LWT - Food Science and Technology 57 (2014) 106–115

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Thermo-compression of biodegradable thermoplastic corn starch films containing chitin and chitosan

O. Lopez [a,b,*], M.A. Garcia [b], M.A. Villar [a], A. Gentili [d], M.S. Rodriguez [c], L. Albertengo [c]

[a] *Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Departamento de Ingeniería Química, UNS, Camino La Carrindanga km. 7, 8000 Bahía Blanca, Argentina*

[b] *Centro de Investigación y Desarrollo en Criotecnología de Alimentos, CIDCA (UNLP-CONICET), Facultad de Ciencias Exactas, UNLP, 47 y 116, 1900 La Plata, Argentina*

[c] *Instituto de Química del Sur, INQUISUR (UNS–CONICET), Laboratorio de Investigaciones Básicas y Aplicadas en Quitina, LIBAQ-Departamento de Química, UNS, Bahía Blanca, Argentina*

[d] *Departamento de Biología, Bioquímica y Farmacia, UNS, Bahía Blanca, Argentina*

ARTICLE INFO

Article history:
Received 2 August 2013
Received in revised form
3 January 2014
Accepted 17 January 2014

Keywords:
Thermoplastic corn starch films with chitosan and chitin
Thermo-compression
Structural characterization
Barrier and mechanical properties
Antimicrobial capacity

ABSTRACT

Films based on thermoplastic corn starch (TPS) and chitosan/chitin were obtained by melt-mixing and thermo-compression. Chitosan and chitin incorporation to TPS matrix induced some structural modifications due mainly to the interactions between starch hydroxyl and chitosan/chitin amino groups. Crystallinity degree of TPS films was increased with biopolymers incorporation. Enthalpy melting values for TPS–chitosan/chitin films resulted lower than those corresponding to TPS control ones. Films had homogeneous and smooth surfaces, without pores and cracks and no glycerol migration was evidenced by Scanning Electronic Microscopy. Films fracture surfaces were uniform without the presence of unmelting starch granules neither chitosan/chitin agglomerates. Films with chitosan/chitin presented higher color, UV absorption capacity and opacity than TPS films. Addition of 10 g chitosan or chitin/100 g starch decreased 35 and 56% water vapor permeability, respectively. Biopolymers addition to TPS increased tensile strength and elastic modulus, and decreased elongation at break. Starch and glycerol-rich domains where evidenced in TPS matrixes by Dynamic Mechanical Analysis. Finally, TPS–chitosan films reduced *Staphylococcus aureus* and *Escherichia coli* growth in the contact zone.

1. Introduction

Packaging films, made of synthetic polymers, cause serious ecological problems due to their non-biodegradability. The major concern of consumers for environmental protection led packaging industries to increase research in biodegradable packaging materials (Fajardo et al., 2010). Materials based on polysaccharides are mostly ecological because they can degrade without leaving behind ecologically harmful residues, in contrast to those which are made from synthetic polymers (Simkovic, 2013). In this sense, polysaccharides are considered good candidates for biodegradable films since they are widely distributed in nature and have been regarded as structural materials. Among them, starch has been broadly used due to its abundance, low cost, and renewability (Xu, Kimb, Hanna, & Nag, 2005), being corn the major commercial starch source in the world (Mali, Karam, Pereira Ramos, & Grossmann, 2004). Unfortunately, starch films are sensitive to environmental humidity and brittle, as well as, difficult to process. Thus, their technological applications require the improvement of films mechanical and barrier properties. In order to overcome this limitation, corn starch has been blended with several synthetic and natural polymers. For example, wheat starch multilayer films with different aliphatic polyesters (Martin, Schwach, Avérous, & Couturier, 2001), films based on thermoplastic starch/natural rubber blends (Carvalho, Job, Alves, Curvelo, & Gandini, 2003) and blown-extrusion starch–pectin films (Fishman, Coffin, Konstance, & Onwulata, 2000), have being developed among others. An alternative, largely used to improve starch films properties, is the addition of chitosan to formulations, mainly due to the more hydrophobic character of chitosan compared to starch (Chillo et al., 2008; Fajardo et al., 2010; Lazaridou & Biliaderis, 2002; Pelissari, Yamashita, & Grossmann, 2011; Pelissari et al., 2012; Quattara, Simard, Piette, Begin, & Holley, 2000).

Chitosan is a partially deacetylated form of chitin, which is the most abundant natural polymer after cellulose (Rinaudo, 2006).

---

[*] Corresponding author. Planta Piloto de Ingeniería Química, PLAPIQUI (UNS-CONICET), Departamento de Ingeniería Química, UNS, Camino La Carrindanga km. 7, 8000 Bahía Blanca, Argentina.

E-mail address: ovlopez75@yahoo.com.ar (O. Lopez).

0023-6438/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.lwt.2014.01.024

Chitin is found in the skeletal materials of crustaceans, insects and cell walls of bacteria and fungi. Although in the literature are several studies related to starch-based films with chitosan, chitin use has not been reported. Chitosan is nontoxic, biodegradable, compatible with other biopolymers and is used to functionalize many others polysaccharides (Zhai, Zhao, Yoshii, & Kume, 2004). Moreover, the antibacterial and antifungal properties of chitosan have been studied by several authors; molecular weight and amino groups are the responsible of chitosan antibacterial capacity (Le et al., 2001; Liu, Huan, Yang, Li, & Yao, 2001; Zhai et al., 2004).

