Electrical Behavior of Chitosan and Poly(hydroxyethyl methacrylate) Hydrogel in the Contact System

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ABSTRACT: Semi-interpenetrating polymer networks (semi-IPNs), as polymer hydrogels composed of chitosan and poly(hydroxyethyl methacrylate) (PHEMA), exhibiting electrical-sensitive behavior, were prepared. The swelling behavior of the chitosan/PHEMA hydrogels was studied by immersing the gels in various concentrations of aqueous NaCl solution. The electrical responses of the semi-IPN hydrogel, in applied electric fields, were also investigated. When the semi-IPN hydrogels were swollen, where one electrode was placed in contact with the gel and the other fixed 30 mm apart from one, they exhibited bending behavior on the application of an electric field on a contact system. The electroresponsive behavior of the present semi-IPN was also affected by the electrolyte concentration of the external solution. The semi-IPN also showed various degrees of increased bending behavior depending on the electric stimulus. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 915–919, 2004

Key words: chitosan; (poly(hydroxyethyl methacrylate); electrical properties; hydrogels; interpenetrating networks

INTRODUCTION

Polymer hydrogels have attracted much attention as "smart materials" because of their characteristic material forms. Many smart polymer hydrogels have been studied, with a particular investigative emphasis on their reversible volume changes in response to external stimuli, such as the ionic strength of the bath medium, pH, solvent, temperature, crosslink density of the materials, and electric field.[1–4] The systems experience shape changes and generate contractile forces in response to environmental stimuli. These kinds of phenomena are occasionally referred to as mechano-electrochemical (MEC) behaviors.[3,4]

Chitosan has many useful peculiarities, such as its hydrophilic, biocompatibility, and antibacterial properties.[5] Poly(hydroxyethyl methacrylate) (PHEMA) hydrogels have gained widespread recognition for their suitability in soft tissue and subcutaneous applications, attributed to their good mechanical strength, chemical resistance, and relatively high water content.[6] Much attention has been focused on improving their chemical and physical properties in the swollen state.

For the realization of a powerful actuator, or a material with properties closely resembling those of skeletal muscles, it is necessary to have a polymer gel with both fast and sensitive electric responses, and a high degree of mechanical strength. This kind of system can transform chemical free energy directly into mechanical energy, giving an isothermal energy conversion. Polymer gels have been studied for their application to a variety of fields (e.g., chemical engineering, medicine). Their electric voltage applications in sensors, robotics, drug-delivery systems, artificial muscle systems, and other biomechanical devices have also been investigated.[7–9] Kim et al.[9] reported that interpenetrating polymer networks (IPNs), composed of poly(vinyl alcohol) and poly(acrylic acid), exhibited electrical-sensitive behavior. Yuk and Lee[10] demonstrated the reversible bending of a crosslinked acrylamide gel, induced by electric current in aqueous NaCl solution, and proposed a mechanism for the bending phenomenon. In this study, changes in the swelling of a chitosan/HEMA semi-IPN, caused by various concentrations of NaCl solution, were examined. The bending behavior of the chitosan/HEMA semi-IPN, under an applied electric field to the contact system and the factors influencing the electrical sensitivity, were investigated.

EXPERIMENTAL

Materials

Chitosan (average molecular weight of 2.0×10^5; 76% degree of deacetylation) was supplied by Jakwang Co. (Ansung, Korea). The acetic acid was supplied by Duksan Pure Chemical Co. (Ansan, Korea). The HEMA and ethylene glycol–dimethacrylate (EGDMA) were purchased from Aldrich Chemical Co. (Milwaukee, WI), and the azobisisobutyronitrile (AIBN) was purchased from Junsel Chemical Co. (Osaka, Japan).

