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ORIGINAL ARTICLE

Improved Physicochemical Properties of Tapioca Starch / Bovine Gelatin Biodegradable Films with Zinc Oxide Nanorod

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ABSTRACT: The effects of zinc oxide nanorod (ZnO-N) incorporation on the_physicochemical properties of tapioca starch / bovin gelatin composite film such as water absorption capacity (WAC), water solubility and permeability to water vapour (WVP) were investigated. In this search, ZnO-N was homogenized by sonication and added into tapioca starch / bovine gelatin dispersions at different concentrations (e.g. 0.5, 2, and 3.5% w/w total solid). Incorporation of 3.5% of nanoparticles to tapioca starch / bovine gelatin films decreased the permeability to water vapor by 18%. Water absorption capacity and Solubility of the films were decreased by increasing the ZnO-N contents. These properties suggest that ZnO-N has the potential as filler in starch /gelatin-based films for using in pharmaceutical and food packaging industries

INTRODUCTION

Nanotechnology has attracted the idea of researchers, population and manufacturers, in recent years. The National Nanotechnology Initiative defines nanotechnology as the understanding and control of matter at dimensions of roughly 1-100 nm, where unique phenomena enable novel applications. Two building strategies are currently used in nanotechnology: 1) the "top down" approach, and 2) the newer "bottom up" approach, which allows nanostructures to be built from individual atoms or molecules that are capable of self-assembling. Nanostructures can be also use in food packaging [1]. Nanofillers exist in different shapes and sizes and can be mainly classified into three categories:

(1) Plate-like nanofillers: The most well-known 1D nanofillers are layered silicates including smectic clays, layered double hydroxides as well as grapheme sheets.

(2) Nanofibers: Carbon nanotubes, nanocellulose substrates, and so on all fall under this category.

(3) Nanoparticles: The most popular 3D fillers are silica particles, metal oxides and polyhedral oligomeric silsesquioxane. In nanoparticles, inverse relationship is between surface area-to-volume ratios with diameter (the smaller the

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diameter, the greater the surface area per unit volume). For layered nanosized filler, the surface area/volume is dominated by low thickness. The second term in equation 2/t + 4/l (t: thickness, l: length) has a very small influence and generally omitted, compared to the first one [2].

In recent decade the demand for environmentally friendly polymers is growing, which intends to reduce the human impact on the environment. Biopolymers are obviously tendency subset of this stream and numerous bioplastics have been developed[3].Natural biopolymer bionanocomposites-based packaging materials have advantages over the plastic for example biopolymers are biodegradable and renewable materials. Biopolymers have great potential for increasing food quality, safety, and stability as a novel packaging [1]. Biocomposite packaging can act as carriers for functionally active substances, and provide nutritional supplements [4].

Currently, many researchers have focused on active packaging with inorganic materials such as ZnO, TiO_2, MgO, and CaO instead of organic materials like essential oils or bacteriocins have been widely studied for their antimicrobial properties and tested for their potential application in polymeric matrices as antimicrobial packaging. Metal oxide can efficiently be used in active packaging because of high stability under harsh condition processes and no effect on health animals and human [5, 6].

There are a few reports about the improvements of biopolymer properties by incorporation of nano zinc oxide [7, 8 and 9]. Zinc oxide has been used as food additive in food industries subsequently listed as a generally recognized as safe (GRAS) material by the U.S. Food and Drug Administration (21CFR182.8991) [10]. Bionanocomposites are mixture of polymers with nanosized inorganic or organic fillers with particular size, geometry, and surface chemistry properties. The polymers used are normally hydrocolloids, such as proteins, starches, pectins, and other polysaccharides [11]. Bionanocomposites formed using a melt intercalation, an In situ intercalative polymerization or a solvent intercalation method [12]. Bionanocomposites exhibit significant improvements in mechanical strength, dimensional stability, and water vapour permeability with respect to the pristine polymer. Bionanocomposites also offer extra benefits like low density, good flow, better surface properties, and recycle ability [13, 14].

UV-vis spectra of the films showed that the UV transmission becomes about zero with the incorporation of small amounts of ZnO-N to the biopolymer matrix. Moreover, ZnO can block UV-A, UV-B, and UV-C. Nano zinc oxide in different shapes, such as rods, discs, tubes, wires and spheres, have been easily synthesized by the catalyst free combust oxidized mesh process as described by Shahrom and his colleague and through the precipitation of surfactants followed by hydrothermal processes (120°C) [15, 16 and 17].

