

Electric Stimuli Responses to Poly(vinyl alcohol)/Chitosan Interpenetrating Polymer Network Hydrogel in NaCl Solutions

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ABSTRACT: An interpenetrating polymer network (IPN) hydrogel composed of poly(vinyl alcohol) (PVA) and chitosan exhibited electric-sensitive behavior. The PVA/chitosan IPN hydrogel was synthesized by an ultraviolet (UV) irradiation method that is used in several biomedical and industrial fields. The swelling behavior of the PVA/chitosan IPN hydrogel was studied by immersion of the gel in NaCl aqueous solutions at various concentrations. The swelling ratio decreased with increasing concentration of NaCl solution. The stimuli response of the IPN hydrogel in electric fields was also investigated. When a swollen PVA/chitosan IPN was placed between a pair of electrodes, the IPN exhib-

ited bending behavior in response to the applied electric field. The bending angle and the bending speed of the PVA/chitosan IPN increased with increasing applied voltage and concentration of NaCl aqueous solution. The PVA/chitosan IPN also showed stepwise bending behavior depending on the electric stimulus. In addition, thermal properties of PVA/chitosan IPN were investigated by differential scanning calorimetry (DSC) and dielectric analysis (DEA). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2285–2289, 2002

Key words: hydrogels; swelling; bending behavior; electric field

INTRODUCTION

Polymer gels have attracted attention as “intelligent materials” because of their peculiar material forms.¹ They consist of an elastic crosslinked network and a fluid filling the interstitial spaces of the network.² Polymer hydrogels can change their volume and shape reversibly depending on several external physicochemical factors; such as, temperature, solvent composition, pH, and ionic concentration.^{3–10} Therefore, 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 these possibilities, electric-sensitive polymer hydrogels actuated by an electric stimulus seem to be particularly interesting because mechanical energy has been triggered by an electric signal.¹¹ These hydrogels have also been developed and studied with regard to the application to several biomedical and industrial field; for examples, controlled drug delivery systems, muscle-like soft linear actuators, biomimetic energy transducing devices, and separation techniques.^{12,13}

There have been a number of reports of electrically induced phenomena in charged polymer networks.

Tanaka et al.¹⁴ 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. Kim et al.¹⁵ reported bending of a copolymer of 2-acrylamido-2-methyl-1-propane sulfonic acid and butyl methacrylate in NaCl solution on the application of electric current. Yuk and Lee¹⁶ demonstrated reversible bending of crosslinked acrylamide gel induced by electric current in aqueous NaCl and proposed a mechanism for the bending phenomenon. Kim et al.¹¹ reported that interpenetrating polymer networks (IPNs) composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) exhibited electric-sensitive behavior. 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 IPN system could be a promising candidate to meet these requirements because it can induce quite strong mechanical properties. Therefore we report here on an IPN hydrogel composed of PVA, with high mechanical strength and easy processibility,¹¹ and chitosan, with excellent biocompatibility and mechanical properties.^{17,18}

In the present study, we would like to report on the preparation and swelling properties of this novel electrolyte concentration-dependent hydrogel. The bending behavior of the PVA/chitosan IPN under an electric field and factors influencing the electric sensitivity

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were investigated. In addition, differential scanning calorimetry (DSC) and dielectric analysis (DEA) studies were performed to determine the thermal properties of the PVA/chitosan IPN hydrogel.

EXPERIMENTAL

Materials

Chitosan, with average of molecular weight of 2.0×10^5 and degree of deacetylation of 76%, was obtained from Jakwang Company (Korea) and used without purification. PVA and acryloyl chloride were purchased from Aldrich Chemical Company, and the average molecular weight of PVA was 1.5×10^5 . 2,2-Dimethoxy-2-phenylacetophenone (DMPAP) was used as a photoinitiator and all other chemical reagents were of extra pure grade.

Preparation of PVA/chitosan IPN hydrogel

PVA was added to deionized water and heated at 80 °C for 1 h to make a solution containing 10 wt % PVA by weight. Acryloyl chloride and DMPAP in tetrahydrofuran (THF) were added to the PVA aqueous solution. Chitosan was dissolved in 4 wt % acetic acid aqueous solution to prepare a 3 wt % chitosan solution, and then the chitosan solution was added to the PVA mixture. The weight ratio of the PVA/chitosan mixture was adjusted to 3:1. This mixture was mixed for 30 min. The mixed solution was poured into a Petri dish and stored in a box and exposed to a 450 W UV lamp (Ace Glass Company, USA) placed above the mould at a height of 20 cm for 1 h under N₂ atmosphere. The irradiated sample was dried in the oven at 50 °C for 12 h, and the dry film was obtained and washed with deionized water to remove any unreacted materials that were not incorporated into the network.

