



Active bilayer films of thermoplastic starch and polycaprolactone obtained by compression molding



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ABSTRACT

Bilayer films consisting of one layer of PCL with either one of thermoplastic starch (S) or one of thermoplastic starch with 5% PCL (S95) were obtained by compression molding. Before compression, aqueous solutions of ascorbic acid or potassium sorbate were sprayed onto the S or S95 layers in order to plasticize them and favor layer adhesion. S95 films formed bilayers with PCL with very good adhesion and good mechanical performance, especially when potassium sorbate was added at the interface. All bilayers enhanced their barrier properties to water vapour (up to 96% compared to net starch films) and oxygen (up to 99% compared to PCL pure). Bilayers consisting of PCL and starch containing 5% PCL, with potassium sorbate at the interface, showed the best mechanical and barrier properties and interfacial adhesion while having active properties, associated with the antimicrobial action of potassium sorbate.

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1. Introduction

In the last few years, the need for replacing petroleum-based plastics by biodegradable polymers has led to a great number of studies focused on the design of environmentally friendly materials. In particular, starch and its derivatives have been widely studied since they could offer an inexpensive solution to such problems (Bastioli, 2001). Starch is obtained from renewable resources, is widely available and low cost and it can be used to obtain biodegradable films for food applications, as it has the ability to form films or coatings with very low oxygen permeability (Jiménez, Fabra, Talens, & Chiralt, 2012; Zhang, Rempel, & McLaren, 2014, chap. 16). However, starch-based materials show several disadvantages which reduce their applicability as packaging material, such as their highly hydrophilic character, limited mechanical properties and the retrogradation phenomena that occur during aging. The blending of starch with other, more hydrophobic, polymers is a widely studied strategy used to improve properties of starch films. The aliphatic polyesters, such as polycaprolactone (PCL) or polylactic acid (PLA), are synthetic biodegradable materials of a more hydrophobic nature that can be combined with starch in different

ways to modulate the properties of mixed films. Of them, PCL has the advantage of great stretchability and low water vapour permeability (Averous, Moro, Dole, & Fringant, 2000). Nevertheless, the starch–PCL materials obtained by simple blending are not adequate due to the low affinity of both polymers, which leads to polymer phase separation with limited adhesion between the polymer interfaces, thus resulting in poor film properties (Avella et al., 2000). To overcome this, several authors have studied the improvement in the starch–PCL compatibility by using different compounds, which can increase the polymer affinity via different mechanisms, such as PCL-co-pyromellitic anhydride (Avella et al., 2000) methylenediphenyldiisocyanate (Wang, Sun, & Seib, 2001) or dioctyl maleate (Zhang & Sun, 2004). Nevertheless, the use of these kinds of compounds can compromise the use of films for food packaging due to their potential toxicity. Other authors reported that hydrogen bonds can be established to a certain extent between the starch hydroxyls and the PCL carbonyls at the interface region, which could allow the incorporation of small amounts of PCL in starch matrices without notable polymer separation, improving film properties (Matzinos, Tserki, Kontoyiannis, & Panayiotou 2002; Ortega-Toro, Collazo-Bigliardi, Talens, & Chiralt, 2015).

The development of multilayer films using starch and PCL layers could be a good alternative for developing packaging materials for food applications. A multilayer packaging material can be defined as two or more materials with specific properties combined in a single layered structure. The multilayer films with petrochemical-based materials are already widely used in food packaging applications.

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(Fang et al., 2005; Mensitieri et al., 2011). The PCL-starch multilayers could exhibit some advantages, such as the decrease in the overall moisture sensitivity and the improvement in the mechanical properties (Yu, Dean, & Bi, 2006), by combining the properties of each material (Fabra, Busolo, Lopez-Rubio, & Lagaron, 2013). Therefore, starch-PCL multilayers could maintain the excellent gas barrier properties of the starch and the high water vapour barrier of the PCL, which would be difficult to achieve with a single biopolymer-based material. Layered structures based on biopolymers containing antimicrobial compounds have been obtained by co-extrusion (Alix et al., 2013) or compression-molding (Takala et al., 2013).

The incorporation of antioxidant and antimicrobial agents in biodegradable films has been widely studied to obtain active packaging materials with controlled release of bioactives (Ayranci & Tunc, 2003; Wook et al., 2013) to enhance food stability and shelf life. These agents have often been included in the biopolymer dispersions used for casting films (Cian, Salgado, Drago, González, & Mauri, 2014; Gómez-Guillén, Ihl, Bifani, Silva, & Montero, 2007; Jiménez, Fabra, Talens, & Chiralt, 2013). Nevertheless, the usual thermal processing of bioplastics make their incorporation necessary during the extrusion or other hot melting steps used at industrial level. Some losses of active compounds can occur during this step due their thermosensitive. For instance, Wook et al. (2013) reported losses of resveratrol and α -tocopherol incorporated in PLA/starch blend films during the polymer melt blending, ranging between 4 and 26%, depending on the film formulation.

