



Crosslinking capacity of tannic acid in plasticized chitosan films

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ABSTRACT

Plasticized and unplasticized chitosan films with tannic acid addition were developed. The crosslinking capacity of tannic acid was studied by evaluating both the structural modification produced on chitosan films and its effect on physicochemical, barrier and mechanical properties. Likewise the changes of these properties during the storage were analyzed; formulations containing tannic acid increased 29% tensile strength whereas decreased 24% water vapor permeability. Film solubility decreased at 100 °C, confirming that exposure at high temperatures facilitates the crosslinking process. The presence of tannic acid and glycerol simultaneously showed a synergic effect on the studied properties, all of which presented intermediate behavior in relation to those determined with the addition of either acid or plasticizer. The effect of the storage was also relevant since the films evidenced their tendency to a more stable structure due to the reorganization toward an anhydrous conformation, as was demonstrated by X-ray diffraction and FTIR analysis.

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1. Introduction

Chitosan is an attractive polymer for a number of uses since it is non-toxic and renewable, two properties which are extremely important in the biomaterial development. Chemical and biochemical reactivity of chitosan is strongly related to the free primary amine groups distributed regularly through its molecular chain that allow to customize its functionality. Thus chitosan applications have been the focus of a wide number of studies which reported their potential uses in the pharmaceutical, medical and food fields (Arvanitoyannis, Kolokuris, Nakayama, Yamamoto, & Aiba, 1997; Arvanitoyannis, Nakayama, & Aiba, 1998; Ravi Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004).

Polymer network can be modified by crosslinking treatments (Bigi, Cojazzi, Panzavolta, Rubini, & Roveri, 2001; Chambi & Grosso, 2006; Sabato et al., 2000). Crosslinking is an important step in the preparation of hydrocolloid films to ensure their stability and mechanical resistance (Mathew & Abraham, 2008). Crosslinking modifications occur mainly through two different reactions either Schiff base or Michael-type adducts (Ravi Kumar et al., 2004).

Glutaraldehyde, the most studied chemical agent, is synthetic and cytotoxic (Bigi et al., 2001; Sung, Huang, Huang, & Tasi, 1999) whereas transglutaminase, which is commonly used for enzymatic

reactions, is expensive (Carvalho & Grosso, 2004). Nowadays natural alternatives are been studied such as genipin (Bigi, Cojazzi, Panzavolta, Roveri, & Rubini, 2002), hydroxycinnamic (Rice Evans, Miller, & Paganga, 1996), citric (Reddy & Yang, 2010), ferulic and tannic acid (Cao, Fu, & He, 2007), as well as proanthocyanidin (Kim, Nimni, Yang, & Han, 2005).

Tannic acid, a gallic ester of D-glucose is recognized by its antioxidant capacity due to their multiple phenolic groups that can interact with biological macromolecules (Aelenei, Popa, Novac, Lisa, & Balaita, 2009).

To the best of our knowledge, the use of tannic acid to crosslink chitosan-based films has hardly been reported; thus this could be an alternative to achieve better film properties.

The development of plasticized and unplasticized chitosan films with the addition of tannic acid was carried out. The crosslinking capacity of tannic acid was studied by evaluating both the structural modification produced on the chitosan films and its effect on physicochemical, barrier and mechanical properties. Likewise the changes of the abovementioned properties during the storage were analyzed.

2. Materials and methods

2.1. Reagents

Commercial chitosan from crab shells with a minimum deacetylation degree of 85% and Mw of 1474 kDa was purchased from Sigma (St. Louis, MO, USA).

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Glycerol (analytical grade), used as plasticizer, was provided by J.T. Baker (Xalostoc, México). Tannic acid (analytical grade) was purchased by Anedra (Buenos Aires, Argentina).

2.2. Film-forming solution preparation

Chitosan solution of 1.5% (w/w) was prepared by solubilization in 1.5% (v/v) acetic acid solution under stirring for 24 h, as it was described in a previous work (Rivero, García, & Pinotti, 2009).

A screening of glycerol (P) and tannic acid (TA) was assayed in order to select the optimum concentrations. Glycerol was added as plasticizer to chitosan solution; the concentrations tested were: 0.25, 0.5, 0.75, 1 and 1.5% (g glycerol/100 ml solution).

Different amounts of crosslinking agent, tannic acid (20, 40, 60, 80 mg TA/g chitosan), were incorporated to plasticized and unplasticized chitosan solutions to select the optimum concentration.

