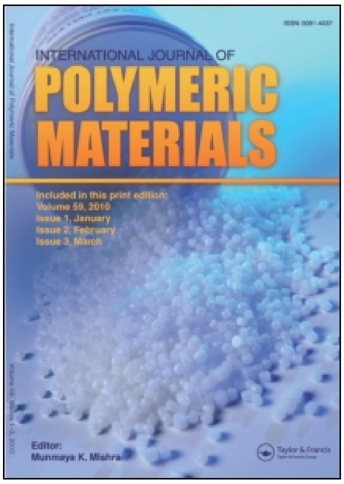

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Poly(vinyl alcohol) Based pH Responsive Semi-IPN Hydrogels: A Comparative Swelling Investigation

K. Sambasivudu[a]; K. John[a]; P. S. Keshava Murthy[a]; Y. Mani[a]; Y. Murali Mohan[a]; J. Sreeramulu[b]; K. Mohana Raju[a]
[a] Synthetic Polymer Laboratory Department of Polymer Science & Technology, Sri Krishnadevaraya University, Anantapur, A.P., India [b] Department of Chemistry, Sri Krishnadevaraya University, Anantapur, A.P., India

To cite this Article Sambasivudu, K. , John, K. , Murthy, P. S. Keshava , Mani, Y. , Mohan, Y. Murali , Sreeramulu, J. and Raju, K. Mohana(2007) 'Poly(vinyl alcohol) Based pH Responsive Semi-IPN Hydrogels: A Comparative Swelling Investigation', International Journal of Polymeric Materials, 56: 11, 1099 — 1111

To link to this Article: DOI: 10.1080/00914030701283030

URL: http://dx.doi.org/10.1080/00914030701283030

International Journal of Polymeric Materials, 56:1099–1111, 2007

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030701283030

Poly(vinyl alcohol) Based pH Responsive Semi-IPN Hydrogels: A Comparative Swelling Investigation

K. Sambasivudu
K. John
P. S. Keshava Murthy
Y. Mani
Y. Murali Mohan
Synthetic Polymer Laboratory, Department of Polymer Science & Technology, Sri Krishnadevaraya University, Anantapur, A.P., India

J. Sreeramulu
Department of Chemistry, Sri Krishnadevaraya University, Anantapur, A.P., India

K. Mohana Raju
Synthetic Polymer Laboratory, Department of Polymer Science & Technology, Sri Krishnadevaraya University, Anantapur, A.P., India

The semi-interpenetrating polymer network (IPN) hydrogels composed of poly (vinyl alcohol) (PVA) and random copolymers of poly(acrylamide-co-sodium methacrylate), poly(AAm-co-NMA); poly(acrylamide-co-potassium methacrylate), poly(AAm-co-KMA); poly(acrylamide-co-maleic acid), poly(AAm-co-MA) were prepared by conventional co-polymerization employing ammonium persulphate (APS)/N,N,N^1,N^1-tetraethylmethylenediamine (TMEDA) as redox initiating system in presence of N,N^1-methylenebisacrylamide (MBA) as a crosslinker. The swelling behavior of these semi-IPN hydrogels were compared in detail in various swelling media, including different pH, salt, and biological fluids.

Received 2 November 2006; in final form 7 February 2007.

The authors thank the Defence Res. & Dev. Organisation (DRDO) and Ministry of Defence, Govt. of India, New Delhi for the financial support.

Present address of Y. Murali Mohan: Department of Pharmaceutical Sciences, College of Pharmacy, University of Nebraska Medical Center, Omaha, NE 68198-6025, USA.

Address correspondence to Prof. K. Mohana Raju, Synthetic Polymer Laboratory, Department of Polymer Science & Technology, Sri Krishnadevaraya University, Anantapur-515 003, A.P., India. E-mail: kmrmohan@yahoo.com or Y. Murali Mohan, Department of Pharmaceutical Sciences, College of Pharmacy, University of Nebraska Medical Center, Omaha, NE 68198-6025. E-mail: mohanaym@yahoo.co.in

Keywords: diffusion coefficient, hydrogel, poly(vinyl alcohol) swelling behavior, semi-interpenetrating polymer network

