Bending of Poly(Vinyl Alcohol)-Poly(Sodium Acrylate) Composite Hydrogel in Electric Fields

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SYNOPSIS

Bending of poly(vinyl alcohol) hydrogel mixed with poly(sodium acrylate) chains, PVA–PAA gel, under the influence of dc electric fields was studied. The PVA–PAA gel was prepared by repeatedly freezing and thawing a mixture of PVA and polyacrylic acid aqueous solutions. The PVA–PAA gel was a hydrogel with the PAA chains, which were entangled with the PVA polymer network and were fixed in the gel. The PVA–PAA gel bent toward the negative electrode in electrolyte solutions under dc electric fields as did the polyelectrolyte gel with negatively charged polyions. The PVA gel, free of PAA, was insensitive to dc electric fields. The deflection of the bending and the bending speed were influenced by the field intensity, the concentration of the polyion in the gel, and the thickness of the gel. The bending of the PVA–PAA gel was qualitatively explained by a bending theory of polyelectrolyte gel, based upon the change of the osmotic pressure due to the ion concentration difference between the inside and the outside of the gel.

INTRODUCTION

Polyelectrolyte gel is a hydrogel with ionizable groups bonded chemically in its polymer network. The gel exhibits shrinking, swelling, or bending in an electrolyte solution under the influence of dc electric fields.[1,2] The electric field-associated deformation has not been observed in nonionic hydrogels. The deformation of the polyelectrolyte gel shows the feasibility of purely polymeric machinery systems, which convert electrical energy into mechanical energy. In designing the systems, it is important to improve the mechanical properties of the polyelectrolyte gel because the hydrogel has low impact strength and it is broken to pieces under a small stress.

Recently poly(vinyl alcohol), PVA, hydrogel was prepared by repeatedly freezing and thawing a PVA solution.[3] The PVA polymer chains are physically crosslinked in the freeze–thaw cycling, and the solution is changed into a gel. The PVA hydrogel has high tensile strength and high elasticity. However,

the PVA hydrogel is insensitive to dc electric fields because it has no ionizable groups. In the previous article,[4] we reported the preparation of PVA hydrogel mixed with poly(sodium acrylate) chains, PVA–PAA gel. The composite hydrogel has PAA chains, having ionizable groups physically entangled with the PVA polymer network, and it seems to be a polyelectrolyte gel. Therefore, we expect the PVA–PAA gel to show bending in an electrolyte solution under dc electric fields. The aim of this article is to study the bending of the PVA–PAA gel experimentally induced by dc electric fields.

BENDING THEORY OF POLYELECTROLYTE GEL[2]

The bending motion of polyelectrolyte gel has been observed in an electrolyte solution when the gel rod is placed not touching a pair of electrodes. Polyelectrolyte gel with negatively charged polyions, such as poly(sodium acrylate) gel, swells where it faces to the positive electrode in a basic solution, such as NaOH or Na_2CO_3, and bends toward the negative electrode like a bimetal (Fig. 1). The bending is the deformation in a swelling.
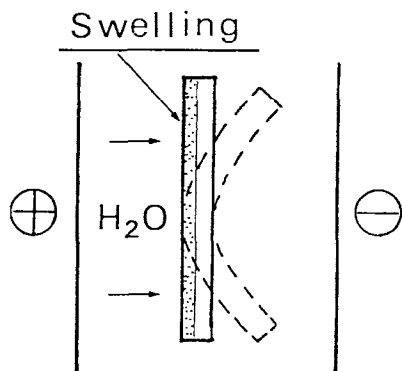
Figure 1 Schematic illustration of bending.

The swelling of polyelectrolyte gel can be explained by Flory's theory of the osmotic pressure.[5] The deformation is related to the application of electric fields, which causes the ion drift in the gel. So the osmotic pressure, π, due to the ion concentration difference between the inside and the outside of a gel, changes in a dc electric field. When π increases, the gel swells. When the gel rod with negatively charged polyion is subjected to a dc electric field, the counterion of the polyion move toward the negative electrode, while the polyion remains immobile. The free ions in the surrounding solution also move toward their counterelectrodes and come into a gel. Then, the osmotic pressure of the positive electrode side, π_1, increases and becomes larger than that of the negative electrode side, π_2. Therefore, the pressure difference, $\Delta\pi$ ($\pi_1 - \pi_2$), occurs in the gel, and the gel is bent like a bimetal due to $\Delta\pi$. When $\Delta\pi > 0$ and $d\pi_1/dt > 0$, the gel swells and bends toward the negative electrode. The gel swells and bends toward the positive one when $\Delta\pi < 0$ and $d\pi_2/dt < 0$.

