



# Effect of amylose content and nanoclay incorporation order in physicochemical properties of starch/montmorillonite composites



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## ABSTRACT

The effects of the amylose content and the preparation sequence in physicochemical properties of starch/montmorillonite (MMT) composites were studied in this work. Native (30%) and high amylose Hylon VII (70%) starches were considered for assessing the effects of amylose content. Glycerol and MMT were used as additives to evaluate the effects of the former as plasticizer and the latter as reinforcer. The glycerol was incorporated before (Method M1) and after (Method M2) the addition of MMT. FTIR studies indicated that water bonding was affected by amylose content. Sorption isotherms indicated that method M2 favoured water adsorption and method M1 reduced water adsorption due to competition for active sites for interaction. TGA showed that method M1 induced a higher degradation rate than method M2. Wettability analysis by contact angle measurements showed that plasticizer promoted the hydrophilicity of the film, whereas MMT promoted a hydrophobic surface for both cases of amylose content.

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## 1. Introduction

The recent decades have witnessed a growing interest in the use of biodegradable polymers for packaging materials aimed to reduce the environmental pollution caused by synthetic plastic wastes. Starch, one of the natural biodegradable polymers, has been considered as one of the most promising candidates primarily because of its attractive combination of high availability, biodegradability and relatively low cost. However, native starch has several drawbacks, such as poor processability and hydrophilic behavior that shares with most natural polymers. Some strategies have been developed to improve the barrier and mechanical properties of starch-based biodegradable films, including (a) the addition of synthetic biodegradable polymers like poly vinyl alcohol and polylactide to produce materials with intermediate properties to the two components (Chen, Julian, & Evans, 2005), (b) the incor-

poration of new plasticizers such as urea or formamide (Ma, Yu, & Feng, 2004), and (c) the use of clays to improve mechanical and barrier properties (Sinha & Okamoto, 2003). The most commonly clays used for this purpose are montmorillonite (MMT), hectorite, saponite and their modifications. Clays offer some advantages, such as environmentally friendly, naturally abundance and inexpensive processing. MMT, hectorite and saponite are layered silicates belonging to the general family 2:1 or phyllosilicates. Their crystal structure consists of layers made up of two silica tetrahedral fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Some of the aluminum atoms are replaced with magnesium creating a difference in valences and a negative charge distribution within the platelets. These charges are balanced by positively charged ions such as Na<sup>+</sup>. Hydration of these sodium ions causes the clay to swell and provides the ability to host polymer chains between the layers, which are facilitated by attractive forces such as hydrogen bonds (Paul & Robeson, 2008).

The presence of nanoclay in polymer formulations increases the tortuosity of the diffusive path for a penetrating molecule,

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and changes the molecular mobility, which in turn enhances thermal, mechanical and barrier properties. Starch is compatible with Na<sup>+</sup>MMT due to interaction between its polar hydroxyl groups and inorganic Na<sup>+</sup> ions of nanoclay. This gives well intercalated or exfoliated nanocomposites, which help to improving the mechanical and barrier properties of the starch films (Avella et al., 2005; Dean, Yu, & Wu, 2007; Dean, Do, Petinakis, & Yu, 2008; Tang, Alavi, & Herald, 2008). The intercalated nanocomposites arise from the penetration of polymer into the interlayer region of the clay, resulting in an ordered multilayer structure with alternating polymer/inorganic layers at a repeated distance of a few nanometers. Exfoliated nanocomposites involve extensive polymer penetration, with the clay layers delaminated and randomly dispersed in the polymer matrix (De Azeredo, 2009; Weiss, Takhistov, & McClements, 2006).

The structure of starch-clay nanocomposites has been studied in the recent years. Potato starch/MMT composite presented an increase in tensile strength (TS) and decrease in water vapor transmission rate (Park et al., 2002, Park, Lee, Park, Cho, & Ha, 2003). Also, an increase of about 70% in TS was observed in Cará root starch/hectorite composite with 30% of clay as compared with its counterpart without clay (Wilhelm, Sierakowski, Souza, & Wypych, 2003). Wheat starch/MMT nanocomposite presented higher thermal stability and lower water absorption than the material without MMT (Chiou et al., 2007). It was found that plasticizers like glycerol and urea/ethanolamine have only a marginal effect in the dispersion of the MMT clays into matrices (Zeppa, Gouanvé, & Espuche, 2009). The above mentioned studies used unmodified normal starch (around 30% amylose content) from different botanical sources, although systematic studies using unmodified starch with high amylose content are scarce.