INTRODUCTION

Hydrogels are one of the most promising types of polymers being used for novel material design and developments. Hydrogels are composed of crosslinked three-dimensional network polymeric chains that exhibit swellable behavior in aqueous solutions [1–4]. The network structural features are provided not only by crosslinked covalent bonds between polymeric chains but also by other inter-molecular attractive forces. The excellent features of hydrogels are high water uptake, good thermal and mechanical stability, non-toxicity, and soft and rubbery nature. Further, their hydrophilicity, biocompatibility, and possessing similar to that of living tissues characteristics of the hydrogels have prompted their use in controlled drug delivery systems, soft contact lenses, wound dressings, artificial implants, dialysis membrane, surgical prostheses, and so on [4–5]. In addition to the aforementioned applications, these materials are also exclusively employed in other applications, such as soil conditioners for agriculture and horticulture, feminine napkins, disposable diapers, water blocking tapes, absorbent pads, gel actuators, drilling fluid additives, polymer cracks blocking materials, firefighting, extraction of precious metals, extraction of solvents, release of agrochemicals, and so on [6–13].

One easy approach to obtain crosslinked network structure is interpenetrating network (IPN) formation. IPNs can be prepared by co-polymerizing the relevant monomers in the presence of some other natural/synthetic polymers [14]. IPN is a well-known method to get hydrogel networks with combined properties of the two individual polymers. Interpenetrating hydrogel networks based on poly(acrylamide-co-acrylic acid) [P(AAm-co-AA)] and poly(vinyl alcohol) (PVA) were developed to evaluate their biomedical applications [15]. Gudeman and Peppas reported the preparation of interpenetrating networks from PVA and poly(acrylic acid) (PAA) [16]. Bajpai and Saini developed spongy PVA-casein cryogels being biocompatible, biodegradable, nontoxic, and noncarcinogenic in nature [17]. Various PVA-based IPN hydrogels were studied with poly(acrylamide) (PAAm) [18–19], poly (N-isopropylacrylamide) (PNIPAm) [20–22], N-isopropylacrylamide-co-acrylamide (PNIPAAm-AAm) and N-isopropylacrylamide-co-2-acrylamido-2-methylpropyl-sulfonic acid (PNIPAAm-AAMPSA) [23], poly (dimethylsiloxane)(PDMS)-chitosan [24], poly(acrylic acid) (PAA) [25–26], poly(methacrylic acid) (PMAc) [27], lactosilated chitosan [28], hyaluronic acid [29], and poly(diallyldimethylammonium chloride) [30].

Bajpai investigated the pH sensitivity of poly(acrylamide-co-maleic acid) gels [31]. The Polyelectrolyte hydrogel, namely poly(acrylamide-co-maleic acid), was employed for controlled release of terbinafine hydrochloride [32]. The adsorption of bovine serum albumin (BSA) onto the surface of poly(acrylamide-co-maleic acid) [poly(AAm-MA)] and poly(acrylamide-co-2-hydroxypropyl methacrylate-co-maleic acid) [poly(AAm-HPMA-MA)] hydrogels was investigated [33–34]. The higher swelling capacity of hydrogels has allowed the presence of more BSA molecules in the water present in the hydrogels. Therefore, it is essential to improve the swelling capacity of the hydrogels. This can be achieved by incorporating a third hydrophilic polymer into the hydrogel networks. The PVA and acrylamide based hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biodegradability, and biocompatibility. Based on the aforementioned information, the present investigation involves the preparation of semi-IPN hydrogels based on PVA and polyacrylamide copolymers, with a view to have high swelling and pH sensitivity and also to compare their swelling behavior in detail.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA), acrylamide (AAm), methacrylic acid (MA), ammonium persulphate (APS), N,N^1-methylenebisacrylamide (MBA), N,N,N^1,N^1-tetramethylethylenediamine (TMEDA), maleic acid (MA), and other common reagents were purchased from S.D. Fine Chemicals Ltd. (Bombay, India) and used as received. Double distilled water was used for the polymerization reactions as well as for swelling studies. Sodium methacrylate (NMA) and potassium methacrylate (KMA) were prepared by complete neutralization of methacrylic acid with sodium hydroxide and potassium hydroxide, respectively [35–36].

Preparation of Semi-Interpenetrating Network Hydrogels

The semi-interpenetrating network hydrogels were prepared by copolymerization of acrylamide (AAm) with sodium methacrylate (NMA)/potassium methacrylate (KMA) or maleic acid (MA) in the presence of poly(vinyl alcohol). All the polymerization reactions were carried out in 100 ml beakers. Different amounts of acrylamide and sodium methacrylate/potassium methacrylate/maleic acid in aqueous solutions were taken in a beaker, and then the crosslinker (MBA) (1 ml, 1 wt%), ammonium persulphate (APS) (1 ml, 5 wt%) and TMEDA (2 ml, 1 wt%) were sequentially added to this solution containing PVA. After the completion of the reaction time (one day), the polymer gels obtained were washed with ethanol and water and then dried in vacuum oven at 60°C to a constant weight. The dried gels were re-weighed and cut into small pieces. All the gels are transparent in nature.

