Electrical Sensitivity Behavior of a Hydrogel Composed of Polymethacrylic Acid/Poly(vinyl alcohol)

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ABSTRACT: An interpenetrating polymer network (IPN) composed of polymethacrylic acid (PMAA) and poly(vinyl alcohol) (PVA) was prepared and exhibited electrical sensitivity behavior. The swelling behavior of the PMAA/PVA IPN hydrogel was studied by immersion of the gel in aqueous NaCl solutions at various concentrations and pH values. The stimuli response of the PMAA/PVA IPN hydrogel in electric fields was also investigated. When swollen IPN hydrogel was placed between a pair of electrodes, the PMAA/PVA IPN hydrogel exhibited bending behavior upon the application of an electric field. The PMAA/PVA IPN hydrogel also showed stepwise bending behavior depending on the electric stimulus. Also, for biomedical applications, the bending behavior of PMAA/PVA IPN hydrogel in Hank's solution at pH 7.4 was studied. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3613–3617, 2004

Key words: polymethacrylic acid; poly(vinyl alcohol); interpenetrating polymer network; bending behavior; polyelectrolytes

INTRODUCTION

In recent years, new polymers have emerged that respond to electrical stimulation with a shape or size change, and this progress has added an important capability to these materials. This capability of electroactive polymers has attracted the attention of engineers and scientists[1]: thus there have been a number of reports that investigated the factor of bending behaviors. Yuk and Lee[2] demonstrated the reversible bending of crosslinked acrylamide gel induced by electric current in aqueous NaCl solution. Park et al.[3] reported on the chemomechanical bending behaviors of ionizable thin film, and showed the time profile of deformation and return of the film to its original position with changing pH. Shiga and Kurauchi[4] reported the deformation of polyelectrolyte gels under the influence of electric field, and interpreted the deformation behavior after removal of the electric field. In this study, the bending behavior as a function of NaCl concentration, pH, electric voltage, and in Hank's solution was investigated.

To realize a powerful actuator or a material closely resembling skeletal muscles with respect to contractility, it was necessary to have both fast and sensitive electric responses and a high degree of mechanical strength for a polymer gel. The interpenetrating polymer network (IPN) system can be a promising candidate to meet these requirements because it could induce quite strong mechanical properties.[5] Therefore we are reporting on a IPN hydrogel composed of polymethacrylic acid (PMAA) and poly(vinyl alcohol) (PVA).

The industrial importance and the wide use of polyelectrolytes such as polyacrylic acid and PMAA has been well established. PMAA is known to be a model hydrophilic system and the crosslinked polymer of PMAA proved to be very useful in many biomedical applications.

PVA is a water-soluble polyhydroxy polymer, used in practical applications because of its easy preparation, excellent chemical resistance and physical properties, and because it is completely biodegradable.[6] Chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biocompatibility, and biodegradability.[7–9]

EXPERIMENTAL

Materials

PVA (average molecular weight: 8.50×10^4–1.46×10^5), *N,N′*-methylenebisacrylamide (MBAAm), methacrylic acid (MAA), and ammonium peroxydisulfate (APS) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Glutaraldehyde (GA, 25 wt % solution in water), hydrochloric acid (HCl), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were purchased from Yakuri Chemical Co. (Japan). All other chemicals were reagent grade and used without further purification.

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Preparation of PMAA/PVA IPN

PMAA/PVA IPN hydrogel was prepared using the sequential IPN method. PVA was dissolved in deionized water and heated at 80°C for 5 h to make a 5 wt % aqueous solution. Then, the MAA monomers were mixed in the desired proportion (1 : 1 wt %). After homogeneous mixing, PVA was crosslinked in the presence of MAA, using GA and HCl as a crosslinking agent and catalyst, respectively. MAA was then polymerized with APS, TMEDA, and MBAAm as an initiator, accelerator, and crosslinking agent, respectively, at room temperature for 48 h. The contents of the initiator and accelerator were 1 wt % of the monomer and the contents of the crosslinking agent were 3 mol % of the monomer. To remove unreacted agent, the film was dipped in deionized water for 2 days and dried in a 40°C vacuum oven for 1 week.

Swelling properties of IPN hydrogel

To measure the swelling ratio, preweighed dry samples were immersed in NaCl aqueous solutions. After excess surface water was removed with filter paper, the weight of the swollen samples was measured at various time intervals. The procedure was repeated five times after there was no further weight increase. The swelling ratio was determined according to the following equation:

$$\text{Swelling ratio (\%)} = \left(\frac{W_s - W_d}{W_d}\right) \times 100$$

where W_s and W_d represent the weight of swollen and dry states samples, respectively.

