

Preparation and Characterization of Carboxymethyl Cellulose Hydrogel Fibers

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ABSTRACT

Carboxymethyl cellulose (CMC) hydrogel fibers were prepared via a solution spinning method with aluminum sulfate as the crosslinking agent. The preparation process of the CMC hydrogel fibers was optimized via orthogonal experiments. FTIR, POM, SEM and TGA were used to characterize the structure and properties of the hydrogel fibers. The mechanical properties and absorption ability of the hydrogel fibers were also investigated. The results indicated that an even structure was formed in the hydrogel. The mechanical properties of the hydrogel fibers were improved with increasing CMC degree of substitution. The hydrogel fibers had excellent moisture absorption performance, and are well-suited for biomedical applications such as wound dressings.

Keywords: Carboxymethyl cellulose hydrogel, fibers, preparation, characterization, moisture absorption

INTRODUCTION

Hydrophilic polymer networks containing a large amount of water or other biological fluids are known as hydrogels. They can simulate the function of natural gels in living organism including swelling, but they do not dissolve in water [1]. The swelling capability of a hydrogel depends on the skeleton and crosslinking density of its network [2-3]. There is a strong interest in hydrogels because these polymeric materials can trap large amounts of water and solutes, and form a solid-like gel structure [4-5]. In particular, the relatively high water content and soft, rubbery consistency gives hydrogels a strong resemblance to many soft living tissues [6].

CMC is an ether derivative of cellulose in which the H atoms of the hydroxyl groups are replaced by carboxymethyl groups (-CH₂COOH). It is often used as its sodium salt, Na-CMC, and exhibits pH

sensitivity. It is used in various biomedical applications primarily due to its easy availability, high viscosity, good water solubility, nontoxicity, low price, biocompatibility, biodegradability, and good film-forming ability [7-12].

Hydrogels prepared via CMC crosslinking are highly absorbent and have excellent physical properties and dynamic viscoelasticities [13]. Due to its unique properties, the CMC hydrogel is a potential candidate for wound dressings [14]. CMC hydrogel fibers have similar properties as CMC hydrogels. Moreover, they can be further processed into other forms of biomedical materials. Thus, the hydrogel fiber has attracted increasing attention in many fields [15-16].

Aluminum sulfate, with its cationic species in the effective forms of Al³⁺, provides multivalent positive charges and abundant sites for cross-linking with anionic groups. Aluminum sulfate has been widely used as a cross-linking agent in the preparation of biomaterials; it exhibits excellent performance and low toxicity [17]. In the present study, a novel electrostatic complexing method is proposed for the preparation of CMC/HEC hydrogels with aluminum ions as a cross-linker [18].

In this study, we propose to use aluminum ions as a cross-linking agent to prepare CMC hydrogel fibers via a solution spinning method. The optimum preparation process of CMC hydrogel fibers was investigated. The CMC hydrogel fibers were characterized with various instrumental techniques.

EXPERIMENTAL

Materials

Carboxymethyl cellulose (CMC) with the same molecular weight but different degrees of substitution

(0.47, 0.59, 0.77 and 0.94) was prepared with cotton pulp as the raw materials according to Ramli *et al.* [19]. Analytical grade $\text{Al}_2(\text{SO}_4)_3$, glycerol and KBr were purchased from China National Pharmaceutical Group (Beijing, China). All reagents were used as obtained without further purification.

Preparation of CMC Hydrogel Fibers

CMC was dissolved in distilled water under constant stirring to obtain final CMC concentration of 3, 3.5, 4 and 4.5 wt%. The well-mixed CMC solution was then transferred to a centrifuge tube that was then centrifuged in a refrigerated centrifuge at 5000 rad/s, 20°C for 3 min. The resulting clear CMC solution was used as a spinning solution and was extruded into $\text{Al}_2(\text{SO}_4)_3$ solution via a needle tube at 25°C. The as-spun fibers were washed in distilled water at 25°C after 2–8 s and then air-dried to afford white fibers.

Characterization

FTIR Study

1 mg dry sample was ground, mixed well with 100 mg KBr powder, and compressed into a transparent disk. The FTIR spectra of the fibers and raw materials were recorded on a Bruker Tensor 27 spectrometer in the range of 4000–400 cm^{-1} using an average of 32 scans with a resolution of 1 cm^{-1} .

