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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

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.

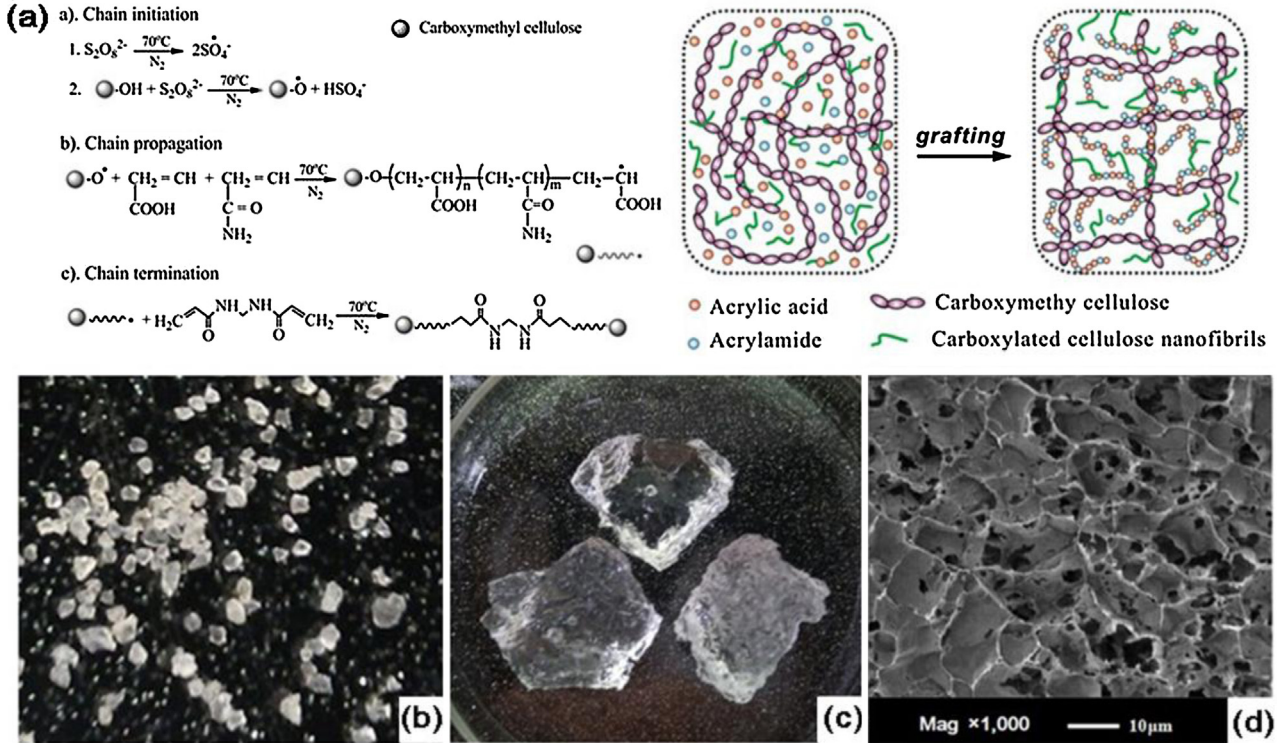

Fig. 1. (a) Proposed reaction mechanism for the synthesis of superabsorbent nanocomposites, macroscopic image of (b) dry and (c) swollen CMC-g-p(AA-co-AM)/CCNFs hydrogels, and (d) SEM images of hydrogels inner structure.

For deswelling kinetic, the pre-weighted swollen hydrogel samples equilibrated in distilled water were immersed in 10 or 100 mM NaCl solution, and taken out at predetermined time intervals. For the water retention at different temperatures, swollen samples were placed in an oven at 35 or 80 °C. The samples were weighed every hour for 10 h. Both the percentage water retention (*WR*) was defined as follows:

$$WR = \frac{W_i - W_d}{W_s - W_d} \quad (2)$$

where W_i is the weight of wet samples at time t. The other symbols are the same as defined above.

