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Effects of different concentrations of ethanol and isopropanol on physicochemical properties of zein-based films

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ABSTRACT

In this study, biodegradable and biocompatible zein films were prepared by casting from alcoholic solutions. The effects of different types and concentrations of alcoholic solutions (ethanol and isopropanol) on hydrophobicity, mechanical and surface properties of zein during the plasticization process were investigated. It was demonstrated that at the initial phase, tensile strength of films increased with the increase of the concentration of ethanol and isopropanol solutions, reaching upon the maximum value (74.2 MPa and 57.5 MPa, respectively). In addition, the results of water contact angle, water vapor permeability, water absorption and transmittance indicated that the hydrophobicity of zein film prepared by ethanol was substantially higher than that prepared by isopropanol. Moreover, DSC (differential scanning calorimetry) and FTIR (Fourier transform infrared spectroscopy) revealed that the thermability and the secondary structure of zein film were affected by the presence of ethanol and isopropanol, respectively. In conclusion, the findings of this study may contribute to pragmatically formulate ideal surface morphology and the degree of hydrophobicity of zein based films fulfilling the different requirements from academia and industry.

1. Introduction

Currently majority materials are derived from fossil fuels. In the past few decades, increased fossil fuel consumption has led to globally rapid depletion of petroleum reserves and soaring petroleum price. Hence, scientists and researchers are devoted attempt to reduce the dependence on limited petroleum resources. Compared to petroleum based materials, biodegradable polymers obtained from renewable resources have received much attention due to their sustainability and environmental biocompatibility (Sessa and Woods, 2011; Feng et al., 2013, 2012; Hayes et al., 2012). Zein is an odorless and tasteless group of proteins, generally consisting of: polypeptides α-, β-, γ-, and δ-zeins (Shukla and Cheryan, 2001). It is commercially available from corn gluten meal, a byproduct of corn wet milling processing in large-scale bioenergy refineries (Lawton, 2002). The main structure of zein is described as a helical wheel conformation containing nine homologous repeating units in an anti-parallel form (Argos et al., 1982). The surface of zein molecule includes defined hydrophobic (>50%) and hydrophilic domains (Lai et al., 1999).

As prolamins, the hydrophobic property of zein is highly associated with the high proportion of non-polar amino acid residues, such as, leucine, proline, and alanine (Shukla and Cheryan, 2001). Traditionally, the presence of binary mixtures of aqueous ethanol (60–95%, v/v) and water enables the improvement of the solubility and dispensability of zein particles (Kim and Xu, 2008; Wang and Padua, 2010). The microstructure of zein is highly linked with the concentration of zein, the concentration of aqueous ethanol and the employment of surfactants in the mixtures (Qin et al., 2008; Wang and Padua, 2010). Alternatively, during evaporation of binary solution, the morphology of self-assembled structure of zein can vary depending on the type and concentration of solvents and solutes (Wang and Padua, 2010).

The careful and rational design of the microstructure of food based polymers in the media can benefit the utilization of food based polymers as a delivery system for nutraceuticals (Patel et al., 2010; Ye and Harte, 2013), and antimicrobials (Zhang et al., 2010) or in food packaging applications along with other functions, for instance, the fat replacer (Feng et al., 2012). In the literature, zein based biopolymers have been investigated as packaging zein films (Biswas et al., 2009; Chen et al., 2013a; Ozcalik and Tihminlioglu, 2013; Panchapakesan et al., 2012; Yoshino et al., 2002), or zein based film combining with lysozyme (Gucbilmez et al., 2007) and oleic acid (Scramin et al., 2011), along

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with incorporating into a Liposome system (Baohua and Youling, 2006).

As mentioned previously, alcoholic solutions have been widely used to enhance the solubility and dispensability of zein for further applications (Chen et al., 2013b). Although the synthesis of zein films in ethanol and acetone in combination with a plasticizer e.g. glycerol, glycol, fatty acids, tributyl citrate, etc., have been investigated in many previous reports, currently, little is known about the comprehensive effects of different concentrations and types of common alcoholic solutions, such as isopropanol, on hydrophobicity, mechanical and surface properties of zein film during the plasticization process. Therefore, the specific objective of this work was to investigate the effect of the concentrations of ethanol and isopropanol on the microstructure of zein film. In addition, thermal behavior, hydrophobicity, and mechanical properties of zein films prepared by casting from alcoholic solutions provided insight into the preparation of zein film in alcoholic solutions. The underlying understanding of zein microphase behavior at two kinds of common alcoholic solutions (ethanol and isopropanol) is anticipated to contribute to the development of zein applications, including the synthesis of zein film for potentially packaging applications and the formation of nano sphere particles for delivery systems.

