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Rheological properties of nanocomposite-forming solutions and film based on montmorillonite and corn starch with different amylose content

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ABSTRACT

Nanoparticles (montmorillonite, MMT) can enhance biopolymer-based film properties. The structure–property relationship between polymers and nanoparticles may be explained by the rheological tests of nanocomposite forming solutions (NFS). The aim of this work was to study the effect of MMT concentration and amylose content on the rheological properties of NFS based on corn starch and glycerol following two preparation methods, through steady shear and dynamic tests. The organization level of NFS was influenced by the addition order of the components. Decreasing in flow index behavior when increasing amylose content was attributed to interactions between the starch components. In all NFS, G′ was higher than G″ indicating a gel-like behavior and suggesting that the MMT reinforced the starch matrix as observed by the increase in the storage modulus of films with MMT. Films obtained from method 2 have better mechanical properties probably due to the starch-MMT interactions.

1. Introduction

Using natural biopolymers as biodegradable materials for packaging has disadvantages including higher gas or water vapor permeability and lower mechanical properties compared to synthetic materials. An alternative to improve the properties of biopolymer-based films is using nanoparticles as a reinforcement additive to produce a material known as nanocomposite (Mu et al., 2013). Nanomaterials are characterized by having at least one component in the nanometric dimension, i.e. between 1 and 100 nm (Aouada, Mattoso, & Longo, 2011).

Nanocomposites are hybrid materials comprising a biopolymer matrix reinforced with well-dispersed nanoscale fillers. The tremendous interfacial interactions between the biopolymer and the nanoparticle result in significant modifications of mechanical, barrier and thermal properties (Alboofetileh, Rezaei, Hosseini, & Abdollahi, 2013; Rhim, 2012). In the biopolymer films technology for food applications, montmorillonite (MMT) is the most used nanoparticle to prepare film nanocomposites. MMT has been used to load films based on gelatin (Flaker, Lourenco, Bittante, & Sobral, 2015), zein (Park et al., 2012), starch (Cyras, Manfredi, That, & Vasquez, 2008) and chitosan (Kasirga, Oral, & Caner, 2012), among others.

The montmorillonite is a layered silicate characterized by a moderate negative surface charge (Tunc et al., 2007). The perfect crystalline structure of the nanoparticles is formed by a two-dimensional layer having a central octahedral sheet of aluminum oxide (Al_2O_3) and magnesium oxide (MgO) linked with two external silica tetrahedrons (Alexandre & Dubois, 2000).

Corn starch has attracted scientific interests because different amylose/amylopectin ratio can be obtained from natural resources and the multiphase transitions exhibited during thermal processing (Chen, Yu, Chen & Li, 2006; Chen, Yu, Kealy, Chen, & Li, 2007; Liu, Yu, Xie, & Chen, 2006). Previous studies have reported that materials based on high-amylose starch show superior strength and toughness (Dean, Yu, & Wu, 2007).

Rheological studies of nanocomposite-forming solutions can help to understand the structure-property relationship between polymer and nanoparticles (Hassanabadi & Rodriguez, 2012), as well as to optimize the nanostructured film production, especially the casting and spreading techniques (Coronado-Jorge et al., 2014).

This work aimed to study the effect of montmorillonite and amylose

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content on the rheological properties of nanocomposite-forming solutions based on corn starch, montmorillonite and glycerol, through steady shear and dynamic tests. The relationship between the dynamic-mechanical properties of the films and the rheological properties of the nanocomposite-forming solutions was assessed.

2. Material and methods

2.1. Materials

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

2.2. Preparation of nanocomposite-forming solutions

Nanocomposite-forming solutions (NFS) were prepared following two methods in which the materials were added in different order, the percentages of glycerol and MMT were based on starch weight. For method 1 (M1), nanocomposite-forming solutions were prepared using 4 g of starch, 30% w/w of glycerol, and 100 mL of distilled water. The mixture was gelatinized using an autoclave (121 °C for 20 min) for HVII or using a stirred hot plate at 90 °C for NS. The difference in the preparation temperature relies on the fact that NS can achieve complete gelatinization at 90 °C, in contrast, the HVII is thermally stable and requires autoclave conditions for its complete gelatinization. In both cases, the final effect is a uniform aqueous dispersion of starch. MMT at 15% w/w was dispersed into 20 mL of distilled water and sonicated (Bransonic 1510R-MTH) during 1 h. The MMT dispersion was added to the starch dispersion at 80 °C and maintained at this temperature for 10 min while stirring. In method 2 (M2), the same quantities were used, but the glycerol was added later. After starch gelatinization (autoclaving or hot plate), the MMT dispersion was added to the starch dispersion at 80 °C and maintained at this temperature for 10 min while stirring, then the glycerol was added, and the mixture was stirred for 5 more min. Control samples with no MMT added were prepared following the same procedures.

2.3. Rheological measurements of nanocomposite forming solutions

The rheological properties of the solutions were measured in an Anton Paar (Physica MCR 101) using a plate–plate geometry of 20 mm with a distance between plates of 1 mm.