Polarizing Microscope Photographs

Dry CMC hydrogel fibers were immersed into distilled water. After 30 min, the fibers were removed and the surface was dried with a filter paper. Afterwards, the dry and wet CMC hydrogel fibers were put onto glass slides separately. Images were collected with a digital camera and evaluated with a polarizing microscope.

Scanning Electron Microscopy

The micro morphological structure of the CMC hydrogel fibers was studied with Phenom-World BV SEM. Prior to examination, the fiber samples were fractured in liquid nitrogen, the fiber sections were coated with gold, and the sample was then observed and photographed.

Thermogravimetric Analysis

Thermogravimetric analyses were conducted on a Netzsch TG 209 thermal gravimetric analyzer. The sample was heated from 50 to 800°C at 10°C/min under a nitrogen flow of 50 mL/min.

Measurements of Properties

Mechanical Properties

After air-drying, the tensile strength and elongation at break of the CMC hydrogel fibers were measured on a Textechno fiber electron tensile tester at constant temperature and humidity. The gauge length was 100 mm, and the crosshead speed was 100 mm/min. Ten individual fiber samples were tested from each group and the measurements were reported as the mean \pm standard deviation.

Water-absorption Values (WAVs) and Water-retention Values (WRVs)

WAVs and WRVs were calculated using the following Eq. (1) and Eq. (2), respectively.

$$\text{WAV} = (W_1 - W_0)/W_0 \times 100\% \quad (1)$$

$$\text{WRV} = (W_2 - W_0)/W_0 \times 100\% \quad (2)$$

Here, W_0 denotes the original weight of fiber that was dried at 70°C until a constant weight was achieved; W_1 is the weight of the fiber after 30 min immersion in distilled water; W_2 is the weight of the fully swollen fiber after being centrifuged at 2500 rpm for 5 min. All experiments were done at least in triplicate.

Moisture Absorption Kinetics

The dried fibers were immersed into distilled water or 0.9 wt% NaCl aqueous solution or “A Solution” (mimic blood containing 142 mmol/L Na^+ and 2.5 mmol/L Ca^+) at room temperature ($\sim 25^\circ\text{C}$). The samples were removed from aqueous solution at regular time intervals and weighed after the surface was dried with a filter paper.

RESULTS AND DISCUSSION

The Crosslinking Mechanism

CMC is a white, powdery or flocculent polymer material [20]. The free segments of CMC entangle with each other after the CMC powder is dissolved into water with increasing CMC content. The viscosity increases and the flow index decreases. The CMC hydrogel mold samples formed after the CMC solution was dried in glass dishes. A thin layer of the CMC hydrogel surface was dissolved when immersed into a coagulation bath containing $\text{Al}_2(\text{SO}_4)_3$. The crosslinking mechanism of CMC

hydrogel is shown in *Figure 1*. The carboxymethyl groups of CMC were ionized and were negatively charged. Thus, a thin reticular film was formed on the surface of the CMC hydrogel samples via a combination of chemical bonds of carboxymethyl groups of CMC and aluminum ions. The crosslinking films could keep CMC from dissolving in water and lock the free water inside the samples to form hydrogel. Thus, the crosslinking thickness of the hydrogel surface could be controlled via the soaking time of the coagulation bath. At the beginning, crosslinking occurred on the surface layer while the CMC inside the samples could still be dissolved. The hydrogel rapidly absorbed water with a large swelling ratio when the dried hydrogel was immersed into water again.

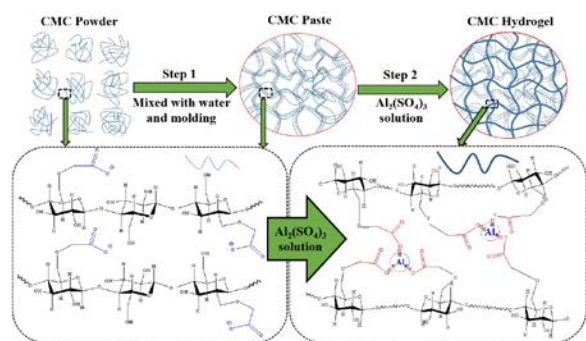


FIGURE 1. CMC hydrogel crosslinking mechanism.

Orthogonal Experiment

The orthogonal experiment could be designed to obtain the optimal preparation process for CMC hydrogel fibers [21]. The main factors are (1) the substitution degree (DS) of CMC (X_1), (2) the CMC concentration (X_2), (3) the $Al_2(SO_4)_3$ concentration (X_3), and (4) the coagulation time (X_4). Details of the four factors in the experiments are presented in *Table I*.