3. Results and discussion

3.1. Mechanism of hydrogel formation

The superabsorbent nanocomposites were synthesized by graft copolymerization of acrylic acid (AA), and acrylamide (AM) onto carboxymethyl cellulose (CMC) in the presence of crosslinking agents (MBA) and cellulose nanofibrils (CCNFs). Ammonium persulfate (APS) was performed as a free radical initiator. The proposed mechanism for the chemically grafting and crosslinking reactions are outlined in Fig. 1a. Firstly, the APS initiator is decomposed and generates sulfate anion-radicals under heating. The radicals extract hydrogen from the hydroxyl groups in the CMC, resulting in the formation of some more active groups such as alkoxy radicals (Li et al., 2012). Then the monomer molecules, close to those reaction sites, become acceptor of CMC radicals resulting in propagating a new polymeric chain and thereafter themselves become free radical donor to neighboring molecules, in this way a new brunch grows. During the chain propagation, the polymeric chains may react synchronously with the end vinyl groups of the MBA, a cross-linked structure can be formed (Bao et al., 2011; Pourjavadi, Jahromi, Seidi, & Salimi, 2010). The function of CCNFs in the polymerization reaction can be considered as a crosslinking agent or a physical inhibitor to prevent the polymeric chains from growing (Spagnol et al., 2012a). The macroscopic image of dry (Fig. 1b) and swollen (Fig. 1c) CMC-g-p(AA-co-AM)/CCNFs hydrogels in distilled water, and SEM image (Fig. 1d) of hydrogels inner structure are also shown in Fig. 1. As can be seen the macroscopic morphology is quite translucent, indicating the homogeneous-dispersed CCNFs in the hydrogel matrix. The SEM images of nanocomposite hydrogels show interlaced and highly porous network. The reason maybe that the incorporation of CCNFs into the hydrogel matrix reduces the crosslinking dots on the polymeric chains and broaden the network voids, which make the diffusion of liquids into the hydrogel matrix easier and faster. This structure is convenient for the penetration of water into the polymeric network, and then may be of benefit to water absorbency of corresponding superabsorbent.

3.2. FTIR spectroscopy

Fig. 2 shows the FTIR spectra of CMC, CCNFs, CMC-g-p(AA-co-AM) and CMC-g-p(AA-co-AM)/CCNF samples, respectively. The spectra of CMC and CCNFs are quite similar, both present characteristic absorptions of cellulose structures, including the absorption around 3400 cm^{-1} (hydroxyl stretch influenced by hydrogen bonding), 2905 cm^{-1} (methylene), 1060 cm^{-1} (β-1,4-glycosidic bond) and 1428 cm^{-1} (skeletal C=C stretching vibrations in the aromatic rings) (Wu et al., 2012). Besides, the absorption peaks around 1607 cm^{-1} are related to the carboxylate of both samples. Based on the above FTIR data, it can be concluded that the TEMPO-mediated oxidation does not affect the main chemical structure of the CCNFs, but introduce carboxylate groups on its chains (Saito et al., 2006). For CMC-g-p(AA-co-AM) hydrogels, some absorption peaks are changed as compared with CMC. The characteristic bands at 1033–1162 cm^{-1} are obviously weakened after polymerization which indicates the participation of hydroxyl groups of CMC in chemical reaction. The absorption peak at 1670 cm^{-1} is

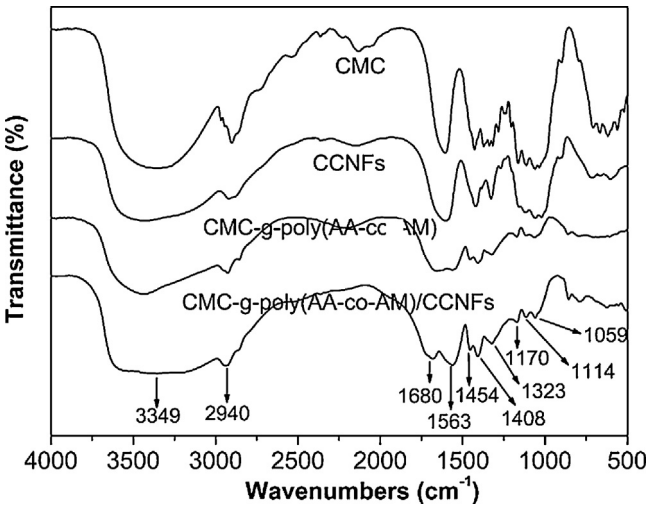

Fig. 2. FTIR spectra of CMC, CCNFs, CMC-g-p(AA-co-AM) and CMC-g-p(AA-co-AM)/CCNF hydrogels.

