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Superabsorbent nanocomposite hydrogels made of carboxylated cellulose nanofibrils and CMC-g-p(AA-co-AM)

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ABSTRACT

Superabsorbents based on carboxylated cellulose nanofibrils (CCNFs) and carboxymethyl cellulose-g-poly(acrylic acid-co-acrylamide) were synthesized. A series of experiments were performed to evaluate the influence of factors such as CCNFs amount, solution pH, temperature, salt solution type and concentration on the swelling behaviors of the hydrogels. The water uptake of the hydrogels strongly depended on the CCNF content, the swelling capacity in distilled water increased dramatically from 245.8 to 458.7 g/g with the addition of CCNFs up to 2.5 wt%. Furthermore, the incorporation of CCNFs improved salt resistance properties of the hydrogels with slower deswelling rate and higher water retention capacity at deswelling equilibrium. Besides, the CCNF nanocomposite hydrogels presented better responsive behavior in relation to pH presence and showed an increase in water retention capacity at various temperatures. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) were employed to examine the structure and morphologies of the prepared superabsorbent hydrogels.

1. Introduction

Superabsorbent hydrogels are high-performance water absorbent and retention materials with three-dimensional network structures connected by chemical and/or physical crosslinking (Bao, Ma, & Li, 2011; Kuang, Yuk, & Huh, 2010; Umeda, Nakade, & Kakuchi, 2011). They are able to absorb large amounts of aqueous fluids in a relatively short time and can maintain a swollen state even under some pressure (Jin et al., 2011; Liu, Miao, Wang, & Yin, 2009; Spagnol, Rodrigues, Neto, et al., 2012). Superabsorbents can be prepared for a specific application, such as agriculture, horticulture, hygienic products, wastewater treatment, as well as drug delivery and water blocking tapes (Besemer, Verwilligen, & Thornton, 2012; Chang, Duan, Cai, & Zhang, 2010; Flautt, Priest, Stotler, & Hager, 2009; Savich, Olson, & Clark, 2010; Wu, Liu, & Liang, 2008). Recently, a good strategy applied to produce superabsorbent materials relies on polysaccharide-based natural polymers, such as cellulose, starch and chitosan (Güçlü et al., 2010; Spagnol et al., 2012a; Wang, Wang, Kang, & Wang, 2011), which could increase their biocompatibility, biodegradability, water uptake capacity as well as decrease the toxicity. Cellulose, the most abundant one, has been the subject of academic and industrial studies for many decades (Marcı, Mele, Palmisano, Pulito, & Sannino, 2006; Pan & Ragauskas, 2012; Sannino, Demitri, & Madaghiele, 2009). However, the strong hydrogen bondings (intermolecular and intramolecular) between the hydroxyl groups along the chain backbone not only limit the water solubility but also lead to the poor reactivity of cellulose. Carboxymethyl cellulose (CMC) is a representative cellulose derivative, which can be easily manufactured and the polar carboxyl groups on the backbone render the cellulose soluble, chemically reactive and strongly chelate. Thus the application of CMC in adsorbent fields becomes attractive and promising (Bao et al., 2011; Reeves, Ribeiro, Lombardo, Boyer, & Leach, 2010).

Nanocomposites exhibit improved or even novel properties when compared to micro- and macro-composites. Inherent advantages of nanofillers and the strong interfacial interactions between the dispersed nanofillers and the polymer matrix, lead to enhanced mechanical, thermal and barrier properties, as well as swelling and adsorption behavior of the virgin polymer (Hubbe, Rojas, Lucia, & Sain, 2008). Carboxylated cellulose nanofibrils (CCNFs) can be obtained when cellulose is treated by the combination of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation and mechanical homogenate. TEMPO-mediated oxidation induced the regioselective conversion of the primary hydroxyl groups to carboxylate ones in aqueous media under mild conditions. Subsequently, significant amounts of carboxylate and aldehyde groups were introduced into native celluloses, maintaining their fibrous morphologies (diameters of 20–40 nm and lengths

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Abbreviations: CCNFs, carboxylated cellulose nanofibrils; CMC-g-p(AA-co-AM), carboxymethyl cellulose-g-poly(acrylic acid-co-acrylamide); FTIR, Fourier transform infrared spectroscopy; SEM, scanning electron microscope; TEMPO, 2,2,6,6-tetramethylpiperidine-1-oxyl radical; AA, acrylic acid; AM, acrylamide; APS, ammonium persulfate; MBA, *N*,*N*′-methylenebisacrylamide; MCC, microcrystalline cellulose; CNWs, cellulose nanowhiskers.

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of 10–30 μm) and crystallinities and having the ability to form interactions among the polymer matrix and the outer stimulus (Hirota, Tamura, Saito, & Isogai, 2009; Saito, Kimura, Nishiyama, & Isogai, 2007; Isogai, Yanagisawa, & Isogai, 2009). Furthermore, the inherent advantages of high mechanical strength and stiffness, and excellent dispersion stability, allow the application of CCNF nanofillers for manufacturing superabsorbent composites with special performance (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009; Li, Renneckar, & Barone, 2010).

Nanocomposites filled with acid-hydrolyzed cellulose nanofibrils or nanowhiskers have been reported to show unique properties that were distinctly different from the original ones (polymers without fillers) (Eichhorn, 2011; Spagnol et al., 2012b). However, the use of CCNFs (obtained from TEMPO-mediated oxidation) as reinforcement nanofillers in polymer matrix is poorly explored. In present study, CCNFs were prepared and used as nanofillers in carboxymethyl cellulose-g-poly(acrylic acid-co-acrylamide) hydrogel matrix to improve or even create new properties. The effects caused by the incorporation of CCNFs into the hydrogel matrix on the water uptake capacity were evaluated. The swelling and deswelling kinetics, as well as water retention at various pH, temperature and salt solutions were investigated.

