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Electroresponsive Behavior of Sodium Alginate-g-Poly (acrylic acid) Hydrogel Under DC Electric Field

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A novel sodium alginate-graft-poly(acrylic acid) (SA-g-PAA) hydrogel was prepared by radical graft copolymerization with ammonium persulfate (APS) as initiator and N,N'-methylene-bis-(acrylamide) (MBAA) as crosslinker, and its swelling properties and electroresponsive behavior in aqueous NaCl solutions were studied. The results indicated that the water take-up ability of the hydrogel decreased with the increasing ionic strength of aqueous NaCl solution. The hydrogel swollen in a NaCl solution bent toward the cathode under non-contact dc electric fields, and its bending speed and equilibrium strain increased with the increasing of applied voltage. With the increasing of ionic strength of aqueous NaCl solution, the equilibrium strain of the hydrogel increased first and then decreased gradually. The maximum equilibrium strain occurs when the ionic strength of aqueous NaCl solution is 0.03. By changing the direction of the applied potential cyclically, the hydrogel exhibited good reversible bending behavior.

Keywords: Sodium alginate-graft-poly (acrylic acid) copolymer, hydrogels, electroresponsive behavior, bending, swelling

1. Introduction

Polymer hydrogel is a kind of material which has a three-dimension, hydrophilic, polymeric network capable of imbibing large amounts of water. In recent years, polymer hydrogels have attracted much attention as "intelligent materials" because of their special characteristics. They can change their volume and shape reversibly in response to external stimuli, such as changes in pH (1, 2), solvent composition (3, 4), temperature (5), light (6) and electric field (7, 8), etc. Among all kinds of intelligent hydrogels, the electric field responsive hydrogel seems to be particularly interesting in connection with the fact that electric field is the most conventional and convenient stimulus from the point of signal control. Therefore, the researches of electroresponsive hydrogels become very hot in recent years. (9–14).

Alginate is a linear anionic polysaccharide composed of (1,4)-linked α-L-guluronate and (1,4)-linked β-D-mannuronic acid residues and are obtained mainly from brown algas belonging to the Phaeophyceae (15). An aqueous solution of the sodium alginate (SA) readily transforms into a hydrogel on the addition of metallic divalent cations such as Ca^{2+}. Because of its remarkable gelation properties, alginates and their derivatives are widely used in food (16), cosmetic (17), drug delivery (18) and agriculture applications (19). Kim et al. (20) reported the electroresponsive properties of poly (methacrylic acid)/sodium alginate interpenetrating polymer network (IPN) hydrogel, in which the sodium alginate was cross-linked with Ca^{2+}. However, for a polyelectrolyte hydrogel, a key factor of its electroresponsive ability is the number of polyions on the polymer network (21). Therefore, the approach that by adding calcium ions into sodium alginate will significantly reduce the number of carboxyl groups on the sodium alginate polymer chains, and reduce the electroresponsive performances of the hydrogels. Meanwhile, the electroresponsive behavior of Kim's hydrogel was investigated in hydrochloric acid solutions (20), which will inevitably cause inconvenience to its practical applications. Liu et al. (22) studied the electroresponsive behaviors of gelatin/alginate semi-interpenetrating polymer network (semi-IPN) membranes, which were composed of cross-linked gelatin with glutaraldehyde and linear alginate and showed good electroresponsive properties.

PAA is a typical polyelectrolyte polymer, and the electroresponsive behaviors of hydrogel based on PAA/PVA (23, 24) and PAA (25) have been reported.

In this paper, a novel sodium alginate-graft-poly (acrylic acid) (SA-g-PAA) hydrogel was synthesized and its swelling properties and electroresponsive behaviors were studied. The synthesized hydrogel has two parts, one is sodium alginate which is a natural polymer molecule, and another is PAA which is a synthetic material. So it may include

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both of the advantages of natural and synthetic polymers and have potential applications in the high-tech fields, such as artificial muscles, actuators, electric current modulated drug delivery systems, etc.

2. Experimental

2.1 Materials

Sodium alginate (SA) was purchased from Dongsheng Chemicals Manufacturer (Wenzhou, China). Acrylic acid (AA) (Analytical grade) was purchased from Bodi Chemical Co., Ltd. (Tianjin, China). N,N'-methylene-bis-(acrylamide) (MBAA) (Analytical grade) was supplied by Shandong Zibo Linzi Wenchang Petrochemical Co., Ltd. (Zibo, China), and the Ammonium persulfate (APS) (Analytical grade) was purchased form Jingdong Tianzheng Fine Chemical Reagent Plant (Tianjin, China). Sodium hydroxide and Sodium chloride (all analytical grades) were purchased from Tianjin Chemical Factory (Tianjin, China). All the materials were used without further purification.