TABLE I
Composition and Designation of Chitosan/PHEMA Semi-IPN Hydrogels

Sample designation	Chitosan (wt %)	Poly (hydroxyethyl methacrylate) (wt %)
CSHM11	1	1
CSHM13	1	3
CSHM15	1	5

Preparation of semi-IPN hydrogel

The crosslinked PHEMA hydrogels were prepared by the polymerization of an aqueous reaction mixture, containing a monomer, a crosslinking agent, and an initiator. Mixtures of HEMA, AIBN, and EGDMA were dissolved in aqueous solution and stirred for 4 h at 60°C. The chitosan was completely dissolved in 1 wt % acetic acid. The chitosan and the HEMA mixing solution were mechanically stirred for 3 h. The detailed compositions and designations of the chitosan/ PHEMA semi-IPNs are listed in Table I. The mixed solutions were poured into petri dishes, and maintained in an oven at 60°C for 24 h. They were then dried in an oven at 50°C for 24 h. The products obtained were washed in distilled water for 1 week to remove any unreacted monomer and acetic acid. The film was dried in a vacuum oven at 40°C for 24 h.

Swelling properties of the semi-IPN hydrogel

To measure the swelling ratios, the preweighed dry samples were immersed in deionized water and in various aqueous solutions of NaCl, prepared with deionized water, and at various pHs, using buffer solutions at room temperature. After the excess surface solutions had been removed by blotting with a filter paper, the swollen samples from the various aqueous NaCl solutions were weighed again. The swelling ratio was determined according to the following equation:

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

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

Bending-angle measurement under electric stimulus

The schematic for the technique of measuring the bending angle in a contact dc electric field is shown in Scheme 1. An aqueous NaCl solution was poured into an instrument equipped with two parallel carbon elec-

trodes. The space between the electrodes was about 30 mm. The semi-IPN hydrogel was fully swollen in the aqueous NaCl solutions at room temperature and cut into strips [15 $\times$ 3 $\times$ 0.14 mm (length $\times$ width $\times$ thickness)]. One electrode was placed in contact with the gel, and the other fixed 30 mm apart from one. When an electric stimulus was applied, the degree of bending was measured by reading the deviated angle from the vertical position. The deformation was recorded onto a videoscreen using a CCD camera (Mitsubishi, Tokyo, Japan), as shown in Scheme 1.

RESULTS AND DISCUSSION

Swelling properties of the semi-IPN hydrogel

The chitosan/PHEMA semi-IPN hydrogels exhibited electrolyte concentration–dependent swelling behavior. The effects of the various concentrations of the aqueous NaCl on the equilibrium swelling of the semi-IPN hydrogels were investigated. The semi-IPN hydrogels swelled extremely rapidly, reaching equilibrium within 1 h.

Figure 1 shows the equilibrium swelling ratio (ESR) of the semi-IPN hydrogels in the various concentrations of aqueous NaCl at room temperature. It shows that the swelling ratios decrease with an increase in the NaCl concentration. Generally, the swelling ratio of polyelectrolyte gel depends on the association state of the ionic group within the polymer and on the affinity of hydrogel for water. On the other hand, according to the Donnan osmotic pressure equilibrium, an increase of the movable counterions in a solution leads to a decrease in the osmotic pressure within the gel, thus causing the gel to shrink.[14,15]
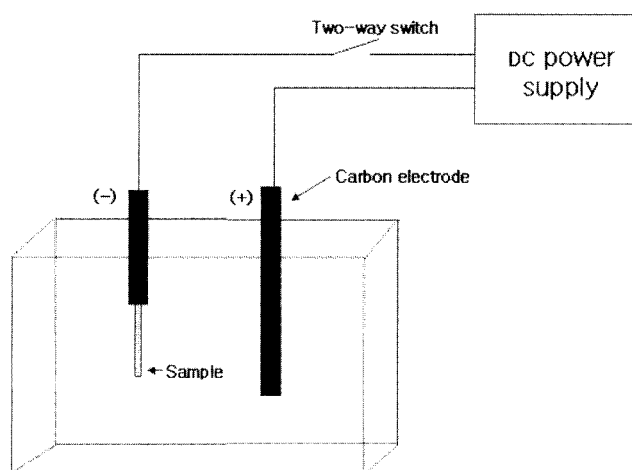
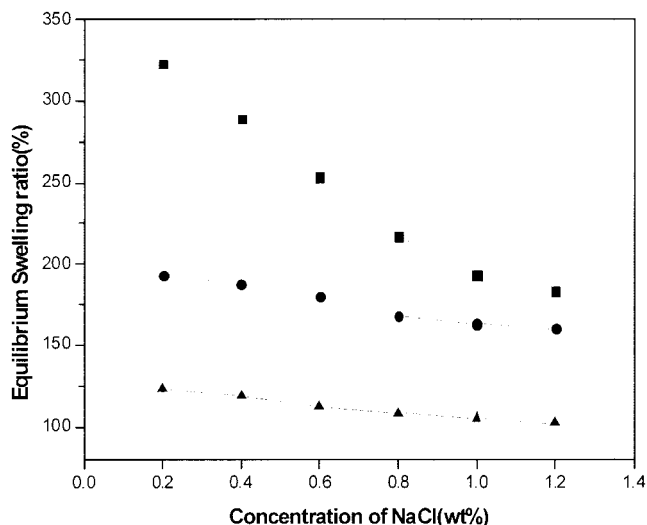**Scheme 1**   Schematic diagram of the bending device.