2. Experimental

2.1. Materials

Acrylic acid (AA) and acrylamide (AM) were supplied by Tianjin Chemical Co., Ltd. (Tianjin, China). Ammonium persulfate (APS), *N,N′*-methylenebisacrylamide (MBA) and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) were obtained from Aladdin Chemistry Co., Ltd. (Guangzhou, China). Sodium carboxymethyl cellulose (CMC), microcrystalline cellulose (MCC), sodium bromide and sodium hypochlorite solution were purchased from Shanghai Reagent Corp (Shanghai, China). All reagents were of analytical grade and used without further purification. The deionized water was used throughout the work and the measured pH value of the water is around 6.9.

2.2. Carboxylated cellulose nanofibrils (CCNFs)

CCNFs were prepared at two steps (Saito, Nishiyam, Putaux, Vignon, & Isogai, 2006). Firstly, 1 g MCC (particles could pass through 200 mesh sieve) was suspended in 100 mL distilled water containing TEMPO (0.1 mmol) and NaBr (1 mmol). The oxidation process was started by adding 6% NaClO solution (5.0 mmol) under gentle agitation at room temperature. The pH was maintained at 10.5 by adding 0.5 M NaOH using a pH stat until no NaOH consumption was observed. Secondly, the oxidized cellulose was ultrasonicated for 10 min in an ice bath, using an ultrasonic homogenizer (JY92-IID, China) with an output power of 500 W. The slurry thus obtained was centrifuged several times (5000 rpm, 15 min) and dialyzed against distilled water until the pH reached 7. The resultant product was lyophilized (−45 °C, 48 h) and stored before further analysis. The carboxylate content of the obtained CCNFs was determined to be 0.94 mmol/g using an electric conductivity titration method.

2.3. Synthesis of CMC-g-p(AA-co-AM)/CCNFs nanocomposite hydrogels

CMC solution has been prepared by slow addition of weighted amount of CMC powder to distilled water in a 250 mL three-necked flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen line. The solution was heated to 60 °C, and after being purged with N_2 for 30 min, 0.15 g APS was added and kept for 5 min to generate free radicals. After cooling the reactants to 40 °C, the mixture of AA (monomer), AM (monomer), CCNFs (nanofillers) and MBA (crosslinker) were added to the flask. Then the temperature was risen to 70 °C and maintained for 2 h to complete the polymerization process (Bao et al., 2011; Wu, Zhang, Liu, & Yao, 2012). The N_2 atmosphere was maintained throughout the reaction period. The reaction mixtures were then all transferred into a glass straw with a diameter of 6 mm. After waiting for 24 h for good gelation at room temperature, cellulosic hydrogels were obtained. The resultant product were deprotonated through the dropping of dilute NaOH solution, and washed with large volumes of distilled water several times until the solution pH was neutral, and then extracted with acetone at room temperature for 24 h to dissolve the homopolymer (Spagnol et al., 2012a; Wu et al., 2012). The precipitate was dried to constant weight at 70 °C, gently manual milled in an agate mortar (Φ = 60 mm, obtained from Shanghai Reagent Corp, China) and sifted through 20–80 mesh sieves for further experiment. The control sample (CMC-g-p(AA-co-AM)), without adding CCNFs, was prepared according to the same procedures described above.

2.4. Methods of characterization

The chemical structures were characterized using a Fourier transform infrared spectrophotometer (FTIR, Bruker Vector 33), operating in the range of 4000–400 cm^{-1}, resolution of 4 cm^{-1}. The dried samples were blended with potassium bromide (KBr, optical grade) powder and pressed into small pellets before spectrum acquisition. The morphology of the nanocomposite hydrogels were evaluated through a scanning electron microscope (SEM, Quanta 200) system using an acceleration voltage of 3 kV. Prior to analysis, the dried hydrogels were coated with gold using an Emitech K 550 Coater.

2.5. Swelling studies

The gravimetric method was employed to measure the swelling behaviors of the hydrogel samples (CMC-g-p(AA-co-AM) and CMC-g-p(AA-co-AM)/CCNFs) in the distilled water, salt solutions, and pH solutions. For swelling kinetic, pre-weighted dried samples were immersed in excessive distilled water or 0.9 wt% NaCl solutions at room temperature to reach the swelling equilibrium. At predetermined time intervals, the hydrogel samples were taken out from the aqueous solution by a 200-mesh cloth and weighed after removing the excess water on the surfaces with wet filter paper. The equilibrium water uptake was calculated by the following equation:

$$Q_{eq} = \frac{W_s - W_d}{W_d} \quad (1)$$

where Q_{eq} (g/g) is the water absorbency per gram of dried sample, W_d (g) and W_s (g) are the mass of dried and swollen samples, respectively.

To investigate the water absorbency in different salt solutions, hydrogel samples were immersed in various saline solutions (NaCl, $CaCl_2$, and $FeCl_3$) with different concentration at room temperature. All solutions presented constant ionic strength (I = 0.1 M), and the swelling capability was determined according to the procedures described previously.

To explore the water absorbency at various pH values, test solutions with various acidic and basic pH values were prepared by diluting aqueous NaOH (pH 13.0) and HCl (pH 1.0) solutions. The ionic strength of the pH solutions was 0.1 M, which was obtained by adding an appropriate amount of NaCl. The measurement of water absorbency was the same as described previously.