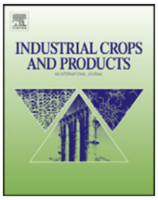
Industrial Crops and Products 34 (2011) 1502–1508

Contents lists available at ScienceDirect

Industrial Crops and Products

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



New strategies in the preparation of exfoliated thermoplastic starch–montmorillonite nanocomposites

Fauze A. Aouada[a,b,*], Luiz H.C. Mattoso[b], Elson Longo[a]

[a] Laboratório Interdisciplinar de Eletroquímica e Cerâmica (LIEC), Chemistry Institute, São Paulo State University, Araraquara campus, 14801-907, Araraquara, SP, Brazil
[b] National Nanotechnology Laboratory for Agriculture –LNNA – Embrapa Instrumentation – CNPDIA, 13560-970, São Carlos, SP, Brazil

ARTICLE INFO

Article history:
Received 31 January 2011
Received in revised form 29 April 2011
Accepted 6 May 2011
Available online 1 June 2011

Keywords:
Intercalation from solution
Mechanical properties
Melt-processing
Montmorillonite clay
Thermal properties
Thermoplastic starch

ABSTRACT

A simple method based on the combination of the intercalation from solution and melt-processing preparation methods was used to prepare highly exfoliated and compatible thermoplastic starch (TPS) and montmorillonite clay (MMT) nanocomposites. The effects of the MMT content on the thermal, structural, and mechanical properties of the nanocomposites were investigated. XRD diffraction was used to investigate the MMT exfoliation/intercalation degrees in the TPS matrix. Data from thermogravimetric analysis and differential scanning calorimetry revealed that the addition of MMT increased the thermal stabilities of TPS nanocomposites. Young's modulus and tensile strength increased from 8.0 to 23.8 MPa and 1.5 to 2.8 MPa with an increasing MMT content from 0 to 5 wt% without diminishing their flexibility. The improvement in such properties can be attributed to the good dispersion/exfoliation of MMT in the TPS matrix. Combining both methods, it was possible to obtain homogenous and transparent nanocomposites with excellent thermal and mechanical properties for application as packaging materials.

1. Introduction

Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: (1) environmental concerns and (2) the realization that our petroleum resources are finite (Yu et al., 2006). In recent years, the environmental pollution from consumed polymers has become serious, particularly from packaging materials and single-use plastic bags and cups. The application of biodegradable polymers instead of non-biodegradable polymers is one promising way to solve environment pollution problems caused by polymer wastes (Zhang et al., 2007).

Starch, one of the natural biodegradable polymers, has been considered as one of the most promising candidates primarily because of its attractive combination of availability and price (Schlemmer et al., 2010). Starch is composed of amylose (poly-α-1,4-D-glucan) and amylopectin (poly-α-1,4-D-glucan and α-1,6-D-glucan) which is a biodegradable and biocompatible polymer from many renewable resources (Avérous, 2004; Avérous and Halley, 2009; Ning et al., 2009; Wang et al., 2010). It is based on α(1–4) (around 95%) and α(1–6) linkages (around 5%) constituting branching points which are localized every 22–70 glucose units (Avérous, 2004) and generate a type of grape branched-like structure with attached chains (Avérous and Halley, 2009).

Thermoplastic starch or TPS can be obtained by the destruction of the starch granules in the presence of plasticizers under specific conditions. Polyols such as glycerol, glycol, sorbitol, and sugars are the most widely used plasticizers (Orts et al., 2007; Wang et al., 2007; Sreekumar et al., 2009; Wu et al., 2010). The main disadvantages of TPS are its pronounced hydrophilic character, the fast degradation rate and, in some cases, unsatisfactory mechanical properties (Wang et al., 2008). However, these features can be significantly improved by blending with MMT (Daí et al., 2009). In this way, MMT in nano-scale (usually below 5 wt%) can increase the mechanical properties, thermal stability and water resistance of TPS dramatically (Dean et al., 2007; Ray et al., 2007; Wang et al., 2009; Majdzadeh-Ardakani et al., 2010). The main reason for such improvement compared to conventional composites is the large surface area which results in high interactions between the polymer matrix and the nanofillers when these nanoparticles are well dispersed. The behavior of the TPS/MMT nanocomposites has been related to the dispersion of the MMT in the TPS matrix; which lead to the formation of intercalated/exfoliated nanostructures (Mondragón et al., 2009). MMT is a 2:1 layer type phyllosilicate composed of two silica tetrahedral sheets and one alumina octahedral sheet. Due to its high swelling capacity, large specific surface area, high cation exchange and adsorption capac-

---

* Corresponding author at: Laboratório Interdisciplinar de Eletroquímica e Cerâmica (LIEC), Chemistry Institute, São Paulo State University, Araraquara campus, 14801-907, Araraquara, SP, Brazil. Tel.: +55 16 2107 2800;
fax: +55 16 2107 2902.
E-mail address: faouada@yahoo.com.br (F.A. Aouada).

0926-6690/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.indcrop.2011.05.003

ity, excellent mechanical and thermal resistance characters, MMT is widely used in many and diverse industrial fields (Zhao et al., 2010).

The aim of this paper was to propose advances in the preparation of exfoliated thermoplastic starch–montmorillonite (TPS–MMT) nanocomposites based on the novel and simple procedure by combination of the intercalation from solution and melt-processing preparation methods. The effect of MMT content on the thermal, structural, and mechanical properties of the nanocomposites was investigated.

