



Improvement of properties of glycerol plasticized starch films by blending with a low ratio of polycaprolactone and/or polyethylene glycol



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water (PubChem CID: 952)
Diphosphorus pentoxide (PubChem CID: 14812)
Magnesium nitrate (PubChem CID: 25212)

ABSTRACT

The effect of the melt blending of polycaprolactone (PCL) (5 and 10 wt. %) and polyethylene glycol (PEG 4000 D) (2 wt. %) with corn thermoplastic starch (with 30% glycerol) on film properties was studied through the characterization of the structural, thermal and physical properties of the films obtained by compression moulding, after 1 and 5 storage weeks. PCL and PEG decreased the glass transition temperature of starch, whereas no changes in PCL melting properties were observed. Starch films could incorporate 5% PCL without a notable phase separation, leading to more stretchable and stable films. Blend films with 10% PCL showed clear phase separation, without any improved tensile properties, but with lower water vapour permeability. In ternary systems, PEG reduced the PCL-starch affinity, enhancing phase separation, whereas it did not improve the film properties with respect to starch films.

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1. Introduction

Synthetic polymers have been widely used for food packaging because of their accessible cost and suitable properties. However, the growth of environmental problems caused by petrochemical-based plastics has aroused interest in the use of biodegradable alternatives coming from renewable sources (Petersen et al., 1999; Weber, Haugaard, Festersen, & Bertelsen, 2002).

Among the natural polymers, such as polysaccharides and proteins, starch is a promising candidate from which to develop biodegradable films. Starch has high film-forming capability, low cost, wide availability from renewable sources and is relatively easy

to handle (Bertuzzi, Armada, & Gottifredi, 2007; Romero-Bastida et al., 2005; Talja, Helén, Roos, & Jouppila, 2007). Many studies have reported the development of starch-based films as a means of reducing the environmental impact of synthetic plastics (Averous & Boquillon, 2004; Park, Yang, Kim, & Lee, 2004).

Starch based-films exhibit good barrier properties to oxygen (Dole, Joly, Espuche, Alric, & Gontard, 2004), carbon dioxide and lipids, biodegradability (Iovino, Zullo, Rao, Cassar, & Gianfreda, 2008) and compostability (Lörcks, 1998). However, starch itself has poor thermoprocessability and exhibits some drawbacks such as a strong hydrophilic character (Teixeira et al., 2009), and poor mechanical properties compared to conventional synthetic polymers (Averous & Boquillon, 2004; Teixeira et al., 2009), which limit its use as packaging material.

Chemical modification (López, Zaritzky, & García, 2010),

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plasticization and blending with other polymers and additives (Jiménez, Fabra, Talens, & Chiralt, 2012) are common methods used to overcome the starch limitations. The most common plasticizers used on starch-based materials are polyols, principally glycerol and sorbitol (Mali, Grossmann, García, Martino, & Zaritzky, 2002; McHugh, Avena-Bustillos, & Krochta, 1993; Sothornvit & Krochta, 2005).

Different polymers used in starch blends are poly (β -hydroxyalkanoates) (PHA), Poly(lactic acid) (PLA) and poly (ϵ -caprolactone) (PCL). PCL is a linear, partially crystalline, hydrophobic polyester (Li, Espartero, Foch, & Vert, 1997) with good mechanical properties and high extensibility. Its elongation and tensile strength at break point is higher than 1100% and 33 MPa, respectively (Matzinos, Tserki, Gianikouris, Pavlidou, & Panayiotou, 2002; Ortega-Toro, Collazo-Bigliardi, Talens, & Chiralt, 2015).

Starch and PCL blends have been extensively studied by several authors (Avella et al., 2000; Averous, Moro, Dole, & Fringant, 2000; Li & Favis, 2010; Matzinos et al., 2002; Ortega-Toro et al., 2015; Singh, Pandey, Rutot, Degée, & Dubois, 2003; Wu, 2003). Several disadvantages of pure starch-based films, such as their low resilience, high degree of moisture sensitivity and high shrinkage have been overcome by adding PCL to the starch matrix (Averous et al., 2000). However, the main problem of the starch/PCL blend is the phase separation of both incompatible polymers and the weak interfacial adhesion due to the lack of chemical affinity between polymers. To overcome this problem, compatibilizers have been used or the polymers have been modified (Avella et al., 2000). Nevertheless, the incorporation of small amounts (10%) of PCL into starch films led to a very fine dispersion of PCL in the starch matrix, decreasing the starch glass transition temperature and improving the water vapour barrier properties of starch films (Ortega-Toro et al., 2015).

Polymer compatibilizers, such as amphiphilic, low molecular weight compounds (Yokesahachart & Yoksan, 2011), ionomers (Landreau, Tighzert, Bliard, Berzin, & Lacoste, 2009) or partially miscible polymers in both blend components (Parulekar & Mohanty, 2007) generally improve the blend film properties. Kim, Choi, and Park (2000) reported that the mechanical and structural properties of 40/60 (wt. %) starch-PCL blend films were greatly improved when 10% (wt. %) polyethylene glycol (PEG) of intermediate molecular weight (MW: 3,400 D) was added. PEG of intermediate molecular weight could be used as a possible compatibilizer in starch-PCL blend films, while acting as a starch plasticizer.

