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New polyelectrolyte complex from pectin/chitosan and montmorillonite clay

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ABSTRACT

A new nanocomposite hydrogel was prepared by forming a crosslinked hybrid polymer network based on chitosan and pectin in the presence of montmorillonite clay. The influence of clay concentration (0.5 and 2% wt) as well as polymer ratios (1:1, 1:2 and 2:1) was investigated carefully. The samples were characterized by different techniques: transmission and scanning electron microscopy, X-ray diffraction, thermogravimetric analysis, infrared spectroscopy, swelling degree and compression test. Most samples presented swelling degree above 1000%, which permits characterizing them as superabsorbent material. Images obtained by transmission electron microscopy showed the presence of clay nanoparticles into hydrogel. The hydrogels' morphological properties were evaluated by scanning electron microscope in high and low-vacuum. The micrographs showed that the samples presented porous. The incorporation of clay produced hydrogels with differentiated morphology. Thermogravimetric analysis results revealed that the incorporation of clay in the samples provided greater thermal stability to the hydrogels. The compression resistance also increased with addition of clay.

1. Introduction

Natural polymers have attracted the attention of many researchers both for their natural abundance and widespread applications as biomaterials. They are a major class of biomaterials, a group of water-soluble polymers that have been utilized to prepare hydrogels, due to their ability to form gels under well-defined conditions. Among these materials are pectin and chitosan (Prajapati & Sawant, 2009; Lee & Mooney, 2012). Polysaccharides can be classified as non-polyelectrolyte or polyelectrolyte, which are divided into positively and negatively charged materials. These complexes exhibit unique physical and chemical properties, as the electrostatic interactions within the polyelectrolyte complex gels are considerably stronger than most secondary binding interactions (Argin-Soysal, Kofinas, & Lo, 2009; Jana, Banerjee, & Gandhi, 2014; Moura, Rubira, & Muniz, 2008). The conformation of the polysaccharide chains is not only dependent on pH and ionic strength of the medium, but also on the temperature and concentration of certain molecules (Alvarez-Lorenzo, Blanco-Fernandez, Puga, & Concheiro, 2013; Borgogna, Bellich, & Cesaro, 2011; Das & Pal, 2015).

In this work, two biopolymers were used, chitosan (CS) and pectin (PECT), classified as polycationic ($-NH_3^+$) and polyanionic ($-CO_2^-$), respectively. The combination of these natural polymers (polysaccharides) was undertaken in order to form an interpenetrating network in which one polymer is crosslinked with the other, in other words, two polymers are crosslinked together, producing a hydrogel (Aguilar & Román, 2014, Chapter 1; Ige, Umoru & Aribo, 2012). Due to their special characteristic, hydrogels have been widely applied in a variety of fields, such as medical applications, agriculture, cosmetics, and foodstuffs, due to their biodegradability, biocompatibility and drug interaction behaviors (Vroman & Tighzert, 2009).

Pectin is an alternative to add value to usable residues from plants, as well as to minimize the volume of unusable residues to be discarded. It is a complex, non-toxic biopolymer that is naturally present in many plants as a component of the middle lamella. It plays a key role in the cell wall structure, comprising a group of polysaccharides rich in galacturonic acid units. Two forms are available commercially: high methyl- and low methyl-esterified pectin. Galacturonic acid (GalA) (α1–4 linked) forms the homogalacturon (HG) backbone. The acid groups along the chain are mainly esterified with methoxy groups in the natural product.

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There can also be acetyl groups present in the free hydroxy groups. Galacturonic acid's main chain also has an occasional rhamnose group present, which disrupts the chain's helix formation (Ahmed, 2016; Canteri, Moreno, Wosiacki, & Scheer, 2012; Carbinatto et al., 2014Carbinatto, Casto, Evangelista, & Cury, 2014; Chen et al., 2010; Tsai et al., 2014).

Chitosan, a crystalline polysaccharide, is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans. The presence of chemical reactive groups (hydroxyl groups and highly reactive amino groups) makes it an attractive adsorbent for removing many kinds of pollutants from effluents (Unagolla & Adikary, 2015). Because of the great advantage provided by the use of polymers obtained from renewable sources, chitosan has been one of the most attractive biopolymers due to its biocompatibility, biological activity and biodegradability (Lavorgna et al., 2014; Wicker et al., 2014).

One of the factors that have enabled the development of tailored biomaterials using pectin and chitosan is their potential to form a polyelectrolyte complex through ionic interaction. While the pK_a values of the carboxyl groups of pectin range between 6 and 8, the pK_a of amino groups in chitosan is ~6.5. It is assumed that the carboxylate moieties of pectin will ionically interact with the protonated amines of chitosan to form a three-dimensional matrix known as a physically crosslinked hydrogel. Thereby, due to the difference in pK_a values of chitosan and pectin, we attempted to synthesize composite hydrogels from binary mixtures of these biopolymers by incorporation of sodium-montmorillonite nanoclay (Taleb, Hegazy, & Ismail, 2012; Unuabonah & Taubert, 2014; Zheng, Xie, & Wang, 2012).