Bending angle measurements under electric stimulus

Aqueous NaCl solution was poured in a petri dish equipped with two parallel carbon electrodes. The space between the electrodes was 30 mm. The PMAA/PVA IPN hydrogel was swollen in NaCl aqueous solutions at room temperature and cut into strips [20 × 5 × 0.2 mm (length × width × thickness)]. One end of the sample strip was fixed and the gel was placed in the center of the petri dish. When an electric stimulus was applied, the degrees of bending were measured by reading the deviated angle from the vertical position. The deformation was recorded with a video screen using a CCD camera (Mitsubishi, Tokyo, Japan).

Preparation of Hank's solution

For biomedical application, the *in vivo* tests are complicated, so research on the swelling and bending behavior in simulated body fluids (Hank's solution) was performed to simulate the bending behavior of PMAA/PVA IPN hydrogel in the fluid system of the human body. The composition of Hank's solution used in this article is listed in Table I.

TABLE I
Composition of Hank's Solution

Composition	Concentration (g/L)
NaCl	8.00
Glucose	1.00
KCl	0.40
$NaHCO_3$	0.35
$CaCl_2$	0.14
$MgCl_2 \cdot 6H_2O$	0.10
$Na_2HPO_4 \cdot 2H_2O$	0.06
KH_2PO_4	0.06
$MgSO_4 \cdot 7H_2O$	0.06

RESULTS AND DISCUSSION

When an electric field is applied to a strip of the PMAA/PVA IPN hydrogel in aqueous NaCl solution, Hank's solution, and pH buffer solution, the gel showed significant and quick bending toward the cathode. When the electric stimulus was removed, the PMAA/PVA IPN hydrogel returned to its original position. Also, if the polarity of the electric field was altered, the PMAA/PVA IPN hydrogel bent in the opposite direction. To understand the mechanism of this kind of behavior, it is generally thought that the deformation of a polymer hydrogel under an electric field is attributed to the voltage-induced motion of ions and the concomitant expansion of one side of the polymer and the contraction of the other side of the polymer.[4,10,11] However, it has not been completely explained because there is still a lack of well-developed theories for such chemomechanical kinetics.

Effect of pH

The pH-sensitive characteristics of IPN hydrogels were studied in swelling tests using the pH range 2 to 10. As shown in Figure 1, the swelling ratio of the IPN hydrogel increased as pH values increased. When the carboxylic acid groups in PMAA are below the pK_a value (~ 5.5), they are in the form of COOH. As the pH of the solution increased, COOH become ionized to COO^-, the IPN hydrogel swelled, and there was a large change in volume resulting from the development of a large osmotic swelling force because of the presence of the ions.

Figure 2 shows the influence of pH on the bending behavior of the PMAA/PVA IPN hydrogel in response to an electric stimulation. In the lower pH region, there were larger size pores in the PMAA/PVA IPN hydrogel. For this reason, the ions could diffuse and move more

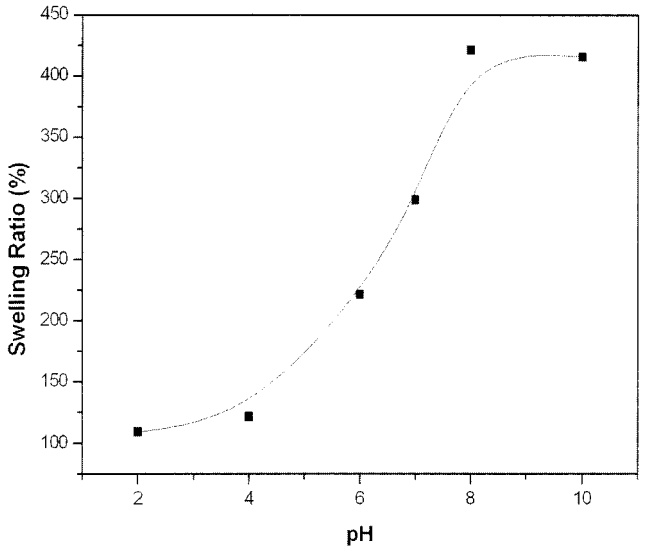

Figure 1 Swelling ratio of PMAA/PVA IPN hydrogel as a function of pH.