TABLE I. Factors and levels of the orthogonal experiments.

Level	(X_1)	(X_2)	(X_3)	(X_4)
	DS of CMC	CMC concentration (wt%)	$Al_2(SO_4)_3$ concentration (wt%)	coagulation time (s)
1	0.4	3	0.2	2
2	0.6	3.5	0.3	4
3	0.8	4	0.4	6
4	0.9	4.5	0.5	8

The orthogonal experiment was designed to obtain the optimal preparation process for CMC hydrogel fibers using water-absorption values (WAVs) and water-retention values (WRVs) as an index. The results in *Table II* show that the order of impact of the four factors on WAV follows the sequence: DS of CMC > coagulation time > $Al_2(SO_4)_3$ concentration > CMC concentration. The preparation process was optimized as follows: the DS of CMC was 0.94, the CMC concentration was 4 wt%, $Al_2(SO_4)_3$ concentration was 0.4 wt%, and the coagulation time was 4 s. The WRV impact was as follows: DS of CMC > $Al_2(SO_4)_3$ concentration > coagulation time > CMC concentration. The preparation process was optimized as follows: the DS of CMC was 0.94, the CMC concentration was 3 wt%, $Al_2(SO_4)_3$ concentration was 0.4 wt%, and the coagulation time was 4 s. The optimal levels obtained via the WAV index remained consistent with that of the WRV index, except for the CMC concentration that has the least influence on WAV and WRV of the fibers. However, the concentration of the CMC solution has important effects on the fibers' physical properties. A better quality of fiber would be possible by applying higher concentrations of spinning solution. While more CMC can give higher hydrogel tensile strength, it is disadvantageous to the spinnability of the spinning solutions. Therefore, in this study, 0.94 DS of CMC, 4 wt% CMC concentration, 0.4 wt% $Al_2(SO_4)_3$ concentration, and a 4 s coagulation time were selected for the further spinning experiments.

TABLE II. Analysis of the orthogonal experiments.

Test No.	X ₁	X ₂	X ₃	X ₄	WAV (%)	WRV (%)
1	0.47	3	0.2	2	12.51	10.19
2	0.47	3.5	0.3	4	24.15	16.41
3	0.47	4	0.4	6	19.86	13.96
4	0.47	4.5	0.5	8	19.5	12.26
5	0.59	3	0.3	6	21.7	18.04
6	0.59	3.5	0.2	8	22.2	19.6
7	0.59	4	0.5	2	28.24	21.09
8	0.59	4.5	0.4	4	29.05	25.6
9	0.77	3	0.4	8	39.88	31.32
10	0.77	3.5	0.5	6	31.25	26.76
11	0.77	4	0.2	4	35.21	24.06
12	0.77	4.5	0.3	2	33.18	29.66
13	0.94	3	0.5	4	52.44	40.5
14	0.94	3.5	0.4	2	44.08	37.16
15	0.94	4	0.3	8	45.54	38.71
16	0.94	4.5	0.2	6	42.48	32.23
K1	19.005	31.633	28.1	29.483	WAV	
K2	25.297	30.4	31.142	35.212		
K3	34.88	32.212	33.197	28.822		
K4	46.115	31.052	32.858	31.78		
R	27.11	1.812	5.097	6.39		
Optimal	0.94	4	0.4	4		
F1	13.205	25.012	21.52	24.525	WRV	
F2	21.083	24.983	25.705	26.643		
F3	27.95	24.455	27.01	22.748		
F4	37.15	24.938	25.152	25.473		
R	23.945	0.557	5.49	3.895		
Optimal	0.94	3	0.4	4		

FTIR Studies

Figure 2 shows the FTIR spectra of CMC powder and CMC dried hydrogel fibers. The CMC powder and CMC dried hydrogel fibers showed absorption bands at 3450, 1618, 1423 and 1060 cm⁻¹, which are attributed to the ν (-CH₂-), ν_a (-COOH), δ (-CH-), ν (-COOH) and ν (C-O) resonances, respectively, in agreement with the literature. Differences between the infrared spectra of CMC powder and CMC hydrogel fibers include the following: (1) The bands of CMC hydrogel fibers at 601 cm⁻¹ are due to the cross-linking function between Al³⁺ and carboxyl groups of CMC. (2) The absorption peak of carboxyl

groups (-COOH) included asymmetrical stretching for CMC powder at 1600 cm⁻¹, but the absorption peak of the CMC hydrogel fibers shifted to higher wavenumbers (1626 cm⁻¹). The carboxyl groups produced via ionization possessed a multi-electron π bonds system (π₃⁴), in which the two C-O bonds may resonate. However, after CMC crosslinking with Al³⁺, the π₃⁴ system was destroyed, and the double bonds of the carboxyl groups were strengthened. Moreover, the asymmetric vibrations of the carboxyl groups exhibited a violet shift, indicating that the carboxyl groups take part in the coordination. This confirmed the presence of -C-O-Al-.

