Swelling Behavior of Semi-Interpenetrating Polymer Network Hydrogels Composed of Poly(Vinyl Alcohol) and Poly(Acrylamide-*co*-Sodium Methacrylate)

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels based on poly(vinyl alcohol) (PVA) and poly(acrylamide-*co*-sodium methacrylate) poly(AAm-*co*-SMA) were prepared by the semi IPN method. These IPN hydrogels were prepared by polymerizing aqueous solution of acrylamide and sodium methacrylate, using ammonium persulphate/N,N,N^1,N^1-tetramethylethylenediamine (APS/TMEDA) initiating system and N,N^1-methylene-bisacrylamide (MBA) as a crosslinker in the presence of a host polymer, poly(vinyl alcohol). The influence of reaction conditions, such as the concentration of PVA, sodium methacrylate, crosslinker, initiator, and reaction temperature, on the swelling behavior of these IPNs was investigated in detail. The results showed that the IPN hydrogels exhibited different swelling behavior as the reaction conditions varied. To verify the structural difference in the IPN hydrogels, scanning electron microscopy (SEM) was used to identify the morphological changes in the IPN as the concentration of crosslinker varied. In addition to MBA, two other crosslinkers were also employed in the preparation of IPNs to illustrate the difference in their swelling phenomena. The swelling kinetics, equilibrium water content, and water transport mechanism of all the IPN hydrogels were investigated. IPN hydrogels being ionic in nature, the swelling behavior was significantly affected by environmental conditions, such as temperature, ionic strength, and pH of the swelling medium. Further, their swelling behavior was also examined in different physiological bio-fluids. J Appl Polym Sci 98: 302–314, 2005

Key words: crosslinker; hydrogels; interpenetrating polymer network; poly(vinyl alcohol); superabsorbent; swelling ratio

INTRODUCTION

Poly(vinyl alcohol) (PVA) is of great interest in numerous biomedical and pharmaceutical applications because of certain advantages that make it an excellent candidate for biomaterials, including its nontoxic, noncarcinogenic, bio-adhesive, good strength, low fouling potential, temperature, and pH stability, as well as its ease of processing behavior.[1–6] Further, it has a simple chemical structure and modifications are possible by chemical reactions. Moreover, PVA gels exhibit a high degree of swelling in water as well as in biological fluids and they are rubbery/elastic in nature, making it employable as a biomaterial for various applications, including contact lenses, lining for artificial hearts, skin replacement, artificial cartilage replacement, and drug delivery.[1,7]

Hydrogels are three-dimensional networks of hydrophilic polymers containing a large amount of water, permeability to a variety of molecules, and good biocompatibility.[8,9] The high water content in the hydrogels aids compatibility with natural tissues. Hydrogels, which exhibit significant changes in response to environmental signals, such as temperature, pH, ionic strength, solvent, pressure, electric stimuli, and so forth, are called stimuli-responsive hydrogels.[1,10–17] Among them, temperature and pH sensitive hydrogels are the most investigated, because of their easy control and wide-ranging applicability of these signals in the biotechnology, chemical processing, and medical fields.

Dhara and coworkers[18] reported a tricomponent IPN system composed of poly(acrylamide-*co*-acrylic acid) [P(AAm-*co*-AA] with poly(vinyl alcohol), used for biomedical applications. PVA and poly(acrylamide) [P(AAm)] were chosen due to their good compatibility and versatility.[19,20] Bajpai reported the synthesis, swelling, and de-swelling behavior of poly(acrylamide-*co*-maleic acid) [poly(AAm-*co*-MA)] hydrogels.[21] The study also included the pH-dependent swelling behavior. Gudeman and Peppas prepared interpenetrating networks from PVA and poly(acrylic acid) (PAA).[12] Crosslinked poly(acrylic acid) and

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poly(acrylic acid-*co*-2-hydroxyethylmethacrylate) [P(AA-*co*-HEMA)] hydrogels were employed for the transport of ionizable drugs and proteins. Öztop and coworkers[22] studied the adsorption of bovine serum albumin (BSA) onto the surface of a novel terpolymeric hydrogel prepared with acrylamide (AAm), 2-hydroxypropyl methacrylate (HPMA) and maleic acid by a radiation technique.[23]

Novel pH and temperature responsive IPN hydrogels composed of PVA and PAA crosslinked by ultraviolet (UV) radiation and the freeze-thawing method were developed and evaluated for their swelling behavior.[24,25] Bajpai and coworkers[7] synthesized hydroxyapatite impregnated (HAP) semi-interpenetrating polymer networks of PVA and poly(acrylamide-*co*-acrylic acid), which are of great importance for the development of biomaterials. One of the main advantages of these HAP/polymer composites with respect to HAP biomaterials is the possibility to modulate biodegradability, bioactivity, and mechanical properties. Shin and coworkers[23] studied the permeation of solutes such as theóphylline, riboflavin, cefazoline-sodium, vitamin B_{12}, and BSA through interpenetrating polymer network hydrogels composed of PVA and PAA.

Poly(acrylamide) based hydrogels have been used for hygienic, agricultural, horticultural, biomedical, and pharmaceutical applications.[19,20,26–28] Poly(acrylamide) [P(AAm)] and neutralized poly(methacrylic acid) are widely known hydrophilic polymers and are widely used in making water-sorption materials. Realizing the vital role of PVA in biomedical engineering, the present investigation involves the preparation of semi-interpenetrating polymer networks (semi-IPNs) of PVA and poly(acrylamide-*co*-sodium methacrylate) [poly(AAm-*co*-SMA)] to improve the swelling behavior of the semi-IPN system as well as to investigate the pH, temperature, and chemical environment sensitivity.

EXPERIMENTAL

Materials

Acrylamide (AAm), ammonium persulphate (APS), poly(vinyl alcohol) (PVA) ($M_w \approx 1{,}25{,}000$), and N,N^1-methylene-bisacrylamide (MBA) were obtained from S.D. Fine-Chem Ltd (Mumbai, India). Methacrylic acid (MA), 1,4-butanediol diacrylate (BDDA), 1,2-ethyleneglycol dimethacrylate (EGDMA), diallyl phthalate (DP), and N,N,N^1,N^1-tetramethylethylenediamine (TMEDA) of Aldrich Chemical Company, Inc. (Milwaukee, WI) were received from Sigma Aldrich Pvt. Limited (Secunderabad, India). All the chemicals and reagents were used as received. Double distilled water was used for making all solutions and swelling experiments.

Stock solutions of MBA (1g/100 mL dist. water), BDDA (1g/100 mL methanol), EGDMA (1g/100 mL methanol), DP (1g/100 mL methanol), APS (5g/100 mL dist. water), and TMEDA (1g/100 mL dist. water) were prepared. Sodium methacrylate (SMA) was prepared by neutralization of methacrylic acid with sodium hydroxide.

Preparation of PVA/P(AAm-*co*-SMA) semi-IPN hydrogel

PVA/Poly(AAm-*co*-KMA) semi-IPN hydrogels were prepared as per the method reported for PVA/poly-(acrylamide-*co*-acrylic acid) by Dhara and coworkers.[18] The polymerization was initiated by the APS/TMEDA system in an aqueous solution of a desired concentration of acrylamide, sodium methacrylate, a crosslinker, and PVA. In a typical polymerization (IPN-NMA 1), 0.25 g of PVA was dissolved in 5 mL of distilled water in a 100-mL beaker and heated at 50°C for 2–3 h to obtain PVA solution. To this solution, 10.46 mM of AAm, 0.46 mM of SMA, 0.013 mM of MBA (0.2 mL MBA solution), 0.219 mM of APS (1 mL APS solution), and 0.086 mM of TMEDA (1 mL TMEDA solution) were added sequentially. Finally, the whole reaction mixture transferred in poly(vinyl chloride) PVC straws (3 mm dai) to obtain gels in the form of rods (cylindrical shape). Semi-IPNs were obtained in the form of transparent gels within 30 min. However, the reaction continued for 24 h to get complete gelation in all cases at room temperature.

