



Physical and microstructural properties of biodegradable films based on pea starch and PVA



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ABSTRACT

The effect of storage time on the physical properties of pea starch (PS) and polyvinyl alcohol (PVA) films and their blend was studied to develop biodegradable packaging materials for food applications. To this end, an analysis was performed of the microstructural and physical properties (solubility, moisture content, barrier, mechanical and optical properties) of PS, PVA and PS:PVA films stored for five weeks (25°C–53%RH). Whereas SEM micrographs showed a homogenous appearance for PS films, PVA presented irregularities typical of semi-crystalline structures. Blend films showed a structure which was more similar to PVA films. After 5 weeks, the physical properties of PVA films did not change; in the case of PS, however, the elastic modulus and tensile strength increased markedly but the stretchability and gloss significantly decreased, which was associated with water loss in the starch matrix. All the physical properties of blend films remained unchanged throughout time, except the elastic modulus and the tensile strength, which slightly increased. Therefore, the incorporation of PVA into pea starch films improved their physical properties and inhibited the changes that occurred in the starch matrix caused by ageing.

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1. Introduction

In the last few years, an important effort has been made by the scientific community to search for bioplastics, which represent an environmentally-friendly and sustainable alternative, whose production has greatly increased over the last few years (Avérous and Pollet, 2012).

Starch is the one of the most important polysaccharides used to develop biodegradable films due to its potential to form a continuous matrix at low cost (Gupta et al., 2014). It is well known that starch has a granular structure and is composed of two macromolecules: amylose and amylopectin. Both polymers are responsible for the starch crystallization which leads to changes in the mechanical response (increased stiffness) of starch products (Talja et al., 2007). The amylose:amylopectin ratio depends on the source of starch, ranging from 15:85 to 35:65. Several studies have reported the use of starches from various sources to prepare biodegradable films and coatings with different properties (Chen et al., 2008; Bonilla et al., 2013; Gupta et al., 2014; Jiménez et al., 2012; Luo et al., 2012 and Ortega-Toro et al., 2014). Of the different kinds of starches, pea starch has a high-amylose content, which normally leads to an improvement in both the mechanical strength

and the gas barrier properties of starch-based films (Han et al., 2006). Films based on starch are odorless, colorless, transparent and with very low oxygen permeability. Nevertheless, starch films present some drawbacks, such as poor water vapor barrier properties and high rigidity, which increase throughout the storage time due to the progress of crystallization in high relative humidity conditions and chain aggregation due to the progressive formation of hydrogen bonds (Cano et al., 2014; Forssell et al., 1999; Myllärinen et al., 2002; and Rindlav-Westling et al., 1998).

Different attempts have been made to overcome these problems when designing starch-based biodegradable films, the most common being to obtain blends with other biopolymers or bioplastics (Bonilla et al., 2013; Gupta et al., 2014 and Ortega-Toro et al., 2014) which are obtained from renewable sources or synthesis and which are biodegradable or compostable. Of the bioplastics, polyvinyl alcohol (PVA), aliphatic polyesters, such as poly B-hydroxyalkanoates (PHA) and polylactic acid (PLA) or poly ϵ -caprolactone (PCL), represent interesting alternatives because of their good mechanical properties and, in some cases, hydrophobic nature, which can contribute to modulate starch properties. Of the different bioplastics, PVA presents the greater compatibility with starch molecules at lower cost (Lu et al., 2009), which is important to ensure the competitive cost of the blend.

Polyvinyl-alcohol is a synthetic bioplastic, which is fully degradable and water soluble. Recently, PVA has received attention

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because of its biocompatibility and its good physical properties, which are due to the presence of OH groups and the hydrogen bond formation (Bonilla et al., 2014). PVA also has good film forming capability, giving rise to odorless, non-toxic films with high tensile strength and flexibility, good oxygen and aroma barrier properties, good transparency and chemical resistance.

Different studies into starch-PVA blends can be found in the literature, thus showing the increasing interest produced by these systems. Some of them mainly focus on biodegradability studies (Gupta et al., 2014; Lu et al., 2009 and Siddaramaiah et al., 2004). Other authors have analyzed the effect of the incorporation of different additives to the starch: PVA blends, such as citric acid, glutaraldehyde or urea (Gupta et al., 2014; Luo et al., 2012; Ramaraj, 2007 and Shi et al., 2008), calcium chloride (Jiang et al., 2012), or nanoparticles (Yoon et al., 2012) for different purposes (compatibility enhancement or biomedical and packaging applications). Few of them studied the effect of different starch:PVA ratios on film properties (Chen et al., 2008; Siddaramaiah et al., 2004 and Sreekumar et al., 2012).

Siddaramaiah et al., (2004) studied the influence of crystal imperfections caused by starch on the mechanical and optical properties of films. Their results support the formation of hydrogen bonds between the hydroxyl groups of PVA and starch in the polymer network. Chen et al. (2008) studied the effect of pea starch nanocrystals (PSN) and native pea starch (NPS) on the structure and physicochemical properties of the PVA films. They concluded that PSN are smaller in size and more homogeneously dispersed in the PVA matrix than the NPS, resulting in stronger interactions with PVA and better mechanical behavior.