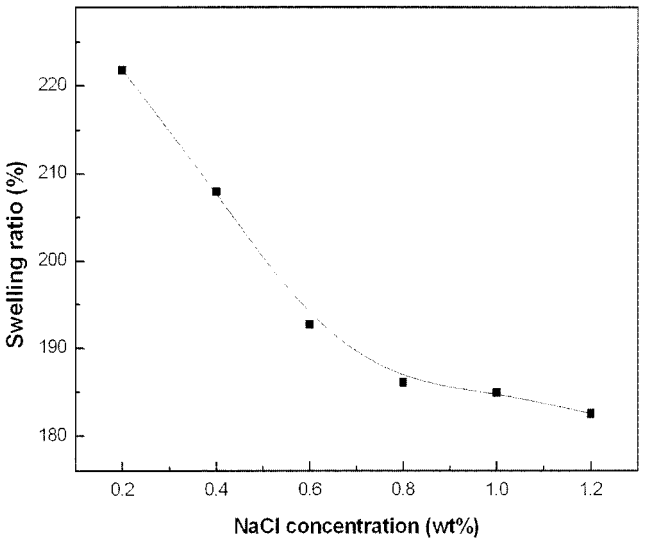

Figure 3 Swelling ratio of PMAA/PVA IPN hydrogel as a function of concentration of aqueous NaCl solution.

easily through large pores under an electric field. Meanwhile, in the medium with a higher pH region, the pores became smaller because of the collapse of the complex, resulting in a relatively slow diffusion of ions.

Effect of medium ionic concentration

The effect of the concentration of the NaCl aqueous solution on the equilibrium swelling was studied for the PMAA/PVA IPN hydrogel. Figure 3 shows the equilibrium swelling ratio of the PMAA/PVA IPN hydrogel in aqueous NaCl solutions at room temperature. It is shown that the swelling ratio decreased with an increase in the concentration of NaCl solution. Generally, the swelling ratio of PMAA/PVA IPN hydrogel depends on the association state of the ionic group within the polymer and on the affinity of the complex for water. According to the Donnan osmotic pressure equilibrium, an increase of movable counterions in a solution leads to a decrease in osmotic pressure within the gel and causes shrinkage of the gel.

Figure 4 shows the influence of medium ionic concentration on the bending behaviors of the PMAA/PVA IPN hydrogel in response to an electric stimulation by varying the concentration of the NaCl solution

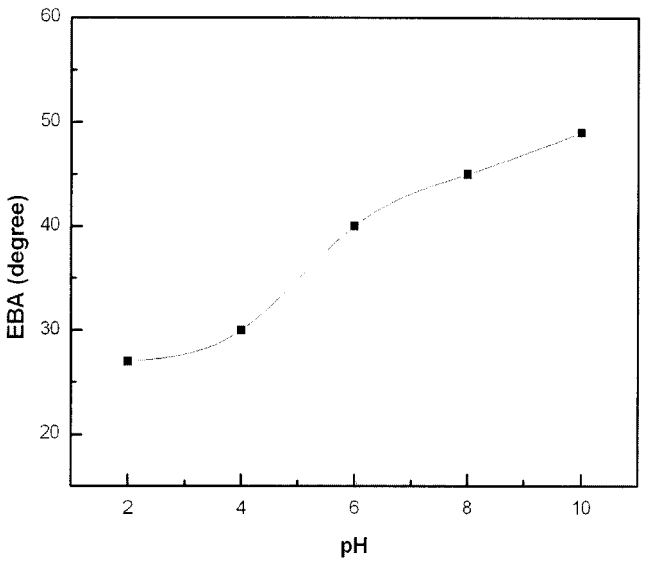

Figure 2 Equilibrium bending angle of the PMAA/PVA IPN hydrogel as a function of pH at 15 V constant voltage.

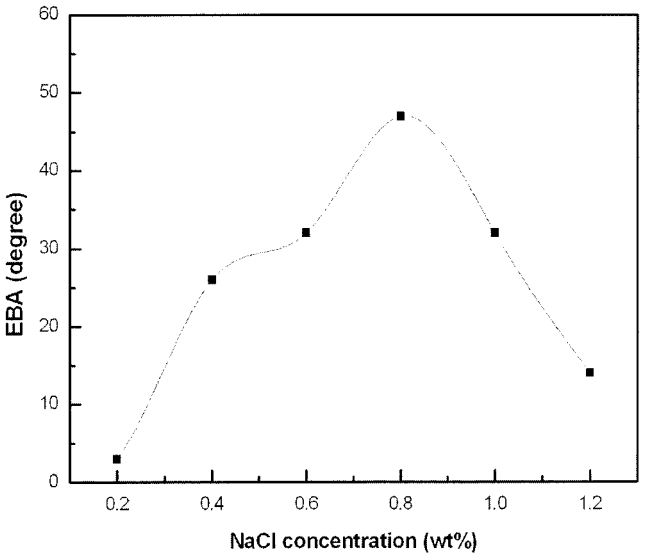

Figure 4 Equilibrium bending angle of the PMAA/PVA IPN hydrogel as a function of NaCl concentration at 15 V constant voltage.

