Electrostimulus Responsive Behavior of Poly(acrylic acid)/Polyacrylonitrile Semi-Interpenetrating Polymer Network Hydrogels

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels composed of poly(acrylic acid) and polyacrylonitrile were prepared with UV irradiation, and their bending behaviors between two electrodes were studied under various conditions. The swelling ratio of the IPN hydrogels decreased with an increasing NaCl concentration in an aqueous solution. The fastest bending speed was observed in a gel synthesized in a 0.6 wt % NaCl aqueous solution. As the applied voltage increased, the bending speed increased. The deformation of the IPN hydrogels was reversible when the applied voltage was turned on and off. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1473–1477, 2004

Key words: hydrogels; interpenetrating networks (IPN); swelling

INTRODUCTION

Hydrogels are crosslinked, three-dimensional hydrophilic polymer networks that swell, but do not dissolve, when brought into contact with water. In the swollen state, they are soft and rubbery and resemble living tissue. Some hydrogels also possess excellent biocompatibility.[1,2] The water uptake by these hydrogels can be sensitive to several factors, including the temperature, the pH, the ionic strength of the swelling solution, the presence of a magnetic or electric field, and even UV light.[3,4] Hydrogels are mainly used in the fields of medicine, pharmacy, biotechnology, and agriculture. In recent years, they have been used for the immobilization of enzymes, proteins, antibodies, and antigens, and they have been applied in many ways in biomedicine and biotechnology.[5]

Interpenetrating polymer networks (IPNs) for hydrogels have also been the subject of many investigations.[6−8] IPNs are a combination of two or more network polymers synthesized in a juxtaposition.[9] IPNs are an important class of materials. They have attracted broad interest from both the scientific community and industry. IPNs are normally composed of two or more incompatible crosslinked polymers; the function of the crosslinking is to increase the extent of network mixing.[10−12]

Poly(acrylic acid) (PAAc) is a pH-sensitive and electrically sensitive material because of the ionic repulsion between its charged anionic groups, and so it forms polymer complexes with polybases, such as poly(ethylene oxide), poly(vinylpyrrolidone), and polyacrylamide. Polyacrylonitrile (PAN) is a semicrystalline vinylic homopolymer with the —$(CH_2—CHCN)$— repeating unit, and it usually occurs in the atactic form.[13] PAN is mainly used in soft cloth furnishings, but it is also an important carbon fiber precursor. PAN is a versatile polymer that is widely used for making membranes. It shows good mechanical strength in film form.[14]

PAAc is a hydrophilic material, and it imparts hydrophilicity to hydrogels formed from composites of PAAc and another mechanically stronger and hydrophobic material, such as PAN. Therefore, it is interesting to investigate the formation of such composite semi-IPN hydrogels with the unique properties of PAAc and PAN.

The mechanism of the stimuli response of these gels in direct-current (dc) electric fields has often been discussed, but it is still controversial. Grimshaw et al.[15] applied an electrodiffusion theory to explain the swelling pattern of a poly(methacrylic acid) gel. De Rossi et al.[16] explained an observed anisotropic deswelling at the anode of poly(vinyl alcohol)/PAAc membranes as arising from a decrease in the local pH associated with the electrolysis of water. Kim et al.[17] proposed a theory involving the depletion of polarization to explain the bending of gels in a dc electric field. Tanaka et al.[18] reported an anisotropic contraction when electrodes were in contact with negatively charged gels, and this was explained by the electrophoretic migration of the negatively charged gel toward the anode.

In this study, semi-IPN hydrogels composed of PAAc and PAN were prepared, the swelling behavior of the IPN hydrogels was characterized in aqueous NaCl solutions, and their deformation under an electrical stimulus under various conditions was observed.

EXPERIMENTAL

Materials

Acrylic acid was purchased from Junsei Chemical Co. (Japan). PAN, with an average molecular weight of 8.6 × 10³, was purchased from Aldrich Chemical Co. (United States). Methylenebisacrylamide (MBAAm), used as a crosslinking agent, was obtained from Aldrich Chemical and was used without any further purification. 2,2-Dimethoxy-2-phenylacetophene (DMPA), used as a photoinitiator, was purchased from Aldrich Chemical. All the other chemicals used in the experiments were reagent-grade and were used without any further purification.

