Properties and ageing behaviour of pea starch films as affected by blend with poly(vinyl alcohol)

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ABSTRACT

Pea starch (S) and poly(vinyl alcohol) (PVA) blends with different ratios were produced in order to elucidate the possible advantages of blend films to overcome the common drawbacks of starch films. Starch, poly(vinyl alcohol) and blends (S:PVA ratios of 2:1, 1:1 and 1:2) were obtained by casting and microstructure and thermal behaviour were characterized. Moreover, barrier, mechanical and optical properties were evaluated after 1 and 5 storage weeks at 25 °C and 53% relative humidity in order to study the effect of poly(vinyl alcohol) on the ageing process of starch. The incorporation of PVA into pea starch films implied the formation of interpenetrated networks of both incompatible polymers with partial solubilisation. S-PVA blend films were much more extensible and stable during storage, with improved water barrier properties and reduced water sorption capacity especially when the S:PVA ratio were 1:1 and 1:2. Starch-poly(vinyl alcohol) blend films are environmentally friendly, low cost materials, with good functional properties.

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1. Introduction

The reduction in petroleum reserves and the great environmental impact of petroleum-derived plastics have led to the development of biodegradable materials that may be used in packaging applications. Bioplastics are biodegradable or compostable products, from renewable sources or synthesis, whose global production has increased considerably in the last few years. They have hydrolytically or enzymatically labile bonds or groups (Lu, Xiao, & Xu, 2009). These biodegradable materials provide opportunities to reduce the waste through biological recycling in order to achieve a sustainable ecosystem.

Starch is considered as a bioplastic and is one of the most abundantly-occurring natural polymers, second only to cellulose (Ramaraj, 2007). It is also especially attractive because of its biodegradability and low cost (Chen, Liu, Chen, Chen, & Chang, 2008; Han, Seo, Park, Kim, & Lee, 2006; Lafargue, Lourdin, & Doublier, 2007). Starch has the ability to form films that are odourless, colourless, transparent, and with very low oxygen permeability (Jiménez, Fabra, Talens, & Chiralt, 2012a; Vásconez,

Flores, Campos, Alvarado, & Gerschenson, 2009). Native starch has a granular structure and presents different properties depending on its amylose/amylopectin ratio. Gelatinized starch shows a great film-forming capacity and, as is well known, its two macromolecules are responsible for starch recrystallization, which leads to changes in the mechanical response of starch-based films (Cano, Jiménez, Cháfer, González, & Chiralt, 2014; Jiménez et al., 2012a; Talja, Helén, Roos, & Jouppila, 2007). Besides their poor mechanical properties, starch films are highly hydrophilic in nature, which confers a great water vapour sensitivity and poor water barrier properties. Some authors have tried to overcome these aspects by blending starch with other compounds, such as sodium caseinate (Jiménez, Fabra, Talens, & Chiralt, 2012c), sorbitan esters of fatty acids (Ortega-Toro, Jiménez, Talens, & Chiralt, 2014a, 2014b), soy protein isolate (Galus, Lenart, Voilley, & Debeaufort, 2013; Galus, Mathieu, Lenart, & Debeaufort, 2012) or biodegradable synthetic polymers (Arvanitoyannins, 1999).

Poly(vinyl alcohol) (PVA) is a synthetic water-soluble polymer, widely used in different industrial, commercial, medical and food applications (Ramaraj, 2007). PVA has been extensively studied because of its biocompatibility and interesting physical properties, which are due to the presence of OH groups and the hydrogen bond formation (Alexy et al., 2003; Bonilla, Fortunati, Atarés, Chiralt, &

Kenny, 2014). Films obtained from PVA are fully biodegradable, odourless, transparent, non-toxic and have useful physical properties, such as high tensile strength and flexibility, good oxygen and aroma barrier properties and transparency (Ramaraj, 2007).

Different studies into starch-PVA blends have been carried out, focussing on biodegradability studies (Priya, Gupta, Pathania, & Singh, 2014; Lu et al., 2009; Siddaramaiah, Raj, & Somashekar, 2004) or the effect of the incorporation of different additives to the blends, such as citric acid, glutaraldehyde or urea (Priya et al., 2014; Luo, Li, & Lin, 2012; Ramaraj, 2006; Shi et al., 2008), calcium chloride (Jiang et al., 2012), poly(methyl methacrylate-co-acrylamide) nanoparticles (Yoon, Park, & Byun, 2012) for different purposes (compatibility enhancement or development of biomedical and packaging materials).

Chen et al. (2008) studied the effect of pea-starch nanocrystals (PSN) and native pea starch (NPS) on the structure and physico-chemical properties of the PVA films. They found that PSN were more homogeneously dispersed in the PVA matrix than the NPS, resulting in stronger interactions with PVA and better mechanical behaviour. Sreekumar, Al-Harthi, and De (2012) found a partial miscibility of the polymers in blends of corn starch and PVA, by analysing X-ray diffraction and thermal and mechanical response. Polymer compatibility and PVA crystallinity greatly decreased when the starch content rose, which affected the mechanical response of the films.

