



Fabrication of bio-nanocomposite films based on fish gelatin reinforced with chitosan nanoparticles



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ABSTRACT

The paper focuses on the synthesis of chitosan nanoparticles (CSNPs) by ionic gelation between chitosan (CS) and sodium tripolyphosphate (TPP) and subsequently its use as filler in a fish gelatin (FG) matrix to produce bio-nanocomposite films. The obtained particles exhibited a spherical shape with size range of 40–80 nm, and a positively charged surface with a zeta potential value of +10 mV. XRD results confirmed the cross-linking reaction between CS and TPP. SEM images showed that CSNPs could be well dispersed in FG polymer matrix at low content, while higher CSNPs loadings (8%, w/w) resulted in the aggregation of particles in the composites. FTIR spectroscopy results confirmed the interaction between CSNPs and FG through hydrogen bonding. The nucleating effect of the CSNPs was confirmed by DSC analysis. Results indicated that the addition of CSNPs caused remarkable increase in the tensile strength (TS) and elastic modulus (EM), which leading to stronger films as compared with individual FG films, but decreased the elongation at break (EAB). Furthermore, addition of CSNPs contributed to the significant decrease ($p < 0.05$) of water vapor permeability (WVP), leading to a 50% decline at 6% (w/w) filler. The light barrier measurements presented low values of transparency at 600 nm of the FG-based nanocomposite films, indicating that these films are very transparent (lower in transparency value) while they have excellent barrier properties against UV light. The results presented in this study show the feasibility of using bio-nanocomposite technology to improve the properties of biopolymer films based on FG.

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1. Introduction

Increasing and widespread environmental awareness, as well as efforts to reduce the volume flow of wastes and increase the use of renewable raw materials have placed emphasis on the disposal properties of different materials (Endres & Siebert-Raths, 2012). The non-degradable and non-renewable nature of plastic packaging has led to a renewed interest in packaging materials based on biopolymers derived from renewable sources. The use of biopolymer-based packaging materials can solve the waste disposal problem to a certain extent (Kumar, Sandeep, Alavi, Truong, & Gorga, 2010). The increasing interest in biopolymer based packaging has resulted in the development of protein-based films from soy protein, whey protein, casein, collagen, corn zein, gelatin, and wheat gluten (Cuq, Gontard, & Guilbert, 1998). Among all the

protein sources, gelatin has also been extensively studied for its film forming capacity and applicability as an outer covering to protect food against drying, light and oxygen (Gómez-Guillén et al., 2009).

Fish gelatin (FG) has gained great interest in recent years as the demand for non-bovine and non-porcine gelatin has increased, due to religious and social reasons, and also the bovine spongiform encephalopathy (BSE) crisis (Bae et al., 2009). Furthermore, fish skin, which is a major byproduct of the fish-processing industry, causing waste and environmental pollution, could provide a valuable source of gelatin (Badii & Howell, 2006). The elaboration of edible films from fish gelatin has been recently studied (Gómez-Estaca, Gómez-Guillén, Fernández-Martín, & Montero, 2011; Hosseini, Rezaei, Zandi, & Farahmandghavi, 2013; Núñez-Flores et al., 2012; Nur Hanani, Roos, & Kerry, 2012).

However, these biodegradable fish gelatin films do have some limitations in their use, such as low tensile strength (TS) and high water solubility (Gómez-Estaca et al., 2011). In order to improve the mechanical property as well as barrier characteristic of gelatin films, recently, a new class of materials namely bio-nanocomposites

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(biopolymer matrix reinforced with nanoparticles) has introduced as a promising option (Bae et al., 2009). Fillers with at least one nano-sized dimension (nanofillers or nanoreinforcements) have better interfacial adhesion with the polymer matrices, when compared to the respective micro/macroscale reinforcements. A uniform dispersion of nanofillers leads to a very large matrix/filler interfacial area, changing the molecular mobility, improve the relaxation behavior, and the consequent thermal and mechanical properties of the resulting nanocomposite (Ludueña, Alvarez, & Vasquez, 2007). Nanocomposite technology using nanofillers such as carbon nanotubes (CNTs) (Ma, Yu, & Wang, 2008), nanoclay (Bae et al., 2009; Casariego et al., 2009), and nanosilica (Ahmed, Varshney, & Auras, 2010) has already proved to be an effective way to improve the mechanical, physical, and thermal properties of polymers. Newly, considering the applications for edible films and/or food packing, much attention has been focused on polysaccharide nanofillers. Chitosan (CS) is a naturally occurring nontoxic, biocompatible, biodegradable, and cationic polysaccharide (Shahidi, Arachchi, & Jeon, 1999).

