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Effect of TiO_2 nanoparticles on the physico-mechanical and ultraviolet light barrier properties of fish gelatin/agar bilayer film

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ABSTRACT

Bilayer gelatin/agar films containing different concentrations of TiO_2 (0.5, 1, and 2 g/100 g) were prepared by incorporation of anatase titanium dioxide nanoparticles in the fish gelatin layer of the bilayers. Gelatin/agar bilayer film was produced from the monolayers using the casting method in two steps and their microstructural, physical, mechanical and optical characteristics were studied. Results showed that the addition of TiO_2 decreased water vapor permeability of the bilayers more than 30%, upon increasing TiO_2 content to 2 (g/100 g). However, swelling ratio and moisture content increased with the increase in the nano-TiO_2 content, probably due to the hydrophilic nature of the TiO_2 nanoparticles. The tensile strength of the bilayer films increased from 10.80 to 13.91 MPa upon increasing nano-TiO_2 content from 0 to 0.5 (g/100 g); however, tensile strength decreased with further increase of the nanoparticle concentration. In addition, the metallic nature of nano-TiO_2 considerably improved the barrier properties of the bilayer films against UV light at low concentration, while it increased their opacity. This property might help in the preservation of light-sensitive foods, but more studies on real food systems are required.

1. Introduction

Increasing environmental problems with petrochemical-based plastic packaging have caused a rising inclination to use biodegradable packaging materials from natural polymers (Weber, Haugaard, Festersen, & Bertelsen, 2002). Among these proteins, gelatin is considered a good candidate for food packaging because it is inexpensive and has good film-forming capability, as well as high availability and biodegradability (Farris et al., 2011).

Gelatin is obtained from the skins and bones of bovine, porcine and fish wastes. Recently, the use of fish gelatin, given the increasing risk of transmitting pathogens like bovine spongiform encephalopathy, has increased (Kim & Mendis, 2006a, 2006b). However, studies have shown that fish gelatin films are brittle (Yakimets et al., 2005), and their hydrophilic nature connotes high water solubility and water vapor permeability. Different strategies have been suggested to overcome these weaknesses, including chemical modification and adding crosslinking agents (Martucci & Ruseckaite, 2009), adding nanoparticles (Kanmani & Rhim, 2014) and developing film blends and bilayers with polysaccharides (Rhim & Wang, 2013).

In this regard, agar is a polysaccharide extracted from marine red algae, which is biocompatible, has high mechanical strength and possesses good film-forming properties (Freile-Pelegrín et al., 2007). Agar is relatively insoluble in water and its films possess good water resistance. This polysaccharide has the ability to produce strong gels which can help to reduce the water vapor permeability of films (Pavlath, Gosset, Camirand, & Roberton, 1999).

Preventing food spoilage from light-induced oxidation is one of the greatest concerns in the food industry (Li et al., 2011). Despite having good mechanical and relatively good oxygen barriers properties (Martucci & Ruseckaite, 2009), protein- or polysaccharide-based films do not have adequate barrier properties against UV light (Ramos et al., 2013) and cannot properly prevent the photooxidation of lipids. Recently, the use of nanoparticles is turning into a promising option to improve mechanical and barrier properties of biodegradable biopolymer-based films (Abdollahi, Rezaei, & Farzi, 2012).

Among nanoparticles, metal oxides like TiO_2 have evidenced

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good potential to improve functional properties (such as anti-radiation and antimicrobial activities) of biodegradable films (Li et al., 2011). With its low price and nontoxic and photostable properties, TiO_2 has gained special attention among proponents of these metal nanoparticles (Feng et al., 2007). In addition, when TiO_2 is incorporated into a biopolymer matrix, it may decrease transmittance in light's visible, UVA and UVB regions (Li et al., 2011). Therefore, TiO_2 might be a good way to prevent spoilage from light-induced oxidation in food packaging systems. However, there is no published study about the combined effect of agar layer and TiO_2 nanoparticle on the properties of fish gelatin-based film.

Thus, the present study aimed to develop a new biodegradable bilayer gelatin/agar film incorporating TiO_2 for food packaging, with minimum water sensitivity and maximum UV light barrier properties. The gelatin/agar films, with or without TiO_2, were characterized using SEM and XRD analysis. Film transparency, surface color, water vapor permeability and mechanical properties of the bilayer films were also examined.

2. Materials and methods

2.1. Materials

Agar–agar (analytical grade) and glycerol were obtained from Merck Co., Germany. Gelatin from cold water fish skin was purchased from Sigma–Aldrich (St. Louis, MO, USA). TiO_2 nanoparticles obtained from TEKCAN Co., Iran were in the anatase and rutile phase, ranging from 10 to 15 nm.

