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Electroresponsive Behavior of Gelatin/Alginate Semi-interpenetrating Polymer Network Membranes Under Direct-Current Electric Field

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Novel gelatin/alginate semi-interpenetrating polymer network (semi-IPN) membranes were prepared by the introduction of linear alginate into a crosslinked gelatin hydrogel network, and their swelling properties and electroresponsive behavior were studied. The results indicated that the water take-up ability of the semi-IPN membranes increased with the increasing alginate content within the network. The semi-IPN membranes swollen in a neutral NaCl solution bent toward the cathode under non-contact dc electric fields, and their bending speed and equilibrium strain increased with the increasing of applied voltage and the alginate content within the hydrogel networks. In addition, the effect of crosslinker concentration of glutaraldehyde on the bending behavior has been studied. The equilibrium strain decreased as the GA concentration increased. By changing the direction of the applied potential cyclically, the semi-IPN hydrogel membranes exhibited good reversible bending behavior. The bending of the semi-IPN hydrogel membranes was initially explained by a bending theory of polyelectrolyte hydrogel based on the change of osmotic pressure due to the ion concentration difference between the inside and the outside of the hydrogel.

Keywords gelatin/alginate, semi-interpenetrate polymer network, hydrogel, electroresponsive behavior, bending

Introduction

Intelligent hydrogels, which show the abilities of changing volume and shape reversibly in response to environmental stimulus, such as pH (1, 2), temperature (3, 4), ionic strength (5), solvent composition (6), and electric field (7–10), magnetic field (11), or light (12), have attracted much attention not only because of their unique properties but also because of their potential for significant technological and biomedical applications (13–16). Among all intelligent hydrogels, electric field responsive hydrogel seems to be particularly interesting in connection with the fact that the electric field is the most conventional and convenient stimulus from the point of signal control. Electric field-induced

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bending deformation or volume change of polyelectrolyte hydrogels can transform chemical free energy directly into mechanical work to give isothermal energy conversion, and can be used as actuators, electromechanical engines, artificial muscles (17–23), chemical valves (14), and controlled drug delivery devices (24–26). However, the literature on research activities in this area focuses on synthetic polymer hydrogels.

Gelatin is a high-molecular-weight polypeptide obtained by a controlled hydrolysis of collagen. It is a good film and particle-forming material, and has been used in medicine as a plasma expander, wound dressing, adhesive and controlled drug delivery, etc. (27–29). Alginate derived from brown sea algae is an anionic linear polysaccharide composed of 1,4-linked β-D-mannuronic acid units and 1,4-linked α-L-guluronic acid units in varing proportions. Alginate is hydrophilic, biocompatible and relatively economical. It is a particularly attracting material to form hydrogels for biomedical applications (30–32). Recently, Kim et al. prepared a IPN hydrogel composed of crosslinked poly(methacrylic acid) and crosslinked alginate with ca^{2+}, and studied its electroresponsive behavior under a dc electric field (33). However, hydrogels based on crosslinked alginate with ca^{2+} may lead to a decrease in the electrical sensitivity of the hydrogels because of the reduction of the carboxyl groups in alginate and the mobility limitation of the alginate chain due to ca^{2+} crosslinking. Considering that electroresponsive hydrogels are usually made of polyelectrolytes (34), we have studied the electromechanochemical behavior of crosslinked gelatin in NaCl solution (35), but there has not been any reports on the electromechanochemical behavior of hydrogel containing linear alginate as yet.

In the present work, novel semi-IPN hydrogel membranes composed of crosslinked gelatin with glutaraldehyde and linear alginate were prepared, and their swelling properties and bending behavior under dc electric field in neutral NaCl solution were studied. In addition, influencing factors on the electric sensitivity of the hydrogel membranes were investigated.

