

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Swelling Behavior of Semi-Interpenetrating Polymer Network Hydrogels Based on Chitosan and Poly(acryl amide)

Seon Jeong Kim^a; Su Ryon Shin^a; Nam Gyun Kim^b; Sun I. Kim^a

^a Department of Biomedical Engineering, Hanyang University, Seoul, Korea ^b Department of Bionics and Biomedical Engineering, Chonbuk National University, Chonju, Korea

To cite this Article Kim, Seon Jeong , Shin, Su Ryon , Kim, Nam Gyun and Kim, Sun I.(2005) 'Swelling Behavior of Semi-Interpenetrating Polymer Network Hydrogels Based on Chitosan and Poly(acryl amide)', Journal of Macromolecular Science, Part A, 42: 8, 1073 – 1083

To link to this Article: DOI: 10.1081/MA-200065934

URL: <http://dx.doi.org/10.1081/MA-200065934>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Swelling Behavior of Semi-Interpenetrating Polymer Network Hydrogels Based on Chitosan and Poly(acryl amide)

SEON JEONG KIM,¹ SU RYON SHIN,¹ NAM GYUN KIM,²
AND SUN I. KIM¹

¹Department of Biomedical Engineering, Hanyang University, Seoul, Korea

²Department of Bionics and Biomedical Engineering, Chonbuk National University, Chonju, Korea

Semi-interpenetrating polymer networks (semi-IPNs) composed of chitosan and polyacrylamide (PAAm) hydrogels have been prepared, and the effect of changing pH, temperature, ionic concentration, and applied electric fields on the swelling of the hydrogels was investigated. The swelling kinetics increased rapidly, reaching equilibrium within 60 min. The semi-IPN hydrogels exhibited a relatively high swelling ratios of 385%–569% at T = 25°C. The swelling ratio increased with decreasing pH below pH = 7 due to the dissociation of ionic bonds. The swelling ratio of the semi-IPN hydrogels was pH, ionic concentration, temperature, and electric field dependent. Differential scanning calorimetry (DSC) was used to determine the volume of free water in the semi-IPN hydrogels, which was found to increase with increasing PAAm content.

Keywords chitosan, polyacrylamide, swelling behavior, pH sensitivity, electric field

Introduction

Hydrogels can be defined as three dimensional hydrophilic polymer networks that swell, but do not dissolve, when brought into contact with water (1, 2). Hydrogels have been actively studied, with particular emphasis on their reversible volume changes in response to external stimulus, such as changes in pH, solvent composition, temperature, ionic concentration, and electric field (3–6). Hydrogels are mainly used in the fields of medicine, pharmacy, biotechnology, and agriculture. In recent years, due to their versatile application in biomedicine and biotechnology, hydrogels have been used for the immobilization of enzymes, proteins, antibodies, and antigens (7, 8).

Semi-interpenetrating polymer networks (semi-IPNs) are defined as compounds in which one or more polymers are cross-linked (either linearly or branched). Cross-linked polymers exhibiting high equilibrium swelling in water or aqueous solutions can be based exclusively on macromolecules with a high hydrophilicity and flexibility, which

Received September 2004, Accepted March 2005

Address correspondence to Sun I. Kim, Department of Biomedical Engineering, Hanyang University, Sungdong P.O. Box 55, Seoul 133-605, Korea. Tel: +82-2-2290-8280; Fax: +82-2-2296-5943; E-mail: sunkim@hanyang.ac.kr

are often a function of the polyelectrolytic nature of the chains. Cross-linked polymers are one component that can be used to improve the wet strength. Chitosan is a high molecular weight carbohydrate polymer that is manufactured from chitin (9, 10). It owes its cationic nature to the free amino groups left by the partial removal of the acetyl groups of chitin. Chitosan is more useful in biomedical applications and for the dehydration of aqueous solutions than chitin, since it has both hydroxyl and amino groups that can easily be chemically modified (11, 12). For these uses, the key properties of chitosan are: its biocompatibility, nonantigenicity, nontoxicity (its degradation products are known natural metabolites), its ability to improve wound healing and/or blood clotting, its ability to absorb liquids, its ability to form protective films and coatings, and its selective binding of liquids. Therefore, it can be used for lowering serum cholesterol levels (13).

Polyacrylamide is a well-known hydrogel, with a swelling capacity that is not very sensitive to pH or to electrolytes (14). Polyacrylamide hydrogels that are commonly used as support matrices are readily fabricated by an aqueous free radical polymerization of the monomer acrylamide and cross-linked *N,N'*-methylenebisacrylamide (MBAAm) using a redox initiator system, such as ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (15–18). The pH of the reaction medium is also important, since hydrolysis of amide groups occurs at high pH, whereas imidization is favored at low pH and high temperatures (19).