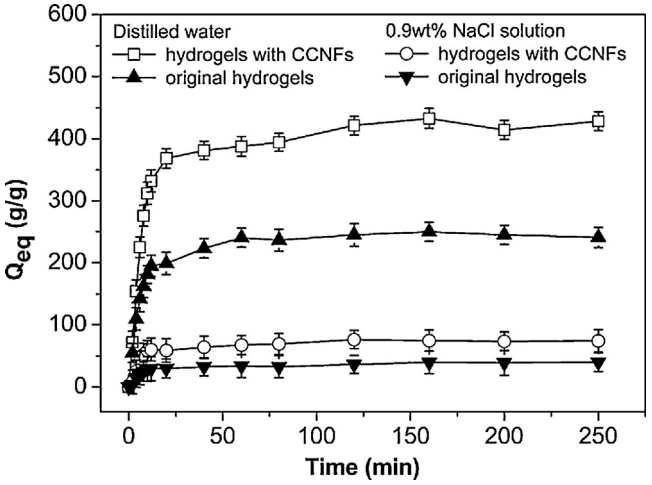

Fig. 4. Swelling kinetic curves of hydrogels (with and without CCNFs) in distilled water and 0.9 wt% NaCl solution.

assigned to carboxamide, causing by the superposition of C=O in amide I (1659 cm^{-1}) and C=O in COOH (1718 cm^{-1}). Besides, the band at 1552 cm^{-1} is due to C=O asymmetric stretching in carboxylate anion, and that is reconfirmed by peaks at 1456 and 1408 cm^{-1} which is related to the symmetric stretching of the carboxylate anion. The spectrum of CMC-g-p(AA-co-AM)/CCNFs exhibits a similar pattern compared with CMC-g-p(AA-co-AM). All the characteristic peaks associated with carboxylate groups become sharper after CCNF reinforcement, regarding to TEMPO-mediated regioselective oxidation of the primary hydroxyl groups to carboxylate ones of the cellulose nanofibrils, which confirm the nanocomposite formation. Therefore, the superabsorbent nanocomposites comprise a crosslinking structure of CCNFs and CMC with side chains that carry AA and AM.

3.3. Effect of CCNF content

Fig. 3 shows the effect of CCNF content on water absorbency of CMC-g-p(AA-co-AM)/CCNFs nanocomposite hydrogels. According to the results, when 2.5 wt% of CCNFs was filled into the hydrogel matrix the water uptake capacity received the maximum value. This behavior can be attributed to two possible reasons. First, there

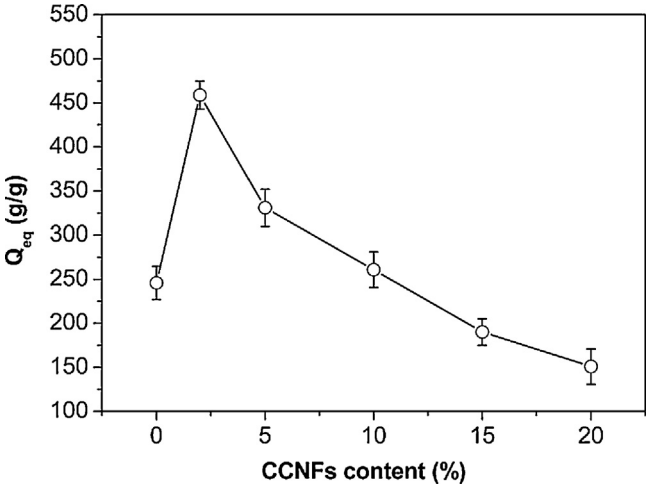

Fig. 3. Effect of CCNF content on water uptake capacity of CMC-g-p(AA-co-AM)/CCNF hydrogels.

