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Synthesis and Properties of Poly(AAm-KMA-MA) Hydrogels

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In this investigation, poly(acrylamide-co-potassium methacrylate-co-maleic acid) hydrogels, poly(AAm-KMA-MA) were synthesized by redox copolymerization in aqueous solution. The effect of reaction parameters, such as concentration of maleic acid, crosslinking agent, initiator and activator, on the swelling behavior was investigated in detail. The swelling/diffusion characteristics were also evaluated for 1,4-butanediol diacrylate (BDDA) and 1,2-ethyleneglycol dimethacrylate (EGDMA) crosslinked hydrogels having different amounts of maleic acid. The results indicate that the water diffusion of hydrogels was of a non-Fickian type. The hydrogels were characterized by IR spectroscopy and thermogravimetric analysis (TGA). Their surface characteristics were observed by using scanning electron microscopy (SEM). Furthermore, their swelling phenomena in different pH and salt solutions and simulated biological fluids was also studied.

Keywords superabsorbent polymer (SAP), hydrogel, diffusion, crosslinking agent, swelling characteristics

Introduction

Superabsorbent polymers (SAPs) or hydrogels are hydrophilic water insoluble polymers which can absorb and hold large amounts of water even under pressure (1, 2). The water imbibing capacity is not only responsive to the pH, (3, 4) temperature (5–8) and ionic strength(7, 8) of the swelling medium but also to the network structure of macromolecular chains such as hydrophilic functionality, (9–11) crosslinking density, (12–14) chain flexibility, osmotic potentials (9, 11) and free volume (5). The high water content of hydrogels not only imparts a soft and rubbery texture to the material but also improves antithermogenicity in the gel matrix because of lower free energy of the

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hydrated interface. Their excellent physico-chemical properties enables them to be employed as potential biomaterials in bioengineering, medicine, pharmacy, and veterinary fields (14–18). In addition to the above applications, superabsorbent polymeric materials are also widely employed as soil conditioners for agriculture and horticulture, disposable diapers, water blocking tapes, absorbent pads, gel actuators, drilling fluid additives, polymer cracks blocking materials, feminine napkins, firefighting, extraction of precious metals, extraction of solvents, release of agrochemicals, etc. (1).

In most of the above applications, the swelling and water retention properties are most important. To obtain high water absorbency, as well as to reduce the cost of production, these materials have to be suitably modified or produced by copolymerization. The composite and porous superabsorbents were also developed for a higher and sharp swelling capacity, as well as for reducing the cost of the material (19–22). W-F. Lee and coworkers have reported the synthesis of crosslinked poly(sodium acrylate-co-hydroxyethylmethacrylate), poly(SA-HEMA) (23), poly(sodium acrylate-co-sodium,2-acryalamido-2-methylpropanesulfonate) poly(SA-AMPS) (24), poly[sodium acrylate-co-3-dimethyl(methacryloy-loxyethyl) ammonium propane sulfonate], poly(SA-DMAPS) (25) and poly(sodium acrylate-co-sulfobetaines) poly(SA-SB) (26) for higher swelling capacity in water and salt solutions.

The removal and separation of proteins were found to have many applications in the immobilization of enzymes and the adsorption of proteins onto polymeric materials has been studied (27–29). Polymeric materials (hydrogels or SAPs) were also utilized as adsorbents for adsorption, purification, and chromatographic separation of biomolecules. The different clinically important hydrogels were found to have applied for various short and long term implants and devices, resulting in a process called thrombosis often caused by the formation of thromboemboli. Because of these consequences, D. Saraydin et al. (30) have reported the adsorption of bovine serum albumin (BSA) onto the surface of poly(acrylamide-co-2-hydroxypropyl methacrylate-co-maleic acid)[-poly(AAm-HPMA-MA)] hydrogels. The poly(acrylamide-co-maleic acid) hydrogels were also employed for controlled release of terbinafine hydrochloride (31). The high swelling of hydrogels have permitted the presence of more BSA molecules in water present in the inside of hydrogel. Due to the high importance of hydrogels made from acrylamide and maleic acid, as well as to further improve their water absorbency, a third hydrophilic monomer has to be incorporated into the hydrogel. In continuation of our study on superabsorbent terpolymers based on acrylamide, as well as to reduce the cost of the product for various applications, (9–11) we report here the synthesis and swelling studies of poly(acrylamide-co-potassium methacrylate-co-maleic acid) hydrogels [poly(AAm-KMA-MA)] using ammonium persulfate (APS)/N,N,N′,N′-tetramethylethylenediamine (TMEDA) initiating system in the presence of a BDDA or EGDMA crosslinker at room temperature. The hydrogels were characterized by IR, TGA and SEM analysis.

