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Surface, mechanical and barrier properties of bio-based composite films based on chitosan and whey protein

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ABSTRACT

Mono-component and composite bilayer and blend films composed of chitosan and whey protein were made. Colour, microstructure, water contact angles, swelling, water vapour sorption, barrier properties (oxygen, water vapour), water vapour diffusion coefficients and mechanical properties were determined. The influence of water vapour on barrier properties was studied in relation to the surface and structural properties. Mono-component and bilayer films were transparent with a homogeneous surface. Contrarily, blend films were translucent. Bilayer films had significantly lower water vapour permeability in comparison to mono-component and blend films. In all bilayer films, the air side (chitosan) was characterized by swelling, while the support side (whey protein) swelled after initial absorption. At low relative humidities, blend films were excellent barrier to oxygen and they completely lost their gas barrier performance in a humid environment. Bilayer films had enhanced mechanical resistance. The films with higher chitosan content showed higher capacity for elongation. Lamination and blending of chitosan and whey protein is a useful method to obtain new materials with desired functional properties.

1. Introduction

Bio-based polymer films are principally prepared from polysaccharides, proteins and/or lipids, and they are generally biodegradable, non-toxic and edible materials. Furthermore, in certain circumstances, they can replace synthetic polymers, be used in multi-layer packaging and provide opportunities for new product development (Debeaufort, Quezada-Galo, & Voilley, 1998). They can enhance the organoleptic properties of packaged foodstuff, supplement the nutritional value, and serve as carriers for antimicrobial and antioxidant agents. In addition, they can regulate moisture, oxygen, carbon dioxide, lipid, and aroma and flavour compounds migration between components of multi-component food products, and between food and surroundings (Sanchez-Gonzalez, Vargas, González-Martínez, Chiralt, & Cháferm, 2009). The interest in these materials in food packaging applications has also increased

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Abbreviations: CS, chitosan film; WP, whey protein film; FFS, film forming solution; CS/WP, chitosan/whey protein bilayer film; CS + WP, chitosan/whey protein blend.

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due to large surpluses of raw materials, which are produced in large amounts as by-products of agro-industrial processes.

Currently, special attention is given to chitosan (CS), N-acetyl-D-glucosamine (Kurita, 2001). This polysaccharide polymer is a by-product from some crustacean industries, biodegradable; stable, it has low toxicity and it is a relatively low cost material. Whey protein isolate (WP) is also a very well-known film forming material. It is obtained from milk whey, a by-product of cheese-making (Foegeding, Davis, Doucet, & McGuffey, 2002) and has interesting mechanical properties (Kokoszka, Debeaufort, Lenart, & Voilley, 2010). Even though both protein and polysaccharide matrices generally show good film-forming abilities, their barrier and mechanical properties are naturally limited. The film properties depend on the type of material used and the process conditions employed, which in turn determine their applications (Krochta & De Mulder-Johnston, 1997; Rao, Kanatt, Chawla, & Sharma, 2010). Indeed, the barrier properties of CS and WP films, mainly with reference to moisture, are inferior to those of plastic packaging materials. Chitosan is not very permeable in a dry state, but as with other hydrophilic polymers, the permeability increases significantly with an increase in water content (Kurek, Ščetar, Voilley, Galić, & Debeaufort, 2012).

To improve physical, functional and barrier properties of both CS and WP film and with respect to the above-mentioned problems, in the present study blending and laminating these two materials has been proposed. In particular, whey proteins can interact with polysaccharide to form either soluble or insoluble complexes, depending on the colloidal properties and compatibility of protein/polysaccharide systems. These properties are related not only to the individual functionality of both components but also to the nature and strength of the interactions between them (de Souza, Bai, Gonçalves, & Bastos, 2009). Improvement of material formulation, its production and combination of protein and polysaccharide matrices offers opportunities for the development of new sustainable polymers with application in food industries (Dickinson, 2008). Recently, different chitosan blends were studied, e.g. quinoa protein/chitosan (Abugoch, Tapia, Villamán, Yazdani-Pedram, & Díaz-Dosque, 2011), HDPE/chitosan (Mir, Yasin, Halley, Siddiqia, & Nicholson, 2011) and chitosan–whey protein (Ferreira, Nunes, Delgadillo, & Lopes-da-Silva, 2009).