are large amounts of active groups, including —OH, —CHO and —COOH (water affinity: —COOH > —CHO > —OH) on the surface of CCNFs, which make the hydrogels more hydrophilic. Besides, these active groups can participate in the polymerization reaction as well as the construction of tridimensional network, which prevent the polymeric chains from intertwining and weaken the hydrogen bonding interactions among the hydrophilic groups. For these reasons, the interactions of the hydrogels with the water molecules are increased and a higher absorption capacity is reached. On the other hand, the water uptake capacity decreased when the content of CCNFs was over than 5 wt%. In this stage the CCNFs shows a typical behavior of inert filler (Dai & Kadla, 2009). Great amounts of CCNFs enhance the crosslinking density and narrow the network voids of the hydrogels. Besides, the excessive CCNFs may physically entangled inside the network voids, and some voids are plugged up. All of these result in decreased water holding capability.

3.4. Swelling kinetics

To determine the swelling behaviors in different aqueous environments, distilled water and 0.9 wt% NaCl solutions were chosen as the swelling media. Fig. 4 shows the swelling kinetics for the hydrogel samples of CMC-g-p(AA-co-AM)/CCNFs and CMC-g-p(AA-co-AM). The observed trends of swelling kinetics for both hydrogels are quite similar. The swelling ratio increased quickly during the initial 20 min after the immersion, reaching about 90% of the equilibrium value. After that, the swelling ratio increased slowly and achieved equilibrium around 120 min. It can be seen that the presence of CCNFs in the CMC-g-p(AA-co-AM) polymer matrix improve the water uptake capacity at equilibrium and reduce the necessary time to reach adsorption balance. During the swelling process, water need to continuously overcome the osmotic pressure inside the absorbents. The substantial hydrophilic groups (—COO^-, —CHO and —OH) on the surface of CCNFs enhance the electrostatic repulsion in the hydrogel network, and thus strengthen the osmotic pressure difference. The larger the osmotic pressure difference, the faster the water permeates into the absorbents (Li et al., 2012). As a result, the hydrogels reinforced with CCNF fillers have a much higher swelling rate. The CMC-g-p(AA-co-AM) hydrogels presented absorption capacity at equilibrium of 240.6 g/g (distilled water) and 40.1 g/g (NaCl solution) while CMC-g-p(AA-co-AM)/CCNFs had higher capacity of 428.4 g/g (distilled water) and 73.9 g/g (NaCl solution), respectively. It is also demonstrated that the ionic strength of a medium has a strong effect on the water

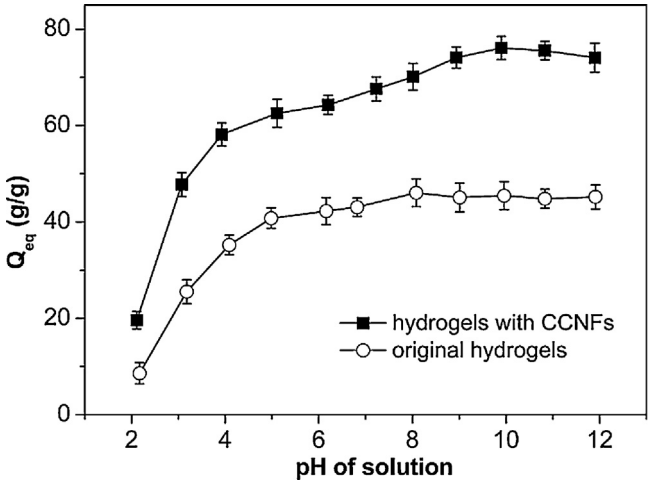

Fig. 5. Effect of pH on the water uptake capacity of hydrogels (with and without CCNFs).