Novel studies have indicated that some anticancer drugs could be assembled with biocompatible nanomaterials, which could effectively sustain drug delivery for the target carcinogenic cells and reduce the relevant toxicity towards normal cells and tissues. Recently, the combination of cancer therapy with ZnO nanoparticles have been the focus of cancer research, due to single modality treatment is not always effective [11].

At the same time, zinc oxide nanoparticles also has been reported to exhibit strong antimicrobial activities due to antimicrobial effects of zinc oxide[18].

In this study, ZnO nanorods were used as filler to prepare tapioca starch/bovin gelatin/ZnO-N bionanocomposites. The films were characterized for their barrier, hydrophobicity properties.

MATERIALS AND METHODS

Bovine gelatin (Type B) was purchased from Sigma Chemical Co (St. Louis, MO, USA) and tapioca starch was purchased from SIM Company Sdn. Bhd (Penang, Malaysia) .Liquid sorbitol and glycerol was purchased from Liang Traco (Penang, Malaysia). All chemicals were of analytical grade. Zinc oxide nanorod was obtained from University Sains Malaysia (USM). Environmental scanning electron microscopy (ESEM) (Figure 1) reveals that ZnO-N has a dimension in nanometer.

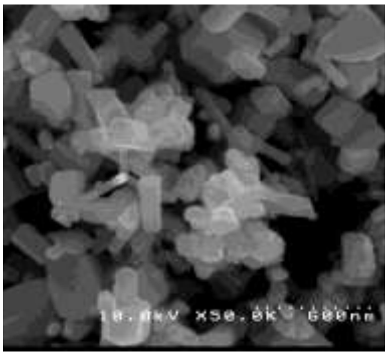

Figure1. ESEM micrograph of nanorod-rich ZnO

Film preparation

ZnO-N aqueous dispersing was prepared at different concentrations (0.5%, 2%, and 3.5%, w/w of dried bases),stirred for 1 h .The dispersing solution was sonicated using an ultrasonic equipment (Marconi model, Unique USC 45 kHz, Piracicaba, Brazil) for 60 min to ensure homogenization was completed. Bionanocomposite solutions were prepared according to casting method through dispersing starch at 4% (w/w) and bovin gelatin %10 (w/w) of total starch. Sorbitol and glycerol at the concentration of 40% w/w of starch/gelatin was added as plasticizers in accordance with Mohammadi Nafchi and his colleagues [19]. Starch/gelatin nanocomposites were heated to 87°C ± 5°C and held for 45 min to allow gelatinization. Then the suspension was cooled to 37°C. Eighty five grams of the dispersion was cast on 16 × 16 cm^2 special plates and dried at 30°C and 50% relative humidity (RH) in a humidity chamber. Control films were prepared similarly but without addition of nanoparticles. Dried films were separated from casting plate and stored at 23°C ± 2 °C and 50 ± 5% relative humidity (RH) until evaluation.

Water vapor permeability

Permeability to Water vapor of the bionanocomposites films was carried out following the modified method[20] of ASTM standard E96-05 [21].The test cups were filled with water up to 1.5 cm below the film. A plot of gained weight versus time was used to measurment the WVTR. The regression coefficients should be 0.99 or greater. Water vapor permeability of the edible films was estimated by multiplying the WVTR by the edible film thickness and dividing that by the water vapour pressure difference across the film.

Water absorption capacity

Water absorption capacity of the bionanocomposite films was measured according to Kiatkamjornwong and others [22] with some modifications. Bionanocomposite samples were cut in special dimension (2 × 2 cm) and were placed in desiccators with diphosphor penta oxide (0% RH) for 2 days. Samples were weighed to the nearest 0.0001 g and placed into desiccators with 200 mL deionized water for 1 day (18 MΩ). The amount of water retained by the films per dried weight of the films was calculated as water absorption capacity

Water solubility

Water solubility test on the edible films was determined according to Maizura and others (2007) [21] .Pieces of film were cut from each film (2 × 3 cm) and were stored in a desiccators with $CaCl_2$ (0% RH) in an oven at 40 °C for 24 h. Then Samples placed into beakers with 80 mL deionized water (18 MΩ). The samples were stirred via agitator for 1 h at 25°C. The remaining samples of bionanocomposite film after soaking were separated through tissue(Whatman no.1), followed by oven drying at 60°C to constant weight. Solubility in Water of films was calculated as follow:

$$\text{Solubility}(\%) = \frac{\text{Initial film w} - \text{Final filmw}}{\text{Initial film w}}$$

STATISTICAL ANALYSIS

ANOVA and Duncan’s Post Hoc tests were used to compare means of physicochemical properties of Bionanocomposite films at 95% confidence level. Results were analyzed by GraphPad Prism 6 (GraphPad Software Inc., 2236 Avenida de la Playa, La Jolla, CA 92037, USA).

