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The effects of ultrasonic/microwave assisted treatment on the properties of soy protein isolate/titanium dioxide films

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ABSTRACT

Soy protein isolate (SPI, 5.0 g/100 mL,) films embedded with nano-TiO_2 (0, 0.5, 1.0, 1.5 and 2.0 g/100 mL) were prepared by solution casting and modified by ultrasonic/microwave assisted treatment (UMAT). The effects of nano-TiO_2 content and UMAT time on the films' physical properties and structure were investigated. Incorporation of nano-TiO_2 significantly enhanced films' mechanical properties and barrier properties, because of the intermolecular force between nano-TiO_2 and SPI. UMAT time ≤20 min obviously improved films' tensile strength values (15.77 MPa, 245% higher than the control), and reduced water vapor permeability (1.8457×10^{-11} g cm^{-1} s^{-1} Pa^{-1}, 72.11% lower than the control) and oxygen permeability values (0.8897×10^{-5} cm^3 m^{-2} d^{-1} Pa^{-1}, 57.66% lower than the control). SEM images also revealed a more compact and dense structure of films when UMAT time ≤20 min. Films' water adsorption properties were evaluated. GAB and Henderson models exhibited the best to fit experimental data, thus it was predicted that films (1.5 g nano-TiO_2/100 ml) could be stable at low moisture content (0.27 kg of water/kg dry mass).

1. Introduction

The application of edible coatings and films in the food industry has attracted great attention because of their potentiality for increasing the shelf life of many food products (Nunes et al., 2013; Wu, Zhong, Li, Shoemaker, & Xia, 2013; Zúñiga, Skurtys, Osorio, Aguilera, & Pedreschi, 2012). Edible film is defined as a thin layer of material, which can be eaten as part of the whole product, providing a barrier to mass transfer (moisture, gas, flavors, etc.) between the food and the environment or in the food itself (Broumand, Emam-Djomeh, Hamedi, & Razavi, 2011; Sun, Wang, Kadouh, & Zhou, in press; Wang, Shang, Ren, & Leng, 2010; Zúñiga et al., 2012). In recent years, soy protein isolate (SPI) has attracted great attention due to its biodegradability, biocompatibility, and wide availability (Restuccia et al., 2010; Shao, Yang, Wang, & Luo, 2012; Wang, Zhu, Li, Fu, & Shi, 2012; Wang et al., 2013).

Nevertheless, the use of SPI films was limited because of their inherent water susceptibility and relatively low tensile strength, especially in moisture environment (Broumand et al., 2011; Jiang, Xiong, Newman, & Rentfrow, 2012; Wang et al., 2010).

Since now, nanomaterials have been added to overcome some limitations of biopolymers (George & Siddaramaiah, 2012; Lupoi & Smith, 2011; Zhang, Ma, Guo, & Zhao, 2012), which could improve the polymers' properties and extend their application field (Chen & Mao, 2007; Wang et al., 2012). Among them, titanium dioxide (TiO_2) nanoparticles have been widely studied because they are cheap, nontoxic, and photostable in compliance with the recommended safe dosage. When nano-TiO_2 were incorporated into a polymer matrix such as packaging material, they will provide protection against foodborne microorganisms as well as odor, staining deterioration, and allergens on the presence of radiation of relatively low wavelength near the ultraviolet region (Arora & Padua, 2010; Chen & Mao, 2007). When used in food packaging, nano-TiO_2 could be able to withstand the stress of thermal food processing, transportation, and storage (Arora & Padua, 2010). Regardless, nanoscale fillers still need to be well dispersed in the polymer matrix for better film forming properties.

SPI/TiO_2 (ST) composite films had been prepared and their antibacterial activities were evaluated (Chen & Mao, 2007; Wang et al., 2012). However, ST were inhomogeneous, and their mechanical properties, oxygen permeability and water vapor permeability were not discussed. In our previous studies, ultrasonic/

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microwave assisted treatment (UMAT) was used to modify microcrystalline wheat-bran cellulose (MWC), leading to smaller particle size, larger surface area, and more free hydroxyls on the surface of MWC, thus modified MWC as fillers significantly improved the films' abilities such as water vapor and oxygen barrier; Additionally, UMAT was also used to improve stearic acid and oleic acid integration in SPI matrix (Wang et al., 2013, 2014).

Thus, in this study, UMAT will be used to disperse nano-TiO_2 in SPI matrix and modify films' properties. The effects of nano-TiO_2 content and UMAT on films' physical properties and structure were discussed. Additionally, the stability of films was also evaluated using moisture sorption isotherms and models.

2. Materials and method

Soy protein isolate (SPI, 90%) was purchased from Gushen Biotechnology Group Ltd. (Shandong, China). Titanium dioxide nanoparticles (VK-TA18H, particle size 15–30 nm) were purchased from Hangzhou Wanjing New Material Co., Ltd. (Zhejiang, China). Distilled water was used for all sample preparations. All other chemicals used were analytical grade.