SEM analysis

The dry PVA/poly(AAm-*co*-SMA) semi-IPNs were coated with a thin layer of palladium gold alloy, and their morphological variations were observed by using a JEOL JSM 840A (Tokyo, Japan) scanning electron microscope (SEM).

Swelling studies

The conventional gravimetric method was employed for the determination of the swelling ratio (S) and the equilibrium water content (EWC%) of semi-IPN hydrogels.[29–34] The swelling ratio of hydrogels at equilibrium is called the equilibrium swelling ratio. In the swelling studies, about 50–60 mg of semi-IPN was placed in 100 mL of distilled water/swelling medium. The weight of swollen semi-IPN was determined at different time intervals, and the swelling experiment was continued to a constant weight. At every measurement, the excess water was removed superficially by filter paper and then weighed accurately. By using the swelling experimental weights of semi-IPNs, the swelling ratio and equilibrium water content of semi-

IPN hydrogels were calculated using the following equations:

$$S = \frac{[\text{Weight of swollen gel}(W_s) - \text{Weight of dry gel}(W_d)]}{[\text{Weight of dry gel}\ (W_d)]} \quad (1)$$

EWC(%)

$$= \frac{[\text{Weight of swollen gel at equilibrium}(W_{eq}) - \text{Weight of dry gel}(W_d)]}{[\text{Weight of swollen gel}\ (W_{eq})]} \times 100 \quad (2)$$

Swelling and diffusion characteristics

To evaluate the mechanism of the swelling process of hydrogels, several kinetic models are used to test the experimental data. A simple kinetic analysis is the second order equation,[34–36] $dS/dt = k_S\ (S_{eq} - S)$,[2] where S_{eq}, S, and k_S denote the equilibrium swelling (theoretical), swelling at any time, and swelling rate constant, respectively. The integration of the above equation over the limits $S = S_0$ at $t = t_0$ and $S = S$ at $t = t$, gives $t/S = A + Bt$, where $B = 1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A = (1/k_S S_{eq}^2)$ is the reciprocal of the initial swelling rate of the hydrogel, and k_s is the swelling rate constant. To examine the above kinetic model for these semi-IPNs, t/S versus t graphs were plotted, and the initial rate of swelling (r_i), swelling rate constant (k_S), and theoretical equilibrium swelling (S_{eq}) values of semi-IPNs were calculated from the slope and intersection of the lines obtained in the graphs.[32]

The dynamics of the water sorption process were investigated by monitoring the change in the amounts of water imbibed by the hydrogel at various intervals. In the present diffusion study also, the previous swelling results were utilized. For the kinetic analysis, the swelling results obtained were utilized only up to 60% of the swelling curves,[37,38] $F = W_s - W_d / W_d = k\ t^n$, where F, W_s, and W_d denote the fraction swelling ratio at time t, the weight of the swollen hydrogel at t, and the weight of the dried hydrogel at time $t = 0$, respectively; k is a swelling constant related to the structure of the network; and n is the swelling exponent, which indicates the water transport mechanism. When $n = 0.5$, the release is Fickian in nature and diffusion controlled, whereas values of n between 0.5–1.0 indicate non-Fickian diffusion (anomalous diffusion). In anomalous diffusion, diffusion and relaxation are said to be isochronal effective.[37,38] If n value is exactly equal to unity, then the diffusion is designed as Case II diffusion. In very few cases, the n value is found to exceed unity and is called super Case II diffusion ($n > 1$). To estimate the swelling exponent (n) by using the above equation up to 60% of the swelling ratio values, ln S versus ln t graphs were plotted to obtain straight lines. The swelling exponent was calculated from the slope of the lines of ln S - ln t plots.

The diffusion coefficients of these IPNs were calculated by using the short time approximation method.[36,39] This method is valid for the first 60% of the swelling results. The cylindrical IPN hydrogels diffusion coefficients were calculated using the following equation:

$$S = 4[D/\pi r^2]^{1/2} t^{1/2}$$

where D, r, S, and t represent the diffusion coefficient of the hydrogel, the radius of the hydrogel, fractional swelling, and time, respectively. To investigate the diffusion coefficient of hydrogels, S versus $t^{1/2}$ plots were plotted and the diffusion coefficients were calculated from the slopes of these lines.

pH solution preparation

Buffer solution A was prepared by mixing 12.3 g of anhydrous boric acid (0.20*M*) and 10.51 g of citric acid (0.05*M*) in 1000 mL distilled water, and buffer solution B was prepared by dissolving 38.01 g of trisodium phosphate (M) in 1000 mL distilled water. To prepare a specific buffer solution, the two pH solutions (solutions A and B) were mixed at different volumes based on Shugar and Dean.[40]

Physiological fluids preparation[41]

To study the water uptake and water transport phenomena of hydrogels in biological media, different simulated biological fluids were made in 100 mL distilled water. The solutions prepared were: saline water, 0.9 g NaCl/100 mL; synthetic urine, [0.8 g NaCl + 0.10 g $MgSO_4$ + 2.0 g urea + 0.06 g $CaCl_2$] / 100 mL; urea, 5 g/100 mL; and D-glucose, 5 g/100 mL.

RESULTS AND DISCUSSION

The semi-IPN hydrogels were prepared from PVA and poly(acrylamide-*co*-sodium methacrylate). The obtained semi-IPNs were subsequently utilized for swelling experiments. It is believed that the polymerization process starts with the reaction between APS and TMEDA to form an activated TMEDA molecule containing unpaired valence electrons. The unpaired valence electrons may interact with acrylamide, sodium methacrylate, and/or crosslinker, thereby initiating the polymerization, copolymerization, and crosslinking process simultaneously to form a crosslinked network of structured semi-IPN hydrogels. In this process, the polymerization of acrylamide and sodium methacrylate was conducted in the

presence of PVA to obtain PVA/poly(AAm-*co*-SMA) semi-IPNs. PVA was distributed throughout the crosslinked networks of semi-IPN hydrogels. This approach is widely useful for the production of semi-IPN hydrogels with required crosslinked networks (crosslink density), which is an important influencing factor on the swelling properties of hydrogels.

Hydrogels are characterized by swelling capacity, which can be measured from their absorption mechanism that in turn is caused by the diffusion process. The diffusion process represents the affinity between the polymeric networks and the external solution. Therefore, the swelling behavior depends on the nature of the polymer network involving the strength of hydrophilic groups, crosslinking density, and elasticity of the polymer network.[25,26] Further, the swelling behavior also depends on the type of external solution and the characteristics of the external solution. The variation in semi-IPN network structure of PVA/P(AAm-*co*-SMA), which directly influences the swelling capacity, can be achieved by varying the reaction parameters, such as the concentration of sodium methacrylate, crosslinker and type of crosslinker, initiator, and activator. In the present investigation, the influence of various reaction parameters on swelling capacity of semi-IPN hydrogels was studied, and detailed results are tabulated in Tables I and II.

Influence of PVA content on swelling behavior

Incorporation of a hydrophilic polymer into a crosslinked gel network is expected to increase the swelling capacity of the hydrogel. In the present study, too, the influence of PVA content in the feed mixture of the semi-IPN was investigated on the swelling capacity of the semi-IPN by varying the amount of PVA from 0.15 to 1.0 g. The results, shown in Figure 1, demonstrate that the swelling ratio increases with increase of PVA from 0.15 to 0.45 g, and decreases with further increase of the PVA content. This behavior is due to the fact that the initial increase in the concentration of PVA leads to an increase in hydrophilicity of the semi-IPN, which normally results in improved sorption behavior. But, beyond 0.45 g of PVA content in the semi-IPNs, higher dense macromolecular chains are formed, restricting the penetration of water molecules into the semi-IPN, thereby decreasing the swelling ratio of the semi-IPN.