Swelling Studies

The swelling studies of the prepared PVA-based semi-IPNs in distilled water were performed by placing the dry IPN gel (W_0) in a 100 ml-beaker containing 50 ml of distilled water or different pH/salt/physiological solutions. The swollen IPN gels were removed from the solution at different time intervals and the excess water on the surface of IPN gels was removed superficially by wiping with a tissue paper and their weights (W_t) were measured with a 4 digit analytical balance. The swelling studies continued until the weight of the IPN gels (W_{eq}) remained constant (equilibrium stage). By using the swelling experimental weights of semi-IPNs, the swelling ratio (S) and swelling capacity (Q) or equilibrium swelling (S_{eq}) of semi-IPN hydrogels were calculated using the following equations:

$$\text{Swelling ratio (S)} = [(W_t - W_0)/W_0]$$

$$\text{Swelling capacity (Q)} = [(W_{eq} - W_0)/W_0]$$

where W_0, W_t, and W_{eq} are the weights of the IPN gel sample in the dry state, at time t and completely swollen state (equilibrium), respectively. The swelling capacity (Q) or equilibrium swelling (S_{eq}) is referred as the highest swelling ratio value of semi-IPNs in various aqueous media.

RESULTS AND DISCUSSION

Swelling Behavior of Semi-IPN Hydrogels

The swelling behavior of hydrogels is attributed to the electrostatic repulsive forces of the ionic charges present in the networks. Therefore, the ionic charge content in the hydrogel network structure is the most important factor for obtaining the swelling capacity. In the present study, sodium methacrylate, potassium methacrylate, and maleic acid (hydrophilic monomers) were employed as co-monomers in the copolymerization reactions with acrylamide in the presence of PVA. Figure 1 illustrates the dynamic swelling behavior of PVA-based semi-IPN hydrogels containing different amounts of acrylamide and potassium methacrylate or sodium methacrylate or maleic acid [(1.0:0.0 (IPN 1), 0.8:0.2 (IPN 2), 0.6:0.4 (IPN 3), 0.4:0.6 (IPN 4), 0.2:0.8 (IPN 5)]. NMA, KMA, and MA codes indicate an IPN series of poly(acrylamide-co-sodium methacrylate)/PVA, poly(acrylamide-co-potassium methacrylate)/PVA, and poly(acrylamide-co-maleic acid)/PVA, respectively.

Initially, all the semi-IPNs swelled rapidly within a time limit of 150 min and slowly leveled off. The maximum swelling ratio was obtained between 300 to 350 min for all these IPNs. For all the semi-IPNs systems, the swelling behavior varied significantly according to the comonomer NMA, KMA, and MA content in the IPN composition. As shown in Figure 1, it changed monotonically with comonomer concentration. Further, PVA/poly(AAm-co-NMA) and PVA/poly(AAm-co-KMA) semi-IPN hydrogels showed a similar swelling pattern but there is a deviation in the swelling behavior of PVA/poly(AAm-co-MA), hydrogels. The lower swelling values observed for PVA/poly(AAm-co-MA) semi-IPN hydrogels are due to difference in pore network structure. This nature is due to variation in the network structure/crosslinking phenomenon of the networks (IPNs). Pore networks are defined as free space between the crosslinked polymer networks. The free-space is comparatively less for PVA/poly(AAm-co-MA) semi-IPN hydrogels because each MA repeating unit has two ionic (COO^-) groups that make a densely crosslinked structure (less pore structure) of the gel products whereas the other two semi-IPN hydrogels containing sodium methacrylate or potassium methacrylates have one ionic (COO^-) per repeating unit and that is why these products yield highly porous network structures for which higher swelling ratios were recorded experimentally.

Figures 1A and 1B clearly show that the swelling ratio increases from 8.74 to 140.79 g/g and 8.74 to 132.07 g/g with increase of NMA and KMA contents from 0 to 0.8 wt%, respectively. In the case of PVA/poly(AAm-co-MA) semi-IPNs (Figure 1C), the swelling ratio increased from 8.74 to 25.84 g/g by varying the MA content from 0 to 0.6 wt%. However, above 0.6 wt% of MA, a drastic fall in the swelling ratio is observed. This nature can be explained as the excess of ionic units leads to an increase in the solubility of the copolymer at a fixed crosslinker concentration in the swelling medium and thus decreased the swelling capacity [37]. In detail, at a fixed crosslinker concentration up to a certain monomeric composition in the polymerization results in highly insoluble hydrogel.