We selected the gelatin/alginate system mainly for two reasons. First, both gelatin and alginate are natural polyelectrolytes, water soluble, and they can form binary solutions over a very wide compositional range. Second, the preparation of gelatin/alginate semi-IPN hydrogel membranes is simple and genial. Crosslinked gelatin as an initial network was synthesized inside the alginate solution by using glutaraldehyde as crosslinker, then the alginate chain was physically entangled with the gelatin polymer network and fixed in the hydrogel.

Experimental

Materials

Gelatin (Chemical grade) with an isoelectric point of about pH 4.9 was purchased from Qingdao Chemicals Manufacturer (Qingdao, China). Alginate was purchased from Dongsheng Chemicals Manufacturer (Wenzhou, China). Sodium chloride and glutaraldehyde (GA) aqueous solution (25%) (all analytical grades) were used without further purification.

Preparation of Gelatin/Alginate Semi-IPN Hydrogel Membranes

Various ratios of gelatin and alginate were dissolved in 20mL distilled water at 45°C, and then 0.7 mL of 1% GA aqueous solution was added. The mixture was poured into a mold of poly(methyl methacrylate) and was maintained at 40°C for hydrogel formation. After

24 h, the hydrogel formed was immersed in distilled water for three days to remove all water-soluble and unreacted moieties, and the water was replaced every 12 h. Finally, the swollen hydrogel was dried at 40°C in a vacuum oven to constant weight, so the hydrogel membrane in dry state was obtained. The feed compositions for the semi-IPN membranes are shown in Table 1.

In order to study the effect of the crosslinker concentration (GA) on the bending behavior, gelatin/alginate semi-IPN hydrogel membranes with different crosslink densities were prepared by adding a different volume of 1% GA solution to the 20 mL mixed solution with the same weight ratio of gelatin to alginate as the specimen of $3^{\#}$ during the process of material preparation, and the procedure of preparation is just the same as mentioned above.

Swelling Properties of Gelatin/Alginate Semi-IPN Hydrogel Membranes

The pre-weighed initially dry samples (approximately 40 mg) were immersed in distilled water at room temperature and the weight of the swollen samples were measured against time after excessive water on the surface of hydrogel membrane was removed using chemical qualitative analysis filter paper (Hangzhuo, China). The swelling ratio (S_w) of each sample at time t was calculated by the following equation:

$$S_w = (W_t - W_d)/W_d$$

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

Electroresponsive Behavior Measurement of Gelatin/Alginate Semi-IPN Hydrogel Membranes Under DC Electric Field

The gelatin/alginate semi-IPN network hydrogel membrane was swollen in a 0.01 mol/L NaCl solution and reached its equilibrium state at room temperature and was cut into $12 \times 1.0 \times 0.4\,\text{mm}^3$ strips. After one end of the sample strip was fixed and placed vertically between two parallel carbon electrodes ($23 \times 25\,\text{mm}^2$) in 0.01 mol/L NaCl solution, its electroresponsive behavior was investigated under an electric field Figure 1. The

Table 1
Feed composition for the preparation of the semi-IPN hydrogel membranes

	Component			
Sample code	Gelatin (g)	Alginate (wt%)[a]	GA (mL)	H_2O (mL)
Ge	0.4	0	0.7	20
$1^{\#}$	0.4	4%	0.7	20
$2^{\#}$	0.4	12%	0.7	20
$3^{\#}$	0.4	20%	0.7	20
$4^{\#}$	0.4	25.5%	0.7	20
$5^{\#}$	0.4	36%	0.7	20

[a] The percentage is based on the total mass of gelatin and alginate.

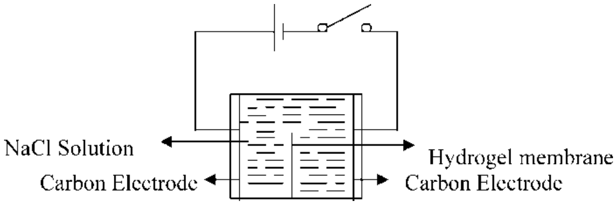

Figure 1. Schematic illustration of measurement under dc electric field.

distance between the two electrodes was 32 mm. The bending deformation was recorded and measured by a video camera (Sony, Japan). The deflection of bending is expressed in terms of the distance between the ends of a hydrogel before and after bending, and the sign of the deflection is defined positive when a hydrogel bends to the cathode. The strain of bending (ε) is calculated by Equation (1) (19):

$$\varepsilon = 6DY/L^2 \tag{1}$$

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 membranes, the polarity of the electric field was altered every 90 sec by changing a two-way switch, and the bending deformation was recorded and measured by the video camera.