Many researchers have reported specific polymer-water interactions. Yao et al. (20) reported on the swelling kinetics of chitosan/polyether semi-IPN hydrogels cross-linked by glutaraldehyde. Sun et al. (21) reported on hydrogel fibres composed of chitosan and poly(propylene glycol). Kim et al. (22) reported on the drug release behavior of electrical-responsive PVA/PAAc IPN hydrogels under an electric stimulus. In regards to using pH as another external stimulus for stimuli-sensitive hydrogels, Yao et al. (23), have studied pH-sensitive hydrogels.

In this study, semi-IPN hydrogels composed of chitosan and PAAm were prepared, and the characterization of the pH, temperature, ionic concentration, and electric field dependence of their swelling behavior, resulting from the chitosan and PAAm amino groups is described. In addition, DSC studies were performed to gain an understanding of the nature of the swollen semi-IPN hydrogels.

Experimental

Materials

Chitosan samples with an average molecular weight of 2.0×10^5 and a 76% degree of deacetylation was supplied by the Jakwang Co., Korea. The acetic acid used was supplied by the Duksan Pure Chemical. Co. Ltd, Japan. The acrylamide (AAm), *N,N'*-methylenebisacrylamide (MBAAm) and ammonium peroxydisulfate (APS) used were purchased from the Aldrich Chem. Co., US. The *N,N,N',N'*-tetramethylethylenediamine (TMEDA) used was purchased from the Yakuri Chem. Co., Japan. All the other chemicals used were of reagent grade, and were used without further purification.

Preparation of the Semi-IPN Hydrogels

The crosslinked PAAm was prepared by free radical solution polymerization. Individual mixtures of AAm, MBAAm (2 wt% of the AAm monomer), and TMEDA (3 wt% of the AAm monomer) were dissolved in an aqueous solution, and stirred for 1 h at room

temperature. The chitosan was completely dissolved in 1 wt% acetic acid (i.e., the solid content in the solution was 1 wt%), and was then mixed with the AAm using mechanical stirring for 24 h. The APS initiator (1 wt% of the AAm monomer) was added to the mixture, which was then stirred for a further 12 h. The detailed compositions and designations of the chitosan/PAAm semi-IPNs are listed in Table 1. The mixed solutions were then poured into petri dishes and kept in an oven maintained at 30°C for 24 h. The samples were then dried in an oven at 40°C for a further 24 h. The obtained products were then soaked in distilled water for one week to remove any unreacted monomer and formic acid. The films were then dried at 40°C in a vacuum oven for 24 h. Scheme 1 shows structure of chitosan/PAAm semi-IPN hydrogel.

Characterization

The dried gels were immersed in 50 ml of deionized water maintained at various temperatures. The swelling ratios were obtained by weighing the samples' initial and swollen state at various time intervals. To measure the swelling ratios, preweighed dry samples were immersed in deionized water. After the excess surface water had been removed with filter paper, the weight of the swollen samples was measured at various temperatures, pH, ionic strength, electric field, and time intervals. The swelling ratio was determined according to the following Equation 1 (24):

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

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

The equilibrium water content (EWC) was calculated using the following Equation 2 (3):

$$\text{EWC (\%)} = \frac{(W_e - W_d)}{W_e} \times 100 \quad (2)$$

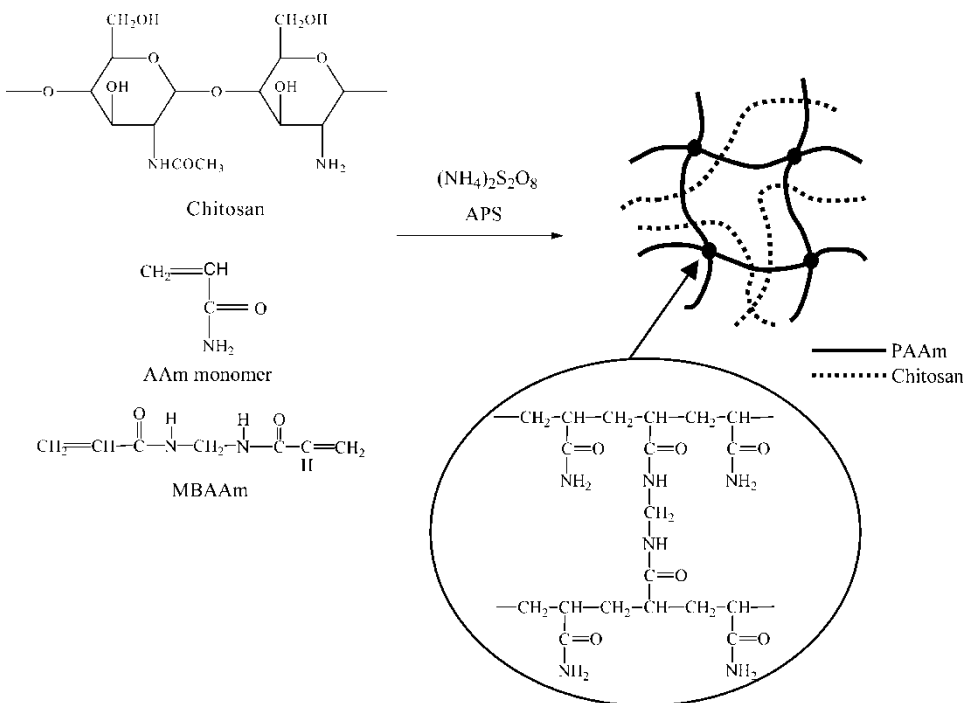
where W_e and W_d represent the weight of the swollen state at equilibrium and the dry state samples, respectively.

