



Modification of physicochemical and thermal properties of starch films by incorporation of TiO₂ nanoparticles



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ABSTRACT

In this research, potato starch and TiO₂ nanoparticles (0.5, 1 and 2 wt%) films were developed. Influences of different concentrations of TiO₂ on the functional properties of nanocomposite films (water-related properties, mechanical characteristics, and UV transmittance) were investigated. XRD, FTIR, and DSC analyses were used to characterize the morphology and thermal properties of the films. The results revealed that TiO₂ nanoparticles dramatically decreased the values of water-related properties (water vapor permeability: 11–34%; water solubility: 1.88–9.26%; moisture uptake: 2.15–11.18%). Incorporation of TiO₂ led to a slight increment of contact angle and tensile strength, and a decrease in elongation at break of the films. TiO₂ successfully blocked more than 90% of UV light, while opacity and white index of the films were enhanced. Glass transition temperature and melting point of the films were positively affected by the addition of TiO₂ nanoparticles. The result of XRD study exhibited that due to a limited agglomeration of TiO₂ nanoparticles, the mean crystal size of TiO₂ increased. Formation of new hydrogen bonds between the hydroxyl groups of starch and nanoparticles was confirmed by FTIR spectroscopy. In conclusion, TiO₂ nanoparticles improved the functional properties of potato starch film and extended the potential for food packaging applications.

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1. Introduction

The demand for sustainable/green packaging is being increased globally in recent decades to keep the environment clean and pollution-free. Therefore, considerable efforts are being made for the production of toxin-free packaging materials from natural resources. Biopolymers such as proteins, fats and carbohydrates have good film formability and exhibit high potential to be used as an alternative to synthetic plastics [1,2]. These bioplastics or green packaging materials contribute to an estimated 5–10% of the current plastic market (about 50,000 t) in Europe [2,3]. A new market research report to states that the global green or sustainable packaging market was valued at US\$ 132.4 billion in 2014 and is predicted to reach US\$ 203.1 billion by 2021 (<http://www.transparencymarketresearch.com>).

Natural polymers are polar materials, therefore, permeability inhibition of nonpolar gases such as oxygen and CO₂ by them, increases the shelf life of fresh products such as fruits and vegetables. Inhibitory to volatile compounds, aroma and oils maintain the quality of the food production and distribution cycle [3].

Starch is one of the raw materials used for food packaging due to its low price, biodegradability and renewability. Starch films have advantages over other biopolymer films. They are stronger than polysaccharides and protein film. Starch films are colorless, transparent or translucent, tasteless and flavorless [4]. Many studies have been reported on starch-based films made from various sources such as corn, wheat and cassava and potato. The amount of phosphorus present in the amylopectin of potato starch (PS) has a negative charge and repulsive little faster because there may be swelling of potato starch granules in hot water and high viscosity, high transparency and it is involved in low retrogradation speed of potato starch pastes [3]. Potato-starch-based films have good transparency at ambient humidity compared to films made with synthetic polymers.

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However, due to the hydrophilic nature of bio-polymeric materials, starch films have some disadvantages such as high permeability to water vapor, weak mechanical properties and high sensitivity to the environmental changes such as humidity, temperature, and pH [5]. Mechanical properties of starch films are influenced by many factors such as source, amylose to amylopectin ratio and preparation methods. In addition, the film plasticizers used to reduce the brittleness of starch films are also reported to weaken the barrier properties [2]. In addition, potato-starch-based films only have limited ability to block light radiation.

Recently, nanotechnology has help to solve these problems. Composite materials containing polymers and nanoparticles can provide high-performance novel materials which find applications in many industrial fields such as food packaging [6]. Nanofillers have large specific surface area and high surface energy, thus they have excellent interfacial interactions in polymer and significantly enhance polymer properties such as mechanical, thermal and barrier properties [7,8].

Metal oxides are often used to extend or improve the functional properties of biodegradable films. Titanium dioxide (TiO₂) is an inert, nontoxic and cheap material with potential activity against a wide variety of microbes, odors, staining, deterioration and allergens due to its photocatalytic activity. In compliance with the recommended safe dosage, TiO₂ has been used extensively in food and cosmetic applications to block light and give a white appearance. Although the incorporation of TiO₂ nanoparticles into biopolymer films such as whey protein isolate [9,10], soy protein isolate [11] and kefiran-whey protein isolate [12] have been reported to improve some physicochemical properties but TiO₂ nanoparticles-reinforced starch films have not been investigated so far. We hypothesized that the application of low-concentration TiO₂ into potato starch film would lead to an improved film hydrophobicity, mechanical, thermal properties and the construction of a bio-polymeric film with UV and water vapor shielding. Therefore, the major objective to undertake the present study was to develop a sustainable potato starch-based nanocomposite film using TiO₂ nanoparticles to enhance their functional properties.