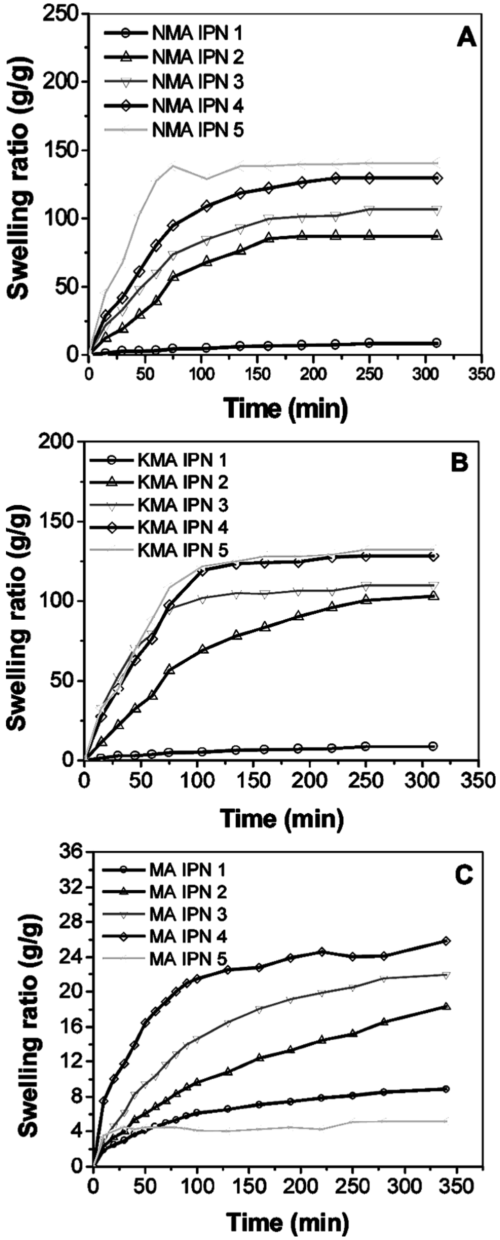

FIGURE 1 Swelling behavior of (A) PVA=poly(AAm-co-NMA), (B) PVA/poly (AAm-co-KMA), and (C) PVA=poly(AAm-co-MA) semi-IPN hydrogels.

Thereafter an increased concentration of monomeric MA leads to less crosslinked structure or even un-crosslinked polymeric chains, and/or higher ionic repeating units exist in the polymeric network structure that are responsible for the soluble portions. Therefore, in the case of PVA/poly(AAm-co-MA) semi-IPNs containing higher concentrations of MA received lower swelling values.

Effect of pH on Swelling Behavior of Semi-IPNs

The pH of the swelling medium strongly affects the swelling behavior of hydrogels, when the hydrogel is polyelectrolyte in nature. PVA-based semi-IPN gels contain either sodium methacrylate or potassium methacrylate or maleic acid, as comonomeric units that are anionic in nature. The equilibrium swelling ratios of these semi-IPN gels in different pH solutions (2–10) are shown in Figure 2. The figure shows the swelling capacity increases with increased pH up to 8, and then decreases. However, the equilibrium swelling ratios are found to be lower for all the semi-IPNs in different pH medium than in distilled water.

At low pH (2.0) (Figures 2A and 2B), the sodium or potassium ions of semi-IPNs dissociate from the carboxylate groups and come out of the gel network structure and these ions are replaced by hydrogen ions of the external solution. At this condition, the total charge present on the semi-IPN networks becomes less than that in the distilled water and hence showed lower equilibrium swelling ratios in this low pH solution. With increased pH of the swelling medium, the replacement of sodium or potassium ions by hydrogen ions decreases and the charges present on the copolymeric chains increase. This causes the expansion of the semi-IPN hydrogel networks and thereby gradually increasing their equilibrium swelling ratios. But, at higher pH medium, the semi-IPNs show again lower equilibrium swelling ratios. This nature can be explained, beyond the pH 8 of the swelling medium, as due to the fact that at higher alkaline range, the charge density in the hydrogel network structure is greater, opposing the penetration of polar water molecules into the gel networks and thereby lowering their swelling capacity. This phenomenon is termed as a salt screening effect.

