Carbohydrate Polymers 151 (2016) 206–212

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Gelatinization and retrogradation phenomena in starch/montmorillonite nanocomposites plasticized with different glycerol/water ratios

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ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 16 May 2016
Accepted 19 May 2016
Available online 20 May 2016

Keywords:
Thermoplastic starch
Montmorillonite clay
Gelatinization
Retrogradation
Plasticizers
Glycerol/water ratio

ABSTRACT

This study aims to gain insights into the intermolecular interactions present in thermoplastic starch (TPS)/montmorillonite (MMT) nanocomposites prepared using water and/or glycerol as plasticizers. Specifically, the impact of using different glycerol/water proportions on the nature of gelatinization and retrogradation processes is studied. Nanocomposites were characterized by rheometry, scanning electron microscopy (SEM) and X-rays diffraction (XRD). It is shown that clay tactoids preferentially interact with glycerol molecules rather than starch macromolecules. Consequently, the effects of MMT incorporation strongly depend on the glycerol/water ratio; when a ratio of 0.5 is used minor variations were observed on the starch gelatinization process—although stronger clays–starch interactions were evident—whereas at higher ratios the addition of clays significantly increased the gelatinization temperature, up to values over 100 °C. In the gelatinization process of starch in TPS samples having only glycerol as a plasticizer, the leaching of amylose and the melting of amylopectin crystalline domains seem to occur simultaneously. This different gelatinization mechanism produces a TPS having a substantially different morphology, which exhibited reduced retrogradation characteristics.

1. Introduction

The development of new materials to replace non-degradable polymers derived from fossil fuels has become relevant due to the mass production of plastic wastes, principally from packaging industries, which produce polymeric materials that are rapidly used and discarded, causing waste accumulation (Gandini, 2008; Jiang & Zhang, 2013). One of the most attractive alternatives that is used to produce biodegradable polymeric packages is starch, due to its wide availability, high biodegradability, low cost and the fact that it is extracted from a wide spectrum of renewable sources such as rice, corn, potato and cassava, among many others (Zhang, Rempel, & Liu, 2014). In its native form, starch is not processable as a thermoplastic since its melting temperature is higher than its degradation temperature, so that it is necessary to add plasticizers, heat and/or mechanical work to induce the starch gelatinization process and produce a thermoplastic material, thermoplastic starch (TPS) (Liu, Xie, Yu, Chen, & Li, 2009). Starch gelatinization is a complex process in which starch granules swell and get disrupted, by the action of a plasticizer, and starch macromolecules crystallinity is partially or completely lost (Jiang & Zhang, 2013); it has been extensively studied in the scientific literature (Lin et al., 2013; Lin, Wang, & Chang, 2008; Liu et al., 2009; Taghizadeh & Favis, 2013; Xie et al., 2009).

In spite of its benefits, TPS has exhibited rather poor mechanical and barrier properties when compared to conventional thermoplastic polymers. Additionally, variations in macroscopic properties over time have been reported, also limiting its applications, due to TPS retrogradation after processing. TPS retrogradation is a complex phenomenon that consists of reorganization (recrystallization) of starch macromolecules (amylose and amylopectin) (Kohyama, Matsuki, Yasui, & Sasaki, 2004). In order to try to overcome TPS flaws, several authors have tried to use different approaches such as the use of different types of plasticizers or the blending of TPS with other thermoplastics (Arroyo, Huneault, Favis, & Bureau, 2010; Gáspár, Benkő, Dogossy, Réczey, & Czigány, 2005; Ma, Yu, He, & Wang, 2007). Glycerol, typically combined with water at a specific glycerol/water ratio, is still by far the most common plasticizer used. Some researchers have studied the effects of different glycerol/water ratios in the starch gelatinization and ret-

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http://dx.doi.org/10.1016/j.carbpol.2016.05.065
0144-8617/

Table 1
Samples formulations.

Samples	Starch (%)	Glycerol (%)	Water (%)	Clay (%)
G20W80C0	100	20	80	0
G40W80C0	100	**40**	**80**	**0**
G80W80C0	100	80	80	0
G120W0C0	100	**120**	**0**	**0**
G40W80C2	100	40	80	2
G40W80C4	100	40	80	4
G40W80C6	100	40	80	6
G120W0C2	100	120	0	2
G120W0C4	100	120	0	4
G120W0C6	100	120	0	6

rogradation phenomena. Bergo et al. (2008) reported an increase in the starch chains mobility causing recrystallization when the amount of glycerol was increased for cassava starch films plasticized with water and glycerol. Li, Sarazin, and Favis (2008) studied the effects of different amounts of water and glycerol used as plasticizers on the time/temperature boundaries required for the successful plasticization of TPS blends.

In a different approach, several authors have proposed the addition of clays (typically montmorillonite) as fillers to try to overcome TPS mechanical and barrier properties drawbacks, as well as retrogradation problems (Avella et al., 2005; Chivrac, Pollet, & Avérous, 2009; Dean, Yu, & Wu, 2007; Huang, Yu, & Ma, 2004; Pandey & Singh, 2005; Park, Li et al., 2003; Park, Lee, & Park, 2003; Tang, Alavi, & Herald, 2008). Huang et al. (2004) reported that the addition of sodium montmorillonite increases TPS Young modulus, tensile strength and restrains corn starch retrogradation. These results have been attributed to strong intermolecular interaction between TPS matrix and montmorillonite (MMT), which uniformly dispersed in the TPS matrix.

