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Chitosan-based electroactive hydrogel

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ABSTRACT

A natural amphoteric polyelectrolyte hydrogel film was prepared by solution blending of chitosan and its derivative carboxymethylchitosan, and cross-linked with glutaraldehyde. Under electric stimulus such a hydrogel quickly bends toward one electrode, showing an electrical sensitive behavior. Because of its amphoteric nature, the hydrogel bends either toward anode ($pH \leq 7$) or cathode ($pH > 7$), depending on the pH of the electrolyte solution. Besides pH value, other factors, such as ionic strength, electric field strength, thickness of the hydrogel and the amount of cross-linking agent also influence the electromechanical behavior of the hydrogels. Compared with chitosan/carboxymethylcellulose hydrogel, which we reported previously, chitosan/carboxymethylchitosan hydrogel exhibits better overall mechanical properties and electrical sensitivity, suggesting its great potential for microsensor and actuator applications, especially in the biomedical field.

1. Introduction

Electroactive hydrogel is one kind of intelligent (smart) hydrogel, which can swell, shrink or bend under electric stimulus [1]. As they can directly transform the electrical energy into mechanical work, electroactive hydrogels have many potential applications in the field of smart gel-based devices, such as sensors, artificial muscles, film separation devices, and drug delivery systems [2–10].

Numerous synthetic polymers have been used to make electroactive hydrogels, such as polyvinyl alcohol/poly(sodium maleate-*co*-sodium acrylate) [11], acrylic acid/vinyl sulfonic acid copolymer [12] and sulfonated polystyrene [13]. In addition to synthetic polymers, some natural polyelectrolytes have been blended with synthetic polymers to prepare such hydrogels. For example, alginate/poly(methacrylic acid) [14], chitosan/polyaniline [15], and hyaluronic acid/poly(vinyl alcohol) [16] hydrogels have also been reported in the literature. However, few reports were found on pure natural polymer-based electroactive hydrogels, and comparing them with those made from synthetic and synthetic/natural polymer blend materials. It is well accepted that natural polymers have better biocompatibility and less latent toxic effect than most synthetic polymers [17–19], so pure natural polymer-based hydrogels would be more suitable for application in biomedical fields. In our previous work, we successfully prepared a natural amphoteric hydrogel based on chitosan (CS) and carboxymethylcellulose (CMC) [20]. Such a CS/CMC hydrogel exhibited a good electromechanical response over a wide pH range and could change its bending direction depending on the pH of the buffer solution.

In order to improve the electrical sensitivity and mechanical properties of hydrogels based on natural polymer, here we use carboxymethylchitosan (CMCS) instead of CMC to prepare a different kind of natural amphoteric hydrogel — CS/CMCS hydrogel. CMCS is a water-soluble CS derivative, containing both –COOH and $–NH_2$ groups [21]. Due to its low toxicity, good biocompatibility and other unique properties, CMCS has been used widely in biomedical fields [22–24]. Compared with CS/CMC hydrogels, CS/CMCS hydrogels show a faster bending rate, a larger bending angle, and a higher tensile strength, which suggests great potential for their application as natural polymeric electroactive hydrogels.

2. Experimental section

2.1. Materials

CS (molecular weight = 1100 kDa, deacetylation degree = 75%) was purchased from Jinan Haidebei Marine Biological Product Co. Ltd. (Jinan, China). After further deacetylation, the deacetylation degree of CS was increased to 90% and the molecular weight was reduced to 460 kDa. Monochloroacetic acid, isopropanol, ethyl alcohol, sodium hydroxide, sodium sulfate, potassium chloride, boric acid, phosphoric acid, acetic acid and glutaraldehyde were

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purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China), and were used without further purification.