In the case of PVA/poly(AAm-co-MA) gels, the equilibrium swelling ratio increases with increasd pH of the swelling medium. A closer observation of Figure 2C reveals that the increase in the equilibrium swelling ratio is rather more pronounced at pH 7 of the medium. This is only due to the complete dissociation of acidic groups of maleic acid at a particular pH value, caused by the second pK_a of maleic acid,

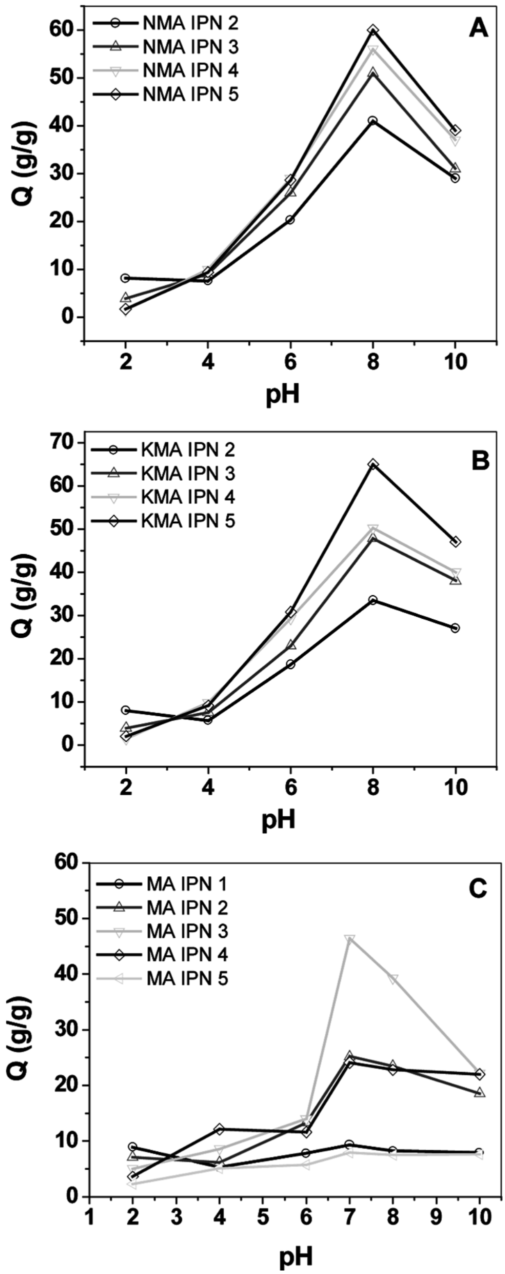

FIGURE 2 Swelling behavior of semi-IPNs of (A) PVA=poly(AAm-co-NMA), (B) PVA/poly(AAm-co-KMA), and (C) PVA=poly(AAm-co-MA) semi-IPN hydrogels in different pH swelling media.

which is about 6.06. Therefore, when the pH of the swelling medium exceeds 6.06, the ionization of carboxylic groups in the IPN matrix causes sudden rise in the equilibrium swelling ratio due to increased ion osmotic swelling pressure as well as chain relaxation resulting from the electrostatic repulsions among the carboxylate groups inside the IPN matrix. But, the swelling behavior of IPNs was not studied below pH 2, where the first pK_a of maleic acid is around 1.85. In conclusion, the observed increase in equilibrium swelling ratio of the hydrogels with increase in pH of the swelling medium arises not only from the increase of ion osmotic swelling pressure but also to some extent from a chain relaxation process.

The pH-dependent swelling reversibility of the semi-IPN hydrogels was examined in acidic (pH 4) and basic (pH 10) media. Figure 3 presents successive swelling and de-swelling cycles for the semi-IPNs when the gels kinetics are followed in external pH medium 4.0 and pH 10. The hydrogels are found to exhibit a number of cycles without undergoing any shape deformation. Owing to insignificant difference between PVA/poly(AAm-co-NMA) and PVA/poly(AAm-co-KMA) semi-IPNs (COONa and COOK groups), the reduction and increment in their swelling characteristics at two different pHs are very close together. Whereas the swelling and de-swelling phenomena varied with the aforementioned semi-IPNs compared to PVA/poly(AAm-co-MA) only due to the carboxylic groups of maleic acid.

