



Properties of starch–hydroxypropyl methylcellulose based films obtained by compression molding



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ABSTRACT

Corn starch–glycerol (1:0.3) films, containing or not citric acid (1 g/100 g starch) and HPMC (10 and 20 g/100 g starch), are obtained by compression molding. The microstructure of the films, the thermal behavior, the X-ray diffraction spectra and the physical properties (mechanical, barrier and optical) were analyzed after 1 and 5 storage weeks at 25 °C and 53% relative humidity. The bonded citric acid and film solubility were also determined. Starch–HPMC blend films showed a dispersed phase of HPMC in a continuous, starch-rich phase with lower glass transition than HPMC-free films. The addition of citric acid also provoked a decrease in glass transition in line with the partial hydrolysis of starch chains. Both components implied a decrease in the water vapour permeability while the oxygen permeability slightly increased. Although citric acid only provoked a small hardening effect in the films, it greatly decreased their extensibility (weak cross-linking effect), which seems to increase during film storage. Starch crystallization during storage was inhibited by both citric acid and HPMC.

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1. Introduction

Society's awareness of the importance of both environmental conservation and green technologies, and the growing environmental contamination caused by synthetic polymers based on petroleum, have led to an increased interest in developing environmentally friendly materials, such as biodegradable polymers based on polysaccharides. In the development of biodegradable materials, starch is the most promising of the polysaccharide polymers, due to its low cost, great processability, and abundance (Ghanbarzadeh, Almasi, & Entezami, 2011; Yoon, Chough, & Park, 2006). Starch films exhibit some good properties, such as high barrier to oxygen, carbon dioxide and lipids. However, poor water vapor permeability and mechanical properties, and the recrystallization during storage, are limitations of this material (Arif Kibar & Us, 2013; Kester & Fennema, 1986).

The deficiencies in the properties of starch films can be improved by different methods. The phenomenon of the recrystallization of starch films could be solved by combining starch with other polymers, as has been proven by other authors (Funami et al., 2005; Jiménez, Fabra, Talens, & Chiralt, 2012a). Hydroxypropyl methylcellulose (HPMC) is a cellulose-derived polymer commonly used

for obtaining edible, biodegradable films (Albert & Mittal, 2002; Sánchez-González, Vargas, González-Martínez, Chiralt, & Cháfer, 2009; Villalobos, Hernández-Muñoz, & Chiralt, 2006) with good availability and processability (Fahs, Brogly, Bistac, & Schmitt, 2010; Jiménez et al., 2012a) which have excellent film-forming properties (Villalobos et al., 2006). Compared to other polymers, HPMC films have great mechanical strength, (Jiménez, Fabra, Talens, & Chiralt, 2010, 2012a) but limited barrier properties. In this sense, Jiménez et al. (2012a) observed that the oxygen permeability of HPMC films obtained by casting was approximately 100 times higher than cornstarch films, while the water barrier properties are similar for films made from both polymers.

Nevertheless, the thermal stability of HPMC films means that they can be thermally processed using industrial equipment, and previous studies (Jiménez et al., 2012a) revealed inhibition of starch crystallization when blend films were obtained by casting the aqueous dispersions, the films showing a more amorphous character. So, HPMC–starch blends could be used to obtain thermally processed films with interesting properties, although phase separation in corn starch–HPMC films obtained by casting has been observed by scanning electron microscopy (Jiménez et al., 2012a), with the films exhibiting a starch-rich phase and a HPMC-rich phase in what is practically a bi-layer film.

The poor compatibility of these polymers can be limited by the incorporation of compatibilizer compounds, which promotes the esterification of the starch–OH groups. For this purpose,

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cross-linking agents, such as phosphorus oxychloride, sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin, and 1,2,3,4-diepoxybutane, were used (Reddy & Yang, 2010; Seker & Hanna, 2006). These substances are relatively toxic and expensive (Reddy & Yang, 2010), so their use in food packaging is not recommendable. However, using polycarboxylic acids as cross-linking agents is a good alternative. This is especially so in the case of citric acid, a low cost organic acid widely used in the food industry, that acts as a cross-linking agent due to the presence of several carboxyl groups in its molecular structure (Ghanbarzadeh, Almasi, & Entezami, 2010). These groups can react with the hydroxyl groups of starch molecules through the formation of esters. According to Reddy and Yang (2010), the esterification reaction using polycarboxylic acids occur with the polymer hydroxyl groups, at high temperatures (about 160 °C), through the formation of anhydride groups (Yang, Wang, & Kang, 1997). This interaction can decrease the retrogradation and recrystallization of starch during storage time (Ghanbarzadeh et al., 2011). The compatibilizer effect of the citric acid in the starch–polymer blends, as well as an improvement in the properties of starch films, has been reported in several studies (Ghanbarzadeh et al., 2010, 2011; Ma, Chang, Yu, & Stumborg, 2009; Reddy & Yang, 2010; Shi et al., 2008; Yu, Wang, & Ma, 2005). The most promising results derived from the addition of citric acid to the polymeric matrix are the increase in thermal stability and the improvement in the barrier properties (Reddy & Yang, 2010; Yu et al., 2005).

