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Effect of the addition order and amylose content on mechanical, barrier and structural properties of films made with starch and montmorillonite

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ABSTRACT

This study considered the effect of amylose content (30% and 70%), montmorillonite (MMT) fraction (5 and 15%) and preparation method on mechanical and barrier properties of starch/clay nanocomposites prepared by casting. In Method 1, (30% w/w) glycerol was incorporated before starch gelatinization and MMT addition, while in Method 2 after gelatinization and MMT addition. Nanocomposites with higher amount of MMT showed the highest tensile strength and Young's modulus for both preparation methods. Method 1 favored nanocomposite properties of films with less amylose content, meanwhile Method 2 favored nanocomposites properties with higher amylose content. Water vapor permeability did not decrease significantly in starch films with different amylose content with the two different preparation methods. X-ray diffraction of the starch films indicated intercalated structures. Higher melting temperature (T_m) was found for nanocomposites with Method 2, indicating more ordered structures. Films with 70% amylose content have higher T_m than films with 30% amylose.

1. Introduction

Pollution is a serious and growing environmental concern that has motivated the development of biodegradable materials showing comparable properties with existing polymeric materials at equivalent cost. Starch, the dominant carbohydrate reserve material of higher plants, is an abundant and relatively inexpensive biopolymer. Starch granules are composed of amylose and amylopectin macromolecules, both of which are polymers of glucose. The main structural difference between these macromolecules is that amylopectin is a highly branched molecule with high molecular weight (1×10^8 g/mol), whereas amylose is mainly linear with average molecular weight of 1×10^6 g/mol. Most starches typically contain 25% amylose and 75% amylopectin, through some genotypes of nearly pure amylopectin or high amylose content do exist (Buleon, Colonna, Planchot, & Ball, 1998). It is documented that amylose form stronger films than amylopectin, which is attributed to the ability of its lineal chains to interact by hydrogen bonds to a higher extent than the branched amylopectin chains. In amylopectin films, weaker inter-chain hydrogen bonds are found as induced by the higher degree of entanglement caused by extensive branching and the short average length of the polymeric chain (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998; Rindlava, Hulleman, & Gatenholma, 1997).

Films from typical starch sources can be readily obtained, although resulting in very brittle material (Liu, Chaudhary, Yusa, & Tadé, 2011). This undesired property is a result of strong cohesive energy of the polymers. Films made from high-amylose corn starches show excellent oxygen barrier properties, lower water vapor solubility, lower retrogradation temperature, and more stable mechanical properties at high relative humidity (RH) than those made from normal starch (Stading, Rindlav-Westling, & Gatenholm, 2001). High-amylose starch is a very useful film-forming material because of it has strong gelation properties and helical linear polymer structure (Juliano, 1985). Films made from high-amylose starch from rice and pea have excellent oxygen barrier property with high stretch ability, but are largely affected by environmental relative humidity (Mehyar & Han, 2004). Films made from normal native starch had lower Young's modulus than films with higher amylose content (Chaudhary, Miler, Torley, Sopade, & Halley, 2008).

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In general, starch films are water sensitive and present inferior mechanical properties than synthetic polymers. This weakness could be improved by the preparation of composites with inorganic natural reinforcing materials (Huang, Yu, & Ma, 2004; Wilhelm, Sierakowski, Souza, & Wypych, 2003; Cyras, Manfredi, Ton-That, & Vázquez, 2008). The introduction of fillers to a polymeric matrix increases its strength and stiffness due to its small particle size and intercalation properties. Among these fillers, special attention has been paid to sodium montmorillonite (MMT), which is composed of hydrated aluminosilicate layers (Murray, 2000). Due to the presence of sodium cations between the interlayer spaces, is hydrophilic and miscible with hydrophilic polymers like starch (Park, Lee, Park, Cho, & Ha, 2003). Research has been carried out with normal starch from different sources like potatoes (Cyras et al., 2008), cará (Wilhelm et al., 2003), corn and wheat (Majdzadeh-Ardakani, Navarchian, & Sadeghi, 2010) adding MMT into the film formulation. Physical and mechanical properties of glycerol-plasticized starch/clay nanocomposites are affected by MMT content, type of clay and mixing type. The hydrophilicities of clays had significant effects on the properties, showing a higher tensile strength and better barrier properties than control films (Gao, Dong, Hou, & Zhang, 2012). Young's modulus increased with the MMT content, this behavior was attributed to the oriented backbone of the polymer chain in the gallery of the clay bonded by hydrogen interactions between them (Huang et al., 2004). The deformation decreases with the MMT content due to that silicate layers acts as a mechanical reinforcement of starch reducing the flexibility of the polymer that is the reason for the lower percentage of elongation (Cyras et al., 2008). It was noted that the amylose to amylopectin ratio in conventional starch sources did not affect the final properties of nanocomposites (Majdzadeh-Ardakani et al., 2010).

