Nanocomposite-forming solutions based on cassava starch and laponite: Viscoelastic and rheological characterization

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ABSTRACT

Nanocomposites-forming solutions (NFS) based on cassava starch and laponite were prepared and next characterized by means of dynamic oscillatory and steady shear rheological tests to evaluate their ability to be processed by knife coating. The effects of speed (rpm) and homogenization time on the laponite dispersion characteristics were first analyzed. Laponite dispersions were affected by both process parameters. High speed (rpm), i.e. 20,000 or 23,000 rpm for 30 min or prolonged homogenization time (10,000 rpm $\leqslant$ speed agitation $\leqslant$ 23,000 rpm, for 60 min) led to high ζ-potential values, with laponite particles size <80 nm. With addition of laponite nanoparticles to cassava starch dispersion, an evident transition in NFS from liquid-like viscous to solid-like elastic behavior was observed. Rheological results indicated that laponite nanoparticles induced new interactions with starch chains allowing to obtain a network structure typical of a semi-rigid gel which shows some spread ability.

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1. Introduction

Nanomaterials are characterized by having at least one dimension of its particles in nanometric dimension, i.e. between 1 and 100 nm (Aouada et al., 2011). 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 material (Aouada et al., 2011; Jorge et al., 2014). Thus, this behavior is associated with the specifics size of nanomaterials such as their high surface to volume ratio (Hassanabadi and Rodrigue, 2012).

Among nanomaterials, there are some thin and flexible materials based on biopolymers charged with nanoparticles. This is a consequence of an approach to improve the mechanical and barrier properties of conventional polymer and biopolymers based films, then producing composites in nanoscale or nanocomposites (Tang and Alavi, 2012; Jorge et al., 2014). Nanocomposites should exhibit a notable enhancement in rigidity and resistance, reduced water vapor and gas permeability, and lower flammability (Tang and Alavi, 2012).

In the biopolymer films technology for food applications, the montmorillonite is the nanoparticle most used in studies on development of films nanocomposites. It has been used to load films based on gelatin (Flaker et al., 2015), zein (Park et al., 2012), starch (Cyras et al., 2008), chitosan (Kasirga et al., 2012), among others. A nanoparticle not so much studied in biopolymer based film is the laponite. Laponite or hydrous sodium lithium magnesium silicate ($Na_{0.7}^{+}[(Si_8\,Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$) is a synthetic hectorite clay with particle disk-shape with a thickness of 1 nm, and a diameter of approximately of 25 nm (Nicolai and Cocard, 2000; Cummins, 2007). Laponite disk have an octahedral configuration with Mg^{2+} ions in the octahedral sites and also Li^+ ions in minor amount and Na^+ ions in the interlayer domain (Perotti et al., 2011). In water, laponite disk hydrates and swells to form clear colloidal dispersions with high stability due to its negative surface charge density of 0.014 e-/$Å^2$ (Nicolai and Cocard, 2000; Herrera et al., 2004).

Laponite has been broadly used in agriculture, construction, personal care, surface coatings and polymer industry (Kumar et al., 2008). Shibayama et al. (2004) reported that the laponite addition in hydrogels based of *N*-isopropylacrylamide led a notable high strength and elongation at break in excess of 1000%. Similar results were reported by Haraguchi et al. (2005) and Haraguchi and Li (2006) for hydrogels reinforced with laponite. Most recently, Chung et al. (2010), Aouada et al. (2011), Tang and Alavi (2012) and Perotti et al. (2014) demonstrated that laponite can improve the

resistance, rigidity, water resistance and water vapor permeability in films based on corn starch, then laponite could be a compatibilizer and cross-linking agent between starch chains.

Besides, the laponite has attracted attention of researcher because its rheological behavior in high concentrated solution in water, which behaves as dilatant fluids (Abou et al., 2003; Joshi et al., 2008). Nevertheless, rheological studies on more diluted solutions of laponite have been not studied, neither on film-forming solutions containing that nanoparticle.

Rheological analyzes of nanocomposite-forming solutions can help to understand the structure–property relations between polymer and nanocomposites (Hassanabadi and Rodrigue, 2012), as well as to optimize the nanostructured film production, specially the casting and spreading techniques (Jorge et al., 2014) since rheology studies interplay between flow and material properties. No information about the effect of laponite on the rheological properties in starch filmogenic solution was reported to date. Hence, this work aimed to study the effect of laponite concentration on the viscoelastic and rheological behavior of nanocomposite-forming solutions (NFS) based on cassava starch by means of dynamic oscillatory and steady shear tests.

2. Materials and methods

2.1. Materials

Cassava starch (humidity = 10.70 ± 0.10% wet basis) was purchased from local market in Pirassununga city (São Paulo, Brazil) and was used as biopolymer for nanocomposite-forming solutions (NFS). Glycerol was supplied by Synth company (São Paulo, Brazil) and used as plasticizer. Laponite RD (Southerm Clay Products Inc. Reference number 23224) was used as nanoparticle. Distilled water was used to disperse laponite and as a solvent in NFS based on cassava starch. Deionized water and potassium hydroxide (KOH) 1 M were used in the sample preparation for particle size distribution and ζ-potential analysis respectively.

