Properties of Electroresponsive Poly(vinyl alcohol)/Poly(acrylic acid) IPN Hydrogels Under an Electric Stimulus

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ABSTRACT: Interpenetrating polymer networks (IPNs) composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc) exhibited electrical-sensitive behavior. PAAc as an initial network was prepared inside a PVA solution using UV irradiation; then, PVA networks as a secondary network were formed by a repetitive freeze-thawing process. Their mechanical properties were influenced by the swelling ratio, crosslinking by UV radiation and a freeze-thawing process, and intermolecular force by hydrogen bonding. When a swollen PVA/PAAc IPN was placed between a pair of electrodes, the IPN exhibited bending behavior upon the applied electric field. The equilibrium bending angle (EBA) and the bending speed of the PVA/PAAc IPN increased with the applied voltage and the content of the PAAc network having negatively charged ionic groups within the IPN. The electroresponsive behavior of the present IPN was also affected by the electrolyte concentration of the external solution. Particularly, IPN37 showed a maximum EBA when the critical ionic strength was 0.1. Anisotropic deswelling of the IPN was observed in a direct contact with a pair of electrodes under aerobic conditions. The PVA/PAAc IPN also showed stepwise bending behavior depending on the electric stimulus. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1675-1683, 1999

INTRODUCTION

Polymer gels have been studied for applications in a variety of fields, such as in chemical engineering, medicine and pharmaceuticals, food, and agriculture.^{1–3} Polymer gels, solid–liquid coexistent materials, can change their volume and shape reversibly, depending on several external physicochemical factors, such as temperature, solvent composition, pH, and ionic concentration,^{4–11} namely, the large volume or shape change of a polymer gel, induced by supplying thermal, chemical, or electrical energy,

offers various possibilities for advanced functional polymers.

Among them, electric-current-sensitive hydrogels actuated by an electric stimulus seem to be particularly interesting in connection with the fact that the mechanical energy was triggered by an electric signal.^{12–24} Electric-current-sensitive hydrogels are usually made of polyelectrolytes and an insoluble, but swellable polymer network which carries cations or anions. This system can transform chemical free energy directly into mechanical work to give an isothermal energy conversion. A typical function of a gel containing ionic groups is to bend reversibly under the influence of an electric field, making it useful in some actuators driven by an electric field. From the viewpoint of mechanical engineering, great hopes

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are set on these materials as new actuators,^{12–20} especially in the fields of robotics and medical welfare instruments. In fact, the realization of lightweight, soft touch, and powerful actuators is an important subject. Besides, the volume change has been utilized for solute permeation control through membranes, in electromechanical engines (energy conversion), and in controlled drug delivery.²¹

Several research groups have focused their studies on the behavior of polyelectrolyte gels under the influence of applied electric fields.¹²⁻²⁴ Yannas and Grodzinsky reported that collagen fibers immersed in an electrolyte bath could deform and thereby perform mechanical work under an external electric stimulus.²³ Tanaka et al. showed that a partially hydrolyzed polyacrylamide gel underwent phase transition on application of an electric field and collapsed if the gel was placed in a solvent such as a 50% acetone-water binary mixture.²⁴ They interpreted the phenomenon using the Flory-Huggins theory. Osada et al. reported that a hydrogel made of weakly crosslinked poly(2-acrylamido-2-methylpropanesulfonic acid) possessed motility in water by the contraction and curvature of a strip of a gel.^{14,17} The system was based on an electrokinetic molecular assembly reaction of surfactant molecules on the hydrogel. There have been several investigations on hydrogels or membranes composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc). Suzuki made a hydrogel out of PVA, PAAc, and polyallylamines and studied their mechanical properties for use as an artificial muscle.¹⁸ Rossi et al. found that a change in shape of the composite membrane composed of PVA/PAAc and polypyrrole occurred when dc was applied.¹⁹

However, these studies focused mainly on the electric responses of polymer gels. To realize a powerful actuator or a material close to skeletal muscles, it was necessary to have both fast and sensitive electric responses and a strong mechanical strength of a polymer gel. The interpenetrating polymer network (IPN) system could be a promising candidate to meet these requirements because it could induce quite strong mechanical properties. Therefore, we report here IPN hydrogels composed of PVA with high mechanical strength and easy processibility and PAAc containing carboxyl groups that become ionized at pH values above 4.7.

