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Transparent organic–inorganic nanocomposites membranes based on carboxymethylcellulose and synthetic clay

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ABSTRACT

In this work, transparent organic–inorganic nanocomposites membranes have been prepared by casting process using carboxymethylcellulose (CMC) as organic matrix and synthetic clay (laponite) as reinforcement inorganic filler. Pristine CMC and CMC-laponite nanocomposites films were prepared using different clay-to-polymer ratios and all the obtained membranes are optically transparent on the UV–vis range. Field emission scanning electron microscopy (FE-SEM) images of the nanocomposite films evidenced a homogeneous dispersion of clay in the polymer matrix. As result, mechanical properties of the membranes are deeply affected by the presence of clay, increasing the Young's modulus and tensile strength values when clay content is increased. On the other hand, maximum strain values decrease when clay concentration is over 10 wt% in comparison to pristine CMC membrane. Thermal properties of CMC films are also influenced by the presence of clay platelets. The main weight loss step of the nanocomposites is shifted toward higher temperatures when compared to pristine CMC membrane, indicating that laponite particles are capable of protecting the polymer chains from thermal and oxidative decomposition. Water vapor permeability (P_w) trend also reveals a decrease in these values for the nanocomposites when clay concentration is high, achieving its minimum permeability at 17 wt% of clay content (which corresponds a decrease of 42% on P_w value in comparison to pristine CMC membrane).

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1. Introduction

Environmental concern is moving the attention of researchers toward the search for alternatives to replace the non-renewable polymeric sources in nanocomposites, especially the petroleum-based ones. They are an interesting alternative to replace the non-renewable sources, especially oil-based plastics. Some examples of biopolymers that have been used for this purpose in composites field are starch, cellulose, bacterial cellulose (BC) and carboxymethylcellulose (CMC) (Barud et al., 2011; De Salvi et al., 2012; Hessler and Klemm, 2009; Legnani et al., 2008; Marins et al., 2013; Perotti et al., 2013, 2014; Salvi et al., 2014; Wang et al., 2012), among others.

Cellulose and its derivatives are a significant class of biopolymers. Particularly CMC, a natural polymer derived from cellulose, is a typical anionic linear polysaccharide and an important industrial polymer with high viscosity and no harmful effects on human health (is both non-toxic and non-allergenic), being widely applied to flocculation, drug delivery, drug reduction, detergents, textiles, papers, foodstuff, cosmetics, pharmaceuticals and composites. CMC films usually present high water content and good biodegradability properties due to the numerous hydroxyl and carboxylic groups present in CMC structure (Reifler et al., 2010; Su et al., 2010; Wang et al., 2012; Yadav et al., 2014).

Some applications include the association with starch, which may be useful for the improvement of the texture, moisture control and water mobility (Tongdeesoontorn et al., 2011) of polymer films. Other applications are related to biodegradable edible films, as those comprising CMC and soy protein isolate (SPI) developed by Su et al. (2010). The development of medical applications is also reported by Jiang et al. (2008), who obtained freeze-dried three-dimensional scaffolds through the incorporation of CMC into nano-hydroxyapatite/chitosan, and by Wong and Ramli (2014), who prepared sodium carboxymethylcellulose (SCMC) films for wound healing.

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There is a considerable interest in polymer systems that are based on biopolymers once they are ecologically safe and biodegradable. Although biopolymers like CMC have a broad range of applications in diverse fields, they present very poor mechanical properties. A common approach to overcome this drawback is the preparation of blends and composites in order to improve their mechanical properties (Mondal et al., 2013).

In this way, organic–inorganic nanocomposites are becoming an important issue, mainly the nanocomposites combined with inorganic fillers containing at least one dimension in nanometric scale, such as clay minerals (Gabr et al., 2013; Lysenkov et al., 2012). These organic–inorganic nanocomposites, when composed by biopolymers, should be used in our daily life to replace synthetic polymers in diverse fields (industry, food, composites) (Romero et al., 2013).

Clays such as bentonite, and hectorite are usually applied to obtain clay nanocomposites. Some polymers often used in this preparation are poly(methyl methacrylate) (PMMA), poly(ethylene terephthalate) (PET), polypropylene (PP), epoxy resin, polyimide, ethylene vinyl acetate (EVA) and many others. Among biopolymers, the mostly used are chitosan, poly(lactic acid) (PLA), cellulose and its derivatives, starch and poly(hydroxybutyrate) (PHB) (Perotti et al., 2011). The incorporation of clays into organic polymers has received special attention last years due to their ability to improve thermal and mechanical resistance in polymers (Bochek et al., 2011). Another characteristic present in some clay based materials is the transparency, as related by Ebina and Mizukami (Ebina and Mizukami, 2007) in the preparation of flexible and transparent films with heat-resistance and gas-barrier properties.

