# Electrical Response Characterization of Chitosan/Polyacrylonitrile Hydrogel in NaCl Solutions

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Received 27 November 2002; accepted 31 December 2002

**ABSTRACT:** A semi-interpenetrating polymer network (semi-IPN) hydrogel composed of chitosan and polyacrylonitrile (PAN) exhibited electrical-sensitive behavior. The swelling behavior of the semi-IPN was studied by immersion of the gels in aqueous NaCl solutions at various concentrations. The swelling ratio decreased with an increase in the concentration of the electrolyte solution. The stimulus response of the semi-IPN hydrogel in electric fields was also investigated. When swollen, the semi-IPN was placed between a pair of electrodes, and it exhibited bending behavior upon application of an electric field. The electro responsive behavior of the semi-IPN was also affected by the electrolyte concentration of the external solution. The semi-IPN also showed various degrees of increase in bending behavior depending on the electrical stimulus. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 91–96, 2003

**Key words:** hydrogel; interpenetrating polymer networks (IPN); swelling; bending

## INTRODUCTION

Chitosan is obtained from the deacetylation of chitin that is poly[(1,4)-2-acetamido-2-deoxy-B-D-glucose].[1,2] It has been widely studied and applied in the biomedical field because of its superior biocompatibility, nonantigenicity, nontoxicity (its degradation products are known to be natural metabolites), and its ability to improve wound healing and/or blood clotting, to absorb liquids, to form protective films and coatings and to perform selective binding of liquids, thereby lowering serum cholesterol levels. As a cationic flexible polyelectrolyte, water-swollen chitosan is a tough elastic material, but its mechano-electro-chemical behaviors have not yet been reported.[3]

Polyacrylonitrile (PAN) is a semicrystalline vinylic homopolymer with the repeating unit–($CH_2$—CHCN)–, usually in atactic form.[4] Several studies have shown that the use of PAN in electrolyte systems can have several advantages. PAN systems show good mechanical strength as films and are thermally stable.[5]

Polymer hydrogels have attracted attention as 'smart materials' because of their peculiar material forms. Hydrogels are three-dimensional, hydrophilic, polymeric networks capable of imbibing large amounts of water or biological fluids. The networks are composed of homopolymers or copolymers and are insoluble due to the presence of chemical or physical cross-links, such as entanglements or crystallites.[6] Many smart materials are made of polyelectrolytes, the deformation of which depends on their composition, structure, and other factors, such as the electric potential, pH, ionic strength of the bath medium, geometric size, and the crosslink density of materials.[7] A system that undergoes shape change and produces a contractile force in response to environmental stumuli is chemomechanical system. This system can transform chemical free energy directly into mechanical work to realize isothermal energy conversion, as can be seen in living organisms, for example, in muscle, flagella, and ciliary movement.[8] Polymer gels have been studied for their application in a variety of fields, such as chemical engineering, foodstuffs, agriculture, medicine and pharmaceuticals (e.g. controlled drug delivery systems). They may also have applications as muscle-like soft linear actuators, robotics, sensors, biomimetic energy transducing devices and separation techniques.[9]

There have been a number of reports of electrically induced phenomena in charged polymer networks. Yuk and Lee[10] demonstrated reversible bending of crosslinked acrylamide gel induced by an electric current in aqueous NaCl and proposed a mechanism for the bending phenomenon. Kim et al.[9] reported that interpenetrating polymer networks (IPNs) composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc) exhibited electrical-sensitive behavior. Sun and coworkers[7,11] reported the mechano-electro-chemical behavior of chitosan/poly(propylene glycol)

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Contract grant sponsor: Advanced Biometric Research Center (ABRC), supported by the Korea Science and Engineering Foundation (KOSEF).

Journal of Applied Polymer Science, Vol. 90, 91–96 (2003)
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composite fibers. These studies focused mainly on the electrical responses of polymer gels. To synthesize a powerful actuator or a material close in nature to skeletal muscles, it was necessary for the polymer gel to have both fast and sensitive electrical responses and strong mechanical strength. The IPN system was expected to be a promising candidate to meet these requirements because it could provide strong mechanical properties.[9]

In our present study, we examined changes in the swelling of a chitosan/PAN semi-IPN by NaCl solutions of various concentrations to confirm the bending mechanism of the semi-IPN under an electric stimulus. The bending behavior of the PAN/chitosan semi-IPN under an electric field and factors influencing the electric sensitivity were investigated.

