The Effects of ZnOnanorodson the Characteristics of Sago Starch Biodegradable Films

R. Alebooyeh, A. MohammadiNafchi, M. Jokar

Food Biopolymer Research Group, Food Science and Technology Department, Damghan Branch, Islamic Azad University, Damghan, Semanan, Iran

Abstract: Nowadays tend to use biodegradable packaging; including edible coatings and films for free from synthetic chemicals and do not cause environmental pollution, the industry is growing day by day. The aim of this research was to preparation and characterization of biodegradable films supported with ZnOnanorods. In this study, sago starch based films were prepared and plasticized with sorbitol/ glycerol by casting method. ZnOnanorod with 0, 1, 3and 5%(w/w)was added to the films before casting the films. Films were dried at controlled conditions. Physicochemical properties such as water absorption capacity (WAC), permeability to water vapor (WVP) and water solubility of the films were measured. Also, the effects of addition of nano particles were measured on the antimicrobial properties of the films by agar diffusion method. Results showed that by increasing concentration of ZnOnanorod, solubility in water, WAC, and WVP of the films significantly (p <0.05) decreased. Furthermore, the addition of zinc oxide nanorods showed antimicrobial properties against E. Coli. In summary sago starch films supported with ZnOnanorodscan were used as active packaging for agricultural products as well as food industry.

Keywords: Biodegradable film, ZnOnanorods, Physicochemical properties, Antimicrobial properties

INTRODUCTION

In recent years, biopolymer-based packaging has received increasing attention from researchers and industry as a potential alternative to synthetic polymer-based food packaging materials these so-called green packaging materials, or biopolymers contribute an estimated 5-10% of the current plastic market (about50,000 t) in Europe [1]. Various natural biodegradable polymers, such as protein- and polysaccharide-based films, might be feasible materials for environmentally friendly packaging [2]. Tend to use biocompatible packaging of edible coatings and films due to natural materials, the ability of non-renewable and environmental pollution, is growing day by day [2]. Edible films that are used in foods, are crevasse environmental analysis capabilities to the basic elements to make a living micro-organisms and soil particles are projected. In other words, are sprinkled with the natural biological cycle. In general, natural polymers can be polysaccharide- or protein- based. Starches are universally available, with low cost and good film formability. Among the starch materials, sago starch is relatively unknown. It is obtained from an uncommon source (Metroxylon sagu palm tree) in Southeast Asia at a very low cost compared with common starches [3]. The advent of nanotechnology in food packaging, application solutions in relation to human life is put on preserving foods. In truth, what has caused the emergence of this technology over the surface to volume ratio of particles with dimensions in nanometers? This ratio has a direct relationship with the radius of the spherical nanoparticles. With decreasing particle size in the nanometer range, the power can be increased activities of surface material and the material reacting with the surrounding environment due to the increase in the active site becomes more shallow [4]. For the past decade, nano scale science and other related technologies has been the leading technology [5]. Incorporation of nanoparticles into composite materials has attracted a great deal of attention due to its 48 ability to enhance polymer properties such as thermal, mechanical, and gas barrier [6]. Bionanocomposites represent the new generation of nanocomposites, and comprises of the combination of biopolymers and an inorganic material that has at least one nanometer scale dimension. Bionanocomposites is an emerging group of nanostructured hybrid materials in the frontier between nanotechnology, material science, and life science [7]. In addition, biopolymer-based materials are known as a green technology and have shown biodegradability and biocompatibility in pharmaceutical, food packaging, and agriculture technologies [8, 9]. Recently, inorganic materials such as metal and metal oxides have been the focus of nanotechnology research due to their ability to withstand harsh processing conditions [4]. Among the metal oxides, ZnO, TiO2, MgO, and CaO have received particular interest because they are safe for animals and human [9]. In addition, the use of zinc oxide nanoparticles is considered to be a viable method for the prevention of infectious diseases through the antimicrobial effects of zinc oxide [10, 11]. The size, morphology, crystallinity, composition, and shape of particles are critical parameters of the intrinsic properties of nanoparticles [12].

