Self-recovery magnetic hydrogel with high strength and toughness using nanofibrillated cellulose as a dispersing agent and filler

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ABSTRACT

Fe$_3$O$_4$ nanocomposite hydrogels, with intrinsic magnetism, can be potentially applied in extensive fields. However, the poor mechanical properties and complex fabrication processes of conventional magnetic hydrogels seriously limit their advanced applications. Herein, this work demonstrates an efficient and easily industrialized method to prepare self-recovery magnetic hydrogels with excellent mechanical performances. In this method, Fe$_3$O$_4$ nanoparticles were facilely dispersed in polyacrylamide (PAM) hydrogels with the assistance of nanofibrillated cellulose (NFC), resulting in good magnetism. The tensile strength and elongation at break of hydrogels increase from 150 to 780 KPa, 1400% to 2960%, respectively, due to the unique network structure and the strong hydrogen bonding interaction between NFC and PAM. Moreover, the obtained hydrogels possess the satisfactory self-recovery ability, thermal stability, and shear resistance. We believe this efficient and simple method can expand the application of high-performance composite hydrogels in biological, medical and environmental fields.

1. Introduction

Intelligent nanocomposite gels with responses to the change of light, electricity, and magnetism can be obtained by introducing inorganic nanoparticles with optical, electrical and magnetic properties into gels (Han et al., 2017; Shao et al., 2018; Wen et al., 2017). Fe$_3$O$_4$, a conventional magnetic material, is usually incorporated into hydrogel systems to afford magnetism (Bhattacharya, Eckert, Boyko, & Pich, 2007; Danieldasilva et al., 2009; Xulu, And, & Zrínyi, 2012). Magnetic hydrogels have attracted much attention because of the property of perception, response to the external magnetic field, unique flexibility and permeability. And they have been widely used in drug delivery (Paulino et al., 2012), separation (Ozay et al., 2010), image enhancement (Kim, 2012), valves (Satarkar, Zhang, Eitel, & Hilt, 2009) and artificial muscle (Ramanujan & Lao, 2006). Unfortunately, conventional magnetic gels often require delicate fabricated process, such as self-assembly (Adriane, Huang, Ding, Chen, & Liu, 2006), microfluidic devices (Hwang, Dendukuri, & Doyle, 2008) and specific molecular design (Czaun, Hevesi, Takafuji, & Ihara, 2008), which limits their large-scale manufacture. Mixing or embedding Fe$_3$O$_4$ magnetic particles into a hydrogel matrix is a relatively easy way to fabricate magnetic hydrogels, and the obtained composites usually have considerable stability and processability. However, the major challenge of this method is that it is hard to evenly disperse magnetic particles in the matrix (Hayashi, Fujikawa, Sakamoto, Inoue, & Yogo, 2008). Due to their agglomeration, only a few particles can be well dispersed in the matrix, causing poor magnetic properties. Furthermore, the mechanical properties of magnetic hydrogels are generally weak. These problems restrict the practical and progressive applications of magnetic gels.

Nanofibrillated cellulose (NFC) extracted from abundant natural cellulose fibers is a mesoscopic material featuring high aspect ratio, high specific surface area, impressive mechanical properties, and low weight (Akira, Tsuguyuki, & Hayaka, 2011; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Qing et al., 2013; Zimmermann, Bordeanu, & Strub, 2010). So it has been broadly applied to reinforce composite hydrogels (Han, Lei, & Wu, 2014; Mckee et al., 2014; Nair, Zhu, Deng, & Ragauskas, 2014). Especially, NFC prepared by 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidized, with the presence of hydroxyl groups and charged groups (−COO$^-$) on its surface, is stable and well-dispersed in water without aggregation, and can be easily combine with other nanoparticles for the construction of novel hybrid materials (Li, Chen, Che, & Tian, 2017; Shi, Phillips, & Yang, 2013; Saito, Kimura, Nishiyama, & Isogai, 2007; Yan et al., 2014). So far, as a stabilizer and dispersant for nanomaterials, NFC has received wide attention in academia and industry. For example, Xiong, Lu, Wang, Zhou, and Zhang (2013) prepared Fe$_3$O$_4$/Ag nanocomposites