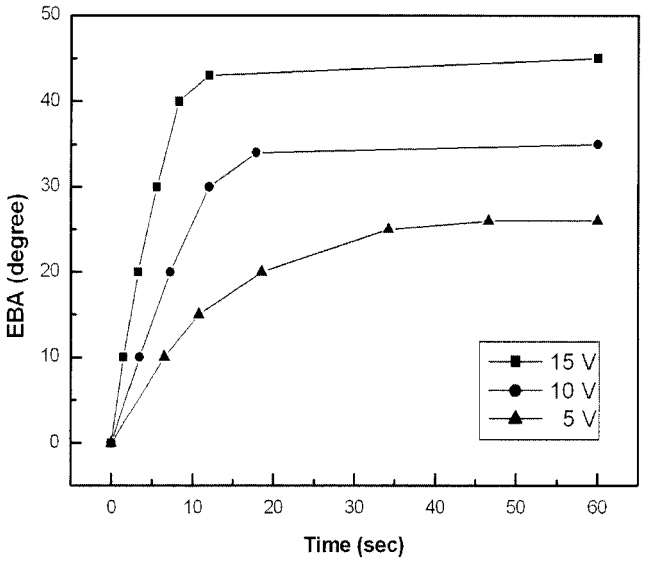

Figure 5 Bending kinetics of the PMAA/PVA IPN hydrogel as a function of the applied voltage in aqueous NaCl 0.8 wt %.

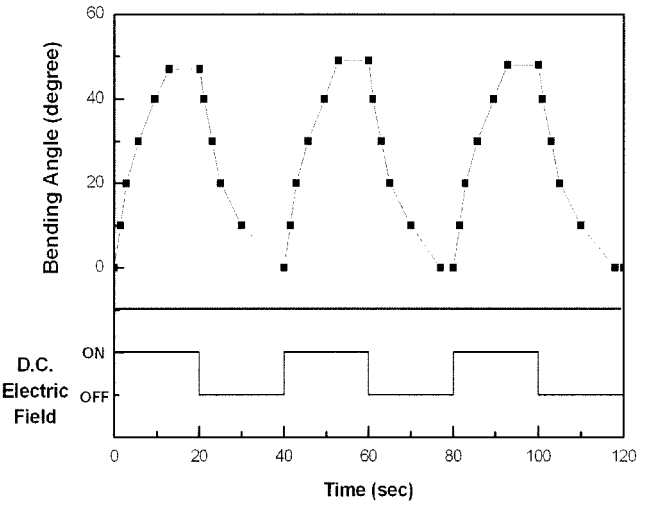

Figure 6 Reversible bending behavior of the PMAA/PVA IPN hydrogel in 0.8 wt % NaCl solution with changes in the applied voltage of 15 V.

from 0.0 to 1.2 wt %. The equilibrium bending angle (EBA) of the PMAA/PVA IPN hydrogel showed an apparent peak with aqueous NaCl 0.8 wt %. The bending degree increased with the concentration of the NaCl solution when the concentration of the NaCl solution was <0.8 wt %. Meanwhile, the bending degree decreased with a concentration of NaCl solution > 0.8 wt %. As described above, an increase in electrolyte concentration in a solution induces an increase of free ions moving from the surrounding solution toward their counterelectrode or into the PMAA/PVA IPN hydrogel. As a result, the bending degree of the PMAA/PVA IPN hydrogel could increase. However, if the concentration of the NaCl solution is greater than its critical concentration, a shielding effect of the polyions by the ions in the electrolytic solute occurs, leading to a reduction in the electrostatic repulsion of the polyions and a decrease in the degree of bending. As shown in Figure 3, the swelling ratio of the PMAA/PVA IPN hydrogel in the solution with the lower ionic concentration was greater than that of the higher ionic concentration. Therefore, if it is compared with the bending results, depending on the concentration of the solution in Figure 4, it could be considered that the swelling of the PMAA/PVA IPN hydrogel according to the degree of concentration does not significantly affect the bending behavior of the PMAA/PVA IPN hydrogel.

Effect of electric voltage

The effect of electric voltage is shown in Figure 5. It shows the variation of the bending angle of the PMAA/PVA IPN hydrogel as a function of the applied voltage in aqueous NaCl 0.8 wt %. The EBA and bending speed increase with an increase in voltage across the gel, indicating that bending is induced by an electric current. Also, as shown in Figure 6, the PMAA/PVA IPN hydrogel exhibited a reversible bending behavior according to the application of an electric field.