## EXPERIMENTAL

### Materials

Chitosan with an average molecular weight of $2.0 \times 10^5$ and 76% deacetylation was supplied by Jakwang Co., Korea. PAN was purchased from Aldrich Chemical Co., USA. Glutaraldehyde (25 wt % solution in water) (GA) was purchased from Yakuri Chemical Co., Japan. Acetic acid and dimethyl sulfoxide were supplied by Duksan Pure Chemical Co., Ltd., Japan.

### Preparation of Semi-IPN hydrogel

Chitosan was dissolved completely in 50 wt % acetic acid. PAN was dissolved in dimethyl sulfoxide. A solution of equal parts chitosan and PAN was obtained by mechanical stirring for 12 h. The mixed solution was poured into petri dishes and dried in an oven at 60°C for 48 h. The film was removed from the petri dishes and washed with deionized water. Crosslinking of a sample was carried out by immersing the film in a GA solution at room temperature. To remove the nonreactive agents, the film was dipped into deionized water for 48 h and dried in a 40°C vacuum oven for one week.

### Swelling properties of Semi-IPN hydrogel

To measure the swelling ratio, preweighed dry samples were immersed in NaCl aqueous solutions of various concentrations. After excessive surface NaCl solution was removed with filter paper, the weight of the swollen samples was measured at various concentrations. The procedure was repeated until there was no further weight increase and then five more times. The swelling ratio was determined according to the following equation:

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

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

### Bending-angle measurement under electrical stimulus

Schematically, the technique for measuring bending angles in the non-contact DC electric field is shown in our previous work.[12] Aqueous NaCl solution was poured into a petri-dish equipped with two parallel carbon electrodes. The space between the electrodes was about 20 mm. The chitosan/PAN semi-IPN hydrogels were swollen in NaCl aqueous solutions at room temperature and cut into $20 \times 2$ mm samples. A hydrogel specimen 20 mm long was placed in the middle of the petri dish filled with 20 mL of solution. Voltage was then applied across the solution between the electrodes. The deformation was recorded and displayed on a video screen via a CCD camera (Mitsubishi, Japan) interfaced with a Compaq-Pentium computer. To test bending, one end of the specimen was fixed between the two electrodes. The amount of bending within a period of 1 s was recorded with a manual counter. A protractor-style scale was drawn on white paper and then placed beneath the petri dish. When the electric stimulus was applied, the angle of bending was measured by reading the deviated angle from the vertical position. The applied electric potentials were set at 5, 7, 10, 13 and 15 V. The bath medium was a 0.9 wt % NaCl solution.

## RESULTS AND DISCUSSION

The chitosan/PAN semi-IPN hydrogel exhibited electrolyte–concentration and pH sensitive swelling behavior. The effect of the concentration of NaCl solution on the equilibrium swelling was studied for the semi-IPN. The hydrogel swelled rapidly and reached equilibrium within 2 h. Figure 1 exhibits the swelling ratio of the semi-IPN hydrogel in aqueous NaCl solutions at room temperature. The semi-IPN hydrogel exhibited a high swelling ratio, in the range of 151–206%. It was shown that the swelling ratio decreased with an increasing concentration of NaCl solution. Generally, the swelling ratio of polyelectrolyte gels depends on the association state of ionic groups within the polymer and on the affinity of the hydrogel for water. On the other hand, according to the Donnan osmotic pressure equilibrium,[13] an increase in movable counterions in solution leads to a decrease in osmotic pressure within the gel and causes shrinkage.

When an electric field was applied to a sample of the chitosan/PAN semi-IPN hydrogel in aqueous NaCl solution, the gel showed significant and quick bending towards the anode. When the electric stimulus was removed, the semi-IPN hydrogel returned to its original position. Also, if the polarity of the electric

