Carbohydrate Polymers 137 (2016) 452–458

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion

J.F. Mendes [a], R.T Paschoalin [b], V.B. Carmona [b], Alfredo R Sena Neto [b], A.C.P. Marques [c], J.M. Marconcini [b], L.H.C. Mattoso [b], E.S. Medeiros [d], J.E. Oliveira [e,*]

[a] Programa de Pós-Graduação em Engenheira de Biomateriais, Universidade Federal de Lavras, Lavras 37.200-000, MG, Brazil
[b] Laboratório de Nanotecnologia Nacional de Agricultura (LNNA), Embrapa Instrumentação, São Carlos 13.560-970, SP, Brazil
[c] Departamento de Ciências dos Alimentos, Universidade Federal de Lavras, Lavras 37.200-000, MG, Brazil
[d] Laboratório de Materiais e Biossistemas (LAMAB), Departamento de Engenharia de Materiais, Universidade Federal da Paraíba, João Pessoa 58.100-100, PB, Brazil
[e] Departamento de Engenharia, Universidade Federal de Lavras, Lavras 37.200-000, MG, Brazil

ARTICLE INFO

Article history:
Received 5 August 2015
Received in revised form 17 October 2015
Accepted 29 October 2015
Available online 2 November 2015

Keywords:
Thermoplastic starch
Thermoplastic chitosan
Extrusion
Biodegradable polymers

ABSTRACT

Blends of thermoplastic cornstarch (TPS) and chitosan (TPC) were obtained by melt extrusion. The effect of TPC incorporation in TPS matrix and polymer interaction on morphology and thermal and mechanical properties were investigated. Possible interactions between the starch molecules and thermoplastic chitosan were assessed by XRD and FTIR techniques. Scanning Electron Microscopy (SEM) analyses showed a homogeneous fracture surface without the presence of starch granules or chitosan aggregates. Although the incorporation of thermoplastic chitosan caused a decrease in both tensile strength and stiffness, films with better extensibility and thermal stability were produced.

1. Introduction

In recent decades, the growing environmental awareness has encouraged the development of biodegradable materials from renewable resources to replace conventional non-biodegradable materials in many applications. Among them, polysaccharides such as starches offer several advantages for the replacement of synthetic polymers in plastics industries due to their low cost, non-toxicity, biodegradability and availability (Fajardo et al., 2010; Simkovic, 2013). Corn has been the main source of starch commercially available. Other minor sources include rice, wheat, potato and cassava and starchy foods such as yams, peas and lentils (Bergthaller, 2005).

Starch is composed of amylose and amylopectin with relative amounts of each component varying according to its plant source As an example, cornstarch has about 28 wt.% amylose as compared to cassava starch with 17 wt.%. Film-forming, barrier and mechanical properties, as well as processing conditions, are dependent on amylose to amylopectin ratio. In general, an increasing amount of amylose improves the abovementioned properties (Forssell, Lahtinen, Lahelin, & Myllärinen, 2002; Raquez et al., 2008; Rindlava, Hulleman, & Gatenholma, 1997).

Starch-based films, however, are brittle and hydrophilic, therefore limiting their processing and application. In order to overcome these drawbacks, starch can be mixed with various synthetic and natural polymers. These approaches are: multilayer structures with aliphatic polyesters (Martin, Schwach, Avérous, & Couturier, 2001), blends with natural rubber (Carmona, De Campos, Marconcini, & Mattoso, 2014) or zein (Corradini, De Medeiros, Carvalho, Curvelo, & Mattoso, 2006) and composites with fibers (Rosa et al., 2009). Another widely used approach to improve mechanical properties and processability of starch films is the addition of chitosan.

Chitosan, which is obtained by partial or total deacetylation of chitin, is one of the most abundant polysaccharides in nature, and a promising material for the production of packaging materials due to the attractive combination of price, abundance and thermoplastic behavior, apart from its more hydrophobic nature as compared to starch. Moreover, chitosan is non-toxic, biodegradable, and has antimicrobial activity (Matet, Heuzey, & Ajji, 2014).

Several studies investigated the use of starch and chitosan in the production of biofilms (Bourtoom & Chinnan, 2008; Dang & Yoksan, 2014; Fajardo et al., 2010; Kittur, Harish Prashanth, Udaya Sankar, & Tharanathan, 2002; Lopez et al., 2014; Pelissari, Grossmann, Yamashita, & Pineda, 2009; Pelissari, Yamashita, & Grossmann,

* Corresponding author. Tel.: +55 353829-4609; fax: +55 353829-1481.
E-mail address: julianoufmg@yahoo.com.br (J.E. Oliveira).

http://dx.doi.org/10.1016/j.carbpol.2015.10.093
0144-8617/

2011; Tuhin et al., 2012; Xu, Kim, Hanna, & Nag, 2005). However, since chitosan films are fragile and require plasticizers to reduce the frictional forces between the polymer chains to improve mechanical properties and flexibility, addition of polyols such as glycerol may reduce this drawback (Leceta, Guerrero, & De Caba, 2013; Park, Marsh, & Rhim, 2002; Srinivasa, Ramesh, & Tharanathan, 2007; Kerch & Korkhov, 2011; Leceta et al., 2013). Furthermore, chitosan hydrophobic nature and mechanical properties can also be modified and improved through blends with poly(ethylene glycol), poly(vinyl alcohol), polyamides, poly(acrylic acid), gelatin, starch and cellulose (Arvanitoyannis, Psomiadou, Nakayama, Aiba, & Yamamoto, 1997; Kuzmina, Heinze, & Wawro, 2012; Lee et al., 1998; Zhai, Zhao, Yoshii, & Kume, 2004).