2.2. Preparation of CMCS

CMCS was prepared by the established procedure reported in the literature [21]. 10 g CS, 13.5 g sodium hydroxide, 80 mL isopropanol and 20 mL deionized water were added into a 500 mL flask. The flask was placed into 50 °C water bath and first let CS swell and alkalize for 1 h. Then the mixture solution of 15 g monochloroacetic acid and 20 mL isopropanol was added dropwise into the reaction mixture and reacted for 4 h at the same temperature. The reaction was stopped by adding 200 mL 70% ethyl alcohol into the reaction mixture. The solid in the flask was filtered and rinsed in 70% ethyl alcohol to desalt and dewater, and vacuum dried at room temperature to yield the product, sodium salt of CMCS (NaCMCS). The substitution degree of carboxymethyl groups on CMCS was determined using the ^{1}H NMR method according to literature [21,25]. The total carboxymethyl substitution degree was 1.18, where the *O*-substitution degree was 1.00 and the *N*-substitution degree was 0.18, indicating most of amino groups on the original CS molecular chains were preserved.

2.3. Preparation of CS/CMCS films

CS was dissolved in 2% (v/v) acetic acid aqueous solution to make a 2% CS solution and NaCMCS was dissolved in deionized water to make a 2% NaCMCS aqueous solution. Then 2 volumes of NaCMCS solution were added dropwise into 3 volumes of CS solution at 60 °C under stirring. In the meantime, glutaraldehyde (if not pointed out, the content of glutaraldehyde was 0.5% molar of the amino groups on CS) was added into the solution in order to crosslink the films. After complete mixing at 60 °C for 2 h, the mixture was poured into a poly(ethylene terephthalate) dish and dried at room temperature. Finally, the dried films were put into 0.5% (w/w) NaOH aqueous solution to remove the remaining acetic acid, and then washed repeatedly with deionized water. We chose this ratio (CS/CMCS = 3/2) because it was the highest CMCS content we could achieve to make the best balance of the polycation and the polyanion part in the amphoteric CS/CMCS film. The CS/CMCS hydrogel became unstable in aqueous solution and its mechanical properties decreased significantly when CMCS content exceeded 40% (w/w).

2.4. Characterization of CS/CMCS films

FTIR spectra were recorded with a Nicolet Nexus-470 spectrometer in reflection mode at 4 cm^{-1} resolution using 64 scans. Wide-angle X-ray diffraction measurements were performed with a Philips X'Pert PRO diffractometer, using Ni-filtered Cu Kα radiation ($\lambda = 1.5406$ Å) with 2θ range between 5° and 40° at 40 kV and 40 mA. The morphology of the CS/CMCS film was observed using a Philip XL30 scanning electron microscope (SEM) at 20 kV. The cross section was prepared by fracturing the film under liquid nitrogen and scanned after coating with a thin layer of gold.

2.5. Swelling of CS/CMCS films

The CS/CMCS films were dried in an oven at 60 °C to constant weight and then immersed in Britton–Robinson buffer solutions with different pH values (from 4 to 12) but constant ionic strength (0.1 M) [26]. After the excess solution on the film surface had been removed with filter paper, the weight of swollen samples was immediately measured. The swelling ratio was determined as follows:

$$\text{swelling ratio} = (W_s - W_d)/W_d \quad (1)$$

where W_s and W_d are the weights of the samples in swollen and dry states, respectively.

2.6. Mechanical properties of CS/CMCS films

CS/CMCS films were first put into buffer solution (pH = 6, ionic strength = 0.1 M) to reach swelling equilibrium. Then, the mechanical properties of CS/CMCS films in the swollen state were measured using an Instron 5565 mechanical testing instrument at room temperature. The initial gauge length was 10 mm and the testing rate was 0.1 mm/s.

2.7. Measurement of bending angle of CS/CMCS hydrogel in an electric field

A schematic diagram of the equipment used for studying the electrical response of hydrogels is shown in Fig. 1. All hydrogel strips (10 mm long and 2 mm wide) were first swollen to equilibrium in an electrolyte solution (Britton–Robinson pH buffer solution) to be used later in the bending experiments; the thickness of the hydrogel in a swollen state was 0.145 mm (pH = 6) if not pointed out. Two parallel carbon electrodes, 50 mm apart, were immersed in the electrolyte solutions and the hydrogel strip under investigation was mounted centrally between them. Upon application of a dc electric field, the degree of bending, θ, was measured by reading the angle of deviation from the vertical position. We define the value of bending angle as being positive when the hydrogel bends toward the anode and negative when it bends toward the cathode. The bending behavior was recorded with a digital camera (Kodak, USA).