Influence of concentration of NMA on swelling behavior

For any crosslinked polymer, the water absorbency or swelling capacity can be expressed as a function of crosslinking density through Flory's elastic theory of dilute polymer solutions as represented by the following equation:

$$Q^{5/3} = \frac{[(i/2V_uS^{1/2})^2 + (1/2 - X_i)/V_1]}{[V_e/V_0]} \quad (3)$$

where Q, V_e/V_o, $[(1/2) - X_1]/V_1$, V_u, i/V_u, and S are the swelling capacity or water absorption, the crosslinking density of the polymer, the affinity between the polymer and the external solution, the volume of the structural unit, the fixed charge per volume of polymer, and the ionic strength of the external solution, respectively. Therefore, Q is a function of the ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water. The first and second terms in the numerator belong to forces that favor the promotion of swelling behavior.

In the present investigation, the influence of an ionic monomer, sodium methacrylate, on the swelling behavior was studied by varying the concentration of sodium methacrylate from 0.46 to 9.25 mM in the feed mixture of the semi-IPN hydrogels. The swelling curves of the semi-IPNs depicted in Figure 2 show that the swelling ratio increases from 27.02 to 82.80 g/g with increase of NMA concentration from 0.46 to 1.85 mM. The improved swelling behavior is attributed to the fact that with increasing NMA concentration in the semi-IPN, the concentration of fixed charges, that is, i/Vu, increases within the gel and, as predicted in eq. (3), the swelling ratio increases. It can also be explained that with increasing the number of carboxylate ions (COO^-) along the crosslinked poly(AAm-*co*-SMA) chains, the electrostatic repulsive forces among the COO^- groups become operative, resulting in the loosening of the network structure, causing an enhanced swelling capacity or sorption. However, above 1.85 mM of SMA, a slight fall in the swelling capacity is observed. This 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 decreases the swelling capacity.

Influence of nature and concentration of crosslinker on swelling behavior

The nature of the crosslinking agent and the type of crosslinking agent directly affect the network structure and thereby greatly influence the swelling behavior of the superabsorbent polymer or hydrogels.[9–14,21,31]

The hydrophilic crosslinker N,N[1]-methylenebisacrylamide is employed to evaluate the swelling behavior of PVA/poly(AAm-*co*-SMA) semi-IPN hydrogels at different concentrations, from 0.013 to 0.097 mM, and the results are presented in Figure 3. This study clearly demonstrates that as the concentration of MBA increases from 0.013 to 0.97 mM, the swelling ratio also increases from 25.34 to 68.39 g/g, and further increase in the concentration of the crosslinker de-

TABLE I
Composition, Swelling Ratio, Equilibrium Water Content, and Swelling/Diffusion Characteristics of Semi-IPN Hydrogels Crosslinked with MBA

Polymer code	PVA (g)	NMA (mM)	Crosslinker (mM)	APS (mM)	TMEDA (mM)	Swelling ratio or equilibrium swelling ratio (g water/g gel)	EWC (%)	Theoretical equilibrium swelling ratio (g water/g gel)	Initial swelling rate [(g water/g gel)min)	Swelling rate constant [(g gel/g water)/min]	Swelling exponent	Diffusion coefficient (cm^2/sec^{-1})
IPNPVA1	0.15	2.31	0.065	0.0219	0.0861	82.78	98.80	113.37	0.26	2.03E-05	0.93	3.76653
IPNPVA2	0.30	2.31	0.065	0.0219	0.0861	70.74	98.60	94.60	0.29	3.26E-05	0.96	4.49413
IPNPVA3	0.45	2.31	0.065	0.0219	0.0861	89.75	98.89	119.33	0.36	2.54E-05	0.90	4.12325
IPNPVA4	0.60	2.31	0.065	0.0219	0.0861	77.33	98.72	116.82	0.18	1.38E-05	0.96	3.4693
IPNPVA5	0.75	2.31	0.065	0.0219	0.0861	63.47	98.44	320.51	0.26	2.60E-06	1.20	5.25144
IPNPVA6	1.00	2.31	0.065	0.0219	0.0861	56.47	98.34	120.33	0.22	1.57E-05	1.04	4.7882
IPNNMA1	0.25	0.46	0.013	0.0219	0.0861	27.02	96.43	31.50	0.12	0.000119	0.71	3.74701
IPNNMA2	0.25	0.92	0.013	0.0219	0.0861	65.37	98.49	102.66	0.14	1.33E-05	0.93	3.27905
IPNNMA3	0.25	1.38	0.013	0.0219	0.0861	62.53	98.42	81.56	0.25	3.87E-05	0.95	4.24169
IPNNMA4	0.25	1.85	0.013	0.0219	0.0861	82.8	98.80	106.49	0.37	3.33E-05	0.90	4.32579
IPNNMA5	0.25	2.31	0.013	0.0219	0.0861	73.2	98.65	92.93	0.40	4.71E-05	1.02	5.15908
IPNNMA6	0.25	4.62	0.013	0.0219	0.0861	71.76	98.62	92.67	0.31	3.6E-05	0.87	4.07084
IPNNMA7	0.25	9.25	0.013	0.0219	0.0861	77.14	98.72	95.78	0.41	4.5E-05	0.82	4.34104
IPNMBA1	0.25	2.31	0.013	0.0219	0.0861	25.34	96.28	25.76	1.64	0.002477	1.01	9.86142
IPNMBA2	0.25	2.31	0.026	0.0219	0.0861	29.98	93.38	31.55	0.64	0.000651	1.35	7.79582
IPNMBA3	0.25	2.31	0.032	0.0219	0.0861	34.56	97.04	35.72	0.93	0.000731	0.89	7.20666
IPNMBA4	0.25	2.31	0.039	0.0219	0.0861	36.65	97.40	38.67	0.71	0.00048	1.25	6.98378
IPNMBA5	0.25	2.31	0.052	0.0219	0.0861	62.65	98.42	71.68	0.57	0.000112	1.02	5.88109
IPNMBA6	0.25	2.31	0.097	0.0219	0.0861	68.39	98.55	93.02	0.25	2.94E-05	0.85	3.83556
IPNMBA7	0.25	2.31	0.129	0.0219	0.0861	59.82	98.35	74.73	0.31	5.57E-05	0.95	4.62548
IPNAPS1	0.25	2.31	0.065	0.0438	0.0861	59.38	98.34	74.18	0.28	5.18E-05	0.84	4.138
IPNAPS2	0.25	2.31	0.065	0.0876	0.0861	56.04	98.24	70.87	0.23	4.61E-05	0.84	3.93
IPNAPS3	0.25	2.31	0.065	0.109	0.0861	68.69	98.56	83.19	0.38	5.58E-05	0.89	4.489
IPNAPS4	0.25	2.31	0.065	0.131	0.0861	66.41	98.51	84.38	0.26	3.70E-05	0.87	3.923
IPNAPS5	0.25	2.31	0.065	0.175	0.0861	57.94	98.30	75.87	0.24	4.26E-05	0.92	4.118
IPNAPS6	0.25	2.31	0.065	0.328	0.0861	50.89	98.07	67.34	0.24	5.36E-05	0.96	4.668

[AAm] = 10.55 mM.

