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Development and properties of new chitosan-based films plasticized with spermidine and/or glycerol

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ABSTRACT

Different chitosan solutions were characterized by evaluating zeta potential and particle size, in the absence or presence of spermidine and/or glycerol, and the physicochemical, morphological and antimicrobial properties of the derived films were determined. An increase of film tensile strength and elongation at break was observed by increasing chitosan amounts, whereas only tensile strength and Young's modulus values were revealed higher at all chitosan concentrations when spermidine was absent. Spermidine-containing films were always more extensible exhibiting an elongation at break even higher than that of glycerol-plasticized films. The concurrent presence of appropriate concentrations of spermidine and glycerol further enhanced the extensibility and plasticity of the biomaterial, conferring to it the ability to be heat-sealed, as well as similar permeability in comparison with Viscofan NDX, widely commercialized as protein-based food casing. Finally, all the prepared films exhibited a clear antimicrobial activity, thus representing credible candidates as food preservative coatings and/or wrappings.

1. Introduction

Chitin is the second most abundant biopolymer occurring in nature after cellulose and chitinous waste, mainly produced from sea food processing (crustacean shells), still represents a major environmental issue (Arbia, Arbia, Adour, & Amrane, 2013).

Chitin is not soluble in common solvents, mostly due to its highly cristalline structure, and this property strongly limits the possible re-use of the polysaccharide. Nevertheless, one possible recycling of chitin rich wastes involves the chemical conversion of chitin in chitosan (CH), a random copolymer formed by D-glucosamine and *N*-acetyl-D-glucosamine units, by alkaline deacetylation at high temperatures (Muxika, Etxabide, Uranga, Guerrero, & de la Caba, 2017). Although various factors (e.g. chitin source, alkali concentration, deacetylation temperature and time) may affect its properties, CH (pKa, 6.3) is easily dissolved in acidic solutions, i.e. when its free amino groups are fully protonated (Aljawish, Chevalot, Jasniewski, Scher, & Muniglia, 2015; Babu, O'Connor, & Seeram, 2013; Kaur & Dhillon, 2014; Van den Broek, Knoop, Kappen, & Boeriu, 2015).

The unique physicochemical and biological features of CH make it worthy in regard to various biomedical, pharmaceutical and agricultural applications. Moreover, because of CH broad antibacterial and antifungal properties, CH-based edible films may be promoted as promising "new economy" bio-based plastics (Spierling et al., 2018) also for food coating and protection in addition to the protein-based biomaterials (Han, Yu, & Wang, 2018). In fact, although CH-based films exhibit weak mechanical properties, as well as unsatisfying water vapor (WV) barrier features, they remain the most promising ones among the various hydrocolloid biomaterials so far proposed, because they are biodegradable, biocompatible, non-toxic and obtainable in large quantities from waste products of seafood industries (crustacean shells) (Elsabee & Abdou, 2013; Mayachiew & Devahastin, 2008; Van der Broek et al., 2015). In addition, CH has been considered as a GRAS (Generally Recognized As Safe) food additive for both consumers and the environment (FDA, 2012).

Several advantages have been demonstrated when different food

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products were CH-coated. CH was shown to be able to form a semi-permeable layer on the surface of various fruits and vegetables, and to delay the rate of respiration and their ripening by reducing food moisture and weight loss (Alvarez, Ponce, & Moreira, 2013; Chofer, Sanchez-Gonzalez, Gonzalez-Martinez, & Chiralt, 2012; Gol, Patel, & Rao, 2013; Sun et al., 2014). Moreover, edible CH films have also been used as carriers releasing different bioactive agents like essential oils, as well as antimicrobials and/or antioxidants (Acevedo-Fani, Salvia-Trujillo, Rojas-Graü, & Martín-Belloso, 2015; Avila-Sosa et al., 2012), and to protect fish, red meat, poultry and their processed products, with the aim to decrease color changes, lipid oxidation, growth of pathogenic and spoilage bacteria and to extend product shelf life (Chamanara, Shabanpour, Khomeiri, & Gorgin, 2013; Gómez-Estaca, De Lacey, López-Caballero, Gómez-Guillén, & Montero, 2010; Samelis, 2006).

Many different attempts have been made to improve mechanical, barrier and functionality properties of CH films by blending CH film forming solution (FFS) with other biopolymers like proteins (Baron, Pérez, Salcedo, Córdoba, & Sobral, 2017; Di Pierro et al., 2007, 2006; Escamilla-García et al., 2017). A further way to modify the physicochemical characteristics of the hydrocolloid edible films, and for a subsequent breakthrough in their applications, is the addition of appropriate concentrations of a suitable plasticizer. Generally, plasticizers are added to both synthetic and bio-based polymeric materials to decrease the intermolecular forces along the polymer chains, impart flexibility and lower the glass transition temperature (Mekkonen, Mussone, Khalil, & Bressler, 2013; Vieira, Altenhofen da Silva, Oliveira dos Santos, & Beppu, 2011). Our recent studies have shown that aliphatic polyamines, in particular the triamine spermidine (SPD), are able to influence the morphological, mechanical and barrier properties of pectin- and protein-based films (Esposito et al., 2016; Porta, Di Pierro, Roviello, & Sabbah, 2017). In addition, the combination of different concentrations of both SPD and glycerol (GLY) may give rise to protein-based biomaterials possessing a wide spectrum of functional characteristics (Porta et al., 2017; Sabbah et al., 2017). Since Chanphai and Tajmir-Riahi (2016) recently reported the conjugation of CH nanoparticles with biogenic polyamines SPD and spermine in aqueous solution, we were stimulated to analyze the physicochemical and biological properties of CH-based films by incorporating various SPD and GLY proportions into the host polysaccharide matrix. Based on the present investigation, it is expected that the addition of both plasticizers to polymeric matrix can bring about improved features of the CH films in such a way that a new polysaccharide-based biomaterial can represent a valid alternative to gelatin-based films, such as the well commercialized Viscofan (www.viscofan.com) widely used for food wrapping. In fact, gelatin is one the most controversial of kosher and halal food ingredients and it seems advisable to replace it according to the religion-based dietary restrictions of Muslim and Jewish consumers and the consequent negative impact in their marketplace (Regenstein, Chaudry, & Regenstein, 2003).