In the bending of a gel in aqueous solution with low electrolyte content, $\Delta\pi$ is given approximately by a simple model based on the Donnan equilibrium (eq. 1).

$$\Delta\pi = 2RTC_p \ (V_2/V_1) \ ht \ (1 - ht) \ ^*ht < 1 \quad (1)$$

where R is the gas constant, T is the absolute temperature, C_p is the concentration of the polyion, V_2 and V_1 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 time of applying an electric field.

Equation (1) shows that the polyion plays an important role in the bending and that nonionic gel does not show bending in dc electric fields. Equation (1) suggests that the gel with ionizable groups fixed

physically in the polymer network may be bent in a dc electric field.

The deflection of the bending, Y, is calculated by eq. (2). The deflection is expressed in terms of the distance between the ends of a gel before and after bending. Equation (2) is obtained from the assumptions that the bending of a gel under an electric field is a bending in a three-point mechanical bending test, and that $\Delta\pi$ is equal to a maximum tensile stress, σ, in the mechanical bending test.

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

where E is the Young's modulus, D is the thickness, and L is the length of a gel before bending.

Using eqs. (1) and (2), the deflection of the bending is calculated. The deflection increases with the amount of $\Delta\pi$, which is influenced by the transport rate of the counterion, the field intensity, the polyion concentration, and the time of applying an electric field. When the amount of $\Delta\pi$ is kept constant, the deflection depends on the Young's modulus and on the thickness of a gel. The deflection increases with the decrease of the thickness of a gel. The fibrous gel shows large deflection.

EXPERIMENTAL

Materials

PVA was supplied by Kuraray Co., Ltd. PVA has a viscosity–average degree of polymerization of 2500, with a degree of saponification of 99.5 mol %. Twenty-five percent of the poly(acrylic acid) aqueous solution was available from Waco Chemical Industries, Ltd. Other inorganic and organic materials were commercially available.

Preparation of the PVA-PAA gel

The PVA-PAA gel was obtained as follows: In the vessel, 7.5 g of PVA was dissolved in 50 mL of a 30% dimethyl sulfoxide–70% water solvent. The PVA solution was added the 25% poly(acrylic acid) aqueous solution up to 40 g (Table I). The mixture was poured into plastic pipes and frozen at $-50°C$. The frozen mixture was warmed up to room temperature at the rate of $5°C/h$. When this freezing and thawing process was repeated twice, the mixtures changed into gel. The prepared gel was finally immersed in a 0.02 M NaOH aqueous solution to yield the PVA-PAA gel.

Table I Material Composition

No.	PVA/g	Polyacrylic Acid Solution/g
1	7.5	0
2	7.5	5
3	7.5	10
4	7.5	15
5	7.5	20
6	7.5	30
7	7.5	40

The water content of typical PVA–PAA gel (Specimen no. 6) was 93%. The mechanical properties of the gel (no. 6) at room temperature are shown as follows: 0.23 MPa of tensile strength, 145% of elongation at break, 0.1 MPa of storage modulus, and 0.3 kPa of loss modulus at 10 Hz.

Measurement of Bending

The PVA–PAA gel rods were immersed in sodium carbonate aqueous solutions. The electrolyte concentrations were 1 mM and 10 mM. After the gel was in equilibrium with the solution, the solution was poured into a plastic case equipped with two platinum electrodes. The separation between the electrodes was 60 mm. The immersed gel rod was set parallel to the electrodes, not touching them, in the center of the case. Voltage up to 90 volts dc was then applied across the gel between the electrodes.