2.2 Preparation of Graft Copolymer Hydrogel

Sodium alginate-graft-poly (acrylic acid) (SA-g-PAA) hydrogels cross-linked with N,N'-methylene-bis-(acrylamide) (MBAA) were prepared by radical graft copolymerization with ammonium persulfate (APS) as an initiator. As a general procedure, 0.3 g SA and 0.05 g MBAA was dissolved in 8mL deionized water, and 1.0 g AA was neutralized with 2 mL 1.75 mol/L aqueous NaOH solution. Then, the two solutions were mixed with vigorous stirring at 40°C for about 15 min. 0.01 g APS was dissolved in 0.5 mL deionized water and was slowly added into the mixture. After that, the mixture was mixed with vigorous stirring for 1 min, and then sealed and heated to 70°C. After polymerization for 5 h, the hydrogel was synthesized. Then, it was taken out, and immersed in deionized water for 4 days to remove the unreacted chemicals. During that time the water was changed once every 8 h, then the hydrogel was dried in vacuum oven at 40°C until constant weight was obtained and used for study the swelling kinetics and electroresponsive behaviors under dc electrical fields.

2.3 IR Analysis

IR spectra of the SA-g-PAA hydrogel and SA samples were recorded on a TENSOR27 IR spectrometer (BRUKER Corporation, Germany), using a KBr pellet technique.

2.4 Swelling Properties of SA-g-PAA Hydrogel

To measure the swelling ratio, pre-weighed dry samples of the hydrogels were immersed in aqueous NaCl solutions. After the removal of the excess surface water by filter paper, the weights of the hydrogel samples were measured at various time intervals. The swelling ratio (S_w) was determined according to the following equation:

$$S_w = \frac{W_t - W_d}{W_d} \tag{1}$$

Where W_t and W_d were the weights of samples at time t and in the dry state, respectively.

2.5 Bending Behavior of SA-g-PAA Hydrogel under DC Electric Fields

The aqueous NaCl solution was poured into a plastic case equipped with two parallel carbon electrodes (Fig. 1). The distance between them was 30 mm. SA-g-PAA hydrogel was fully swollen in aqueous NaCl solutions at room temperature, and cut into 11 mm long × 3 mm wide × 1 mm thick strips. One end of the sample was fixed and the hydrogel was placed in the center of the case. The electroresponsive behavior of the hydrogel was investigated by measuring the displacement of its free end, that is, the deflection of bending (Y) before and after applied electric field. The sign of the deflection is defined positive when a hydrogel bends to the cathode. The strain of bending (ε) is calculated by the following equation (26):

$$\varepsilon = \frac{6DY}{L^2} \tag{2}$$

Where Y is the deflection of bending, D is the thickness of the hydrogel and L is the original length of the hydrogel before application of electric field. To test the reversible bending behavior of the hydrogel strips, the polarity of the electric field was altered every 60 sec. by changing a two-way switch.

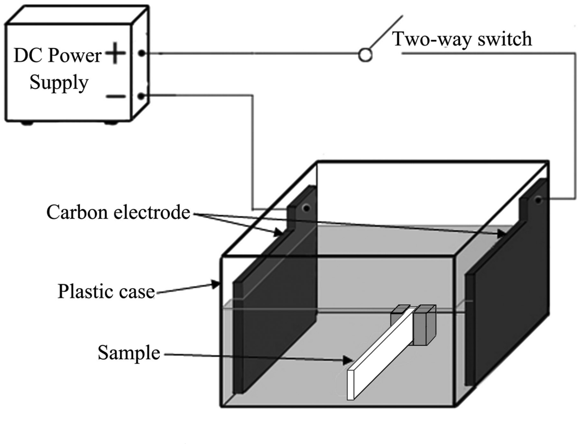


Fig. 1. Self-made equipment of measurement under dc electric field.