Most of the works found in the literature related to starch-chitosan materials based their studies on films obtained by casting method. However, processing methods such as blown extrusion, compression or injection molding are less reported. Solvent-casting has been the most used method at small-scale of biopolymers films preparation, which involves solubilization, casting, and drying steps. Despite, this is a good and adequate technique at laboratory scale, it is considered as a high energy-consuming procedure. On the other hand, high levels and efficient biodegradable films production is required by industrial area. In this sense, scaling-up processing methods using equipments designed for synthetic polymers is indispensable (Sothornvit, Olsen, McHugh, & Krochta, 2007; Thunwall, Kuthanova, Boldizar, & Rigdahl, 2008). In this context, extrusion, blowing, injection, and thermo-compression are viable alternatives due to their energy-efficient combined with their high productivity (Flores, Costa, Yamashita, Gerschenson, & Grossmann Eiras, 2010; Pellissari et al., 2012; Thunwall, Boldizar, & Rigdahl, 2006). Particularly, thermo-compression is useful as a processing method because of its simplicity and capability of producing films without polymer solubilization. In this context, these biomaterials could have feasible applications to develop economical and ecological materials (Simkovic, 2013).

The goal of this paper was the development of biodegradable films based on thermoplastic native corn starch containing chitosan and chitin by thermo-compression. Furthermore, the influence of chitin and chitosan addition on films properties (microstructure, color, water vapor permeability, mechanical and dynamic mechanical behavior and antimicrobial capacity) was also studied.

2. Materials and methods

2.1. Materials

Native corn starch was provided by Misky, Arcor (Tucumán, Argentina) with an amylose content of 23.9 ± 0.7 g/100 g (López, García, & Zaritzky, 2010). Chitin was isolated in the Laboratorio de Investigaciones Básicas y Aplicadas en Quitina (LIBAQ) from shrimp shells waste (*Pleoticus mülleri*) supplied by Ingeniero White Port (Bahía Blanca, Argentine). Chitin was previously characterized reporting moisture and ash contents of 0.38 and 6.5 g/100 g, respectively and 6.5 g/100 g nitrogen content (Pistonesi, 2001). Chitosan was prepared by heterogeneous alkaline deacetylation of chitin (Zuñiga, Debbaudt, Albertengo, & Rodríguez, 2010). Chitosan presented a molecular weight (MW) of 468,200 Da, ash and moisture contents of 2.3 and 10.4 g/100 g, respectively and 82.5% of deacetylation degree (DD). To obtain homogeneous size samples chitin and chitosan were sieved employing a sieve with 0.25 mm opening sizes. Glycerol (Anedra, Argentine) was used as plasticizer.

2.2. Thermoplastic starch mixtures

Assayed mixtures were composed by thermoplastic corn starch (TPS) with chitosan or chitin. TPS was based on corn starch with 30 g glycerol and 45 g distilled water/100 g starch. Formulations with two different chitosan concentrations (5 and 10 g/100 g starch) were prepared and designed as TPS–chitosan5 and TPS–chitosan10, respectively. On the other hand, a formulation with 10 g chitin/100 g starch was also prepared (TPS–chitin10). Chitosan or chitin was premixed with starch and then, glycerol and distilled water were added. Samples were mixed and conditioned at 25 °C during 24 h. Mixtures were processed in a Brabender Plastograph (Brabender, Germany) at 140 °C and 50 rpm for 15 min. They were removed from the mixing chamber, triturated and stored at 25 °C and 60% relative humidity (RH) for a week to improve their processability. Ambient conditions were reached employing an aqueous glycerol solution (72 g glycerol/100 g solution).

2.3. Films preparation

TPS films were obtained by thermo-compression using a thermostatized hydraulic press. Processing conditions were 140 °C for 6 min, increasing the pressure every 2 min (80, 140 and 180 kg/cm^2). An aluminum frame as mold of 1 mm thickness and a relation of 1.9 g sample per cm^3 were used. Material was cooled under pressure up to approximately 50 °C, then the pressure was released and obtained films were removed from the frames.

2.4. Films characterization

Before characterization, films were conditioned at 25 °C and 60% RH for a week. Films thickness was measured at different locations of the specimens, employing a micrometer. Ten measurements were taken on each film and mean values are reported.

2.4.1. Fourier transform infrared (FTIR)

FTIR spectra were obtained using a Thermo Nicolet Nexus spectrophotometer (Nicolet, United States). Samples were prepared by mixing TPS films as fine powder with KBr (Sigma Aldrich) at 3 g/100 g. The mixture was pressed and a transparent sample was obtained. Spectra were achieved from 100 accumulated scans at 4 cm^{-1} resolution in the range 4000–400 cm^{-1}.

2.4.2. X-ray diffraction (XRD)

Crystal structure identification of films was studied by XRD. Diffractograms were obtained in an X-ray diffractometer Philips PW1710 (Philips, Holland) with a detector operating at 45 kV and 30 mA within 2Θ varied from 3 to 60°. Crystallinity degree (CD) was calculated as the ratio between the absorption peaks and the total diffractogram area, expressed as percentage (%).

2.4.3. Differential scanning calorimetry (DSC)

Thermal properties of TPS films were determined by DSC in a Perkin Elmer Pyris I (USA) calorimeter. Approximately 10 mg of film were weighted in hermetic pans in order to avoid water loss. An empty hermetic pan was used as reference. Samples were heated from 20 to 250 °C at 10 °C/min, under nitrogen atmosphere. From the thermograms, the following parameters were obtained: onset and melting temperature and melting enthalpy.

2.4.4. Scanning electronic microscopy (SEM)

Homogeneity and appearance of the films were examined by visual observation and by SEM with a JEOL JSM-35 CF electron microscope (JEOL, Japan) using an accelerating voltage of 10 kV. Samples were cryofractured by immersion in liquid nitrogen. Film pieces were mounted on bronze stubs and coated with a gold layer (~30 Å) using an argon plasma metallizer (sputter coater PELCO 91000).