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Whey protein isolate biodegradable films: Influence of the citric acid and montmorillonite clay nanoparticles on the physical properties

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ABSTRACT

Innovative technologies for the incorporation of nanoparticles into packaging systems are being studied in order to improve performance properties. The objective of this study was to evaluate the influence of the addition of citric acid (CA) and sodium montmorillonite clay nanoparticles (MMT) on the physical properties and thermodynamic equilibrium with water vapor in films from whey protein isolate (WPI). WPI nanocomposites (6% w/v), glycerol (40 g/100 g of WPI), montmorillonite (3 g/100 g of WPI) and citric acid (5 g/100 g of WPI), were developed by the casting technique. The GAB model adequately described the water adsorption isothermal behavior ($E \leq 6.08\%$), the curves were sigmoidal. The combined addition of MMT and CA reduced the adsorption capacity, the moisture content of the monolayer (X_m), permeability to water vapor and moisture in relation to the control film. It was also verified that the combination increased the decomposition temperature and showed less mass loss variation. Thus, the interaction between MMT and CA enabled to obtain nanocomposites with good thermal and barrier properties and higher storage stability for application as packaging materials.

1. Introduction

Materials produced from petroleum derived monomers have good functional properties in the preparation of plastics, but produce serious environmental pollution problems. With advances in technology, and the concern about the environmental impact caused by the use and disposal of plastics, new materials of biological origin have been developed. These materials are mostly from renewable sources, are biodegradable, and in some cases, even edible (Martínez-Romero et al., 2006; Slavutsky & Bertuzzi, 2012).

Proteins, lipids and carbohydrates have been used in developing biodegradable films and have good mechanical properties and barrier properties against O_2 and CO_2. However, the functional properties (mechanical and barrier properties) of these hydrophilic materials are related to their water content because the water vapor strongly interacts with the polymer matrix affecting its structure (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007; Perdomo et al., 2009; Slavutsky, Bertuzzi, Armada, García, & Ochoa, 2014). Water acts as a plasticizer for hydrophilic materials whose mechanical, thermal and barrier properties depend strongly on the water content (Bertuzzi, Armada, & Gottifredi, 2003; Slavutsky & Bertuzzi, 2012).

Films based on whey protein have been studied due to its edible and/or biodegradable film forming properties and show good mechanical strength and excellent barriers to oxygen, lipids and aromas. However, like other protein based films, due to their hydrophilic nature, they have a low moisture barrier (2.1 g mm/kPa h m^2) (Kim & Ustunol, 2001; Miller & Krochta, 1997; Osés et al., 2009).

In order to make biopolymers capable of competing with traditional polymers, there is still need to improve their properties such as thermal and physical stability, as well as mechanical and barrier properties (Wang et al., 2005). Normally the use of small amounts of nanoparticles in the nanocomposites in the order of 3–5% by weight equivalent generates 20–30% improvements in physical properties relative to conventional composites (Vartiainen, Tammelin, Pere, Tapper, & Harlin, 2010). Accordingly, nanotechnology has received great attention, aiming at its application in food packaging, since packaging made from polyolefin or biodegradable materials

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incorporated with nanocomposites, exhibit improved performance properties. The development of new materials, products and processes based on the incorporation of nanocomposites in polymer matrices is perhaps one of the most important application of the nanotechnology in the realm of food science (Bao & Tjong, 2008; Bouwmeester et al., 2009; Vartiainen et al., 2010).

Polymer nanocomposites incorporated with montmorillonite clay (MMT) have been developed to improve the performance of the polymer, since they often have improvements in their barrier, thermal and mechanical properties compared to pure polymers (Echeverría, Eisenberg, & Mauri, 2014; Sorrentino, Gorrasi, & Vittoria, 2007).

In particular, up to 3% improvements in barrier properties (against oxygen and water) of the nanocomposites are reported with minimal clay incorporated in the formulation (Lavorgna, Piscitelli, Mangiacapra, & Buonocore, 2010), which arouses interest in the use of clays for the production of flexible or rigid packaging for food (Silvestre, Duraccio, & Cimmino, 2011).

These improvements in nanocomposites reinforced with MMT were reported when the clay layers were uniformly dispersed in the polymer matrix to form an intercalated and/or exfoliated structure instead of forming aggregates or tactoids (Echeverría et al., 2014; Ray, Yamada, Okamoto, & Ueda, 2003). The complete dispersion of clay layers in the polymer creates a winding path in which the permeable elements have difficulty penetrating the nanocomposites (Echeverría et al., 2014). Furthermore, being hydrophilic, the sodium montmorillonite can form stable suspensions in water, which facilitates their dispersion in water-soluble polymers such as whey protein isolate.