Chitosan nanoparticles (CSNPs) which are composed of a natural material with excellent physicochemical properties, is environmentally friendly, and bioactive (Yang, Wang, Huang, & Hon, 2010). CSNPs can be prepared by the electrostatic interaction and resultant ionotropic gelation between CS polycation and sodium tripolyphosphate (TPP) polyanion (Calvo, Remunán-López, & Vila-Jato Alonso, 1997; Yang et al., 2010). Using of these nanoparticles in edible films would be very promising, due to the food-grade properties of both components. De Moura et al. (2009) found that CS-TPP nanoparticles increases thermal and mechanical properties and decrease water vapor permeability of the hydroxypropyl methylcellulose (HPMC) films. In another study, these polysaccharide nanoparticles have been used as the reinforcing medium in glycerol plasticised-starch (GPS) matrices (Chang, Jian, Yu, & Ma, 2010). They have obtained an improvement of thermal stability, mechanical and barrier properties of GPS composites. More recently, Martelli, Barros, De Moura, Mattoso, and Assis (2013) was also reported that the incorporation of chitosan nanoparticles promoted noticeable improvement of the mechanical properties and acted in reducing the water vapor permeation rate in banana puree films.

Hence, bio-nanocomposite films based on FG and CSNPs could be a good candidate for food packaging applications to extend the shelf life of foods and products. This research focused on fabrication and characterization of CSNPs as well as evaluation of the effects of incorporation of obtained nanoparticles on morphology, mechanical properties, water vapor permeability, light barrier properties, and thermal behavior of FG films.

2. Materials and methods

2.1. Materials

Gelatin from cold water fish skin, chitosan (CS) (medium molecular weight, 75–85% deacetylated) and sodium tripolyphosphate (TPP) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Glycerol (analytical grade) and acetic acid were purchased from Merck Chemicals Co., (Darmstadt, Germany).

2.2. Preparation of chitosan nanoparticles (CSNPs)

CSNPs were prepared based on the ionotropic gelation between CS and TPP with some modifications (Calvo et al., 1997). CS solution (1% (w/v)) was prepared by agitating chitosan in an aqueous acetic acid solution (1% (v/v)) at ambient temperature (23–25 °C) overnight. The mixture was then centrifuged at 9000 rpm for 30 min;

the supernatant was separated and filtered through 1 µm pore size filters. TPP solution (0.4% (w/v)) was added (weight ratios of CS: TPP was 2.5:1) drop wise to CS solution under vigorous stirring for 40 min. The formed particles were collected by centrifugation at 9000 rpm for 30 min at 4 °C, and subsequently washed several times with deionized water. Finally, ultrasonication (50 w) was applied by a sonicator (Bandelin sonopuls HD3200, KE 76 probe, Germany) in an ice bath for 4 min with a sequence of 0.7 s of sonication and 0.3 s of rest, resulting in a homogeneous suspension. The suspensions were immediately lyophilized at –35 °C for 72 h using freeze dryer (GAMMA 1-16 LSC, UK).

2.3. Bio-nanocomposite film preparation

The gelatin films were prepared according to the method described by Gómez-Estaca et al. (2011) with slight modifications. The FG solution was prepared by dissolving 4 g gelatin in 100 ml distilled water for 30 min and then heated at 45 °C for 30 min under continuous stirring. Glycerol (0.3 g/g gelatin) was added as a plasticizer and solutions were again warmed and stirred at 45 °C for 15 min. For the preparation of bio-nanocomposite film forming dispersions, different levels of CSNPs (0, 2, 4, 6 and 8%, w/w), based on dry FG was first dispersed into distilled water (50 ml) and then sonicated for 10 min. Then, the CSNPs suspension were added to FG solution (50 ml) drop wise and gently stirred for 60 min. The film-forming dispersions were degassed under vacuum for 15 min to remove air bubbles. Finally, aliquots of 100 g of film-forming dispersions were poured in rectangular plastic dishes (24 × 12 cm) and dried at ambient temperature (23–25 °C) for 3 days. Dried films were peeled from the plate and conditioned at 25 °C and a relative humidity (RH) of 50 ± 4% RH for 48 h for further analysis.

2.4. Characterization of CSNPs and bio-nanocomposite films

2.4.1. Atomic force microscopy (AFM)

Atomic force microscope (DualScope™ DS95-50, DME, Denmark) was used for morphological characterization and nanoparticles size determination. A drop of diluted nanoparticle suspension (0.05 mg/ml) was spread on the clean glass surface, and dried at room temperature. The image measurement was performed in tapping mode using silicon probe cantilever of 230 micron length, resonance frequency of 150–190 kHz, spring constant of 20–60 N/m and nominal, 5–10 nm tip radius of curvature. The scan rate was used as 1 Hz.

2.4.2. Particle size and zeta potential

The mean particle size, particle size distribution and zeta potential of the nanoparticle suspension were obtained using a Zetasizer Nano ZS 3300 (Malvern Instruments Ltd., United Kingdom) on the basis of dynamic light scattering (DLS) technique. Diluted samples were placed in glass cuvette with square aperture and the scatter intensity was measured at 25 °C.

2.4.3. X-ray diffraction

XRD patterns of CS powder and CSNPs were recorded over a 2θ range of 5–50° using an X-ray diffractometer (Siemens, model D5000) with a step angle of 0.04°/min.

2.4.4. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of CS powder, CSNPs and bio-nanocomposite films were recorded from wavenumber 400–4000 cm⁻¹ by a Bruker Equinox 55 spectrometer (Bruker Banner Lane, Coventry, Germany). For CS powder and CSNPs, samples were prepared using KBr to form pellets. For each spectrum, 16 scans at a resolution of 4 cm⁻¹ were obtained.

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