Experimental

Materials

Acrylamide (AM), ammonium persulfate (APS) and maleic acid (MA) were supplied by S.D. Fine-Chem. Ltd. (India). Methacrylic acid (MA), 1,4-butanediol diacrylate (BDDA), 1,2-ethyleneglycol dimethacrylate (EGDMA) and N,N,N′,N′-tetramethylethylenediamine

(TMEDA) were obtained from Aldrich (Germany). All the chemicals were used as received. Double distilled water was used for all the copolymerization reactions, as well as for swelling studies. Potassium methacrylate was prepared by neutralization of methacrylic acid with potassium hydroxide.

Synthesis of Poly(AAm-KMA-MA) Hydrogels (32)

Poly(AAm-KMA-MA) hydrogels were prepared by free radical polymerization of AAm, KMA, MA in the presence of a crosslinker using a APS/TMEDA redox initiating system at room temperature. In a typical reaction, 14.06 mM of acrylamide, 8.05 mM of potassium methacrylate, and 1.72 mM of MA were dissolved in 2 ml of distilled water in a 100 ml beaker. To this solution, 0.050 mM of BDDA, 0.043 mM of APS and 0.086 mM of TMEDA were added sequentially to the reaction mixture. The polymerization was initiated and continued for 10 h at room temperature, even though the gels were obtained within 1 h. The polymerization reactions were carried out by varying the reaction parameters such as concentration of potassium methacrylate, crosslinker (BDDA and EGDMA), ammonium persulfate and TMEDA. The formed hydrogels were then transferred to a 1 L beaker containing distilled water and left for 24 h by changing the intervals every 2 h in order to remove the un-reacted monomers and other reactants in the hydrogel. The gels were dried completely and cut into square shaped small pieces for further study.

IR Spectra

The IR spectra of hydrogels were carried out on a Perkin-Elmer Spectrophotometer ASCII (Perkin-Elmer Cetus Instruments, Norwalk, CT).

SEM Analysis

The poly(AAm-KMA-MA) hydrogels were coated with a thin layer of palladium gold alloy. The morphological variations of the hydrogels were observed by using a JEOL JSM 840A (Japan) scanning electron microscope (SEM).

Thermal Analysis

The thermal stability of dry hydrogel samples was investigated using a Universal V1 12E thermogravimetric analyzer (TGA). The temperature range covered in this study was 50–700°C with a heating rate of 2°C/min and 50 ml/min of nitrogen flow.

Swelling Studies

To determine the equilibrium swelling ratio (13, 14) (S_{eq}), as well as the equilibrium water content (32) (EWC%) of the hydrogels, the conventional gravimetric method was followed. In this method, about 50–100 mg of superabsorbent hydrogel was immersed in a beaker containing 100 ml distilled water or other swelling medium, and was allowed to remain until the equilibrium swelling was achieved. After attaining the equilibrium swelling, the swollen gel was taken out and the excess water was removed superficially by filter paper and then weighed accurately. The equilibrium swelling ratio and equilibrium water content of SAP were calculated using the following Equations (1) and (2);

$$S_{eq} = \frac{[\text{Weight of swollen gel at equilibrium } (W_{eq}) - \text{Weight of dry gel } (W_d)]}{[\text{Weight of dry gel } (W_d)]} \tag{1}$$

