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Preparation and properties of carboxymethyl cellulose/layered double hydroxide bionanocomposite films

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ABSTRACT

Solution casting method was employed for preparing of carboxymethyl cellulose/layered double hydroxide (CMC–LDH) bionanocomposite films with LDH content ranged from 0 to 8 wt%. The synthesized nanocomposite films were characterized using FTIR, XRD, TEM and SEM analytical methods. XRD and TEM analysis revealed a partially exfoliated structure for nanocomposites with LDH content up to 3 wt%. However, for LDH contents higher than 3 wt%, nanocomposites formed an intercalated structure. Incorporation of LDH significantly decreased water vapor permeability (WVP) of the bionanocomposite films up to 37%. Addition of the LDHs into the CMC matrix is accompanied by a decrease in the film transparency. Mechanical properties of CMC-based films were improved significantly by addition of LDH particles. CMC–LDH nanocomposite film with 3 wt% LDH showed a 148 and 143% increase in the tensile strength and tensile modulus, as well as a 62% decrease in elongation in comparison with the pure CMC film.

1. Introduction

Polymer nanocomposites are a new generation of materials that contain a polymeric matrix and less than 10% by weight of a nanoscale reinforcing particle. The polymer nanocomposites have better interaction with filler compared with the conventional composites. Uniform distribution of nanoparticles in the polymer matrix causes an improvement of the mechanical, thermal, and gas barrier properties of composites (Pavlidou & Papaspyrides, 2008). Bio-nanocomposites are an emerging class of composites that formed by the combination of a natural polymer and an inorganic or organic nanoparticle. These nanocomposites have attracted much attention in medicine and environmentally friendly materials because of their desirable properties such as biocompatibility and biodegradability (Zhao, Torley, & Halley, 2008).

Among various nanofillers, nanoparticles with a large aspect ratio have proven to be more impressive in polymer matrix reinforcement, such as layered silicates (Namazi, Dadkhah, & Mosadegh, 2012; Namazi, Mosadegh, & Dadkhah, 2009), carbon nanotubes (Chen, Goren, Ozisik, & Schadler, 2012; Shawky, Chae, Lin, & Wiesner, 2011), cellulose nanocrystals (Bitinis et al., 2013; Eichhorn, 2011) and graphite nanoplatelets (El Achaby et al., 2012; Galpaya et al., 2012). Recently, another type of inorganic nanoparticle, layered double hydroxides (LDHs), otherwise called anionic clays, and their intercalation compounds has aroused much attention. LDHs have been used as catalysts, ion exchangers, optical hosts, ceramic precursors and in the preparation of polymer nanocomposites (Kuang et al., 2010; Zümreoglu-Karan & Ay, 2012). In comparison to layered silicates, the LDH structure consists of positively charged brucite-like $[M(OH)_2]$ sheets containing both bivalent and trivalent cations and anions within interlayer galleries. LDHs are represented by the general formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}\cdot[(An^{m-})_{x/m}\cdot yH_2O]$ with representative examples M^{2+} = Mg, Zn or Ca; M^{3+} = Al, Cr or Fe; An^{m-} = $CO_3{}^{2-}$, $C1^-$, OH^-, $NO_3{}^-$ or $SO_4{}^{2-}$, and x taking values between 0.2 and 0.4 (Wang & O'Hare, 2012).

The facile synthesis, versatility and flexibility in composition, biodegradability and biocompatibility of LDHs, makes them, especially attractive in the preparation of bio-nanocomposites and other types of biohybrid materials (Hitzky, Darder, Aranda, & Ariga, 2010; Zhao et al., 2008). Recently, several biopolymers such as casein (Yu, Bian, & Plank, 2010), deoxyribonucleic acid (DNA) (Choy, Kwak, Park, Jeong, & Portier, 1999; Desigaux et al., 2006; Oh, Kwak, & Choy, 2006) and polysaccharides like starch (Chung & Lai, 2010; Wu, Chang, & Ma, 2011), alginate (Alcantara, Aranda, Darder, & Ruiz-Hitzky, 2010; Darder, López-Blanco, Aranda, Leroux, & Ruiz-Hitzky, 2005; Leroux, Gachon, & Besse, 2004; Mandal, Patil, & Mayadevi, 2012), pectin (Darder et al., 2005; Gorrasi, Bugatti, & Vittoria, 2012)

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and i-carrageenan (Darder et al., 2005) have also been successfully intercalated into LDH phases using ion exchange, co-precipitation, delamination-restacking and reconstruction methods.

Carboxymethyl cellulose (CMC) is an anionic, water-soluble cellulose derivative obtained by introducing $-CH_2COOH$ groups into cellulose molecular chain. It has received much interest due to its unique properties such as high viscosity, transparency, hydrophilicity, non-toxic, biocompatibility, biodegradability and good film forming ability. It has been employed for several applications such as drug delivery, textile printing, paper industry, detergents, food, and oil well drilling operations among others (Heinze, Liebert, Klüfers, & Meister, 1999; Stigsson, Kloow, & Germgård, 2006; Wang & Somasundaran, 2005; Yang & Zhu, 2007). To improve its properties, different nano-particles such as copper complexes (Basta & El-Saied, 2008), silver nanoparticles (Singh & Ahmad, 2012; Song, Birbach, & Hinestroza, 2012), Cellulose nanocrystal (Choi & Simonsen, 2006), hydroxyapatite (Zakharov, Ezhova, Kalinnikov, & Chalykh, 2005), calcium carbonate (Shen, Song, Qian, & Yang, 2010), Fe_3O_4 (Chang, Yu, Ma, & Anderson, 2011) and ZnS (Luna-Martinez et al., 2011) and graphene oxide (Yadav, Rhee, Jung, & Park, 2013) have been incorporated into CMC matrix. According to the best of our knowledge, a few reports have been published on using LDHs for preparation CMC–LDH nanocomposites (Kang et al., 2009; Yadollahi & Namazi, 2013). For instance, Kang et al., have prepared CMC–LDH intercalated nanocomposites through coassembly of layered double hydroxide (LDH) nanosheets with carboxymethyl cellulose. They reported a significant enhancement in the thermal stability of CMC after preparation of CMC–LDH nanocomposite (Kang et al., 2009). Additionally, in our previous work (Yadollahi & Namazi, 2013); we reported preparation of CMC–LDH intercalated nanocomposites through co-precipitation method. The obtained nanocomposites revealed a better thermal stability and a pH dependent swelling behavior.