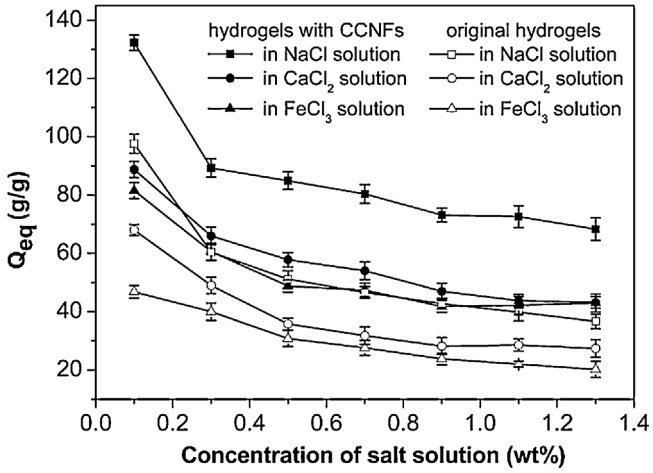

Fig. 6. Effect of salt solutions on water uptake capacity of hydrogels (with and without CCNFs).

absorbency of hydrogels, 0.9 wt% NaCl solution has high concentration of salts, both the hydrogels swell to a lesser degree in NaCl solution than in the distilled water.

3.5. Swelling equilibrium in various pH solutions

Fig. 5 shows the effect of pH on the water absorbency of CMC-g-p(AA-co-AM) and CMC-g-p(AA-co-AM)/CCNF hydrogels. The swelling behaviors of the two hydrogels exhibited clearly pH sensitive. The presence of CCNFs in the hydrogel matrix increased the water uptake capacity at each pH solution. In solutions of pH < 4 or pH > 8, CMC-g-p(AA-co-AM)/CCNFs seemed more sensitive to pH-stimulus. The CMC-g-p(AA-co-AM)/CCNF nanocomposites contain substantial carboxylate groups (from CMC and CCNFs), and thus are mainly anionic-type absorbents. Under acidic conditions (pH < 5), most of the carboxylate groups are protonated ($-COO^- \rightarrow -COOH$), which strengthen the hydrogen-bonding interactions and generate an additional physical crosslinking in the network (Li et al., 2012; Wang & Wang, 2010). Meanwhile, the electrostatic repulsions of the carboxylate are restricted and the network tends to shrink, and thus the swelling capacity is decreased. When pH is higher (6 < pH < 10), the hydrogen-bonding interactions are broken with decreasing effect of the H^+, besides, the reinforcement of the repulsions among the carboxylate groups also make the hydrogels swell more. However, in highly basic solutions (pH > 10), the charge screening effect of the Na^+ counterions in the swelling medium prevent effective anion-anion repulsions and lead to decreased water absorption (Lanthong, Nuisin, & Kiatkamjornwong, 2006). For another nanofiller-cellulose nanowhiskers (CNWs), no additional anion groups but sulfate groups are brought into the synthetic nanocomposites, the pH-sensitive characteristic is attributed only to the hydrogel matrix (Spagnol et al., 2012b). Thus different preparation approaches can obtain cellulose nanofillers with unique chemical or/and physical properties, resulting in manufacturing superabsorbents with special performance.

3.6. Effect of salt solutions on water absorbency

The characteristics of external solution such as charge valencies and salt concentration greatly influence the swelling behavior of the superabsorbents. Fig. 6 shows the water absorbency of the CMC-g-p(AA-co-AM) and CMC-g-p(AA-co-AM)/CCNF hydrogels in various salt solutions. The water absorbency at equilibrium decreased as the concentration of external saline solutions increased. The reason can be that the increasing salt concentration leads to the reduction of the osmotic swelling pressure difference between the polymer matrix and the external solution which prevent water molecules to penetrate inside the hydrogels. According to Fig. 6, the swelling decreasing depended not only on the salt concentration but also on the type of salt added to the swelling medium. Under the presence of excess salt, the counterion contribution to the osmotic pressure increases with the increasing of the ionic charge (monovalent > divalent > trivalent). The trends indicated that, despite the more hydrophilic groups and more loose structure of the CMC-g-p(AA-co-AM)/CCNFs, the nanocomposite hydrogels undergo almost the same influence to the presence of salt as the CMC-g-p(AA-co-AM). The reason can be that the CCNF nanofillers prevent the polymeric chains from intertwining and reduce the crosslinking density. The resultant broaden network of the nanocomposite hydrogels make an positive effect on the neutralization of charges inside the gel by multivalent ions and strengthen the intramolecular and intermolecular complex formation ability (Zhang, Chen, & Wang, 2006; Zhang & Wang, 2007), which in turn stimulate the rapidly shrinking of the CMC-g-p(AA-co-AM)/CCNF network, and thus water uptake capacity is decreased.