3. Results and discussion

3.1. Characteristics of CS/CMCS films

Both CS and CMCS are polysaccharides that have a number of different functional groups, such as amino, hydroxyl and carboxyl groups. Similar to CS and CMC, CS and CMCS can form intermacromolecular complexes by the strong interactions between those functional groups, such as electrostatic interaction and hydrogen bonding [20]. FTIR measurement showed that the $-NH_3^+$ characteristic absorption band in CS and the $-COO^-$ characteristic absorption band in CMCS combined to a new adsorption band in CS/CMCS film (figure not shown), indicating the intermolecular interaction between CS and CMCS. The WAXD pattern of CS/CMCS film showed less crystallinity than the pure CS (Fig. 2) also suggesting the intermolecular interaction between CS and CMCS macromolecular chains that destroys the original crystalline structures of CS. As a result of strong intermolecular interactions between CS and CMCS in CS/CMCS film, it was found that the morphology of CS/CMCS film was quite uniform and there was no obvious macrophase separation (Fig. 3).

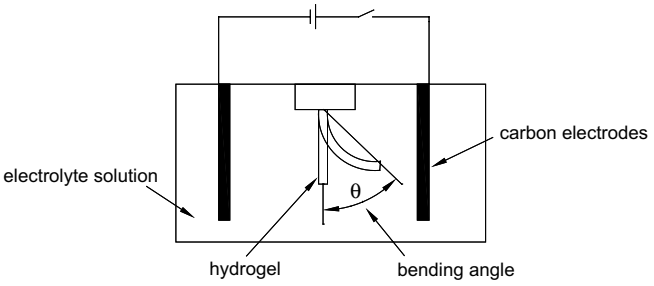

Fig. 1. Schematic diagram for testing the bending behavior of hydrogels.

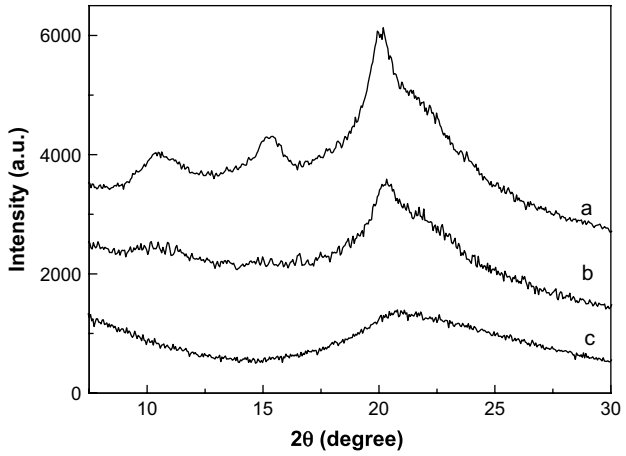

Fig. 2. Wide-angle X-ray diffraction patterns of CS film (a), CS/CMCS film (b) and CMCS film (c).

3.2. The bending behavior of CS/CMCS hydrogels in the electric field

Similar to CS/CMC hydrogel, after applying a dc electric field to CS/CMCS hydrogel strip in buffer solutions, it quickly bends toward the anode or the cathode, depending on the pH of the solution. In acidic or neutral buffer solutions ($pH \leq 7$), the hydrogel bends toward the anode, but it bends toward the cathode in the basic buffer solutions ($pH > 7$). Fig. 4 shows the influence of pH on the swelling ratio and equilibrium bending angle of CS/CMCS hydrogels. With increase in pH of the buffer solution, the swelling ratio first decreases, reaching a minimum at $pH = 7$, and then increases slightly (Fig. 4a). This confirms that CS/CMCS hydrogel is an amphoteric material. For the equilibrium bending angle, the hydrogel shows a maximum value at $pH = 6$ when it bends in the buffer solution with $pH \leq 7$. While in $pH > 7$ buffer solution, the equilibrium bending angle of the hydrogel shows a relative simple tendency to increase slightly with increasing pH value (Fig. 4b).