2. Materials and methods

2.1. Materials

Regular cornstarch containing 28% amylose (Amidex 3001 TM) was kindly supplied by Corn Products Brasil Ltda. Glycerol was purchased from Aldrich. Natural montmorillonite clay with an ion-exchange capacity of 92 mequiv/100 g (cloisite Na$^+$) was supplied from Southern Clay Products, Inc. All chemicals were used as received.

2.2. Preparation of nanocomposites

TPS–MMT cloisite-Na$^+$ nanocomposites were obtained by the combinations of intercalation from solution and melt-processing preparation methods (Scheme 1). The content of glycerol was fixed at 30 wt%. The contents of MMT were 1, 2, 3, and 5 wt% based on starch and glycerol weight. Corn starch powder was first dried overnight at 70 °C in a ventilated oven to remove the free water (≈10 wt% of the materials depending on the relative atmosphere humidity and temperature).

In the first step, a known quantity of MMT was introduced in 200 mL of distilled water and dispersed in an ultra-sonic bath at 25 °C for 2 h, and the corn starch was dispersed into the MMT dispersion under stirring magnetic for 10 min. Then the glycerol was slowly added into the same solution under stirring. After the complete addition of glycerol, the mixture was mixed at high speed (1500 rpm) to obtain a homogeneous dispersion. The mixture was then placed in a ventilated oven at 90 °C for 24 h, allowing vaporization of the bound water and diffusion of the glycerol into the starch granules. In the second step, the mixtures were processed in a Haake Rheomix 600 batch mixer connected to a torque rheometer with roller-like rotors at 120 °C and 50 rpm, for 20 min.

2.3. Nanocomposites characterization

2.3.1. X-ray diffraction (XRD)

XRD studies of the samples were carried out using a Rigaku D/Max 2500PC X-ray diffractometer (40 kV, 150 mA) equipped with Cu K$_\alpha$ radiation) ($\lambda = 0.154$ nm) and a curved graphite crystal monochromator at a scanning rate of 0.5°/min.

2.3.2. Thermogravimetric analysis (TGA)

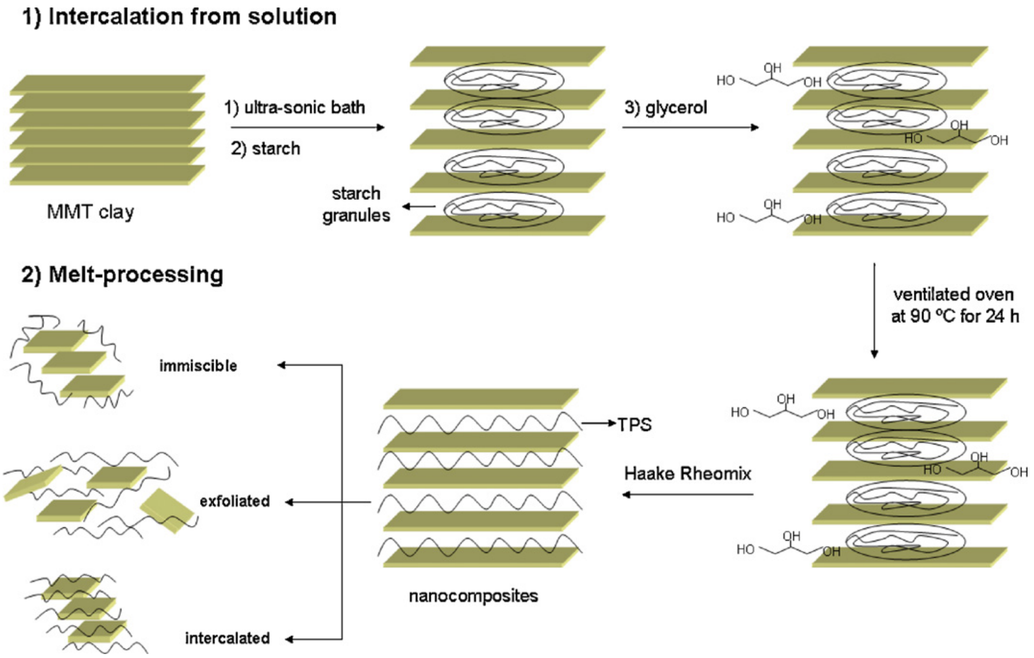
Thermogravimetric analyses were carried out on TGA Q-500 equipment from TA Instruments (New Castle, USA) from room temperature to 600 °C, at a heating rate of 10 °C min^{-1} under a nitrogen flow of 60 mL min^{-1}. TG curves were used to determine the percentage of weight loss, and the decomposition temperature (T_d) was calculated by derivative thermogravimetric curves (DTG) (Schlemmer et al., 2010).

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter (TA Instruments Q100) fitted with a cooling system using liquid nitrogen. It was calibrated with an indium standard. Around 6 mg of MMT, TPS or nanocomposites were accurately weighed into aluminum pans, sealed and then heated from −80 to 200 °C at 10 °C min^{-1} under a nitrogen flow of 60 mL min^{-1}.

2.3.4. Tensile tests

After melt-processing, molded specimens were obtained by hot-pressing at 120 °C by applying 10 MPa pressure for 5 min. The nanocomposite samples were then allowed to stabilize at 53% RH (relative humidity percentage) for 2 weeks in a controlled humidity chamber before characterization. Measurements of the mechanical properties such as tensile strength, Young's modulus and elongation at break were performed according to the method detailed



Scheme 1. Mechanisms of different states of clay dispersion during combinations of intercalation from solution and melt-processing methods utilized to TPS–MMT nanocomposites.