The aim of this work was to analyse the influence of adding PEG of intermediate molecular weight on the structural, thermal and physicochemical properties of compression moulded starch films containing a low ratio (less than 10%) of PCL in order to obtain low cost starch films with improved properties.

2. Materials and methods

2.1. Materials

Corn starch was obtained from Roquette (Roquette Laisa España, Benifaió, Spain). Its moisture content was 10% w/w and amylose percentage was 14%. Glycerol was purchased from Panreac Química, S.A. (Castellar del Vallès, Barcelona, Spain). Polyethylene Glycol (PEG) and the polycaprolactone (PCL) were provided by Aldrich Chemistry (Sigma–Aldrich Co. LLC Madrid, Spain); their molecular weights were 4000 Da and 80,000 Da, respectively. Magnesium nitrate 6-hydrate and phosphorus pentoxide were purchased from Panreac Química, S.A. (Castellar del Vallés, Barcelona, Spain).

2.2. Film preparation

PEG and glycerol were dissolved in water, and then native starch was dispersed in the aqueous solution. Afterwards, the respective amount of PCL was added to the mixture. The starch:glycerol ratio was 10:3 and the starch:water ratio was 2:1 in every case. The other components were added in different proportions depending on the blend. The starch:PEG ratio was 100:2 and the starch:PCL ratios were 100:5 and 100:10. Two control films (S: glycerol plasticized starch and PCL: pure PCL) and 5 blend films were prepared: S-PEG (starch, glycerol and PEG), S-PCL5 (starch, glycerol and PCL at 5%), S-PCL5-PEG (starch, glycerol, PCL at 5%, and PEG), S-PCL10 (starch, glycerol and PCL at 10%) and S-PCL10-PEG (starch, glycerol, PCL at 10%, and PEG).

The formulations were hot-mixed on a two-roll mill (Model LRM-M-100, Labtech Engineering, Thailand) at 160 °C and 8 rpm for 30 min. A visually good miscibility among the components was observed. When the mixing was finished, the paste sheets formed were removed from the mill and conditioned at 25 °C and 53% Relative Humidity (RH), using a Mg(NO₃)₂ oversaturated solution for 48 h, to increase the blend moisture content, thus improving processability. Afterwards, films were made in a compression moulding press (Model LP20, Labtech Engineering, Thailand). Four g of the pre-conditioned paste were put onto steel sheets and pre-heated on the heating unit for 5 min. Compression moulding was performed at 160 °C and 50 bars for 2 min, followed by 6 min at 150 bars; thereafter, the cooling cycle was applied for 3 min. Starch-based films were conditioned at 25 °C and 53% RH for 1 week for the initial time characterization and for 5 weeks for the final time characterization.

2.3. Film characterization

2.3.1. Structural properties

The surface morphology of the films was analysed using an atomic force microscope (AFM) (Multimode 8, Bruker AXS, Santa Barbara, USA) with NanoScope[®] V controller electronics. Measurements were taken from 20 μm^2 areas using the PeakForce QNM mode. Samples conditioned for 1 week at 25 °C and 53% RH were analysed. The maps of Derjaguin–Muller–Toropov (DMT) modulus derived from the model of elastic contact (Derjaguin, Muller, & Toropov, 1975) were obtained from the PeakForce QNM Mode analysis, showing the surface mechanical properties of the materials. Three replicates were considered for every case.

Scanning Electron Microscopy (SEM) of the cross-sections of the films was performed by means of a microscope JEOL JSM-5410, Japan. The film samples were maintained in desiccators with P₂O₅ for 1 week to guarantee that water was not present and 2 samples per formulation were analysed. Film pieces, 0.5 cm² in size, were cryofractured (by immersion in liquid nitrogen and subsequent break) and fixed on copper stubs, gold coated, and observed using an accelerating voltage of 10 kV.

A diffractometer (XRD, Bruker AXS/D8 Advance) was used to obtain the X-ray diffraction patterns of the films. The samples (conditioned for 1 and 5 weeks at 25 °C and 53% RH) were analysed between 2 θ : 5° and 2 θ : 30° using K α Cu radiation (λ : 1.542 Å), 40 kV and 40 mA with a step size of 0.05°, using a sample holder of quartz. For this analysis, samples were cut into 4 cm squares. Pure PEG film was also analysed, so as to identify its characteristic peaks.

Fourier Transform Infrared spectroscopy in Total Attenuated Reflection mode (ATR-FTIR) was used to study the films at initial time. Measurements were carried out using a Tensor 27 mid-FTIR Bruker spectrometer (Bruker, Karlsruhe, Germany) equipped with a Platinum ATR optical cell and an RT-D1a TGS detector (Bruker, Karlsruhe, Germany). During analysis, the diaphragm was set at

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