Figure 1 Equilibrium swelling ratio of the hydrogel, as a function of the concentration of aqueous NaCl solution, at room temperature.

Bending behaviors of semi-IPN hydrogel under electric fields

The influence of the ionic concentration of the media on the bending behaviors of the semi-IPN hydrogel was examined in response to an electric simulation, by varying the concentration of the NaCl solution from 0.2 to 1.2 wt %, while keeping the conditions constant and the pH at 7.

In Figure 2, the equilibrium bending angle (EBA) of the chitosan/PHEMA semi-IPN hydrogel showed an apparent peak with a 1.0 wt % aqueous NaCl solution, and the degree of bending increased with NaCl solution concentrations of less than 1.0 wt %. However, the degree of bending decreased with NaCl solution concentration greater than 1.0 wt %. As described above, an increase in the electrolyte concentration of a solution induces an increase in the free ions moving from the surrounding solution toward their counterelectrodes, or into the chitosan/PHEMA semi-IPN itself. As a result, the bending of the chitosan/PHEMA could increase. However, if the concentration of the NaCl solution is greater than its critical concentration, the shielding effect of the polyions, by the other ions in the electrolytic solute, would occur, leading to a reduction in the electrostatic repulsion of the polyions and a decrease in the degree of bending. When an electric field of 15 V was applied to a sample of the chitosan/PHEMA semi-IPN hydrogel, in an aqueous NaCl solution, the gel quickly bent out of the cathode. When the electric field was removed, the semi-IPN returned to its original position. Also, if the polarity of the electric field was altered, the semi-IPN hydrogels bent in the opposite direction. However, bending behavior was not observed in pure water because pure water is an insulating medium, thus indicating that

the bending behavior is induced by the electric current. To understand the mechanism of this kind of behavior, it is generally thought that the deformation of a polymer hydrogel, under an electric stimulus, is attributed to the voltage-induced motions of the ions, the concomitant expansion of one side the hydrogel, and the contraction of the other.[16-19] When a dc electric field is applied, mobile ions in the surrounding solution move toward their counterelectrode and migrate into the semi-IPN hydrogel. Thus, the osmotic pressure of the gel network near to the positive electrode increases, and becomes larger than that on the negative electrode side. Consequently, an osmotic pressure difference arises within the gel, which is the driving force that controls the bending toward the negative. However, this still remains to be completely explained, given the lack of well-developed theories for such MEC kinetics.

