



Facile fabrication of self-healing carboxymethyl cellulose hydrogels

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ABSTRACT

As a material derived from cellulose, which is abundant in nature, carboxymethyl cellulose (CMC) has been used as an ingredient to synthesize hydrogels for various applications. The introduction of self-healing properties in CMC hydrogels will expand their service life and scope of application. We report a facile way to fabricate CMC hydrogels with self-healing behaviour. The self-healing CMC hydrogel is achieved by acidifying the CMC paste in citric acid solution. The CMC hydrogel can autonomously self-heal without any external stimulus under ambient temperature, and the healed hydrogels can bear the stretching as demonstrated by macroscopic observation. The hydrogel with ~ 2.5 MPa compressive strength exhibits $\sim 80\%$ of healing efficiency. With these superior properties, the developed CMC hydrogel holds great potential for applications in biomedical and industry fields.

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1. Introduction

Hydrogels, identified as soft and wet materials containing a large amount of water in their three-dimensional (3D) network structure, have been widely explored in biomedical and engineering fields, such as tissue engineering, drug delivery, soft actuator and soft machines [1–7]. However, the desired performance of traditional hydrogels usually deteriorates or even gets lost because of their intrinsic brittleness and irreversible deformation, which seriously restrict their service life and scope of application. Self-healing hydrogels possess the ability to solve these problems, due to their ability to repair their damages at macro- or microscale, inhibit damage propagation, and recover the integrity of network structures and functionalities [8]. To equip hydrogels with self-healing features, two major strategies have been proposed. One is based on dynamic covalent bonds, such as phenylboronate ester bond [9,10], acylhydrazone bond [11], disulfide bond [12,13] and Diels–Alder reaction [14,15]; the other is based on non-covalent bonds, such as electrostatic interactions [16–18], hydrophobic interactions [19,20], host–guest recognition [21,22] and hydrogen bonding [23]. The developed self-healing hydrogels can be potentially used in various areas of tissue adhesives, agents for drug/cell delivery, coatings and sealants [8].

Currently, the existing approaches to fabricate self-healing hydrogels are mainly based on designing and synthesizing molecules with preferred functional groups that are necessary for constituting 3D polymer networks, via either specific dynamic covalent bonds or non-covalent bonds. These processes involve some unavoidable drawbacks, such as adopting rigorous reaction conditions, the use of toxic chemicals, and dealing with multi-step synthesis/purification procedures. The

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complexities involved prevent the large-scale production and economic practicality of self-healing hydrogels, which further limit their widespread applications. It remains a challenge to develop strategies for the fabrication of self-healing hydrogels through facile procedures using green, cheap and natural resources.

Carboxymethyl cellulose (CMC) is a cellulose derivative with a large number of carboxymethyl groups on the cellulose backbone [24]. Due to the merits of non-toxicity, water solubility, low-cost and environmental friendliness [25], CMC has been widely used as a natural ingredient for hydrogels, and has been developed for various applications including tissue engineering, drug delivery, wound dressing and plant breeding [24–29]. All these applications expect self-healing performance of CMC hydrogels to enhance their service life and applicability. Currently, the preparation methods of CMC hydrogels are largely based on chemical cross-linking [24–29]. However, breaking the chemically cross-linked CMC networks results in irreversibly damaged polymer networks, and the chemical agents involved are generally toxic. Some reports have been focused on physical cross-linking of CMC chains using organic acid [30,31], but the mechanical performance of the hydrogels is unsatisfactory. Recently, a self-healing CMC hydrogel based on dynamic phenylboronate ester cross-links has been reported [32]. The development of a self-healing CMC hydrogel based on physical bonds via a facile approach is still elusive.

In this contribution, we developed a novel CMC hydrogel with self-healing performance and toughness using green resources. This is realised straightforwardly by immersing free-shaped Na-CMC pastes into citric acid solution, in which the H^+ ions gradually diffuse into the Na-CMC paste and bind CMC polymer chains via hydrogen bonds, resulting in transparent and free-shaped CMC hydrogels. The number of hydrogen bonds, adjusted by controlling the acidification time, can affect the self-healing performance and mechanical properties of CMC hydrogels. As demonstrated by macroscopic observation and beam-shaped strain compression test, the CMC hydrogel can achieve ~ 2.5 MPa of compressive strength and exhibit excellent self-healing behaviour with over 80% of healing efficiency. The proposed facile strategy of achieving tough and self-healing hydrogels can be adapted for other natural polymers, like alginate, broadening the utilisation of natural polymers into various novel functional hydrogel frontiers.

2. Materials and methods

2.1. Materials

Sodium carboxymethyl cellulose (CMC, M.W. 700,000, DS = 0.9, 2500–4500 mPa s) was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China) in a powder form. Citric acid (AR, monohydrate) was obtained from Hengxing Chemical Co. Ltd. (Tianjing, China). Other chemicals were reagent grade. All chemicals were used as received.

2.2. Preparation of hydrogel

The CMC hydrogels were prepared at room temperature through a facile two-step method (Fig. 1a). In the first step, the dry Na-CMC powder was mixed with de-ionised water with a CMC content of 20% and stirred as the CMC paste. The CMC content is defined as the weight of dry Na-CMC powder over the weight of CMC paste. The obtained CMC paste was put into a mould, pressed to remove air bubbles and moulded into the desired shape. At this stage, the CMC polymer chains were uncross-linked. In the second step, the CMC paste was immersed into a citric acid solution (the concentration is in the range of 1 mol/L to saturation) for a predetermined time and then the as-prepared CMC hydrogel was obtained. The CMC hydrogel with the desired shape was formed through physical cross-linking in the second step along with the formation of hydrogen bonds among the polymer chains. The equilibrated CMC hydrogel was obtained by immersing the as-prepared hydrogel into deionized water for 2 days.

2.3. Fourier transformed infrared spectroscopy

Fourier transformed infrared (FTIR) spectroscopy was used to investigate the gelation mechanism of CMC hydrogel. Briefly, the hydrogel was lyophilized for 24 h (Heto power dry LL1500, Thermo, USA) and ground to powder form. Then the dry powder was mixed with KBr (0.5 mg sample/50 mg KBr) and pressed into a disc shape. FTIR spectra of the original Na-CMC powder were also recorded.

2.4. Scanning electron microscopy

The microstructure of the CMC hydrogel was examined using a scanning electron microscope (SEM). For this purpose, the hydrogel samples were frozen at -80 °C and freeze-dried in a lyophilizer (Heto power dry LL1500, Thermo, USA) under vacuum (0.50 mbar) for at least 24 h. The dehydrated samples were cross-sectioned and placed on double-sided tape, sputter coated with gold, and observed by SEM (JSM-7000F, JEOL, Japan).

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