Mechanical and optical properties, wide-angle X-ray scattering, and biodegradation of PVA films containing a small ratio of corn starch (0–10 %) were analysed by Siddaramaiah et al. (2004). Although they report an increase in the haze and diffusion of light, there was only a slight change associated with the tensile behaviour of PVA films, which could be explained in terms of the changes in the crystalline structural parameters.

Pea starch is highly available and one of its advantage is its high amylose content about 24%–65%, depending on variety (Han et al., 2006; Hoover & Sosulski, 1991). In most of the cases the amylose/amylopectin ratio is higher than in corn starch. The high amylose content contributes to improve the tensile strength and gas barrier properties of starch based films (Cano et al., 2014; Lourdin, Della Valle, & Colonna, 1995; Palviainen et al., 2001; Wolff, Davis, Cluskey, Gundrum, & Rist, 1951). The very low oxygen permeability of high amylose starch films make them very useful for preservation of foods sensitive to oxidation process, such as meat and fish products or nuts. No studies have been found into the effect of PVA on the properties of gelatinized pea-starch films and on their ageing behaviour, which is one of the main drawbacks to the practical use of starch films as food packaging material. Although it could be expected a relatively close behaviour of pea-starch-PVA blend films to that obtained for corn starch blends, differences in starch sources (tubercles, cereals or legumes) can imply notable changes in the film's properties (Fredriksson, Silverio, Andersson, & Eliasson, 1998; Hoover & Ratnayake, 2002). Likewise, to prove differences and similarities between starch behaviour from different sources in the films is interesting in order to their possible substitution in the industrial uses.

The aim of this work was to analyse the effect of blending different ratios of PVA and pea starch on the structure, thermal behaviour, physical properties and ageing of blend films, in order to elucidate possible beneficial effects in the starch film properties.

2. Material and methods

2.1. Materials

Pea starch (S) was purchased from Roquette Laisa España S.A. (Benifaió, Valencia, Spain), poly(vinyl alcohol) (PVA) (M_w:

89,000–98,000, degree of hydrolysis >99%, and viscosity: 11.6–15.4 cP) was obtained from Sigma Aldrich Química S.L. (Madrid, Spain) and glycerol and magnesium nitrate-6-hydrate were provided by Panreac Química S.A. (Castellar de Vallès, Barcelona, Spain).

2.2. Preparation of film-forming dispersions and S:PVA blend films

Films were obtained by solvent casting procedure after the preparation of film-forming dispersions (FFDs).

Starch (1% w/w) was dispersed in an aqueous solution at 95 °C for 30 min and, while stirred, to induce starch gelatinization. Thereafter, the dispersion was homogenized using a rotor-stator homogenizer (Ultraturrax D125, Janke and Kunkel, Germany) at 13,500 rpm for 1 min and 20,500 rpm for 3 min. Finally, glycerol was added at a starch:glycerol ratio of 1:0.25, on the basis of previous studies (Jiménez, Fabra, Talens, & Chiralt, 2012b). PVA (2% w/w) was dispersed in an aqueous solution and maintained at 90 °C for 30 min until complete dissolution. For S-PVA blends, PVA was incorporated into the previously gelatinized starch dispersion by using S:PVA ratios of 1:2, 1:1 and 2:1 (named as S1:PVA2, S1:PVA1 and S2:PVA1, respectively). Afterwards, glycerol was also added (ratio starch:glycerol, 1:0.25).

To obtain the films, the FFDs were stirred for 30 min and poured into petri casting plates, in the amount which would provide a density of solid of 145 g·m^{-2}. Films were dried at 40 °C in a convection oven for 48 h and afterwards, peeled off the casting surface. Films were conditioned at 53% RH at room temperature (25 ± 2) °C until further analysis.

2.3. Characterization of S:PVA films

2.3.1. Fourier transform infrared spectroscopy (FT-IR)

Structural analysis was carried out by using the Fourier transform infrared spectra (FT-IR, Jasco FT-IR 615 spectrometer, Easton MD, USA). For the measurement, a few drops of solution were cast on a silicon plate for each formulation and investigated in transmission mode over the 400–4000 cm^{-1} range. Two replicates per formulation were measured.

2.3.2. Film thickness

The film thickness was measured at six random positions with a micrometer (MicrometerStarrett) to the nearest 0.001 mm.

2.3.3. Microstructure of films

The microstructural analysis of the cross-section and surface of the films was carried out using field emission scanning electron microscopy (FESEM) (Supra™ 25-Zeiss, Germany). To this end, films were equilibrated at 53% RH in desiccators by using Mn(NO$_3$)$_2$ solution. Two replicates per formulation were fixed on copper stubs, gold coated, and observed using an accelerating voltage of 2 and 5 kV, for the surface and cross-section observations, respectively.

2.3.4. Thermogravimetric analysis (TGA)

A thermogravimetric analyzer (Seiko Exstar 6300, Italy) was used to obtain the thermal weight loss (TG), and the derivate (DTG), of samples. To this end, the samples were heated from 30 °C to 600 °C at 10 °C/min, using a nitrogen flow (250 mL/min). Prior to the analyses, the samples were conditioned at 25 °C and 53% RH. The thermal degradation temperature was obtained at the maximum of the DTG curves (T$_{max}$). The measurements were taken in triplicate.