2. Materials and methods

2.1. Chemicals

Zein, regular grade, was obtained from Gaoyurixing Industries Inc. (Jiangsu, China) with its composition mainly being 94.7% protein, 2.1% moisture and 1.4% lipid. Other materials included ethyl alcohol (HPLC grade), isopropanol (HPLC grade), glycerol were purchased from Sigma–Aldrich (Shanghai, China). Other chemicals were achieved from Tianyi (Tianjin, China). All commercial chemicals were used without further purification.

2.2. Preparation of zein film

2.2.1. The effect of glycerol concentrations on the properties of cast zein films

Zein (10%, w/w) and glycerol were gently mixed at the different ratios of 0, 10, 15, 20, 25 and 30% of glycerol in 85% alcohol solution (ethanol or isopropanol), respectively. The solution was continuously stirred and maintained at 60 °C until zein was fully dissolved in solution (approximately 10 min). Then, a constant amount (30 mL) of solution was casted onto a polyethylent film (150 mm × 250 mm) using an applicator (model CS-194AV, Toyoseiki Ltd. Japan) and dried at 30 °C for 1–2 h to remove excess alcoholic solutions, followed by drying at 45 °C for 6 h. The slow drying procedure enables the formation of homogeneous casted films. The zein films were placed in 50% relative humidity desiccator under 23 ± 2 °C before further use. After equilibration, the thickness of the zein film was measured with a hand-held micrometer (MDC-25M, Mitutoyo Co., Japan), ranging from 0.045 to 0.065 mm.

2.2.2. The effect of alcoholic concentrations on the properties of cast zein films

Zein (10%, w/w) was carefully blended 20% of glycerol, and subsequently, the mixture was dispersed to a concentration water/ethanol or Isopropanol mixture (65%, 70%, 75%, 80%, 85%, 90%, 95%, v/v ethanol or isopropanol, respectively) by stirring continuously at 60 °C, until zein was fully dissolved in solution. The other procedures are consistent with the above-mentioned method.

2.3. Mechanical property measurement

The film thickness was first measured using a dial gauge with a sensitivity of 0.01 mm. For each specimen, 10 thickness measurements were performed randomly at different locations, and the average values were used.

An electronic universal testing machine (Shenzhen Reger Instrument Co., Ltd., Shenzhen, China) was used to measure the mechanical properties. The films were conditioned in a desiccator at 25 °C and 50% RH for 7 d. The measurement of mechanical properties follows the protocol (Ke et al., 2012) with minor modifications. The tensile strengths and elongations to break of the films were measured. The rectangular test strips of the films had a length of 80 mm and a width of 25 mm, and the cross-head speed was set at 10 mm/min. The temperature of the laboratory environment was maintained at 20–23 °C, and the RH was 50 ± 4%. At least four replications were employed to determine the ultimate tensile strength, elongation to break. Tensile strength was calculated by dividing the maximum load at break by the area of cross-section. Elongation at break (E, %) was expressed as

$$E = 100 \times \frac{L_1 - L_0}{L_0} \quad (1)$$

where L_0 (mm) is the initial length of the film and L_1 (mm) is its length at break.

2.4. Contact angle measurements

Contact angle measurements were carried out using a Data Physics OCA-15 plus setup according to the early publication (Lei-Yan et al., 2011). Droplets of sample liquids were placed on hydrophilic glass slides. The instrument employed a well-established methodology to determine the contact angle value from droplet images where a best fit between a theoretical Laplacian curve and the experimental profiles were recorded. Four measurements of contact angle were taken and averaged for each sample.

2.5. Water absorption measurement

Water absorption was determined by a modification of the ASTM D87016 following the method previously described in the literature with minor modifications (Ke et al., 2012). Initially, films were incubated at 25 °C and 50% relative humidity. After chopped into three 30 mm × 30 mm specimens, samples were stored at 25 °C and 50% relative humidity for two days to reach equilibrium. Beakers were pre-dried at 60 °C for 48 h and the weight was recorded. The chopped sample was immersed in distilled water in a beaker at 25 °C for up to 3 h. Subsequently, after the surface water was carefully wiped off, the weight of the sample was monitored. Water absorption was calculated as a percentage ratio of submerged water to initial dry weight. Loss of soluble materials from the samples after 3 h of soaking was recorded by evaporating away immersing water in the beaker at 60 °C for one day and then weighing the alternation of the beaker.

2.6. Water vapor permeability (WVP) measurement

The WVP of the zein films was measured using the method reported by (McHugh et al., 1993). In this method the zein film was cut to 2 cm in diameter, and the film was used to seal a testing cup containing calcium chloride. This cup was placed in a controlled chamber at 25 °C and 90% RH. The weight of the cup was measured intermittently at intervals of 24 h, up to 96 h. WVP of the zein films was calculated as follows:

$$\mathrm{WVP} = \frac{WL}{tAP}$$