A TA Instruments 2010 differential scanning calorimeter (DSC) was employed to examine the state of the water in the swollen hydrogels with different water contents. The samples were sealed in aluminium pans that were cooled to -30°C and then heated to 30°C using a heating rate of 5°C/min under 60 ml/min of flowing nitrogen

Table 1

The states of the water present in the chitosan and PAAm semi-IPN hydrogels, as estimated by DSC analysis

Sample	Weight ratio (Chitosan/PAAm)	EWC (%)	Free water (%)	Bound water (%)
PAAm	N/A	95.20	39.30	55.90
CSPM18	1 : 8	85.07	29.80	55.27
CSPM16	1 : 6	79.78	24.70	55.08
CSPM14	1 : 4	79.41	24.67	54.74



Scheme 1. The schematics of the synthesis of chitosan/PAAm semi-IPNs.

gas. The fraction of free water in the total water was estimated using Equation 3 from the ratio of the endothermic peak area for the water-swollen hydrogels to the melting point endothermic heat of fusion ($Q_f = 79.7 \text{ cal/g}$) for pure water. The bound water due to hydrogen bonds is expressed as the difference between the total water and the free water content (25).

$$W_b(\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{\text{endo}}/Q_f) \times 100 \quad (3)$$

where W_b is the percentage of bound water, W_f and W_{fb} are the volumes of free and frozen bound water, respectively; and W_t is the equilibrium water content (EWC (%)). When swollen, the semi-IPNs were placed between a pair of electrodes (supplying a non-contact DC electric field in deionized water) (3), and exhibited deswelling on the application of an electric field. The deswelling water ratios of each semi-IPN in an electric field were evaluated using the following Equation 4 (26):

$$\text{Deswelling water ratio} = W_t/W_{t0} \quad (4)$$

where W_{t0} and W_t are the weight of the fully swollen semi-IPN and the weight of the semi-IPN upon the application of an electric field, respectively.

Results and Discussion

Figure 1 shows the water swelling behavior of the PAAm and chitosan/PAAm semi-IPNs. As can be seen in Figure 1, the water swelling occurred rapidly, reaching an equilibrium in water uptake in a time of about 60 min. The swelling ratios of the semi-IPNs were between

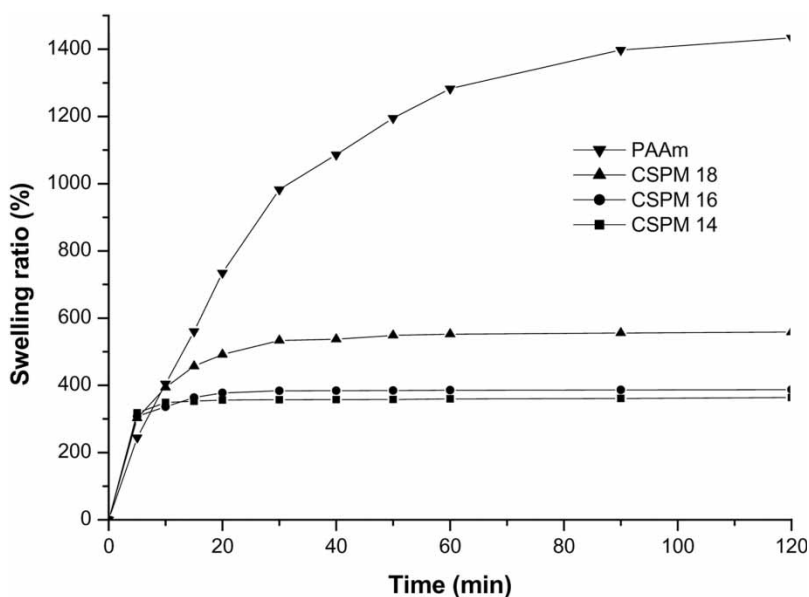


Figure 1. The swelling behavior of chitosan/PAAm semi-IPNs hydrogels at 25°C. Key: (▼) = PAAm, (▲) = CSPM 18, (●) = CSPM 16, and (■) = CSPM 14.