In our previous studies, we synthesized novel PVA/PAAc IPN hydrogels by a unique sequential method through UV irradiation and a freezing-

thawing process.^{25–27} We already reported the swelling kinetics,²⁵ drug-release behavior,²⁶ and permeability of various solutes.²⁷ PVA/PAAc IPNs showed drastic swelling changes by external pH and temperature according to the repulsion of ionic groups and association–dissociation of hydrogen bonds between the two polymers. The release of the drug incorporated into these IPN hydrogels exhibited pulsatile patterns in response to both pH and temperature. Also, the permeabilities of various solutes through the PVA/PAAc IPN hydrogels were regulated as a function of temperature, pH, ionic strength, solute size, and ionic properties of the solutes.

In the present study, we paid attention to the feasibility of a PVA/PAAc IPN hydrogel as a chemomechanical system that can transform chemical free energy directly into mechanical work to give an isothermal energy conversion. We examined the changes in the swelling of a PVA/PAAc IPN by pH and the ionic strength of the solution to confirm the bending mechanism of the IPN under an electric stimulus. The mechanical properties in the wet and dry state were also measured. In addition, the bending behavior of the PVA/PAAc IPN under an electric field and influencing factors on the electric sensitivity were investigated.

EXPERIMENTAL

Materials

Acrylic acid (AAc) monomer was purchased from Junsei Chemical Co. (Tokyo, Japan) and used after purification with an inhibitor removal column (Aldrich Chemical Co., Milwaukee, WI). PVA (DP = 2500; degree of deacetylation = 99%) was obtained from Shinetsu Chemical Co. Methylenebisacrylamide (MBAAm) and 2,2-dimethoxy-2phenylacetophenone (DMPAP), purchased from Aldrich, were used as a crosslinking agent and photoinitiator, respectively. All other chemicals used were regent grade and used as purchased without further purification.

Preparation of PVA/PAAc IPN Hydrogels

The PVA/PAAc IPNs were prepared by a sequential method of IPN synthesis as described in our previous articles.^{25–27} PAAc as an initial network was synthesized inside the PVA solution by using UV irradiation; then, PVA networks as a second-

Sample ^a	Feed Composition PVA : PAAc (mol %)	Mass of AAc (g)	Mass of MBAAm ^b (g)	Mass of DMPAP ^c (g)
IPN64	60:40	2.16	0.023	0.0043
IPN55	50:50	3.26	0.035	0.0065
IPN46	40:60	4.89	0.052	0.0098
IPN37	30:70	5.70	0.061	0.0114

Table I Composition and Designation of PVA/PAAc IPNs

^a Each sample was prepared using 10 wt % PVA aqueous solution.

^b 0.5 mol % of MBAAm was dissolved in AAc.

 $^{\rm c}$ 0.2 wt % of DMPAP was also dissolved in AAc.

ary network were formed by a repetitive freezethawing process. PVA was dissolved in deionized water and heated at 80°C for 2 h to make the 10 wt % aqueous solution. Then, the AAc monomers were mixed with 0.2 wt % DMPAP and 0.5 mol % MBAAm. The molar ratios of the PVA-to-PAAc mixture were adjusted to 6:4, 5:5, 4:6, and 3:7, respectively. The feed composition and designation of each sample are listed in Table I. The mixed solutions were poured onto Petri dishes and irradiated using a 450 W UV lamp (Ace Glass Co.) for 1 h under a N₂ atmosphere. The irradiated samples were placed at -50° C for 6 h and room temperature for 2 h. These freeze-thawing cycles were repeated eight times. The synthesized gels were removed from the Petri dishes, cut into rod or disk shape, and washed by deionized water to remove any unreacted AAc monomers. The swollen gels were dried, first, at 25°C for 1 day and then at 45°C in vacuo for additional 2 days and, finally, at 25°C for 1 day.

