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Self-healing carboxymethyl Chitosan(CMCS) Hydrogel Composites With a Focus on Hydrogels Containing Nanowhiskers of Cellulose (CNWs)

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ABSTRACT

The poor mechanical properties of hydrogels have limited its application. Here, CNWs were fabricated and used to reinforce CMCS hydrogels. A series of CMCS/CNWs films were prepared by CMCS solution with CNWs suspensions homogeneously dispersed. The morphology of the resulting hydrogels was analyzed by scanning electron microscopy (SEM), the enhancement of the mechanical properties of the composites hydrogels were demonstrated by mechanical testing. Among the CNWs contents used, a loading of 2 wt % led to the maximum extension at break 95% and a loading of 3 wt % led to the maximum value of 650KPa for the composite hydrogels. The incorporation of CNWS led to a decrease in the swelling capacity. Besides excellent mechanical properties, CNWS composite hydrogels also have the capability of self-healing. We conclude that the incorporation of CNWs is a simple and promising way to reinforce composite hydrogels without impairing self-healing capacites. In light of these observations, this study provides a novel method to expand the application of CMCS hydrogels.

KEYWORDS Carboxymethyl chitosan, Cellulose nanowhiskers, Acrylamide, Hydrogel, Self-healing

1. Introduction

Hydrogels, due to the abundant hydrophilic groups on the chains and slightly crosslinked structure, can absorb large amounts of water and release the absorbed water in dry conditions. Besides their applications in drug delivery, hydrogels have wide potential applications in the fields of food, biomaterials, agriculture, etc.. Although a wide range of applications have been proposed for the hydrogels due to their unique properties, most of the hydrogels are suffered from short service life due to a lack of strength or easily broken 1.

Naturally occurring polysaccharide chitosan and cellulose are abundant renewable organic materials produced in the biosphere. CNWs have gained much attention not only because of their high mechanical strength and elastic modulus values, but also because of their inherent renewability and sustainability in addition to their abundance. They have been the subject of a wide array of research efforts as reinforcing agents in nanocomposites due to their low cost, availability, renewability, light weight, nanoscale dimension, and unique morphology 2. The main process for the isolation of CNWs from cellulose fibers is based on acid hydrolysis 2-4. The whiskers have a unique ability to act as reinforcing material for several polymers, such as waterborne polyurethane5, starch 6-10, pullulan11, chitosan12, and collagen13.

CMCS has many unique chemical, physical, and biological properties such as low toxicity, biocompatibility,and good ability to form films, fibers and hydrogels 14,15. For this reason, it has been extensively used in many biomedical fields such as moisture-retention agent and bactericide in wound dressings, as artificial bone and skin in blood anticoagulants and as a component in the drug-delivery matrices16, 17.

Hydrogels with the ability to repair themselves after sustaining damage and high strength could extend the lifetimes of materials used in many applications. Often, conventional hydrogels do not possess these properties at the same time. In sequence, we incorporated CNWs in CMCS hydrogels to produce materials with interesting self-healing capacities and high tough properties. To take advantage of the properties of CMCS and CNWs, we have designed a CNWs based composite hydrogel material in which CNWs were dispersed within a CMCS hydrogel matrix to form a rigid network. The morphology, mechanical properties and swelling behavior of the hydrogel composite were examined. The resulting hydrogel composite exhibited a stable mechanical functionality and good ability to repair themselves after damage.

2. Experimental

2.1 Material

Carboxymethyl chitosan, aminocaproic acid, acryloyl chloride, and acrylamide, ammonium persulfate, N,N'-methylene bisacrylamide were of analytical grade and used without further purification.

2.2 Preparation of CNWs nanocomposite hydrogels

2.2.1 Preparation of CNWs

The cotton fibers were firstly soaked in dimethyl sulfoxide (60mL) for 6 h at room temperature. After this, the fibers were washed in deionized water. The CNWs were obtained through cotton fibers acidic hydrolysis using 45wt.% H2SO4 (cellulose/ H2SO4 ratio of 1/20 g/ml) at 75°C for 10 h under vigorous magnetic stirring. After this process, the resulting solution was centrifuged at 10,000 rpm for 5 min and washed thoroughly with deionized water until pH 7. The resultant material was lyophilized at 57°C for 48 h.

