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Preservation properties of *in situ* modified $CaCO_3$–chitosan composite coatings

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ABSTRACT

To improve the dispersibility, hydrophilia constraints of primitive particle size, and reduce the economic cost, *in situ* modified $CaCO_3$–chitosan composite coatings were prepared by tape-casting with different modifiers. The coating structures were characterised, and the preservation properties of the coatings were evaluated by fresh indices of *Sciaenops ocellatus*. The results revealed that the coatings were homogeneous and compact when the *in situ* modifier was sodium stearate. Besides, the amide I group of chitosan disappeared and hydrogen bonds were formed between the nano-$CaCO_3$ and the chitosan. Meanwhile, the preservation effects to *S. ocellatus* of the coatings modified *in situ* by sodium stearate and sodium citrate were better. This was because the coatings effectively prevented oxygen and bacteria from reaching *S. ocellatus*, and thus inhibited the degradation of the proteins and lipids. The *in situ* modified method is conducive to chitosan coating properties, which will be widely used in the food preservation field.

1. Introduction

Green consumerism advocates the rapid development of the food industry. The preservation of seafood varies from the traditional methods such as chilled storage, the addition of chemical additives, to controlled atmosphere packing (Kanatt, Rao, Chawla, & Sharma, 2013; Lerasle et al., 2014; Mohan, Ravishankar, Lalitha, & Srinivasa Gopal, 2012). Besides, many new methods for rendering antimicrobial activities have been used, such as ozone treatment, ionising radiation and biochemical agents, including nisin, essential oils, and gelatin hydrolysate, among others (Bono & Badalucco, 2012; Gao et al., 2014; Kittiphattanabawon, Benjakul, Visessanguan, & Shahidi, 2012; Singh & Pal, 2009). However, low-cost, high-efficiency, practical means are the main corporate aims for any seafood storage.

Chitosan (poly β-1,4-amino-2-deoxy-D-glucopyranose) is derived from chitin by chemical deacetylation and is the second most abundant natural polymer after cellulose (Fernández-Saiz, Sánchez, Soler, Lagaron, & Ocio, 2013; Mathew, Brahmakumar, & Abraham, 2006). Moreover, chitosan has been a focus for research attention because of its non-toxic, biodegradable, and biocompatible cationic polysaccharide nature (Aider, 2010; Elsabee & Abdou, 2013; Shahidi & Abuzaytoun, 2005). Chitosan coatings are widely applied in food-packing for their superior film-forming capability and antimicrobial properties against *Serratia marcescens* (Chen, Jin, Gurtler, Geveke, & Fan, 2012; Leleu et al., 2011), *Escherichia coli* (Celis, Azocar, Enrione, Paez, & Matiacevich, 2011; Kong et al., 2008; Li et al., 2010), *Pseudomonas aeruginosa*, *Staphylococcus aureus* (Fernandez-Saiz, Soler, Lagaron, & Ocio, 2010; Qi, Xu, Jiang, Hu, & Zou, 2004), *Listeria monocytogenes* (Fernandez-Saiz et al., 2010; Sun, Wang, Kadouh, & Zhou, 2014), etc. However, the main drawbacks of chitosan coating are its water solubility and fragility. It is essential to composite additives to improve its properties so as to maintain coating integrity and its barrier properties.

Nano-composite coatings comprise organic coatings and nanometric particles, which can improve the properties of the coatings, such as their mechanical properties, barrier properties, and antibacterial activities (Xu, 2008).

Nano-SiOx, ZnO, TiO_2, and Ag, or their mixtures are the most commonly added materials in such coatings. Nano-SiOx could significantly reduce the water vapour transmission and extend the shelf-life of Huang-guan pears (Feng, 2010). As described by Li, Deng, Deng, Liu, and Li (2010), CS/Ag/ZnO maintained the initial colour of chitosan and had a higher antimicrobial activity than CS/Ag and CS/ZnO. Tao (2011) reported that nano-TiO_2/chitosan coatings have higher values of CO_2-permeability and lower O_2-permeability, while the transmittance of the chitosan composite membrane was lower than the blank group. The properties of

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composite coatings can be improved by addition of nanometric particles. However, the effect of modification faces primitive particle size, dispersibility and hydrophilia constraints. Nano-$CaCO_3$ is widely used as an inorganic nano-material for its non-toxicity, ease of synthesis, and low cost. It is available for the improvement of chitosan coatings. However, nano-particle agglomeration occurred in the traditional method, and the coating properties were affected by the original size of the nano-particles used: *in situ* modification is a new approach to solve these problems. Compared with the other composite coatings, the *in situ* modifications method omitted many steps, such as the synthesis, desiccation and modification of the nano powders before adding into the coatings. So the procedure can be simplified, what's more, the economic cost can be reduced.

Here, *in situ* modification nano-$CaCO_3$–chitosan coatings were synthesised from a nano-$CaCO_3$ suspension with different modifiers, meanwhile *Sciaenops ocellatus* was chosen to examine the preservation properties of nano-composite coatings.

