ARTICLE IN PRESS

Process Biochemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Process Biochemistry

journal homepage: www.elsevier.com/locate/procbio

A novel zein/poly (propylene carbonate)/nano-TiO_2 composite films with enhanced photocatalytic and antibacterial activity

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ARTICLE INFO

Keywords:
Zein
PPC
Nano-TiO_2
Characterization
Photocatalytic activity
Antibacterial activity

ABSTRACT

Composite films were prepared by extrusion technology using zein, poly propylene carbonate (PPC) and nano-TiO_2. The samples were characterized by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR) and mechanical properties experiments. Based on the Halsey equation, the relationship between tensile strength and relative humidity is established to predict the tensibility of the composite films under different humidity conditions. The SEM study revealed that zein and PPC could form a homogeneous network structure and uniform distribution of nano-TiO_2 in films. Furthermore, the composite films presented a good thermal stability. The structural analysis showed that ester groups were major forces responsible for complex formation. In addition, the photocatalytic degradation of methyl orange (MO) followed pseudo first-order kinetics was also investigated, and the removal rate of MO could achieve up to 85.06%. The antibacterial experiment indicated that zein/PPC/nano-TiO_2 film had good activity against the *E. coli*, *S. aureus* and *salmonella*. The obtained results indicated the designed film may be a potential alternative for food packaging.

1. Introduction

Plastic materials play important roles in daily life. However, the solid waste along with their utilization, especially those non-degradable plastic, could lead to the negative impacts on the environment. Therefore, the edible biodegradable films based on naturally renewable biopolymers have attracted more and more attention in the past decades [1]. Zein, a natural polymer, has become an attractive solution to the increasing demand for environment-friendly and biocompatible materials. Many works have intensively investigated materials from regenerated zein films due to their excellent transparency, film forming ability and biocompatibility [2,3]. However, pure zein also exists several disadvantages, such as poor mechanical properties, nano-aggregates self-dissociate and lack antimicrobial activity compared to conventional synthetic polymers and other biopolymers, which results in its bottleneck in packaging application.

Chemical modification or combination with other polymers would be a promising approach to overcome the existing challenge of zein [4,5]. Poly (propylene carbonate) (PPC) is a highly biocompatible, nontoxic synthetic polymer with excellent mechanical properties. It has a promising industrial application potential in many fields because of its film-forming, low permeability, high water resistance and barrier properties (oxygen barrier) [6]. Furthermore, it exhibits strong compatibility with other materials. To expand the application scope of PPC, great efforts have been devoted to improve the thermal, mechanical and barrier properties by incorporating it into other polymers [7,8]. Our preliminary experimental results showed that PPC can be also used to increase the mechanical properties for zein. However, zein/PPC based films have limited application in functional packaging due to the weak antibacterial activity. Thus, improving the antibacterial activity of zein/PPC based composite films is significant.

Among the inorganic nanoparticles, titanium dioxide (TiO_2) has been considered as an effective antibacterial agent that exhibits excellent photocatalytic properties along with biological and chemical inertness, high oxidizing power, and longer chemical stability [9]. It has been approved that TiO_2 can be used in human food or compounded in food contact materials at a low nanoparticle dose [10,11]. In photocatalysis, a semiconductor material interacts with light of sufficient energy to generate reactive oxygen species (ROS), which has been shown to be capable of killing a wide range of organisms, including Gram-negative and Gram-positive bacteria [12]. Due to its enriched properties, TiO_2 can act as a suitable thin film coating on implant devices which could help in preventing the bacterial adhesion [13]. Bactericidal and fungicidal function of TiO_2 on *Escherichia coli* (*E. coli*),

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https://doi.org/10.1016/j.procbio.2018.03.029
Received 6 November 2017; Received in revised form 28 March 2018; Accepted 28 March 2018
1359-5113/

Please cite this article as: Li, S., Process Biochemistry (2018), https://doi.org/10.1016/j.procbio.2018.03.029

Staphylococcus aureus (*S. aureus*), *Pseudomonas aeruginosa and Penicillium expansum* have been reported [14,15].

To the best of our knowledge, few studies have been conducted on the preparation and characterizations of antibacterial composite films based on zein/PPC/nano-TiO_2. The objective of this study was to explore the feasibility of producing photocatalytic and antibacterial zein/PPC film by incorporating with TiO_2 nanoparticles. Characterization, structural analysis, photocatalytic and antibacterial activity of zein/PPC/nano-TiO_2 were investigated.

2. Material and method

2.1. Chemicals and reagents

Zein, regular grade, was obtained from Gaoyurixing Industries Inc. (Jiangsu, China). Anatase TiO_2 nanoparticles with the crystalline size of 18 nm and the specific surface area of 60 m^2/g were purchased from Xuancheng gold Ruixin Material Co. Ltd. (Anhui, China). PPC was obtained from Tianguan Industries Inc. (Henan, China) with a molecular weight of 10000. Other chemicals were achieved from Tianyi Inc. (Tianjin, China). The reagents and solvents were analytical grade and used as received. The microorganisms (such as *E. coli, salmonella* and *S. aureus*) used in this study were obtained from Tianjin University of Science and Technology (Tianjin, China) and were stored at 4 °C before use.