The correlation between the ESR and EBA is shown in Figure 3. By fixing the concentration at 0.2 or 1.2 wt %, the semi-IPN hydrogel experienced an increased ESR with increases in the PHEMA content. However, the EBA decreased with increasing PHEMA content. The ESR versus EBA of the semi-IPN hydrogel is osmotic pressure dependent. The swelling pressure caused by the ions can be expressed by the difference in the osmotic pressure attributed to the solute in the gel and the outer solution. In an electric field, the concentrations of ions in the gel and outer solution, at the sample–solution interface, change with time as a result of their transport through the gel. This showed that the bending angle of the gel is dependent on the ionic strength; that is, the gel swelling dependency on ionic strength determines the maximum bending angle when an electric current flows.
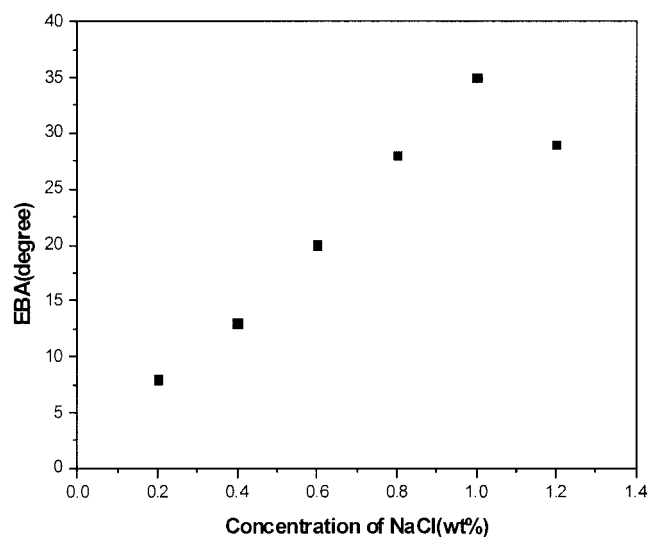

Figure 2 Effect of the aqueous NaCl solution concentration on the equilibrium bending angle (EBA) at a constant 15 V.
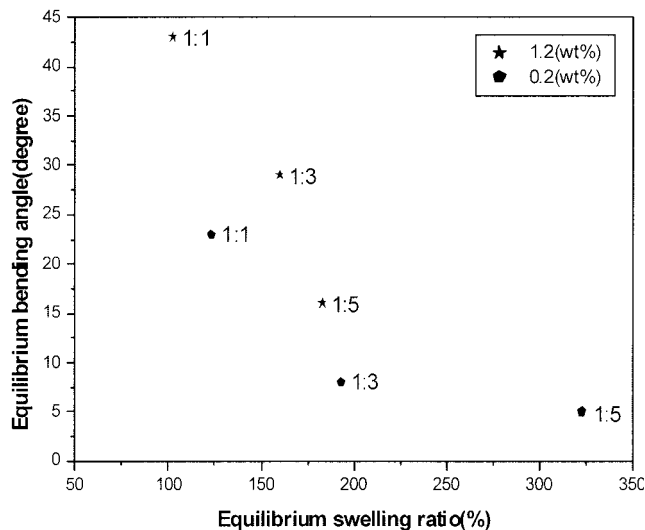
Figure 3 Influences of the electric field in the contact system on the bending kinetics at various voltages.

Figure 5 Effect of the electric field on the bending kinetics at various voltages in the contact system.