According to literature, the bending behavior of hydrogel in the electric field can be explained by Flory's theory of osmotic pressure [27,28]. When an electric field is applied, the counterions of the polyions in the hydrogel and the free ions in the solution move toward their counter-electrodes, which results in an ionic gradient along the direction of the electric field. The ionic concentrations inside and outside the gel are thereby different such that the osmotic pressure of the anode side π_1 is not equal to that of the cathode side π_2. Thus the polymer gel will bend due to the osmotic pressure difference $\Delta\pi$ ($\Delta\pi = \pi_1 - \pi_2$). For polyanionic hydrogel, $\Delta\pi > 0$, the hydrogel swells on the anode side and shrinks on the cathode side and it thereby bends toward the cathode side. In the case of polycationic hydrogel, as $\Delta\pi < 0$, it bends toward the anode side. The detailed explanation of the bending mechanism can be referred to our previous publication [20].

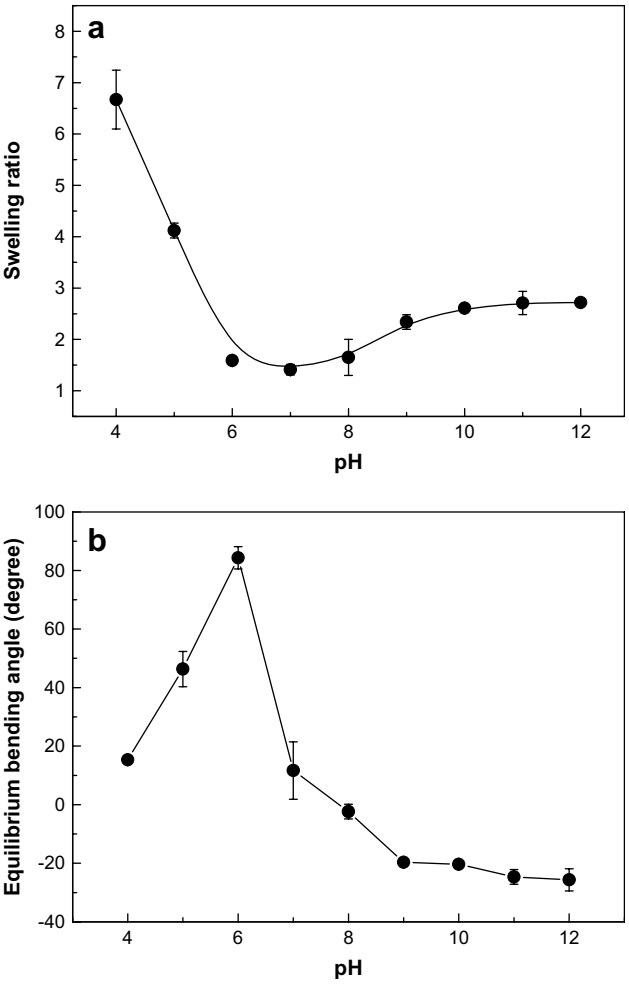

Fig. 4. Effect of pH on the swelling ratio (a) and equilibrium bending angle at 15 V (b) of CS/CMCS hydrogels in different pH buffer solutions (ionic strength = 0.1 M).