385% and 569%, and these changed with PAAm content. In contrast, the water uptake of the initially dry PAAm took a long time to reach equilibrium. The swelling ratios of the PAAm hydrogels were higher than those of the hydrogels of Samples CSPM14, CSPM16, and CSPM18. Higher equilibrium swelling ratios were obtained by increasing the PAAm content of the hydrogel structures. This was attributed to the PAAm having a large hydrophilic content. This behavior may be due to the degree of crosslinking of the chitosan/PAAm network, but also to the mass of PAAm present, which has a large number of water-binding sites (5). Therefore, the water molecules could penetrate into the polymer chains more easily, resulting in an improvement of the semi-IPN hydrogel water-swelling properties in aqueous solution. Generally, the state of water in the polymer can be distinguished as “free water” and as “bound water”. The free water is that portion of water not associated with, or not bound to the polymer, which means that it undergoes no interaction with the polymer chains. However, bound water is the most popular term used to describe any associated water, and particularly, that associated with secondary forces, such as that hydrogen bonded to the polymer matrix. The heat of melting of the frozen water (i.e., intermediate and free water) was determined from the area under the endothermic peak, and was calibrated using pure distilled water as a standard, as was described in the work of Mansor and Malcolm (25).

Figure 2 shows the DSC thermograms of a water-swollen semi-IPN sample as a function of the PAAm content. An endothermic peak appeared between -20 and 10°C , which was attributed to the presence of free water in the semi-IPN hydrogels. The EWC values and the free and bound water contents were calculated, and are listed in Table 1. The bound water was expressed as the difference between the total and free water contents. The bound water content of the semi-IPN samples ranged between 54.74% and 55.90% of the total water content. The volume of free water was observed to increase with increasing PAAm content in the semi-IPN hydrogels. This indicates

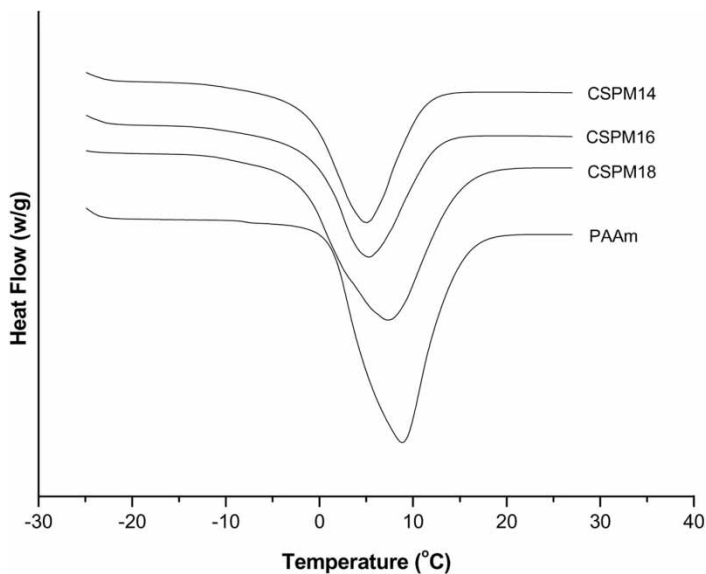


Figure 2. DSC thermograms of the swollen PAAm and chitosan/PAAm semi-IPN hydrogels in aqueous solution at 25°C.

that the increase in the swelling ratio could be mainly attributed to the free water content of the semi-IPN hydrogels.

The swelling behavior of the semi-IPN hydrogels was investigated as a function of temperature. As shown in Figure 3, all the hydrogels exhibited significant changes in

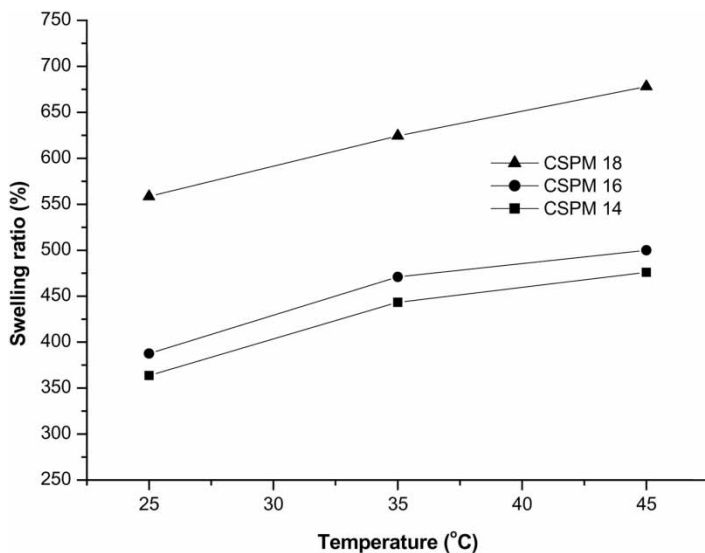


Figure 3. The equilibrium swelling ratios as a function of temperature ($T = 25, 35,$ and 45°C) for the chitosan/PAAm semi-IPNs in aqueous solution. Key: (\blacktriangle) = CSPM 18, (\bullet) = CSPM 16, and (\blacksquare) = CSPM 14.