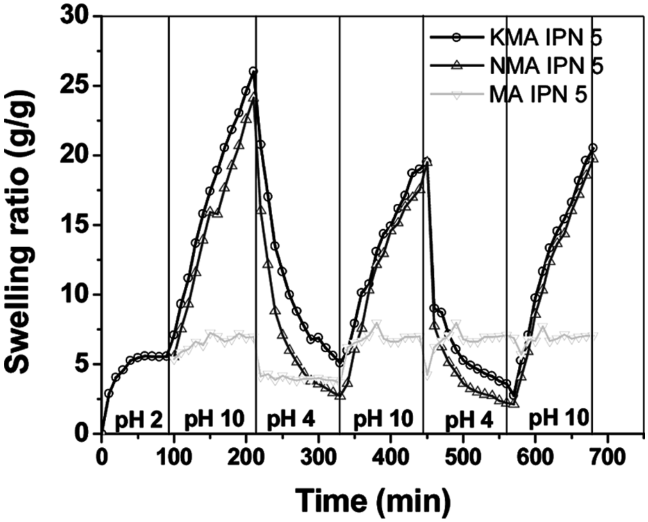

FIGURE 3 pH-responsive (reversible) swelling behavior of semi-IPNs.

Effect of Salt Solutions on Swelling Behavior of Semi-IPNs

In general, the swelling behavior of hydrogel depends mainly on the chemical structure of the hydrogel and the medium. The swelling capacity can be obtained either by increasing the concentration of ionizable groups in the networks or by lower crosslink density. The presence of salt in the swelling medium greatly influences the swelling nature of hydrogels, which is responsible for the diffusion coefficient of any drug release. The presence of salt ions in the swelling medium alters the osmotic pressure due to difference in the ionic concentration in the interior of the gel and in the external solution. Therefore, the equilibrium swelling or swelling capacity of the synthesized hydrogels was performed in different saline solutions. The test results shown in Figure 4 indicate that the swelling ratio of these semi-IPN hydrogels decreases in sodium chloride solutions as the ionic concentration of the salt solution increases [37]. This behavior is quite acceptable and can be explained as the gel network expansion decreased due to operation of repulsive forces of counter ions acting on the IPN networks shielded by the bound ionic charges. Therefore, the resulting osmotic pressure decreased with increase in the ionic strength of the saline concentration.

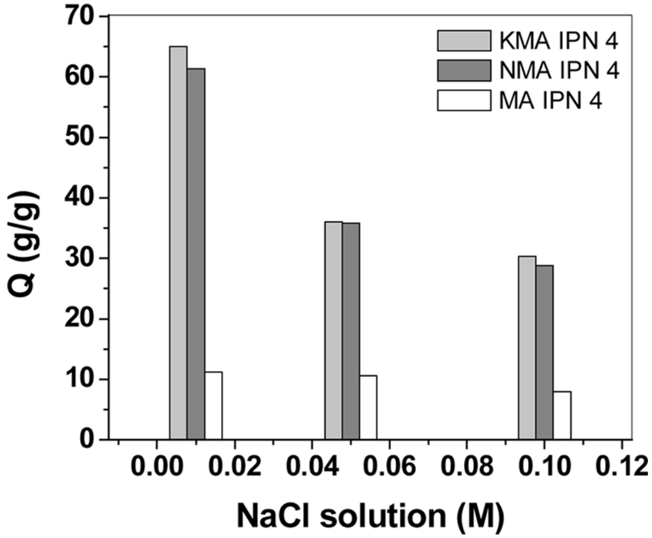

FIGURE 4 Influence of sodium chloride concentration on swelling behavior of semi-IPNs.

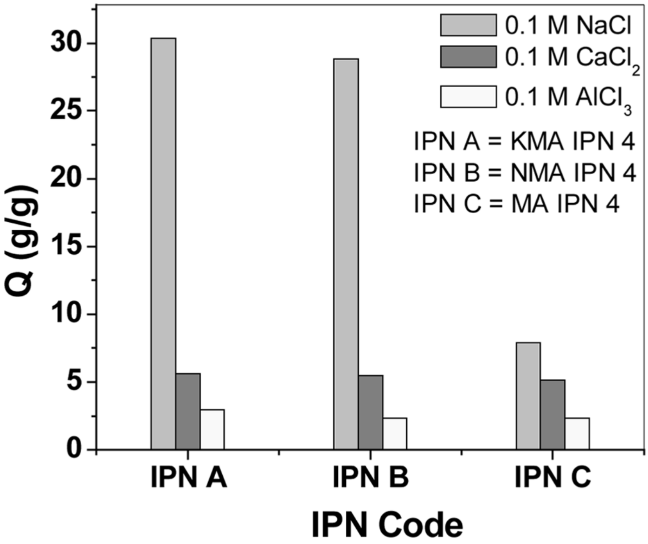

FIGURE 5 Swelling dependency on metal cation solutions of semi-IPNs.