A limited number of studies have been carried out with high amylose starch and MMT (Chaudhary et al., 2008; Mondragón, Mancilla, & Rodríguez-González, 2008; Tang, Alavi, & Herald, 2008). In particular, the effect of amylose and amylopectin in starch films added with MMT on the physicochemical and mechanical properties is still poorly understood. Addition of MMT in waxy, normal and high amylose starch films showed that 2% of MMT produced exfoliated structure meanwhile at 10% MMT was intercalated, affecting the mechanical and barrier properties of the films (Mondragón et al., 2008). The clay dispersion in starch films with different amylose content could be related to the physical properties of the filmogenic solution. These properties depend on the amount of amylose leached from the granule, the swelling of granules, the entanglement of amylose and amylopectin molecules in the matrix, and the interactions between components (Tang et al., 2008).

In the elaboration of nanocomposites, polymer chains from the bulk could penetrate inside the silicate layers and depending on penetration extent, an intercalated or exfoliated structure may be formed. Different parameters determine this behavior: degree of diffusion, type of clay, polar–polar interactions, molecular weight of polymer, packaging density inside the gallery, concentration of filler, etc. (Pandey & Singh, 2005). A determinant factor to form intercalated or exfoliated polymer-clay nanocomposites is a good interfacial interaction, which occur when the surface polarities of clay and polymer are similar. It has been reported that changing contents of amylose affected the formation of intercalated/exfoliated clay structures and the interactions with plasticizer. It was hypothesized that as amylose content increased there is more chains to interact with the MMT (Tang et al., 2008). The reinforcement of polymeric systems by clay has been attributed to the nanometric dispersion of silicate layers, the interaction between polymers and clay, the formation of partially immobilized polymer phases due to silicate layers and the orientation of silicate layers (Ramos Filho, Mélo, Rabello, & Silva, 2005; Aouada, Mattoso, & Longo, 2011; Slavutsky, Bertuzzi, & Armada, 2012).

The aim of this study was twofold: (i) to evaluate the effect of amylose and MMT content, and (ii) to assess the effects of the addition order of the components on the mechanical and barrier properties of starch films. The motivation for carrying out this study relies in the fact that the order of addition of components plays an important role in the interactions among the fractions in the matrix, and hence in the properties of the film obtained.

2. Materials and methods

Normal corn starch (30%) and high amylose Hylon VII (70%) were purchased from Ingredion (formerly, Corn Products and National Starch at Bridgewater, N.J.). Glycerol (G7757). Sodium montmorillonite (682659) was purchased from Sigma Aldrich (Sigma, St Louis, MO).

2.1. Elaboration of films

Method 1: Film forming solution was prepared using 4 g of starch, 30% w/w of glycerol, and 100 ml of distilled water. The mixture was gelatinized in autoclave (121 °C for 20 min) for high amylose starches, and in a hot plate with a stirring device for normal starch at 90 °C. A specified amount (5, 10, 15% w/w) of MMT was dispersed into 20 ml of distilled water and sonicated (Bransonic 1510R-MTH) for 1 h. After, the nanoclay dispersion was added to the starch suspension at 80 °C and held at this temperature for 10 min. The final slurry was cast into acrylic plates (20 × 20 cm) and incubated in an oven (*IBTF-050*) at 65 °C for 6 h. The dried films were peeled and stored until further analysis.

Method 2: Film forming solution was prepared as before but without glycerol. After starch gelatinization (autoclaving or hot plate) the nanoclay dispersion was added to the starch suspension at 80 °C and held at this temperature for 10 min. Subsequently, glycerol was added and the stirring continued for five more minutes. The final slurry was cast into acrylic plates and dried as made in Method 1.

2.2. Thickness measurement

Thickness was measured using a manual micrometer (Fowler, USA). Measurements were performed on ten different points along the film.

2.3. Water vapor permeability (WVP)

WVP test was conducted following the ASTM E96-66 method. An acrylic cup (55 mm height and 65 mm in diameter) was employed as a permeation device. Each film was sealed over a circular opening of the cup and inside the cup a saturated salt solution (75% HR) was used. This cup allows a transference area of 53 mm in diameter. The cup was placed inside the permeability chamber containing silica gel (0% HR) with temperature control at 30 °C. The water vapor transport was determined from the weight gain of the permeation cup against time. Data was automatically recorded every 30 min during a period of 6 h in an analytical balance connected to a computer. The coefficient of the straight line, obtained by linear regression, was considered the water vapor transmission rate. The water vapor permeability can be calculated including the difference of water vapor pressure of the environment, the thickness of the material and the transference area. Films were conditioned at 57% RH for 72 h before testing and all tests were conducted in triplicate.