Characteristics of Electrical Responsive Chitosan/Polyallylamine Interpenetrating Polymer Network Hydrogel

Seon Jeong Kim, Sang Jun Park, Mi-Seon Shin, Sun I. Kim

Department of Biomedical Engineering, Hanyang University, Seoul 133-791, Korea

Received 6 August 2001; accepted 30 January 2002

ABSTRACT: An interpenetrating polymer network (IPN) hydrogel composed of chitosan and polyallylamine exhibited electric-sensitive behavior. The chitosan/polyallylamine IPN hydrogel was synthesized by radical polymerization using 2,2-dimethoxy-2-phenylacetophenone (DMPAP) and methylene bisacrylicamide (MBAAm) as initiator and crosslinker, respectively. The swelling behavior of the IPN was studied by immersion of the gel samples in aqueous NaCl solutions at various concentrations and pHs. The swelling ratio decreased with increasing concentration and pH of electrolyte solution. The stimuli response of the IPN hydrogel in electric fields was also investigated. When a swollen the IPN was placed between a pair of electrodes, the IPN exhibited bending behavior in response to the applied electric field. The IPN also showed stepwise bending behavior depending on the electric stimulus. In addition, thermal properties of the IPN were investigated by differential scanning calorimetry (DSC) and dielectric analysis (DEA). © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2290–2295, 2002

Key words: hydrogels; bending behavior; electric field; thermal analysis

INTRODUCTION

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 because of the presence of chemical or physical crosslinks, such as entanglements or crystallites.[1] Smart polymer hydrogels have been studied with a particular emphasis on their reversible volume changes in response to external stimuli, such as the pH, solvent composition, temperature, ionic concentration, and electric field.[2–9] The system that undergoes shape change and produces contractile force in response to environmental stimuli is called a 'chemomechanical system'. This system can transform chemical free energy directly into mechanical work to give isothermal energy conversion and this can be seen in living organisms; for examples, in muscle, flagella, and in ciliary movement.[10] Polymer gels have been studied for applications in a variety of fields (e.g., chemical engineering, medicine and pharmaceuticals, food, and agriculture) for a variety of uses (e.g., controlled drug delivery systems, muscle-like soft linear actuators, robotics, sensors, biomimetic energy transducing devices, and separation techniques).[11–13]

There have been a number of reports of electrically induced phenomena in charged polymer networks. Tanaka et al.[14] reported that a hydrolyzed acrylamide gel (~20% of amide groups were converted to carboxyl groups) collapsed in an acetone/water (50% by volume) binary mixture on application of an electric field. They interpreted the phenomenon using the Flory–Huggins theory. Yuk and Lee[15] 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) (PAAc) exhibited electric-sensitive behavior. Sun et al.[16,17] reported mechano-electro-chemical behavior of chitosan/poly(propylene glycol) composite fibers. 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.[11] Therefore we report here on an IPN hydrogel composed of chitosan and polyallylamine. Chitosan is a deacetylated derivative of chitin that is poly((1,4)-2-acetamido-2-deoxy-β-D-glucose). It has been widely studied and applied in the biomedical field because of its

Correspondence to: S. I. Kim, Sungdong P.O. Box 55, Seoul 133-605, Korea (sunkim@hanyang.ac.kr)

Journal of Applied Polymer Science, Vol. 86, 2290–2295 (2002)

good biocompatibility, biodegradability, nontoxicity, and easy availability.[16]

In our previous study,[18] we synthesized novel PVA/chitosan IPN hydrogels by ultraviolet (UV) irradiation and reported the swelling ratio and the bending behavior of PVA/chitosan IPN. The swelling ratio decreased with increasing concentration of aqueous NaCl solution. The equilibrium bending angle and the bending speed of the PVA/chitosan IPN increased with the applied voltage and concentration of NaCl solution.

In the present study, we would report on the preparation and swelling properties of novel electrolyte concentration- and pH-dependent hydrogel. Also, the bending behavior of the chitosan/polyallylamine IPN under an electric field and factors influencing the electric sensitivity were investigated. In addition, differential scanning calorimetry (DSC) and dielectric analysis (DEA) studies were performed to determine the thermal properties of the chitosan/poly-allylamine IPN hydrogel.