TABLE II
Composition, Swelling Ratio, Equilibrium Water Content, and Swelling/Diffusion Characteristics of Semi-IPN Hydrogels Crosslinked with BDDA and EGDMA

Polymer code	PVA	NMA	Crosslinker	APS	TMEDA	Swelling ratio (g water/g gel)	EWC (%)	Equilibrium swelling ratio (g water/g gel)	Initial swelling rate [(g water/g gel)min)	Swelling rate constant [(g gel/g water)/min]	Swelling exponent	Diffusion coefficient (cm^2/sec^{-1})
IPNBDDA1	0.25	2.31	0.010	0.044	0.0861	37.38	97.39	40.01	0.77	0.000481	1.11	6.92582
IPNBDDA2	0.25	2.31	0.020	0.044	0.0861	27.69	96.51	29.31	0.67	0.000786	1.18	7.01686
IPNBDDA3	0.25	2.31	0.030	0.044	0.0861	96.97	98.98	117.37	0.73	5.36E-05	1.32	6.16824
IPNBDDA4	0.25	2.31	0.040	0.044	0.0861	76.30	98.70	88.49	0.64	8.26E-05	1.21	6.3886
IPNBDDA5	0.25	2.31	0.050	0.044	0.0861	115.66	99.14	127.67	0.38	5.02E-06	1.06	3.98531
IPNBDDA6	0.25	2.31	0.100	0.044	0.0861	66.86	98.52	81.43	0.36	5.5E-05	1.14	5.16608
IPNEGDMA1	0.25	2.31	0.010	0.044	0.0861	12.91	92.81	13.36	0.81	0.004545	0.84	10.7787
IPNEGDMA2	0.25	2.31	0.020	0.044	0.0861	53.55	98.16	88.65	0.25	3.24E-05	0.81	4.4169
IPNEGDMA3	0.25	2.31	0.030	0.044	0.0861	83.90	98.82	127.55	0.57	3.51E-05	1.39	6.75662
IPNEGDMA4	0.25	2.31	0.040	0.044	0.0861	82.93	98.80	132.97	0.41	2.33E-05	0.75	4.41464
IPNEGDMA5	0.25	2.31	0.050	0.044	0.0861	88.19	98.87	133.51	0.60	3.39E-05	1.35	6.7568
IPNEGDMA6	0.25	2.31	0.100	0.044	0.0861	119.12	99.16	176.67	0.84	2.71E-05	1.29	6.75781

[AAm] = 10.55 mM.

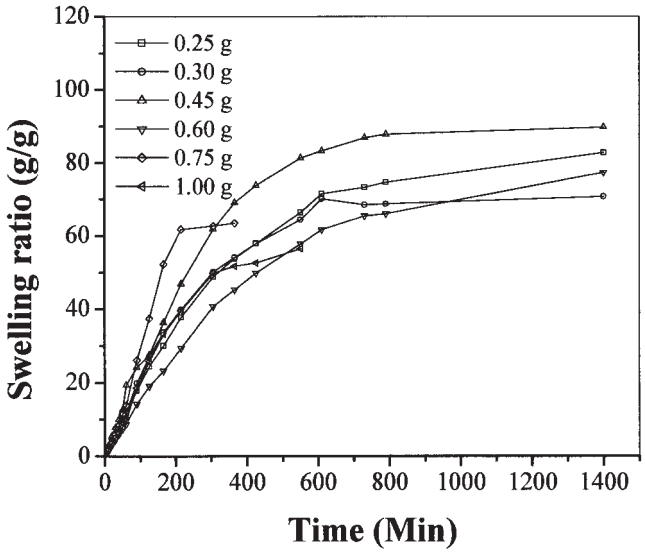

Figure 1 Influence of PVA content on swelling behavior of semi-IPN hydrogels.

creases slightly the swelling capacity. Similar swelling results were also obtained in our previous studies.[26–28]

The variation in the morphology of PVA/poly(AAm-*co*-SMA) semi-IPN hydrogels with change of crosslinker (MBA) concentration was investigated by using SEM. The SEM photographs of cross-sectional areas of PVA/poly(AAm-*co*-SMA) semi-IPN hydrogels (15 KV and ×500 magnification) are presented in Figure 4. The cross-sectional views of SEM images of these semi-IPN hydrogels display more irregular crosslinked network structure at lower concentration, whereas very fine network structure is ob-

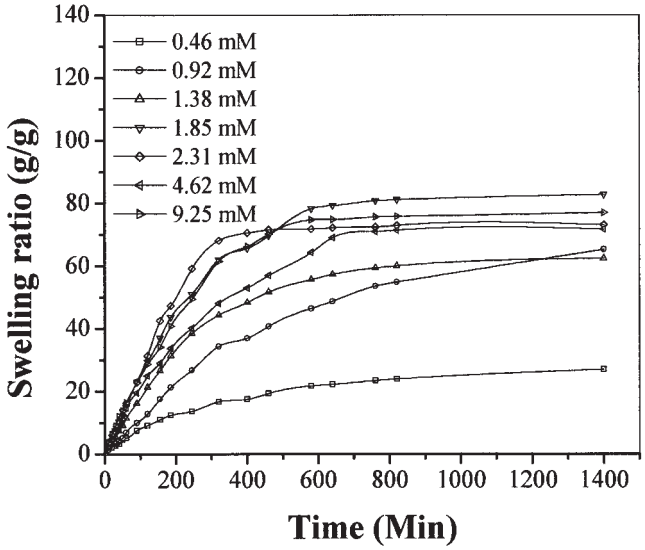

Figure 2 Influence of NMA concentration on swelling behavior of semi-IPN hydrogels.

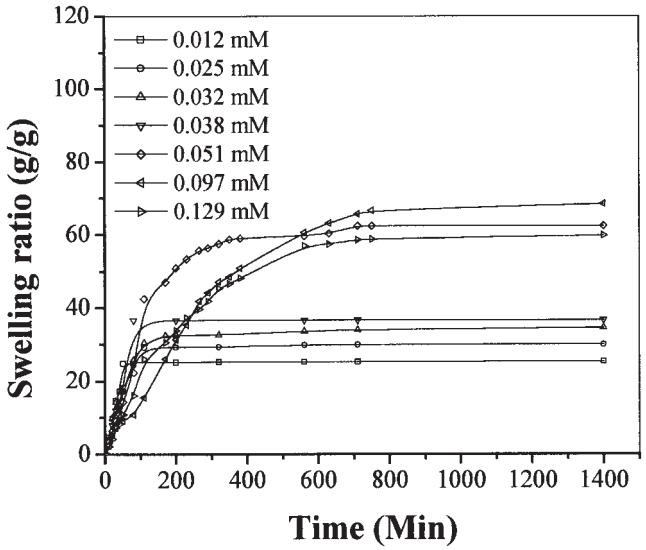

Figure 3 Influence of MBA concentration on swelling behavior of semi-IPN hydrogels.

served at higher crosslinker concentration in the reaction feed, indicating higher crosslink density. Similarly, variation in the surface area of crosslinked network structures also showed significant variations in the SEM photographs at two different magnifications (×500 and ×2000), as shown in Figures 5 and 6, respectively, with increase of crosslinker concentration in the reaction feed in semi-IPN hydrogels.

To evaluate the influence of the nature of the crosslinker on the swelling pattern of PVA/poly(AAm-*co*-SMA) IPN hydrogels, three different crosslinkers, namely, 1,4-butanediol diacrylate (BDDA), 1,2-ehtyleneglycol dimethacrylate (EGDMA), and diallyl phthalate (DP), were employed. The concentrations of BDDA and EGDMA were varied in the range of 0.01–0.10 mM in the feed of PVA/poly(AAm-*co*-SMA) semi-IPN hydrogels. As the BDDA concentration varied in the feed of semi-IPN hydrogels, different swelling capacities were observed (Fig. 7). However, at 0.50 mM of BDDA, the highest swelling ratio is noticed. A similar pattern of swelling behavior was observed in the case of EGDMA crosslinked semi-IPN hydrogels (Fig. 8). The highest swelling ratio (119.12 g/g) was attained at 1.00 mM of EGDMA. But, in the case of DP crosslinked semi-IPNs, the gels obtained are very smooth in nature and are soluble in water within 5 h. This indicates that DP crosslinked semi-IPNs have very loosely crosslinked networks, which may promote solubility in water. Therefore, their swelling ratios are not determined.