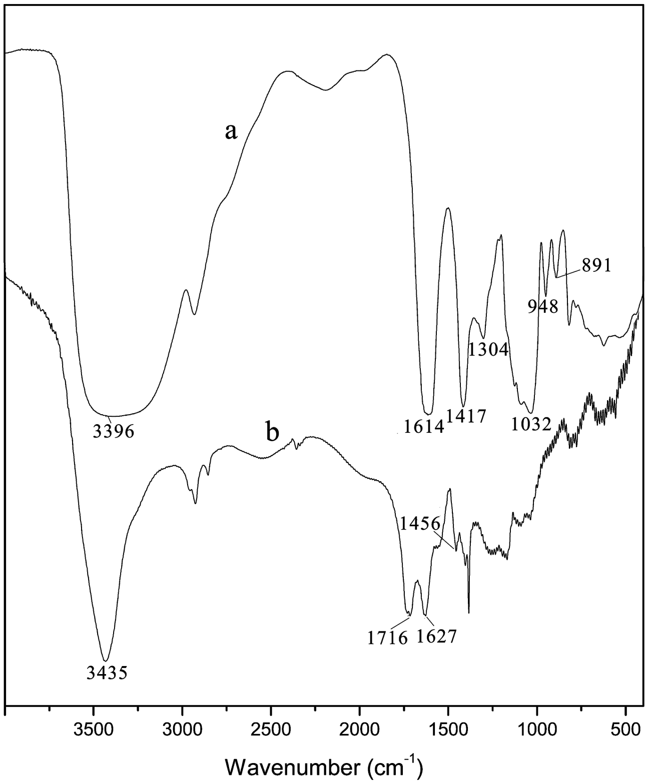


Fig. 2. IR spectra of (a) SA and (b) SA-g-PAA.

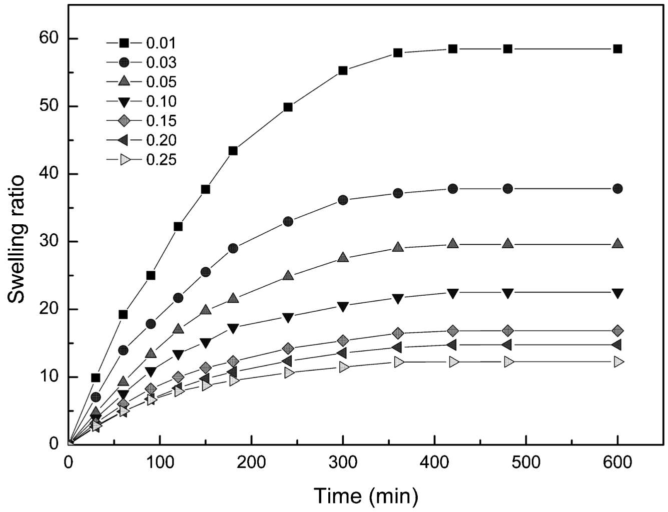
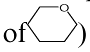
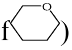
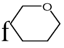
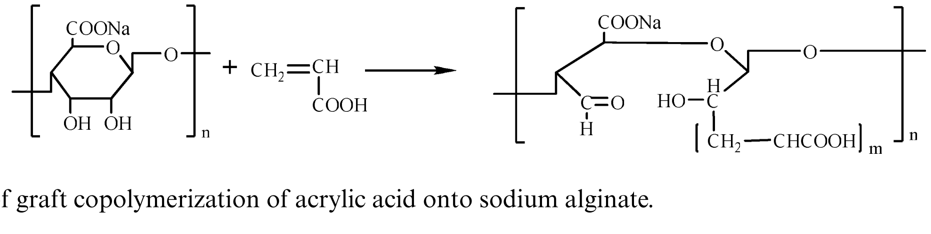


Fig. 3. Swelling kinetic curves of the SA-g-PAA hydrogel in different ionic strength of the aqueous NaCl solution.

3. Results and Discussion

3.1 IR Analysis

The IR spectra of the SA and SA-g-PAA are shown in Figure 2. Comparing with the IR spectrum of SA (Fig. 2(a)), the absorption bands at 1614 cm^{-1} (asymmetric stretching vibration of–COO$^-$) and 1417 (symmetric stretching vibration of –COO$^-$) shift to 1627 and 1456 cm^{-1}, respectively, and the absorption bands at 1716 cm^{-1} (C=O stretching vibration of –COOH) appeared in the IR spectrum of SA-g-PAA (Fig. 1(b)). Meanwhile, the absorption bands at 948 cm^{-1} (C-H bending vibration of) and 891 cm^{-1} (stretching vibration of) disappeared in the IR spectra of the SA-g-PAA, indicate that the ring structure of in sodium alginate has been non-existent. These indicated that AA has been grafted onto SA successfully, in accordance with the research result of Hua et al. (15). The reaction of graft copolymerization (27) is as follows:



Sch. 1. The reaction of graft copolymerization of acrylic acid onto sodium alginate.

3.2 Swelling Properties of SA-g-PAA Hydrogel

Figure 3 shows the curves of swelling ratio of the SA-g-PAA hydrogel against ionic strength in aqueous NaCl solutions. The swelling ratio was shown to decrease with increasing concentration of the NaCl solution. This can be explained that with the increasing concentration of the NaCl solution, the shielding effect caused by the counterions in the electrolytic solution would occur, leading to a reduction in the electrostatic repulsion of the polyions and a decrease of swelling ratio of the hydrogel. This phenomenon shows that the SA-g-PAA hydrogel has a concentration-dependent swelling behavior.