EXPERIMENTAL

Materials

Chitosan, with an average of molecular weight of 2.0 $\times 10^5$ and a degree of deacetylation of 76%, was obtained from Jakwang Company, Korea. Polyallylamine, purchased from Sigma Company (USA), had an average molecular weight of 6.5×10^4. 2,2-Dimethoxy-2-phenylacetophenone (DMPAP) and methylene bisacrylicamide (MBAAm) were purchased from Sigma Company and Aldrich Company (USA) and were used for hydrogels preparation without further purification. All other chemical reagents were used extra pure grade.

Preparation of the IPN hydrogels

Polyallylamine was mixed with 1 wt % DMPAP and 0.5 mol % MBAAm in tetrahydrofuran (THF). Herein, DMPAP and MBAAm were used initiator and crosslinker, respectively. Chitosan was dissolved in 1 wt % acetic acid aqueous solution to prepare a 2 wt % chitosan solution. Later, the 2 wt % chitosan solution was added to the polyallylamine reaction mixture. This mixture was heated at 65 °C for 3 h. The solutions were poured in a Petri dish and dried at 50 °C for 12 h. 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 the IPN

To measure the equilibrium water content (EWC), preweighed dry samples were immersed in various pHs and 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:

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

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

Bending-angle measurement under electric stimulus

Aqueous NaCl solution was poured in a Petri dish equipped with two parallel carbon electrodes. The separation between the electrodes was ~30 mm. The chitosan/polyallylamine IPN hydrogel samples were swollen in NaCl aqueous solutions at room temperature and cut into 20-mm-long × 5-mm-wide sheets. 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 vertical position.

Thermal properties of the IPN

DSC (TA Instruments DSC 2010) was used to characterize the thermal properties of the IPN at a 10 °C min^{-1} heating rate and a 65 mL min^{-1} N_2 flow rate. Dielectric measurements were conducted to observe the glass transition temperature (T_g) and relaxation behavior of IPN. Dielectric constant, ε', and dielectric loss factor, ε'', were determined by DEA with a dielectric analyzer (TA Instruments DEA 2970) equipped with a parallel plate ceramic sensor. The experiment was conducted at −60–200 °C at a rate of 3 °C min^{-1}, with dry nitrogen adjusted to a flow rate of 50 mL min^{-1}. Applied frequencies were 100 and 500 Hz, and 1 kHz.

RESULTS AND DISCUSSION

Swelling properties of the IPN hydrogel

The IPN composed of chitosan and polyallylamine was synthesized by radical polymerization, using DMPAP and MBAAm as initiator and crosslinker, respectivelyThe chitosan/polyallylamine IPN hydrogel exhibited electrolyte concentration- and pH-sensitive swelling behavior. The effect of concentration of NaCl aqueous solution on the equilibrium swelling was studied for the IPN. The hydrogel swelled rapidly

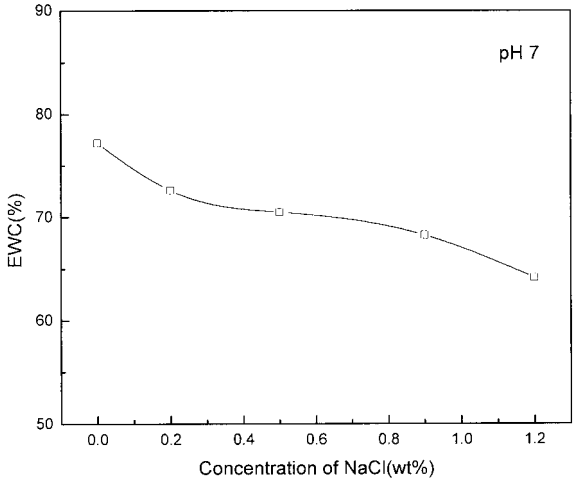

Figure 1 Equilibrium water content (EWC) of chitosan/polyallylamin IPN hydrogel as function of concentration of aqueous NaCl solution at room temperature.

