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Research paper

Physical and morphological properties of nanocomposite films based on gelatin and Laponite

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ABSTRACT

The aim of this research was to study the effect of Laponite concentration on some physical and morphological properties of gelatin films produced by casting technique. The studied properties were thickness, gloss, color, opacity, moisture content, solubility in water, water vapor permeability, microstructure, crystallinity, chemical structure, and thermal and mechanical properties. The results suggested that the mechanical properties (elastic modulus, tensile strength and puncture force) of gelatin matrix were significantly improved with the increase of the concentration of Laponite. Others properties such as surface rugosity and solubility in water also were altered with the increase of the concentration of Laponite. X-ray analyses suggested a good dispersion of Laponite into gelatin matrix, confirmed by atomic force microscopy micrographs. The analysis by Fourier transform infrared spectroscopy revealed the alterations of bands at 1080 and 997 cm^{-1} with Laponite addition to the gelatin matrix. Laponite gelatin nanocomposite films could be potentially used as a novel packaging in food and pharmaceutical industries.

1. Introduction

Packaging based on biopolymers films can offer alternatives for disposal and biodegradation when compared to synthetic plastics packaging in food industry (Oliveira et al., 2015; Flaker et al., 2015). Proteins and polysaccharides are the principal biopolymers used for production of biodegradable material for food packaging (Nisperos-Carriedo, 1994; Genadios et al., 1994).

Gelatin is a protein from animal source, which is water soluble at temperatures above its sol-gel transition (Genadios et al., 1994). Particularly, gelatin has excellent film-forming properties and has been widely used as a single biopolymer in studies on biodegradable and/or edible films (Sobral et al., 2001; Vanin et al., 2005; Bergo and Sobral, 2007; Hanani et al., 2014). Gelatin-based films have excellent color and opacity properties (Wittaya, 2012), however, with limited mechanical and water vapor barrier properties when compared with synthetic films (Sobral et al., 2001).

A recent alternative to improve physical properties in films based on biopolymers is their reinforcement with clay minerals (Chen and Zhang, 2006; Tunc et al., 2007; Angellier-Coussy et al., 2008; Vanin et al., 2014). Clay minerals are characterized by having at least one dimension between 1 and 100 nm (Aouada et al., 2011). It is well accepted that when the particle size is equivalent to the dimension of a molecule, the atomic and molecular interactions can have a significant influence on the macroscopic properties of that system (Aouada et al., 2011; Jorge et al., 2014).

Particularly, montmorillonite (Mt) is the most studied clay mineral in biopolymers films (Tunc et al., 2007; Angellier-Coussy et al., 2008; Bae et al., 2009; Sothornvit et al., 2010; Vanin et al., 2014; Flaker et al., 2015). Mt concentrations between 3% and 5% (based on the weight of biopolymer) have improved mechanical properties in gelatin films (Vanin et al., 2014; Flaker et al., 2015).

Several researches reported that water vapor permeability in films decreased with increasing Mt concentration, however the optimal Mt concentration to be used in biopolymer films still is not clear, varying between 3% and 5% (Tunc et al., 2007; Angellier-Coussy et al., 2008; Bae et al., 2009; Sothornvit et al., 2010; Vanin et al., 2014).

Another clay mineral not so much studied in biopolymer-based film is the Laponite (Lap). Lap ($Na^{+}_{0.7}[(Si_8\ Mg_{5\cdot 5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$) is a synthetic hectorite with particle disk-shape with a thickness of 1 nm, and a diameter of approximately 25 nm (Nicolai and Cocard, 2000). Recent reports indicated that Lap improved mechanical properties, water vapor permeability and thermal stability in corn and cassava starch films (Aouada et al., 2011; Tang and Alavi, 2012; Perotti et al., 2014).

Rao (2007) produced Lap gelatin nanocomposite films using the spreading technique and reported that the elastic modulus increased in approximately 58% when Lap concentration was 14% (based on the volume of biopolymer). In addition, thermal transitions were sensitive to Lap content, hence melting temperature increased and melting enthalpy decreased, both with Lap concentration. Thermal results

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indicated that the crystallinity in gelatin films was depressed by the addition of this nanoclay. And, Li et al. (2015) produced Lap gelatin nanocomposite films using the casting technique, and reported an increase in mechanical properties (tensile strength and elongation at break). Water vapor permeability and water absorption also increased in gelatin films with Lap. Then, more information about physical properties of Lap gelatin nanocomposite films could be interesting to elucidate the effect of the Lap load on this material. Hence, this work aimed to study the effect of Lap concentration on some physical properties of gelatin films produced by casting technique.

2. Materials and methods

2.1. Materials

Pigskin gelatin, type A, bloom 245 and molecular mass 5.2×10^4 Da (Gelita South America, São Paulo, Brazil) was used as biopolymer, and glycerol (Synth, Brazil) was used as plasticizer. Laponite RD (Southern Clay Products Inc. Reference number 23224) was used as nanoparticle. Distilled water was used as solvent.