Swelling Properties of PVA/PAAc IPN Hydrogels

To measure the swelling ratio of the IPNs, a dried PVA/PAAc IPN was placed in a buffer medium of different pH values and ionic strengths at 25°C until the hydrated weight reached a constant value. It was confirmed from our previous experiments²⁵ that the swelling of these PVA/PAAc IPN disks was enough to reach the equilibrium state within 24 h. After excessive water appeared on the surface of the IPN, a disk was removed using filter paper and the hydrated weight of swollen gel was measured. The swelling ratio of each sample was evaluated from the following equation:

Swelling ratio =
$$(W_s - W_d)/W_d$$
 (1)

where W_s and W_d are the fully swollen and dry weight of each sample, respectively.

Mechanical Properties of PVA/PAAc IPN Hydrogels

A universal testing machine (Hounsfield 10KM) was used to measure the tensile strength and elongation of each PVA/PAAc IPN sample in dry and wet states with an extension rate of 10 mm/ min at room temperature. For the wet-state measurement, the IPNs were immersed into water until equilibrium was achieved. Reported values are the mean of five samples and the deviation from the mean is within $\pm 5\%$.

Bending-Angle Measurement Under Electric Stimulus

The PVA/PAAc IPNs hydrogels were swollen in a NaCl aqueous solution at room temperature and cut into $50 \times 2 \times 2$ -mm rectangular columns. After one end of the sample column was fixed and placed vertically between two carbon electrodes in the NaCl aqueous solution, its bending behavior was investigated under an electric field. The bending degree of the PVA/PAAc IPNs hydrogels from the vertical position was measured by varying the applied electric potential, charge density due to the ionic group within IPN, and the ionic strength of the medium.

Deswelling in Electrode Contact System Under Aerobic Conditions

The PVA/PAAc IPN was swollen to an equilibrium condition in distilled-deionized water at room temperature. The swollen IPN was placed between two 15×15 -mm platinum plates. To prevent changing the area of contact between the surface of the PVA/PAAc IPN and the platinum plates, we applied a constant dead weight on the platinum plate. The released water from the IPN was continually removed using filter paper and the weight change of the swollen PVA-PAAc IPN was checked periodically under an electric field.



Figure 1 Swelling ratio change of PVA/PAAc IPN hydrogel by varying pH, ionic strength of the external solution, and the content of ionic groups within the IPN.

The deswelling water ratio of each IPN was evaluated from following equation:

Deswelling water ratio = W_t / W_{t0} (2)

where W_{t0} and W_t are the initial weight of the fully swollen IPN and the weight of IPN at the deswelling time t, respectively.

RESULTS AND DISCUSSION

Factors Influencing the Swelling Properties

We already reported that PVA/PAAc IPNs were successfully synthesized by a sequential method, that is, UV polymerization of AAc in the mixture of the PVA aqueous solution, followed by a freeze-thawing process to prepare elastic hydrogels. In addition, pH- and temperature-sensitive swelling behaviors of this PVA/ PAAc IPN were reported in our previous articles.²⁵⁻²⁷ All PVA/PAAc IPNs exhibited a temperature-responsive swelling behavior due to the association/dissociation of the hydrogen bonding between the hydroxyl groups in the PVA and the carboxyl groups in the PAAc within the IPN. Also, it showed the pH-sensitive swelling behavior to be attributed to the increase of the free volume in a polymer matrix by ionic repulsion of the carboxyl groups in the PAAc.