2.2. Preparation of composite films

The composite films preparation route of current work can be referred to our previous work, which is a modified version of zein/propylene carbonate films [16]. The formation process of zein/PPC/nano-TiO_2 films was shown in Fig. 1. PPC was dissolved in pure acetone (PPC: acetone = 1:10 w/v) and heated to 80 °C on a stir plate to make sure PPC was totally dissolved. After zein was completely dissolved in 80% ethanol, glycerin (20%) and nano-TiO_2 (0.5%) were dispersed into solution. Then, it was mixed with PPC solution (25%), heated to 80 °C and adequately stirred. Finally, the zein/PPC/nano-TiO_2 solution was coated on OHP plastic-sheet base and extruded to film with a thickness of 0.06–0.08 mm. The samples were dried at 55 ± 2 °C in a drying oven and the properties of dried films were tested.

2.3. Mechanical properties

Film tensile strength (TS) and breaking elongation (BE) were measured by an electronic universal testing machine (RGF5, China). The tensile rate of film (33 mm × 6 mm) was set at 20 mm/min. Five groups of repeated trials were averaged for each sample.

2.4. Equilibrium moisture content

The Equilibrium moisture content (EMC) test was conducted according to DIN EN ISO 12271 standard method [17]. Five kind saturated salt solutions (LiCl, MgCl2, K2CO3, NaCl and KNO3) were placed in the closed boxes. The boxes were placed at 23 ± 1 °C to form different relative humidity levels (11%, 32%, 53%, 75%, 93%). For each recipe and humidity level, three samples (110 mm × 10 mm) of the same materials were used as replicates. The climate conditions inside the box were monitored by the combined T/RH sensors. After one week, when relative humidity inside the box became a constant, the samples were weighed and the moisture contents were calculated.

2.5. Water absorption capacity

Film samples (40 mm × 10 mm) dried in desiccators were weighed (± 1.0 mg) in glass dishes. The water absorption capacity (WAC) measurement of designed film was carried out through soaking the samples in 500 mL of deionized water, and then monitoring the weight of samples after 24 h. The details were described as follows: the samples were taken out from the deionized water for 30 s and dried with gauze. Triplicate trials of WAC were obtained for each type of film with individually prepared films as replicated experimental units. The WAC was calculated by the following equation.

$$WAC = \frac{W_2 - W_3}{W_1} \tag{1}$$

where W_1 was the dry mass of the sample (g) before absorbing water, W_2 was the mass (g) of the sample after absorbing water, W_3 was the mass (g) of the sample dried for 24 h at 50 °C after absorbing water.

2.6. Scanning electron microscopy

The morphology of the films was examined under a Quanta 200 scanning electron microscope (Philips-FEI Co., AMS, The Netherlands) with an accelerating voltage of 20 kV. Prior to the observation, the sample was placed on the sample table with conductive adhesive and coated with a thin film of gold (Au) under vacuum.

2.7. Thermal properties

The films were subjected to thermal analysis using differential scanning calorimeter (Shimadzu DSC-60A, Japan). A portion of the films (7–10 mg) was hermetically sealed in aluminum pans, heated up from room temperature to 300 °C and put in the nitrogen flow of 60 mL/min. The heating rate was kept constant at 10 °C/min. Empty aluminum pan was used as the control.

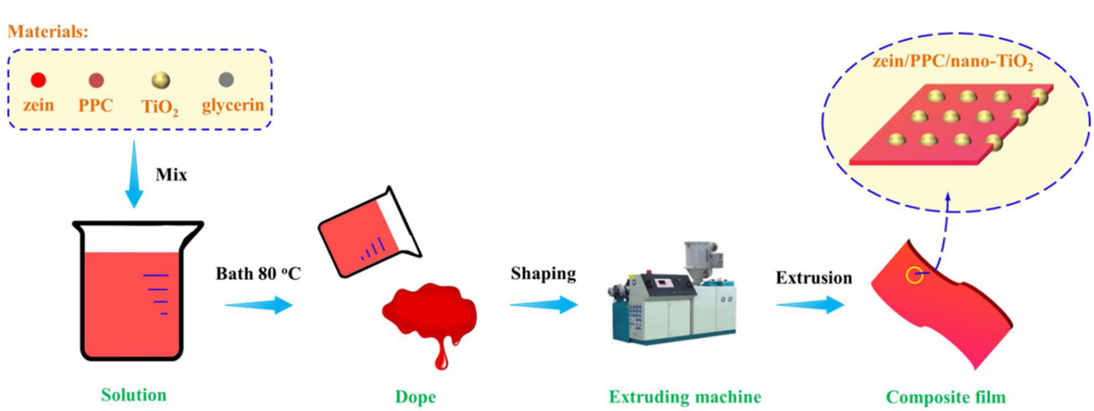

Fig 1. The formation process of zein/PPC/nano-TiO_2 films.