In this study, we describe the synthesis and characterization of carboxymethyl cellulose/LDH exfoliated nanocomposite films by casting CMC and LDH aqueous solution. The microstructures, mechanical and thermal, optical and barrier properties of CMC/LDH nanocomposites films were examined a function of LDH concentration by X-ray diffraction (XRD), TEM, SEM analysis, UV–vis, water vapor permeability and mechanical tests. The LDH concentration of the nanocomposite films ranged from 0 to 8 wt%.

2. Experimental

2.1. Materials

Sodium carboxymethyl cellulose (CMC), degree of substitution (DS) 0.55–1.0 and viscosity 15,000 mPas/s (1% in H2O, 25 °C) was obtained from Nippon Paper Chemicals Co., Ltd., Japan. $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and NaOH and glycerol were purchased from Merck. All the chemicals were used as received without further purification. Bi-distilled water was used throughout this work.

2.2. Preparation of LDH

Mg–Al-LDH was prepared by co-precipitation method. First, an aqueous solution (50 ml) of $Mg(NO_3)_2{\cdot}6H_2O$ (33.5 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (16.5 mmol) was prepared, followed by drop-wise addition of NaOH solution (50 ml, 2 M) with constant stirring under N_2 atmosphere. Afterwards, the slurry was aged for 24 h at 95 °C, keeping the pH at 9–10 by adjusting with NaOH (2.0 M) solution. After washing, the wet sample was divided into two portions. One portion was dried at 50 °C under vacuum for 24 h. Another portion was dispersed in water and subjected to ultrasonic irradiation for 10 min at full power to disperse the LDH particles. The LDH content in the colloidal dispersion was measured by air drying (3%, w/w). The suspension was used directly in our experiments.

2.3. Preparation of CMC–LDH nanocomposite films

CMC–LDH bionanocomposite films with 1, 3, 5 and 8 wt% were prepared by a casting/evaporation method as follows: typically, 2 g CMC and desired amount of LDH suspension contains 0.02–0.16 g LDH and 1 g of glycerol were added into 100 ml bi-distilled water. A homogeneous solution was obtained by constant stirring of the mixture at 90 °C for 24 h. The solution was then subjected to ultrasonic irradiation for 10 min at full power to disperse the LDH particles and reduce aggregation. Then, the obtained homogenous solution was poured into a Teflon mold (18 cm × 18 cm) and heated to 50 °C for approximately 24 h to evaporate water. After drying, the films were removed from the mold and different of analytical tests were carried on them.

2.4. Film characterization

Infrared spectra were obtained on an FTIR spectrometer (Bruker Instruments, model Aquinox 55, Germany) in the 4000–400 cm^{-1} range at a resolution of 0.5 cm^{-1} as KBr pellets. UV–vis spectroscopy was carried out on a Perkin-Elmer Lambda 35 UV–vis absorption spectrometer at room temperature. The X-ray diffraction patterns of the samples were obtained by Siemens diffractometer with Cu-Kα radiation at 35 kV in the scan range of 2θ from 2 to 70°. All of analyzed samples were in powdery form. The d-spacing was calculated by Bragg's equation where λ was 0.154 nm. Transmission electron micrograph (TEM) was conducted by LEO 906E transmission electron microscope operating at 80 kV. Scanning electron micrographs (SEM) were obtained with LEO 1430VP scanning electron microscope operating at 15 kV. Tensile properties of free films were investigated by a universal test machine (MTS, model 10/M, USA) according to ISO 527 at room temperature. Five films were cut into 2 cm × 15 cm strips. Films were held parallel with an initial grip separation of 10 cm and pulled apart at a head speed of 25 mm/min.

Water vapor permeability of films (g m^{-1} h^{-1} Pa^{-1}) was gravimetrically determined at 20 °C using a method described by Tunc et al. (2007). Prepared nanocomposite films were hermetically sealed with silicone grease in glass cups (4.8 cm × 3.8 cm × 4.0 cm) containing 15 ml distilled water. The cups were placed at 20 °C in desiccators containing silicagel, thus obtaining an RH gradient equal to 100%. The water vapor transfer through the exposed film area (18.24 cm^2) was measured from the cup weight loss as a function of time. The cups were weighed using a four-digit balance every 24 h over a 5-day period, after steady-state vapor flow had been reached. At least three samples of each type of film were tested, and water vapor permeability (WVP) was calculated from the following equation:

$$\mathrm{WVP} = \frac{S \times d}{A \times \Delta P}$$

where S is the slope of the weight loss versus time (g h^{-1}), d is the film thickness (m), A is the area of exposed film (m^2) and ΔP is the differential of water vapor pressure across the film (at 20 °C, $\Delta P = 2.33 \times 103$ Pa, assuming that the RH on the silicagel is negligible).

3. Results and discussions

3.1. FTIR analysis

Fig. 1 illustrates the corresponding FTIR spectra for CMC film, the pristine Mg–Al-LDH and CMC–LDH nanocomposite film with