2.2.2 Synthesis of acryloyl-6-aminocaproic acid (A6ACA)

0.1mol 6-aminocaproic acid and 0.11mol NaOH were dissolved in 80 mL deionized water in ice bath under vigorous stirring. To this, 0.11mol acryloyl chloride in 15 mL tetrahydrofuran was added dropwise. The pH was maintained at 7.5 until the reaction was complete. The reaction mixture was then extracted with ethyl acetate. The clear aqueous layer was acidified to pH 3.0 and then extracted again with ethyl acetate. The organic layers were collected, combined, and dried over sodium sulfate. The solution was then filtered, concentrated, and precipitated in petroleum ether. Further purification was achieved by repeated precipitation and the product was lyophilized 18.

2.2.3 Synthesis of CNWs nanocomposite hydrogels

The reaction system generally consisted of CNWs, water-soluble monomers(CMCS, A6ACA and AM), N,N′-methylene bisacrylamide, ammonium persulfate, and water. The hydrogels were prepared by free radical polymerization in dispersion of CNWs containing certain amounts of 86 wt.% distilled water, reactants (CMCS: A6ACA :AM=1:5:2 mass ratio), 0.6 wt.% N,N′-methylene bisacrylamide, 0.5 wt.% ammonium persulfate (initiator) were added to a reaction bulb and dissolved in, polymerized for 24 h at 37 °C.

2.3 Methods

IR spectra were recorded by FTIR (Nicolet iN10Thermo Fisher Scientific China) in the region of 400–4000 cm−1. The cellulose nanowhiskers structure was analyzed on an atomic force microscopy (Shimadzu, SPM-9600).The morphological characterization of gel was performed with scanning electron microscopy (S-3400N, Hitachi, Japan). The tensile stress–strain measurements were performed by using an Instron 3365 Universal Testing Machine (Norwood, MA) with the following parameters: sampling rate, 10.000 pts/sec; beam speed, 100 mm/min; full scale load range, 0.1000 kN; humidity, 25%; and temperature, 24 °C. The strip shape gel samples were 100mm *10mm * 3mm and the original, length between top and foot clamps was 25mm.

The gravimetric method was employed to measure the swelling ratios of the gels in distilled water at 25°C. After immersion in distilled water for about 48 hr to reach swelling equilibrium, the gel samples were taken out and weighed after removing the excess water on the surfaces. Each data was measured three samples, and the average value of three measurements was taken. The equilibrium swelling ratio (SR) was calculated as SR = Ws/Wd, where Ws is the weight of the swollen gel andWd is the weight of the gel at the dry state.

3. Results and discussion

3.1 The synthesis of the CNWS composite hydrogels

Disordered or paracrystalline regions of cellulose are preferentially hydrolyzed, whereas crystalline regions having a higher resistance to acid attack remain intact 2. Followed with an acid treatment that hydrolyzes the cellulose, then cellulose rod-like nanocrystals (CNWs obtained from acid hydrolysis are 2–20 nm wide and 0.3-1μm long, Figure 1 atomic force microscopy) are produced. CNWs here used were isolated from cotton. A CMCS -based composite material in which CNWS were dispersed within a CMCS matrix to form a rigid network (Fig.1) was designed. During the free radical polymerization, the reactive double bonding groups on the surface of CNWS and CMCS form highly branched polymer networks, which lead to CNWS and CMCSs act as multifunctional cross-links and bridges the adjacent CNWS and CMCS. As seen in Fig.1, except for the covalent bonds in CNWS, CMCS and poly(AM-co- A6ACA), there may also exist noncovalent interactions in $-CONH_2$, -COOH, $-NH_2$ and –OH. The self-healing reported here is rapid, occurring within seconds of the juxtaposition of two separate hydrogel pieces, as shown in Figure 1. The above finding suggests that the self-healing properties of the hydrogels along with their flexible side chains might be able to mediate hydrogen bonding across two hydrogel interfaces through the hydroxyl, amino, amide and carboxylic functional groups. Thus, the above noncovalent interactions mechanism in hydrogels network contributes to the self-healing behaviors 19.

3.2 Characterization of the CNWS composite hydrogels

Figure 2 shows the FTIR spectra of the CNWS composite hydrogels. As shown in Figure 2a, the principal characteristic bands of CMCS are attributable to the amide groups in the structure and appear as a peak at 1654 cm–1 corresponding to the band C=O stretching vibrations of carbonyl groups, a peak at 1240 cm-1 due to the amide C-N and N-H stretching. CNWS and CMCS exhibit characteristic absorption peaks at 3350, 2920, 1650, 1409, and 1066cm–1, which arise from the chain ascribed to C-O and O-C-O stretching vibrations Figure 2. After free-radical copolymerization with A6ACA, the spectra showed several new absorption bands in addition to the original peaks of pure CMCS. The new absorption band at 1720 cm-1 was assigned to the C=O stretching vibration of the amide group, and those appearing at 1570 cm-1 and 1410 cm-1 were assigned to the asymmetric and symmetric stretching vibrations, respectively, 1660cm-1 were assigned to the C=O in the carboxylate group 17. This clearly indicates that CNWS composite hydrogels were successfully performed.