Swelling properties of PVA/chitosan IPN hydrogel

To measure the equilibrium water content (EWC), pre-weighed dry samples were immersed in various NaCl aqueous solutions. After excessive surface water was removed with the filter paper, the weight of swollen samples was measured at various time intervals. The procedure was repeated until there was no further weight increase and then five more times. EWC was determined according to the following equation:

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

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

Bending-angle measurement under electric stimulus

NaCl aqueous solution was poured into a Petri dish equipped with two parallel carbon electrodes for bending-angle measurement in the DC electric field. The separation between the electrodes was ~30 mm. The PVA/chitosan IPN hydrogel samples were swollen in NaCl aqueous solutions at room temperature and cut into $20 \times 5 \times 0.14$ -mm sheet. One end of the sample sheet was fixed, and the gel was placed in the center of the Petri dish. A white paper-drawn scale in angle degree was placed outside of the Petri dish bottom. When an electric stimulus was applied, the degrees of bending were measured by reading the deviated angle from the off-electric field position.

Thermal properties of PVA/chitosan IPN hydrogel

Differential scanning calorimetry (TA Instruments DSC 2010) characterized the thermal property of the IPN at a 10 °C/min heating rate and 65 mL/min N₂ flow rate. Dielectric measurements were conducted to observe the glass transition temperature (T_g) and relaxation behaviors of IPN. Measurements of dielectric constant, ϵ' , and dielectric loss factor, ϵ'' , were carried out by dielectric analysis (DEA; TA Instruments DEA 2970) with a parallel plate ceramic sensor. The experiment was conducted at 40–300 °C at a rate of 3 °C/min, with dry nitrogen adjusted to a flow rate of 50 mL/min. Applied frequencies were 300, 500, and 700 Hz.

RESULTS AND DISCUSSION

Swelling properties of PVA/chitosan IPN

The IPN composed of chitosan and PVA was synthesized by UV irradiation using DMPAP as a photoinitiator. PVA/chitosan IPN exhibited a temperature-responsive swelling behavior due to the association/dissociation of the hydrogen bonding between the hydroxyl groups in the PVA and the amino groups in the chitosan within the IPN. Also, the hydrogel showed electrolyte concentration-sensitive swelling behavior. The effect of concentration of NaCl aqueous solution on the equilibrium swelling was studied for PVA/chitosan IPN hydrogel. The IPN swelled very rapidly and reached equilibrium within 3 h. The swelling ratio of the IPN hydrogel in aqueous NaCl solutions at room temperature is shown in Figure 1. It is evident that the swelling ratio decreases with 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 hydrogels for water.¹⁹ On the other hand, according to the Donnan osmotic pressure equilibrium,²⁰ an increase of movable counterions in

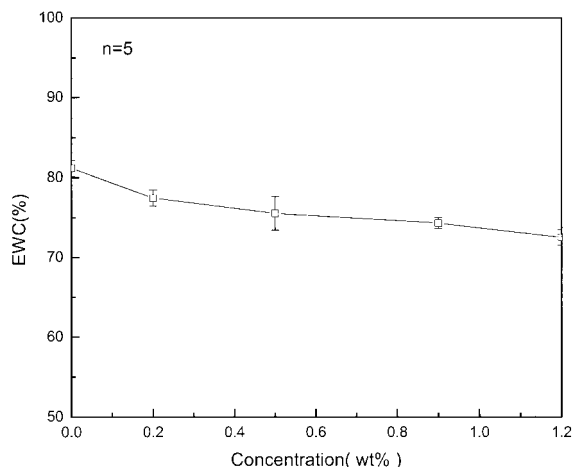


Figure 1 Swelling behavior of PVA/chitosan IPN hydrogel as a function of NaCl concentration of surrounding aqueous medium at pH 7.

solution leads to a decrease of osmotic pressure within the gel and causes shrinkage of the gel.

Bending behavior of IPN hydrogel under electric fields

When an electric field was applied to a sheet of PVA/chitosan IPN hydrogel in the NaCl aqueous solution, the gel showed significant and quick bending toward the negative electrode. 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.

In the bending angle measurement, the initial position of the IPN hydrogel sheet (bending angle = 0°) is the position of non-applied electric field. We could not make straight the hydrogel sheet in a NaCl solution because it is very flexible. However, we tried starting the initial position of the gel sheet (bending angle = 0°, off-DC field) at ~45° horizontally. The gel bent into a curve on the application of the electric potential. We observed the bending behavior of the hydrogel under this electric field for 60s, and the equilibrium bending-angle value had evidently not been attained. However, we focused on the quick response to electric stimulus.