Bending behavior in Hank's solution

For biomedical applications, the swelling kinetic of PMAA/PVA IPN hydrogel in Hank's solution is shown in Figure 7. The equilibrium swelling ratio (ESR) of PMAA/PVA IPN hydrogel in Hank's solution is similar to the ESR of PMAA/PVA IPN hydrogel in NaCl solution at 0.8 wt %. As shown in Table I,

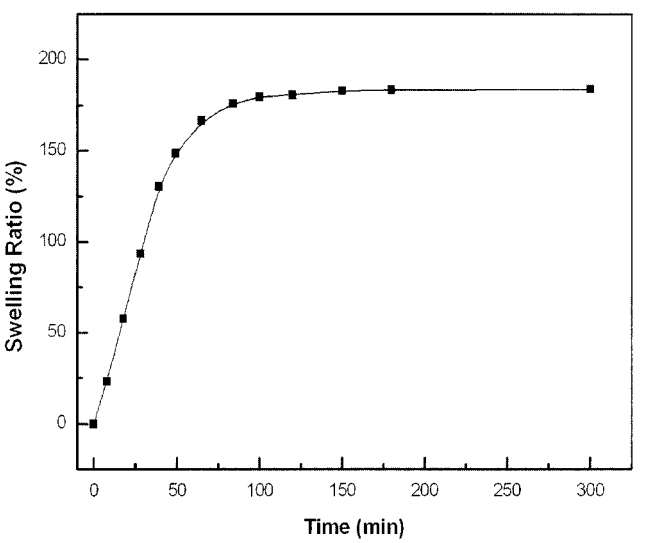

Figure 7 Swelling kinetics of the PMAA/PVA IPN hydrogel in Hank's solution.

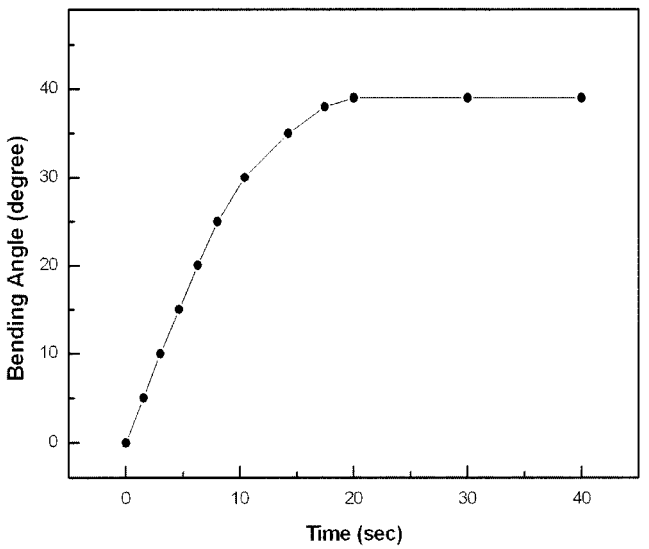

Figure 8 Bending kinetics of the PMAA/PVA IPN hydrogel at 15 V in Hank's solution.

the main component of Hank's solution is NaCl, which played a dominant role during swelling. Figure 8 shows the bending kinetics of the PMAA/PVA IPN hydrogel at 15 V in Hank's solution. The result of the EBA in Hank's solution is lower than that in NaCl solution at 0.8 wt % because the shielding effect of all the other ions in Hank's solution occurs.

CONCLUSIONS

The PMAA/PVA IPN hydrogel was synthesized and its bending behavior was studied. The swelling ratio decreased with increasing the concentration of the aqueous NaCl solution. When the PMAA/PVA IPN hydrogel in NaCl electrolyte solution was subjected to an electric field, the PMAA/PVA IPN hydrogel showed significant and quick bending toward the cathode. When the electric stimulus was removed, the gel returned to its original position. The bending angle of the PMAA/PVA IPN hydrogel was measured in NaCl solution at different concentrations. The bending angle and the bending speed of the PMAA/PVA IPN hydrogel were the greatest in aqueous NaCl 0.8 wt % and increased with an increase in applied voltage. The PMAA/PVA IPN hydrogel also showed stepwise bending behavior depending on the electric stimulus. As a result of the bending behavior in Hank's solution, the present PMAA/PVA IPN hydrogel system can be useful for artificial organ components such as muscle-like contractile structures, sensors, switches, and electric current–modulated drug-delivery systems.

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