Preparation of semi-IPN hydrogels

The IPNs were prepared with the semi-IPN method. The PAN and acrylic acid monomers were dissolved in ethyl alcohol, and then the crosslinker and initiator (MBAAm and DMPA, respectively) were mixed with the solutions. The solutions were then poured into circular glass molds and irradiated with a 450-W UV lamp (Ace Glass Co., United States), placed 20 cm above the samples, for 20 min until gelation occurred. The molds were then kept under reduced pressure to evaporate the solvent. After 1 day, dry films were obtained, which were washed for the removal of any unreacted chemicals. Three IPNs were prepared from 2:1, 3:1, and 4:1 weight ratios of PAAc to PAN; they are denoted AN21, AN31, and AN41, respectively.

Characterization

The dried gels were immersed in 50 mL of deionized water at 20°C. The swelling ratios were calculated through the weighing of the initial and swollen samples at various time intervals. For the measurement of the swelling ratio, preweighed dry samples were immersed in aqueous NaCl solutions of various concentrations. After the excess surface water was removed with filter paper, the weights of the swollen samples were measured at various pH levels, temperatures, and time intervals. The swelling ratio was determined with the following equation:

$$\text{Swelling ratio (\%)} = [(W_s - W_d)/W_d] \times 100 \quad (1)$$
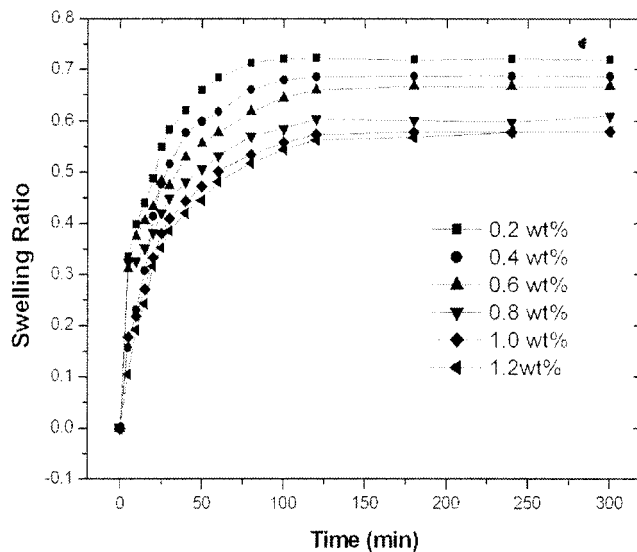

Figure 1 Swelling ratios of the AN41 sample as a function of the NaCl concentration in aqueous solutions at room temperature.

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

Bending angle measurements under an electrical stimulus

An aqueous NaCl solution was poured into a petri dish equipped with two parallel carbon electrodes set 30 mm apart. The PAAc/PAN IPN hydrogel was allowed to swell in the aqueous NaCl solution at room temperature, and then it was cut into strips (20 mm long, 5 mm wide, and 0.2 mm thick). The sample was placed in the center of the petri dish, and one end of the sample was immobilized. When an electric stimulus was applied, we measured the degree of bending by reading the angle of deviation from the vertical position. The deformation was recorded on a video screen with a CCD camera (Mitsubishi, Japan).

RESULTS AND DISCUSSION

Figure 1 shows the swelling ratios of the AN41 samples in aqueous NaCl solutions at room temperature. The hydrogel samples swelled rapidly, reaching equilibrium within a period of 2 h. The IPN hydrogel samples generally exhibited swelling ratios in the range of 57–72%, which decreased as the concentration of NaCl increased. The swelling ratio was different by a factor of 1.24 in terms of the volume in the range of salt concentrations studied. This means that the linear dimension was different only by 7%. The effect of the salt concentration was small. However, Figure 1 shows that the swelling behavior of the AN41 IPN hydrogel depended on the salt concentration.
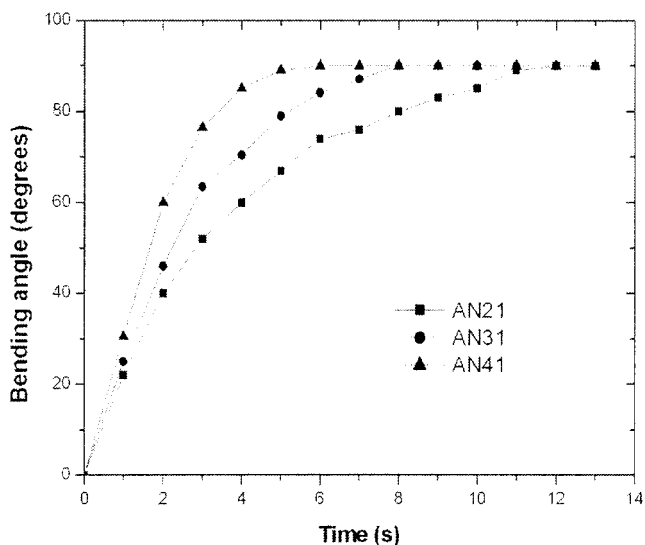
Figure 2 RT_{90} values of the PAAc/PAN IPN hydrogels with the PAAc content in 0.6 wt % NaCl solutions under an applied voltage of 20 V at room temperature.