The swelling experiments of different crosslinked semi-IPN hydrogels indicate MBA crosslinked IPNs have lower swelling ratio values at all concentrations than BDDA or EGDMA crosslinked semi-IPN hydrogels. This is due to the variation in the reactivity of different crosslinkers. Due to the high solubility nature of MBA, it forms a good network structure, which ultimately reduces the mesh size, leading to lower swelling capacity. The other crosslinkers, BDDA and EGDMA, are insoluble in the aqueous phase, less reactive than MBA, and may not form a very fine network structure in the semi-IPNs, leading to high elastic behavior, thereby increasing the swelling behavior. Further, due to the employment of methanol in crosslinker solutions, porosity is generated in the gel networks, which is further responsible for enhanced swelling behavior. Thus, the order of swelling capacity of semi-IPN hydrogels crosslinked by different crosslinkers is EGDMA > BDDA > MBA.

Influence of concentration of initiator

The process of crosslinking in redox-polymerization is influenced by the concentration of the initiator[42] and activator, and it also contributes to the extent of the degree of inhomogeneity and molecular weight between two crosslinking points. The lower initiator

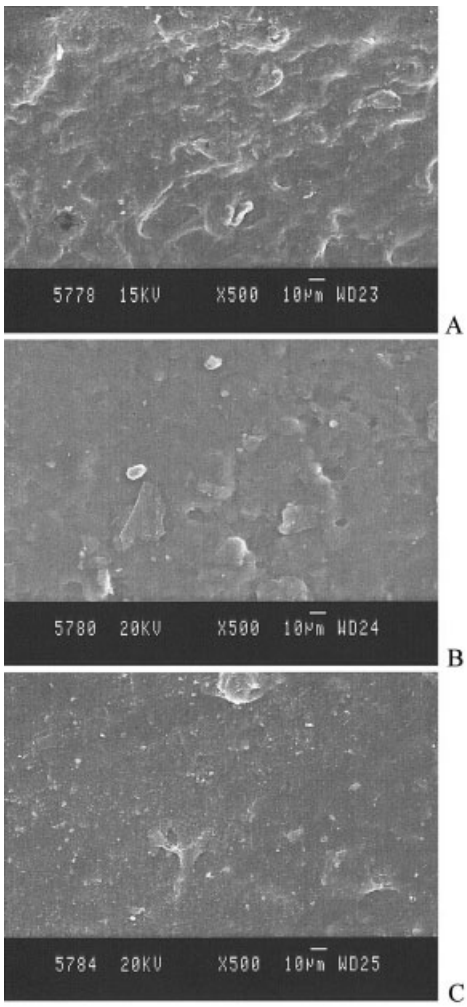

Figure 4 SEM photographs of cross-sectional area of semi-IPN hydrogels.

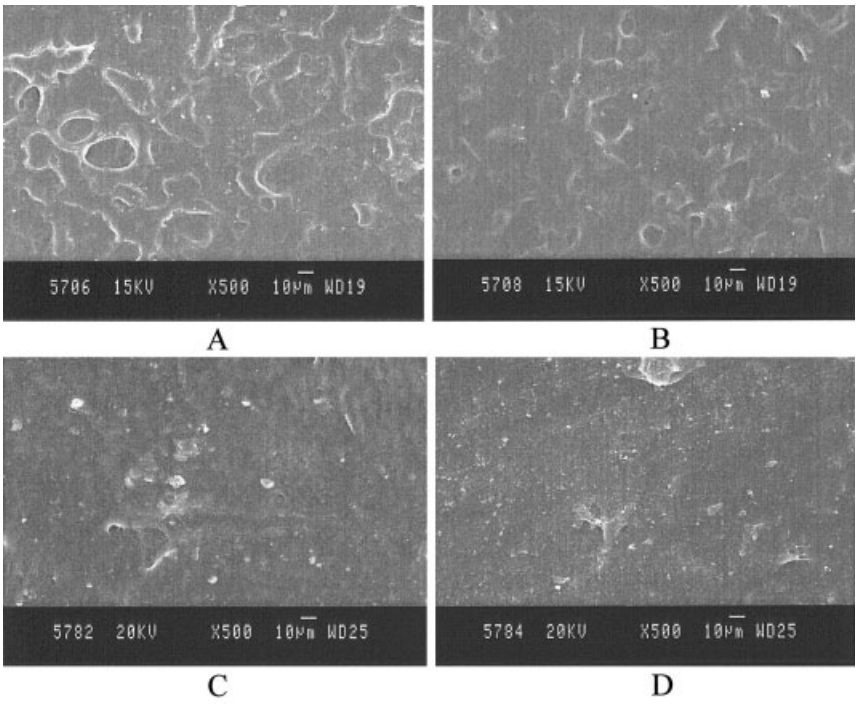

Figure 5 SEM photographs of surface area of semi-IPN hydrogels (×500 magnification): (A) IPNMBA 1, (B) IPNMBA 3, (C) IPNMBA 5.

concentration results in decrease of crosslinking degree and conversion, whereas the molecular weight of the polymer increases based on the principle of kinetic chain length.[21,36] In the present investigation, ammonium persulphate is employed as the initiator. The APS concentration is varied from 0.043 to 0.328 mM in

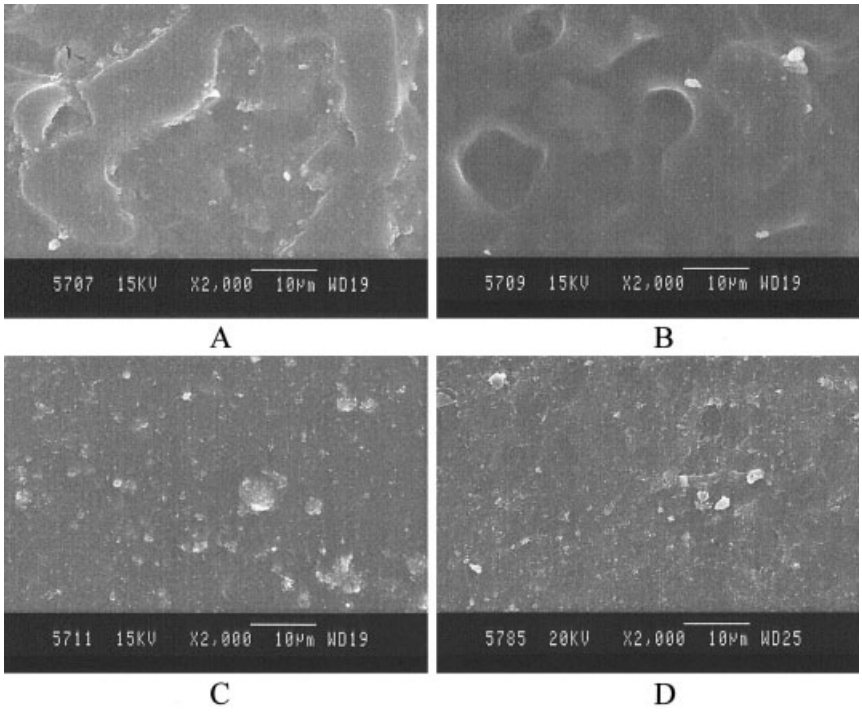

Figure 6 SEM photographs of surface area of semi-IPN hydrogels (×2000 magnification): (A) IPNMBA 1, (B) IPNMBA 3, (C) IPNMBA 5, (D) IPNMBA 7.

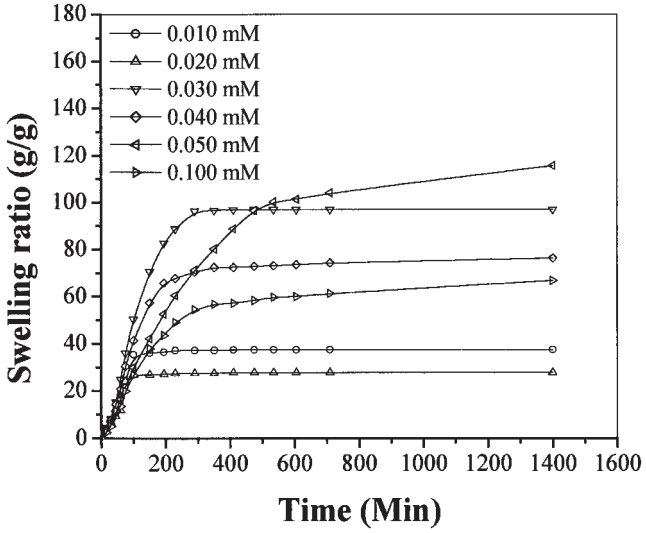

Figure 7 Influence of BDDA concentration on swelling behavior of semi-IPN hydrogels.