their swelling ratios over the temperature range 25 to 45°C. It is clear that this type of polymer network has a positive thermosensitivity, i.e., they exhibit higher swelling levels with increasing temperature. When the mass of PAAm in the hydrogels was increased, the swelling ratios also increased. The water molecules associated with the polymer will increase their enthalpies when the temperature increases, and the hydrophilic groups on the chitosan and PAAm will form intramolecular hydrogen bonds under these conditions. All the chitosan/PAAm networks exhibited a temperature-responsive swelling behavior, which was due to the association and dissociation of the hydrogen bonds formed by the amine groups on both the chitosan and PAAm molecules (3).

Figure 4 shows the swelling ratios of different samples in various pH buffered solutions at 25°C. The semi-IPNs swelled at pH = 2, and shrank at pH = 7. The protonation of the amino groups of the hydrogels became easier in acidic rather than basic media. Because the positively charged amine groups of the chitosan and PAAm are incorporated into the polymer network, the gel swells at low pH due to the ionic repulsion of the protonated amine groups. The shrinkage at high pH is due to the unprotonated amine groups. Conversely, alkaline hydrogen bonds tend to associate because $-\text{NH}_3^+$ groups can change into $-\text{NH}_2$ groups at low H^+ concentrations. In an acidic solution, the protonation of the amino groups ($-\text{NH}_2$) in the hydrogels, and the dissociation of the hydrogen bonds, induce the hydrogel to swell and develop an internal ion osmotic pressure (13). The swelling capacities of the hydrogels increases as the acidity of media increases, and the highest swelling ratios were obtained at pH = 2, the lowest pH used in these experiments.

Figure 5 shows the ionic strength dependency of the swelling of semi-IPN hydrogel Sample CSPM18. The effect of salt concentration on the swelling ratio of the hydrogel was investigated by increasing the ionic strength of the external solution by the addition of sodium ions to the external solution in the concentration range $[\text{Na}^+] = 0.2\text{--}1.2\text{ wt}\%$. Increasing the ionic strength of the solution caused a deswelling of the hydrogels.

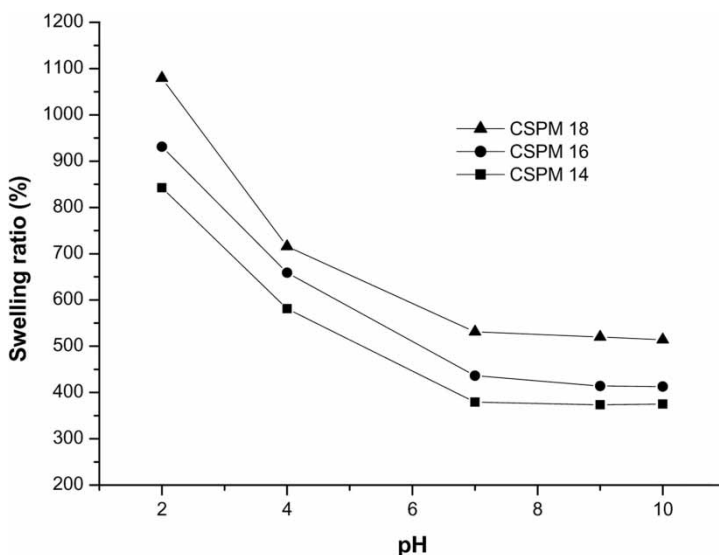


Figure 4. The pH-dependent swelling behavior of chitosan/PAAm semi-IPNs at 25°C. Key: (▲) = CSPM 18, (●) = CSPM 16, and (■) = CSPM 14.