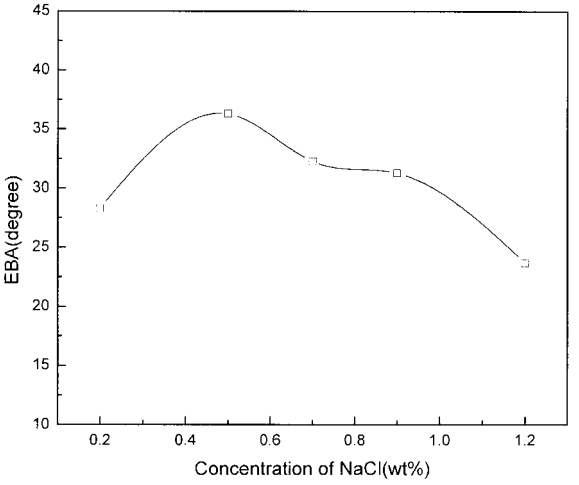

Figure 3 Effect of concentration of NaCl solution on the equilibrium bending angle (EBA) at 5 V constant voltages.

and reached equilibrium within 2 h. All swelling behaviors are plotted as the average of FIVE trials. The swelling ratios of the IPN hydrogel in aqueous NaCl solutions at room temperature are shown in Figure 1. The swelling ratio decreased 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 solution leads to a decrease of osmotic pressure within the gel and causes shrinkage of the gel.

pH-dependent swelling behavior was observed at 35 °C, with changes in pH 2–10 buffer solution, as shown in Figure 2. The IPN showed a lower specific solution content at basic pH compared with acidic pH. There is hydrogen bonding between —OH of chitosan and —NH_2 from polyallylamine. There are —NH_3^+ groups on the molecular backbone of the chitosan/polyallylamine IPN hydrogel in an acid medium. These ionizable groups have the property of connecting and disconnecting with the —OH in the chitosan in different solvent media. In the acidic medium, hydrogen bonds tend to dissociate, which results in a decrease of interaction among chains and an increase in equilibrium volume. On the other hand, in the alkaline medium, hydrogen bonds tend to associate because —NH_3^+ groups could be changed into —NH_2 because of the low concentration of H^+.

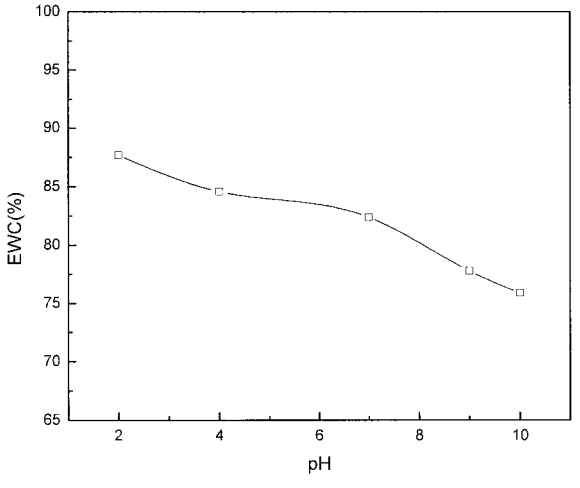

Figure 2 Equilibrium water content (EWC) of chitosan/polyallylamin IPN as function of pH at 35 °C.

Bending behavior of the IPN under electric fields

When an electric field is applied to a sheet of the chitosan/polyallylamine IPN hydrogel in aqueous NaCl solution, the gel showed significant and quick bending toward the cathode. 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. The mechanism of this kind of behavior 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 and contraction of the other side of the polymer.[21–23] However, this behavior has not been exactly understood because there is still a lack of well-developed theories for such chemomechanical kinetics.

We examined the influence of the medium ionic concentration on the bending behaviors of the IPN in response to an electric stimulation by varying the concentration of NaCl solution from 0.2 to 1.2% by weight while keeping the pH and other conditions constant. As shown in Figure 3, the equilibrium bending angle (EBA) of the IPN showed an apparent peak with aque-

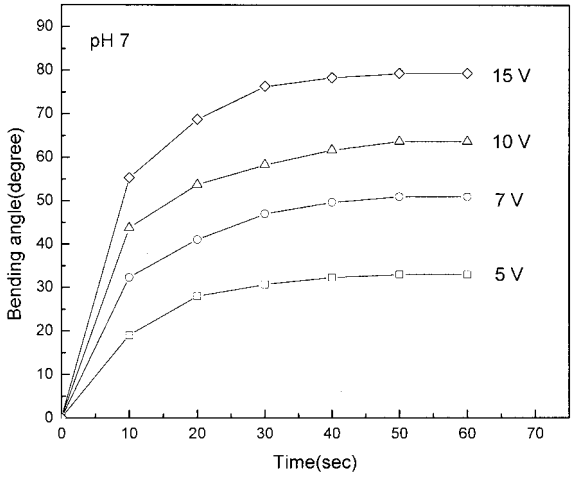

Figure 4 Bending kinetics of the IPNs as a function of the applied voltage in aqueous NaCl at 0.5% by weight.