To study the influence of cations on the swelling capacity of PVA-based ionizable hydrogels, 0.1 M chloride salt solutions of Na^+, Ca^{2+}, and Al^{3+} were utilized. Figure 5 illustrates the equilibrium swelling results of different PVA-based IPNs with respect to different salt solutions. It is obvious from the figure that aqueous Al^{3+} medium has shown lower swelling ratio than the other two ionic mediums. The order of equilibrium swelling ratio of cations in the aqueous solutions is, $Na^+ > Ca^{2+} > Al^{3+}$. The IPN hydrogels contain carboxylate groups on the polymeric chains that can interact with cations. The possible reason for lower swelling capacity for IPN hydrogels in $AlCl_3$ and $CaCl_2$ solution is that the trivalent aluminum ions or bivalent calcium ions increase the crosslinking density because of interaction of Al^{3+} or Ca^{2+} with carboxylate ions leading to "ionic crosslinking."

Effect of Simulated Biological Fluids

The swelling of hydrogel is the net result of osmotic and the restoring elastic pressure. It is noticed that the presence of a solute in the surrounding aqueous medium is capable of altering the swelling behavior of hydrogels. Figure 6 clearly indicates the solute-dependant swelling property of hydrogels in different biological solutions. The results obtained clearly show that IPN hydrogels have higher swelling

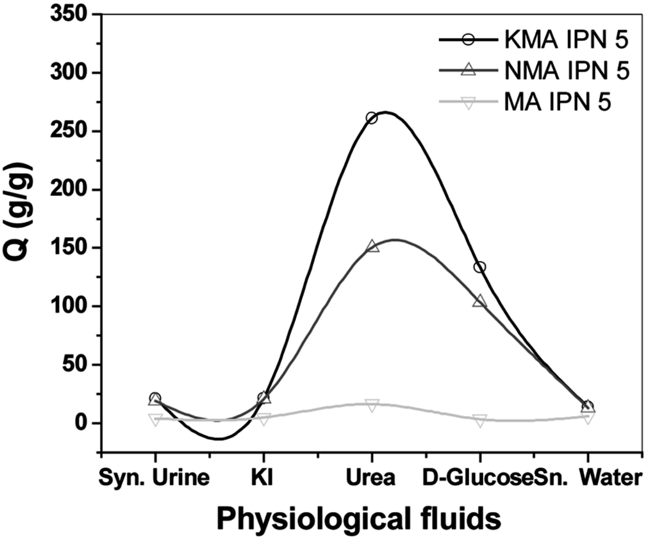

FIGURE 6 Semi-IPNs swelling capacity variation with different physiological fluids.

capacity in urea solution than in other biological solutions. This may be due to hydrogen bonding between the polymeric chains and the swelling media (urea) and hence the capability to hold huge amounts of water inside the hydrogel networks. Further, the order of swelling capacity for IPN hydrogels in different biological fluids is found to be urea > glucose > synthetic urine > saline water.

CONCLUSION

Semi-interpenetrating polymer network hydrogels show swelling capacity in the order: PVA/poly(AAm-co-KMA) > PVA/poly(AAm-co-NMA) > PVA/poly(AAm-co-MA). The swelling pattern of these semi-IPN hydrogels is discussed in detail in various swelling media, including different pH, salt, and biological fluids. Moreover, pH reversibility of these semi-IPN hydrogels was also revealed.

REFERENCES

[1] Gil, E. S. and Hudson, S. M., *Prog. Polym. Sci.* **29**, 1173 (2004).
[2] Tanaka, Y., Gong, J. P., and Osada, Y., *Prog. Polym. Sci.* **30**, 1 (2005).
[3] Chen, J., Park, H., and Park, K., *Proc. ACS. Div. Polym. Mat. Sci. Eng.* **79**, 236 (1998).

[4] Hoffman, A. S., *Adv. Drug. Deli. Rev.* **43**, 3 (2002).

[5] Osada, Y., Gong, J. P., and Tanaka, T., *J. Macromol. Sci. Part C: Polym. Rev.* **44**, 78, (2004).

[6] Buchholz, F. L., *Chemtech.* **24**, 38 (1994).

[7] Mohana Raju, K., Padmanabha Raju, M., and Murali Mohan, Y., *Polym. Int.* **52**, 768 (2003).