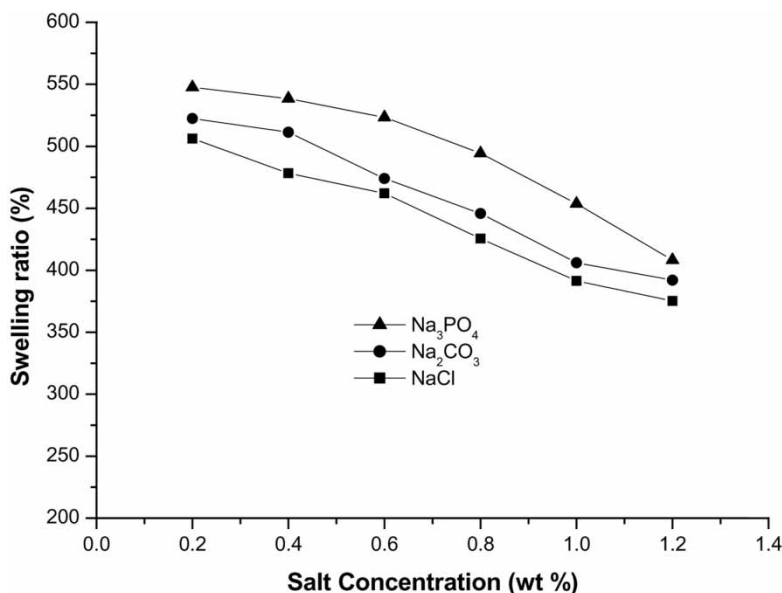


Figure 5. The effect of the medium's ionic strength on the swelling ratio of semi-IPN hydrogel Sample CSPM18 at 25°C. Key: (▲) = Na₃PO₄, (●) = Na₂CO₃, and (■) = NaCl.

According to the Donnan osmotic pressure equilibrium (27), an increase in the movable counterions of a solution leads to a decrease in the osmotic pressure within the hydrogel, causing the gels to shrink. The osmotic pressure results from the difference in the mobile ion concentrations between the interior of the hydrogel network and the external immersion medium. Increasing the ionic strength of the solution shields the charge of the polymeric network, therefore reducing the difference in mobile ion concentration between the polymer gel and external medium (i.e., the osmotic swelling pressure), which in turn reduces the gel volume, i.e. the gel shrinks. Our results show that the relative effect of the addition of anions increases in the following order:



This series may be explained by the fact that the PO₄³⁻ and CO₃²⁻ ions can form ion-pairs with the sodium ions, and, therefore, reduce their effective concentration in the external solution. This results in a decrease in the swelling capacity, but this is still less than that produced by the Cl⁻ ions, which, because they are monovalent, have a greater effective concentration in the external solution. This explains the observed order of the relative effectiveness of the salt additions.

The deswelling water ratios of the semi-IPN were calculated using Equation 4 to quantify the degree of deswelling. Figure 6 shows the remaining water ratio dependency on the applied voltage and the PAAm ionic group content in the semi-IPN hydrogels. As shown in Figure 6, the volume of remaining water in the semi-IPN hydrogels reduced with the increasing applied voltage and PAAm content in the semi-IPN hydrogels. That is, the semi-IPN hydrogel shrank when an electric field was applied. This phenomenon can be explained by attributing the shrinkage to the osmotic ion pressure difference that occurred as a consequence of mobile ion transport to the anode or cathode side of the

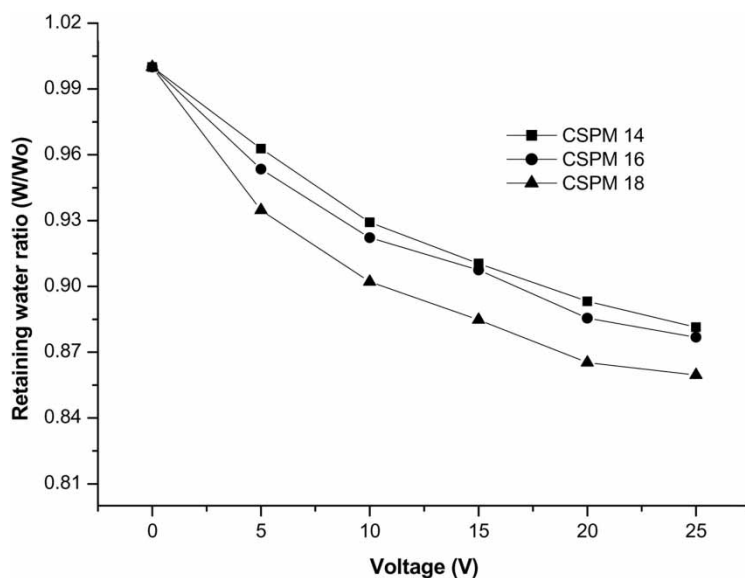


Figure 6. The equilibrium retained water ratios of the chitosan/PAAm semi-IPN hydrogels with applied electric field at 25°C. Key: (▲) = CSPM 18, (●) = CSPM 16, and (■) = CSPM 14.

polymer, combined with local pH changes around the electrodes as a result of electrochemical reactions.