In recent years, the preparation of organic/inorganic nanocomposite hydrogels has attracted increasing attention (Nie et al., 2014; Yadav & Rhee, 2012). The incorporation of inorganic fillers in a biopolymer matrix increases its strength and stiffness. Among inorganic compounds, special attention has been paid to clay minerals for use in nanocomposites because of their small particle size and intercalation properties (Alboofetileh, Rezaei, Hosseini, & Abdollahi, 2013; Kiatkamjornwong, 2007). The use of polysaccharides and inorganic clay minerals can both improve their performance as super absorbents and also reduce their cost (Feng, Ma, Wu, Wang, & Lei, 2014).

In this experiment by in the current study, we aimed to prepare a nanocomposite hydrogel compound by forming a crosslinked hybrid polymer network of chitosan and pectin in the presence of montmorillonite clay (MMT). The incorporation of MMT can both reduce production cost and improve certain properties (such as swelling ability, gel strength and thermal stability) (Fig. 1) (Camargo et al., 2009Camargo, Satyanarayana, & Wypych, 2009; Zhang, Cheng, & Ying, 2006).

2. Materials and methods

2.1. Materials

Chitosan was supplied by Sigma Aldrich Chemical Co. The viscosity average molar mass,–Mv was calculated by applying the equation of Mark-Houwink-Sakurada. The–Mv value was 2.60×10^6 g mol^{-1}.The intrinsic viscosity determination was performed at 25.00 ± 0.05 °C, using an Ubbelohde C529 capillary viscometer with capillary diameter of 0.63 mm, in a ThermoHaake DC30 temperature controlled bath apparatus. Aqueous solution of acetic acid (CH_3COOH 0.1 mol/L) and sodium chloride (NaCl 0.2 mol/L) was prepared. By the method of graphic extrapolation to infinite dilution, experimental determination was done by timing the flow time five dilutions of the polymer-solution. The degree of deacetylation (DD) was determined by elemental analysis using elemental analyzer model VARIO MACRO CHNS in a combustion temperature of 1150 °C. The elemental composition of the chitosan was carbon (39.19%), hydrogen (7.33%) and nitrogen (7.42%). The DD was calculated based in literature (Tian, Liu, Hu & Zhao, 2004), giving 94%.

Pectin was supplied by Vetec. The degree of esterification (DE) of the pectin was determined by FT-IR spectra according to a method previously described (Gnanasambandam & Proctor, 2000) and defined as follows: (number of esterified carboxylic groups/number of total carboxylic groups) × 100. The DE was 22.5%.

The clay, Cloisite 10A, was purchased from Southern Clay Products, USA.

The electrical conductivity measurement procedure was performed on a microprocessor conductivity meter BEL engineering, Model W12D with electrode DJS-1 and conductivity range of 200.0–1999 μS/cm at 25 °C. The measurements were performed by dipping the electrode directly in the solution to be analyzed (pectin and chitosan).

2.2. Preparation of hydrogels

First of all, an acid solution (acetic acid 2% wt/v, pH 2.72) of 1.5% wt chitosan (pH 2.98) was prepared at room temperature under stirring during 24 h. Then the solution was divided into two parts and 0.5 or 2% nanoclay was added in each part. These compositions were placed in an ultrasound bath (Ultra cleaner 1400 model) for 1 h to disperse the clay in the chitosan solution completely. At the same time, an aqueous solution of pectin was prepared at a concentration of 3% w/v (pH 7.63) at room temperature also under stirring for 24 h.

The solutions were mixed to obtain a volumetric composition ratio of polysaccharides (PECT/CS = 1/1, 1/2 or 2/1) and then allowed to stand for 24 h at room temperature. The samples were washed with distilled water and dried in an oven at 40 °C for 48 h.

Three series matching to a composition of hydrogels (PECT/CS, BH1 and BH2) were prepared. The samples BH1 and BH2 correspond the incorporation of 0.5 and 2.0% of clay, respectively. The concentrations of the solutions of pectin (PECT) and chitosan (CS) were kept constant (PECT = 3.0% and CS = 1.5% wt/v).

2.3. Degree of swelling (S_w)

The degree of swelling was determined from dry samples. The samples were weighed and placed in a sufficient amount of distilled water to cover the entire sample (~50 mL) in a beaker. Then, the swollen samples were withdrawn from water at different time intervals (t = 1, 3, 6 or 24 h) and weighed (W_s) for comparison with their initial weight. Each sample was weighed three times to minimize error and the average values of these three measurements were taken. The percent degree of swelling was calculated using following equation (Eq. (2)):

$$S_w = \frac{W_s - W_o}{W_o} \times 100 \tag{2}$$

where W_o is the mass weight of the dry gel and W_s is the mass weight of the swollen gel.

2.4. Thermal stability analysis

Thermogravimetric analyses (TG/DTA) of samples were performed using Q500 V20. Build39, in the 20–900 °C temperature range, at a heating rate of 20 °C/min^{-1} under nitrogen atmosphere. The maximum temperature (T_{max}) was based on the material's degradation speed curve (DTG).