To examine the electrokinetic phenomena of the PVA/PAAc IPN in the electric stimulus system, the swelling ratio of the IPN was investigated and is shown in Figure 1 to depend on the pH and the electrolyte concentration of the buffer solution. Figure 1(a) exhibits the swelling ratio of the PVA/PAAc IPN in the buffer solution of pH 7 in which the ionic strength was adjusted to 0.01 and to 0.1. As we increased the content of the PAAc network having ionic groups within the IPN, the swelling ratio of the IPN drastically increased. Also, PVA/PAAc IPN has a higher swelling ratio at an ionic strength of 0.01 than that of 0.1, indicating that the ionic repulsion between the fixed charge of the carboxylate ion in PAAc and an external solution became more intense when the electrolyte concentration in the external solution increased.

Note that the pK_a value of PAAc is 4.7.²⁸ Therefore, the ionization of carboxylic acid in the IPN by the change of pH significantly affected the swelling as shown in Figure 1(b). Also, an interaction between ionic groups in the IPN and electrolytes in the buffer solution became more intense when the pH of the buffer solution changed from 4 to 7; namely, when the pH was below the pK_a value of PAAc (at pH 4) in which the carboxylic acid group in the IPN hydrogel was in a hydrogenated state, the effect of the ionic strength on swelling was less than that when the pH was above the pK_a value of PAAc (at pH 7) in which the carboxylic group in the IPN hydrogel was in an ionized state, as can be seen in Figure 1(b).



Figure 2 Mechanical properties of PVA/PAAc IPN with different compositions and water content: (a) dry state; (b) wet state.

Mechanical Properties

Figure 2 exhibits the tensile strength and elongation of the PVA/PAAc IPN hydrogels with different compositions of PVA to PAAc and water content inside the gel. For IPNs in the dry state shown in Figure 2(a), the tensile strength decreases, but elongation increases as each composition of PVA or PAAc inside the IPN increases. IPN55, with a similar ratio of PVA and PAAc, has greater tensile strength and smaller elongation than those of other IPNs. The increase of tensile strength could be explained in that not only crosslinking by UV radiation and the freezethawing process but also intermolecular force by hydrogen bonding should have been maximized when the composition ratios of two materials were equal. In the case of a fully swollen IPN, however, both tensile strength and elongation decreased with increasing PAAc content inside the IPN as shown in Figure 2(b), indicating that the mechanical property of the PVA/PAAc IPN was influenced more by the degree of swelling rather than by the crosslinking density within the IPN in a fully swollen state.

Bending Behavior of Polyelectrolyte Gel Under Electric Fields

There are three competing forces acting on the gel polymer network: the rubber elasticity, the polymer–polymer affinity, and the ion pressure. These forces, collectively called the osmotic pressure, determine the equilibrium state of the gel^{13,15}; namely, the osmotic pressure π is given as the

sum of π_1 , π_2 , and π_3 , which corresponds to the osmotic pressure due to the rubber elasticity, the solubility of the solvent in the polymer chain, and the ion concentration difference between the inside and outside of the gel, respectively. Therefore,

$$\pi = [\ln(1-v) + v + xv^{2}]RT/V_{1} + (v^{1/3} - v/2)RTv_{e}/V_{0} + \left(\sum C_{i} - \sum C_{j}\right)RT$$
 (3)

where v is the volume fraction of the polymer network; x, the solubility parameter; V_0 , the volume of the polymer network under the dry condition; v_e , the number of chains; V_1 , the molar volume of the gel; R, the gas constant; and T, the temperature. Since the composition between these forces determines the osmotic pressure, the changing balance of these forces induces the volume change of the gel polymer network. The osmotic pressure π of the gel is equal to that of the surrounding aqueous solution, π_0 , at equilibrium. Therefore, π_1 , π_2 , and π_3 have definite values. When an electric field is applied on the negatively charged gel 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 counterelectrode and come into the gel. Thus, the osmotic pressure of the gel



Figure 3 Bending kinetics and EBA of PVA/PAAc IPN as a function of the applied voltage in NaCl electrolyte solution (ionic strength = 0.1): (a) bending kinetic of IPN 37; (b) EBA of IPN 37 depending on applied voltage.