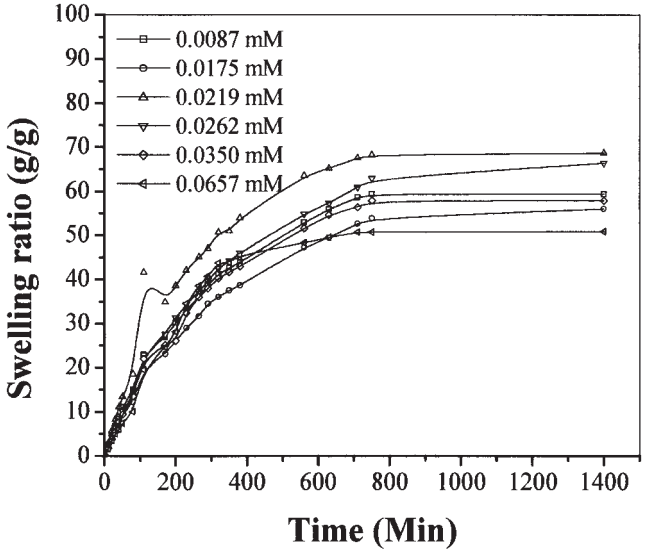

Figure 9 Influence of APS concentration on swelling behavior of semi-IPN hydrogels.

the feed of PVA/poly(AAM-*co*-NMA) semi-IPN hydrogel reactions. The results are shown in Figure 9. The swelling ratio of semi-IPN hydrogels increases as APS concentration proceeds from 0.043 to 0.1.09 mM, and then decreases with further increase in the concentration of APS. This is due to the production of more radicals as the concentration of APS increases, which increases the total number of chains, leading to more network formation.

Swelling and diffusion analysis

To determine the swelling kinetic parameters, such as initial swelling rate (r_i), maximum equilibrium swelling ratio (S_{eq}), and swelling rate constant (k_s), for semi-IPN hydrogels, a graph is drawn of t/S versus t, as shown in Figure 10. The above parameters were calculated as per the equation reported in the literature. The parameters calculated for all the semi-IPN hydrogels for different reaction parameters are tabulated in Table I. Table I indicates that the swelling parameters varied as the concentration of reaction parameter varied. However, in most of the cases, the highest equilibrium swelling ratio and initial swelling ratio values are observed for semi-IPN hydrogels having higher swelling capacity.

The porosity and free volumes of varied mesh sizes present in semi-IPN hydrogels favor the penetration

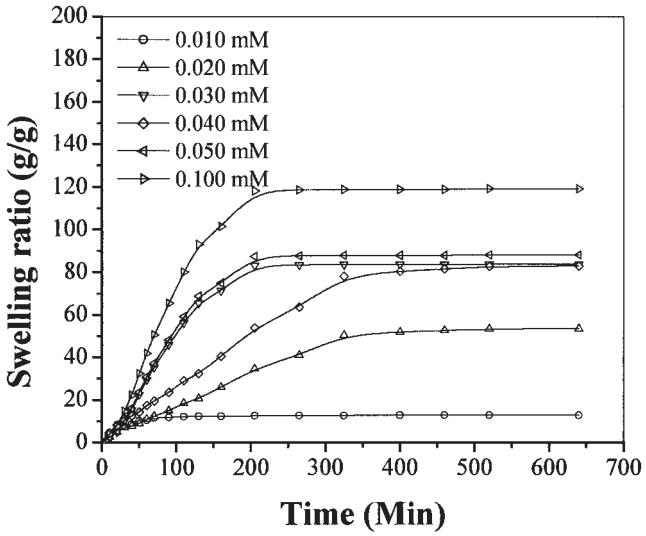

Figure 8 Influence of EGDMA concentration on swelling behavior of semi-IPN hydrogels.

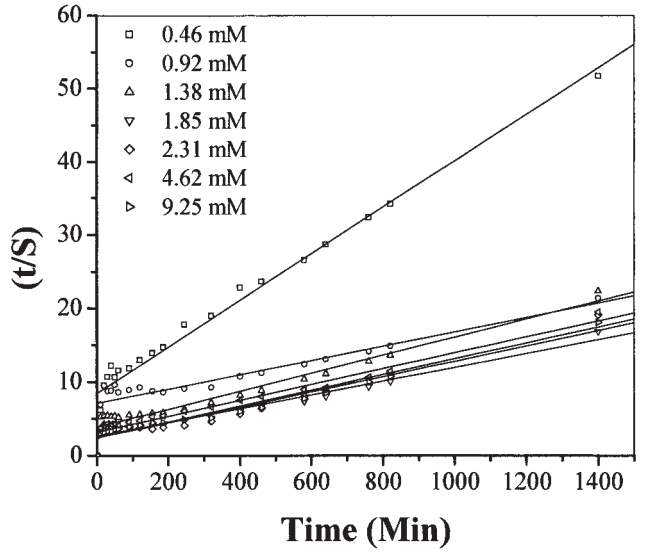

Figure 10 t/S and t graph of semi-IPN hydrogel of different NMA concentrations.

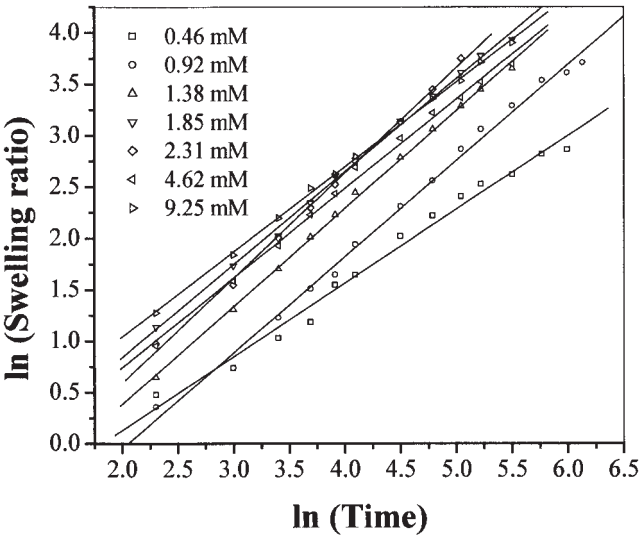

Figure 11 ln S and ln t of semi-IPN hydrogel of different NMA concentrations.

of water molecules into the crosslinked networks. As the penetrant solvent (water) invades the semi-IPN hydrogel surface, a moving front is observed that clearly separates the unsolvated glassy copolymer region ahead of the front from the swollen and rubbery gel phase behind it. Just ahead of the front, the presence of solvent plasticizes the polymer and causes it to undergo a glassy to rubbery transition. Therefore, the following possibilities may arise.

If the glass transition temperature (T_g) of the copolymer is well below the swelling medium temperature, the copolymer will be in the rubbery state possessing higher copolymer chain mobility and allowing for easier penetration of water molecules. This results in a Fickian diffusion (Case I), which is represented as solvent diffusion rate, R_{diff} < copolymer relaxation rate, R_{relax}. If the experimental temperature is below the Tg of the copolymer, the copolymer chains may not have sufficient flexibility to create free volume of different meshes, which are responsible for immediate penetration of the solvent into the copolymer matrix. Therefore, it may follow anomalous diffusion ($R_{diff} \sim R_{relax}$) and non-Fickian diffusion (Case II) ($R_{diff} > R_{relax}$).