Citric acid (CA) is a natural organic acid found in citrus foods. In packaging films, citric acid is added to increase the antimicrobial, plasticizing and dispersing effect of montmorillonite in nanocomposites, and to improve the mechanical properties and water vapor permeability (Cagri, Ustunol, & Ryser, 2004; Shi et al., 2007; Wang, Zhang, Han, & Bai, 2009). Research has been conducted evaluating the effect of the interaction between citric acid and montmorillonite clay in the structural, mechanical, morphological and barrier properties of biodegradable films, but nothing has been reported for whey protein isolate. Thus, the objective of this study was to evaluate the influence of the addition of citric acid and sodium montmorillonite clay nanoparticles on the physical properties and thermodynamic equilibrium with water vapor in films from whey protein isolate. Investigation of this study were focused on moisture content, water vapor permeability, differential scanning calorimetry, thermogravimetric analysis and water sorption isotherms of the films.

2. Material and methods

2.1. Materials

Whey protein isolate (WPI 9400) with 90% protein was obtained from *Hilmar Ingredients* (Hilmar CA, USA). Glycerol from *Sigma–Aldrich* (Brazil), granular citric acid anhydrous, *Cargill* (Uberlândia, MG, Brazil) and the montmorillonite clay (Cloisite Na^+) nanoparticles was provided by *Southern Clay Products, Inc.* (Gonzales, TX, USA).

2.2. Film preparation

(WPI) films were developed, WPI and glycerol being fixed at 6 w/v and 40 g/100 g of WPI, respectively. The MMT0CA0 film (control) was prepared by dissolving 6 g (w/v) of WPI in 44 mL of distilled water with 2.4 g of glycerol (GLY) (based on the WPI weight) in 56 mL of distilled water both separately subjected to continuous agitation on a magnetic stirrer for 30 min at room temperature. After stirring, the solutions were poured together and kept under continued agitation for 10 min at room temperature. The pH was then adjusted to 8 with NaOH 2N and the final solution submitted to an ultrasonic homogenizer (*Sonifier Cell Disruptor Branson – Model* 450D, Manchester, UK) for 10 min at output 80 W/25 °C. Subsequently, the solutions were heated at 90 °C for 30 min in a water bath, cooled to room temperature and poured on glass plates. The other films shown in Table 1, were developed as was the MMT0CA0 film, the MMT (3 g/100 g of WPI) and citric acid (5 g/100 g of WPI) being dispersed in glycerol. The thickness control was accomplished by the volume applied to the support, corresponding to 110 mL. Then, the films with dimensions of 18 × 30 cm were dried at room temperature for 48 h to ensure slow evaporation of the solvent and film formation.

2.3. Film conditioning and thickness

All films were stored at a controlled temperature of 23 ± 2 °C and 50 ± 5% relative humidity for 48 h before analysis, according to the D618-00 method (ASTM, 2000). The average thickness the films was measured by reading at ten distinct points, randomly chosen in each test body, using a *Mitutoyo* digital micrometer (accuracy 0.01 mm Mitutoyo, Suzano, SP, Brazil).

2.4. Moisture content

Film samples of (3 × 3 cm) were cut and weighed, before and after drying, at 105 °C under forced air circulation for 24 h. The moisture values were determined relative to the initial weight and weight lost during drying (ASTM, 2007), and reported on a wet basis.

2.5. Water vapor permeability

The water vapor permeability (WVP) of the films was determined by the accumulation method according to ASTM E398-03 (ASTM, 2003b), with *Permatran*W *1/50 G* equipment (*Minneapolis*, MN, USA). The equipment was calibrated with reference film provided by the manufacturer and the nitrogen gas pressure used was 200–300 kPa during the test. Tests were performed in three replicates and WVP (g m^{-1} s^{-1} Pa^{-1}) was calculated according to Equation (1):

$$WVP = \frac{(WVTR \cdot \delta)}{\Delta P} \quad (1)$$

In which: δ is the film thickness, WVTR is the water vapor transmission rate and ΔP represents the difference in vapor pressure between the two faces of the film: $\Delta P = S(R_1 - R_2)$; S is the saturated vapor pressure at the test temperature (6.5537 kPa), R_1 is the RH on the wet side of the capsule (50%), R_2 is the RH on the dry side of the capsule (10%).

2.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed in a model DSC TA 60 calorimeter (*Shimadzu Corporation*, Kyoto, Japan).

Table 1
Composition of nanocomposites WPI/MMT/CA.

Films	MMT (g 100 g^{-1} WPI)	CA (g 100 g^{-1} WPI)
MMT0CA0	0	0
MMT0CA5	0	5
MMT3CA0	3	0
MMT3CA5	3	5