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Fabrication and characterization of soluble soybean polysaccharide and nanorod-rich ZnO bionanocomposite

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ABSTRACT

In this study, a novel bionanocomposite film was prepared by the casting method. Different concentrations [i.e., 0%, 1%, 2%, and 4% (w/w)] of nanorod-rich ZnO (ZnO-nr) were incorporated into soluble soybean polysaccharide (SSPS). The mechanical, thermophysical, antimicrobial, and barrier properties of the resultant bionanocomposite films were evaluated. Incorporation of 4% ZnO-nr into the SSPS matrix reduced water vapor permeability from 8.19×10^{-11} to 5.25×10^{-11} ($g\,m^{-1}\,s^{-1}\,Pa^{-1}$) and oxygen permeability from 223 to 127 ($cm^3\,\mu m\,m^{-2}\,day^{-1}\,atm^{-1}$). The elongation at break and heat seal strength of the films increased by over 20%. The moisture content, glass transition temperature, and tensile strength of the SSPS films significantly decreased by ZnO-nr incorporation. SSPS/ZnO-nr (4%) films showed 0% UV transmittance and were able to absorb over 70% of the near-infrared spectrum. The SSPS/ZnO-nr films exhibited excellent antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*. In summary, ZnO-nr is an excellent potential filler for SSPS-based films used as packaging materials.

1. Introduction

The use of synthetic materials has become increasingly popular worldwide [1,2]. Some plastic packaging materials, such as PE, PET, and PP, are favored because of their good mechanical and barrier properties, low cost, and heat sealability. Despite these features, however, the use of these materials should be avoided because of their non-environment-friendly properties [3]. Polymers derived from bio-based resources have been considered potential alternatives to oil-based plastic films because of their availability and biodegradability [4,5]. Sustainable materials for food and non-food packaging in the form of films or coatings have recently been developed [6–9]. However, bio-based polymers present the main disadvantages of moisture susceptibility and poor mechanical properties.

Soluble soybean polysaccharides (SSPS) are extracts from the cell-wall material of soybean cotyledons [10]. SSPS has a pectin-like structure featuring a galacturonan backbone of homogalacturonan (α-1,4-galacturonan) and rhamnogalacturonan (repeating units composed of α-1,2-rhamunose and α-1,4-galacturonic acid) with branches of β-1,4-galactan and α-1,3- or α-1,5-arabinan chains [10]. Recent research has indicated that SSPS may be formed into films [11], but the material obtained is highly soluble and very sensitive to moisture.

In the last decade, nanoscience has been coupled with other fields to develop various novel materials and applications [12]. Nanotechnologies have been developed to solve common problems [13]. Bionanocomposites are a new generation of nanocomposites made from the combination of inorganic materials with at least one-nanometer scale dimension and a biopolymer [14]. Active packaging efficiency, good barrier properties, UV-shielding, and improvements in overall physicochemical properties are some of the main advantages of bionanocomposites [13].

Incorporation of nanoparticles (e.g., nanoclay, CaO, Ag, SiO_2, and TiO_2) into packaging materials have been reported to improve the functional properties of the composite materials compared with those of pure matrices [6,15–18]. ZnO is a functional filler that has been widely used in UV-shields for application in pharmaceutical materials, cosmetics, pigments, and coating materials [19,20]. ZnO nanoparticles also present antimicrobial properties, making them a viable approach to prevent infectious diseases [21,22].

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Particle shape, size, morphology, and crystallinity are critical parameters of the intrinsic properties of nanoparticles [23]. While incorporation of ZnO nanoparticles into biopolymer films has been reported to improve some film properties [17,24,25], to the best of our knowledge, the functional properties of ZnO nanorod-reinforced SSPS have not yet been investigated. In this study, ZnO nanorods incorporated in high soluble matrix, while in previous studies the polymeric matrix were not soluble as SSPS. Also the approach for characterization of antimicrobial activity of SSPS/ZnO-nr is based on dynamic method that so much accurate than static method reported in other studies [6].

We hypothesize that application of low-concentrations of ZnO nanorods (ZnO-nr) into SSPS films will improve film hydrophobicity and yield biopolymeric films with antimicrobial properties and UV shielding. The proposed film can be applied to the packaging industry. In this study, ZnO-nr was used as filler to prepare SSPS/ZnO-nr bionanocomposites. We characterized the films by evaluating their thermal, physicochemical, antibacterial, mechanical, barrier, and hydrophobic properties.

2. Materials and methods

2.1. Materials

The SSPS used in this work was provided by Fuji Oil (Osaka, Japan). ZnO-nr was synthesized ((Fig. 4a and b) via the catalyst-free combust-oxidized mesh process described by Mahmud and Abdullah [26]. For antimicrobial assays, *Escherichia coli* O157:H7 and *Staphylococcus aureus* cultures were obtained from the culture collection center of the Microbiological Laboratory, Islamic Azad University, Damghan, Iran). All other chemicals used were of analytical grade.