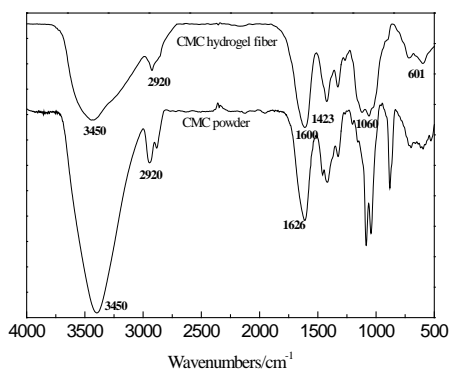
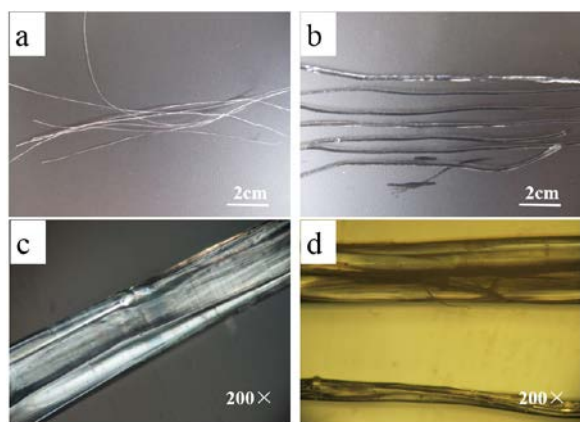


FIGURE 2. FTIR spectrum of CMC powder and CMC hydrogel fibers.

Surface Morphology

The surface morphology of the CMC hydrogel fibers in the dry state and in the gelatinous state were examined with a digital camera (Figure 3a and Figure 3b) and polarization microscope (Figure 3c and Figure 3d). As shown in Figure 3a, the dried fibers are similar to nylon fibers for fishing net, but they do not have curves. The surface morphology of the fibers soaked in distilled water for 30 minutes were swollen, transparent and gel-like (Figure 3b). Versus dry fibers, the gelatinous fibers were soft and had good elasticity. Figure 3 and Figure 4 present a smooth and straight morphology. The volume of the gelatinous fibers was much larger than that of the dry fibers. The cross sections of the CMC hydrogel fibers (Figure 4) showed a smooth and homogeneous morphology without cracking and peeling. This suggests an even distribution of CMC with no layers inside.



(a), (b) Digital photos; (c), (d) polarizer photos.

FIGURE 3. The surface morphology of the CMC hydrogel fibers.

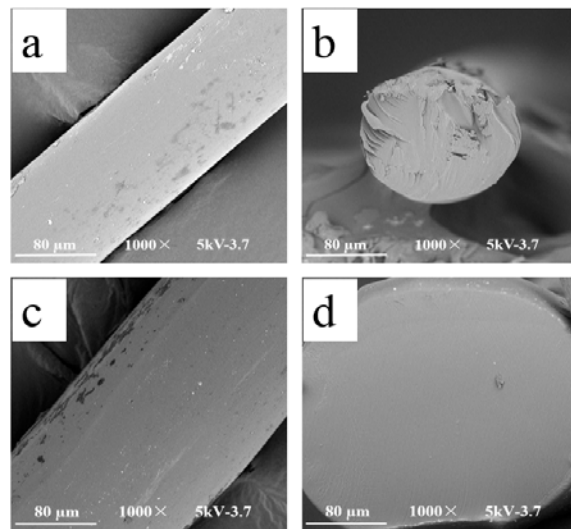


FIGURE 4. SEM photos of CMC hydrogel fibers.

Thermal Stability

The thermal stability of the pulp, CMC powder and CMC hydrogel fibers were investigated using TG analyses. The TG curves are shown in Figure 5. The thermal decomposition temperature of the CMC hydrogel fibers was about 230°C, which was much lower than that of the pulp (310°C) and slightly lower than that of CMC powder (250°C). This can be explained by the fact that alkalization and etherification as well as the intensive agitation during the dissolution of CMC powder destroyed the crystalline regions of the pulps to some extent [23]. This resulted in a relatively lower thermal stability of the CMC hydrogel fibers.