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using nanofibrillated cellulose as a stabilizer for Fe_3O_4 nanoparticles (Xiong et al., 2013). Li et al. (2013) reported a magnetic nanopaper by using nanocellulose as a dispersing agent for Fe_3O_4 nanoparticles (Li et al., 2013). And the prepared nanocomposites present excellent mechanical performances and magnetism. Thus, in the presence of NFC serving as a dispersing agent and filler, the preparation of magnetic nanocomposite hydrogels is a breakthrough compared with conventional ways.

In this work, we fabricated free-standing magnetic nanocomposite hydrogels with excellent mechanical and self-recovery properties. First, NFC prepared by TEMPO-mediated oxidation was used as a stabilizer to uniformly disperse Fe_3O_4 nanoparticles in an aqueous medium. Then, acrylamide was dissolved in the homogeneous Fe_3O_4/NFC aqueous solution. Finally, homogenous Fe_3O_4 nanocomposite hydrogels were synthesized by free radical polymerization. Due to the unique structure formed by NFC and PAM chains and the strong hydrogen bonding interaction between NFC and PAM, the obtained hydrogels were simultaneously reinforced and toughened. The tensile strength, elongation-at-break, and energy at break of the obtained hydrogels preponderated over those of reported hydrogels. Additionally, we characterized other comprehensive properties, such as thermal stability, shear resistance, and self-recovery property by thermogravimetric analysis, rheological test and cyclic tensile test in this study. We believe this integration of straightforward and green process is beneficial to broaden the practical application of composite hydrogels in modern industries.

2. Experimental

2.1. Materials

Microfibrillated cellulose (MFC, Celish MFC KY100-S) was purchased from Daicel Chemical Industries, Ltd., Japan. Fe_3O_4 nanoparticles were obtained from Nanjing Emperor Nano Material Co., Ltd., China. TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy, 98 wt%) was obtained from Sigma Aldrich. Sodium bromide (NaBr), sodium hypochlorite (NaClO) solution, sodium hydroxide (NaOH), acrylamide (AM) and *N*,*N*-methylenebisacrylamide (MBA) were supplied by Chengdu Kelong Chemical Reagent Factory, China. Tetramethylethylenediamine (TEMDA), and potassium persulfate (KPS) were from Tianjin Bodi Chemical Industry Ltd., China. All reagents used in this work were of analytical grade, and distilled water was used for the preparation of aqueous solutions.

2.2. Preparation of NFC

NFC was prepared according to an existing method (Yang et al., 2017). Firstly, 78 mg TEMPO, 514 mg NaBr together with 5 g MFC were mixed together in 1000 mL distilled water. TEMPO oxidation of cellulose was triggered by adding NaClO at room temperature with gentle agitation. During the oxidation process, the pH was maintained at 10.5 by adding 0.5 M NaOH solution. After TEMPO treatment, the cellulose was thoroughly washed with distilled water and disintegrated by sonication for 15 min at a power of 300 W in an ice bath. NFC dispersion was achieved by centrifugation at 10,000 rpm for 10 min to remove the unfibrillated cellulose. The tested solid content of NFC in suspension is 0.88 wt%.