2.1. Film preparation

A solution of SPI (5%, *w*/*v*) was denatured by heating to 80 °C for 30 min, the solution was then cooled and the pH adjusted to 10.0 with 1 mol/L NaOH. Subsequently, glycerol (2%, *v*/*v*) was added into SPI solution and magnetically stirred for 20 min at room temperature (Schmidt, Giacomelli, Soldi, & Soldi, 2005; Shao et al., 2012), and vacuum degassing was conducted to remove trapped air bubbles in the solution. It was demonstrated in our previous studies that excellent SPI films were obtained (Wang et al., 2013). Then, various amounts of nano-TiO_2 (0 g, 0.5 g, 1.0 g, 1.5 g, and 2.0 g) were added into the SPI solution, and the detailed composition could be shown in Table 1. The slow addition and intense stirring could help nano-TiO_2 uniformly disperse into SPI matrices before they aggregate, and form colloid composite with SPI molecules (Chen & Mao, 2007). A volume of 100 mL of film solutions was degassed under a vacuum degassing for 20 min and then cast on square plastic dishes (20×20 cm^2). The dishes were placed on a level surface to obtain films of homogenous thickness. The film solutions were dried in a drying chamber at 50 °C for 7 h. Dried films were peeled-off and conditioned at 50% relative humidity (RH) and 25 ± 1 °C for 48 h prior to testing.

2.2. Ultrasonic/microwave assisted treatment

The prepared films were assessed by determining mechanical properties, oxygen permeability and water vapor permeability. Films which have the highest tensile strength or the lowest oxygen permeability or the lowest water vapor permeability were selected to modify using a microwave and ultrasonic combination reaction system (SL-SM50, Nanjing Shunliu Instruments Co., Ltd, Nanjing, China). In our previous studies, ultrasonic/microwave assisted treatment (UMAT) at 20 °C and 500 W could significantly improve films' properties. Therefore, SPI/TiO_2 (ST) films were treated by UMAT at 20 °C, 500 W for 0 min, 10 min, 20 min, 30 min and 40 min, respectively.

Table 1
Thickness of SPI/TiO_2 (ST) films with different ratio of SPI to TiO_2.

Sample	SPI (g/100 ml)	TiO_2 (g/100 ml)	Glycerol (ml/100 ml)	Thickness (μm)
ST0	5	0	2	180 ± 3a
ST1	5	0.5	2	185 ± 4a
ST2	5	1	2	191 ± 2b
ST3	5	1.5	2	197 ± 4bc
ST4	5	2	2	200 ± 2c

[a–c]For each measurement, the data marked by different letters in a column indicate significant difference ($p < 0.05$).

2.3. Film thickness

Thickness of ST was determined to the nearest 0.01 mm using a micrometer (Mitutoyo Manufacturing, Tokyo, Japan). Measurements were made in at least five random locations on each film. The average was calculated for mechanical properties, water vapor permeability and oxygen permeability.

2.4. Mechanical properties

Mechanical properties of the films, such as tensile strength (TS, MPa) and elongation at break (*E*, %), were determined at 25 ± 1 °C using a Testometric Machine (PARAM XLW (B) Auto Tensile Tester, Jinan, China) according to the ASTM (2001) standard method D882-01. Briefly, films were cut into 120 mm × 15 mm strips. Stripes were equilibrated at 50% RH and 25 ± 1 °C for 48 h in a desiccator using saturated salt solutions of $Mg(NO_3)_2$ prior to further analysis.

The films were fixed with an initial grip separation of 80 mm and stretched at a cross-speed of 50 mm/min. A microcomputer was used to record the strength and elongation data. Tensile strength was calculated as the maximum load on the film before failure divided by the cross-sectional area of the specimen. Elongation was defined as the percent change in specimen length compared to the initial length between the grips. For each film, at least five replicate measurements were performed.

2.5. Water vapor permeability

Water Vapor Permeability Tester (PERME TSY-TIL, Labthink Instruments Co., Ltd, Jinan, China), was used to test the water vapor permeability (WVP, $\times 10^{-11}$ g cm^{-1} s^{-1} Pa^{-1}) of the films according to the ASTM (1994) standard method (E96). The water vapor transmission rates were determined at 25 ± 1 °C and 50% RH using saturated salt solutions of $MgCl_2$ or $Mg(NO_3)_2$. The specimen was fixed to form a sealed environment with 2/3 distilled water in the vessel. Between the two sides of the specimen, water vapor was transmitted through the specimen and entered the drier side. The water vapor transmission rate and transmission coefficient were determined by measuring the weight loss of distilled water over time. For each film, at least five replicates were tested.

2.6. Oxygen permeability

A gas permeability tester (GDP-C) (Brugger Feinmechanik GmbH, Germany), was utilized to test the oxygen permeability (OP, $\times 10^{-5}$ cm^3 m^{-2} d^{-1} Pa^{-1}) of the films according to the ASTM (1995) standard method (D3985-95). Oxygen transmission rates were determined at 25 ± 1 °C and 50% RH using saturated salt solutions of $Mg(NO_3)_2$. The sample was mounted in a gas transmission cell to form a sealed semi-barrier between chambers. One chamber contained O_2 at a specific high pressure and the other, lower pressure chamber received the permeating O_2. The lower pressure chamber was initially evacuated and the transmission of the gas through the test specimen was indicated by an increase in pressure. The O_2 stream was set to 100 ml/min and the oxygen transmission rate (OTR) was recorded. The OP was calculated by multiplying the OTR by the film thickness (FT) then dividing by the partial pressure difference of oxygen (ΔP) as follows: