



Dual physically crosslinked healable polyacrylamide/cellulose nanofibers nanocomposite hydrogels with excellent mechanical properties



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ABSTRACT

To develop healable hydrogels with excellent mechanical properties is still a challenge topic. In this study, a novel class of physically crosslinked polyacrylamide based nanocomposite hydrogels reinforced with cellulose nanofibers (CNF) were fabricated using radical polymerization, followed by further strengthening through ferric ions via strong ionic coordination interactions between Fe^{3+} and carboxyls on CNF surfaces. Then the obtained gels were characterized by FTIR, tensile and compressive measurements as well as healing experiments. The increase of CNF amount or Fe^{3+} concentration generated positive effect on the improvement of hydrogel mechanics, demonstrating facilely modulatable mechanical properties through simply changing CNF dosages in formulations and/or Fe^{3+} concentrations in posttreatment. The obtained nanocomposite hydrogels show remarkable mechanical properties with high stiffness and toughness, quick recovery and healing abilities owing to the distinctive roles of dual physical crosslinks. This work provides a promising view for designing novel high strength hydrogels with fully physical crosslinks.

1. Introduction

Hydrogels have attracted broad attentions due to their various applications such as structural biomaterials, masks, drug delivery, wound dressing and so on (Buenger, Topuz, & Groll, 2012; Burdick & Prestwich, 2011). However, conventional polymer hydrogels as soft and wet materials often exhibit low mechanical strength, limited toughness as well as poor recovery owing to their brittle three-dimensional network structure, which has restricted their application in some special fields. To address this issue, many efforts have been made to develop mechanically robust hydrogels. Some novel concepts were proposed, which include micro- or nano-composite hydrogels (Huang, Xu, Jiao, Zhu, Brown, & Wang, 2007; Thoniyot, Tan, Karim, Young, & Loh, 2015; Can et al., 2016), double network hydrogels (Gong, Katsuyama, Kurokawa, & Osada, 2003), topological hydrogels (Okumura & Ito, 2001), tetra-poly(ethylene glycol) hydrogels (Sakai et al., 2008), and hydrophobic hydrogels (Oliveira et al., 2016). Generally, covalent chemical crosslink is a usually adopted method to fabricate hydrogels. However, its major drawback is that the network structure would be permanently fractured once the chemical crosslinks are broken, so that the produced hydrogels are mostly lack of good recoverability. Thus dynamic physically crosslinked hydrogels with efficient energy dissipation mechanism have been developed recently, which apply non-

covalent interactions such as hydrogen bonding, ionic bonds, crystallization, metal coordination bonds, and so on (Bilici, Ide, & Okay, 2017; Hu, Vatankhah-Varnoosfaderani, Zhou, Li, & Sheiko, 2015; Lee, Narkar, & Wilharm, 2016; Sun et al., 2013). Here, with regard to various metal coordination bonds for hydrogel construction, reversible ferric ion-carboxyl interaction represents an important research branch to get high-performance hydrogels (Chen et al., 2016; Hu, Du et al., 2016; Lin, Ma, Wang, & Zhou, 2015; Zhang, Zuo, Hu, & Chang, 2017; Zheng et al., 2016; Zhong et al., 2015). For example, Zheng and coworkers reported a species of poly(acrylamide-co-acrylic acid) based physical hydrogels solely crosslinked by Fe^{3+} , which exhibited high stiffness and toughness, fatigue resistance, and stimulation-triggered healing along with shape memory and processing abilities (Zheng et al., 2016).

Various species of physically crosslinked nanocomposite hydrogels have emerged since the first report of poly(N-isopropylacrylamide)-clay hybrid gels was published by Haraguchi and coworkers (Haraguchi & Takehisa, 2002). Polymer hydrogels composited with inorganic nanoparticles such as laponite, layered double hydroxide, montmorillonite, graphene oxide and boron nitride (Gao, Du, Sun, & Fu, 2015; Hu, Liu et al., 2016; Hu & Chen, 2014; Liu et al., 2012; Zhu et al., 2006), revealed excellent mechanical properties with superior flexibility and high strength despite the absence of any chemical crosslinkers. Inside the networks, nanoparticles served as noncovalent crosslinkers besides

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as nanofillers, and thus self-healing ability was realized simultaneously in some systems. Recently, a novel type of natural nanomaterials, nanocellulose, has been applied in nanocomposite hydrogel fabrications (De France, Hoare, & Cranston, 2017; Shah, Ul-Islam, Khattak, & Park, 2013). Usually nanocellulose is classified into bacterial cellulose (BC), cellulose nanocrystals (CNC), and cellulose nanofibers (CNF). BC composited polyacrylamide (PAM) hydrogels showed improved strength no matter BC existed in the form of interpenetration or cluster dispersion within the networks (Velichko et al., 2017; Yuan et al., 2016). CNC reinforced hydrogels including PAM, poly(acrylic acid) (PAA) and poly(ethylene glycol) (PEG) systems, were systematically researched by Yang et al., and some microscopic strengthening mechanism was investigated (Yang et al., 2012; Yang, Han, Duan, Xu, & Sun, 2013; Yang, Han, Duan, Ma et al., 2013; Yang, Zhao, Xu, & Sun, 2013; Yang, Han, Zhang, Xu, & Sun, 2014; Yang, Zhao et al., 2014). CNF, by virtue of its propensity for entanglement and flexibility, also has been used as reinforcing agents to construct tough yet highly flexible polymer gels through straightforward mixing, in situ polymerization, or heat-treatment (De France et al., 2017).