2.2. Preparation of bilayer films

Gelatin/agar bilayer films were prepared by a two-step casting technique. First, the agar layer was produced by solubilization of 1.5 g of agar powder in 100 mL of distilled water heated at 90 °C for 30 min under 600 rpm magnetic stirring. Then, glycerol (as plasticizer) was added at a concentration of 35% (g/100 g of agar powder). The agar film-forming solution was cast onto Petri dishes (8 cm in diameter) and allowed to dry in an oven at 45 °C for 24 h. In the next step, the gelatin film-forming solution (4 g/100 mL) was prepared by hydrating 4 g of the fish gelatin in 100 ml distilled water for 30 min, and then heating it at 55 °C for 30 min under continuous stirring. Glycerol was also added at a concentration of 35% of the total dry basis. Next, the TiO_2 dispersions (in ratios of 0, 0.5, 1 and 2 g/100 g of the gelatin) were added to the gelatin solution and stirring was continued for 1 h. Then, it was sonicated with assistance of a probe ultrasound (S-4000 Ultrasonic Processor, Misonix, Farmingdale, NY, USA) for 30 min, and stirring was subsequently continued for 1 h. Next, the solutions were degassed under vacuum for 15 min to remove air bubbles. Solutions were then cast atop the agar film and dried at 25 °C in the oven for 24 h. Finally, the obtained bilayer film was stored in desiccators containing saturated magnesium nitrate solution at 25 °C and 52.89% relative humidity for 48 h.

2.3. X-ray diffraction (XRD) analysis

Crystallinity of TiO_2 in the gelatin/agar bilayer films was determined by XRD analysis. Film samples were cut into rectangular pieces (3 × 2 cm), mounted on glass supports and used for the analysis. XRD patterns of the films were obtained using a D8 ADVANCE Polycrystal X-ray Diffractometer (Bruker Co., Germany) with a nickel-filtered Cu Kα radiation beam in an angular range of 20–80 (2θ) at a voltage of 40 kV and current of 40 mA.

2.4. Scanning electron microscopy (SEM)

The surface morphology of the gelatin/agar-TiO_2 bilayer films was examined by scanning electronic microscopy using a Philips XL 30 scanning electron microscope with an operating voltage of 20.0 kV (Philips, Eindhoven, the Netherlands). All samples were mounted on metal stubs, sputtered with gold for conductivity and observed at various magnifications.

2.5. Apparent surface color measurement

Film color was determined by a colorimeter (BYK-Gardner, Columbia, MD, USA). The film samples were placed on a standard white plate ($L^* = 94.63$, $a^* = -0.88$ and $b^* = 0.65$). Color parameters such as L (lightness), a (green-red), and b (blue-yellow) values were determined from the average of eight readings from each sample. The total color difference (ΔE) and whiteness index (WI) of the films were determined as follows:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

$$WI = 100 - \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}} \quad (2)$$

where ΔL, Δa and Δb are the differences between the color of the standard color plate and the film samples.

2.6. Spectrophotometric analyses

Transmission spectra of the bilayer film in the wavelength range of 200–800 nm were measured by a UV–VIS spectrophotometer (Lambda 25, PerkinElmer, Fremont, CA, USA). Each film specimen was cut into rectangles and placed directly in a spectrophotometer test cell, and ambient air was used as reference. Opacity of the bilayer films was evaluated according the method described by Abdollahi, Alboofetileh, Rezaei, and Behrooz (2013). Light absorbance of the bilayer film specimens at 600 nm was used to calculate opacity according the following equation:

$$\text{Opacity} = \frac{\text{Abs } 600}{t} \quad (3)$$

Where Abs600 is a value of absorbance at 600 nm and t is the film thickness (mm). Measurements were performed in at least three replicates.

2.7. Mechanical properties

The mechanical properties of each film sample were measured by analyzing the tensile strength (TS) and elongation at break (EB) according to ASTM standard method D 882-02 (ASTM, 2002) with an Instron Universal Testing Machine (Model A1 700, Gotech, Taiwan). Samples were cut into rectangular strips measuring 2.54 × 10 cm. The initial grip separation was set at 50 mm and crosshead speed at 50 mm/min. Measurements were performed on at least five film specimens.

2.8. Moisture content (MC)

MC of each film sample was measured by drying small specimens of films (2.5 cm × 2.5 cm) in a hot air oven at 105 ± 1 °C for 24 h. Samples were placed on glass Petri dishes that were weighed before and after oven drying. MC values were analyzed in at least triplicate and results were expressed as (g/100 g).