2.2. Characterization of laponite powder

Laponite morphology was analyzed using low vacuum scanning electron microscopy (LV-SEM, TM-3000, HITACHI, Japan) at an accelerated voltage of 15 kV. Before analysis, laponite powder was conditioned under vacuum by 12 h and then fixed on aluminum stubs by means of conductive carbon tape. No additional preparation was necessary for analysis using this LV-SEM (Flaker et al., 2015). Energy dispersive spectroscopy (EDS) of laponite was analyzed in the same equipment.

2.3. Production of laponite dispersions

To disperse laponite in distilled water, 1 g of laponite was added to 99 g of distilled water and then dispersed under vigorous stirring using a high speed homogenizer (ultraturrax, Ika, model T25) at room temperature. To study the effect of control process variables in ultraturrax, comparative experiments were carried out to examine the effect of different speed (10,000; 15,000; 20,000 and 23,000 rpm) and dispersion time (30 and 60 min) on the quality of laponite dispersion in distilled water.

2.4. Characterization of laponite dispersions

The pH of laponite dispersions was analyzed by means of a digital pH meter (PG1400 Gehaka). Dynamic light scattering (DLS) measurements were performed using a Zetaplus equipment (Brookhaven Instrument Company, EUA) to determine the particle size distribution and surface charge (ζ-potential). These determinations were obtained at room temperature. Laponite dispersions were stored at 4 °C until use.

Atomic force microscopy (AFM) images were obtained using a SolverNext (NT-MDT, Russia). Laponite dispersions were diluted to a designed concentration, and then 10 μL were pipetted onto a piece of freshly cleaved mica sheet. The dispersion was then allowed to evaporate in an enclosed Petri dish under ambient conditions (40% relative humidity) for 24 h (Balnois et al., 2003). The nanostructures were characterized using the semi-contact mode in AFM with a resonance frequency of 240 kHz, force contact of 11.8 N/m and scan speed 0.3 Hz.

The rheological properties of laponite dispersions were obtained at 25 °C with a rheometer (AR2000 Advanced Rheometer, TA Instruments, New Castle DE, EUA), using a double concentric cylinder geometry (internal radius = 16.0 mm, external radius = 17.5 mm, height = 53 mm and gap = 2000 μm). For each test, 12 mL of laponite dispersions was used. The dispersions were analyzed by applying steady shear rates ranging from 0.1 to $100\ s^{-1}$, being submitted to two shear rate sweeps, increasing then decreasing, with duration of 2 min each (Moraes et al., 2009; Jorge et al., 2014). All resulting flow curves were measured at least three times for each laponite dispersion.

2.5. Production of NFS based on cassava starch and laponite

The NFS were produced using (C_{cs}) 2 and 4 g of cassava starch/100 g of NFS, and 30 g glycerol/100 g of cassava starch. Laponite dispersed in distilled water at 20,000 rpm for 30 min (see preliminary dispersion tests reported in Section 3.2) was added in different concentrations (C_{Lap}): 0, 5, 10, 15 and 20 g laponite/100 g cassava starch. Distilled water was added to complete 100 g of NFS. The NFS were heated at 95 ± 1 °C for 30 min to promote starch gelatinization (Chen et al., 2009), and later cooled down to 25 °C within 30 min, covered with a preservative film to minimize the loss of moisture during heating and cooling (Che et al., 2008).

2.6. Rheological characterization of NFS

All rheological tests were carried out with the same rheometer as in Section 2.4.

2.6.1. Dynamic oscillatory characterization

For all tests, nearly 4 mL NFS were loaded in the cone and plate geometry (cone angle 4°, 60 mm diameter) of the rheometer. Right after loading, a pre-shear at a shear rate of $1\ s^{-1}$ was applied during 1 min to erase any flow history and rejuvenate the NFS, thus ensuring test reproducibility. Temperature was controlled using a Peltier system and the water evaporation in NFS was avoided using mineral oil and a solvent trap accessory (Jorge et al., 2014). All results were analyzed using the software Rheology Advantage Data Analysis V.5.3.1 (TA Instrument).

Firstly, the linear viscoelastic region was determined at 25 °C by performing small amplitude oscillatory strain (SAOS) sweep tests on all NFS, and using strain values between 0.01% and 100% and 1 Hz of frequency (Moraes et al., 2009). From the results of these tests, a strain amplitude of 1%, within the linear viscoelastic domain in NFS, was chosen to perform all remaining SAOS tests. A time sweep test at 1 Hz on new NFS loaded samples was first performed to check for sample equilibrium after loading and pre-shear. Then, a stress sweep test was performed at 1 Hz and for stress values between 0.1 and 180 Pa, or a frequency sweep test for frequency values between 0.01 to 10 Hz was performed. All characterizations were realized at least three times for each NFS.