Preparation and Electroresponsive Property of Poly(vinyl alcohol)/Sodium Alginate Composite Hydrogel*

R. X. Li,[1] X. Z. Zhang,[1] J. S. Zhao,[2] J. M. Wu,[1] Y. Guo,[1] J. Guan[1]

[1]*Institute of Medical Equipment, TianJin, China*
[2]*School of Materials Science and Engineering, Tianjin Polytechnic University, TianJin, China*

Received 19 January 2006; accepted 24 March 2006
DOI 10.1002/app.24521
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(vinyl alcohol) (PVA)/sodium alginate composite hydrogel was prepared by solidifing the blending solution of PVA and sodium alginate, then freezing and thawing repeatedly. In the direct current electric field, the composite hydrogel in aqueous NaCl solution swelled, contracted, and bent. The gel's bending speed and maximum bending degree increased with increase in the electric field intensity and the concentration of NaCl solution. The maximum bending degree increased with increase in the sodium alginate content in the composition hydrogel. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3493–3496, 2006

Key words: poly(vinyl alcohol); sodium alginate; composite hydrogel; electroresponsive; bending

INTRODUCTION

Polyelectrolyte gel is a hydrogel with ionizable groups bonded chemically in its polymer network. Hydrogels have been used primarily in the pharmaceutical field as carries for delivery of various drugs, peptides, and proteins. Stimuli-sensitive materials respond to changes in environment, whether it is change in temperature, pH, mechanical pressure, light, or electronic stimulation. In the application, the best stimulus is an electric field because it can be controlled easily. The polyelectrolyte gel exhibits electroresponsive property, i.e., the gel can change their volume or shape under the influence of electric field. The electroresponsive hydrogels can convert electricity energy to mechanical energy, so they may become of particular importance to some unique applications in the engineering and medical professions. Tanaka[1,2] firstly prepared polyacrylamide gel and found it could deform under the influence of electric fields. After this, many scholars like Yannas and Grodzinsky,[3] Osada et al.,[4] Suzuli,[5] Chirelli et al.[6] studied the deformation and mechanism of other polyelectrolyte gels.

Poly(vinyl alcohol) (PVA) gel can be prepared by repeatedly freezing and thawing a PVA solution. The PVA gel has high tensile strength and high elasticity. In this paper, the preparation and electroresponsive property of PVA/sodium alginate composite hydrogel were described.

*Supported by NSFC (10172093)
Correspondence to: R. X. Li (limxinxin@yahoo.com.cn).

EXPERIMENTAL

Materials

PVA was supplied by Tianjin University chemical laboratory. PVA has a degree of polymerization of 1750. Sodium alginate was supplied by Shanghai Chemical Regent Co., Shanghai, China.

Preparation of gel

Gels with different blend proportions of PVA and sodium alginate were prepared. PVA and sodium alginate were dissolved in distilled water and then put into a mold. Then the molds were immersed into a solidification bath to obtain the gel. The gel was then frozen and thawed repeatedly for four times. The dimensions of the specimen were 30 mm × 2 mm ×2 mm.

Measurement of deformation

Aqueous NaCl solution was poured into a case with two parallel platinum electrodes. The distance between the two electrodes was 45 mm. The specimen was immersed in aqueous NaCl solution for equilibration, and then was placed in the middle of the two electrodes. Voltage was applied between the two electrodes. The deformation of the gel was calculated using the following equation:

$$\varepsilon = [(L_t - L_0)/L_0] \times 100\% \quad (1)$$

where L_0 and L_t are, respectively, the distance of gel ends before and after application of electric field, and ε is the deformation of gel (Fig. 1).

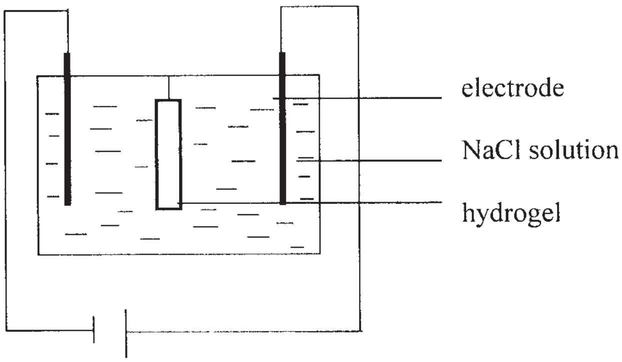

Figure 1 Schematic figure of specimen under an applied electric field.

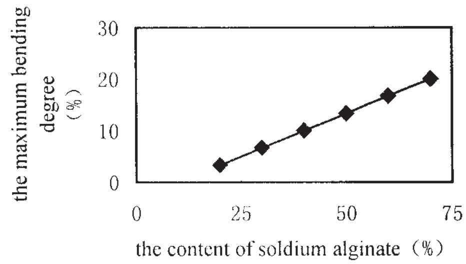

Figure 2 Effect of the content of sodium alginate on the maximum bending degree.