From an extensive review of the scientific literature, it was found that bilayer chitosan and whey protein films have been investigated to a much lesser extent. Thus in the present study, WP and CS laminated bilayer films with different layer thicknesses were developed. The detailed understanding of the characteristics of bilayer films is of great practical and commercial importance. Developed bilayer films were compared with blends and single composite CS and WP films. Regarding barrier properties, the critical compounds that can penetrate the packaging materials and degrade food quality are water vapour and oxygen. Thus, the water vapour and the oxygen permeability were determined. The influence of RH on the surface and on the barrier properties was tested in order to verify whether interactions between chitosan and protein enhanced properties of investigated films. In addition, the film microstructure and the mechanical properties were also determined.

2. Materials and methods

2.1. Materials and reagents

Commercial grade chitosan (France Chitine, Marseille, France, powder 652, having a molecular mass of 165 kDa, low viscosity, food grade, degree of deacetylation of >85%) was used as the carbohydrate film-forming matrix. Whey protein isolate (BiPRO, ~90% protein, Davisco Foods International Inc., La Sueur, MN, USA) was used to prepare protein-based film-forming matrix. Glycerol (Fluka Chemicals, Seelze, Germany) and acetic acid (glacial 100%, Merck, Darmstadt, Germany) were used either to improve mechanical film properties or to enhance the solubilization of polymer powders. Silica gel, magnesium chloride ($MgCl_2$), magnesium nitrate ($Mg(NO_3)_2$), sodium chloride (NaCl), potassium chloride (KCl) and deionized water were used to prepare saturated salt solutions to fix the RH for water vapour and gas permeability measurements. Deionized water was also used for surface analysis. No further purification of chemicals has been done and freshly prepared solutions were always used.

2.2. Film preparation

2.2.1. Chitosan films (CS)

A chitosan solution was prepared by dissolving the chitosan powder in a 1% (v/v) aqueous acetic acid, to obtain 2% (w/v) film forming solutions (FFS). To achieve complete dispersion of chitosan, the solution was stirred for 2 h at room temperature. The pH of chitosan FFS was 4.6–5. In order to improve the mechanical properties of the films, glycerol (at 30% (w/w) of chitosan) was added to the CS solution under stirring. An exact amount of the FFS (75 mL) was then poured into glass Petri dishes to obtain dry films of 80 ± 5 μm. Films were dried in a ventilated climatic chamber (KBF 240 Binder, ODIL, France) at 25 °C and 50% RH. After drying, they were peeled off and stored in the same ventilated climatic chamber at 25 °C and 30% RH before measurements.

2.2.2. Whey protein films (WP)

Aqueous dispersions of 2% (w/w) of whey protein isolate were heated at 80 °C for 30 min under stirring. WP solution was heated to denature the whey proteins. WP solution without heating is not able to make a continuous self-standing film after drying. Glycerol was used at 30% (w/w of protein). The pH of protein FFS was ~7. An exact amount of the FFS was then poured into glass Petri dishes to obtain dry films of 80 ± 5 μm. Films were dried and stored as described in Section 2.2.1.

2.2.3. Chitosan/Whey protein bilayer films (CS/WP)

The bilayer films were prepared by a two-step coating technique. This method includes first the formation of one film and then, after drying, the polymer solution of the second layer is poured directly on top of the previously dried first layer. WP was used as a support layer whereas CS solution was poured on the top of it. FFS of each layer was prepared as described in Section 2.2.1. Firstly, WP films were made. Then, chitosan FFS was poured on top of the WP film. When CS was used as a supporting layer, the formation of a bilayer was