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Preparation and characterization of bionanocomposite film based on tapioca starch/bovine gelatin/nanorod zinc oxide

Mohammad Mehdi Marvizadeh[a], Nazila Oladzadabbasabadi[b], Abdorreza Mohammadi Nafchi[c,*], Maryam Jokar[d]

[a] Young Researchers and Elite Club, Damghan Branch, Islamic Azad University, Damghan, Semnan, Iran
[b] Department of Chemical Engineering, Shahrood Branch, Islamic Azad University, Shahrood, Iran
[c] Food Biopolymer Research Group, Food Science and Technology Department, Damghan Branch, Islamic Azad University, Damghan, Semnan, Iran
[d] Research Group for Nano-Bio Science, National Food Institute, Technical University of Denmark, Mørkhøj Bygade 19, 2860 Søborg, Denmark

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ABSTRACT

To exploring a nano-packaging materials for using as coating or edible films, tapioca starch/gelatin/nanorod ZnO (ZnO—N) bionanocomposites were prepared via solution casting technique. The effects of nanofiller addition on the mechanical, physicochemical, and crystalline structures, as well as the barrier properties of bionanocomposite films were investigated. X-ray diffraction analysis showed that the bionanocomposite film incorporated with ZnO—N at a concentration of 3.5% w/w exhibited high intensity peaks compared with control samples. Results of UV–vis spectra analysis showed that incorporation of ZnO—N into the films can absorb the whole UV light. Tensile strength of the films was increased from 14 to 18 MPa whereas elongation at breaks decreased from 18 to 8 percent and oxygen permeability decreased from 151.03 to 91.52 cm^3 $\mu m/(m^2-day)$ by incorporation of 3.5% ZnO—N into biopolymer matrix. In summary combined starch/gelatin films supported by ZnO—N showed better properties compared to starch or gelatin alone. Thus, the bionanocomposite films can be used in food, medicine, and pharmaceutical packaging.

1. Introduction

The aim of food packaging is to increase food shelf life by avoiding bacterial contamination, spoilage, or the loss of food nutrient [1,2]. Petroleum-derived polymers that are currently used in food industries are from non-renewable resources and yield non-biodegradable plastic materials [3]. With advantages such as abundance, relatively low cost, biodegradability, and edibility, natural polymers, such as starch and gelatin, have been the focus of current research. Starch is a widely available renewable resource and can be obtained from different by-products of harvesting and raw material industrialization. The unique capacities of proteins to form network and induce plasticity and elasticity are beneficial in preparing biopolymer-based packaging materials. Hence, bovine gelatin can be used as a basic raw material for the development of food packaging films [4]. Coating and biodegradable films are used not only to protect food quality but also to enhance safety and stability [5]. The properties of natural packaging may lead to the development of new products, such as individual packaging of particulate foods, nutrient supplements, and carriers for different additives [6,7].

The use of nanotechnology in food packaging has led to extended shelf life, better traceability of food products, healthier food, and safer packaging. The oxidation of fats and oils and the growth of microorganisms present a major problem owing to oxygen inside food packaging. In addition, oxygen accelerates the processes inside food packaging, leading to discoloration, changes in texture, rancidity and off-odor, and flavor problems [8]. Nanotechnology can effectively produce oxygen scavengers for sliced processed meat, nuts, beverages, cooked pastas, and ready-to-eat snacks, moisture absorber sheets for fresh meat, poultry, and fish, and ethylene-scavenging bags for fruit and vegetable packaging [9].

There are many efforts to finding application of biocomposites in pharmaceutical and medical application by mixing different source of biopolymers [2,10]. The main limitation of biopolymer application in food and pharmaceutical application is hydrophilic nature of the biopolymers. Recent reports on nanoparticle application were showed that application of metal oxide nanoparticles can decrease hydrophilic nature of biopolymers and can improve

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* Corresponding author.
E-mail addresses: fstiau@gmail.com, fstiau@damghaniau.ac.ir (A. Mohammadi Nafchi).

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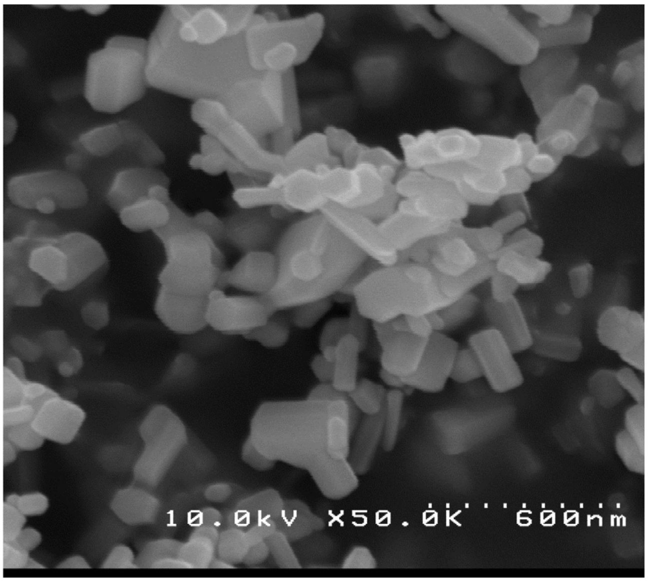

Fig. 1. Environmental scanning electron microscopy micrograph of nanorod-rich ZnO.