3.3 Mechanical properties of the CNWS composite hydrogels

Hydrogels normally present poor mechanical properties. Cellulose nanocrystals have been used to manufacture mechanical adaptive materials as reinforcement due to the excellent mechanical strength and strength diminishing in the presence of water. Using CNWS to prepare hydrogels could improve the mechanical strength of the hydrogels 20-21. Therefore, CNWS have been used to reinforce numerous polymer matrices 20-21. In sequence, we incorporated CNWs in CMCS hydrogels to produce materials with interesting self-healing capacities and high tough properties.

The effect of CMCS on mechanical properties was studied by varying the content of CNWS (1 wt.%, 2 wt.%, 3 wt.%,4wt.%, and 5 wt.% in related to the amount of solid content), while the rest of variables were unchanged. As shown in Figure 3, the composite hydrogels exhibited an increased extension at break as the CNWS content increased to a maximum of 2wt% CNWS, and then the extension at break gradually decreased at 2 wt% and 5 wt% of the incorporated CNWS. With increasing amounts of CNWS, the stress has a maximum value of 650KPa as the 3wt% CNWS content. The results show that CNWS accelerated the formation of the hydrogels and increased the effective crosslinking density; that is, it was suggested that the CNWS acted as a multifunctional crosslinking agent.The significant reinforcement observed for CMCS / CNWS nanocomposites hydrogels can be attributed to the formation of rigid whisker networks in which stress transfer is facilitated by hydrogen bonding between the whiskers. Owing to their strongly interacting surface hydroxyl groups, cellulose nanofibers have a strong tendency for self-association 22-23.

In addition, the addition of a small fraction of CNWS led to a significant increase in extension at break and stress. The low density of crosslinks, the homogeneous network structure, and the multifunctionality of CNWS within the primary chains promoted the remarkable strength of the hydrogels 24. The concentration of CNWS is too large will lead to easy to agglomerate, at the same time, the excessive cross-linking can lead to the degradation of mechanical properties.

3.4 The SR of the CNWS composite hydrogels

The ability of the scaffold to absorb water is one of the important factors in determining the properties of a hydrogel. CNWS is a highly hydrophilic material because of its chemical and physical structure. The swelling properties of composite films mainly depended on the hydrophilic ability of the functional groups and the effective cross-link density of the hydrogels. Equilibrium swelling experiments were conducted to study water absorption as a function of CNWS content, and the results are summarized in Figure 4. The equilibrium swelling ratios of the composite hydrogels were strongly dependent on the CNWS content, and a decrease in the swelling ratio occurred with increasing content of CNWS. The results show that CNWS increased the effective crosslinking density, that is, it was suggested that the CNWS acted as a multifunctional crosslinking agent. In this case, the presence of CNWS decreased the swelling ability of such composite hydrogels, this indicated that the CNWS acted as a multifunctional crosslinker and reinforced the hydrogel system25. This suggested the existence of physical and chemical interactions between the polymer matrix and the CNWS 24-26.

4. Conclusion

In this study, CMCS -based composite hydrogels reinforced with CNWS were successfully prepared using a simple, rapid, and effective method. Composite hydrogels comprise a matrix components (CMCS, AM, A6ACA) and CNWS, whereby the matrix component supports the reinforcement material (CNWS) by maintaining relative positions, and the CNWS impart mechanical properties that enhance the hydrogels properties. The results confirmed that CNWS are an attractive reinforcing agent for integration into CMCS matrices, the incorporation of CNWS improved the interior ordering and stability of the composite films and led to an increase in the swelling capacity.