MATERIALS AND METHODS

Materials

Starch from sago (12% moisture) was purchased from SIM Company (Penang, Malaysia). Food grade glycerol and liquid sorbitol were purchased from Liang Traco (Penang, Malaysia). Zinc oxide nanorod was obtained from University Sains Malaysia (USM). All chemicals were of analytical grade.

Preparation of nanobiocomposite films

Zinc oxide nanorod was dispersed in water at different concentrations (1%, 3%, and 5%; w/w of total solid),
stirred for 1 h, and then sonicated in an ultrasonic bath (Marconi model, Unique USC 45 kHz, Piracicaba, Brazil) for 30 min. The solution was used to prepare the aqueous starch dispersion at 4% (w/w). A mixture of sorbitol and glycerol (3:1) at 40% (w/w) of total solid was added as plasticizers in accordance with [13]. Starch nanocomposites were heated to 85 ± 5°C and held for 45 min to allow gelatization. Upon completion of starch gelatinization, the solution was cooled to room temperature. A portion (90 g) of the dispersion was cast on Perspex plates fitted with rings around the edge to yield 16 × 16 cm² film-forming areas. Films were dried under controlled conditions in a humidity chamber (25 °C and 50% RH). Control films were prepared similarly but without addition of nanoparticles. Dried films were peeled and stored at 23 ± 2°C and 50 ± 5% relative humidity (RH) until experimentiation. The thickness of each film was measured at five different locations and to the nearest 0.01 mm with a hand-held micrometer.

**Water vapor permeability (WVP)**

The modified gravimetric cup method based on ASTM E96-05 [14] was used to determine the water vapor permeability (WVP) of films. The test cups were filled with 20 g of silica gel (desiccant) to produce a 0% RH below the film. The sample was placed between the cup and the ring cover of each cup coated with silicone sealant (high vacuum grease, Lithelin, Hannau, Germany). The air gap was at approximately 1.5 cm between the film surface and desiccant. The water vapor transmission rates (WVTR) of each film were measured at 55 ± 2% RH and 25 ± 2°C. The initial weight of the test cup was measured, and the cup was placed into an incubation chamber with an air velocity rate of 125 m/min. Weight gain measurements were taken by weighing the test cup to the nearest 0.0001 g with an electronic scale (Sartorious Corp.) every day for 7 days. A plot of weight gained versus time was used to determine the WVTR. The slope of the linear portion of this plot represented the steady state amount of water vapor diffusing through the film per unit time (g/h). The WVTR was expressed in grams per square meter per day. Six samples per treatment were tested. The slopes yielded regression coefficients of 0.99 or greater. The WVP of film was calculated by multiplying the steady WVTR by the film thickness and dividing that by the water vapor pressure difference across the film.

**Solubility of films**

Solubility of the films in water was determined according to Maizura and others [15] with some modifications. Pieces of film (2 × 3 cm) were cut from each film and were stored in a desiccators with P₂O₅ (0% RH) for 2 days. Samples were weighed to the nearest 0.0001 g and placed into beakers with 80 mL deionized water (18 MΩ). The samples were stirred with constant agitation for 1 h at room temperature. The remaining pieces of film after soaking were filtered through filter paper (Whatman no.1), followed by oven drying at 60 °C to constant weight. Samples were measured in triplicates and the percentage of total soluble matter (% solubility) was calculated as follow:

\[
\text{Solubility(%) = } \frac{(\text{Initial film w - Final film w})}{\text{Initial film w}} \times 100
\]

**Antimicrobial assay**

Antimicrobial activity test on the films was carried out using the agar diffusion method according to Maizura[15]. Antimicrobial effects of the films were determined by inhibition zone against E. coli O157:H7 on solid media.