2.3. Film preparation

Plasticized and unplasticized chitosan films with and without TA were prepared by casting 20 g of filmogenic solutions onto Petri dishes (9 cm diameter) and drying at 37 °C in an oven until reaching constant weight (approximately 24 h). The ratio of film-forming solution weight to acrylic plate area was maintained in order to guarantee a constant film thickness. The obtained films were removed from the dish and stored for 48 h prior to the determinations of structural, physicochemical, barrier and mechanical properties. The films were conditioned in a controlled room during 30 days (final time) at 20 °C and 65% relative humidity (RH) to evaluate the effect of the storage time on the properties studied.

Film nomenclature used was for chitosan films CH; plasticized chitosan films CHP; chitosan films containing tannic acid CHTA and films containing both tannic acid and glycerol CHPTA. Besides letter I was added for initial time and F for stored samples.

2.4. Physicochemical characterization

2.4.1. Film solubility in water

Samples of 2 cm × 2 cm were cut from each film, weighed to the nearest of 0.0001 g and placed into test beakers with 80 ml deionized water. The samples were maintained under constant agitation for 1 h at 20 °C or at 100 °C. The remained pieces of the films after soaking were dried again in an oven at 105 ± 1 °C to constant weight. Film solubility (%) was calculated as follows:

$$\% \text{ Solubility} = \left[\frac{\text{initial dry weight} - \text{final dry weight}}{\text{initial dry weight}} \right] \times 100$$

All samples were analyzed at least in triplicate.

2.4.2. Moisture content

Film moisture contents were determined by measuring their loss of weight, upon drying in an oven at 105 ± 1 °C until reaching constant weight (dry sample weight). Samples were analyzed at least in triplicate and results were expressed in grams of water per 100 g of sample.

2.4.3. Color

Film color was determined using a Minolta colorimeter CR 400 Series (Osaka, Japan) calibrated with a standard ($Y = 93.2, x = 0.3133, y = 0.3192$). The CIE Lab scale was used; lightness (L) and chromaticity parameters a^* (red–green) and b^* (yellow–blue) were measured. Color differences ΔE were also calculated (Rivero et al., 2009). Assays were performed by placing the film samples over the standard. Samples were analyzed in triplicates, recording four measurements for each sample.

2.5. Water vapor permeability

Water vapor permeability (WVP) tests were conducted based on a modified ASTM (1995) method E96 using a specially designed permeation cell that was maintained at 20 °C as it was described in a previous work (Rivero, García, & Pinotti, 2010). After steady-state conditions were reached, eight measurements were performed over 8 h. Each informed value corresponded at least to four determinations.

2.6. Microstructural studies by transmission electron microscopy

The morphology of films was examined using a transmission electron microscope (JEM 1200EX II Jeol, Japan) equipped with a digital camera (ES500W Erlangshen CCD Gatan). Small pieces from the center of the films were prepared according to Denavi et al. (2009).

2.7. X-ray diffraction

Plasticized and unplasticized chitosan films with and without tannic acid were analyzed by X-ray diffraction in an X'Pert Pro P Analytical Model PW 3040/60 (Almelo, The Netherlands). The CuK α radiation (1.542 Å), operated at room temperature, was generated at 40 kV and 30 mA, and the relative intensity was recorded in the scattering range of (2θ) 3–60° with a step size 2θ 0.02°.

2.8. Mechanical properties

The tensile test of the preconditioned films was performed at room temperature in a texturometer TA.XT2i—Stable Micro Systems (England) as it was described in a previous work (Rivero et al., 2009) using a tension grip system A/TG at a constant rate of 1 mm/s. Film probes of 6 cm length and 0.7 cm width were used.

To evaluate if the crosslinking process had been developed in a preferential direction, CHTA films were casted onto rectangular plates (10 cm × 20 cm) and longitudinal and transverse probes relative to the major dimension were cut and tested.

The curves of force (N) as a function of deformation (mm) were automatically recorded by the Texture Expert Exceed software. The elongation at break, EB (% of the original probe length) and the tensile strength (MPa) were also calculated according to the ASTM D638-01 method (2001). Each informed value corresponded at least to six determinations.

2.9. FTIR spectroscopy

The Fourier transform infrared (FTIR) spectra of the films were recorded in an IR spectrometer (Vertex 50, Bruker, Germany) in the wavenumber range 4000–400 cm⁻¹ by accumulation of 60 scans at 4 cm⁻¹ resolution. For each film formulation the spectra were obtained at initial time and after stored for 30 days. The samples were conditioned at 20 °C and 65% relative humidity (RH).

2.10. Statistical analysis

Systat-software (SYSTAT, Inc., Evanston, IL, USA) version 10.0 was used for all statistical analysis. Analysis of variance (ANOVA), linear regressions and Fisher LSD mean comparison test were applied. The significance levels used were 0.05 and 0.01.

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