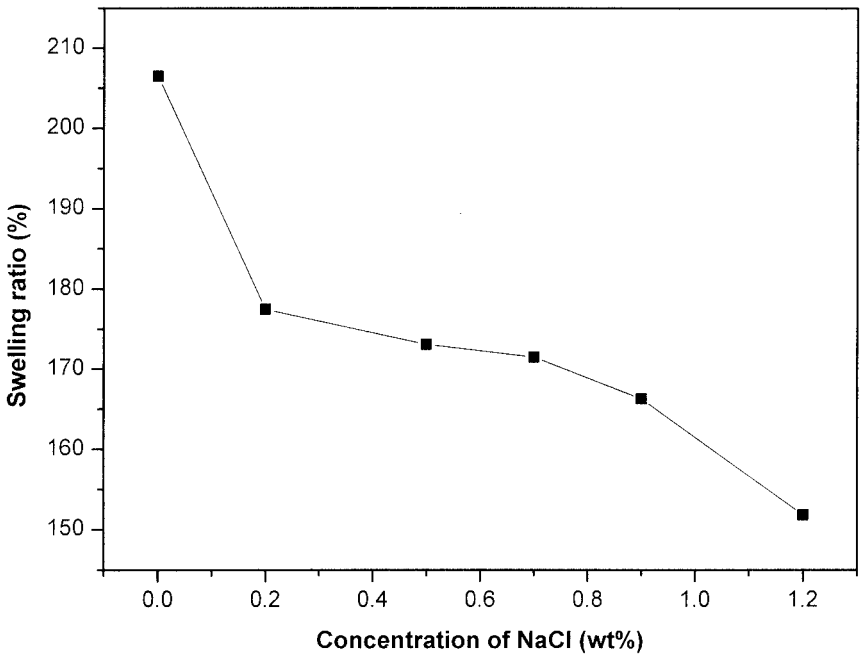


**Figure 1** Swelling ratio of chitosan/PAN semi-IPN hydrogel as a function of concentration of aqueous NaCl solution at room temperature.

field was altered, the semi-IPN hydrogel bent in the opposite direction. The mechanism of this kind of behavior is generally attributed to the idea that the deformation of a polymer hydrogel under an electric field is due to the voltage-induced motion of ions and the concomitant expansion of one side and contraction of the other. As a polycation, a chitosan/PAN specimen can experience greater swelling pressure on the side near the cathode than on the side near the anode. Thus, the specimen tended to bend toward the anode.[7,9] However, this has not been completely understood because there is a lack of well-developed theory for such chemomechanical kinetics.

The sample was allowed to reach its swelling equilibrium in the corresponding bath medium before electric stimulation. As soon as an electric field was applied, this equilibrium could not be maintained. The influence of medium ionic concentration on the bending behaviors of the semi-IPN hydrogel in response to an electric stimulation was studied by varying the concentration of NaCl solution from 0 to 1.2% by weight while keeping the other conditions constant. As shown in Figure 2, the equilibrium bending angle (EBA) of the semi-IPN hydrogel showed an apparent peak with an aqueous NaCl solution of 0.9% by weight. The bending degree increased with an increase in the concentration of the NaCl solution when the concentration of NaCl solution was less than 0.9% by weight, while the bending degree decreased with an NaCl solution of greater than 0.9% by weight. This is because an increase 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 semi-IPN hydrogel.[12] As a result, the bending angle of the semi-IPN hydrogel could increase. However, when the concentration of NaCl solution was greater than the 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. Similar results were reported by Sun and Mak[7] in their study of mechano-electrochemical behaviors of a hydrogel fiber based on chitosan/poly(ethylene glycol). As shown in Figure 1, the swelling ratio of the semi-IPN in the solution with a lower concentration of electrolyte was greater than that of a solution with a higher electrolyte concentration. Therefore, if the swelling ratio is compared with the bending results depending on the concentration of the solution (Fig. 2), it could be considered that swelling of the semi-IPN according to the concentration of the NaCl solution does not significantly affect the bending behavior of the semi-IPN.

Figure 3 shows the bending angle of the semi-IPN as a function of time in a 0.9 wt % NaCl solution at room temperature. The rate of bending is high, and the maximum bending angle is reached at 0.4 s. When the semi-IPN hydrogel in the NaCl electrolyte solution is subjected to an electric field, the semi-IPN bends toward the anode.

Figure 4 shows the variation of the bending angle of the semi-IPN hydrogel as a function of the applied voltage in aqueous 0.9 wt % NaCl. The equilibrium bending angle and bending speed increase with in-