**RESULTS AND DISCUSSION**

**Permeability to water vapor**

The results of WVP studies are presented in Table 1. The significant decrease in WVP after the addition of zinc oxide nanorodmay be attributed to the greater water resistance of Zinc oxide nanorod compared with the biocomposite matrix, so that the incorporation of these nanorods to the matrix introduces a tortuous pathway for oxygen and water vapor molecules to pass through [16]. Permeability reduction in zinc oxide nanorod incorporated starch films can be described based on the Nielsen simple model of tortuosity [17].

Table 1: Water vapor permeability (WVP) of sago starch films supported with zinc oxide nanorod.

<table>
<thead>
<tr>
<th>Zinc oxide nanorod (%)</th>
<th>WVP x 10⁻¹ ( \text{g m}^{-1} \text{h}^{-1} \text{Pa}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.37±0.27²</td>
</tr>
<tr>
<td>1</td>
<td>0.74±0.19²</td>
</tr>
<tr>
<td>3</td>
<td>0.52±0.02²</td>
</tr>
<tr>
<td>5</td>
<td>0.47±0.09²</td>
</tr>
</tbody>
</table>

Values are mean \( n=3 \) ± SD. Different letters on WVP values represent significant difference at 5% level of probability among sago starch films.

**Solubility in water**

The solubility of the Zinc oxide nanorod/sago starch films are presented in Table 2. The introduction of zinc oxide nanorod into sago starch matrix significantly decreased the solubility of the biocomposites. This finding may be attributed to the interactions between ZnO and starch or gelatin in the biopolymer film structure. Studies have reported that increasing the nanoparticle (ZnO) content of films results in the formation of more hydrogen bonds the ZnO and the matrix components [17]. Thus, free water molecules do not interact as strongly with nanocomposite films compared with composite films alone. These results are consistent with the sorption isotherm and previous reports on nanobioocomposites [9,15].

**Antimicrobial assay**

Effects of sago starch film reinforced with zinc oxide nanorod on the growth of E.Coli were investigated. The inhibition zone of nano-incorporated films was significantly increased by increasing zinc oxide nano rod contents, suggesting (Fig. 1) that sago starch film incorporated with zinc oxide nano rod can act as an active film against...
microorganisms. Excellent antimicrobial activity of ZnO nanoparticles against Escherichia coli and the corresponding mechanism of action have also been demonstrated by other researchers [10, 11]. Mechanisms of the antibacterial behavior of ZnO have been detailed by Zhang et al. [11]. They have categorized this behavior as chemical and/or physical interaction between ZnO particles and the cell envelope of microorganism.

Table 2: Water solubility of sago starch films supported with zinc oxide nanorod

<table>
<thead>
<tr>
<th>Zinc oxide nanorod (%)</th>
<th>Water solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23.12±1.0a</td>
</tr>
<tr>
<td>1</td>
<td>21.16±1.4b</td>
</tr>
<tr>
<td>3</td>
<td>17.39±1.36c</td>
</tr>
<tr>
<td>5</td>
<td>17.40±2.01c</td>
</tr>
</tbody>
</table>

Values are mean (n=3) ± SD. Different letters in each column represent the significance difference in 5% level of probability among sago starch films.

The Zn$^{2+}$ could penetrate through the cell wall of microorganism and react with interior components that finally effects on viability of the cells. Another possible mode of action is generating of H2O2 due to presence of Zinc oxide particles. Zhang et al. [11] also reported that nano size of ZnO is more effective than micro size due to easy penetration through cell wall of microorganisms. In this study, the nanorods could act as needle and easily penetrates through cell wall. Sawai, also reported the same results and he demonstrated that among ZnO, CaO, and MgO, ZnO was the most effective for E. coli [16].

Fig. 1: Antimicrobial assay of zinc oxide nanorod supported films.

CONCLUSION

In this study, we prepared zinc oxide nanorod and introduced it to the sago starch matrix to fabricate bionanocomposites. After incorporation of low levels of the filler (1%), we observed significant differences in film properties, especially in WVP, and antimicrobial activity. Since zinc is one of the essential trace elements for human body that is under strict regulation, bionanocomposites based on zinc oxide nanorod may have potential applications in the medical, pharmaceutical, and food packaging industries.

REFERENCES