Results and Discussion

Swelling Behavior of Gelatin/Alginate Semi-IPN Hydrogel Membranes

The swelling curves of gelatin and gelatin/alginate semi-IPN hydrogel membranes as a function of time in distilled water are given in Figure 2. The results indicated that the swelling ratio of the semi-IPN membranes increased with the increasing of the alginate content within the network, in agreement with the introduction of more hydrophilic alginates.

Electroresponsive Behavior of Gelatin/Alginate Semi-IPN Hydrogel Membranes Under DC Electric Field

When the gelatin/alginate hydrogel in the NaCl electrolyte solution is subjected to an electric field, it bends toward the cathode. Figure 3 shows the relationship between strain of specimen of $3^{\#}$ as a function of time and the voltage of the applied electric field in a 0.01 mol/L NaCl solution at room temperature. As shown in Figure 3, the gradient slope in the plot of the strain of bending vs. time became steeper with increasing applied voltage and then leveled off at a steady state. The equilibrium strain increases with the applied voltage up to 15 V. When it is more than 15 V, the maximum strain is kept constant.

The electro-stimulate response mechanism of hydrogels in dc electric fields has been discussed frequently, but it is still controversial. De Rossi explained the anisotropic deswelling of poly(vinyl alcohol) (PVA)/poly(acrylic acid) (PAAc) membranes at the anode by a local pH decrease associated with water electrolysis (20).

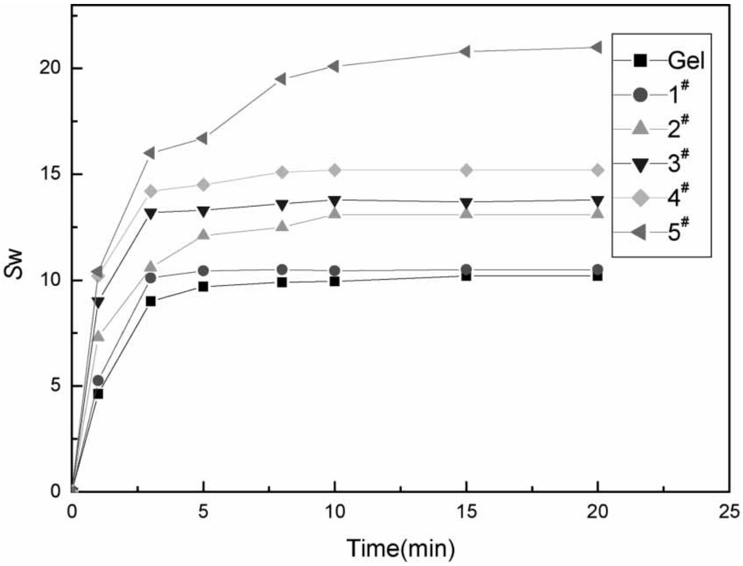

Figure 2. Swelling kinetics of gelatin and gelatin/alginate semi-IPN hydrogel membranes measured as a function of time in distilled water.

Grimshaw applied an electrodiffusion theory to explain the swelling pattern of a poly(methacrylic acid) hydrogel (8). Shiga explained that the bending deformation of a polyelectrolytic hydrogel is induced by a change in the osmotic pressure based on a difference in mobile ion concentrations between the inside and the outside of the hydrogel (36).