To estimate the swelling exponent (n), 60% of the swelling ratio values in Figure 1 are utilized and the graphs are plotted ln S versus ln t (Fig. 11). The graphs are obtained as straight lines. The swelling exponent was calculated from the slope of the lines of ln S - ln t plots. Similarly, the n values were found by utilizing the swelling ratio values of corresponding series. In the present investigation, semi-IPN hydrogels prepared under different reaction conditions, such as varying the PVA content, concentration of NMA, crosslinker (MBA, BDDA, EGDMA), initiator (APS), and activator (TMEDA), have obtained n values fluctuating between 0.71–1.00 and above 1.00, indicating non Fickian and super case II type of water transport phenomena of semi-IPNs, respectively.

To determine the diffusion coefficient of IPN hydrogels, the slopes of the lines of S-$t^{1/2}$ plots were taken, and the complete results are tabulated in Tables I and II for IPN hydrogels prepared under different reaction parameters. A representative S-$t^{1/2}$ graph of IPN hydrogels is depicted in Figure 12. The diffusion coefficient of the water to the hydrogel varies as the reaction conditions varied.

Influence of salts on swelling behavior

The concentration of salt and its charge valencies also affect the swelling phenomena of any hydrogel or SAP. The presence of a salt can influence the swelling behavior of hydrogels due to change in the gel matrix, which is responsible for the mechanical properties of the gel and the diffusion coefficient of drug release. The possible consequences of salt ions in the swelling medium is to vary the osmotic pressure due to differences in the ionic concentration of the interior of the gel and the external solution. Donnan equilibrium theory is generally used to determine the osmotic pressure π_{ion}, which indirectly reveals the swelling behavior of any gel that follows the equation $\pi_{ion} = RT \Sigma_i (C_i^g - C_i^s)$, where C_i is the mobile ion concentration of species I and superscripts g and s represent gel and solution phases, respectively.

To study the effect of different anions and cations on the swelling ratio of IPN hydrogels, the halide anions of potassium (KCl, KBr, and KI) and chloride salts of K^+, Ca^{2+}, and Fe^{3+} were added, respectively, to the

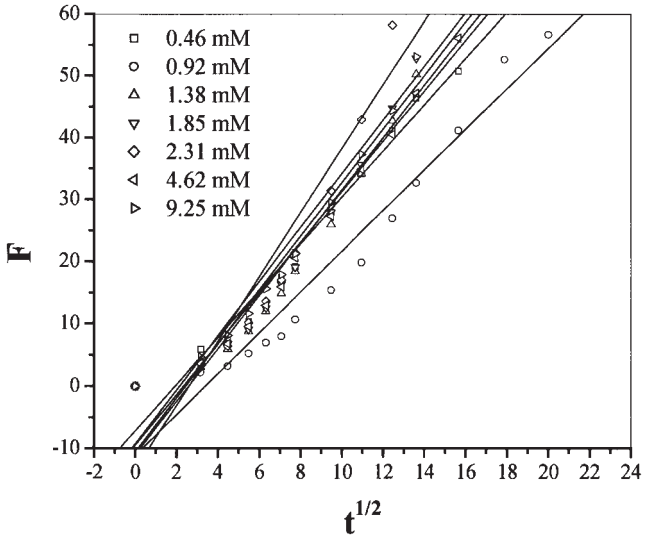

Figure 12 Diffusion curves of semi-IPN hydrogel of different NMA concentrations.

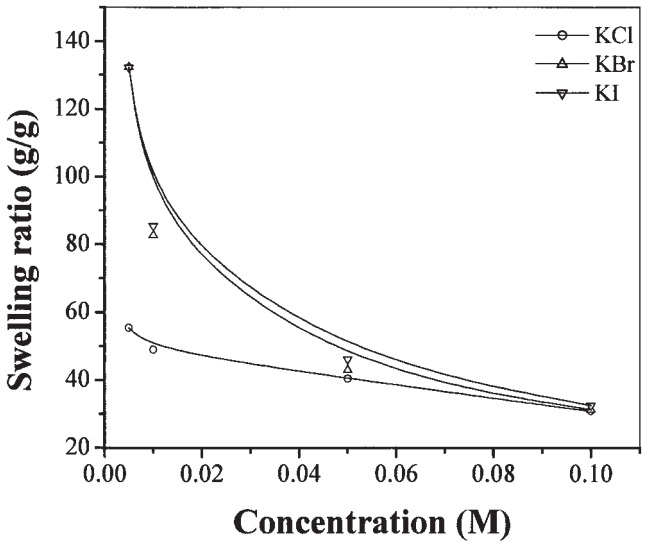

Figure 13 Influence of the halide anions of potassium on swelling behavior of IPNPVA3 hydrogel.

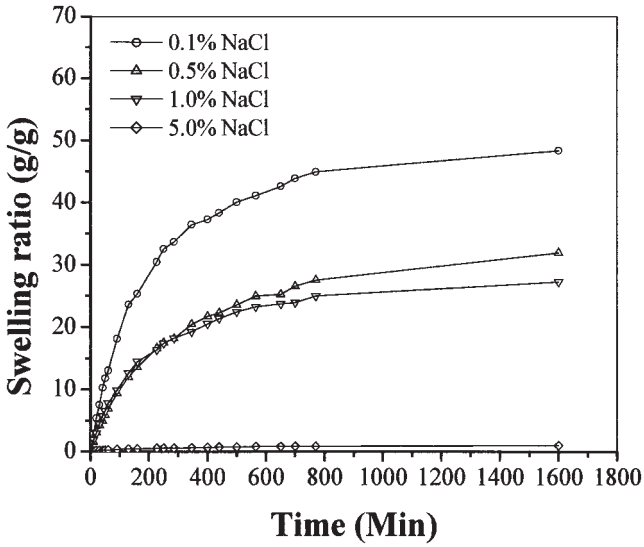

Figure 15 Influence of different wt % of sodium chloride solution on swelling behavior of IPNPVA3 hydrogel.

swelling medium. The results are presented in Figures 13 and 14 for anions and cations. The results clearly demonstrate that the swelling ratio of the hydrogel decreases with increasing ionic concentration and followed the order of the swelling behavior, that is, $I^- > Br^- > Cl^-$ (anions) and $Fe^{3+} > Ca^{2+} > K^+$ (cations). The results are acceptable because, with increase of the concentration of salt ions, the numerical value calculated by the term (C_i^g - C_i^s) gives lower values, which in turn lowers the degree of swelling. Similar results were also published by Bajpai and coworkers[21] and Lee and colleagues.[43–45]

Further, the effect of the concentration of the sodium chloride solution on the swelling behavior of semi-IPN hydrogels was investigated. Figure 15 illustrates the swelling ratio of semi-IPN hydrogels as a function of the concentration of the sodium chloride solution. The results indicate that the swelling ratio of the hydrogel decreases in the salt solution as the ionic concentration of the salt solution increases. This is due to decrement in the expansion of the gel network because of repulsive forces of counter ions acting on the polymeric chain shielded by the bound ionic charges. Therefore, the difference in the osmatic pressure between the gel network and the external solution decreased with an increase in the ionic strength of the saline concentration.

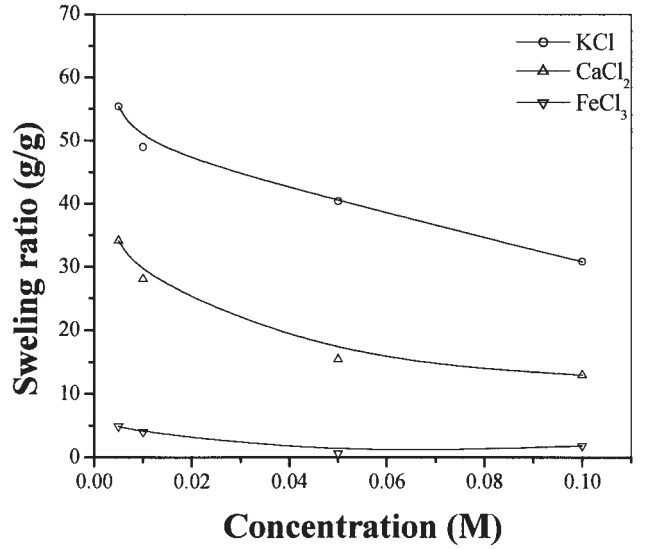

Figure 14 Influence of the chloride salts of K^+, Ca^{2+}, and Fe^{3+} on swelling behavior of IPNPVA3 hydrogel.