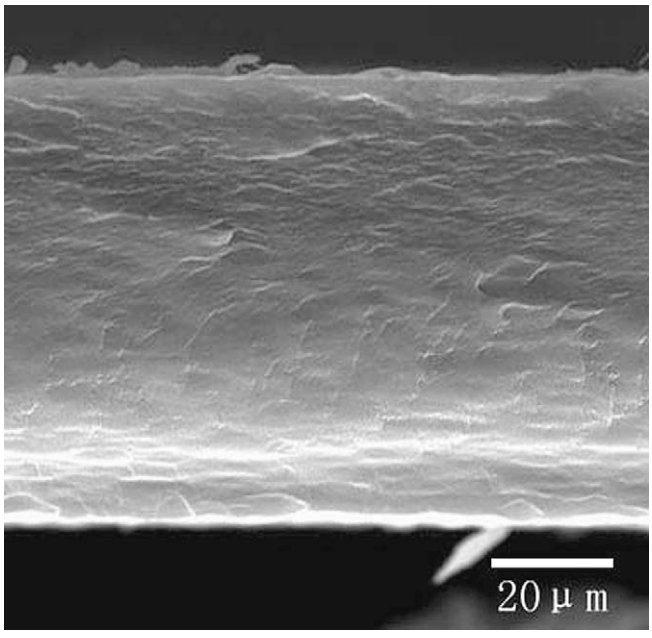

Fig. 3. SEM image of the cross-section of dry CS/CMCS film.

Alternatively, the bending behavior of hydrogel in the electric field can be explained simply and pellucidly as follows. For polyanionic hydrogel, in an ionic gradient along the direction of the electric field, the negatively charged functional groups are balanced by the positively charged ions moving toward the cathode side, but they repel from each other in the anode side. This makes the hydrogel swells on the anode side and shrinks on the cathode side and it thereby bends toward the cathode side. In the case of polycationic hydrogel, the positively charged functional groups are balanced in cathode side and repel in the anode side, thus bends toward the anode side.

In this case, CS/CMCS hydrogel is amphoteric due to the existence of amino and carboxyl groups on CS and CMCS. In $pH \leq 7$ buffer solutions, the amino groups are protonated to become $-NH_3^+$ while the carboxyl groups remain as –COOH, so it behaves as

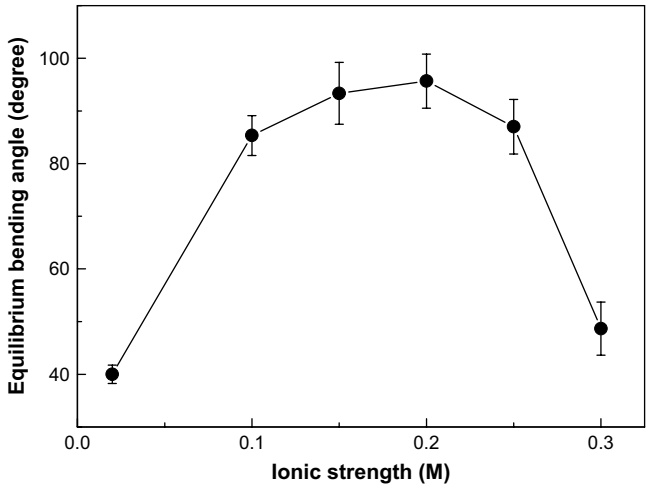

Fig. 5. Effect of ionic strength on the equilibrium bending angle of CS/CMCS hydrogels in pH = 6.0 buffer solution at 15 V.

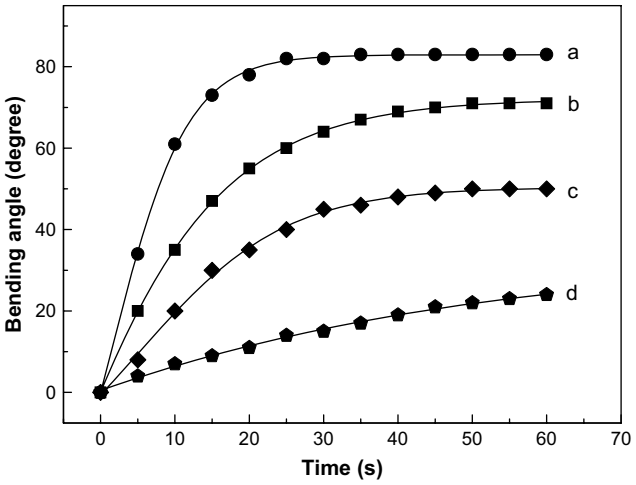

Fig. 6. Bending behavior of CS/CMCS hydrogels with various thickness in swollen state in pH = 6 buffer solution at 15 V. (a) 0.145 mm; (b) 0.155 mm; (c) 0.184 mm; (d) 0.266 mm.