RESULTS AND DISCUSSION

The PVA–PAA gel rod bends toward the negative electrode in the electrolyte solution as polyelectrolyte gel such as the poly(sodium acrylate) gel does when subjected to the influence of dc electric fields. The strain time curves of the PVA–PAA gel rod with a length of 80 mm and a diameter 8 mm are shown in Figure 2. The strain is calculated by the equation (strain $= 6DY/L^2$; Y: deflection; D: thickness of the gel; L: length of the gel before bending). The gel shows large deflection in the solution with high content of the electrolyte, and so the bending motion has been activated by the electrolyte in the surrounding solution. In the deformation, poly(sodium acrylate) chains have not been removed from the gel. As the original shape of the deformed polyelectrolyte gel can be recovered by reversing the field polarity, the same can also be done to the PVA–PAA gel. In the bending and straight-
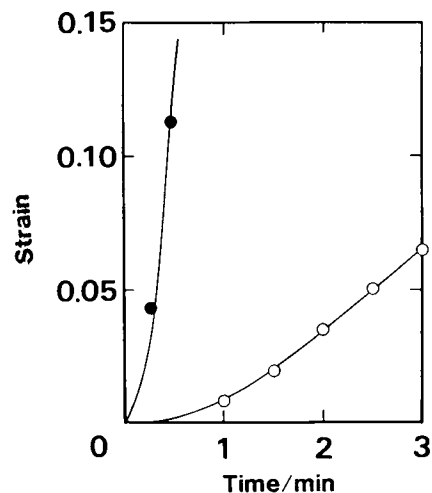

Figure 2 Strain time curves of the specimen (no. 6) under 10 V/cm, in Na_2CO_3 aq; (○) 1 mM, and (●) 10 mM. The strain was calculated by using the equation, strain $= 6DY/L^2$, D: thickness of the gel, Y: deflection, and L: length of the gel before bending. The size of the specimen is 8 mm in diameter and 80 mm in length in Figures 2–5.

ening, the bending speed is almost equal to the recovering speed. The PVA–PAA gel can bend up to 50 cycles in the same speed as that of the first cycle.

The amount of the strain in bending increases gradually with time, and reaches a maximum of 0.21
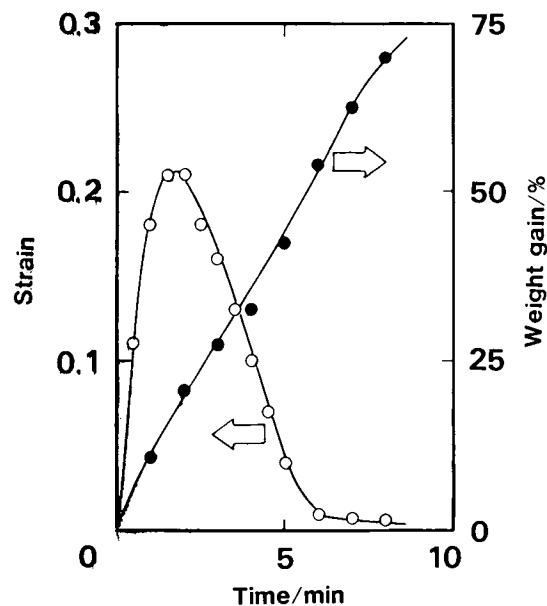
Figures 3 Strain in bending and weight gain of the specimen (no. 6) under 10 V/cm. The data shown in Figures 3–6 were obtained from the bending in 10 mM Na_2CO_3 aq.
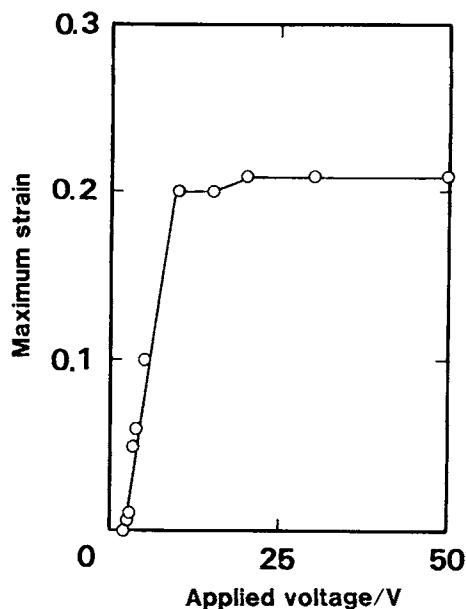
Figure 4 Relationship between the maximum strain in bending and the applied voltage (specimen no. 6).

Figure 5 The effect of the concentration of the polyion in the gel on the bending speed. Strain ($t = 30$ s) is the strain in 30 sec, and this represents bending speed. The amount of the polyacrlic acid solution is the amount used in preparation of gel, and this reflects the concentration of the polyion.

(Fig. 3). At 0.16 of the strain, the part of the gel facing the positive electrode elongates about 20%, and the gel bends in a semicircular. The rod deflected by 0.11 of the strain in 30 sec. The gel straightens in 7 min under 10 V/cm. The gel rod gains weight on bending, and the weight gain is about 15% at 0.2 of the strain. Figure 3 indicates that the bending phenomenon has been observed in a swelling of the polymer gel rod.