RESULTS AND DISCUSSION

Permeability to water vapor

Water vapor permeability (WVP) of the films are given in Table 1. The significant decrease in WVP after the incorporation of ZnO-N may be attributed to the greater water resistance of ZnO-N compared with the biopolymer matrix, so that the addition ZnO-N to the biopolymer introduces a tortuous pathway for water vapor molecules to pass through [20]Permeability reduction in ZnO-N incorporated tapioca starch / bovin gelatin films can be explained based on the Nielsen[24] simple model of tortuosity. It states that each layer of nanoparticle is perpendicularly oriented to the diffusion pathway, indicating that gases molecule should transfer in a longer diffusive path for the permeability coefficient to decrease. Yu et al. [20] incorporated ZnO nanoparticles into pea starch structure and found that water vapor permeability decreased markedly with the addition of nanoparticles.

Table 1. Water vapor permeability (WVP) of tapioca starch / bovine gelatin nanocomposites

ZnO-N(%)	WVP × 10^{-7}[g/ m Pa h]
0	4.20±0.01a
0.5	4.15±0.01b
2	4.01±0.02c
3.5	3.42±0.02d

Values are mean (n=3) ± SD. Different letters in WVP column values represent significant difference at 5% level of probability among tapioca starch / bovine gelatin films.

Capacity to absorb water

The results of water absorption capacity are presented in Table 2. Incorporation of nanoparticles to tapioca starch / bovin gelatin films decreased the water absorption capacity. This could be attributed to the interactions between zinc oxide and bovin gelatin or tapioca starch in biopolymer film structure. Accordingly Tunc et al. [25] have suggested that when the nanoparticle (ZnO) content of films was increased, more hydrogen bonds formed between the ZnO and the matrix components. For this reason, free water molecules do not interact as strongly as with nanocomposite films as with composite films alone.

Table 2.water absorption capacity (WAC) of tapioca starch / bovine gelatin nanocomposites

ZnO-N(%)	WAC [g water/g dried film]
0.0	2.00±0.01a
0.5	1.87±0.01b
2.0	1.80±0.01c
3.5	1.77±0.01d

Values are mean (n=3) ± SD. Different letters in WAC columnvalues represent significant difference at 5% level of probability among tapioca starch / bovine gelatin films.

Solubility in water

The solubility of the Zinc oxide nanorod/tapioca starch /bovin gelatin films is presented in Table 3. The introduction of zinc oxide nanorod tapioca starch /bovin gelatin matrix significantly decreased the solubility of the biocomposites. These results may be related to the interactions between ZnO and the matrix constitute. Increasing the nanoparticle (ZnO) content of films results in the formation of more hydrogen bonds the ZnO and the matrix constitute [26].Thus, free water molecules do not interact as strongly with nanocomposite films compared with composite films alone. These results in are consistent with previous reports on bionanocomposites [6, 23].

Table 3. solubility of tapioca starch / bovine gelatin nanocomposites

ZnO-N (%)	Solubility(%)
0	40.34±0.06a
0.5	39.27±0.25b
2	38.25±0.23c
3.5	37.25±0.12d

Values are mean (n=3) ± SD. Different letters in solubility column values represent significant difference at 5% level of probability among tapioca starch / bovine gelatin films.

CONCLUSION

We introduced nano-ZnO to the tapioca starch / bovine gelatin matrix to fabricate bionanocomposites. With the incorporation of the nano filler, starch/gelatin-based materials generally show improvement in some of their properties such as permeability to water vapour and water absorption capacity properties. Besides, the use of starch / gelatin-based nano-biocomposites as new packaging materials would be based on their biodegradation and improved solubility and other properties. Under strict regulation, bionanocomposites based on nano-ZnO may have potential applications in the food and pharmaceutical packaging industries.

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