a polycationic hydrogel that bends to the anode. Conversely, the carboxyl groups in CS/CMCS hydrogel are ionized to $-COO^-$ in pH > 7 buffer solutions, but amino groups remain in their uncharged form to give a polyanionic hydrogel, which bends toward the cathode. However, a phenomenon to be noted is that in acidic buffer solutions the equilibrium bending angle does not increase as pH decreases, but reaches a maximum at pH = 6. As we suggested for CS/CMC hydrogel [20], the reason is the decrease of fixed charge density in the hydrogel due to the significant swelling when pH < 6 (Fig. 4a). In addition, the increase of the thickness of the hydrogel in consequence of swelling maybe another reason for the decrease of the equilibrium bending angle. The discussion later will reveal the influence of the thickness on the bending behavior of the hydrogel, but here we don't consider the effect of the thickness, though it obviously changes with the variation of pH.

Another important factor to affect the bending behavior of CS/CMC hydrogel we discussed was ionic strength of the buffer solution [20], which had a similar effect here on CS/CMCS hydrogel. With the increase of ionic strength, the equilibrium bending angle increased at first, reaching a maximum value when the ionic strength was 0.2 M, and then decreased with further increase in ionic strength (Fig. 5). The equilibrium bending angle of CS/CMCS hydrogel can reach a high value (85°–96°) over quite a wide range of ionic strength (0.1–0.25 M).

The electric voltage applied to the hydrogel also had an influence on its bending behavior. However, the effect of the electric voltage was quite simple, i.e., the higher the electric voltage applied, the faster the bending rate and the greater the equilibrium bending angle the hydrogel showed [20]. Therefore, in this article we do not discuss the effect of electric voltage in detail, but discuss other two factors, the thickness of the hydrogel and the content of cross-linking agent.

3.3. Effect of thickness on the bending behavior of CS/CMCS hydrogels

Shiga and Kurauchi have used a three-point mechanical bending model to explain the bending behavior of gels [27]. That is, when hydrogels bend under electric stimulus, the osmotic pressure difference between the anode and the cathode sides, $\Delta\pi$, is balanced by the stress caused by the strain on the polymers. Therefore, in a three-point bending test, $\Delta\pi$ is equal to the maximum tensile stress σ.

$$\Delta\pi = \sigma = 6DEY/L^2 \quad (2)$$

where E is Young's modulus, Y is the amount of the deflection (the distance between the ends of the polymer gel before and after bending), D is the thickness, and L is the length of the polymer gel before bending.

When a constant value of electric field is applied to the hydrogel, $\Delta\pi$ is constant. If the length and Young's modulus of the hydrogel are also kept constant, the bending deflection for a given hydrogel is in inverse proportion to its thickness. Fig. 6 shows the influence of thickness on the bending behavior of CS/CMCS hydrogel. A thin hydrogel (0.145 mm, curve a) had a high bending rate (20 s to reach the bending equilibrium) and a large equilibrium bending angle (more than 80°). However, if the thickness is increased, both the bending rate and the equilibrium bending angle decrease. When the thickness of the hydrogel was about twice that of curve a in Fig. 6 (0.266 mm, curve d), the bending angle was only 24° after 60 s and seemed still not to have reached equilibrium.

3.4. Effect of the content of the cross-linking agent on the mechanical properties and the bending behavior of CS/CMCS hydrogels

Similar to CS/CMC hydrogel, we used glutaraldehyde as a cross-linking agent in the preparation of CS/CMCS hydrogel to prevent CMCS from dissolving in the aqueous solution and to enhance the strength of CS/CMCS hydrogel. As pointed out in Section 2, we have kept as many amino groups as we can (about 82% amino groups were not carboxylmethylate) during the preparation of CMCS, so glutaraldehyde cross-linked via amino groups on both CS and CMCS macromolecular chains and forms an interpenetrating polymer network (IPN). Table 1 shows the mechanical properties of CS/CMCS hydrogels with different glutaraldehyde content. It was found that a glutaraldehyde content in the range 0.5–1.0% gave an

Table 1
Effect of cross-linking agent content on mechanical properties of CS/CMCS hydrogels.