2.2. Laponite gelatin nanocomposite film preparation

The Lap gelatin nanocomposite films were produced from a mixture of gelatin (solution A) and Lap dispersion in water containing glycerol (solution B). Solution A was prepared with 4 g of gelatin/100 g of solution as follows: gelatin was hydrated for 30 min at room temperature, and then dissolved at 70 °C for 30 min using a thermostatic water-bath (Marconi TE 184, Brazil) (Vanin et al., 2014; Jorge et al., 2014). At the same time, solution B was prepared as follows: firstly, Lap was dispersed at room temperature in distilled water to a concentration of 1% (%w/w), using a high speed homogenizer (ultraturrax, Ika, model T25) at 20,000 rpm for 30 min as reported by Valencia et al. (2015). Later, glycerol (30 g of glycerol/100 g of gelatin) was added to Lap dispersion and mixed for 10 min in a magnetic stirrer (Tecnal TE 0852, Brazil). Then, solution A and B were mixed conveniently to produce solutions with Lap concentration (C_{Lap}) of 0, 1.5, 3, 4.5 and 6 g of Laponite/100 g of gelatin. After that, the solutions were homogenized for 15 min at 70 °C in the same thermostatic water-bath.

The Lap gelatin nanocomposite films were produced by casting process. The quantity of solution poured onto the Petri dishes was calculated to obtain a constant weight of dry matter of approximately 8 mg/cm^2. Solutions were applied to Petri dishes (diameter 14 cm) and dried in an oven with forced air circulation (Marconi, MA037, Brazil) at 30 °C and controlled relative humidity (55–65%), for 18–20 h. At last, it was obtained Lap gelatin nanocomposite films.

Before characterization, the Lap gelatin nanocomposite films were conditioned in desiccators containing saturated solutions of NaBr (58% relative humidity, RH) at 25 °C for at least 7 days. Samples analyzed by atomic force microscopy, X-ray diffraction and Fourier transform infrared spectroscopy were conditioned in desiccators over silica gel, for at least 7 days.

2.3. Laponite gelatin nanocomposite film characterization

All characterizations were performed at least three times for each Lap gelatin nanocomposite film.

2.3.1. Thickness

Thickness was determined using a digital micrometer (0.001 mm; Mitutoyo), averaging ten different positions in each Lap gelatin nanocomposite film (Sobral et al., 2001; Oliveira et al., 2015).

2.3.2. Gloss

The gloss of the Lap gelatin nanocomposite films was determined using a glossmeter (Rhodopoint NGL 20/60), at angle of 60° and in 10 points of the sample, according to ASTM D2457 standard (Villalobos et al., 2005; Flaker et al., 2015). Gloss measurements were performed on the drying surface of the Lap gelatin nanocomposite films.

2.3.3. Color and opacity

The color of the Lap gelatin nanocomposite films was determined using a colorimeter Miniscan XE (HunterLab) in the reflectance mode, with the CIELab scale and illuminant/angle D65/10° and with a measurement opening of 30 mm. Samples were placed on the surface of the standard white plate and the parameters L^* (representing lightness index), a^* (representing the tons from red to green color) and b^* (representing the tons from yellow to blue color) were determined. The total color difference (ΔE^*) was then calculated using the Eq. (1):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where $\Delta L^* = L^*_{sample} - L^*_{standard}$ (92.58 ± 0.92); $\Delta a^* = a^*_{sample} - a^*_{standard}$ (−0.88 ± 0.06); $\Delta b^* = b^*_{sample} - b^*_{standard}$ (1.26 ± 0.02).

The opacity was measured with the same equipment as for color measurement, according to the Hunterlab method, in the reflectance mode. Opacity (Y) values were calculated as the relationship ($Y = Y_b/Y_W$) between the opacity of Lap gelatin nanocomposite film superimposed on the black standard (Y_b), and that of the same sample superimposed on the white standard (Y_W).

2.3.4. Moisture content and solubility in water

The moisture content of Lap gelatin nanocomposite films was determined by oven drying at 105 °C for 24 h (Gontard et al., 1992; Oliveira et al., 2015). Moisture content values were expressed as g of water/100 g of wet material.

For determination of Lap gelatin nanocomposite films solubility in water, samples with approximately 2 cm in diameter (known initial dry weight) were immersed in distilled water (50 ml) and placed in a shaker (Marconi, MA141) under slight stirring for 24 h at 25 °C. The material was filtered through filter paper (Nalgon) and dried in an oven at 105 °C for 24 h for determination of final dry weight. Solubility (%) was then calculated as dry weight difference (Gontard et al., 1992).

2.3.5. Water vapor permeability

The water vapor permeability (WVP) was determined gravimetrically, according to the standard ASTM E96 (Gontard et al., 1992). Lap gelatin nanocomposite films were disposed on aluminum cells containing silica gel (0% RH) and placed in a dessicator containing distilled water (100% RH). Aluminum cells were weighed (±0.01 g) daily for 7 days to guarantee the steady state permeation. WVP was calculated using the Eq. (2):

$$WVP = \frac{\Delta g}{\Delta t}\left(\frac{x}{A\Delta P}\right) \quad (2)$$

where $\Delta g/\Delta t$ is the rate of weight change (g/h), x is the sample thickness (mm), A is the permeation area (0.0032 m^2) and ΔP is the partial pressure difference across the Lap gelatin nanocomposite film (3.169 kPa at 25 °C).

2.3.6. Atomic force microscopy

Atomic force microscopy (AFM) analyses were carried out using an atomic force microscope (model NT-MDT Solver Next Brand, Russia) equipped with software for images analysis (New Model 3.1.0 program PX). The Lap gelatin nanocomposite films were characterized using the semi-contact mode with a resonance frequency of 240 kHz, contact force of 11.8 N/m and scan speed 0.3 Hz. Analyses were performed in areas of 50 μm × 50 μm and using five different specimens.

The average roughness (R_a) and root mean square roughness (R_q) were calculated using the software of AFM. Additionally, texture image analysis was applied to quantify the surface microstructure of