Effect of swelling behavior with pH

Lee and coworkers[43–45] reported the pH and temperature dependence swelling behavior of PVA/Poly-(acrylic acid) IPNs as well as the permeation of various solutes through these IPNs. A detailed relationship between the changes in the molecular structure in the IPN hydrogels and the electrolytes in the buffer solution was also reported. Gudeman and Peppas[12] prepared PVA/Poly(acrylic acid) IPNs and evaluated their responsiveness to pH, ionic strength, and temperature; and determined their crosslinked network structure parameters, such as molecular weight between crosslinkers, crosslinking density, mesh size, and maximum swelling behavior. Recently, Dhara and coworkers[18] studied pH dependent swelling as well as the structural parameters of superabsorbent hydrogel interpenetrating networks of PVA and poly(acrylamide-*co*-acrylic acid).

pH sensitivity of hydrogels has gained much importance in various applications in the biomedical field.

TABLE III
Ionic Strength of Buffer Solution at Different pHs

Desired pH	Solution A (ml)	Solution B (ml)	Ionic strength (mol ion dm^{-3})
2	97.50	2.50	0.1866
3	88.00	12.00	0.1762
5	67.00	33.00	0.1521
7	49.50	50.50	0.1243
9	34.50	65.50	0.1048
11	22.00	78.00	0.0886
12	8.50	91.50	0.0711

Thus, the aim of the present investigation is to study the influence of pH on the swelling behavior of the PVA/poly(AAm-*co*-SMA) semi-IPN hydrogels. Table III gives the details of buffer solutions along with their ionic strengths. The pH sensitivity results of semi-IPN hydrogels are presented in Figure 16, which shows the dependence swelling behavior of hydrogels in all pH solutions ranging from 2 to 12. The pH dependent swelling behavior was noticed by varying the pH. From this investigation, it is clear that the swelling behavior of the IPN hydrogel is dependent on the pH. The swelling behavior of the IPN hydrogel was found to increase from pH 2 to 7, and further increment of pH from 7 to 11 decreased the swelling ratio. Based on the studies reported by Lee and coworkers,[42–44] this behavior can be explained as below.

When pH of the medium is low (pH = 2), the carboxylic groups of poly(sodium methacrylate) are almost in an un-dissociated state and, therefore, these polymeric chains are closely packed through hydrogen bonding. When pH of the swelling medium increases from pH 2, the carboxylic groups dissociate into negatively charged COO- and result in relaxation

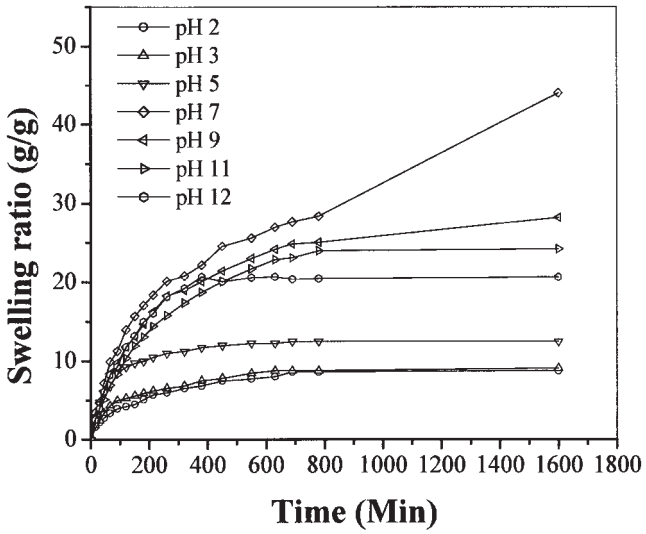

Figure 16 Influence of pH on swelling behavior of IPN-PVA3 hydrogel.

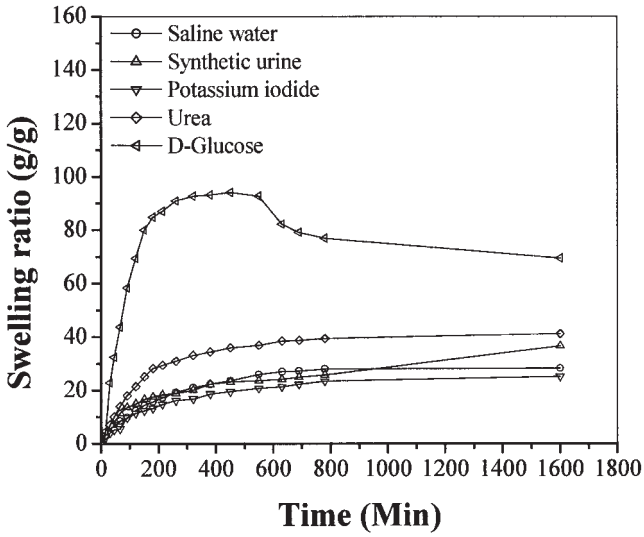

Figure 17 Influence of stimulated biological fluids on swelling behavior of IPNPVA3 hydrogel.

of the networks by breaking the hydrogel bonds. This in turn increases the diffusion of water molecules into the network, thereby increasing the swelling ratio. When the pH of the swelling medium is greater than 7, indicating the alkaline range where the number of carboxylate anions reaches the maximum level, no more repulsions could be expected in the crosslinked IPN hydrogel. This leads to greater relaxation of the macromolecular chains of the IPN hydrogel, which causes expulsion of water molecules from within the IPN hydrogel into the swelling medium due to the weakening of the hydrogen bonds formed between water molecules and crosslinked IPN hydrogel chains. This causes lowering of the swelling ratio of the IPN hydrogel.

Influence of simulated biological fluids on swelling behavior

It is widely known that swelling is the net result of osmotic and the restoring elastic pressures. The presence of solute in the surrounding aqueous medium is capable of tilting this balance, resulting in variations in the swelling behavior of any hydrogel. To investigate the influence of swelling phenomena of semi-IPN hydrogels in simulated biological fluids, five different biological fluids were employed, and the results are shown in Figure 17. The results indicate that the swelling ratio values are low in all biological fluids when compared to water as a swelling medium. This nature is attained due to the presence of different ionic species in the swelling medium. The order of swelling behavior of IPN hydrogels in different biological fluids is as follows: glucose > urea > synthetic urine > saline water > potassium iodide.

CONCLUSIONS

Semi-IPN hydrogels composed of PVA and poly(AAm-*co*-NMA) were prepared by polymerizing acrylamide and sodium methacrylate using APS/TMEDA as the initiating system with a crosslinker in the presence of poly(vinyl alcohol). The influence of various reaction parameters, including PVA content, concentration of ionic monomer (NMA), crosslinker (MBA, BDDA, EGDMA), and initiator (APS), on swelling behavior was investigated in detail. For all these semi-IPN hydrogels, the swelling/diffusion characteristics as well as equilibrium water contents were also investigated. The network structural difference in semi-IPN hydrogels at different MBA concentration was observed using SEM. Further, different types of crosslinker also were employed to study their effect on the swelling behavior of IPN hydrogels. The salt, simulated biological fluids, and pH-dependent swelling behavior of PVA/poly(AAm-*co*-NMA) semi-IPN hydrogels was also investigated. The semi-IPN hydrogels developed in the present investigation may find applicability in various biomedical applications.

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