Glutaraldehyde content (%)	Young's modulus (MPa)	Breaking strength (MPa)	Elongation at break (%)
0	4.1 ± 0.6	4.4 ± 0.6	135 ± 17
0.5	4.8 ± 0.4	6.3 ± 1.3	167 ± 21
1.0	7.0 ± 0.8	5.9 ± 0.7	142 ± 20
2.0	6.2 ± 0.6	1.9 ± 0.6	49 ± 10
3.0	2.8 ± 0.6	0.5 ± 0.3	23 ± 10

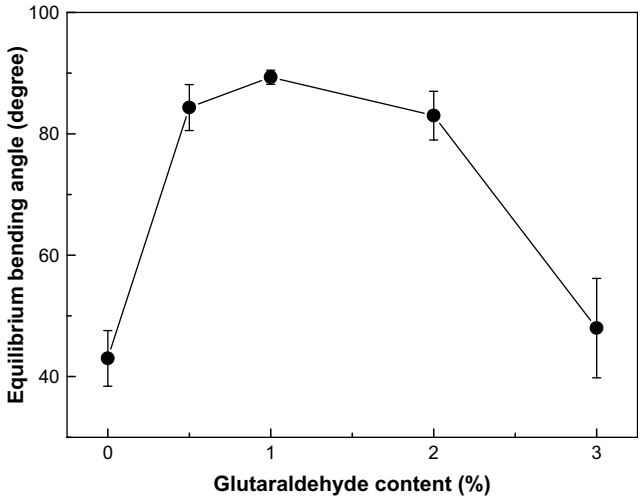

Fig. 7. Effect of cross-linking agent content on the equilibrium bending angle of CS/CMCS hydrogels in pH = 6.0 buffer solution at 15 V.

optimum balance of enhanced Young's modulus, breaking strength and elongation at break.

Besides mechanical properties, cross-linking was also found to increase the electrical sensitivity of CS/CMCS hydrogel in pH ≤ 7 buffer solutions. Fig. 7 shows that CS/CMCS hydrogels bend to larger equilibrium bending angles (80°–90°) when the glutaraldehyde content was in the range 0.5–2.0%, and reached a maximum when glutaraldehyde content was 1.0%. Such a result can be suggested due to the increase of free amino groups in CS/CMCS hydrogel, as found in several other cases [29,30]. Although there are many of amino groups in CS and CMCS, many of them form hydrogen bonds within themselves or between CS and CMCS in the CS/CMCS polymer network, so the free amino groups that are responsible for the electrical sensitivity are actually limited. Therefore, this was the reason why the equilibrium bending angle of CS/CMCS hydrogel without cross-linking was only 40°, though the absolute number of amino groups in the hydrogel was the highest. Cross-linking with glutaraldehyde can break the hydrogen bonds to some extent and increase the number of free amino groups [29], thus enhancing the electrical sensitivity to obtain a large equilibrium bending angle. However, further increase in cross-linking (for example, when glutaraldehyde was 3.0%) consumed more amino groups and made the hydrogel more rigid, which resulted in a decrease of equilibrium bending angle again.

Table 2
Mechanical properties of CS/CMC and CS/CMCS films in swollen state.

Sample	Young's modulus (MPa)	Breaking strength (MPa)	Elongation at break (%)
CS–CMC	5.6 ± 1.5	4.9 ± 1.2	81 ± 17
CS–CMCS	4.8 ± 0.4	6.3 ± 1.3	167 ± 21

3.5. Comparison of CS/CMCS hydrogel with CS/CMC hydrogel

We find that CS/CMCS hydrogel presented here has a number of advantages over CS/CMC hydrogel reported previously [20]. Firstly, the overall mechanical properties of CS/CMCS hydrogel are better than those of CS/CMC hydrogel (Fig. 8). Though Young's modulus of CS/CMCS hydrogel was slightly lower, its breaking strength and elongation at break were both higher than those of CS/CMC hydrogel (Table 2). Therefore, CS/CMCS hydrogel is tougher than CS/CMC hydrogel, which should be very important in future applications.