RESULTS AND DISCUSSION

Effect of blend proportion on the electroresponsive property of composite gel

Blend proportions of PVA and sodium alginate used in the preparation of the gels are listed in Table I.

The deformation of each specimen was tested in 0.1 mol/L NaCl solution under 10 V. The results are shown in Figure 2.

PVA gel is insensitive to DC electric fields because it has no ionic groups, so sodium alginate is the main body that is responsive to electric field. Figure 2 shows the effect of the content of sodium alginate on the maximum bending degree. The maximum bending degree of composite gel increases linearly with sodium alginate content. The amount of the moving ions and polyions increases with increase in the sodium alginate content in the composite gel, so the expulsive force between the polyions increases in same NaCl solution and under same voltage, and the osmotic pressure increases between the ends of gel; as a result, the maximum bending degree increases.

Effect of electric field intensity on the electroresponsive property of gel

The deformations of sample 3 in 0.1 mol/L NaCl solution under different electric voltages were tested, and the results are exhibited in Figures 3 and 4.

TABLE I
The Blend Proportion of PVA and Sodium Alginate

Sample	PVA:sodium alginate (mass)
1	8:2
2	7:3
3	6:4
4	5:5
5	4:6
6	3:7

The deformation of the specimen under different electric voltages is shown in Figure 3. The slope of curve, which is deformation velocity of gel, increases with increase in the electric voltage. According to Flory's theory of the osmotic pressure, the osmotic pressure is related to concentration of ions. When a DC electric field is applied between electrodes, ions move toward their opposite electrode. In the present experiments, H^+ and Na^+ in the aqueous NaCl solution move toward cathode and OH^- and Cl^- move toward anode. In the gel, polyions are immobile, and Na^+ moves toward the cathode. As a result of this, a concentration gradient is formed. Because of the difference of ion concentration in the two sides of the gel, the gel bends towards the cathode. Electric field intensity increases with increase in the voltage between the two poles. Hence the velocity of ions increased. The osmotic pressure difference relates to velocity of the ions, and so the gel deformation velocity increased. Figure 3 shows that there is a maximum at different voltages, and it is similar to the electroresponsive property of PVA/PAA hydrogel fiber[7]. There are two mechanisms in the course of gel bending. In the former part of the curve, the main cause of gel deformation is the transfer of ions. In the latter part of the curve, the main cause of gel deformation is the pH gradient. In the middle part of the curve, the two mechanisms are in equilibrium. Figure 3 shows that the time required for maximum bending degree decreases with increase in the voltage, and the probable reason is the quickening of the two mechanisms.

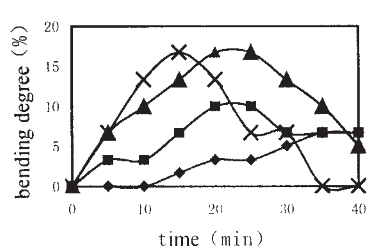

Figure 3 Effect of time on bending degree of sample 3: (♦) 5 V, (■) 10 V, (▲) 15 V, (×) 20 V.

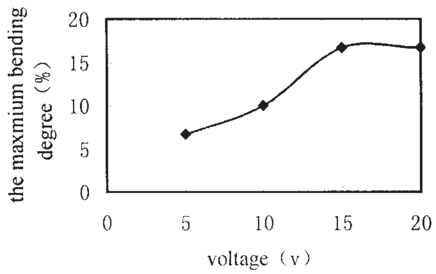

Figure 4 Effect of voltage on the maximum bending degree of sample 3.

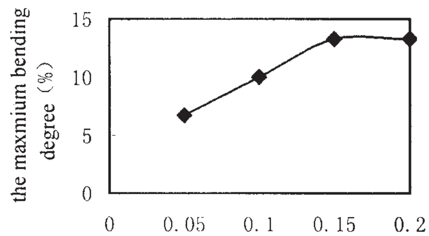

Figure 6 Effect of the NaCl concentration on the maximum bending degree.

Figure 4 shows that the effect of electric voltage on the maximum deformation of sample 3. The maximum deformation exhibits S-type curve with increase in the voltage.

Effect of electrolyte solution on the electroresponsive property of gel

Figures 5 and 6 show the results of the deformation of sample 3 in different concentrations of NaCl solution, at 10 V DC.

Figures 5 and 6 show that the effect of NaCl solution concentration on the gel deformation is similar to electric field intensity. The gel's deformation velocity increased with increase in the concentration of NaCl. This behavior is similar to the electroresponsive property of PVA/poly(acrylic acid) hydrogel.[8] The ion move velocity increased with increase in the electrolyte solution concentration; as a result, the osmotic pressure at the sides of the gel changes quickly. Hence the deformation velocity increased.