Most works related to the production of biodegradable films based on starch and chitosan are obtained by casting (Ibrahim, Aziz, Osman, Refaat, & El-sayed, 2010; Leceta, Peñalba, Arana, Guerrero, & De Caba, 2015; Sindhu Mathew, 2008; Xu et al., 2005). In most of these studies, starch is pre-gelatinized prior to chitosan addition and pouring into a mold. Such methods are not adequate to large-scale production of films, therefore limiting their industrial application. On the other hand, processing of starch–chitosan by methods such as extrusion and injection molding have been relatively neglected.

In this work, cornstarch–chitosan blends were produced by extrusion so as to evaluate the effect of chitosan addition on blend morphology, and mechanical and thermal properties, envisioning a large scale, mass production material, for industrial packaging application.

2. Experimental

2.1. Materials

Chitosan with a molecular weight of 90–310 kDa and a degree of deacetylation of 75–85% was purchased from Polymar (Foratelza-CE, Brazil). Cornstarch, containing 70% amylose and 30% amylopectin (Amidex® 3001), was supplied by Corn Products Brasil (Balsa Nova—PR, Brazil). Glycerol, and citric and stearic acid were purchased from Synth (Rio de Janeiro, Brazil).

2.2. Starch–chitosan blending by extrusion

Thermoplastic starch (TPS) was prepared from native corn starch:glycerol:water (60:24:15 wt.%). The thermoplastic chitosan (TPC) was obtained from the physical mixture of chitosan powder, acetic acid, glycerol and water at the following proportions: 17, 2, 33 and 50 wt.%, respectively. Glycerol was first added to chitosan and a 2 wt.% acetic acid solution was subsequently added to form a paste following the procedure described by Epure, Griffon, Pollet, and Avérous, (2011) in order to obtain the TPC. Additionally, 1 wt.% of stearic acid and 1 wt.% citric acid were added to both compositions as processing aid.

Each of these mixtures was pre-mixed manually and then extruded using a model ZSK18 co-rotating twin-screw extruder (Coperion Ltd., SP, Brazil), with $L/D = 40$, screw diameter (D) = 18 mm equipped with seven heating zones. The temperature profile (from the feeder to the matrix) and screw speed were: 120/125/130/135/135/140/140 °C and 300 rpm for TPS, and 108/90/90/100/100/110 °C and 200 rpm for TPC. The TPS/TPC blends were prepared using 5 (TC5) and 10 (TC10) wt.% in the abovementioned extruder with the following temperature profile and screw speed: 101/104/109/109/107/106/107 °C and 350 rpm. These conditions were established based on previous works reported by our group (Carmona, Corrêa, Marconcini, & Mattoso, 2015; Carmona et al., 2014; Sengupta et al., 2007; Giroto et al., 2015; De Campos et al., 2013).

Extruded polymers and blends were pelletized using an automatic pelletizer (Coperion Ltd., SP, Brazil), do produce 2-mm pellets that were subsequently extruded in a single screw extruder (AX Plasticos Ltda., São Paulo, Brazil) operating at 120 rpm and a temperature profile of 80/90/100 °C. This extruder is equipped with a slit die to produce sheets that were then hot-pressed into films of about 800 μm in thickness.

2.3. Characterization

2.3.1. Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy measurements were obtained using a FTIR model Vertex 70 Bruker spectrophotometer (Bruker, Germany). Spectra were recorded at a spectral range between 3500 and 6000 cm^{-1} at a scan rate of 180 scans and spectral resolution of 2 cm^{-1}. The FTIR spectrum was employed in the transmittance mode. FTIR analyses were performed to study the effect of the addition of thermoplastic chitosan in thermoplastic starch, to verify possible interactions among starch, chitosan and glycerol.

2.3.2. X-ray diffraction (XRD)

The crystal structures of TPS and blends with TPC were analyzed from diffraction patterns obtained on a model XRD-6000 Shimadzu X-ray diffractometer (Shimadzu, Kyoto, Japan). Samples were scanned from 5 to 40 (2θ) using a scan rate of 1° min^{-1}. The diffraction patterns were fitted using Gaussian curves, after peak deconvolution using a dedicated software (Origin 8.0™). Crystallinity index (CI) of TPC and blends were estimated based on areas under the crystalline and amorphous peaks after baseline correction. The IC of TPS was estimated as a function of the B and Vh crystal form according to Hulleman, Kalisvaart, Janssen, Feil, and Vliegenthart (1999).

2.3.3. Scanning electron microscopy (SEM) analyses

Qualitative evaluation of the degree of mixture (distribution and dispersion of the TPC phase in TPS) was performed by using a model JSM 6510 JEOL SEM, operating at a 5 kV. Samples were mounted with carbon tape on aluminum stubs. Cross-sections of fractured samples were mounted with the cross-section positioned upward on the stubs. All specimens were sputter-coated with gold in a sputter (Balzer, SCD 050).

2.3.4. Thermogravimetric measurements

TG/DTG analyzes of the copolymers and blends were performed on a TGA Q500 TA Instruments TG (TA Instruments, USA). Thermogravimetric curves were performed under synthetic air atmosphere. Approximately 6 mg samples were loaded to a platinum crucible heated at a heating rate of 10 °C min^{-1} from 25 to 600 °C.

2.3.5. Film thickness

Film thickness was measured using a digital micrometer (IP65 Mitutoyo) at five random positions. The mean values were used to calculate barrier and mechanical properties.

2.3.6. Mechanical properties

Tensile strength, maximum elongation at break and elastic modulus were measured using a model DL3000 universal testing machine (EMIC, São Paulo, Brazil). Tests were carried out according to ASTM D882-09. Test samples of mid-section 15 mm wide; 100 mm long and 0.8 mm in thickness were cut from the extruded films. At least six samples were tested for each composition. Clamp-to-clamp distance, test speed and load cell were