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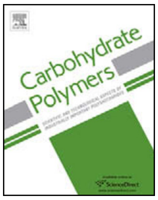

Preparation, characterization, mechanical, barrier and antimicrobial properties of chitosan/PVOH/clay nanocomposites

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ABSTRACT

In the current study low molecular weight poly(vinylalcohol) (PVOH) was used to prepare chitosan/PVOH blends and chitosan/PVOH/montmorillonite nanocomposites via a reflux – solution – heat pressing method. The effect of PVOH content and montmorillonite type (hydrophylic vs. organically modified) on the morphology, mechanical, thermomechanical, barrier and antimicrobial properties of the obtained polymer blends and nanocomposite films was studied. Higher amounts of PVOH (20 and 30%) resulted in plasticization of the films, with an increase in the elongation at break and decrease of the stiffness and the strength while effective blending between chitosan and PVOH chains was observed based on the XRD and DMA findings. Addition of PVOH was beneficial for water and oxygen barrier properties of the obtained films while it did not influence the antimicrobial activity of films against the growth of *Escherichia coli*. Intercalated structures were obtained after the addition of hydrophilic and organo-modified clays leading into stiffening of the nano-modified films and enhancement of their barrier and antimicrobial properties.

1. Introduction

Chitosan (CS), is a very promising biodegradable biopolymer, with good film forming properties and immense potential as active food packaging material due to its antimicrobial activity (Zheng & Zhu, 2003), non-toxicity and low oxygen permeability. CS the cationic (1-4)-2-amino-2-deoxy-β-D-glucan, is industrially produced in various quality grades from chitin, the second most abundant polysaccharide in nature (Muzzarelli, 2012).

Many strategies have been explored to improve the water resistance and mechanical properties of chitosan based biodegradable films including the addition of plasticizers or other biodegradable aliphatic polyesters, such as poly-caprolactone, poly(butylene succinate), poly(lactic acid), poly(butylene terephthalate adipate), and poly(butylenesuccinate adipate).

Polyvinylalcohol (PVOH) has been widely utilized for the preparation of blends and composites with several natural, renewable polymers (Chiellini, Corti, D'Antone, & Solaro, 2003). PVOH is a semicrystalline, water-soluble synthetic polymer, with good biodegradability, excellent chemical resistance and good mechanical properties linked to the presence of —OH groups and their hydrogen bond formation ability (Abdelrazek, Elashmawi, & Labeeb, 2010). Many reports have been published on the preparation of blended CS/PVOH films for food packaging applications (Bahrami, Kordestani, Mirzadeh, & Mansoori, 2003; Bonilla, Fortunati, Atarés, Chiralt, & Kenny, 2014; Nakano et al., 2007; Park, Jun, & Marsh, 2001; Parparita, Cheaburu, & Vasile, 2012; Srinivasa, Ramesh, Kumar, & Tharanathan, 2003; Tripathi, Mehrotra, & Dutta, 2009; Yang, Sua, Leub, & Yang, 2004), biomedical uses (Costa-Júnior, Barbosa-Stancioli, Mansur, Vasconcelos, & Mansur, 2009; Naveen Kumar et al., 2010) or other applications such as proton batteries (Kadir, Majid, & Arof, 2010). In Ref. Srinivasa et al. (2003) CS/PVOH films were prepared and found that an increment in the PVOH concentration resulted in an increase of the moisture content. In Ref. Tripathi et al. (2009) a novel antimicrobial coating based on CS and PVOH was developed and evaluated its effect on minimally processed tomato by means of microbiological analyses. As previously reported (Bonilla et al., 2014) biodegradable films of

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CS/PVOH blends were prepared. Reduction in the UV-transmittance and an increase of the antimicrobial activity upon the addition of chitosan was observed. In Ref. Yang et al. (2004) CS/PVOH films were prepared and an increase in the water vapor transmission rates of the membranes with increasing chitosan content was demonstrated, while the antibacterial activity of all tested membranes was similar.

In recent years, many studies have been devoted in evaluating the benefits of clay addition in biodegradable polymers, especially for the control of the transport properties of the obtained nanocomposite films (Azeredo, 2009; Bordes, Pollet, & Avérous, 2009; Haerudin et al., 2010; Ray & Bousmina, 2005; Rhim, Hong, Park, & Ng, 2006; Rhim, Park, & Ha, 2013;Wang et al., 2005; Tang et al., 2009; Xu, Ren, & Hanna, 2006). Although CS/PVOH blended films and CS/clay nanocomposites have attracted much attention there are only two publications dealing with CS/PVOH/clay nanocomposites. The Ref. Parida, Nayak, Binhani, and Nayak (2011) where CS/PVOH/Closite 30B nanocomposites have been applied for controlled release of the anticancer drug curcumin and the Ref. Huang, Mu, and Wang (2012) where rod-like sepiolite has been used as reinforcing filler in CS/PVOH blends for food packaging applications.