The variation of bending angle of the IPN hydrogel as a function of the applied voltage in aqueous NaCl at 0.2 and 0.9% by weight is shown in Figures 2 and 3, respectively. The PVA/chitosan IPN exhibited a reversible bending behavior according to the application of the electric field. The bending angle increases with increasing voltage across the gel, but bending is not found in pure water, indicating that bending is induced by the electric current. When an electric field was applied to the gel immersed in a NaCl electrolyte solution, electrochemical reactions (positive electrode:

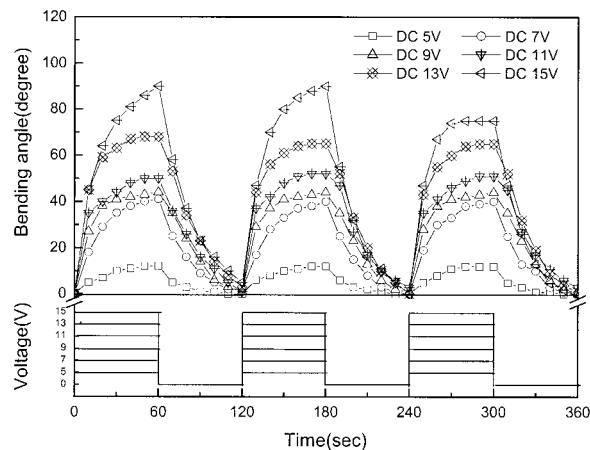


Figure 2 Variation of bending angle as a function of the applied voltage in aqueous NaCl at 0.2% by weight.

$2\text{Cl}^- \rightarrow 2\text{Cl}_2 + 2\text{e}^-$; negative electrode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$) occurred.²¹ On the application of electric current, mobile ions (Na^+ and OH^-) move toward their counterelectrodes. The diffusion coefficient of OH^- in aqueous solution at infinite dilution at 25 °C is five times larger than that of Na^+ . As a consequence, ion concentration gradients are induced and the osmotic pressure on the positive electrode side becomes larger than that on the negative side. This osmotic pressure difference is the driving force of bending toward the negative electrode.¹⁶

The influence of concentration of NaCl solution on the bending angle and bending speed of PVA/chitosan IPN at 7 V constant voltage is shown in Figure 4. The bending angle increases with increasing concentration of NaCl solution. As already shown in Figure 1, the swelling ratio of the PVA/chitosan IPN in the solution with the lower concentration of electrolytes was greater than that of the higher electrolyte concentration. Therefore, if this result is compared with the bending results depending on the concentration of the

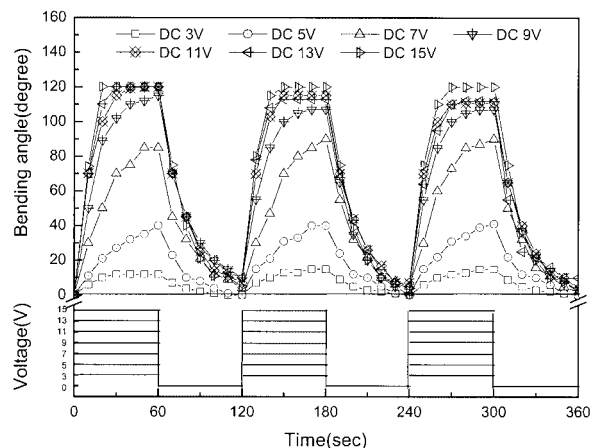


Figure 3 Variation of bending angle as a function of the applied voltage in aqueous NaCl at 0.9% by weight.

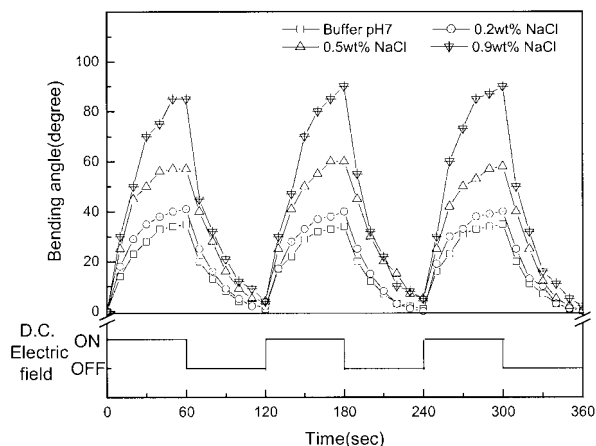


Figure 4 Influence of concentration of NaCl solution on the bending angle and bending speed of PVA/chitosan IPN at 7 V constant voltage.

solution in Figure 4, we could consider that the swelling of the PVA/chitosan IPN by the concentration does not significantly affect the bending behavior of the IPN.

