



# Physical properties and antioxidant capacity of starch–sodium caseinate films containing lipids

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## ARTICLE INFO

### Article history:

Received 5 November 2012  
Received in revised form 4 January 2013  
Accepted 13 January 2013  
Available online 31 January 2013

### Keywords:

Starch  
Sodium caseinate  
 $\alpha$ -Tocopherol  
Barrier properties  
Antioxidant

## ABSTRACT

Biodegradable films based on starch, sodium caseinate, glycerol and lipids (oleic acid and/or  $\alpha$ -tocopherol) were obtained and evaluated in terms of microstructure, mechanical behaviour, barrier and optical properties and antioxidant capacity. The effect of film storage time on these properties was also analysed. The lipid incorporation provoked phase separation due to the different interaction between each polymer and lipids, although structural rearrangement of components during storage could be deduced from the change in mechanical behaviour. After storage, all films showed similar mechanical properties, but lipid containing films were more stretchable. Lipid addition did not induce a notable decrease in water vapour permeability of the films, but oxygen permeability highly increased when they contained oleic acid. All films were highly transparent, with very small differences among formulations, although their gloss values increased when lipids were added. The incorporation of  $\alpha$ -tocopherol greatly increased the antioxidant capacity of the films which affected oxygen permeability.

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## 1. Introduction

Due to the severe environmental pollution caused by plastic food packaging, there has been a growing amount of interest in the production of edible and biodegradable films (Yan et al., 2012). In this sense, there are a great number of studies focusing on solving the problems produced by plastic waste and obtaining environmentally friendly materials (Jiménez et al., 2012a). Several works study the possibility of substituting the petro-based plastics for biodegradable, low cost materials with similar properties (Pso-miadou et al., 1996; Mali et al., 2002, 2006; Famá et al., 2007). In this sense, starch is the most abundant natural polysaccharide and it is described as a renewable resource, inexpensive and widely available (Lourdin et al., 1995). Starch-based films exhibit appropriate physical characteristics, since these films are isotropic, odourless, non-toxic, biodegradable, tasteless, colourless and constitute a good barrier against oxygen transfer (Krochta et al., 1994; Yan et al., 2012). Nevertheless, starch films exhibit several drawbacks which it would be beneficial to overcome to increase their potential use. One of the main disadvantages of starch is that the mechanical behaviour of films can be negatively affected by retrogradation phenomena. Jiménez et al. (2012b) found that starch re-crystallizes during film formation and storage, increasing the elastic modulus and decreasing the flexibility of films. In a recent work, they found that recrystallization of starch was also

influenced by the amylose–lipid interactions, thus giving rise to V-type crystalline forms for amylose (Jiménez et al., 2013). Composite films of starch with other biopolymers showed a lower degree of re-crystallization, thus minimising mechanical changes associated to starch retrogradation. This was observed in corn starch–sodium caseinate and corn starch–hydroxypropylmethylcellulose (HPMC) films (Jiménez et al., 2012a,c).

Sodium caseinate has a satisfactory thermal stability and can easily form films from aqueous solutions, due to its random coil nature and ability to form extensive intermolecular hydrogen, electrostatic and hydrophobic bonds (Arvanitoyannis and Biliaderis, 1998). Different aspects of this polymer as a matrix of edible and biodegradable films have been extensively studied (Siew et al., 1999; Kristo et al., 2008; Patzsch et al., 2010).

The addition of sodium caseinate to starch matrices reduced the degree of crystallinity of starch films and inhibited starch recrystallization during film storage (Jiménez et al., 2012a). Mixtures of both hydrocolloids provide films which are less stiff and resistant to fracture but more flexible and deformable than pure starch films, but with similar water vapour permeability values as starch films (Jiménez et al., 2012a). In the case of starch, this disadvantage has been avoided by different methods such as surface esterification (Ren et al., 2010), surface photocrosslinking (Zhou et al., 2008) or blending starch with other hydrophobic polymers (Averous et al., 2000; Fang and Fowler, 2003). For sodium caseinate, hydrophobic additives, such as fatty acids, waxes or oils, were incorporated in the films in order to improve the resistance to water vapour transfer (Morillon et al., 2002; Pereda et al., 2010).

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Fatty acids have been tested widely in film formulation to improve their water vapour barrier ability (Hagenmaier and Shaw, 1990; Koelsch and Labuza, 1992; Ayranci and Tunc, 2001; Fernández et al., 2006). In sodium caseinate matrices, oleic acid (C<sub>18:1</sub>) acts as a plasticizer, greatly increasing the film extensibility (Fabra et al., 2008).

Another lipid that has been used in film formulation is  $\alpha$ -tocopherol, which improves water barrier properties while conferring antioxidant capacity to the film (Fabra et al., 2011). This component is a lipid-soluble antioxidant whose antioxidant activity has been clearly documented (Rupérez et al., 2001; Manzanarez-López et al., 2011). Like other tocopherols (tocopherols and tocotrienols),  $\alpha$ -tocopherol acts as a free radical scavenger specifically within cell membranes, by preventing the oxidation of polyunsaturated lipids by free radicals, especially hydroxyl radical OH (Hejtmánková et al., 2010). This antioxidant has been used in film formulation, by using both synthetic (Lee et al., 2004; Granda-Restrepo et al., 2009) and natural polymers (Martins et al., 2012).

The aim of this work is to evaluate the effect of the addition of oleic acid and/or  $\alpha$ -tocopherol on the properties of corn starch–sodium caseinate composite films, through the analyses of the microstructural, mechanical, barrier and optical properties of films, as well as their antioxidant capacity. This was carried out in newly prepared/conditioned films and in those stored for 5 weeks.