The aim of this work is to analyze the properties of starch-PCL bilayer films obtained by compression molding by incorporating a common food antimicrobial (potassium sorbate: PS) and an antioxidant (ascorbic acid: AA) at the layers' interface. The interactions of these compounds with both phases could improve the layers' adhesion, while conferring active properties to the layered film. Bilayer films formed with starch layers containing 5% PCL was compared with those formed with pure starch layers in order to discover the potential improvement of starch-PCL interfacial adhesion when a small amount of PCL is present in the starch matrix.

2. Materials and methods

2.1. Materials

Corn starch was purchased from Roquette (Roquette Laisa España, Benifaió, Spain). Its moisture content was 10% (w/w) and amylose percentage was 14%. Glycerol was from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain). Polycaprolactone (PCL) was from Aldrich Chemistry (Sigma-Aldrich Co., LLC, Madrid, Spain), with a molecular weight of 80,000 daltons. Potassium sorbate, ascorbic acid, magnesium nitrate 6-hydrate, sodium chloride and phosphorus pentoxide were from Panreac Química, S.A. (Castellar del Vallès, Barcelona, España).

2.2. Film preparation

Three kinds of monolayer films were obtained by melt blending and subsequent compression molding: thermoplastic starch (S), thermoplastic starch with 5% (g/100 g of starch) PCL (S95) and pure PCL (PCL). To prepare S films, native starch and glycerol were dispersed in water using a starch:glycerol:water ratio of 1:0.3:0.5 (w/w). When starch films contained PCL, this was added to aqueous dispersions in 1:0.05, w/w starch:PCL ratio.

A two-roll mill (Model LRM-M-100, Labtech Engineering, Thailand) was used for the hot-mixing process where polymers were heated at 160 °C and 8 rpm for 30 min. The resulting sheets

were ground and conditioned at 25 °C and 75% RH using NaCl oversaturated solutions for 48 h. Afterwards, the monolayer films were obtained using a compression molding press (Model LP20, Labtech Engineering, Thailand). The following process conditions were used: (a) pre-heating cycle at 160 °C for 5 min, (b) compression-molding at 50 bar for 2 min, (c) compression-molding at 150 bar for 6 min, and (d) cooling cycle at 150 bars for 3 min.

Subsequently, the bilayer films were obtained by means of a second compression-molding step where the corresponding two layers were compressed together. The process conditions were 80 °C and 150 bars for 4 min and cooling cycle for 2 min. The obtained bilayer films always had one PCL layer and an S or S95 layer. Before the second compression, 1 mL of distilled water (H₂O) or aqueous solutions containing ascorbic acid (AA) or potassium sorbate (PS) were sprayed onto the S or S95 layers in order to plasticize starch and promote layer adhesion. The obtained bilayer films were coded by indicating if the starch layer was S or S95 and the kind of solution sprayed onto the interface (H₂O, AA or PS); e.g. S-H₂O indicates that the bilayer film contains S plus PCL layers sprayed with pure water. AA and PS aqueous solutions were prepared in such a way that 1 mL of solution contained 0.1 g of compound/g of starch film. The bilayer films were conditioned at 25 °C and 53% RH for 1 and 5 weeks before their characterization. The thickness of conditioned films was measured at six random positions with a digital electronic micrometer (Palmer-Comecta, Spain, ± 0.001 mm).

2.3. Film characterization

2.3.1. Scanning Electron Microscopy (SEM)

Cross-section images from resulting films were obtained by means of a scanning electronic microscope (JEOL, JSM-5410, Japan). The conditioned samples (1 and 5 weeks) were stored inside P₂O₅ desiccators for one week before the analysis. Afterwards, the samples were cryofractured, fixed on copper stubs, gold coated, and observed using an accelerating voltage of 10 kV.

2.3.2. Fourier Transform Infrared (FTIR) spectroscopy

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to analyze component interactions in the films. Measurements were performed at 25 °C using a Tensor 27 mid-FTIR Bruker spectrometer (Bruker, Karlsruhe, Germany) attached to a platinum ATR optical cell and an RT-D1a TGS detector (Bruker, Karlsruhe, Germany). The diaphragm was set at 4 mm for the analysis, and the spectra were obtained between 4000 and 800 cm⁻¹ using a resolution of 4 cm⁻¹. The analysis was carried out on both the S or S95 and PCL layers. The data were analyzed using OPUS software (Bruker, Karlsruhe, Germany).

2.3.3. Thermal properties

Thermal degradation of the films and their components was analyzed using a thermogravimetric TGA 1 Star^e System analyser (Mettler-Toledo, Inc., Switzerland), equipped with an ultra-micro weighing scale (± 0.1 μ g), under nitrogen atmosphere. The analysis was carried out using the following temperature program: heating from 25 to 500 °C at a 10 °C/min heating rate. Approximately 4 mg of each sample were used in each test, considering at least two replicates for each one. Initial degradation temperature (Onset) and peak temperature (Peak) were registered from the first derivative of the resulting weight loss curves.

2.3.4. Water content (X_w)

Conditioned films were transferred to a natural convection oven (J.P. Selecta, S.A., Barcelona, Spain) at 60 °C for 24 h. Then, these samples were stored in a P₂O₅ desiccator for 8 days. Moisture

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