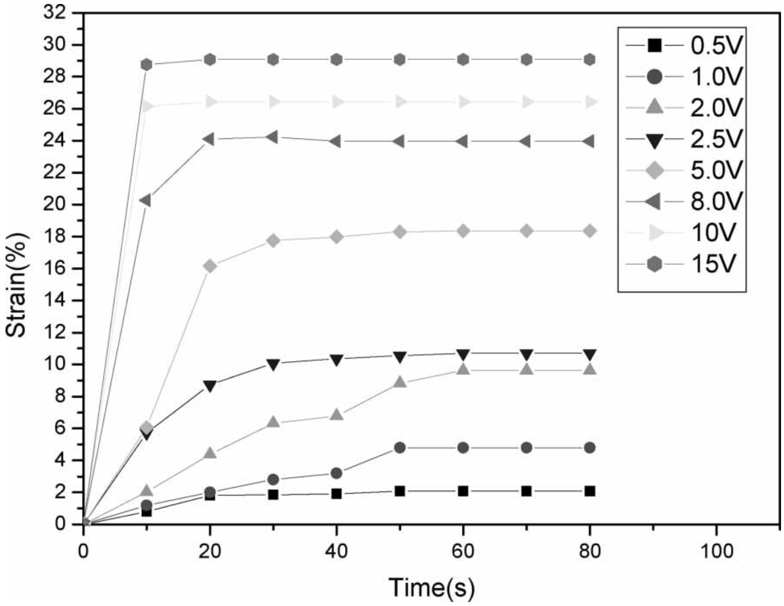

Figure 3. Strain of the specimen of $3^{\#}$ as a function of time under different applied voltages in 0.01 mol/L NaCl solution.

When an electric field is applied on the negatively charged hydrogel in the aqueous solution, the counterion of the polyion, which is an ionic group in the polymer network, 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. On the contrary, the positively charged hydrogel in the aqueous solution will bend toward the positive electrode under an dc electric field.

In the bending of a polyelectrolytic hydrogel in aqueous solution with low electrolyte content, the osmotic pressure difference, $\Delta\pi$ is given approximately by a simple model expressed based on Donnan equilibrium:

$$\Delta\pi = 2RTc_p(V_2/V_1)\,ht(1-ht) \quad (\text{polyanion gel}) \tag{2}$$

$$\Delta\pi = -2RTc_p(V_2/V_1)\,ht(1-ht) \quad (\text{polycation gel}) \tag{3}$$

where R is the gas constant, T is the absolute temperature, c_p is the concentration of the polyions, V_2 and V_1 are the volumes of hydrogel and surrounding solution, h is the transport rate of the counterion of the polyion from hydrogel to solution, or from solution to hydrogel, and t is the time of applying an electric field, $0 < ht < 1$.

Equations (2) and (3) show that the polyion plays an important role in the bending and that nonionic gel doesn't show bending in dc electric fields. In bending, the pressure difference is balanced by the stress caused by the strain on the polymer hydrogel. We assume that the bending of a hydrogel under an electric field is equal to the bending in a three-point mechanical bending test, and that $\Delta\pi$ is equal to the maximum tensile stress, σ, in a three-point bending test. So the following is derived:

$$\Delta\pi = \sigma = 6DEY/L^2 \tag{4}$$

where E is Young's modulus, Y is the amount of the deflection, D is the thickness, and L is the length of a polymer hydrogel before bending.

Using Equations (2)–(4), the deflection of the bending (Y) is calculated. The deflection increases with the amount of $\Delta\pi$, which is influenced by the transport rate of the counterion, the electric field intensity, the polyion concentration, and the time of applying an electric field. For a certain hydrogel, the higher the polyion concentration, the higher the values of $\Delta\pi$ and Y. As the strain of bending is proportional to the value of Y, we know therefore that the increase in polyion concentration increases the strain of bending.