3.3 Bending Behavior of SA-g-PAA Hydrogel under Electric Field

When a SA-g-PAA hydrogel stripe swollen in the aqueous NaCl solution was subjected to a dc electric field, it bent toward the cathode. When the polarity of electric field was changed, the hydrogel stripe first became straight and then bent toward the opposite direction.

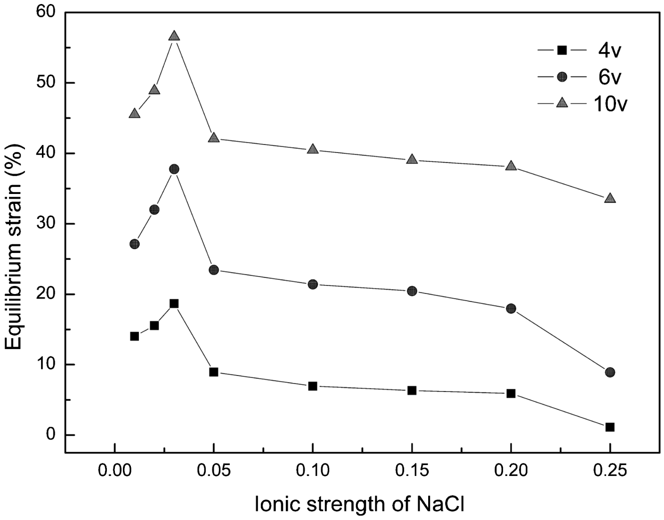
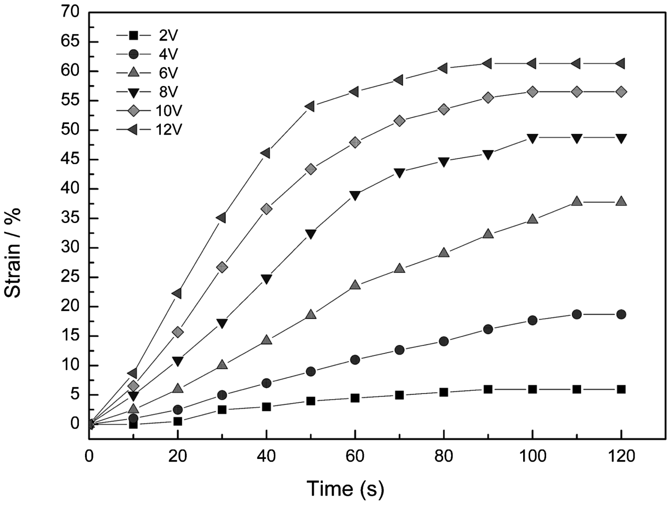


Fig. 4. Effect of ionic strength of the aqueous NaCl solution on the equilibrium strain under different applied voltages of 4 V, 6 V and 10 V.

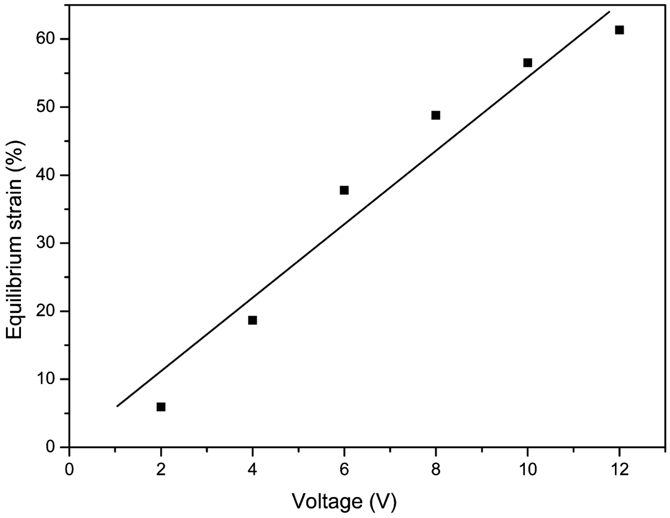
Both of SA and PAA are polyanionic polymers, so the hydrogel product is a polyanionic hydrogel which has –COO$^-$ on its molecule backbone. When an electric field is applied on the negative charged hydrogel in the aqueous solution, the counterion of the polyion moves toward the negative electrode, while the polyion remains immobile. Also, the free ions in the surrounding solution move toward their counter-electrodes and come into the hydrogel. Thus, the osmotic pressure of the hydrogel polymer network near the positive electrode increases and becomes larger than that of the negative electrode side. Consequently, the osmotic pressure difference occurs within the hydrogel, and it is the driving force of bending toward the negative electrode.

