



Effect of equilibrium moisture content on barrier, mechanical and thermal properties of chitosan films



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ABSTRACT

Water molecules modify the properties of biodegradable films obtained from hydrophilic materials. Most studies dealing with thermal, mechanical and barrier properties of hydrophilic films are carried out under one relative humidity (RH) condition. The objective of this work was to evaluate the effect of the moisture content on the thermal, mechanical and barrier properties of chitosan films under several RH conditions. Microclimates, obtained with saturated salt solutions were used for conditioning samples and the properties of the films were evaluated under each RH condition. Chitosan films absorbed up to 40% of moisture at the higher RH studied. The percentage of elongation and the water vapour permeability increased while tensile strength, Young's modulus and glass transition temperature decreased, when the moisture content increased. The results suggest that the water molecules plasticized the polymer matrix, changing the properties when the films were in contact with high RH environments.

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1. Introduction

Hydrocolloids are the biopolymers most used to prepare edible and biodegradable films. These compounds are easy to process and the films have acceptable mechanical and gas barrier properties; however, they have a moderate permeability to water vapour mainly due to their hydrophilic character (McHugh, Avena-Bustillos, & Du, 2009). When a hydrophilic film is used for food packaging or it is exposed to conditions of high relative humidity, water molecules are adsorbed on the polymeric chains, exerting a plasticizing effect on the film structure and resulting in changes in the thermal, mechanical and barrier properties (Kurek, Guinault, Voilley, Galić, & Debeaufort, 2014; Pittia & Sacchetti, 2008; Stading, Rindlav-Westling, & Gatenholm, 2001). Plasticization depends on the degree of interaction between the polymer chains and the adsorbed water molecules. Plasticizers reduce interaction forces between polymer chains, increasing molecular mobility, improving film flexibility, modifying gas permeability and decreasing the T_g value of the films (Cisneros-Zevallos & Krochta, 2002; Gupta, 2010; Suppakul, Chalernsook, Ratisuthawat, Prapasitthi, & Munchukwan, 2013). The water molecules are considered

universal plasticizers of hydrophilic materials affecting the molecular mobility of the structural matrix (Lukasik & Ludescher, 2006). Plasticization can also change the properties of hydrophilic films when they are exposed to different RH conditions during storage or transportation, resulting in changes in the packaging performance for food products (Cisneros-Zevallos & Krochta, 2002; Masclaux, Gouanvé, & Espuche, 2010).

In enclosed systems at constant temperature, a supersaturated salt solution with given a_w values generates a specific equilibrium relative humidity environment which is different for each salt solution (ASTM., 2012; Kitic, Jardim, Favetto, Resnik, & Chirife, 1986). A dry material in contact with those environments absorbs water molecules, to reach an equilibrium moisture content corresponding to an a_w value in the material equal to the a_w of the salt solution (Figura & Teixeira, 2007), as a_w is a relationship between the vapour pressure of water in the material at a given temperature and the vapour pressure of pure water at the same temperature. This phenomenon implies that the a_w value of the material depends on the relative humidity of the environment.

Water vapour sorption isotherms describe the relationship between the moisture content and the a_w at constant temperature (Figura & Teixeira, 2007; Srinivasa, Ramesh, & Tharanathan, 2007). The behaviour of the adsorption isotherms can be described by several mathematical models, including the Guggenheim-Anderson-de

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Boer (GAB) model, which has been widely applied to model isotherms of biodegradable films (Furmaniak, Terzyk, Gołembiewski, Gauden, & Czepirski, 2009; Suppakul et al., 2013).

Chitosan is a natural biopolymer consisting of N-acetyl-D-glucosamine and D-glucosamine units linked by β -(1–4) bonds (Cissé, Montet, Tapia, Loiseau, & Ducamp-Collin, 2012; Dutta & Tripathi, 2004). Chitosan is a deacetylated chitin, the main component of the exoskeleton of crustaceans, arthropods and cell walls of some fungi (Dutta & Tripathi, 2004; Pereda, Aranguren, & Marcovich, 2009) and it is used for preparing biodegradable films with good mechanical properties, low oxygen permeability and a moderate water vapour barrier (Bourtoom & Chinnan, 2008; Pereda et al., 2009). Chitosan-based films have been applied to extend the shelf life of fruits, vegetables and meats (Günlü & Koyun, 2013; Vásquez, Flores, Campos, Alvarado, & Gerschenson, 2009). It is important to notice that the performance of the chitosan film could change as a function of the environmental conditions (Cissé et al., 2012; Kurek et al., 2014). The plasticizing effect of water molecules on several properties of films prepared from hydrophilic materials, such as chitosan, is already known and documented in literature; however, most of the studies, reporting several properties of films, are carried out after conditioning at only one relative humidity (Chillo et al., 2008; Kurek et al., 2014). The objective of this work was to study the effect of moisture content on the thermal, barrier and mechanical properties of chitosan biodegradable films subjected to a wide range of relative humidity conditions.