Gelatin is a polymeric ampholyte with carboxyl (–COOH) and amido ($-NH_2$) on its polymeric network. When pH values are higher than the isoelectric point of gelatin ($pH > 4.9$), it becomes polyanionic because of the dissociation of carboxyl, while amido is protonized at pH values lower than the isoelectric point ($pH < 4.9$) and gelatin turns polycationic. Alginate is a weak polyacid, the pK_a values of 1,4 linked β-D-mannuronic acid units and 1,4 linked α-L-guluronic acid units are 4.0 and 3.5, respectively. Under the experimental conditions, the electrolytic solution is neutral NaCl solution about pH 7.0, both the gelatin and alginate exist as polyanonic because of the dissociation of carboxyl in the gelatin/alginate semi-IPN, so the semi-IPN hydrogel membranes bend to the cathode under dc electric field.

Note that the bending speed and equilibrium strain increase with the applied voltage, 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 polymer 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.

Figure 4 exhibits the effect of the alginate content on the equilibrium strain in 0.01 mol/L NaCl solution at 5 V. The equilibrium strain is increased as the alginate content in the semi-IPN membranes increased. This is due to the increase in concentration of carboxylate groups in the hydrogel network.

Figure 5 shows the effect of crosslinker concentration (GA) on the equilibrium strain of bending in 0.01 mol/L NaCl solution at 5 V. The equilibrium strain decreased as the GA concentration increased. Generally, the higher the crosslinker concentration, the higher the modulus of the hydrogel membrane, as the mobility of the chains were somewhat restricted because of the crosslinkage. With higher modulus, the hydrogel membrane deformation became more difficult. This was the reason the equilibrium strain decreased as the GA concentration increased.

In addition, the reversible bending behavior of the semi-IPN hydrogel membranes depending on the electric stimulus was examined in 0.01 mol/L NaCl solution. After passage of an electric current crossed it, the strip of hydrogel started to bend toward the cathode. When the electric stimulus was removed, the hydrogel was displaced to its original position. Also, if the polarity of the electric field was altered, the deformed hydrogel can be recovered to its original shape and then bent toward the opposite direction. As shown in Figure 6, both the gelatin hydrogel and specimen $3^{\#}$ exhibited good reversible bending behaviors under a cyclically varying electric field from 5 V to −5 V every 90 sec.

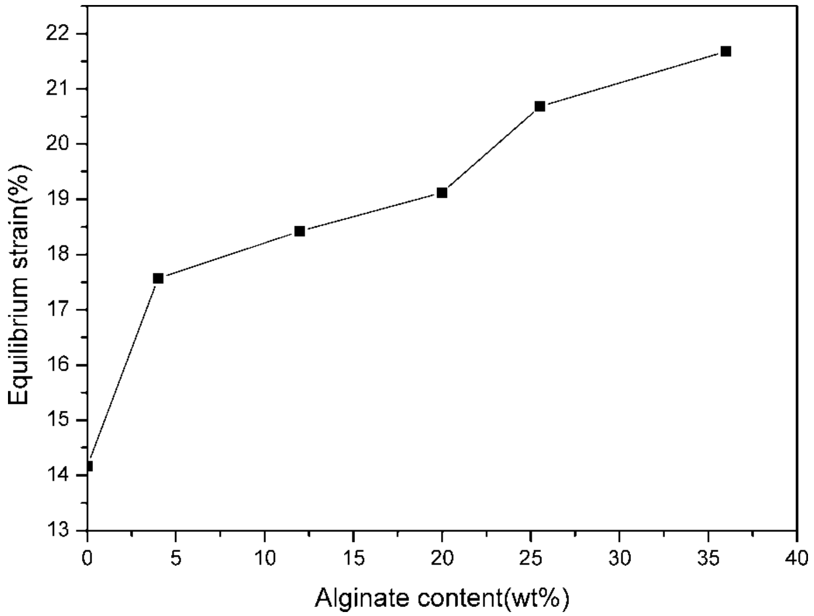

Figure 4. Effect of alginate content in gelatin/alginate semi-IPN membranes on the equilibrium strain of bending in 0.01 mol/L NaCl solution under 5 V constant voltage.