2. Materials and methods

2.1. Materials

Chitosan was purchased from Shanghai Crystal Pure Biological Technology Co., Ltd (China) with a deacetylation degree of 95% and the molecular weight of 200 kDa. Sodium stearate, sodium polyacrylate, sodium citrate, citric acid, quick lime, acetic acid, and glycerol were all of analytical grade and commercially available. Deionised water with a conductivity of less than 0.5 μS/cm was used to prepare all the solutions.

2.2. Preparation of in situ modified $CaCO_3$–chitosan composite coatings

2.2.1. Preparation of in situ modified $CaCO_3$ solution

Ten grams of quick lime and 1000 ml deionised water were mixed and aged at 80 °C for 30 min, and then stood overnight. After the addition of different *in situ* modifiers to the supernate, a gaseous mixture of air and CO_2 was driven off until the pH was 10.3, and the ratio of air to CO_2 was 5:1 (v/v). The modification conditions were 80 °C for 40 min except for citric acid which was used at 30 °C.

2.2.2. Preparation of chitosan coating solution and in situ modified $CaCO_3$–chitosan coating solutions

Firstly, 1.5% (m/v) chitosan was dissolved in 2% (v/v) acetic acid at 40 °C to prepare the chitosan coating solution. Secondly, the *in situ* modification $CaCO_3$ solution was mixed with the chitosan solution at 40 °C, and the *in situ* modification $CaCO_3$–chitosan solution was thus prepared. The solutions were treated by ultrasonication at a frequency of 53 kHz, an applied power of 224 W, at 30 °C, for 15 min. Then 40 ml of the composite coating solution were poured onto an acrylic board (20 cm × 20 cm) and dried at 30 °C for 12 h. The coatings were stored in a desiccator before further use.

2.3. Physico-chemical property measurement

2.3.1. Mechanical properties

Mechanical properties including tensile strength (*Ts*) and elongation at break (*EB*) were determined according to ASTM standard methods (ASTM, 2002) with little modification. Three coatings (25 mm × 70 mm) were tested by texture analyser (TA-XT-PLUS (SMS)) with a load cell of 20 kg. The initial grip gap between the clamps was 40 mm and the cross-head speed was 2.0 mm/min. The values of *TS* and *EB* were calculated as follows:

$$Ts = \frac{F}{S}$$

$$EB\% = \frac{l_1 - l_0}{l_0} \times 100$$

where, *Ts* is the tensile strength (MPa); *F* is the maximum force at rupture (N); *S* is the cross-sectional area of the initial film (mm^2); *EB%* is the percentage elongation at break; l_1 is the elongation at break (mm); and l_0 is the initial distance between the baselines (mm).

2.3.2. Water-vapour permeability (WVP)

WVP was determined following the method of Zhao (2005). The coatings were sealed onto the measuring flasks containing distilled water by using elastic bands: each flask had a diametre of 4 cm and a height of 2.5 cm. These cells were placed in a desiccator at 30 °C, and weighed at 12 hourly intervals for 3 days. The *WVP* was calculated as follows:

$$WVP = \frac{\Delta m}{A \times t}$$

where, *WVP* is the water vapour permeability g/(h m^2); Δm is the mass change over time (g); *A* is the coating area (mm^2); and *t* is the drying time (h).

2.3.3. CO_2 and O_2 permeability

The test was designed by the authors to evaluate the permeability to CO_2 and O_2 according to Chinese Standard GB 1038-70. A large, gas-tight, plastic case was used as the circulation cell: it was provided with both an air inlet and outlet. Three small cylindrical plastic pipes with one open end were used as measuring cells. Besides, rotameters and an O_2/CO_2 detector were used to examine the percentage of CO_2 and O_2 in both circulation and measuring cells.

The coatings were sealed onto the open ends of each measuring cell, and the measuring cells were sealed within a circulation cell. A gaseous mixture of CO_2/O_2 and air was circulated for 5 min, and then the air inlet and outlet were sealed. After 2 min, 50 ml gas were extracted from the circulation cell and discarded, then the other 50 ml of gas were imported to the O_2/CO_2 detector to measure the percentage of CO_2 and O_2. After that, the 50 ml of gas were extracted from the measuring cells, and its percentage of CO_2 and O_2 measured. CO_2 and O_2 permeabilities were calculated as follows:

$$CDP = \frac{V_{CO_2} \times d}{A \times \Delta P} \qquad OP = \frac{V_{O_2} \times d}{A \times \Delta P}$$

where, *CDP* is the carbon dioxide permeability, *OP* is the oxygen permeability (ml mm/(cm^2 d kPa)); V_{CO_2} is the volume of CO_2 permeating the coatings in 24 h, (ml/d); V_{O_2} is the volume of O_2 permeating the coatings in 24 h (ml/d); *A* is the effective area of the coatings (cm^2); and ΔP is pressure differential between the circulating cell and measuring cell (kPa).

2.3.4. Coating transparency

The transparency of the coating was measured by the method described by Xu (2008). An ultraviolet spectrophotometer was used to determine the light transmittance at a wavelength of 450 nm by placing the rectangular coating samples thereon. The coating transparency (*T*) was calculated as follows:

$$T = T_{450} \times d$$