



Composite and bi-layer films based on gelatin and chitosan

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ABSTRACT

The aims of this work were: to develop composite, bi-layer and laminated biodegradable films based on gelatin and chitosan, to determine film barrier and mechanical properties and to characterize their microstructure.

Gelatin and chitosan concentrations used were 7.5% and 1% (w/w), respectively. Glycerol (0.75%) was added as plasticizer.

Physicochemical properties such as moisture content, transparency and color were analyzed. Composite and bi-layer systems showed a compact structure indicating a good compatibility between components.

Water vapor permeability (WVP) was independent of film thickness up to 120 μm for gelatin films and 60 μm for chitosan ones. Both, bi-layer and laminated systems resulted effective alternatives to reduce WVP of composite films (at least 42.5%). Bi-layer systems showed better mechanical properties than laminated ones. The resistance at break increased from 54.3 for composite to 77.2 MPa for bi-layer films, whereas elongation at break values of both composite and bi-layer films were similar (2.2–5.7%).

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1. Introduction

Proteins are biopolymers that can be used successfully in food packaging formulations. Therefore they are an attractive alternative to synthetic plastic materials made from non-renewable resources that can be a hazard to the environment.

Gelatin obtained by partial degradation of collagen has gained more attention as edible films for its abundance and biodegradability. Gelatin has relatively low cost and excellent functional and filmogenic properties (Eastoe and Leach, 1997; Arvanitoyannis et al., 1997a; Arvanitoyannis et al., 1997b; Cao et al., 2007a). Gelatin film itself, as most protein films, does not have ideal water vapor barrier properties. Thus, some chemical treatments can be applied to modify the polymer network through cross-linking of the polymer chains to improve the hydrocolloid film functionality (Arvanitoyannis et al., 1997c; Cao et al., 2007b). Food, pharmaceutical and industries are the main users of gelatin, which has several other technical applications. Their most frequent uses in the biomedical field include hard and soft capsules, wound dressings and adsorbent pads for surgical uses, as well as three-dimensional tissue regeneration (Bigi et al., 2004).

Chitin is the second most abundant biopolymer (after cellulose) found in the exoskeleton of crustaceans and fungal cell walls

(Muzzarelli, 1996; Zhang et al., 2006a; No et al., 2007). Chitosan is a polysaccharide derived from chitin, and is mainly composed by 2-amino-2-deoxy- β -D-glucopyranose repeating units. The importance of chitosan resides in its antimicrobial properties in conjunction with its cationic character and its film-forming properties (Khan et al., 2000; No et al., 2007).

A special property of chitosan is its bioactivity, which determines the medical and veterinary application of this polymer (Wiśniewska-Wrona et al., 2002).

In hydrocolloid films, plasticizers can be added to enhance the functional properties of films, improving both their film flexibility and their manipulation (Sothornvit and Krochta, 2001).

Composite edible films and coatings can be formulated to combine the advantages of each component. Whereas biopolymers, such as proteins and polysaccharides, provide the supporting matrix, lipids provide a good barrier to water vapor (Baldwin et al., 1997; García et al., 2000; Anker et al., 2001). Since gelatin and chitosan are hydrophilic biopolymers with good affinity and compatibility, they are expected to form composite films with good properties (Arvanitoyannis et al., 1998; Sionkowska et al., 2004).

Most of the cited literature about bi-layer films described systems where a lipid forms a second layer over the polysaccharide or protein support (Kamper and Fennema, 1984; Greener and Fennema, 1989; Weller et al., 1998; Perez-Gago, 2005). There are no references about bi-layer systems including two hydrocolloid layers. Previous literature related to characterization and applications of laminated films are scarce, although this is a common practice with synthetic films (Vidal et al., 2007). Besides, there is no

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distinction between bi-layer and laminated systems in the studies performed up to the present and these terms are used indistinctly (Park et al., 1994; Cho et al., 2002). In this work a distinction was made between them, calling bi-layer to a system prepared by the coating technique which is a two-step procedure and laminated to one formed by two independent films, placed one on the other.

The aims of this work were: to characterize the hydrocolloids used in the formulations and the rheological properties of the film forming solutions, to develop composite, bi-layer and laminated biodegradable films based on gelatin and chitosan, to analyze the effect of different film preparation techniques on film barrier and mechanical properties, to evaluate thickness effect on water vapor barrier properties and to characterize their microstructure.

2. Materials and methods

2.1. Reagents

Gelatins of two different sources were used for solution preparation: bovine gelatin type B provided by Gelico (Belo Horizonte, Brazil) (G1) and commercial one (G2) provided by Mallinckrodt Inc (New York, USA).

Commercial chitosan from crab shells with a minimum deacetylation degree of 85% was purchased from Sigma (St. Louis, MO, USA).

Glycerol (analytical grade) was used as plasticizer and was provided by J.T. Baker, (Xalostoc, México).