The preparation method and process condition have strong influence in the characteristics of starch/MMT films. However, it was found that the sequence of addition of components had a significant effect on the nature and properties of composites formed (Pandey & Singh, 2005). It was reported that among glycerol and normal starch, penetration of glycerol into the clay galleries is favored owing to its smaller molecule size. Besides, if plasticizer is added after mixing of clay in the starch matrix, enhanced mechanical properties can be obtained. Hydrophilicity of the nanocomposite films increased with the hydrophilic nanoclay content, which resulted in decreased water contact angle and increased swelling ratio (Rhim, 2011). It was also found that the mechanical properties of samples prepared by solution homogenization are much better than those of nanocomposites prepared by melt blending (Müller, Kapin, & Fekete, 2014). A recent study showed that MMT content and process temperature affected the stability of amaranth starch/MMT films (Diéguez, Pelissari, do Amaral Sobral, & Menegalli, 2015). Nanocomposites made of corn starch with 30 and 70% amylose content and MMT were recently developed (Romero-Bastida, Bello-Pérez, Velazquez, & Alvarez-Ramirez, 2015). It was found that not only the amylose content, but also the sequence of addition were important in the properties of the final film. Films incorporating silver nanoparticles were studied in a recent work, finding that MMT did not modify drastically the average size and size distribution of the silver nanoparticles (Cheviron, Gouanvé, & Espuche, 2016).

Motivated by the aforementioned reports, the focus of this study was on the study of the effects of the amylose content and the preparation sequence in physicochemical properties of starch/MMT composites film.

to evaluate the effect of the humidity on the nanocomposite by sorption isotherms and contact angle, as well as understanding the interaction between the components by thermogravimetric analysis and infrared spectroscopy.

## 2. Materials and methods

### 2.1. Materials

Native starch (30%) and high amylose starch Hylon VII (70%) were purchased from National Starch and Chemical S.A. de C.V. (Toluca, Mexico). Glycerol (G7757) and sodium MMT (682659) were obtained from Sigma-Aldrich (Saint Louis, MO, USA).

### 2.2. Film preparation

Films were prepared for native (NS) and high amylose (VII) starches. Additives were glycerol (G) and montmorillonite (MMT). Film forming solutions were prepared using two methods in which the order of addition of glycerol is changed; namely, before (Method M1) and after (Method M2) clay addition. For method M1, film forming solutions were 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 starch (VII), and in a hot plate with a stirring device for native starch (NS) at 85 °C. The difference in the preparation temperature relies on the fact that native starch can achieve complete gelatinization at 85 °C. In contrast, the high amylose starch (VII) is thermally stable, such that its complete gelatinization requires stringent autoclave conditions. In both cases, the final effect is a uniform aqueous dispersion of starch chains to form homogeneous films. A specified amount (15% w/w) of MMT was dispersed into 20 ml of distilled water and sonicated (Bransonic 1510R-MTH) for 1 h. Subsequently, the MMT dispersion was added to the starch suspension at 80 °C and maintained at this temperature for 10 min. The final slurry was cast into acrylic plates (20 × 20 cm) and dried using an oven (IBTF-050) at 65 °C for 6 h. The dried films were peeled and stored until further analysis.

In method M2, film forming solution was prepared as described above but without glycerol addition. After starch gelatinization (autoclaving or hot plate) the MMT dispersion was added to the starch suspension at 80 °C and maintained at this temperature for 10 min. Then, glycerol was added and the stirring continued for 5 min. The final slurry was cast into acrylic plates and dried as in method M1.

### 2.3. MMT characterization

The structure analysis of MMT was performed in a scanning electronic microscope (Carl Zeiss EVO 50, Cambridge UK). MMT samples were dried in an oven at 100 °C for 1 h. For elemental analysis, an energy dispersive X-ray spectroscopy analyzer was used (IXRF Systems, Houston USA). To measure particle size and Z-potential, a Zetasizer (Malvern Instruments, Ltd., UK) was used.

### 2.4. Thermogravimetric analysis (TGA)

The analysis of films was performed using a TGA Q-50 (TA Instruments). Data were collected on samples of 10 mg during a ramp temperature from 40 to 700 °C at 10 °C/min under a nitrogen flux of 60 ml/min. The first derivative (weight/temperature) obtained from the mass loss curves allowed to determine the degradation temperatures of the different films.

### 2.5. Fourier transform infrared spectroscopy (FTIR)

IR spectra were obtained using a Shimadzu spectrometer IR, Prestige-21 (Kyoto, Japan), equipped with an attenuated total reflectance (Kyoto, Japan) cell. The spectra were recorded in absorbance units and the wave number ranged from 4000 to 400 cm<sup>-1</sup>. Each sample was scanned 20 times for spectrum inte-

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