It is known that CNF can be extracted from cellulose pulps through mechanical, chemical or a combination thereof (Abitbol et al., 2016). And 2, 2, 6, 6-tetramethylpiperidine-1-oxyl radical (TEMPO) mediated oxidation in combination with following mild mechanical treatment is a convenient method to produce transparent dispersions of individual CNFs with 3–4 nm in width and several μm in length (Saito, Kimura, Nishiyama, & Isogai, 2007). The crucial point of this method is the selective oxidation of C6 primary hydroxyls into carboxylate groups with high density on the fibril surfaces, guaranteeing the stability of CNF dispersions through the electric repulsion from generated carboxylate moieties (Isogai & Fukuzumi, 2011). Meanwhile, the electronegative nature of CNF surfaces also endows it with potential applications as absorbents to heavy metal cations (Liu, Oksman, & Mathew, 2016; Ma, Hsiao, & Chu, 2012; Sehaqui et al., 2014). Furthermore, CNF surface carboxylate groups were also used as junctions to interplay with multivalent cations for fabricating hydrogels through physical crosslinks (Zander, Dong, Steele, & Grant, 2014). Yang et al. treated covalently crosslinked PAM/CNF composite hydrogels with Ca^{2+} , Zn^{2+} , Al^{3+} , and Ce^{3+} cations, obtaining ionic and covalent dually crosslinked hydrogels with improved mechanics and high self-recovery efficiency (Yang, Xu, & Han, 2017); subsequently, fully physically crosslinked PAA/CNF- Fe^{3+} hydrogels with high strength, toughness and self-healing properties were also published by the same group (Shao, Chang, Wang, Xu, & Yang, 2017).

As for nanocellulose-containing composite hydrogels, especially for PAM ones, hydrogen bonding between hydroxyls and amides on both components plays an important role in their excellent mechanical properties (Yang, Han et al., 2014; Yang et al., 2017; Yuan et al., 2016).

Considering this factor, in combination with strong Fe^{3+} - COO^- ionic coordination, a novel type of PAM hydrogels with dual physical crosslinks are designed and studied in this research. Different from the Yang's works mentioned above, which have dealt with solely physically crosslinked PAA/CNF- Fe^{3+} gels and chemical-physical dually crosslinked PAM/CNF- Ca^{2+} (Zn^{2+} , Al^{3+} , Ce^{3+}) ones, this research focuses on PAM/CNF- Fe^{3+} composite hydrogels with only physical crosslinks. To this end, PAM/CNF physical gels are prepared by in-situ polymerization of AM in CNF dispersion, followed by the posttreatment in FeCl_3 solution. Within the obtained hydrogels, hydrogen bonding and Fe^{3+} - COO^- coordination act as the first and second crosslinks, respectively, and the obtained hydrogels demonstrate excellent and tunable mechanical properties as well as healing ability.

2. Experimental

2.1. Materials

Never-dried hardwood pulp was obtained from Chongqing Lee & Man Paper Mfg. Ltd., China. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from Tianjin Fuchen Chemical Factory, China. Acrylamide (Am, 98%) was supplied from Mitsui Chemicals, Japan. 2, 2, 6, 6-Tetramethylpiperidine-1-oxyl (TEMPO), N, N, N', N'-Tetramethylethylenediamine (TEMED), Ammonium persulfate (APS), and Ethylene diamine tetraacetic acid disodium salt (EDTA 2Na) were bought from Shanghai Richjoint Chemical Reagent Co. Ltd., China.

2.2. Preparation of CNF

Referring to the method developed by Isogai group (Saito et al., 2007), 10 g of wet wood pulp was suspended in 400 mL of water solution containing TEMPO (33 mg) and NaBr (100 mg), to which 10 mL of 10 wt% NaClO aqueous solution was slowly added under stirring. During the reaction, 0.5 M NaOH was dropped into the system to maintain pH 10, and no more decrease of pH indicating the completion of reaction. Finally the pH value was adjusted to 7 using 0.5 M HCl. The product was thoroughly washed with water by filtration for 4 times, and then was sonicated in an ultrasonic cell disrupter for 15 min. The resultant dispersion was stored at 4 °C for later measurements and applications. The concentration of CNF suspension in this work was gravimetrically determined to be 0.2 wt%; the surface carboxylate content of CNF was measured to be 1.56 mmol/g using conductometric titration method; the diameter of CNF was in the range of several nanometers based on TEM image, as shown in Fig. 1.

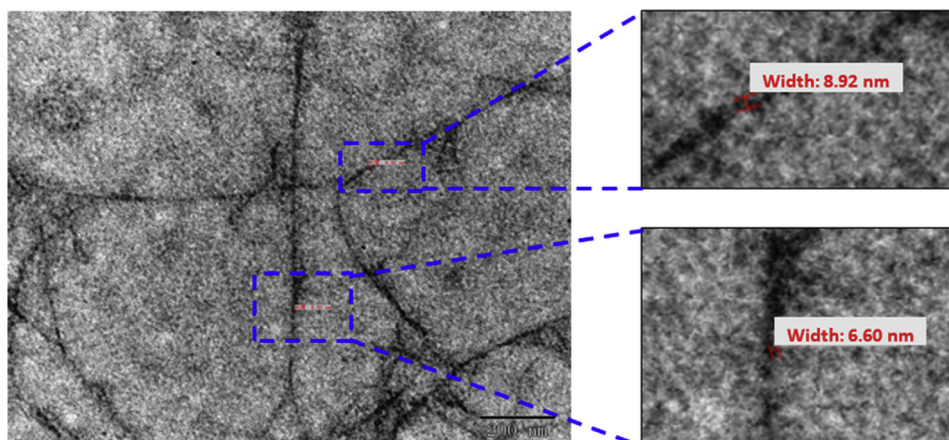


Fig. 1. TEM image of CNF.

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