



Improvement of water barrier properties of starch films by lipid nanolamination



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ABSTRACT

A nanolaminate consists of two or more layers of material with nanometric dimensions that are physically or chemically bonded to each other. Starch based edible films present suitable characteristics for food protection, but their functional properties are affected by film water content. Nanolaminated films were formulated by coating the starch film with lipid nanolayers in order to improve their water resistance and barrier properties. Lipid nanolayer presence was confirmed by SEM images and contact angle measurements. Sorption isotherms of nanolaminated films showed an important reduction in film water adsorption through all the a_w range studied. The effect on permeability of the driving force (a_w difference) and the a_w values at each side of the film, were analysed. Water vapour transport was controlled by water diffusion through hydrophobic nanolayers. Nanolamination of edible films improved the water barrier properties of hydrophilic films by combining starch with lipids materials at nanometric scale.

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1. Introduction

Nowadays, about 150 million tons of plastics are produced annually all over the world, and their production and consumption show a growing trend. Most of these plastics are petroleum based, and their production results in increasing use of non-renewable resource and serious environmental pollution problems (Parra, Tadini, Ponce, & Luga, 2004). Biopolymers produced from renewable resources are an innovating answer to replace conventional petroleum based products and fit with a real sustainable development approach. Biodegradable films based on starch, can be produced at low cost and large scale. However, the mechanical and barrier properties of this promising material have to be enhanced in order to be able to compete with conventional petroleum-based polymers (Averous, 2001; Vieira, Da Silva, Dos Santos, & Beppu, 2011). Starch is a hydrophilic material and their main functional properties depend on their water content. This is due to water vapour strongly interacts with polymer matrix affecting their structure (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007; Perdomo et al., 2009). Many attempts have been done in order to overcome this problem, such as the incorporation of nanofiller of organic or inorganic origin (Bodirlau, Teaca, &

Spiridon, 2013; Kampeerappun, Aht-ong, Pentrakoon, & Srikulkit, 2007), the introduction of lipids as microdroplets inside the film matrix (Debeaufort, Quezada Gallo, Delporte, & Voilley, 2000; Zahedi, Ghanbarzadeh, & Sedaghat, 2010), and the production of laminated films that consist in a lipid layer of micrometric dimensions on a polysaccharide or protein based film (Debeaufort et al., 2000; Phan The, Debeaufort, Luu, & Voilley, 2008).

Incorporation of nanofillers such as montmorillonite and cellulose nanocrystal has been used as an alternative to improve functional properties of starch based film (Chen, Liu, Chang, Cao, & Anderson, 2009; Svagan, Hedenqvist, & Berglund, 2009; Liu, Chaudhary, Yusa, & Tadé, 2011; Slavutsky, Armada, & Bertuzzi, 2012; Slavutsky & Bertuzzi, 2014). The decrease in gas or vapour permeability is due to the increase in tortuosity of the diffusion path of permeant molecules caused by nanoparticles (Slavutsky & Bertuzzi, 2014). Besides, nanoclay addition produces an increase in Young's module and tensile strength and a decrease in film elongation as a consequence of film structure reinforcement (Slavutsky, Bertuzzi, Armada, García & Ochoa, 2014).

Inclusion of lipids into the film can be made by two different methods: lamination or emulsion. Bi-layer films are obtained by lamination of a hydrophobic lipid layer over a preformed hydrophilic film, resulting in the lipid being a distinct layer, of micrometric thickness, atop the hydrophilic film. On the other hand, emulsion films are formed by dispersion of the lipid material throughout the hydrophilic film (Rhim and Shellhammer, 2005).

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Indeed, the association of lipids with a film forming compound, such as protein or carbohydrate (biopolymers), is required due to their non-polymeric nature, and thus, the poor mechanical resistance of solid fat. Mass transfer resistance of lipid compounds against gas and vapour migration is mainly due to their structure and hydrophobic character. The incorporation of lipid compounds in film forming solution, such as sunflower oil and essential lemon oil, could improve mechanical and barrier properties of hydrocolloids based films (Sánchez-González, Chiralt, González-Martínez, & Cháfer, 2011; Vargas, Albors, & Chiralt, 2011). Furthermore, essential oil compounds have a well-documented antimicrobial activity. Water vapour barrier efficiency of emulsion-based edible films depends on the nature of the lipids, the chain length of the fatty acids and the structure of the dried emulsion which constitutes the film. Several studies showed that bi-layer films are more effective barriers against water vapour transfer than emulsion films, due to the continuous hydrophobic phase in the film (Pérez-Gago and Krochta, 2005). Emulsion-based films reduce around 10 times the water vapour permeability of hydrocolloid based films, while bi-layer films have 10–1000 times better barrier efficiency against water transfer than emulsified film (Debeaufort et al., 2000). However, bi-layer films tend to delaminate and exhibit poor mechanical properties due to the fracture or cracking of the lipid layer. These problems are related to the low compatibility between the hydrophilic polymeric matrix and the lipid layer of non-polymeric characteristics.