Flow curves were obtained from rotational tests, using a shear rate of 50 s^{-1} with a temperature sweep from 60 to 25 °C and a cooling rate of 2.5 °C/min. At the final temperature, two measurement cycles were performed, upward and downward from 0.03 to 100 s^{-1}. Mineral oil was used to prevent water evaporation during measurements. The flow behavior was determined in the last cycle. The power law equation of Ostwald-de Waele was applied to the data obtained as a function of the shear stress (τ), where $\gamma = f(\tau)$, to calculate the parameters of the consistency index (K, Pa s^n) and the flow index behavior (n, dimensionless) (Steffe, 1992; Tecante & Doublier, 1999). Determinations were carried out in triplicate.

Oscillatory measurements (frequency sweeps) were performed in samples after 48 h of storage at room temperature, applying a constant stress of 5 MPa once the linear viscoelastic region (LVR) was allocated. No syneresis was observed and the samples were not reheated before measurement. The frequency sweeps were performed at an interval of 0.01–100 Hz. The storage modulus (G′), loss modulus (G″) and complex viscosity (η*, Pa s) were calculated from each test.

For creep-recovery tests, the measurements were carried out after the samples were stored for 48 h at room temperature to allow reorganization of amylose, conforming the matrix and promoting the interaction with MMT. A constant stress of 5 MPa was applied for 4 min and the recovery was measured for 4 more min.

2.4. Film preparation

The nanocomposite-forming solutions were cast in acrylic plates (20 × 20 cm) and dried using an oven (IBTF-050) at 65 °C for 6 h. The dried nanocomposite films were peeled and stored in a dessicator containing silica gel to prevent moisture absorption. Samples were analyzed one week after preparation.

2.5. Dynamical mechanical thermal analysis for films

DMTA measurements were performed in a temperature range from −100 to 100 °C using a Reometrics scientific DMTA V in tension mode working at 1 Hz of frequency, 0.07% of amplitude and 2 °C/min for the heating rate. The sample dimension was 0.5 × 5 × 10 mm. Storage modulus (E′), loss modulus (E″) and tan δ were obtained for the temperature range analyzed.

3. Results and discussions

3.1. Rheology for nanocomposite forming solutions

In the rotational test of nanocomposite-forming solutions (NFS), the power law model successfully described the rheograms; n and k parameters were estimated with $R^2 > 0.9$ (Table 1). In this study, the values of flow index were lower than one ($n < 1$), indicating a non-Newtonian behavior that shows a shear-thinning pattern where the viscosity decreases when increasing the shear rate (Tanner, 2000). This behavior can be observed in the flow curves (Fig. 1) for all the NFS prepared following the both preparation methods. Lopez and García (2012) studied the film-forming solutions from ahipa, cassava and corn, with and without glycerol. The authors found that the glycerol decreased the apparent viscosity of the filmogenic solution. Although in the current study, no filmogenic solution without glycerol was evaluated, in M1, the glycerol had more contact time with starch than in M2 resulting in an important effect on NS, as shown in Fig. 1 where NS-0%-M1 is below NS-0%-M2 indicating a softer system. The viscosity of NS was higher than that of HVII as the matrix was favored by the proportion of amylose and amylopectin, taking into account that glycerol has no as higher interaction with amylose as it has with amylopectin. According to Lopez and García (2012), higher viscosity values suggest a reinforcement effect of the network by the amylopectin; also, the higher swelling ratio of starch with lower amylose content is other possible factor contributing to the high viscosity of the suspension.

The n value became lower when increasing amylose content showing that the cornstarch with lower amylose content had a non-Newtonian behavior. Della Valle, Colona, Patric, and Vergnes, (1996) reported similar results indicating that the main differences observed

Table 1
Parameters of the Ostwald-de Waele (power law) model for nanocomposite forming solutions.

Sample	R^2	n	k
NS-0%-M1	0.994 ± 0.001[a]	0.343 ± 0.034[b]	3.469 ± 0.964[a]
NS-15%MMT-M1	0.994 ± 0.001[a]	0.322 ± 0.106[b]	12.503 ± 8.927[b]
NS-0%-M2	0.993 ± 0.002[a]	0.279 ± 0.008[ab]	9.756 ± 1.561[b]
NS-15%MMT-M2	0.996 ± 0.000[a]	0.447 ± 0.035[c]	1.165 ± 0.460[a]
HVII-0%-M1	0.989 ± 0.004[a]	0.232 ± 0.001[a]	0.389 ± 0.035[a]
HVII-15%MMT-M1	0.988 ± 0.002[a]	0.239 ± 0.002[a]	0.303 ± 0.042[a]
HVII-0%-M2	0.985 ± 0.006[a]	0.290 ± 0.002[ab]	0.434 ± 0.137[a]
HVII-15%MMT-M2	0.991 ± 0.001[a]	0.235 ± 0.032[a]	0.535 ± 0.083[a]

n = flow index behavior; k = consistency index. Values are the average of at least three replicates. Different letters in the column indicate significant differences ($p \leq .05$).