UV-shielding of the respective packaging film materials [11–14]. Bionanocomposites are combinations of natural polymer and organic or inorganic nanofillers with particular geometry, surface chemistry and size, properties [15]. Bionanocomposites exhibit significant improvements in mechanical properties, solvent or gas resistance, and dimensional stability with respect to the pristine polymer [12,16,17]. ZnO, TiO_2, MgO, and CaO among inorganic materials are of particular interest owing to the safety of such materials for animals and humans, as well as the stability under harsh condition processes [18]. Several works have reported on biopolymer improvements by the incorporation of nanoparticles, such as nano-zinc oxide [4,19–21]. To the best of our knowledge there is no report on ZnO nanoparticle in a mixed biopolymeric system, so the purpose of this work was to evaluate ZnO—N effects on XRD pattern, mechanical, physicochemical, opacity, oxygen permeability, and sorption isotherm properties of tapioca starch/bovine gelatin films.

2. Materials and methods

2.1. Materials

Tapioca starch was purchased from SIM Company Sdn. Bhd. (Penang, Malaysia), and bovine gelatin (Type B) was purchased from Sigma Chemical Co (St. Louis, MO, USA). Liquid sorbitol and glycerol were purchased from Liang Traco (Penang, Malaysia). All chemicals include chemicals that used in moisture sorption isotherm (LiCl (aw = 0.11), $KC_2H_3O_2$ (aw = 0.22), $MgCl_2$ (aw = 0.33), K_2CO_3 (aw = 0.44), $Mg(NO_3)_2$ (aw = 0.52), NaBr (aw = 0.58), NaCl (aw = 0.75), KCl (aw = 0.85), KNO_3 (aw = 0.93), and dried P_2O_5(aw = 0.00)) were of analytical grade. Zinc oxide nanorod (ZnO—N) was synthesized through the catalyst-free combust-oxidized mesh (CFCOM) process [22].

The structure of ZnO—N is illustrated in environmental scanning electron microscopy micrographs of Fig. 1. It reveals that ZnO—N possesses dimensions lower than 100 nm.

2.2. Bionanocomposite film preparation

ZnO—N was added to water at different concentrations (0.5%, 2%, and 3.5% w/w of total solid). The dispersion was stirred at 60 ± 5 °C for 60 min. Nano- solutions were exposed to ultrasound in an ultrasonic bath (Marconi model, Unique USC 45 kHz, Piracicaba, Brazil) for 30 min to obtain homogeneous mixture. Nano-film were fabricated according to the solution intercalation technique with formulation 4 g of starch and 3.6 of bovine gelatin. About 1.6 g of glycerol and sorbitol (1:3) was added to dispersion as plasticizer in accordance with Abdorreza et al. [23]. Solutions bionanocomposites were heated to 87 °C for 45 min. Nano- dispersions were cooled to ambient temperature (37 °C). Approximately 92 mL of the solution was cast on casting plates with special dimension (16 cm × 16 cm). The bionanocomposites films were dried in special condition in 30 °C and 50% RH. Tapioca starch/bovine gelatin films were fabricated similarly but without the incorporation of nanoadditives. Edible films based on starch/gelatin were removed from solution casting plates and conditioned at approximately 28 ± 2 °C and 50 ± 5% relative humidity (RH) in a desiccator using saturated magnesium nitrate. Manual micrometer was used for measurment thickness of different films

2.3. Characterization of starch/gelatin nanocomposite films

2.3.1. Hydrophobicity measurements

Hydrophobicity characterization of the starch/gelatin/ZnO—N films was conducted by water contact-angle measurements according the method described by Nafchi et al. [24]. Static contact angle was performed on a contact-angle meter (CAM-PLUS, Tantec, Germany). Static contact angles on each sample surface were measured after the addition of 1 μL deionized water immediately using the Sessile Drop Half-Angle™ Tangent line method. Experiment was carried on eight independent determinations at different sites of the film samples.

2.3.2. Moisture sorption isotherm

The moisture sorption isotherm of the film samples at room temperature was studied according to Bertuzzi et al. [25] with some modifications [26]. Moisture content equilibrium of bionanocomposite films (dried basis) was estimated in triplicate in each a_w that equal to equilibrium relative humidity (ERH) that provided by saturated salts.

A third-order polynomial equation for the sorption isotherm was also fitted to the practical data according Hazaveh et al. [27]:

$$W = Ba^3{}_w + Ca^2{}_w + Da_w$$

where a_w is water activity; B, C, and D are the constant factors of polynomial equation and W is the moisture content (dry basis).

2.3.3. Light absorbance

All films were cut in equipment cell dimension and placed in the location of the sample without cells. Then, the light absorbance of the bionanocomposite films was measured at wavelengths between 190 and 1100 nm by using a UV–vis spectrophotometer model UV-1650PC (Shimadzu, Tokyo, Japan) with air as the reference [28].

2.3.4. FTIR absorption spectra

The functional groups of starch/gelatin based films blending of ZnO—N were observed using an FTIR-attenuated total reflectance (ATR) spectrometer (Thermo Scientific, Madison, USA) [29]. Each thin film was applied onto the ZnSe ATR cell. The spectral range for each spectrum varied from 700 cm^{-1} to 4000 cm^{-1} with 32 consecutive points and a resolution of 4 cm^{-1}.

2.3.5. Color evaluation

CIELAB color values (L^*, a^*, b^*, $c*$, and h) were measured using a colorimeter (Minolta CM-3500D; Minolta Co. Ltd., Osaka, Japan),