Sreekumar et al. (2012) studied the structure and physical properties of different blends of corn starch and PVA, by analyzing X-ray diffraction and thermal and mechanical response. They concluded that the blends presented a partial compatibility, thanks to the addition of glycerol. Likewise, polymer compatibility and PVA crystallinity greatly decreased when the starch content rose, which affected the mechanical response of the films.

To the best of our knowledge, no studies have been found into the effect of PVA on the ageing behavior of starch films, which is one of the main drawbacks for the practical use of starch films as packaging material, as previously commented on.

The objective of this work was to analyze how PVA affects the development of the starch film properties throughout the storage. To this end, optical, mechanical and barrier properties of PS:PVA (1:1) blend films stored for five weeks were analyzed and compared to pure PS and PVA films.

2. Materials and methods

2.1. Materials

Pea starch was purchased from Roquette (Roquette Laisa España, Benifaió, Spain) and Poly (vinyl alcohol) (M_w : 89,000–98,000, degree of hydrolysis > 99%, and viscosity: 11.6–15.4 cP) was supplied by Sigma (Sigma Aldrich Química S.L., Madrid, Spain). Glycerol, as starch plasticizer, was provided by Panreac Química S.A., (Castellar de Vallès Barcelona, Spain).

2.2. Preparation and characterization of films

Films were prepared by casting. For the preparation of pure pea starch films (PS), 2% (w/w) starch aqueous dispersions were heated in a water bath at 95 °C for 30 min to induce starch gelatinization and homogenized for 1 min at 13,500 rpm and for 3 min at 20,500 rpm using a rotor–stator-homogenizer (Ultraturrax D125, Janke and Kunkel, Germany). Finally, glycerol was incorporated

in a ratio of 1:0.25 (Starch:Glycerol) and mixed. For pure PVA films, 1% (w/w) PVA dispersion was dissolved in distilled water by stirring for 30 min at 90 °C. In PS:PVA composite films, PVA was added to the starch dispersion at 90 °C in a ratio of 1:0.5 (PS:PVA) and stirred until dissolved (30 min). 1.5 g of total solids of different film forming dispersions (FFD) were gently spread over a Teflon plate (15 cm diameter) resting on a level surface, which would provide a density of solid of 84.7 g/m². Films were formed by drying at 25 °C and 45%RH for approximately 48 h. The RH was monitored by means of a portable Alarm-Hygrometer testo 608-H2 (Lenzkirch, Germany) placed in the same drying room.

2.3. Film conditioning

After the drying process, films were conditioned in desiccators at 25 °C and 53%RH by using magnesium nitrate-6-hydrate oversaturated solution (Sigma Aldrich Química S.L., Madrid, Spain) for one week (considered as initial storage time, t_0) when the first series of analysis were carried out. One part of the samples was stored under the same conditions for five weeks (final storage time, t_f) in order to perform the second series of analysis of stored films. After this storage period, the physical properties of pea starch films have been shown to remain almost unaffected by time due to its low amylopectin content (Cano et al., 2014).

The film thickness of every sample was measured after these two times at six random positions with a Palmer digital micrometer to the nearest 0.0025 mm.

2.4. Characterization of films

2.4.1. Microstructural analysis

The microstructure of films was observed by Field emission scanning electron (SEM) (JEOL®, model JSM-5410, Japan) in films previously equilibrated (conditioned) at 25 °C and 53%RH for 1 week (initial storage time).

SEM observations were carried out on the film surface and at their cross section. To prepare the samples, films were frozen in liquid N₂ and cryofractured to observe the cross section. Two replicates per formulation were fixed on copper stubs, gold coated, and observed using an accelerating voltage of 2 kV to surface (750×) and 5 kV to cross sections (1.500×).

2.4.2. Solubility

The solubility of films was determined by means of a gravimetric method previously described by Ortega-Toro et al., 2014. For this purpose, the samples were kept in distilled water in a film:water ratio of 1:10 for 48 h, and later on, they were transferred to a convection oven (J.P. Selecta, S.A., Barcelona, Spain) for 24 h at 60°C to remove the free water, and afterwards, they were completely dried in a desiccator with P₂O₅ °C until constant weight. Three replicates were analyzed for each formulation, and results were expressed in g of dissolved film/g dry film.

2.4.3. Moisture content

The films moisture content (MC) was analyzed using a gravimetric method. Five replicates per formulation were dried at 60 °C for 24 h in a vacuum oven, and then they were equilibrated with P₂O₅ until constant weight.

2.4.4. Mechanical properties

Mechanical properties were measured by means of a Universal Machine (TA.XT plus, Stable Micro Systems, Haslemere, England). Equilibrated specimens were mounted in the film-extension grips of the testing machine and stretched at 50 mm min⁻¹ until breaking, following the ASTM standard method D882 (ASTM, 2001). Force-distance curves were obtained and transformed into

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