3.7. Deswelling kinetics in NaCl solutions

The deswelling kinetics of the swollen CMC-g-p(AA-co-AM)/CCNFs and CMC-g-p(AA-co-AM) hydrogels in aqueous NaCl solutions are shown in Fig. 7. All of the swollen hydrogels displayed fast responsive decreasing properties once transferred into NaCl solution and reached equilibrium within 1 h. The CCNF hydrogels have a slower deswelling rate and higher water retention at equilibrium. The equilibrium water retention are 83.3% (10 mmol/L NaCl), 39.3% (100 mmol/L NaCl) for CMC-g-p(AA-co-AM) samples, and 90.1% (10 mmol/L NaCl), 50.1% (100 mmol/L NaCl) for CMC-g-p(AA-co-AM)/CCNFs, respectively. Theoretically speaking, a relatively loose structure of CCNF nanocomposite hydrogels will improve the diffusion of liquids out of the adsorbents. However, the fact is that the CCNF nanofillers increased the water retention of the hydrogels, that partly can be attributed to the excellent mechanical stiffness (as high as 138 GPa) of the nanosized cellulose fibrils, which reinforce the hydrogel skeleton and prevent the tridimensional structure from severe shrinking. Besides, capillary action of the free or interstitial volume of the adjacent CCNFs can also tightly hold water molecules (Bao et al., 2011; Li et al., 2012). As a result, water releasing is suppressed. This new nanocomposite hydrogels

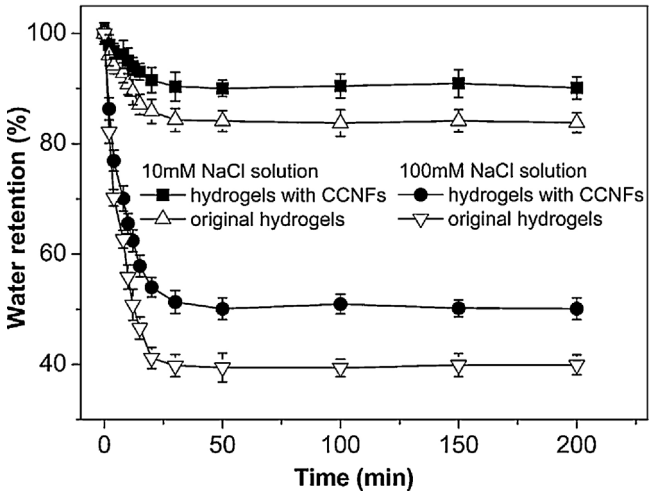

Fig. 7. Deswelling kinetics of hydrogels (with and without CCNFs) in NaCl solutions.

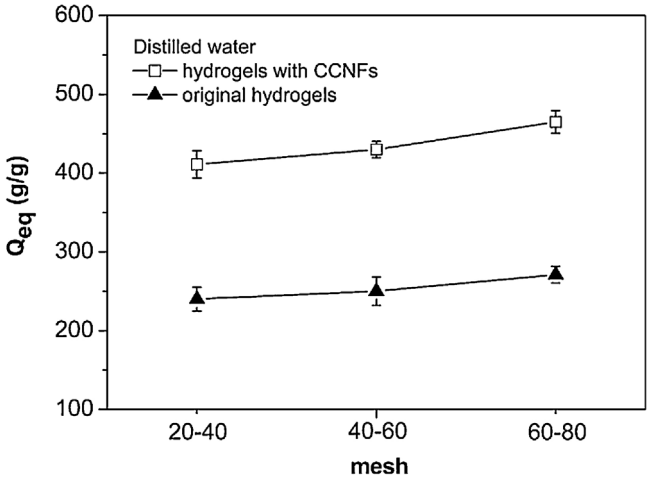

Fig. 9. Effect of particle size on water absorbency of hydrogels (with and without CCNFs).

with good deswelling resistance properties would have potential applications in modern agriculture and horticulture.