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 gel, and it is the driving force of bending toward the negative electrode.

Another factor which influences the bending phenomenon of a gel may be the local pH gradient attributed to water electrolysis. Several researchers reported that ions produced by electrochemical reactions and the movement of ions toward the counterelectrodes induced the pH gradient inside the gel matrix under the flow of electric current.^{19,22} When an electric field was applied to the gel immersed in a NaCl electrolyte solution, electrochemical reactions (positive electrode: $2Cl^- \rightarrow 2Cl_2 + 2e^-$; negative electrode: $2H_2O$ $+ 2e^- \rightarrow 20H^- + H_2$) 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.

To investigate the electroresponsive behavior of a PVA/PAAc IPN hydrogel under an electric stimulus, we measured the bending degree of the IPN by varying several factors: Figure 3 shows the relationship between the bending angle of IPN37 as a function of time and the voltage of the applied electric field in a 0.1M NaCl solution at room temperature. When the PVA/PAAc IPN hydrogel in the NaCl electrolyte solution is subjected to an electric field, the IPN bends toward the anode. As shown in Figure 3, the gradient slope in the plot of the bending angle versus time became steeper with increasing applied voltage and then leveled off at a steady state. Note that the equilibrium bending angle (EBA) and the bending speed 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 of PAAc within the PVA/PAAc IPN from the IPN to the external solution and the free ion moved from the external solution into the IPN as the potential gradient in electric field increased.

Figure 4 exhibits the effect of the PAAc content on the EBA of the IPN in a 0.1M NaCl solution at 10 V. As the content of the PAAc network increased, the EBA increased linearly. The bending speed also increased in proportion to the content of PAAc in the IPN. As can be seen in Figures 3 and 4, this may indicate that the EBA is not a rate-limiting step for bending at the equilibrated state.

In addition, the EBA and bending kinetics of IPN37 were measured in NaCl solutions with different ionic strengths. There was a critical ionic strength for bending of the PVA/PAAc IPN as shown in Figure 5. The bending degree increased with the ionic strength when the ionic strength was less than 0.1, while the bending degree decreased at an ionic strength of greater than 0.1. Furthermore, when the ionic strength of the NaCl solution was 1.0, we could not observe the bending behavior of the PVA/PAAc IPN under the 10 V of applied voltage. As described above, an in-



Figure 4 Effect of PAAc content in PVA/PAAc IPN on the EBA in NaCl electrolyte solution (ionic strength = 0.1) at 10 V constant voltage.

crease of the electrolyte concentration in a solution induces an increase of the free ions moving from the surrounding solution toward their counterelectrode or into the IPN. As a result, the bending degree and bending speed of the IPN could increase. However, if the ionic strength of the solution is greater than a critical concentration, the shielding effect of the polyions by the ions in the electrolytic solute occurred, leading to a reduction in the electrostatic repulsion of the polyions and a decrease in the degree of bending.

As already shown in Figure 1, the swelling ratio of the PVA/PAAc IPN in the solution with the lower concentration of electrolytes (ionic strength = 0.01) was greater than that of the higher electrolyte concentration (ionic strength = 0.1). Therefore, if it is compared with the bending results depending on the ionic strength of the solution in Figure 5, we could consider that the swelling of the PVA/PAAc IPN by the ionic strength does not significantly affect the bending behavior of the IPN.

In addition, the stepwise bending behavior of the PVA/PAAc IPN depending on the electric stimulus was observed for the IPN in the 0.1*M* NaCl solution with changes in the applied voltage of 10 V every 10 min. When the electric stimulus was removed, the IPN was displaced to its original position. Also, if the polarity of the electric field was altered, the IPN bent toward the opposite direction. As shown in Figure 6, the PVA/ PAAc IPN exhibited a reversible bending behavior according to the application of the electric field.