Figure 4 shows the degree of bending of the semi-IPN hydrogel, as a function of the electric field voltage, in a 1.0 wt % aqueous NaCl solution at room temperature. The slope of the plot of bending versus time became steep for a short time, with an increase in the applied voltage after the equilibrium state had been reached. The gel gradually bent out of the cathode on the application of various potentials. This means that the bending behavior is governed by the initial conditions. The degree and speed of bending increased with increasing applied voltage, which could be interpreted as an enhancement in the transfer rate of the immobile ions within the hydrogel network to the external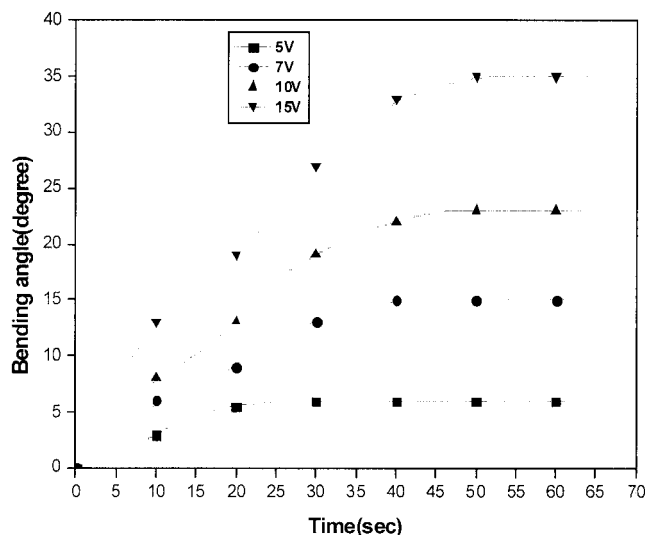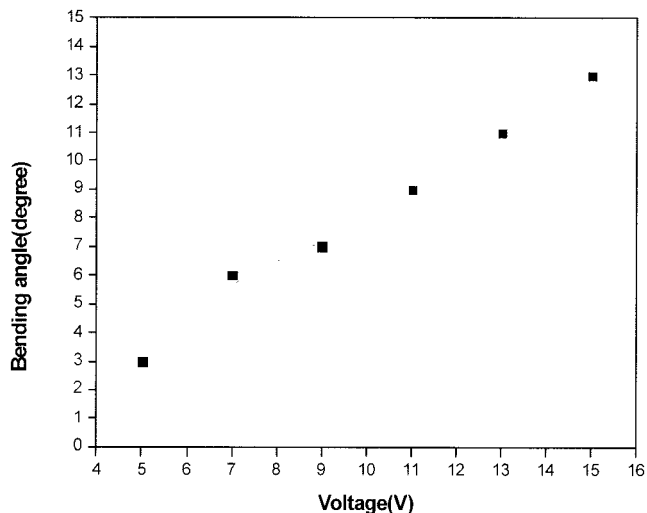 solution, whereas the free ions moved from the external solution into the hydrogel network as the voltage of the electric field was increased.

Figure 5 shows the degree of bending of the semi-IPN hydrogel, as a function of the various applied voltages, reached within 10 s, in a 1.0 wt % aqueous NaCl solution. The increasing degree, speed, and angle of bending, with increases in the applied voltage, of the hydrogel indicate that the bending was induced by the flow of the electric current. However, the bending behavior did not occur in pure water because pure water is an insulating medium. Analysis of the relationship between Figure 3 and Figure 4 showed that the bending speed is proportional to the applied voltage. These quantitative relationships could be useful in the design of actuator devices and artificial actuators.

CONCLUSIONS

The stimuli response of the chitosan/PHEMA semi-IPN hydrogels to applied electric fields was investigated through measurements of the bending behaviors. The EBA and the bending speed of the semi-IPN hydrogels were greatest in a 1.0 wt % aqueous NaCl solution, and increased with increases in the applied voltage. The semi-IPN hydrogels exhibited considerable sensitivity to contact electric stimuli. The bending behavior of the chitosan/PHEMA semi-IPN hydrogel, induced by a dc electric field, was dependent on the applied electric voltage and ionic strength of the medium. The differences in osmotic pressure and electric field in contact with the system were major factors in controlling the bending. These factors can be handled to prompt the chitosan/PHEMA hydrogel to bend further and faster. Increasing the electric voltage can increase the speed of deformation. Thus, these phe-

Figure 4 Bending speed of the hydrogel at various amplitudes of the electric field.

nomena can be useful in artificial organ components, such as controlled drug-delivery systems, musclelike contractile structures, or soft linear actuators, sensors, switches, biomimetic energy-transducing devices, and separation techniques.

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