The aim of this work was to study the effect of citric acid addition on the structural and physical properties of corn starch films obtained by compression molding, combined with different ratios of HPMC, using glycerol as plasticizer. The effect of storage time on the film properties was also analyzed.

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). Hydroxypropyl methylcellulose (HPMC) and citric acid (CA) were provided by Fluka (Sigma–Aldrich Chemie, Steinheim, Germany).

2.2. Film preparation

Native starch and glycerol, as plasticizer, were dispersed in water. HPMC was hydrated in cold water (5%, w/w) under continuous stirring. The HPMC dispersion and the aqueous mixture of starch and glycerol were mixed in different ratios to obtain two blends with 1:0.1 and 1:0.2 starch:HPMC ratios. The polymer:glycerol ratio was 1:0.3. CA was mixed to obtain four blends with and without CA; a constant starch:CA ratio of 1:0.01 was used in every case. Blends of starch–glycerol and starch–glycerol–citric acid, in the previously described ratios, were studied as control formulations. The abbreviations used for the studied formulations were: SG:starch–glycerol; CA: citric acid; H10:10 g HPMC/100 g starch; H20:20 g HPMC/100 g starch.

The formulations were hot-mixed on a two-roll mill (Model LRM-M-100, Labtech Engineering, Thailand) at 160 °C and 8 rpm for 20 min. A visual good miscibility of HPMC, CA and starch was obtained. A trowel was used during mixing to smoothly spread the material on the rolls. The paste sheet formed was removed from the mill and conditioned at 25 °C and 53% relative humidity (RH), using a Mg(NO₃)₂ saturated solutions (Panreac Química, SA, Castellar del Vallès, Barcelona, Spain), for 48 h.

Afterwards, films were obtained by compression molding (Model LP20, Labtech Engineering, Thailand). Four grams of the pre-conditioned paste were put onto steel sheets and pre-heated on the heating unit for about 5 min. Compression molding was performed at 160 °C for 2 min at a pressure of 30 bars, followed by 6 min at 130 bars; thereafter, the cooling cycle was applied for 3 min. The 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. Film thickness

A Palmer digital micrometer was used to measure film thickness to the nearest 0.0025 mm at six random positions around the film.

2.3.2. Scanning electron microscopy (SEM)

The microstructural analysis of the cross-sections and surface of the films was carried out by means of a scanning electron microscope (JEOL JSM-5410, Japan). The film samples were maintained in desiccators with P₂O₅ for 2 weeks to guarantee that water was not present in the sample and observations were taken in duplicate for each film sample and in two films per formulation.

Film pieces, 0.5 cm² in size, were cryofractured from films and fixed on copper stubs, gold coated, and observed using an accelerating voltage of 10 kV.

2.3.3. X-ray diffraction

A diffractometer (XRD, Bruker AXS/D8 Advance) was used to record the X-ray diffraction patterns. All the samples (equilibrated for one and five weeks at 25 °C and at 53% RH) were analyzed at 25 °C and 53% RH, between $2\theta = 5^\circ$ and $2\theta = 30^\circ$ using K α Cu radiation (λ : 1.542 Å), 40 kV and 40 mA with a step size of 0.05°. For this analysis, samples were cut into 4 cm squares. Pure citric acid was also analyzed, so as to identify its characteristic peaks.

2.3.4. Atomic force microscopy (AFM)

Samples equilibrated for 5 weeks at 25 °C and 0% RH, using P₂O₅ saturated solutions (Panreac Química, SA, Castellar del Vallès, Barcelona, Spain), were used. The surface morphology of the films was analyzed using an atomic force microscope (Multimode 8, Bruker AXS, Santa Barbara, USA) with NanoScope[®] V controller electronics. Measurements were taken from several areas of the film surface (20 μm²) using the PeakForce QNM mode. Method ASME B46.1 (ASME, 1995) was used to calculate the following statistical parameters related with sample roughness: average roughness (Ra: average of the absolute value of the height deviations from a mean surface), root-mean-square roughness (Rq: root-mean-square average of height deviations taken from the mean data plane), and factor of roughness (*r*: ratio between the three-dimensional surface and two-dimensional area projected onto the threshold plane). The DMT modulus, derived from the Peak Force QNM Mode, was also applied to obtain the surface maps showing the heterogeneities present in the surface properties. Three replicates were considered for each sample.

2.3.5. Optical properties

The Kubelka–Munk theory for multiple scattering was applied to the reflection spectra to determine the film's transparency (Hutchings, 1999). The surface reflectance spectra were determined from 400 to 700 nm using a spectro-colorimeter CM-3600d (Minolta Co., Tokyo, Japan) on both a white and a black background. As the light passes through the film, it is partially absorbed and scattered, which is quantified by the absorption (*K*) and the scattering (*S*) coefficients. The internal transmittance (*T_i*) of the films

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