Thermal properties of PVA/chitosan IPN

DSC and the DEA were used to determine the thermal properties of the PVA/chitosan IPN. To investigate the state of the IPN hydrogel as a function of temperature, we studied the fundamental thermal properties of the IPN.

The DSC melting thermograms of PVA, chitosan, and IPN hydrogel are shown in Figure 5. PVA reveals a sharp melting endothermic peak at 219 °C, whereas a weak and broad melting endothermic peak of the PVA segment in the IPN, caused by crosslinking reaction and IPN formation, appeared at 218 °C. On the other hand, the melting temperature (T_m) of the chi-

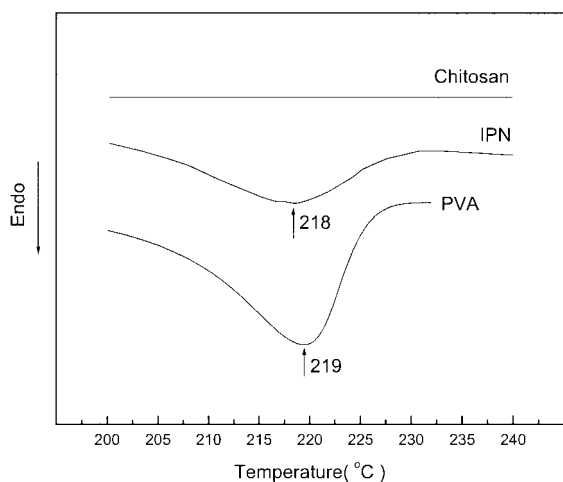


Figure 5 DSC melting endotherms of PVA, chitosan, and IPN.

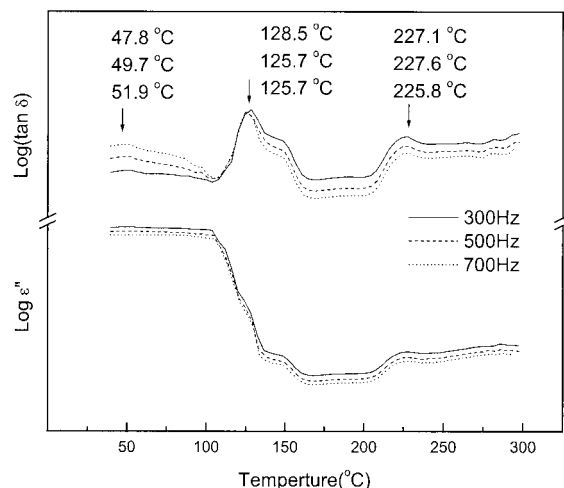


Figure 6 Dielectric analysis of PVA/chitosan IPN.

tosan network cannot be determined from DSC analysis. Although chitosan has crystalline regions, T_m cannot be determined because of the rigid-rod polymer backbone with strong inter- and/or intramolecular hydrogen bonding.²² This behavior is frequently detected in many polysaccharides, such as cellulose and chitin derivatives.²³ In general, the T_g of a crosslinked polymer is difficult to detect using the ordinary DSC technique. Therefore, in this study, the more sensitive DEA was employed to determine the T_g of each component in the IPN. Plots of $\log(\tan \delta)$ versus loss factor ($\log \epsilon''$) of the IPN depending on temperature at 300, 500, and 700 Hz are shown in Figure 6. Three relaxation peaks appeared at ~ 50 , 130, and 230 °C in the IPN. The T_g of chitosan appears at >150 °C.²⁴ Accordingly, the temperature of the maximum $\tan \delta$, ~ 130 °C, is considered to be the T_g of chitosan. Another maximum $\tan \delta$ temperature at 230 °C was thought to be the T_m of PVA segments in IPN, as was seen from DSC analysis. The lowest maximum $\tan \delta$ temperature was assumed to be the T_g of PVA segments in IPN. From the result of DEA, the IPN exhibited two T_g s, indicating the presence of phase separation in the IPN.

CONCLUSIONS

A PVA/chitosan IPN hydrogel was synthesized by UV irradiation, and the properties of the hydrogel were studied. The IPN hydrogel exhibited a high EWC in the range 75–85%. The swelling ratio decreased with increasing concentration of aqueous NaCl solution. When the PVA/chitosan IPN hydrogel in NaCl electrolyte solution was subjected to an electric field, the IPN bent toward the negative electrode. When the electric stimulus was removed, the IPN hydrogel returned to its original position. The bending angle and the bending speed of the PVA/chitosan IPN hydrogel

increased with increasing applied voltage and concentration of aqueous NaCl solution. The PVA/chitosan IPN hydrogel also showed stepwise bending behavior depending on the electric stimulus. The results of DEA show that the IPN exhibited two T_g s, indicating the presence of phase separation in the IPN. Therefore, the present PVA/chitosan 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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