2.2. Film preparation

Different concentrations of ZnO-nr [i.e., 0% (control), 1%, 2%, and 4%; w/w (dried based of SSPS)] were dispersed in water and then homogenized in an ultrasonic bath (Marconi model, Unique USC 45 kHz, Piracicaba, Brazil) for 15 min. These solutions were used to prepare the SSPS dispersion at 8% (w/w wb). A mixture of sorbitol and glycerol (3:1) at 40% (w/w db) of the total SSPS was added to the formulation as a plasticizer to compare the heat seal strength of the bionanocomposite films with those of other biopolymers, following the methodology of Abdorreza et al. [27]. Dispersions were heated to 75 ± 5 °C and stirred for 1 h to achieve homogenized dispersions. Then, 45 g portions of the dispersions were cast on Perplex plates fitted with rims around the edge to create a 16 cm × 16 cm film-forming area. Films were dried in a humidity chamber at 25 °C and 50% RH. Dried films were peeled and stored in a closed desiccator contained saturated magnesium nitrate at 25 ± 2 °C and 50% ± 5% RH. Film thickness was measured at 10 different locations with a hand-held micrometer (Mitutoyo, Tokyo, Japan). All films were prepared in triplicate.

2.3. Water solubility, moisture content and moisture uptake

The water solubility of the bionanocomposite films was determined following Nafchi et al. [17].

The moisture content (MC) of the bionanocomposite films was determined by thermogravimetric analysis (Pyris1 TGA, Perkin-Elmer, Massachusetts, USA) following the method described by Mohammadi Nafchi and Karim [28].

Moisture uptake was estimated following the method described by Vermeiren et al. [29].

2.4. Moisture sorption isotherm estimation

The moisture sorption isotherm of SSPS/ZnO-nr at 25 °C was estimated using the method described by Bertuzzi et al. [30]. MC (dry basis) at equilibrium was measured for each water activity (a_w). The experimental MC data were fitted using the Guggenheim, Anderson, and de Boer (GAB) equations [31].

$$W = \frac{W_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

where W is the MC (dry basis), K and C are GAB parameters, w_m is the monolayer water content, and a_w is the water activity.

A third-order polynomial model for moisture sorption isotherms was also fitted to the experimental data [32,33]:

$$W = B a_w^3 + C a_w^2 + D a_w \quad (2)$$

where W is MC (dry basis), a_w is the water activity, and B–D are polynomial model constants.

2.5. Barrier properties evaluation

Water vapor permeability (WVP) tests were performed based ASTM standard E96-05 with some modifications. Test cups were filled with distilled water up to 2 cm below the film surface. A plot of weight loss versus time (14 h for every 2 h) was used to determine the water vapor transmission rate (WVTR). Five samples were tested per treatment. The WVPs of the films were calculated by multiplying the film thickness by their WVTR and dividing the result by the difference in water vapor pressure across the film area [13].

Oxygen permeability (OP) was evaluated according to the ASTM standard method D3985-05 with Mocon Oxtran 2/21 (Minneapolis, USA) equipped with a patented colorimetric sensor (Coulox®) and WinPermTM permeability software with minor modifications according Mohammadi Nafchi et al. [34]. Permeability coefficients were calculated based on oxygen transmission rate in the steady state by taking the film thickness into account and are presented in units of $cm^3\ \mu m\ m^{-2}\ day^{-1}\ at.^{-1}$.

2.6. Mechanical properties and heat seal strength of SSPS/ZnO-nr films

The mechanical properties of the films were determined according to the ASTM D882-10 method with some modifications [7]. Film strips were cut into 120 mm × 22 mm pieces and conditioned for at least 48 h at 25 °C and 55% RH (in closed desiccators contain saturated magnesium nitrate). A texture analyzer (TA.XT2, Stable Micro System, Surrey, UK) was used to measure the force versus distance of the films. Initial grip separation was 80 mm and the crosshead speed was 0.5 mm/s. Tensile strength (TS), Young's modulus (YM), and elongation at break (EB) were evaluated from the stress-strain data recorded by the equipment. The seal strength of the heat-sealed films (110 °C for 3 s) was determined according to the ASTM F-88-09 standard as modified by Abdorreza et al. [27] for biofilms. Each leg of the sealed film was clamped to the texture analyzer, and each end of the sealed film was held perpendicular to the direction of the pull. The distance between the clamps was 25 mm. A 5 kg static load cell and a test speed of 1 mm/s were used. Seal strength (N/m) was calculated as the ratio of the maximum force required for seal failure to the film width.

2.7. UV–vis transmission spectra

The UV–visible (UV–vis) transmission spectra of the bionanocomposite films were recorded from 190 nm to 1100 nm using a UV–vis UV-1650PC spectrophotometer (Shimadzu, Tokyo, Japan). A blank glass plate was used as a Ref. [35].