2. Materials and methods

2.1. Materials

Potato starch (20% amylose, 12% moisture) was obtained from Alvand Industry (Hamedan, Iran). Glycerol, calcium sulfate and calcium nitrite were purchased from Merck (Darmstadt, Germany). TiO₂ nanoparticles (80% Anatase and 20% Rutile) were provided by Evonik Degussa GmbH (Germany). The average diameter of the particles (as recorded by the company) was about 21 nm. All other reagents were of analytical grade.

2.2. Preparation of potato starch-TiO₂ nanocomposite films

Pilot experiments indicated that filmogenic solutions containing high concentrations of TiO₂ led to the discontinuity of the film network. Thus, we used lower concentrations of the nanoparticle to achieve films with adequate properties. TiO₂ was dispersed in water at different concentrations (0, 0.5, 1 and 2% of total starch solid), stirred for 4 h, and then sonicated in an ultrasonic bath (USD 4R model, AS ONE, 40 kHz, Japan) for 30 min. Starch film was fabricated by the method described by Almasi et al. [13]. The aqueous starch dispersions at 5% (w/w) were prepared by weighing the amount of starch. They were heated to 90 ± 5 °C and held at this temperature for 30 min to complete the gelatinization process. Upon completion of starch gelatinization, PS-TiO₂ composite film forming solutions were prepared by mixing TiO₂ and the starch

solution. To control the dispersion of TiO₂ nanoparticles in starch polymeric hosts, the addition of TiO₂ nanoparticles suspension was very slow with intense stirring (1000 rpm, 5 min) and sonication in an ultrasonic bath for 30 min. Glycerol (40% w/w starch) as the plasticizer of the film was added to PS-TiO₂ solutions before degassing under vacuum. The solutions were then cooled at room temperature, and a vacuum was applied to remove trapped air bubbles in the solution. 15 g of the filmogenic solution were cast onto a polystyrene petri-dish with 10 cm internal diameter. The films were dried at 60 °C for 15 h in an oven. All films (including control) were prepared in triplicate. Dried films were peeled and stored at 20–25 °C and 55% relative humidity. The thickness of the films was determined using a handheld micrometer (Alton M820-25, China) at 10 random positions and to the nearest 0.01 mm and the average value was used as the film thicknesses. Films specimens of 80 μm thickness were selected for all experiments.

2.3. Water solubility

Solubility in water was defined as the percentage of the dry matter of film, which is solubilized after 24 h of immersion in water [14]. Film specimens (20 × 40 mm²) were dried in a 100 °C oven for 24 h. The same films were then immersed in 50 ml of distilled water at 23 °C for 24 h with periodical gentle manual agitation. The Films were removed from the water and placed back in the oven until they reached a constant weight to obtain the final dry weight of the film. The water solubility of the films was calculated using the following Eq. (1):

$$\text{Water Solubility} = [(\text{initial dry wt} - \text{final dry wt}) / \text{initial dry wt}] \times 100(1)$$

Water solubility test for each type of film was carried out in triplicate. All of the films were conditioned at 55% RH and 23 ± 2 °C inside a desiccator over a saturated solution of CaCl₂ for 48 h before the test.

2.4. Moisture uptake

The moisture uptake of the films was determined according to Sadegh-Hassani and Mohammadi-Nafchi [3]. The test specimens were prepared with the dimensions of 20 × 20 mm². They were dried in a 50 °C oven for 24 h, then cooled in a desiccator, and immediately weighed to obtain the initial weight. The specimens were conditioned in a desiccator containing K₂SO₄ saturated solution at 20–25 °C to ensure a relative humidity of 98%. The samples were removed at desired intervals and weighed until the equilibrium state was reached. The moisture uptake values of the samples were calculated as follows (Eq. (2)):

$$\text{Moisture uptake} = \frac{W_t - W_0}{W_0} \times 100 \quad (2)$$

where W_t and W₀ are the weights of the sample after t time conditioning at 98% RH and the initial weight of the sample, respectively. All measurements were triplicated.

2.5. Water vapor permeability (WVP)

WVP tests were carried out according to the standard ASTM standard method E96-05 [15] with some modifications. Special permeation cells, with an average diameter of 2 cm and a depth of 4.5 cm, were utilized to determine WVP of the films. The films were cut into discs with a diameter slightly larger than that of the permeation cell. After placing 3 g of anhydrous CaSO₄ in each permeation cell, they were covered with the film samples. Relative humidity (RH) of 0 was maintained using anhydrous CaSO₄ in the permeation cell. Each permeation cell was placed in a desiccator

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