2.2. Hydrocolloids characterization

2.2.1. Protein content

Protein content was measured by Kjeldahl method (AOAC, 1999). Approximately 0.5 g sample was weighed and poured into digestion tubes. Protein content was determined in duplicates. The nitrogen value determined allowed to compute the protein content multiplying by the nitrogen conversion factor for gelatin, which is 5.55 (AOAC, 1984).

2.2.2. Ash determination

Porcelain crucibles were dried at 105 °C overnight to remove water. The crucibles were placed in a vacuum desiccator to reach room temperature and the weights were recorded. Approximately 1 g of sample was poured onto the porcelain crucibles. Ash content was determined in duplicates in a muffle furnace at 550 °C according to the method described by Harbers (1998).

2.3. Hydrocolloids solutions

Gelatin solutions (G1, G2) were prepared, using a concentration of 7.5% (w/w) in both cases by hydrating gelatin powder (G1, G2) with distilled water for 8 h and then samples were heated at 60 °C until complete dissolution.

Chitosan (CH) solution of 1% (w/w) was prepared by solubilizing in 1% (v/v) acetic acid solution as described in a previous work (García et al., 2006).

Glycerol was added as plasticizer (P); the concentration used was 0.75% (w/w).

Blends of G1 or G2, with and without plasticizer, and CH solutions were also prepared by mixing the corresponding solutions in the proportion 50:50 (w/w).

2.3.1. Gel strength

The gel strength was determined according to the method described by Avena-Bustillos et al. (2006) with some modifications. Gelatin solutions were prepared as described previously using a

concentration of 6.67% (w/v) in both cases. Gels were formed by maintaining the solutions at 10 °C during 18 h. Gel strength was measured at 10 °C using a texturometer TA.XT2i – Stable Micro Systems (Surrey, England) equipped with a SMS P/0-5R plunger of 12.5 mm diameter. Gels were compressed 4 mm and the compression force was registered and expressed in grams.

2.3.2. Rheological characterization of hydrocolloids solutions

Rheological characterization of the filmogenic solutions was performed in a Haake RheoWin 3.0 (Haake, Karlsruhe, Germany) rotational viscometer, at controlled constant temperature 25 °C. MV I P type sensor system of roughened coaxial cylinders was used. Rheological curves were obtained after a stabilization time of 3 min at 25 °C. The shear stress (σ) was determined as a function of shear rate ($\dot{\gamma}$) between 0 and 500 s⁻¹, with the following program: 3 min to reach the maximum shear rate, then it was maintained during 1 min and finally it was allowed to reach 0 shear rate in 3 min. This program allows to evaluate the rheological behavior of the solutions and its time-dependence.

Rheological behavior was mathematically fitted using Newtonian ($\tau = \eta \dot{\gamma}$) or Ostwald de Waele ($\tau = k\dot{\gamma}^n$) model, where η is the viscosity of the Newtonian fluid; k is the consistency coefficient and n the flow behavior index. For non-Newtonian systems apparent viscosity was calculated at 500 s⁻¹.

2.4. Hydrocolloids films

2.4.1. Film preparation

Fig. 1 shows a scheme of the different types of films analyzed in this work: Composite, bi-layer and laminated ones. Gelatin films with (GP) and without (G) plasticizer were obtained; composite films formulated with gelatin and chitosan with (GCHP) and without (GCH) plasticizer were prepared. Both types of gelatins (G1 and G2) were used in single and composite film formulations. Besides, chitosan films (CH) were also analyzed. Film-forming solutions with the same dry matter, for guarantee a constant thickness, were poured onto rectangular acrylic plates (10 × 20 cm). The solutions were dried at 37 °C in an oven to constant weight. Films were stored at 20 °C and a relative humidity (RH) of 65% for barrier and mechanical property determinations.

Only G1 gelatin was used to formulate bi-layer and laminate films. Bi-layer films were formed by the coating technique which is a two-step procedure. Single or composite gelatin G1 based films were casted onto the acrylic plates and then dried in an oven at 37 °C until a firm surface but still with adhesive properties was obtained. In all the bi-layer tested formulations, a second layer of CH solution was added onto these pre-formed gelatin based films (Fig. 1) and finally the system was dried at 37 °C in the oven. Nomenclature used for the bi-layer systems was: G1-CH, G1P-CH and G1CH-CH (one layer of CH and other of G1, G1P or G1CH).

Besides, laminated films were also tested in order to compare their performance with those of bi-layer and composite films. These laminated films were formed by two individual films one on the other (Fig. 1). Nomenclature used for the laminated systems was: G1 + CH, G1P + CH, G1CH + CH (one film of CH and other of G1, G1P, or G1CH).

2.5. Film characterization

2.5.1. Thickness measurement

Film thickness was determined using a coating thickness gauge Check Line DCN-900 (New York, USA) for non-conductive materials on non-ferrous substrates. The informed values correspond to the average of at least fifteen measurements at different positions for each specimen. Besides, thickness was also measured by Scanning

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