Generally, the swelling ratio of the hydrogel depended on the association state of the ionic groups within the polymer and their affinity for water.[19] According to the Donnan osmotic pressure equilibrium,[20] an increase in the number of labile counterions in a solution leads to a decrease in the osmotic pressure within the gel, causing the gels to shrink.

A constant electric voltage across two parallel-plate electrodes can cause PAAc/PAN IPN hydrogels in an aqueous NaCl solution to bend toward the cathode. The mechanism for this behavior is not well understood because of the lack of a well-developed theory for such behavior. However, it is generally thought that the deformation of a polymer hydrogel in an electric field is due to the voltage-induced motion of ions, the concomitant expansion of one side of the polymer film, and the corresponding contraction of the other side of the polymer film. In other words, when an electric field is applied to a negatively charged gel in an aqueous NaCl solution, the positive counterion (H^+) to the polyion ($—COO^-$), which is an ionic carboxyl group of PAAc in the polymer network, moves toward the negative electrode, whereas the polyion remains immobile. In addition, the free sodium ions (Na^+) and water molecules in the surrounding solution also move toward the negative electrodes and into the gel. Thus, the osmotic pressure of the gel polymer network near the positive electrode increases and becomes larger than that on the negative electrode side. Consequently, an osmotic pressure difference arises within the gel and is the driving force that controls the bending toward the negative electrode.

Figure 2 shows the bending angle of the IPN hydro-

gels with the PAAc content in 0.6 wt % NaCl solutions under an applied voltage of 20 V at room temperature. All the IPN hydrogels reached a bending angle of θ = 90°. The time required to reach a bend angle of 90° measured on a protractor scale (RT_{90}) of the AN41 gel sample was about 5 s, which was fastest time of all the gels tested. The speed of bending tended to increase with increasing PAAc content, and this was ascribed to the carboxyl group of PAAc, as the carboxyl group is an anionic group in an aqueous electrolyte and is deformed by an electrical field.

The samples were allowed to reach their swelling equilibrium in the corresponding bathing media before the application of electrical stimulation. As soon as an electric field was applied, the equilibrium state could not be maintained. The influence of the ionic concentration of the media on the bending behavior in response to an electric stimulus was examined as the concentration of NaCl in solution was varied from 0.2 to 1.2 wt % and the other conditions were kept constant. Figure 3 shows the RT_{90} values of the AN41 sample, showing an apparent peak at a 0.6 wt % NaCl concentration in the aqueous solution. The RT_{90} value decreased as the concentration of NaCl increased in solution when the concentration was less than 0.6 wt %, but it increased when the concentration of NaCl in solution was greater than 0.6 wt %. This effect arose because an increase in the electrolyte concentration in the solution induced an increase in the free ions moving from the surrounding solution toward the counter electrode, or into the IPN hydrogel. As a result, the RT_{90} value of the IPN hydrogel decreased. However, if the concentration of the NaCl solution were greater than a given critical concentration, then the shielding effect of the polyions by the other ions in the electro-
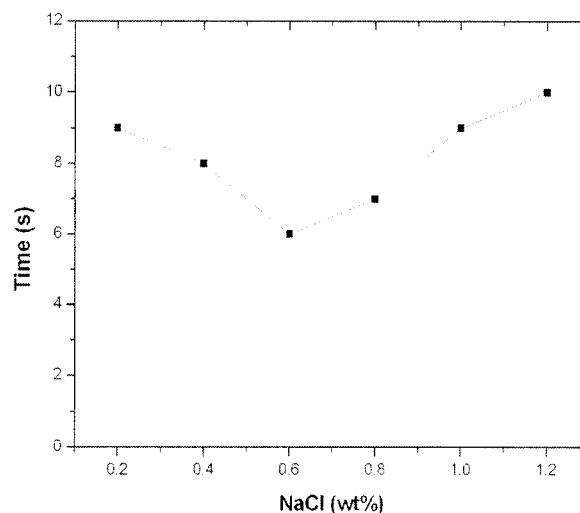

Figure 3 Effect of the NaCl concentration on the RT_{90} values of the AN41 hydrogel sample under an applied voltage of 15 V at room temperature.

lytic solution would occur. This would lead to a reduction in the electrostatic repulsion of the polyions and increase the RT_{90} value. As shown in Figure 1, the swelling ratios of the AN41 hydrogel sample in lower concentration electrolyte solutions were higher than those in solutions with higher electrolyte concentrations. Therefore, if the swelling ratios are compared to the bending results obtained in different solution concentrations (Fig. 3), the swelling of the IPN hydrogels with respect to the concentration of NaCl in solution can be considered not to affect the bending behavior significantly.