[8] Mohana Raju, K., Padmanabha Raju, M., and Murali Mohan, Y., *J. Appl. Polym. Sci.* **85**, 1795 (2002).

[9] Donempudi, S. and Yaseen, M., *J. Polym. Mater.* **11**, 73 (1994).

[10] Kasgoz, H., Ozgumus, S., and Orbay, M., *Polymer* **44**, 1785 (2003).

[11] Bajpai, S. K., *Iran. Polym. J.* **9**, 19 (2000).

[12] Sagasaka, K., Katoh, S., Takai, N., Takahashi, H., and Umezawa, Y., *Sep. Sci. Technol.* **16**, 971 (1984).

[13] Peppas, N. A. and Am Ede, D. J., *J. Appl. Polym. Sci.* **65**, 509 (1997).

[14] Yong, Q. and Park, K., *Adv. Drug Deliv. Rev.* **53**, 321 (2001).

[15] Dhara, D., Nisha, C. K., and Chatterji, P. R., *J. Macromol. Sci. Part C: Polym. Rev.* **36**, 197 (1999).

[16] Gudeman, L. F. and Peppas, N. A., *J. Appl. Polym. Sci.* **55**, 919 (1995).

[17] Bajpai, A. and Saini, R., *Polym. Int.* **54**, 796 (2005).

[18] Aleyamma, A. J. and Sharma, C. P., (1991). In *Blood Compatible Materials and Devices—Prospective Towards the 21st Century*. C. P. Sharma and M. Szycher, Eds., Technomic, Lancaster, PA, p. 123.

[19] Langer, R., *Chem. Eng. Commun.* **6**, 1 (1990).

[20] Shin, B. C., Jhon, M. S., Lee, H. B., and Yuk, S. H., *Eur. Polym. J.* **34**, 171 (1998).

[21] Kim, S. J., Lee, K. J., Kim, I. Y., Lee, Y. M., and Kim, S. I., *J. Appl. Polym. Sci.* **90**, 3310 (2003).

[22] Park, S. J. and Kim, S. I., *React. Funct. Polym.* **55**, 61 (2003).

[23] Szilagyi, A. and Zrinyi, M., *Polymer* **46**, 10011 (2005).

[24] Shin, M.-S., Kim, S. I., Kim, I. Y., Kim, N. G., Song, C. G., and Kim, S. J., *J. Appl. Polym. Sci.* **84**, 2591 (2002).

[25] Peppas, N. A. and Wright, S. L., *Eur. J. Pharm. Biopharm.* **46**, 15 (1998).

[26] Kim, S. Y. and Lee, Y. M., *J. Appl. Polym. Sci.* **74**, 1752 (1999).

[27] Kim, S. J., Yoon, S. G., and Kim, S. I., *Polym. Int.* **54**, 149 (2005).

[28] Masci, G., Husu, I., Murtas, S., Piozzi, A., and Crescenzi, V., *Macromol. Biosci.* **3**, 455 (2003).

[29] Kim, S. J., Yoon, S. G., Lee, Y. M., Kim, H. C., and Kim, S. I., *Biosensors and Bioelectronics* **19**, 531 (2004).

[30] Kim, S. J., Yoon, S. G., Lee, Y. M., An, K. H., and Kim, S. I., *J. Appl. Polym. Sci.* **90**, 1389 (2003).

[31] Bajpai, S. K., *J. Appl. Polym. Sci.* **80**, 2782 (2001).

[32] Sen, M., Uzun, C., and Guven, O., *Int. J. Pharm.* **203**, 149 (2000).

[33] Oztop, H. N., Saraydin, D., Solpan. D., and Guven, O., *Polym. Bull.* **50**, 183 (2003).

[34] Karadag, E., Vzum, D. B., and Saraydin, D., *Eur. Polym. J.* **38**, 2133 (2002).

[35] Murali Mohan, Y., Keshava Murthy, P. S., Rao, K. M., Sreeramulu, J., and Mohana Raju, K., *J. Appl. Polym. Sci.*, **96**, 1153 (2005).

[36] Murali Mohan, Y., Keshava Murthy, P. S., and Mohana Raju, K., *React. Funct. Polym.* **63**, 11 (2005).

[37] Murali Mohan, Y., Keshava Murthy, P. S., Sudhakar, H., Padmanabha Raju, M., Vijaya Kumar Naidu, B., and Mohana Raju, K., *Int. J. Polym. Mat.* **55**, 867 (2006).