However, the effects of glycerol/water ratios in TPS/MMT nanocomposites properties have not been yet, to the best of our knowledge, fully discussed. The overall objective of the present work is to describe the effects caused by the addition of native MMT to cassava starch at different glycerol/water plasticizers ratios in both the gelatinization and retrogradation processes, in order to contribute to a better fundamental understanding of these two complex phenomena in these similarly complex systems. The gelatinization process was monitored through oscillatory rheological tests. TPS morphologies obtained were studied by scanning electron microscopy (SEM) and X-rays Diffraction (XRD). Retrogradation phenomenon was studied by XRD tests performed at different times after TPS production.

2. Materials and methods

2.1. Samples formulations and preparation

All samples studied were prepared with cassava starch (Bell Chem S.A), native clay (montmorillonite, MMT) Cloisite Na^+ (Southern Clay Products, Inc.), distilled water and glycerol (USP grade). Starch moisture content was 11% as received; before using the starch to produce the composites it was dried until 2.5% moisture content was reached.

Different sets of samples with different formulations were evaluated and their respective compositions are presented in Table 1. A reference formulation (sample G40W80C0) was established having the relative amounts of starch, glycerol and water that have exhibited the best TPS processing characteristics and properties, based on our previous works (Salcedo & Lara, 2014). The glycerol/water ratio of this sample is 0.5. To study the individual effects of glycerol-water intermolecular interactions, a set of samples without MMT was first evaluated; in this set the glycerol content was varied and the starch and water content were fixed at the level used in the reference sample (samples G20W80C0, G40W80C0 and G80W80C0). Since a significant increase in the gelatinization temperature was found when the glycerol content was augmented (as will be discussed below in Section 3.1), a specific sample having a formulation in which "all the water content present in the reference sample was replaced by glycerol" was also included in this set (G120W0C0).

The effects of the addition of MMT were studied using two new sets of samples. The first one (G40W80C2, G40W80C4 and G40W80C6) consisted of samples having 2%, 4% and 6% of MMT respectively and maintaining the starch, glycerol and water proportions of the reference sample. The second one (G120W0C2, G120W0C4 and G120W0C6) consisted of samples with the same MMT amounts as in the previous set (2%, 4% and 6%), but using only glycerol as a plasticizer.

TPS samples without clay were prepared by first mixing water and glycerol at 150 rpm during 10 min with an IKA® Eurostar mixer. Then, dried starch was added and mixed at 100 rpm for ten more minutes. TPS samples including clay were prepared by first mixing clays with water and glycerol at 1500 rpm, using a Dispermat mixer during 1 h, and then starch was added and mixed manually until a homogeneous suspension was obtained; finally the suspension was mixed at 50 rpm for ten more minutes.

2.2. Rheological characterization of the gelatinization process

To study the gelatinization process, all the formulations in Table 1 were gelatinized in a rheometer (DHR-1, TA Instruments) with a 20 mm parallel plate geometry with solvent trap. Oscillatory rheological tests at a fixed frequency of 1.0 Hz and a fixed strain of 5% were performed applying a temperature ramp from 20 °C to 160 °C at a heating rate of 5 °C/min. All experiments were carried out by duplicate. Elastic (G′) and viscous (G″) moduli were monitored during the process to determine the gelatinization temperature.

2.3. TPS and TPS/MMT nanocomposites morphology and starch retrogradation evaluations

Formulations G40W80C0, G120W0C0, G40W80C4 and G120W0C4 were also gelatinized in an oven using a temperature ramp from 20 °C to 140 °C at a heating rate of 3 °C/min. After the suspensions were gelatinized they were manually pelletized and molded using a LabTech model LP-S-80 compression molder at 150 °C, with a heating time of 10 min and pressing at 15 bar during 1 min, followed by 1 min more at 85 bar. These TPS compression molded samples were used for two studies, the first one performed to determine the TPS morphology and the second one to investigate the clays dispersion and starch retrogradation. For the first one, formulations G40W80C0 and G120W0C0 were metalized with gold and observed by scanning electron microscopy at 350X magnification in a JEOL JSM-6490L scanning electron microscope. For the second one, samples G40W80C0, G40W80C4, G120W0C0 and G120W0C4 were studied by X-ray diffraction (XRD). Tests were performed using an X'Pert PRO MPD (PANanalytical) diffractometer, using a range of 2θ angles from 2° to 35° at 0.02°/s; XRD tests were performed at 1, 15 and 30 days of aging.

3. Results and discussion

3.1. Starch gelatinization process

Fig. 1 shows the storage modulus (G′) as a function of temperature during starch gelatinization for the set of samples having no MMT. The viscous modulus (G″) follows the same trend for all the samples studied in this work. As reported elsewhere (Teyssandier,