The electroresponsive behavior of the hydrogel was also affected by the ionic strength of aqueous NaCl solution. Figure 4 shows the correlation between the equilibrium strain and ionic strength of aqueous NaCl solution under different voltages at room temperature. It shows that with the increasing of ionic strength of aqueous NaCl solution, the equilibrium strain increased first and then decreased gradually. The maximum equilibrium strain occurs when the ionic strength of aqueous NaCl solution is 0.03. As described above, an increase in the electrolyte concentration of a solution induces an increase in the free ions moving from the surrounding solution toward their counter electrodes, and into the hydrogel itself. As a result, the strain of the hydrogel increases. However, if the ionic strength of the NaCl solution is greater than its critical ionic strength of 0.03, the shielding effect of the polyions caused by the counterions in the electrolytic solution would occur, leading to a reduction in the electrostatic repulsion of the polyions and a decrease in the equilibrium strain.

Figure 5 shows the bending kinetic curves and equilibrium strain of SA-g-PAA hydrogel under different applied voltages in ionic strength of aqueous NaCl solution of 0.03. As shown in Figure 5(a), the gradient slope in the plot of the strain of bending vs. time became steeper with the increasing of applied voltages and then leaved off at a steady state. Note that the bending speed and equilibrium strain increase with the applied voltage increasing, which could be explained by the fact that there was an enhancement in the transfer rate of the counterions of the immobile carboxylate groups on the hydrogel network from the hydrogel to the external solution and the free ions moved from the external solution into the hydrogel as the potential gradient in electric field is increased. Further analysis of the relationship between the voltage amplitude and the equilibrium strain showed a linear correlation between them (Fig. 5(b)). These



(a)



(b)

Fig. 5. Bending kinetic curves (a) and Equilibrium strain (b) of SA-g-AA hydrogel under different applied voltages in 0.03 mol/L NaCl solution.

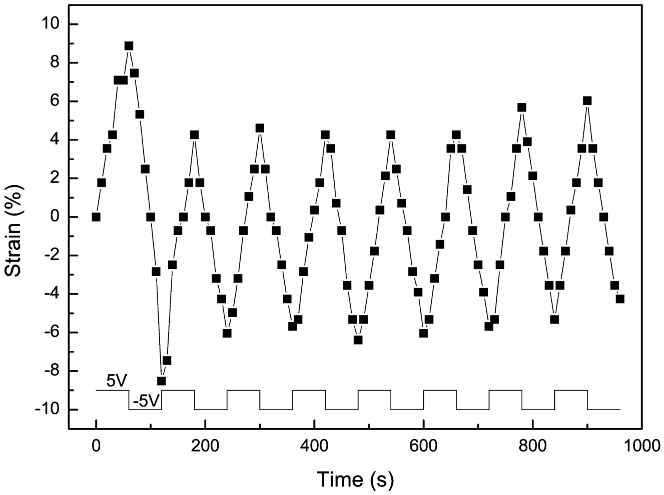


Fig. 6. Response of bending for SA-g-PAA hydrogel under a cyclically varying electric field from 5 V to −5 V every 60 sec. (I = 0.03).

quantitative relationships could be useful in the design of actuator devices.

In addition, the reversible bending behavior of the hydrogel depending on the electric stimulus was examined. When an electric field was applied to it, the strip of hydrogel bent toward the negative electrode. When the electric stimulus was removed, the gel was gradually displaced to its original position. Also, if the polarity of the electric field was altered, the hydrogel bent toward to the opposite direction. When a cycle electric field (the electric field direction changes every time 60 s) was applied, with the reverse of electric field direction, the hydrogel bends quickly to the opposite direction without hysteresis. Figure 6 indicated that the SA-g-AA hydrogel exhibited good reversible bending behaviors under a cyclically varying electric field from 5 V to −5 V every 60 sec.

4. Conclusions

A graft copolymer hydrogel based on sodium alginate and acrylic acid was prepared by radical graft copolymerization. The water take-up ability of the hydrogel increased with the decreasing of ionic strength of aqueous NaCl solution. Under a non-contact dc electric field, the hydrogel stripe shows electroresponsive behavior. The bending behavior can be adjusted via voltage of the applied electric field and the ionic strength of the electrolyte. By changing the direction of the applied potential repeatedly, the hydrogel stripe exhibited good reversible bending behaviors. The hydrogel may have potential applications in the high-tech fields, such as artificial muscles, actuators, electric current modulated drug delivery systems, etc.

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