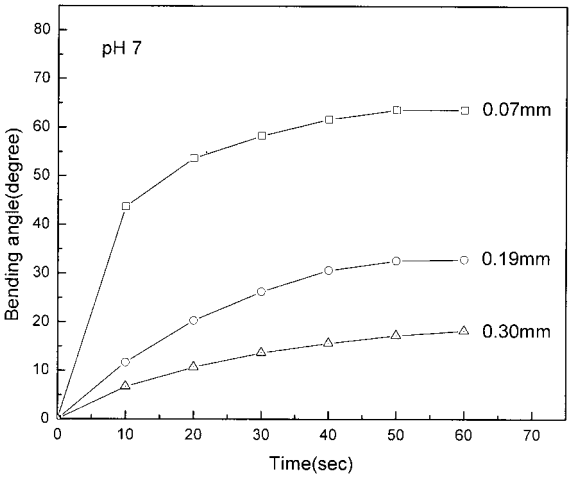

Figure 5 Effect of thickness of IPN on the bending behavior in aqueous NaCl at 0.5% by weight and at 10 V constant voltage.

ous NaCl at 0.5% by weight. The bending degree increased with the concentration of NaCl solution when the concentration of NaCl solution was <0.5% by weight, whereas the bending degree decreased at the concentration of NaCl solution of >0.5% by weight. As already described, 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 IPN. As a result, the bending degree of the IPN could increase. However, if the concentration of NaCl 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. A similar result was reported by Sun and Mak[17] in their study of mechano-electrochemical behaviors of a hydrogel fiber based on chitosan/poly(ethylene glycol). As already shown in Figure 1, the swelling ratio of the IPN in the solution with the lower concentration of electrolytes was greater than that of the higher electrolyte concentration. Therefore, if these results are compared with the bending results depending on the concentration of the solution in Figure 3, we could consider that the swelling of the IPN induced by the concentration does not significantly affect the bending behavior of the IPN.

The variation of bending angle of the IPN hydrogel as a function of the applied voltage in aqueous NaCl at 0.5% by weight is shown in Figure 4. The equilibrium bending angle and bending speed increase with increasing voltage across the gel, but bending is not found in pure water, indicating that bending is induced by the electric current. In a medium with 0.5 wt % NaCl, the IPN thickness could obviously influence the bending rate of the IPN hydrogel samples, as shown in Figure 5. The thinner the IPNs were, the faster they tended to bend under the electric field. A similar result was reported by Homma et al.[24] in their study of an electro-driven polymer hydrogel. Also, as shown in Figure 6, the chitosan/polyallylamine IPN hydrogel exhibited a reversible bending behavior according to the application of the electric field.

Thermal properties of the IPN

The DSC melting thermograms of chitosan, polyallylamine, and IPN hydrogel are shown in Figure 7. Polyallylamine reveals a sharp melting endothermic peak at 110 °C, whereas a weak and broad melting endothermic peak of the polyallylamine segment in the IPN, caused by crosslinking reaction and IPN formation, appeared at 133 °C. On the other hand, the melting temperature (T_m) of chitosan network cannot be determined by DSC analysis. Although chitosan has crystalline regions, T_m cannot be found because of

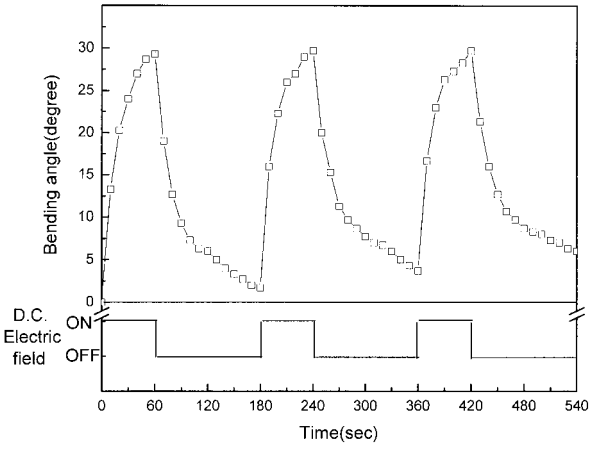

Figure 6 Reversible bending behavior of the IPN in 0.5 wt % NaCl solution (pH 7) with changes in the applied voltage of 7 V.