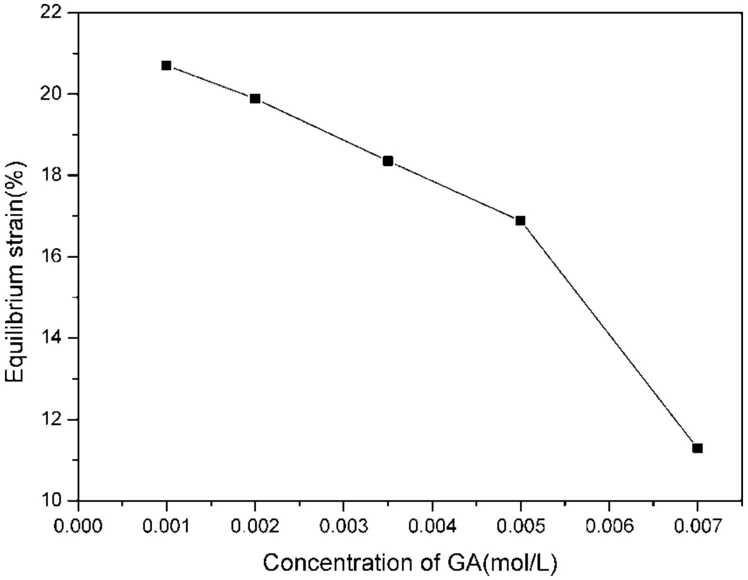

Figure 5. Effect of crosslinker concentration (GA) on the equilibrium strain of bending in 0.01 mol/L NaCl solution under 5 V constant voltage.

Conclusions

Novel semi-IPN hydrogel membranes composed of crosslinked gelatin with glutaraldehyde and linear alginate were prepared. The water take-up ability of the semi-IPN membrane increased with the increasing of alginate content within the network. Under a non-contact dc electric field, the semi-IPN hydrogel membranes show

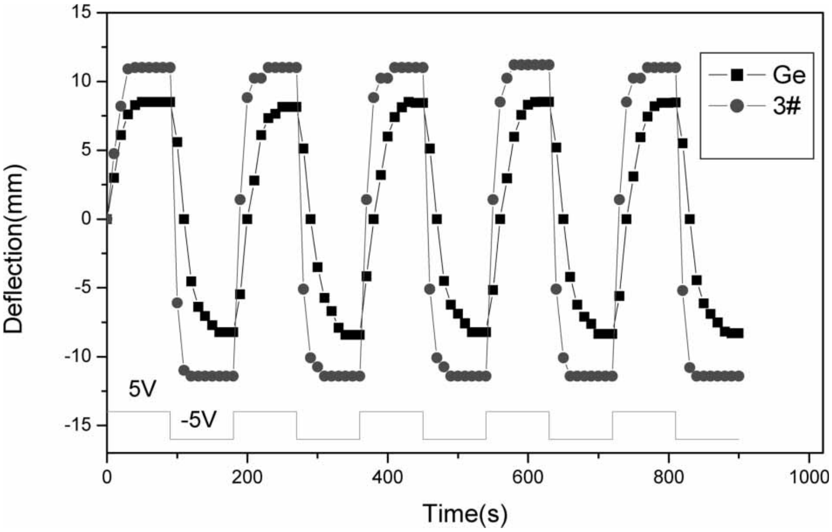

Figure 6. Response of bending for the specimens of Ge and $3^{\#}$ under a cyclically varying electric field from 5 V to −5 V every 90 sec.

electromechanochemical phenomena. The bending behavior can be modulated via voltage of the applied electric field and the concentration of alginate within the hydrogel network. By changing the direction of the applied potential repeatedly, the semi-IPN hydrogel membranes exhibited good reversible bending behaviors. Both gelatin and alginate are biocompatible and biodegradable, and the condition of the gelatin/alginate semi-IPN hydrogel membrane preparation is simple and genial, the present semi-IPN hydrogel membrane as a electric field-controlled drug delivery device or chemomechanical system may be useful for various potential applications.

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