The relationship between the maximum strain in bending and the applied voltage is shown in Figure 4. The bending starts at 2 V. The maximum strain increases with the applied voltage up to 10 V. When it is more than 10 V, the maximum strain is kept constant (=0.21).

The bending speed has been determined by the intensity of the applied electric field and the concentration of the PAA in the gel. Figure 5 shows the relationship between the strain in 30 sec, bending speed, and the amount of the polyacrylic acid solution was used in the preparation of the gels. The latter reflects the polyions in the gel. The gel, free of the polyacrylic acid, is not influenced by dc electric field. In the presence of the polyacrylic acid, bending has been observed. The bending speed of the PVA–PAA gel is proportional to the amount of the polyacrylic acid solution present as is suggested by the bending theory. However, in the gel prepared by 40 g of the solution, the speed is not linear to the amount of the polyacrylic acid solution.

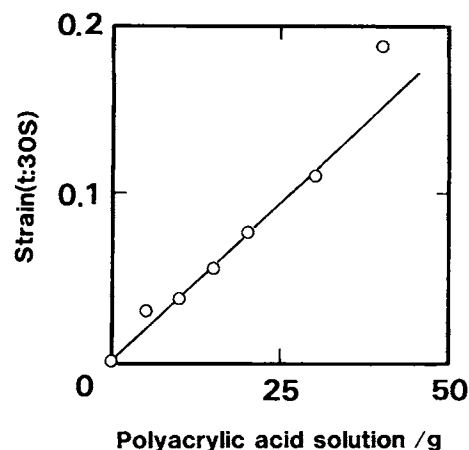The effect of the gel size on the bending speed is

shown in Figure 6. The gel with a length of 50 mm (no. 6) is used in the experiment. The deflection decreases with the increase of the thickness in the gel. The gel with a diameter of 10 mm swells, but doesn't bend in 30 sec. The gel with a diameter of 1.2 mm bends circularly in 30 sec. Figure 6 shows that the fibrous gel produces a high response of dc electric fields. In the case of the gel with 1.2 mm in
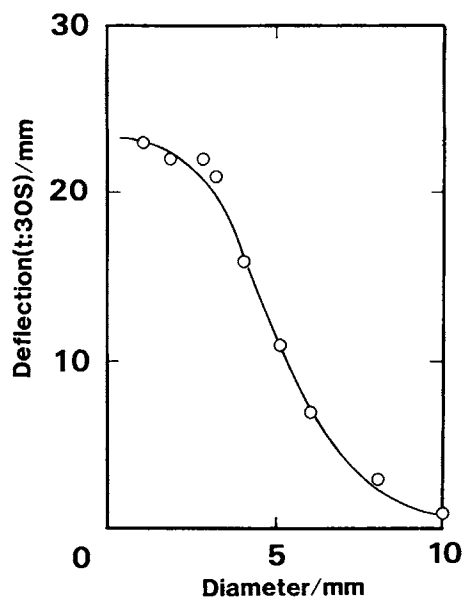

Figure 6 The effect of the diameter in the specimen (no. 6) on the bending speed under 10 V/cm. Deflection ($t = 30$ s) is the deflection in 30 sec. All the specimens are 50 mm in length.

diameter, the gel bends at a velocity of about 1 mm/ sec. The bending is the deformation, which is associated with the ion drift. Here, consider the velocity of sodium ion in the solution. The approximate velocity is given by cumulating the mobility of an ion and the intensity of an electric field. By using $0.0518 \, mm^2/Vsec$, which is the value of the mobility of Na^+ in a dilute solution, as a mobility of Na^+ in the present experiment, the velocity of Na^+ in 10 V/cm becomes 0.0518 mm/sec. Those results indicate that the gel moves at a higher speed than the ion does in the solution.

CONCLUSION

We have presented experimental results on the bending of the PVA–PAA gel in sodium carbonate aqueous solutions under dc electric fields. The PVA–PAA gel is the composite hydrogel with the PAA chains having ionizable groups, which are physically entangled with the PVA polymer network and fixed in the gel. However the PVA–PAA gel deforms in dc electric fields as the polyelectrolyte gel does. The results obtained upon bending the PVA–PAA gel are qualitatively in agreement with the results suggested from the bending theory of polyelectrolyte gel.

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