A nanolaminated film consists of two or more layers of material with nanometric dimensions that are physically or chemically bonded to each other (Rubner, 2003). Multilayer films or coatings of nanometric thickness can be made by successive adsorption of oppositely charged polyelectrolytes on a solid support. They could be used for potential applications such as food preservation and coatings for implant devices (Rudra, Dave, & Hayne, 2006). Carneiro-da-Cunha et al., (2010) and De S. Medeiros, Pinheiro, Carneiro-da-Cunha, and (2012) Vicente studied the impact of hydrocolloid deposition, as nanolayers, over PET films. However, the only mention to a lipid nanolaminated hydrocolloid films was reported by our group in a previous work (Slavutsky and Bertuzzi, 2015). Nanolaminated films were formulated by coating starch film with a lipid nanolayer of sunflower oil, driven by favourable interfacial forces that interact between oil molecules and the starch film. The aims of this work were to formulate starch/oil nanolaminated films combining two different oil nanolayers and to investigate the improvements on water resistance and barrier properties of starch based films.

2. Materials and methods

2.1. Materials

Food grade corn starch (Unilever, Argentina) was used as polymeric matrix for film formulation. Essential lemon oil (ELO) was provided by CITROMAX S.A.C.I. (Argentina). Food grade sunflower oil (SO) was provided by Molinos Río de la Plata (Argentina). Glycerol (Mallinckrodt, USA) was added as plasticizer. Hexane was provided by Aldrich (USA). All salts used to obtain different relative humidity ambient (% RH) were provided by Aldrich (USA).

2.2. Film forming solution

Film forming dispersion was prepared by mixing 5 g of starch, 100 mL distilled water and glycerol in a concentration of 20% w/w of starch. The dispersion was gelatinized in a shaking water bath at 78–80 °C during 10 min. This procedure ensures the disintegration of starch granules to form a homogeneous solution. Starch

solution, while still hot, was cast over plastic dishes. Dishes were placed in an air-circulating oven at 45 °C until films were dry. After that, dishes were removed from the oven and the films were peeled off. Isotropic films were obtained.

2.3. Nanolaminated films

Nanolaminated films consist of oil nanolayers deposited over a starch film support. Starch/ELO/SO films were obtained according the following procedure. Starch films were stored at 53% RH for a week, before the lipid nanolayers were added. In order to form the oil nanolayer, starch films were dipped into ELO during 2 min and then, they were rinsed with hexane. Hexane was evaporated from the samples using an air flow at 25 °C for 24 h. A second layer of SO was deposited using the same procedure.

2.4. Characterization of nanolaminated starch/oil films

2.4.1. Scanning electron microscopy (SEM)

Cross-section and surface of film samples were examined by SEM using a JEOL JSM 6480 LV scanning microscope (Japan). Samples were previously stored in a relative humidity controlled ambient during a week (53% RH). Films were cryofractured by immersion in liquid nitrogen. Samples were stored at 25 °C under silica gel. Then film samples were mounted on aluminium stubs and coated with gold plasma. Samples were observed using an accelerating voltage of 15 kV.

2.4.2. Surface properties

Surface hydrophobicity was evaluated through static contact angle measurements. The contact angle was measured by the sessile drop method (Kwok and Neumann, 1999), using a goniometer (Standard Goniometer with DROP image standard, model 200-00, Ramé-Hart Instrument Co., Succasunna, USA). A small water droplet was released on the film surface, digital pictures were gathered and the image produced was used to calculate the contact angle. Contact angle measurements were taken at 5 s and 30 s for each type of film. Ten replicates were taken on each kind of film.

2.4.3. Moisture sorption isotherms

Constant relative humidity environments were established inside sorbostats (glass jars) using salt solutions. The salts used (LiCl, CH₃COOK, MgCl₂, K₂CO₃, Mg(NO₃)₂, NaBr, NaCl, KCl) were the different salts recommended by the European project COST-90 (Spiess and Wolf, 1983), to cover a water activity (*a_w*) range from 0.10 to 0.90. Film samples (rectangular strips approximately 2 cm² area) were first freeze-dried (Thermovac Industries Corp, USA) and stored in a desiccator during a week. Samples were weighed and placed on a plastic lattice by holding it on a tripod inside the sorbostats that contain the saturated salt solutions and then the sorbostats were sealed. The sorbostats were kept inside an environmental chamber maintained at constant temperature. Film samples were equilibrated in the sorbostats for 4 days before their weights were recorded. The weights of the samples were checked during 3 more days. Equilibrium was judged to have been attained when the difference between two consecutive sample weightings was less than 1 mg/g dry solid. Data were reported for each relative humidity as gram of water sorbed/100 g dry film. Absorption tests were done in quadruplicate at each *a_w*. The moisture sorption determination was done at 25 °C.

The data obtained were fitted by GAB sorption model, as described by Eq. (1):

$$w_e = \frac{w_0 \times C \times k \times a_w}{(1 - k \times a_w)(1 - k \times a_w + C \times k \times a_w)} \quad (1)$$

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