Laponite synthetic clay that presents wide applications in industry, engineering, agriculture, pharmaceuticals, absorbents and ceramics (Laporte, 1990), is classified as a hectorite (2:1 phyllosilicate trioctahedral smectite) clay. In particular Laponite RD, manufactured by Rockwood Additives Ltd. (formerly Laporte Ind. Ltd.), presents chemical composition SiO_2, 65.82%; MgO, 30.15%; Na_2O, 3.20%; LiO_2, 0.83% (Cummins, 2007). Its crystal structure consists of two dimensional layers with a magnesium–oxygen octahedral sheet partially substituted with Li^+ ions, sandwiched between two silicon–oxygen tetrahedral sheets, forming a structure called layer. In order to compensate the excess of negative charges caused by octahedral substitutions, cations are presented between adjacent layers, forming an electroneutral stacked system (Faucheu et al., 2010). Due to its very interesting characteristics, laponite is present in the composition of paints, cosmetics and house cleaning products. Various composite materials have been prepared using laponite. Perotti et al. (2011) have prepared bacterial cellulose – laponite composites which presented high Young's modulus and tensile strength, in comparison with the pristine polymer. Cellulose/laponite composite films obtained by Yuan et al. (2014) and also the bionanocomposites (biopolymers combined to inorganic solids at nanometric scale) prepared by Bitinis et al. (2011) are example of materials to be used as recyclable eco-friendly packages to minimize the plastic waste.

This disk shaped synthetic hectorite clay (diameter of 25 nm for a single particle, layer thickness of 0.92 nm and charge density of $0.0014e^-/Å^2$) (Herrera et al., 2004) has smaller dimensions when compared to natural montmorillonite (MMT) clays (usually within the micrometric scale) (Cummins, 2007). Even though laponite particles are far less anisotropic than conventional MMT, both layers possess tensile strength within hundreds of GPa range, whereas tensile strength for carbohydrate polymers are usually around tenths of MPa (Sun et al., 2010; Suter et al., 2007). This difference of tensile strength, associated with strong hydrogen bonds formed between both organic and inorganic phase are responsible for an improvement of mechanical properties of nanocomposites in comparison to pristine polymer membranes (Paul and Robeson, 2008; Ray and Bousmina, 2005). In addition, since synthetic clays are virtually free of chemical impurities, they are considered potential candidates for polymer/clay nanocomposite studies. Combined with the versatile CMC, synthetic clays are a reliable option for reaching out new transparent organic-inorganic nanocomposite membranes.

This work discusses the production and characterization of CMC-laponite transparent organic–inorganic nanocomposite membranes containing different clay loadings. Clay was added to the polymer system in order to analyze its impact on structural and physical properties of CMC. The prepared materials were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), field-emission scanning electron microscopy (FE-SEM), scanning electron microscopy in back-scattered electrons mode (BSE-SEM), energy dispersive spectroscopy (EDS), stress-strain curves and water vapor permeability (P_w) techniques.

2. Materials and methods

2.1. Materials

The carboxymethylcellulose (CMC) sample used in this work was prepared in our laboratory (DS = 0.7). Bacterial cellulose (BC) was used as raw material. This cellulose was prepared using the procedure described ahead. BC membranes (4 mm thick, 99% water and 1% cellulose) were obtained from cultures of isolated wild strain of *Gluconacetobacter xylinus* isolated in our laboratory. Cultivation was conducted for 96 h at 28 °C in trays 30 × 50 cm, containing the sterile medium composed of a 50 g L^{-1} glucose solution, 4 g L^{-1} yeast extract solution, 2 g L^{-1} anhydrous disodium phosphate solution, 0.8 g L^{-1} heptahydrated magnesium sulphate solution and 20 g L^{-1} ethanol solution. All solutions were prepared using deionized water. BC membranes were washed with 1 wt% aqueous NaOH solution at 70 °C in order to remove bacteria, and washed in water until reach neutral pH value. BC membranes were dried to obtain a paper-like material. After drying, it was crushed and used for the synthesis of the CMC. The synthesis was performed as described by Schlufter and Heinze (2010). The obtained sample showed a degree of substitution of 0.7 and average molecular weight of 280,000.

Laponite RD® was obtained from Bentonit União Nordeste (Brazil) and also used as received.

2.2. Preparation of CMC-laponite nanocomposite

Colloidal suspensions were obtained using laponite RD® as clay source. Clay contents were attained in function of the CMC content (weight/weight). Synthetic clay was dispersed in deionized water (100 mL) at concentrations of 1, 3, 5, 10, 13, 17 and 23% (concerning the CMC amount), under magnetic stirring for 24 h at room temperature. After this time, the samples were immersed in ultrasonic bath for 30 min in order to obtain a laponite clay colloidal dispersion with fully transparent appearance. After this step, the clay dispersion was slowly added to each carboxymethylcellulose suspension at 2% (weight/volume), under magnetic stirring for 24 h. Then the samples were again placed in ultrasonic bath in order to remove some bubbles formed in the mixed suspension during agitation. After this step, the samples were poured into a polystyrene Petri dish of 10 cm diameter and allowed to dry at 37 °C in a vacuum furnace. These samples were named as CMC-Lap 1, 3, 5, 10, 13, 17 and 23%, respectively, for each nanocomposite membrane prepared.

2.3. X-ray diffraction characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Miniflex diffractometer using Cu Ka radiation (λ = 1.5451 Å)

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