Deformation mechanism

There are three competing forces acting on the gel inner network: the rubber elasticity, the polymer–polymer affinity, and the ion pressure[9]. These factors, collectively called the osmotic pressure, determine the equilibrium state of the gel. When an electric field is applied on the gel in the aqueous solution, the counterion of 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 counterelectrode and come into the gel. Thus, the osmotic pressure of the gel polymer network near the anode increases and becomes larger than that of the gel polymer network near cathode. Consequently, the osmotic pressure difference occurs within the gel, and it is the driving force of bending toward the cathode.

Another factor that influences the bending phenomenon of a gel may be the local pH gradient attributed to water electrolysis.[7] Several researchers have reported that ions produced by electrochemical reactions and the movement of the ions toward the counterelectrodes induced the pH gradient inside the gel matrix under the flow of electric current. When an electric field was applied to the gel immersed in a NaCl solution, electrochemical reactions (anode electrode: $2Cl^- - 2e \rightarrow Cl_2$; cathode electrode: $2H_2O + 2e \rightarrow 2OH^- + H_2$) occurred. Then, the movement of the produced ions toward their counterelectrode by the electroattractive force caused the local pH gradient inside the gel and it could influence the bending of the gel.

The osmotic pressure is given approximately by a simple model based on Donnan equilibrium as follows. $\Delta\pi$ is expressed as follows:

$$\Delta\pi = 2RTC_{\mathrm{P\,B}}(V_B/V_C)ht(1-ht) \qquad (2)$$

where R is the gas constant, T is the absolute temperature, $C_{P,B}$ is the concentration of polyion in the gel, V_B and V_C are the volumes of a gel and of a surrounding solution, h is the transport rate of the counterion of the polyion from gel to solution or from solution to gel, and t is the exposed time to an electric field. Equation (2) shows that polyion acts an important role in the deformation of the gel, so the gel free of polyion is not influenced by the electric field and is not deformed under the elelctric field.

We assume that the bending of a gel under an electric flied 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:

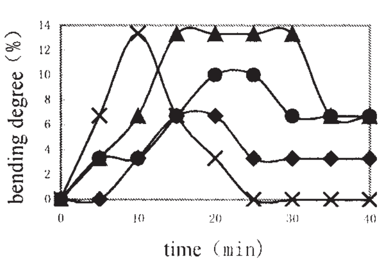

Figure 5 Effect of time on bending degree of sample 3: (◆) 0.05 mol/L, (●) 0.10 mol/L, (▲) 0.15mol/L, (×) 0.20mol/L.

$$\Delta\pi = \sigma - 6DEY/L^2 \quad (3)$$

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

Y can be calculated from equation 2 and 3. Y increased with $\Delta\pi$, and $\Delta\pi$ is determined by the ions move velocity, electric field intensity, ion concentration, and the duration for which electric field is applied. When the concentration is changed and other factors are constant, the ions move velocity increased with increase in the concentration of NaCl. Thus, the deformation velocity and degree increased with increase in the concentration of NaCl.

CONCLUSIONS

PVA/Sodium alginate composite hydrogels were prepared and their deformation in aqueous solutions under direct current fields were studied. The following results were obtained:

1. PVA/sodium alginate composite hydrogel obtained through solidification of the blend solution, then freezing and thawing repeatedly.
2. PVA/sodium alginate composite hydrogel bends toward the cathode. The deformation induced by the electric field is swelling, shrinking, and bending.
3. The bending rate depends on the field intensity, gel content, and the concentration of mobile ions in the solution. The gel's bending speed and maximum bending degree increased with increase in the electric field intensity and the concentration of NaCl. The maximum bending degree increased with the sodium alginate content in the composite hydrogel.

References

1. Tanaka, T.; Nishio, I.; Sun, S.-T.; et al. Science 1982, 218, 467.
2. Doi, M.; Matsumoto, M.; Hirose, Y. Macromolecule 1992, 25, 5504.
3. Yannas, I. V.; Grodzinsky, A. J. J Mechanochem Cell Motil 1973, 2, 113.
4. Osada, Y.; Okuzaki, H.; Gong, J. P. Electro-driven Gel Actuators TRIP 1994, 2, 61.
5. Suzuli, M. Polymer Gel: Fundamentals and Biomedical Applications; Plenum: New York, 1991; p 221.
6. Chiarelli, P.; Umezawa, K.; DeRossi, D. A Polymer Composite Showing Electrocontractle Response, Polymer Gels: Fundamentals and Biomedical Applications. Plenum: New York, 1991; p 195.
7. Fei, J.-Q.; Zhang Z.-P.; Zhong L.-l. J Functional Polym 2001, 14, 185.
8. Bai, Y.-P.; Cheng, Y.; Yang, R.-J. Polym Mater Sci Eng 2002, 18, 74.
9. Shahinpoor, M. Smart Mater Struct Int J 1994, 3, 367.
10. Shiga, T.; Kurauchi, T. J Appl Polym Sci 1990, 39, 2305.