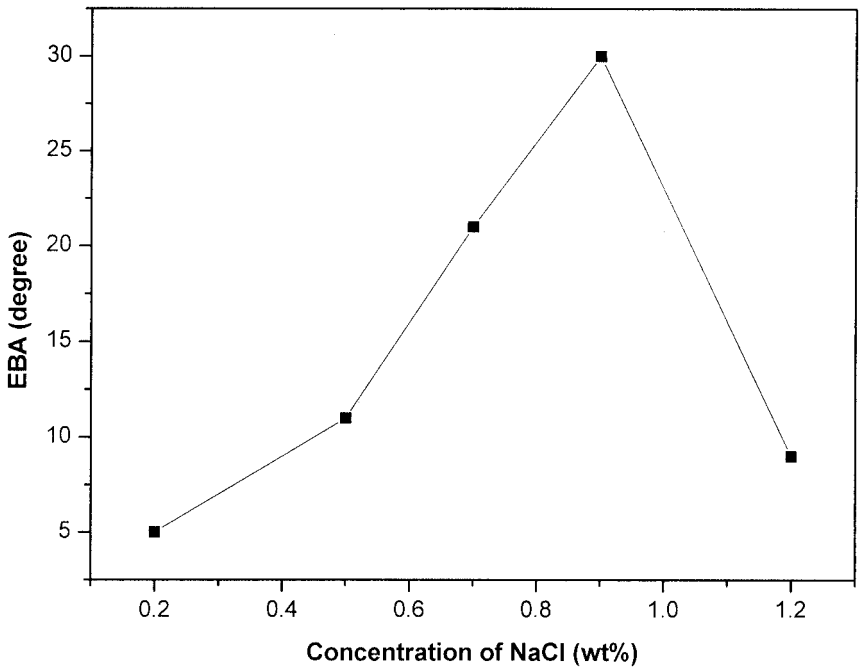


**Figure 2** Effect of concentration of NaCl solution on the equilibrium bending angle (EBA) at a constant 15 V voltage.

creasing voltage. However, bending is not observed in pure water, indicating that bending is induced by the electric current. It is generally thought that the deformation of a polymer hydrogel under an electric field is due to the voltage-induced motion of ions and the concomitant expansion of one side of the polymer and contraction of the other. Also, as shown in Figure 5, the chitosan/PAN semi-IPN hydrogel exhibited reversible bending behavior depending on the application of the electric field.

## CONCLUSIONS

The chitosan/PAN semi-IPN hydrogel was synthesized by radical polymerization and its bending behavior was studied. The semi-IPN hydrogel ex-