In the current study the development of CS/PVOH blends films and CS/PVOH/clay nanocomposite films varying the PVOH content and type of clay nanofiller i.e. hydrophilic sodium–montmorillonite (NaMMT) and organically modified montmorillonite (OrgMMT) with dimethyl-dialkyl(C14-C18) amine groups are presented. The aim of the study is to improve the properties of CS/PVOH and CS/PVOH/clay nanocomposites films towards food packaging applications. In this direction: [i] a reflux – heat pressing method has been selected for the preparation of the CS/PVOH and CS/PVOH/clay nanocomposites films. This method was recently applied for the preparation of CS/clay nanocomposite films and proved to be beneficial for their morphological, mechanical and water barrier properties (Giannakas, Grigoriadi, Leontiou, Barkoula, & Ladavos, 2014; Grigoriadi, Giannakas, Ladavos, & Barkoula, 2015); [ii] while most studies discuss the effect of high molecular weight on the properties of CS/PVOH blends (Costa-Júnior et al., 2009), in order to improve barrier properties of the obtained films, a low molecular weight PVOH has been used here. This study focuses on the morphology of the obtained CS/PVOH and CS/PVOH/clay films characterized using X-ray diffraction, the mechanical and thermomechanical response along with a series of properties that concern food packaging applications such as water sorption, water and oxygen barrier properties and antimicrobial activity.

2. Experimental

2.1. Materials

The materials used were: (i) medium molecular weight CS, 190–310 kDa (MMW) with a deacetylation degree greater than 75%; (ii) NaMMT with commercial name Nanomer® PGV and OrgMMT with ~40% dimethyl-dialkyl (C14–C18) ammonium surfactant and commercial name Nanomer® – I44P; (iii) PVOH with low molecular weight (13,000–23,000) and hydrolysis degree 87–89%; and (iv) glacial acetic acid (HAc) all purchased from Sigma–Aldrich.

2.2. Preparation of CS/PVOH blends and CS/PVOH/NaMMT, CS/PVOH/OrgMMT nanocomposites films

All films were prepared via a reflux-heat pressing method according to our previous publications (Giannakas et al., 2014; Grigoriadi et al., 2015). For the preparation of CS/PVOH blends and CS/PVOH/clay nanocomposites films a 2 w/v% CS solution was prepared by dissolving the CS powder in 1 v/v% aqueous HAc solution, under vigorous stirring for 24 h at 70 °C. Then the mixture (pH 4.4) was left to cool down at room temperature.

Appropriate amount of the 2 w/v% CS solution was mixed with hot water containing PVOH in order to obtain final products with 10, 20 and 30 w/w% PVOH content, respectively. The mixtures were refluxed under stirring for 4 h. Obtained solutions were cast onto plastic dishes (12 cm diameter). The castings were dried at ambient conditions (~22 °C) for ~5 days and then received films were peeled off. After drying films were pressed for 5 min at 130 °C under 3 MPa constant pressure, using a hydraulic press with heated platens. For the preparation of the CS/PVOH/clay nanocomposites appropriate amounts of NaMMT or OrgMMT were added in the PVOH solutions in order to achieve final 5 wt% clay content. The dispersions were left under vigorous stirring for 12 h before the addition of the 2 w/v% CS solution and refluxed under stirring for 4 h. Obtained dispersions were dried and pressed as described above. Code names and exact quantities used for the preparation of the films are presented in Table 1.

Preparation of "blank" samples: samples without the addition of PVOH, i.e. CS/NaMMT and CS/OrgMMT, as well as samples without CS, i.e. PVOH/NaMMT and PVOH/OrgMMT were prepared as "blank" samples for comparison (see Table 1). In all cases samples were refluxed under vigorous stirring for 4 h. The obtained dispersions were also dried and pressed as described above.

2.3. X-ray diffraction (XRD) analysis

The XRD measurements of the films were performed on a Brüker D8 Advanced diffractometer with CuKa radiation ($\lambda = 1.5418$ Å). For the samples containing NaMMT or OrgMMT clays as nanofiller the d-spacing was estimated from the 001 reflection.

2.4. Mechanical properties

The mechanical properties of the obtained CS/PVOH and CS/PVOH/clay nanocomposite films were assessed via tensile measurements, according to ASTM D638 using a Simantzü AX-G 5kNt instrument. Three to five samples of each film were clamped between the grips (30 mm initial distance) and tensioned at a crosshead speed of 5 mm/min. The shape of the samples was dumbbell with gauge dimensions of 10 mm × 3 mm × 0.22 mm. Force (N) and deformation (mm) where recorded during the test. Based on these data and the gauge dimensions the stress, stain and Modulus of Elasticity were calculated. The strain and Modulus of Elasticity results can only be used for comparison, because the strain values are based on the rotational movement of the drive shaft.

2.5. Thermomechanical properties

The thermomechanical properties of the prepared films were measured on a NETZSCH DMA 242C apparatus. Dynamic temperature spectra of the samples were obtained in tensile mode at a vibration frequency of 1 Hz, at temperatures ranging from 40 to 200 °C, at a rate of 3 °C/min. In order to ensure linear viscoelastic response the amplitude of the deformation was set at 30 μm. Since the thermomechanical properties are sensitive to the moisture content the films were dried prior to measurement for 24 h at 100 °C in order to remove unbound water.

2.6. Water sorption

Selected films were cut in small pieces (12 mm × 12 mm), desiccated overnight under vacuum and weighed to determine their dry mass. The weighed films were placed in closed beakers containing