2.3. Preparation of composite hydrogels

In this work, nanocomposite hydrogels were prepared by free radical polymerization of AM in an aqueous dispersion of NFC and Fe_3O_4 nanoparticles at room temperature. The preparation schematic of F/N-PAM hydrogels is illustrated in Fig. 1. Firstly, to obtain the homogeneous Fe_3O_4/NFC (F/N) dispersion, a certain amount of Fe_3O_4 nanoparticles were added into NFC dispersion under high-speed stirring at

3000 rpm for 15 min, then sonicated for 10 min at power of 300 W. Secondly, the solid reagents, including AM, TEMDA, and MBA were initially dissolved in F/N dispersion. Subsequently, deoxygenation was performed by bubbling nitrogen into the homogeneous mixture for 15 min under mechanical stirring, followed by adding 40 mg/5 g KPS water solution. Finally, the mixture was transferred into molds under a nitrogen atmosphere and stayed for 24 h to react completely. The composition of hydrogels and their nomenclature are listed in Table S1. The hydrogels with 0 wt%, 0.4 wt%, 1.2 wt%, 2.0 wt% of Fe_3O_4 (relative to the monomer) were labeled as 0F/N-PAM, 0.4F/N-PAM, 1.2F/N-PAM, 2.0F/N-PAM, respectively. The amount of NFC in the hydrogels with various Fe_3O_4 contents is the same. 0.4F-PAM hydrogels without NFC were prepared in the same way for comparison.

2.4. Characterization

The structure and morphology of NFC and Fe_3O_4 nanoparticles were characterized by transmission electron microscope (TEM, JEM-2010). Scanning electron microscopy (SEM, FEI Inspect F, USA) was employed to investigate the structure and morphology of composite hydrogels as well as the fractured surfaces after tensile tests. All the samples were freeze-dried before SEM tests.

X-ray diffraction (XRD) patterns were recorded by a D/MAX-III X-ray diffractometer (DY1291, Philips, Holland) with Cu Kα (0.154 nm) radiation from 5° to 80° at a rate of 5°/min and at room temperature. Hydrogel samples were placed in a vacuum oven at 50 °C drying to constant weight and then cut in the form of thin slices with a size of $3 \times 3 \times 1$ mm.

The magnetic properties of the composite were measured at 298 K using a vibrating sample magnetometer (model 7300 VSM system, Lake Shore Cryotronic, Westerville OH, USA). Samples were placed in a vacuum oven at 50 °C drying to constant weight and then cut in the form of cubes with a size of 3 mm.

The swelling ratio of hydrogels was tested by following procedures. The hydrogels were cut into smaller rectangular matrices with basically same size and placed in a vacuum oven at 50 °C drying to constant weight. Then these gels were swollen in a large excess of distilled water, placed at room temperature. The gels were taken out at a certain time, and the surface of gels was wiped with filter paper. Then the gels were accurately weighed. Swell ratio (SR) of the gels is calculated as follows:

$$SR = \frac{W_t - W_0}{W_0} \times 100\%$$

where W_0 is the weight of the dry gel, W_t is swelling weight of gel when the time is t. Each sample was tested 3 times and averaged. For all the samples, the amount of extracted polymer (e.g., linear PAM) analyzing by HPLC, if observable, was less than 1.5 wt% of the total organic content.

The thermal stability of hydrogels was characterized with a thermal gravimetric analyzer (TGA, TA Instruments, Q500, USA). Samples were placed in a vacuum oven at 50 °C drying to constant weight before the tests. Samples were heated from 0 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a flow rate of 25 mL/min.

Mechanical properties of hydrogels were characterized by tensile tests and hysteresis tests. Stress-strain tests of the hydrogels were performed by making uniaxial measurements using an Instron tester 4302 (USA). Gels were cut into dumbbell-shaped specimens with a cross-section area of 4×1 mm. Then these specimens were clamped vertically, with a gauge length of 20 mm and tested at a constant rate of 100 mm/min at room temperature. All the samples were stretched until failure. Stress was calculated by dividing the force generated during extension by the initial cross-sectional area. In this work, a parameter to characterize the toughness of the samples was determined by the area under the stress-strain curve until the fracture of the sample. The loading-unloading hysteresis tests of gels were also conducted by the same instrument above. Gel specimens were firstly stretched by a