2. Materials and methods

2.1. Materials

CH (mean molar mass of 3.7×10^4 g/mol) with a degree of 9.0% *N*-acetylation, was a gift from Prof. R.A.A. Muzzarelli (University of Ancona, Italy). The mean molar mass of CH was determined by a viscometric method, as previously described (Costa, Teixeira, Delpech, Sousa & Costa, 2015), by dissolving 0.2 g of CH in 10 mL of 0.1 M acetic acid, containing 0.2 M sodium chloride, and obtaining five different dilutions of the original solution. The degree of *N*-acetylation was determined by the first derivative ultraviolet spectrophotometric method, as described by Muzzarelli and Rocchetti (1985), based on recording of the first derivative of the CH UV spectra at 202 nm by using a standard curve obtained by varying *N*-acetylglucosamine concentrations. Citrus peel low-methylated (7.0%) pectin (Aglupectin USP) was purchased from Silvateam srl (San Michele Mondovi, CN, Italy). Viscofan NDX edible casings were from Naturin Viscofan GmbH (Tajonar-Navarra, Spain). GLY (about 87%) was supplied from the Merck Chemical Company (Darmstadt, Germany), whereas SPD was from Sigma Chemical Company (St. Louis, MO, USA). All other chemicals were analytical grade.

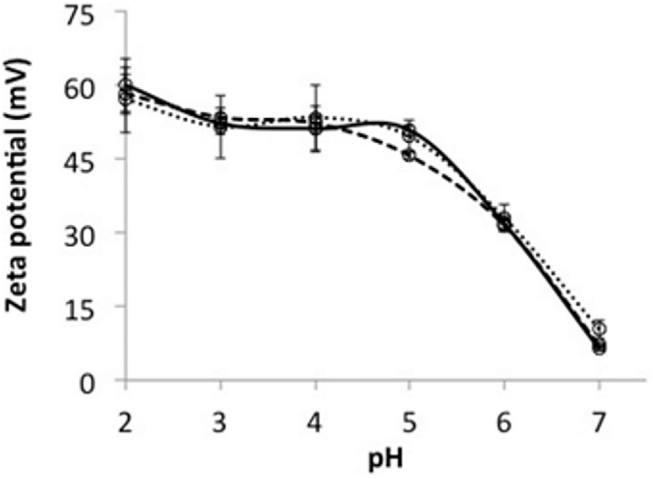

Fig. 1. Effect of either 5 mM SPD and/or 25 mM GLY on zeta potential of 0.2% CH FFSs measured at different pH values. The different FFSs contained only CH (solid line), CH + SPD (point line), CH + GLY (dashed line). The results are expressed as mean ± standard deviation. Further experimental details are given in sections 2.2 and 2.5.

2.2. Titration of CH FFSs

Zeta potential values of different CH solutions (0.2% CH containing or not 5 mM SPD and/or 25 mM GLY) were determined by a Zetasizer Nano-ZSP (Malvern®, Worcestershire, UK) equipped with an automatic titrator unit (MPT-2). The device was equipped with a helium-neon laser of 4 mW output power operating at the fixed wavelength of 633 nm (wavelength of laser red emission). The instrument software programmer calculated the zeta potential through the electrophoretic mobility by applying a voltage of 200 mV using the Henry equation. CH FFSs were prepared at pH 2.0 by using 1.0 N HCl and then the titration was carried out from pH 2.0 to pH 7.0 by adding 1.0, 0.5, and 0.1 N NaOH as titrant solutions under constant stirring at 25 °C. Zeta potential values were measured at each pH in triplicate.

2.3. CH FFS and film preparation

CH stock solution (2%) was prepared by dissolving the polysaccharide in 0.1 N HCl at room temperature under overnight constant stirring at 700 rpm (Di Pierro et al., 2006). FFSs and films were obtained at pH 4.5 by using CH (0.1–0.6%) mixed or not with different concentrations of SPD (2–10 mM; 5–24%, w/w with respect to maximal CH concentration used) and/or GLY (2–40 mM; 3–60%, w/w with respect to maximal CH concentration used). All FFSs were characterized for their zeta potential, Z-average and conductivity by a Zetasizer Nano-ZSP as described above. FFSs were then poured onto polystyrene plates (1 mL x cm^2), most experiments being performed by using 8 cm diameter polystyrene Petri dishes. FFSs were allowed to dry in an adjusted environmental chamber at 25 °C and 45% RH for 48 h and, finally, the dried films were peeled from the casting surface and stored at 25 °C and 50% RH.