## 2. Materials and methods

### 2.1. Materials

Corn starch and sodium caseinate (NaCas) were purchased from Roquette (Roquette Laisa España, Benifaió, Spain) and Sigma (Sigma–Aldrich Chemie, Steinheim, Germany), respectively. Oleic acid (OA) and  $\alpha$ -tocopherol (TOC), selected as the hydrophobic dispersed phase, were also supplied by Sigma. Furthermore, glycerol was provided by Panreac Química, S.A. (Castellar del Vallés, Barcelona, Spain) as plasticizer.

### 2.2. Preparation and characterisation of films

Four different formulations based on corn starch, sodium caseinate, glycerol as plasticizer, and lipids were prepared. Corn starch was dispersed in cold water to obtain 2% (w/w) polysaccharide dispersions. These were maintained, under stirring, at 95 °C for 30 min to induce starch gelatinization. Sodium caseinate was dissolved directly in cool distilled water (2% w/w). Afterwards, both hydrocolloids were mixed to obtain dispersions with a starch:protein ratio of 1:1. Once the mixtures were prepared, a controlled amount of glycerol was added (hydrocolloid:glycerol ratio was 1:0.25). In the case of emulsions containing lipids, these were incorporated prior to the homogenisation step. The hydrocolloid:lipid ratios were 1:0.15 and 1:0.10 for oleic acid and  $\alpha$ -tocopherol, respectively. Dispersions were homogenised for 1 min at 13,500 rpm and for 5 min at 20,500 rpm at 95 °C, under vacuum, using a rotor–stator homogenizer (Ultraturrax T25, Janke and Kunzel, Germany). High temperature homogenisation favoured the denaturation of the protein and polymer interaction as well as the lipid dispersion in the system.

Film-forming dispersions, containing 1.5 g of total solids, were gently spread over a Teflon plate (150 mm diameter) resting on a leveled surface. The dispersions were allowed to dry for approximately 48 h at 45% RH and 20 °C. Dry films could be peeled intact from the casting surface. Film thickness, used in different analyses, was measured with a Palmer digital micrometer to the nearest 0.0025 mm at six random positions. Four kinds of films were pre-

pared: without lipids (control), with only oleic acid (OA) or  $\alpha$ -tocopherol (Toc) and with both of them (OA–Toc).

#### 2.2.1. Film equilibration and storage

Before characterising the films, samples were equilibrated in desiccators at 25 °C and 53% RH, by using magnesium nitrate-6-hydrate saturated solutions (Panreac Química, SA, Castellar del Vallés, Barcelona) for 1 week when the first analyses were carried out. One part of the samples was stored under the same conditions for five weeks in order to perform the second series of analyses.

#### 2.2.2. Tensile properties

A universal test Machine (TA.XTplus model, Stable Micro Systems, Haslemere, England) was used to determine the film elastic modulus (EM), the tensile strength (TS), and elongation at break (E) of the films, according to ASTM standard method D882 (ASTM, 2001). EM, TS and E parameters were determined from stress–strain curves, estimated from force–deformation data. After drying, flawless films were selected to determine their mechanical behaviour. At least eight replicates of each formulation were tested. The cut film samples had a rectangular section of 2.5 cm wide and 10 cm long. Before testing, all samples were equilibrated as explained previously at 53% RH and 25 °C. Equilibrated film specimens were mounted in the film–extension grips of the testing machine and stretched at a rate of 50 mm min<sup>-1</sup> until breaking.

#### 2.2.3. Barrier properties

**2.2.3.1. Water Vapour Permeability (WVP).** WVP of films was determined by using the ASTM E96-95 (ASTM, 1995) gravimetric method, taking into account the modification proposed by Mc Hugh et al. (1993). Films were selected for WVP tests based on the lack of physical defects such as cracks, bubbles, or pinholes. Distilled water was placed in Payne permeability cups (3.5 cm diameter, Elcometer SPRL, Hermelle /s Argenteau, Belgium) to expose the film to 100% RH on one side. Once the films were secured, each cup was placed in a relative humidity equilibrated cabinet at 25 °C, with a fan placed on the top of the cup in order to reduce resistance to water vapour transport. RH of the cabinets (53%) was held constant using oversaturated solutions of magnesium nitrate-6-hydrate (Panreac Química, SA, Castellar del Vallés, Barcelona). The cups were weighed periodically (0.0001 g) and water vapour transmission rate was determined from the slope obtained from the regression analysis of weight loss data versus time, once the steady state had been reached, divided by the film area. From this data, water vapour permeability values were obtained, taking into account the average film thickness in each case. The equation proposed by Mc Hugh et al. (1993) was used to correct the effect of concentration gradients established in the stagnant air gap inside the cup.

**2.2.3.2. Oxygen permeability (OP).** The oxygen barrier capacity of the films was evaluated by measuring oxygen permeability (OP) by means of an Ox-Tran 1/50 system (Mocon, Minneapolis, USA) at 25 °C (ASTM Standard Method D3985-95, 2002). Measurements were taken at 53% in films previously equilibrated at the same RH. Films were exposed to pure nitrogen flow on one side and pure oxygen flow on the other side. The OP was calculated by dividing the oxygen transmission rate by the difference in the oxygen partial pressure on the two sides of the film, and multiplying by the average film thickness. At least three replicates per formulation were taken into account.

#### 2.2.4. Scanning Electron Microscopy (SEM)

Microstructural analysis of the films was carried out using a Scanning Electron Microscope (JEOL JSM-5410, Japan). Film samples were maintained in a desiccator with P<sub>2</sub>O<sub>5</sub> for 15 days. Then films were frozen in liquid N<sub>2</sub> and gently and randomly broken

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