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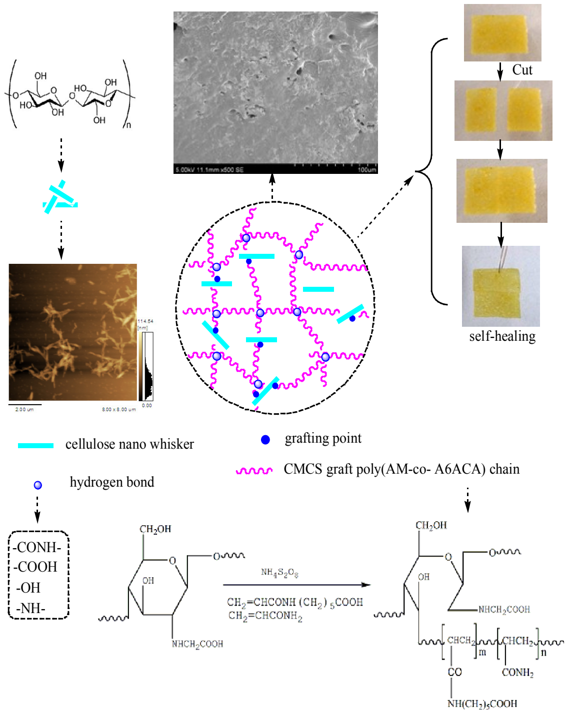


Figure 1 Schematic illustration of the network in hydrogels

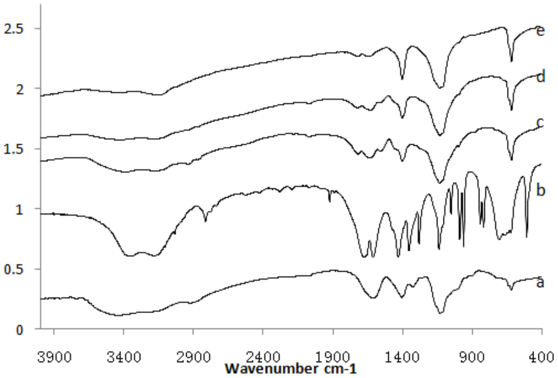
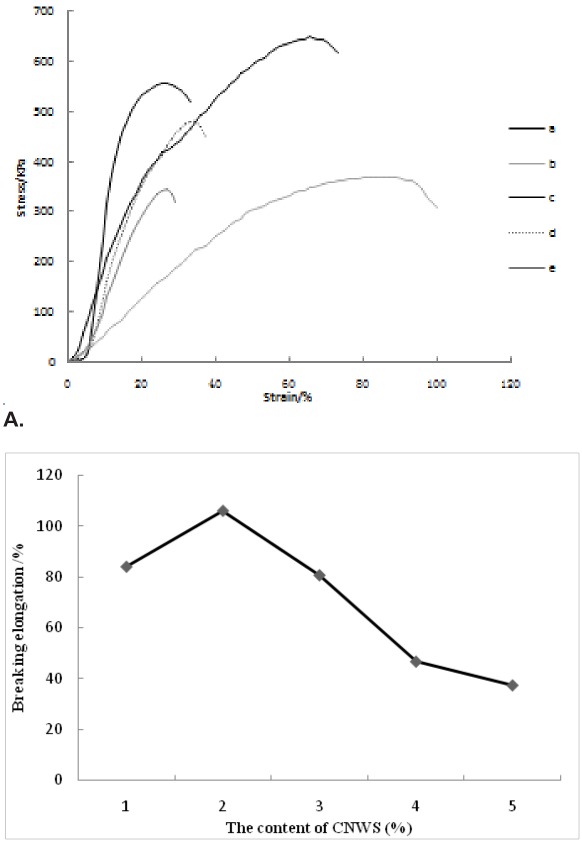


Figure 2 FTIR spectra of CNWS composite hydrogels. (a. CMCS; b. A6ACA ; c. The content of CNWS in the system was 1 wt.% ;d. The content of CNWS in the system was 3 wt.%;e. The content of CNWS in the system was 5 wt.%)



A.

B.

Figure 3 The effect of CNWS content on the mechanical properties of hydrogels (the content of CNWS:a.1 wt.%, b. 2 wt.%, c.3wt.%, d.4 wt.% and e. 5 wt.%)

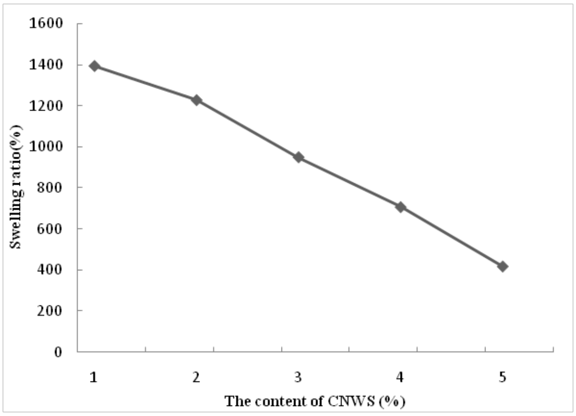


Figure4 The swelling ratio of CNWS composite hydrogels

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