As mentioned above, there are more amino groups in CS/CMCS hydrogel than in CS/CMC hydrogel, so CS/CMCS hydrogel should have better electrical sensitivity in pH ≤ 7 buffer solutions than CS/CMC hydrogel. In addition, according to Eq. (2), the lower Young's modulus of CS/CMCS hydrogel is also favorable to increase its electrical sensitivity. Fig. 9 clearly shows that under the same conditions, CS/CMCS hydrogel exhibits a faster bending rate and a larger equilibrium bending angle than CS/CMC hydrogel.

4. Conclusions

Natural amphoteric CS/CMCS hydrogels were prepared by a simple solution blending of two natural polymers, CS and its derivative CMCS. Such an amphoteric hydrogel gave a fast mechanical response in an electric field (bending toward an electrode) in different electrolyte solutions and over a wide pH range. The bending behavior of the hydrogels was different in different pH buffer solutions, i.e., when pH ≤ 7, it bent toward the anode, but when pH > 7 it bent toward the cathode. The equilibrium bending angle of CS/CMCS hydrogels was influenced by pH, ionic strength, electric strength, the thickness of the hydrogel film, and content of cross-linking agent in the hydrogel. The equilibrium bending angle of the hydrogel reached a maximum that was over 90° in the buffer

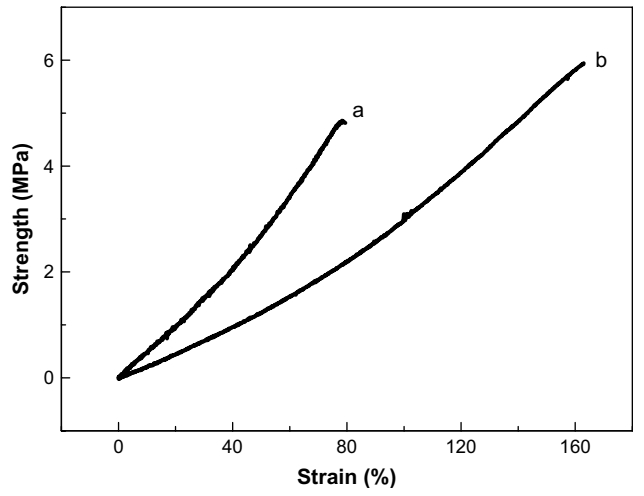

Fig. 8. Typical strain–stress curves of CS/CMC film (a) and CS/CMCS film (b) in swollen state.

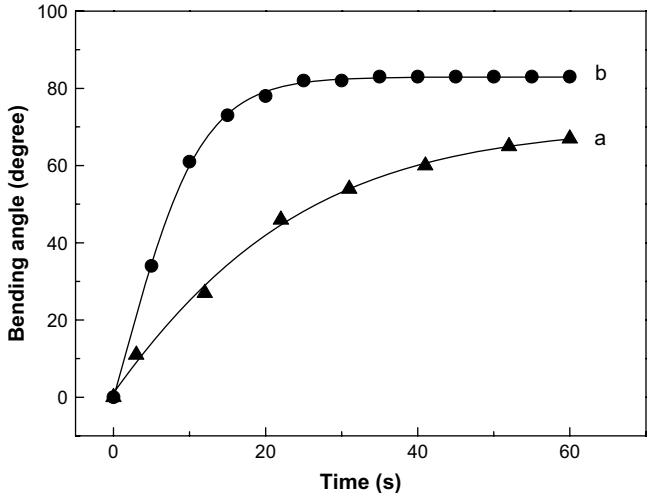

Fig. 9. The electric response of CS/CMC hydrogel (a) and CS/CMCS hydrogel (b) in the same buffer solution at 15 V (pH = 6, ionic strength = 0.1 M).

solution at pH = 6 with 0.2 M ionic strength. In addition, we found that thin hydrogel films and optimised cross-linking was favorable to enhance the electrical sensitivity. The CS/CMCS hydrogel shows better overall mechanical properties and electrical sensitivity than the CS/CMC hydrogel we reported previously, which indicates its great potential for application in artificial muscles, microsensors and actuators, particularly in biomedical fields because all the materials are from chitosan, an excellent natural material.

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