the rigid-rod polymer backbone with strong inter- and/or intramolecular hydrogen bonding.[25] This behavior is frequently detected in many polysaccharides, such as cellulose and chitin derivatives.[26] In general, the T_g of 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. The plots of log(tan δ) and loss factor (log ε″) of the IPN versus temperature at 100 and 500 Hz, and 1 kHz are shown in Figure 8. Three relaxation peaks appeared at ~50, 110, and 170 °C in the IPN. The T_g of chitosan appears at above 150 °C.[27] Accordingly, the temperature of the maximum tan δ, ~170 °C, is considered to be the T_g of chitosan. Another maximum tan δ temperature at 110 °C was thought to be the T_m of polyallylamine segments in IPN, as was seen from DSC analysis. The lower maximum tan δ temperature was taken to be the T_g of polyallylamine segments in IPN hydrogel. In fact, the T_g of polyallylamine itself was −26°C as determined by DSC analysis in this work. DEA showed that the T_g in IPN was much higher than that of polyallylamine and shifted up to ~50 °C. From the results of DEA, the IPN exhibited two T_gs, indicating the presence of phase separation in the IPN.

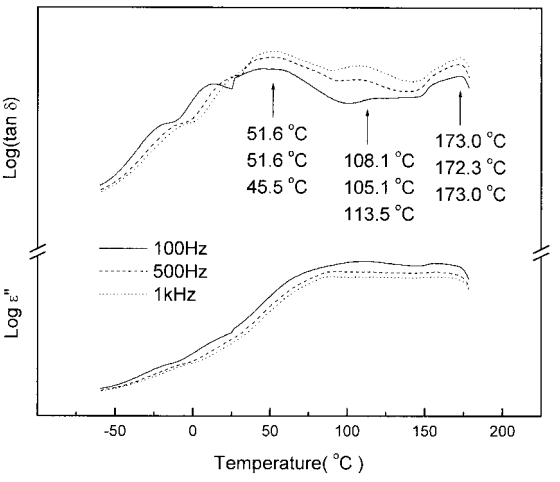

Figure 8 Dielectric analysis of the chitosan/polyallylamine IPN hydrogel.

CONCLUSIONS

A chitosan/polyallylamine IPN hydrogel was synthesized by radical polymerization and its bending behavior was studied. The IPN hydrogel exhibited a high EWC in the range 65–85%. The swelling ratio decreased with increasing concentration and pH of aqueous NaCl solution. When the IPN in NaCl electrolyte solution was subjected to an electric field, the IPN showed significant and quick bending toward the cathode. And when the electric stimulus was removed, the gel returned to its original position. The EBA of IPN was measured in different concentrations of a NaCl solution. The EBA and the bending speed of the IPN were the greatest in aqueous NaCl at 0.5% by weight and increased with increasing applied voltage. The IPN also showed stepwise bending behavior depending on the electric stimulus. From the results of DEA, the IPN exhibited two T_gs, indicating the presence of phase separation in the IPN. Therefore, the present chitosan/polyallylamine IPN system can be useful for artificial organ components, such as muscle-like contractile structures, sensors, switches, and electric-current-modulated drug-delivery systems.

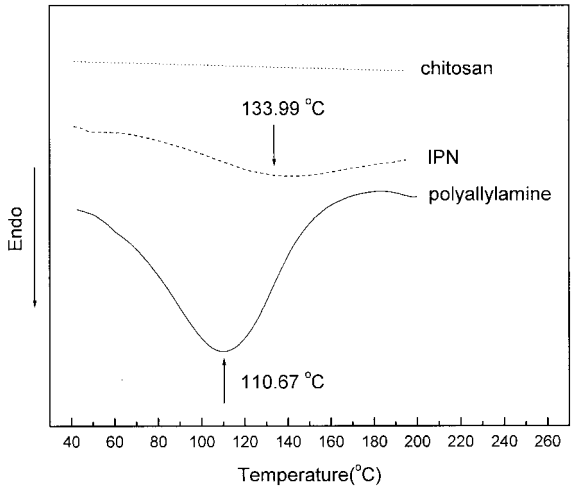

Figure 7 DSC melting endotherms of chitosan, polyallylamine, and IPN.

This work is the result of research activities of Basic Research Grant (2000-2-31400-002-3) and Advanced Biometric Research Center (ABRC) supported by Korea Science and Engineering Foundation.

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