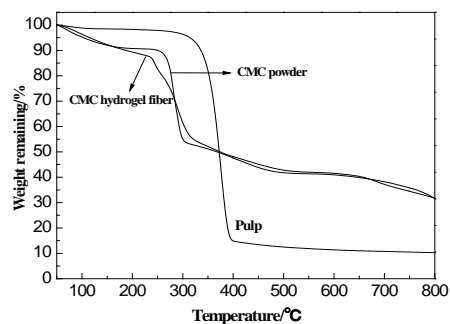


FIGURE 5. TG curves of CMC powder, pulp and CMC hydrogel fibers.

Mechanical Properties

Figure 6 shows the tensile strength and elongation at break of the CMC hydrogel fibers with various CMC degrees of substitution. The data show that the

increase in substitution degree of CMC could greatly improve the mechanical properties of the hydrogel fibers. Note that the tensile strength of the CMC-4 hydrogel fibers was as high as that of cotton fibers, and the elongation at break was much better than that of cotton fibers. The mechanical properties of CMC-4 hydrogel fibers could meet the requirements of medical dressings.

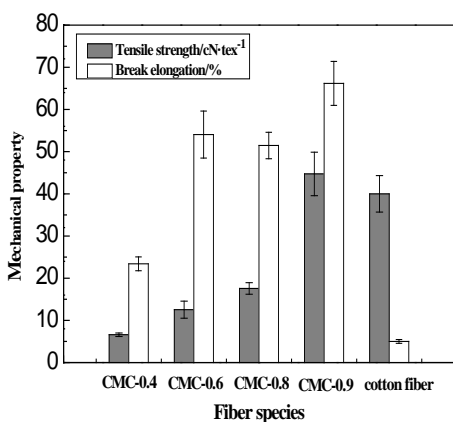


FIGURE 6. Mechanical properties of CMC hydrogel fibers.

Moisture Absorption

The moisture absorption ability plays an important role in the application of hydrogel fibers [22]. Figure 7 shows the moisture absorption rate of the hydrogel fibers at different time. The moisture absorption rate increased very quickly in the first 200 s and subsequently slowed down. This was nearly linear with time up to 210 s; thereafter, it did not change significantly. The hydrogel fibers absorbed up to 712% of distilled water at equilibrium. This is very significant for medical fibers. The “A Solution” absorption effect of the fibers was the worst, but still above 450%. The weight of the fibers remained essentially constant after equilibrium in distilled water, but the weight of the fibers continued to grow after equilibrium in normal saline and “A solution”. This may be because normal saline and “A solution” contain metal ions such as Na⁺ and Ca²⁺.

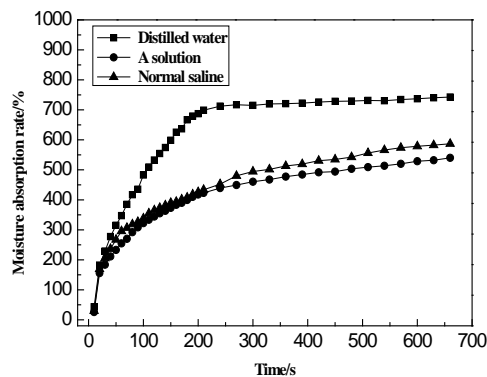


FIGURE 7. Moisture absorption curves of CMC hydrogel fibers.

CONCLUSION

In this study, CMC hydrogel fibers were successfully prepared via a solution spinning method using Al₂(SO₄)₃ aqueous solution as the coagulation bath. The preparation process of CMC hydrogel fibers was optimized as follows through orthogonal test: the DS of CMC was 0.94, the CMC concentration was 4 wt%, Al₂(SO₄)₃ concentration was 0.4 wt%, and the coagulation time was 4 s. The cross sections of CMC hydrogel fibers showed a smooth and homogeneous morphology without cracking or peeling. The tensile strength of CMC-4 hydrogel fibers was as high as that of cotton fibers, and the elongation at break was much better than that of cotton fibers. Furthermore, the moisture absorption performance of the hydrogel fibers was excellent, and the distilled water absorption effect of the hydrogel fibers was up to 712% at equilibrium, making it well-suited for biomedical applications such as wound dressings.

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