Figure 7 shows the remaining water ratio as a function of time, dependent on the PAAm ionic group content in the semi-IPN hydrogels. Figure 7 indicates that the time required to reach equilibrium deswelling was about 100 min, and the differences in

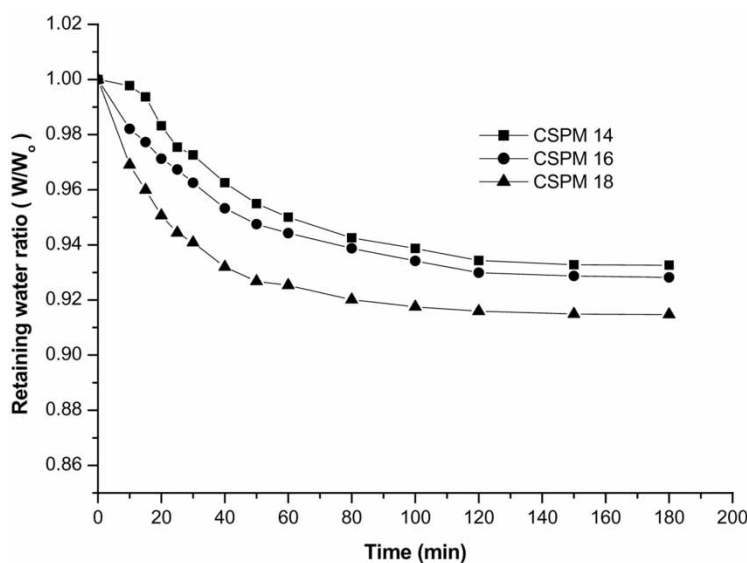


Figure 7. The retained water ratio of chitosan/PAAm semi-IPNs in an electric field of 10 V at 25°C. Key: (▲) = CSPM 18, (●) = CSPM 16, and (■) = CSPM 14.

the retained weight ratio is consistent with the trends shown in Figure 6. In particular, the fully swollen Sample CSPM18 showed an approximate reduction in weight of 8% from its original weight within 100 min in an applied voltage of 10 V. To examine the effects of the ionic groups on the semi-IPNs, the remaining water ratio of semi-IPNs with different compositions were measured for Samples CSPM14, CSPM16, and CSPM18. An increase in shrinkage was observed with time and PAAm content in the semi-IPNs.

Conclusions

Differential scanning calorimetry was used in the quantitative determination of the volumes of free and bound water contained in semi-IPNs. The free water in the semi-IPN hydrogels increased with increasing PAAm content. The semi-IPN hydrogels exhibited sensitivity to pH, temperature, ionic concentration, and an applied electric field. They also exhibited higher swelling ratios with increasing PAAm content. Sample CSPM18, which contained the highest PAAm content, showed the highest pH-dependent swelling ratio behavior. The semi-IPN hydrogels were electro-responsive, and shrank when an electric field was applied. The greatest electro-responsive volume change was shown by Sample CSPM18. This phenomenon can be explained in terms of the osmotic pressure difference caused by the redistribution of fixed and mobile ions. The chitosan/PAAm semi-IPN hydrogels prepared in this study would be useful in biomedicine, in areas such as wound dressing materials or drug delivery systems.

Acknowledgement

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

References

1. DeRossi, D., Kajiwaru, K., and Osada, Y. (1991) Polymer gels, fundamentals and biomedical applications. Plenum Press: New York.
2. Aharoni, S.M. (1992) Synthesis, characterization and theory of polymeric networks and gels. Plenum Press: New York.
3. Kim, S.J., Park, S.J., Kim, Y.I., Shin, M.S., and Kim, S.I. (2002) Electric stimuli responses to poly(vinyl alcohol)/chitosan interpenetrating polymer network hydrogel in NaCl solutions. *J. Appl. Polym. Sci.*, 86: 2285–2289.
4. Basan, H., Gümüşderelioğlu, M., and Orbey, T. (2002) Diclofenac sodium releasing pH-sensitive monolithic devices. *Int. J. Pharm.*, 245: 191–198.
5. Lee, S.J., Kim, S.S., and Lee, Y.M. (2000) Interpenetrating polymer network hydrogels based on poly(ethylene glycol) macromer and chitosan. *Carbohydr. Polym.*, 41: 197–205.
6. Johnson, B., Niedermaier, D.J., Crone, W.C., Moorthy, J., and Beebe, D.J. Society for experimental mechanics, 2002, SEM Annual Conference Proceedings, Milwaukee, WI, 2002.
7. Kim, S.J., Park, S.J., Shin, M.S., Lee, Y.M., Kim, N.G., and Kim, S.I. (2002) Thermal characteristics of IPNs composed of polyallylamine and chitosan. *J. Appl. Polym. Sci.*, 85: 1956–1960.
8. Sutani, K., Kaetsu, I., and Uchida, K. (2001) The synthesis and the electric-responsiveness of hydrogels entrapping natural polyelectrolyte. *Radiat. Phys. Chem.*, 61: 49–54.
9. Park, S.B., You, J.O., Park, H.Y., Haam, S.J., and Kim, W.S. (2001) A novel pH-sensitive membrane from chitosan—TEOS IPN, preparation and its drug permeation characteristics. *Biomaterials*, 22: 323–330.