3.8. Water retention at various temperatures

Fig. 8 shows the water retention capacity of the hydrogels at two temperatures. As can be seen from the curves, the water retention capacity decreased almost linear as the time increased, and reached equilibrium after being heated for 10 h. The CMC-g-p(AA-co-AM)/CCNF nanocomposite hydrogels display slower water releasing rate and have higher equilibrium water retention of 81.1% and 78.9% at 35 and 80 °C, respectively. While the hydrogels without CCNF nanofillers retain 69.0% and 0.6% at 30 and 80 °C, respectively. Water retention capacity can be determined by the H-bonding interaction and Van der Waals force between the water molecules and the superabsorbents (Patra, Pal, & Dey, 2010). The substantial carboxylate groups of the CMC-g-p(AA-co-AM)/CCNF hydrogels make this chemical interaction stronger, furthermore, the high stiffness of the CCNFs firm the physical structure (tensile modulus and strength) of the hydrogel network, which in turn improve the water retention capacity.

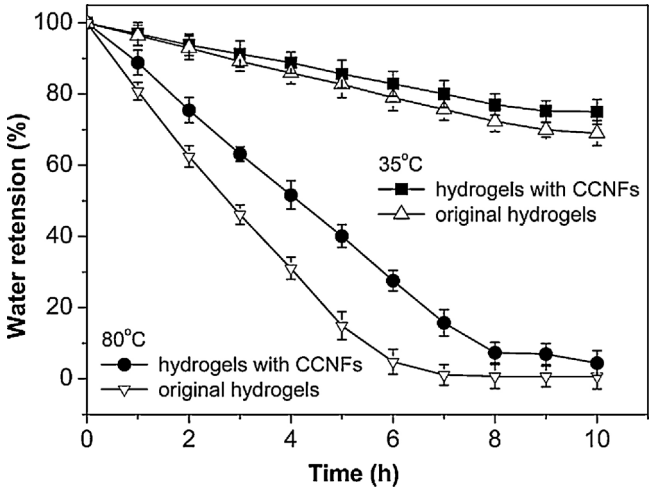

Fig. 8. Effect of temperature on water retention ability of hydrogels (with and without CCNFs).

3.9. Effect of particle size on water absorbency

Fig. 9 shows the effect of particle size on the water absorbency of CMC-g-p(AA-co-AM) and CMC-g-p(AA-co-AM)/CCNF hydrogels. Both the two hydrogels exhibited a little larger swelling capacity in the equilibrium when the particles were small, probably due to the increasing superficial area with decreasing particle size. Even when the particles are in contact, there is some space, called free or interstitial volume, between the particles, which have capillary action and can absorb some additional water (Bao et al., 2011). Since the same mass of small particles has a larger interstitial volume than the large particles, small particles have larger water retention at equilibrium.

4. Conclusion

Nanocomposite hydrogels based on carboxymethyl cellulose-g-poly(acrylic acid-co-acrylamide) and carboxylate cellulose nanofibrils (CCNFs, obtained by TEMPO-mediated oxidation) were successfully synthesized. The result of FTIR spectra showed the nanocomposites comprise a crosslinking structure of CCNFs and CMC with side chains that carry AA and AM. SEM images displayed the hydrogel morphology changed due to the incorporation of CCNFs. The swelling behaviors of hydrogels were affected by CCNF content, salt solution type and concentration, solution pH and temperature. The incorporation of CCNFs up to 2.5 wt% provided a maximal improvement in the swelling capacity due to the substantial hydrophilic carboxylate groups (0.94 mmol/g) on the CCNF surface. Further addition of CCNFs decreased the water uptake because some hydroxyl groups took part in the grafting reaction, which increased the crosslinking density. Besides, the nanocomposite hydrogels presented better responsive behavior in relation to pH. These hydrogels also had excellent salt and temperature resistance properties with lower decreasing rate and higher adsorption capacity at equilibrium. Such characteristics reveal that the inherent advantages of make these nanosized cellulose fillers suitable for high-performance superabsorbent application.

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