Figure 4 shows the relationship between the applied voltage and the bending angle of the AN41 hydrogel as a function of time in a 0.6 wt % NaCl solution at room temperature. The equilibrium bending angle and speed both increased with increasing applied voltage across the gel. However, no bending was observed in pure water, and this indicates that bending is induced by the electric current. It is generally thought that the deformation of a polymer hydrogel in an electric field is due to the voltage-induced motion of the ions and the concomitant expansion of one side of the polymer with the contraction of the other side. The observed rate of bending was fast, reaching its maximum in 5 s when the AN41 hydrogel in a 0.6 wt % NaCl electrolyte solution was subjected to an electric field (20 V). The direction of bending was toward the cathode.

Figure 5 shows that the PAAc/PAN IPN hydrogels exhibited a stimuli-responsive bending behavior according to the magnitude of the electric field applied (15 V) in 0.6 wt % NaCl solutions at room temperature. All the IPN hydrogels exhibited a reversible bending
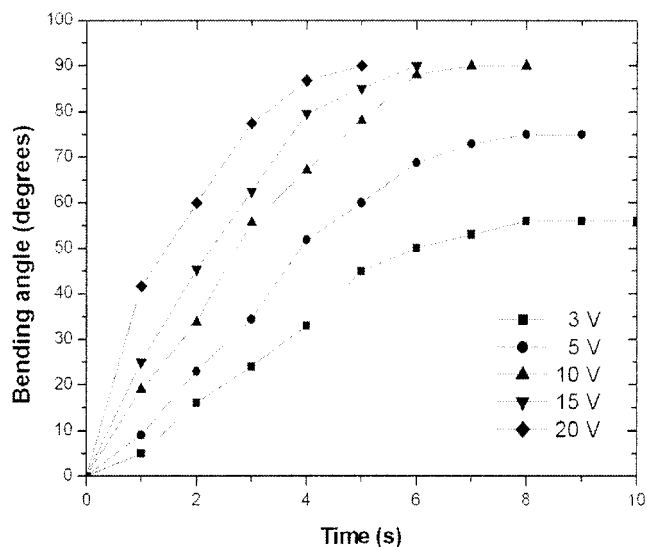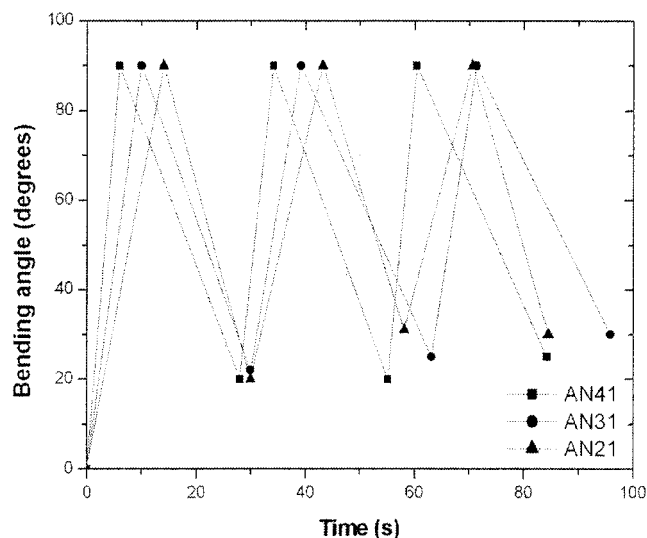

Figure 5 Reversible bending behavior of the IPN hydrogels with an applied voltage of 15 V (on–off) in 0.6 wt % NaCl solutions at room temperature.

behavior. With the electric field turned on, all the samples moved to a 90° position, and when the electric field was turned off, they tended to return to their original positions. When they did not completely return to their original position, then the observed deformation angle was only about 20°. This phenomenon was caused by the penetration of the solution ions. Under an applied voltage, IPN hydrogels bend, and so more solution can penetrate them.

CONCLUSIONS

When an electric field was applied to PAAc/PAN semi-IPN hydrogels, they bent toward the cathode because of the ionic groups of PAAc. IPN hydrogels containing a higher proportion of PAAc were more sensitive to an electric field. The swelling of the IPN hydrogels with respect to the concentration of the NaCl solution did not significantly affect the bending behavior.

Figure 4 Bending kinetics of the AN41 hydrogel sample as a function of the applied voltage in 0.6 wt % aqueous NaCl solutions.

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