10. Mehrdad, Y.P., Jaime, R., and Raul, Q. (2000) Hydrogels based on modified chitosan, 1. Synthesis and swelling behavior of poly(acrylic acid) grafted chitosan. *Macromol. Chem. Phys.*, 201: 923–930.
11. Kang, D.W., Choi, H.R., and Keon, D.K. (1999) Stability constants of amidoximated chitosan-g-poly(acrylonitrile) copolymer for heavy metal ions. *J. Appl. Polym. Sci.*, 73: 469–476.
12. Peniche, C., Waldo, A.M., Davidenko, N., Sastre, R., Gallardo, A., and Roman, J.S. (1999) Self-curing membranes of chitosan/PAA IPNs obtained by radical polymerization: preparation, characterization and interpolymer complexation. *Biomaterials*, 20: 1869–1878.
13. Lee, W.F. and Chen, Y.J. (2001) Studies on preparation and swelling properties of the N-isopropylacrylamide/chitosan semi-IPN and IPN hydrogels. *J. Appl. Polym. Sci.*, 82: 2487–2496.
14. Puig, L.J., Sánchez-Díaz, J.C., Villacampa, M., Mendizabal, E., Puig, J.E., Aguiar, A., and Katime, I. (2002) Microstructured polyacrylamide hydrogels prepared via inverse microemulsion polymerization. *J. Colloid. Interf. Sci.*, 235: 278–282.
15. Liang, L. and Ruckenstein, E. (1995) Polyvinyl alcohol-polyacrylamide interpenetrating polymer network membranes and their pervaporation characteristics for ethanol-water mixtures. *J. Membrane. Sci.*, 106: 167–182.
16. Patras, G., Qiao, G.G., and Solomon, D.H. (1999) On the mechanism of background silver staining during sodium dodecyl sulphate-polyacrylamide gel electrophoresis. *Electrophoresis*, 20: 2039–2045.
17. Mathew, B., Madhusudanan, P.M., and Rajasekharan Pillai, V.N. (1992) Effect of the nature of crosslinking agents on the thermal decomposition of metal complexes of crosslinked polyacrylamide-supported dithiocarbamates. *Thermochim. Acta.*, 207: 265–277.
18. Bartoň, J. and Juraničová, V. (2000) Polymerization of acrylamide in styrene containing inverse microemulsions: Polymerization kinetics and polymer product composition studies. *Polym. Int.*, 49: 1483–1491.
19. Pinotti and Zaritzky, N. (2001) Effect of aluminum sulfate and cationic polyelectrolytes on the destabilization of emulsified wastes. *Waste. Manage.*, 21: 535–542.
20. Peng, T., Yao, K.D., Yuan, C., and Goosen, M.F.A. (1994) Structural changes of pH-sensitive chitosan/polyether hydrogels in different pH solution. *J. Polym. Sci. Part. B: Polym. Chem.*, 32: 591–596.
21. Sun, S. and Mak, A.F.T. (2001) The dynamical response of a hydrogel fiber to electrochemical stimulation. *J. Polym. Sci. Part. B: Polym. Phys.*, 39: 236–246.
22. Kim, S.Y. and Lee, Y.M. (1999) Drug release behavior of electrical responsive poly(vinyl alcohol)/poly(acrylic acid) IPN hydrogels under an electric stimulus. *J. Appl. Polym. Sci.*, 74: 1752–1761.
23. Yao, K.D. and Peng, T. (1993) pH-sensitivity of hydrogels based on complex forming chitosan: Polyether interpenetrating polymer network. *J. Appl. Polym. Sci.*, 48: 343–354.
24. Ju, H.K., Kim, S.Y., and Lee, Y.M. (2001) pH/temperature-responsive behaviors of semi-IPN and comb-type graft hydrogels composed of alginate and poly(N-isopropylacrylamide). *Polymer*, 42: 6851–6857.
25. Mansor, B.A. and Malcolm, B.H.. DSC studies on states of water in crosslinked poly(methyl methacrylate-co-n-vinyl-2-pyrrolidone) hydrogels. *Polym. Int.*, 33: 273–277.
26. Kim, S.Y., Shin, H.S., Lee, Y.M., and Jeong, C.H. (1999) Properties of electroresponsive poly(vinyl alcohol)/poly(acrylic acid) IPN hydrogels under an electric stimulus. *J. Appl. Polym. Sci.*, 73: 1675–1683.
27. Ricka, J. and Tanaka, T. (1984) Swelling of ionic gels: quantitative performance of the Donnan theory. *Macromol.*, 17: 2916–2921.