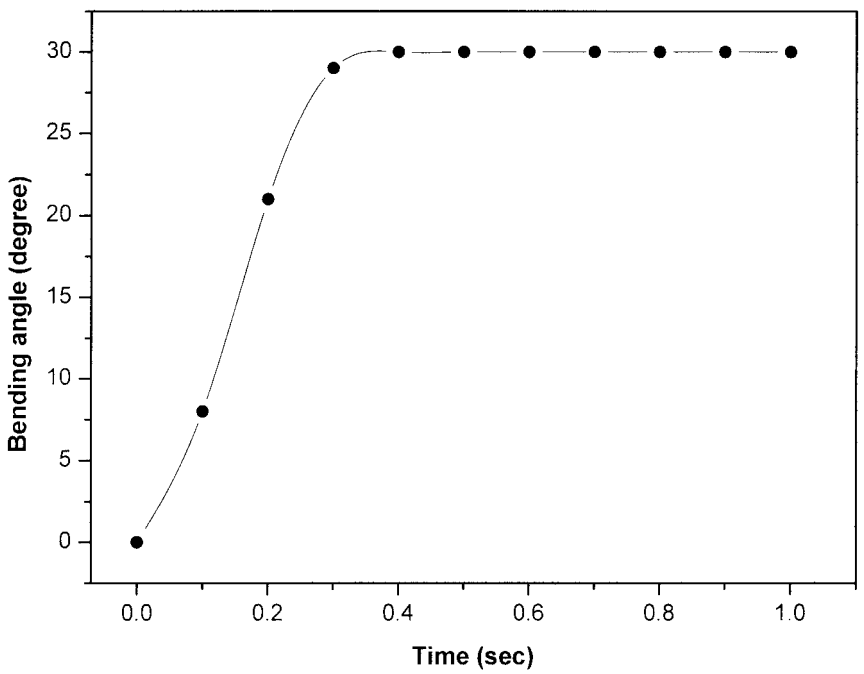


**Figure 3** Bending kinetics of the semi-IPN in a 0.9 wt % NaCl solution with changes in the applied voltage (15 V).

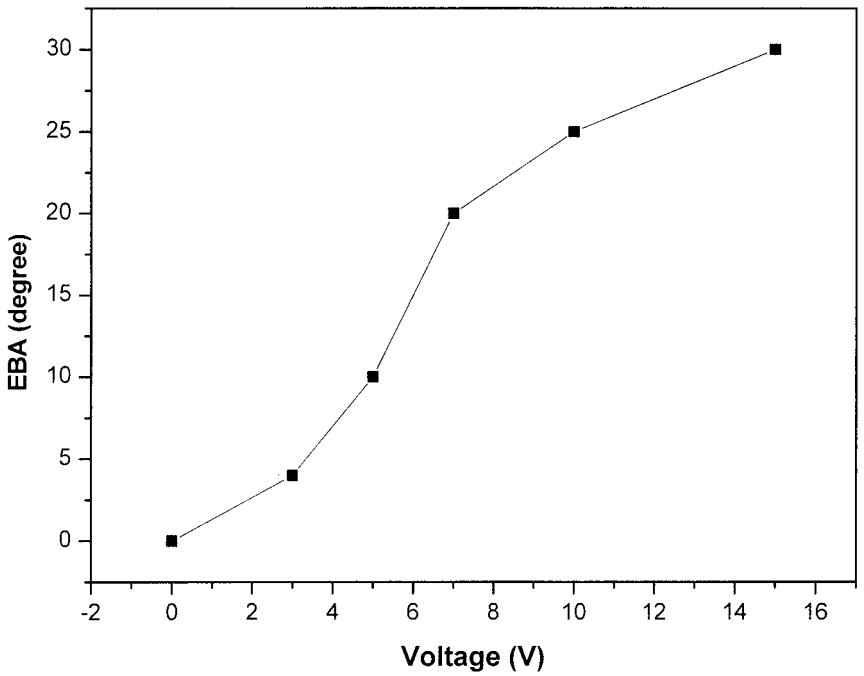


**Figure 4** Bending of chitosan/PAN semi-IPN in response to various amplitudes of the applied electric potential (in 0.9 wt % NaCl solution).

hibited a high swelling ratio in the range of 151–206%. When the semi-IPN hydrogel in NaCl electrolyte solution was subjected to an electric field, the semi-IPN hydrogel showed significant and quick bending toward the anode. When the electric stimulus was removed, the gel returned to its original position. The EBA of the semi-IPN was measured in NaCl solutions of various concentrations. The EBA and the bending speed of the semi-IPN reached a maximum in 0.9 wt % aqueous NaCl and increased with increasing voltage. The semi-IPN also showed stepwise bending behavior depending on the electric stimulus. Therefore, the present chitosan/PAN semi-IPN system can be useful for artificial organ

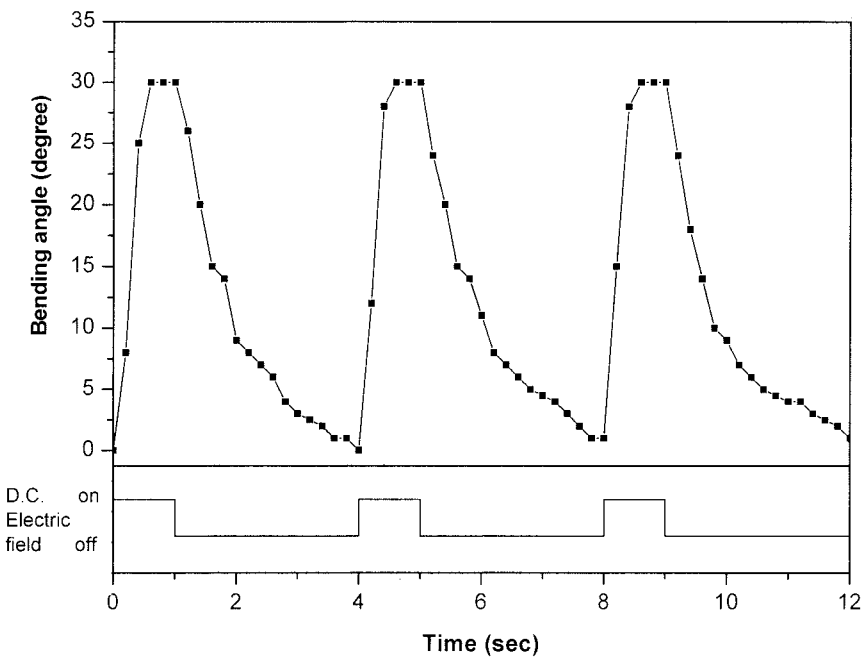


**Figure 5** Reversible bending behavior of the semi-IPN in a 0.9 wt % NaCl solution with changes in the applied voltage (15 V).

components such as muscle-like contractile structures, sensors and actuators.

This work is the result of research activities of the Advanced Biometric Research Center (ABRC), supported by the Korean Science and Engineering Foundation (KOSEF).

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