2. Materials and methods

2.1. Materials

Chitosan (Sigma–Aldrich, United States, degree of acetylation < 75%) from shrimp shell was used, as previous experience had shown that it forms films with excellent properties, and is transparent and easy to handle (Chillo et al., 2008; Srinivasa et al., 2007). Glacial acetic acid (Fermont, Mexico) was used as solvent. Reagent grade salts (Jalmek Científica S.A. de C.V., Mexico) were used to prepare supersaturated aqueous saline solutions to obtain a wide range of equilibrium relative humidity environments.

2.2. Film preparation

Film forming solution was prepared by dissolving 1 g of chitosan in 100 ml of 1% (v/v) acetic acid solution. This concentration is most often used for the preparation of films and coatings (Chillo et al., 2008; Srinivasa et al., 2007). The filmogenic solution was centrifuged at 3000 rpm for 20 min (Eppendorf, model 580HR) to remove any remaining insoluble particle and air bubbles. The films were obtained by the casting method, using 150 mm \times 150 mm glass moulds. Solutions were dried in a dehydrator with forced convection (Excalibur Products, United States) at 35 ± 1 °C for 3 h. After drying, films were placed in plastic bags and stored at room temperature in a desiccator containing silica gel prior to further analysis. The film thickness was measured at 10 random points in the periphery and centre of the film, using a digital micrometer (Truper, model 14401).

2.3. Adsorption isotherm

To evaluate amounts of water that the chitosan films can adsorb under different equilibrium relative humidity conditions, the water vapour adsorption isotherm was determined, using the static method of microclimates, following the methodology developed by the COST90bis Project with some modifications (Wolf, Spiess,

& Jung, 1985); 1 litre acrylic containers with airtight lids were used to obtain microclimates of 11.1%, 22.6%, 32.7%, 43.8%, 57.7%, 75.3%, 84.3% and 90.3% relative humidity environments at 30 °C, using supersaturated saline solutions of LiCl, MgCl₂, K₂CO₃, KCl, NaCl, NaBr and BaCl₂, respectively (ASTM, 2012; Figura & Teixeira, 2007; Kitic et al., 1986). Rectangular samples of chitosan films were placed, in triplicates, on brackets over saline solutions, ensuring that the adsorption of water vapour molecules took place on both sides of the film. The containers were placed in a chamber with controlled temperature (30 ± 0.5 °C) for 7 days. Preliminary studies, weighing the films every 24 h, showed that the equilibrium was reached in 5–7 days. No perceptible changes or microbial growth were appreciated in the films after the conditioning period. At high relative humidity, softening of the structure was observed as expected. After reaching the equilibrium in each microclimate, the samples were weighed, using an analytical balance (0.0001 g sensitivity) according to the ASTM D570–98 standard test (ASTM, 2010) before determining the dry matter, using an oven at 110 °C for 12 h.

The GAB model (Eq. (1)) was used to describe the sorption isotherms and the parameters x_m , C , and K were determined by non-linear regression, using the method of least squares (Furmaniak et al., 2009).

$$X = \frac{x_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

where x_m is the moisture content in the monolayer, C is a constant related to the sorption in the first layer, K is a constant related to the sorption of water molecules in multilayer.

2.4. Moisture content

Water content of films was determined by measuring weight loss upon drying in an oven at 110 °C until constant weight (dry sample weight). Samples were analysed in triplicate. Equilibrium moisture content (%) was calculated, considering the initial weight of each conditioned sample and the dry weight (García, Pinotti, Martino, & Zaritzky, 2004).

2.5. Water vapour permeability (WVP)

To evaluate the behaviour and performance of films in a wide range of a_w , it was necessary to devise two permeability chambers (region of low and region of high RH corresponding to low and high a_w in the film, respectively) in which different water vapour pressure gradients were generated. a_w of the film was assumed as the average of a_w values ($a_w = RH/100$) at both sides of the sample (Fig. 1). Both permeability chambers allowed evaluation of the WVP in a wide range of a_w film from 0.05 to 0.95, which represents almost the entire scale of a_w . To measure water vapour permeability (WVP) of the chitosan films, the standard method ASTM E96–00 (ASTM, 2001b) was followed. Sixteen gradients of water vapour pressure were used to study the effect of moisture content on the WVP of chitosan-based films. Each a_w condition was evaluated in triplicate. An acrylic cell, with height of 55 mm and 65 mm in diameter, was filled with silica gel, water or supersaturated saline solutions. The mouth of the cell was sealed with the film, using a lid which allowed a transfer area of 2.206×10^{-3} m². The cell with the film was placed inside of the temperature controlled (30 ± 0.5 °C) chamber. Two conditions were studied, using a low relative humidity chamber and a high relative humidity chamber (Fig. 1). In the first case, water or saline solutions were placed inside the permeability cell and LiCl solution was used to maintain an environment of 11.1% RH in the chamber. In the high relative humidity chamber, silica gel or saline solutions were placed in

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