Deswelling in Electrode Contact System Under Aerobic Conditions

When the PVA/PAAc IPN swollen until the equilibrated state was in direct contact with a pair of electrodes under an aerobic condition, we could observe the deswelling of the IPN. The anisotropic deswelling of an electrolyte gel was reported by several researchers.^{15,29,30} They explained that the deswelling was attributed to the electroosmosis inside the gel, combined with local pH changes around the electrodes resulting from electrochemical reactions.

We measured the deswelling water ratio of the IPN using eq. (2) to quantify the degree of deswelling. Figure 7 exhibits the remaining water ratio as a function of time depending on the applied voltage and the content of PAAc having ionic groups in the IPN. As shown in Figure 7, the deswelling of PVA/PAAc IPN was enhanced in proportion to the applied voltage. Particularly, fully swollen IPN37 showed about a 50% weight reduction of its original weight within 10 min under the 15 V applied voltage. To examine the effect of the ionic group in the PVA/PAAc IPN, the remaining water ratio of each IPN with different compositions, IPN 55, IPN46, and IPN 37, was measured. It also showed that the deswelling water ratio of the IPN increased with the content of the ionic group.



Figure 5 Influence of ionic strength of NaCl solution on the EBA and bending speed of IPN 37 at 10 V constant voltage.



Figure 6 Reversible bending behavior of IPN 37 in NaCl solution (ionic strength = 0.1) with changes in the applied voltage of 10 V every 10 min.

CONCLUSIONS

The PVA/PAAc IPNs with various compositions were prepared by a sequential synthetic method, that is, UV polymerization of AAc in the mixture of a PVA and AAc monomer aqueous solution, followed by a freeze-thawing process to prepare elastic hydrogels. The PVA/PAAc IPN exhibited different swelling patterns as a function of the pH, ionic strength of the external solution, and content of ionic group in the IPN. The swelling ratio of the IPN drastically increased with the PAAc network having ionic groups within the



Figure 7 Deswelling behavior of PVA/PAAc IPN directly contacted with a pair of electrodes under aerobic condition.

IPN. The PVA/PAAc IPN has a higher swelling ratio at an ionic strength of 0.01 than that of 0.1, attributed to the enhancement of the ionic repulsion between the fixed charge of the carboxylate ion in PAAc and an external solution. In the dry state, not only crosslinking by UV radiation and a freeze-thawing process but also intermolecular force by hydrogen bonding affected the mechanical property of the PVA/PAAc IPNs. On the contrary, the mechanical property of fully swollen IPN was influenced more by the degree of swelling rather than by the density of the crosslinking within the IPN. When the PVA/PAAc IPN hydrogel in a NaCl electrolyte solution is subjected to an electric field, the IPN bends toward the anode. When the electric stimulus was removed, the IPN returned to its original position. Also, if the polarity of the electric field is altered, the IPN bends toward the opposite direction.

The gradient slope in the plot of the bending angle versus time became steeper with increasing applied voltage and then leveled off at a steady state. The EBA and the bending speed increased with the applied voltage. In addition, as the content of the PAAc network having negatively charged ionic groups within the IPN increased, the EBA increased linearly. The bending speed also increased in proportion to the content of PAAc in the IPN. From the results of the EBA and the bending kinetics of IPN37 measured in a NaCl solution with different ionic strengths, there is a critical ionic strength for the bending of PVA/PAAc. In addition, the PVA/PAAc IPN showed stepwise bending behavior depending on the electric stimulus. When the PVA/PAAc IPN swollen until the equilibrated state was in direct contact with a pair of electrodes under an aerobic condition, we could observe the anisotropic deswelling of the IPN in proportion to the applied voltage. Therefore, by controlling the electric sensitivity of the IPN using such influencing factors, the present PVA/PAAc IPN as a chemomechanical system could be useful for various applications.

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