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

In order to study the swelling and diffusion parameters, the extent of swelling behavior is to be determined at different time intervals up to the equilibrium swelling. The extent of equilibrium swelling (S_{ex}) was determined using Equation (3);

$$S_{ex} = \frac{[\text{Weight of swollen gel at time t } (W_t) - \text{Weight of dry gel } (W_d)]}{[\text{Weight of dry gel } (W_d)]} \tag{3}$$

pH Solution Preparation (33, 34)

Buffer solution I 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 the buffer solution II was prepared by dissolving 38.01 g of tri-sodium phosphate (M) in 1000 ml distilled water. In order to prepare a specific buffer solution, the two pH solutions (Solutions I and II) were mixed at different volumes based on Shugar and Dean (33).

Physiological Fluids Preparation (12)

In order 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; KI: 15 g/100 ml; Urea: 5 g/100 ml; and D-glucose: 5 g/100 ml.

Results and Discussion

IR Analysis

The IR analysis of the hydrogels indicated the presence of peaks corresponding to the functional groups of monomeric units, i.e., acrylamide, potassium methacrylate and maleic acid in the copolymeric hydrogel chain. A representative IR spectrum of poly(AAm-KMA-MA) (S_{BD8}) crosslinked with BDDA is presented in Figure 1. A broad peak corresponding to -COOH of maleic acid, as well as NH stretching of acrylamide was observed at 3429 cm^{-1}. The peaks corresponding to CH stretching were observed at 2924 cm^{-1} and 2854 cm^{-1}. Three peaks were observed in the region of 1725–1663 cm¯1, 1725 cm^{-1}, corresponding to the C═O stretching of MA, 1663 cm^{-1}, corresponding to the carbonyl stretching of acrylamide units, and at 1587 cm^{-1}, corresponding to the carbonyl stretchings of KMA and BDDA. In addition to the above peaks, peaks were also observed at 1440 and 1180 cm^{-1} corresponding to –CO–O– coupling interactions of the methacrylate and maleic acid. The above IR analysis indicates the presence of all monomeric units in the crosslinked hydrogel.

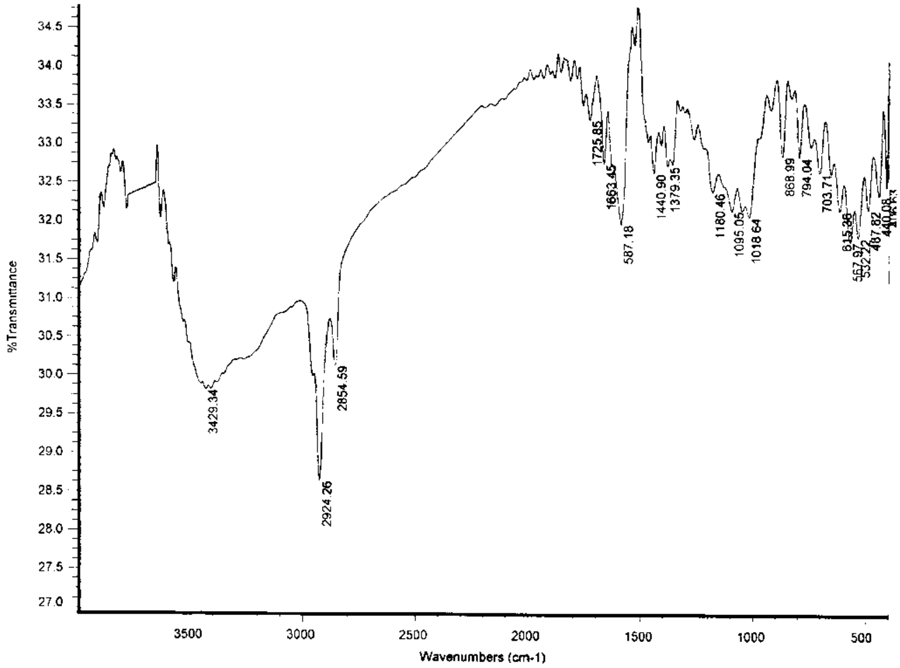

Figure 1. IR spectrum of BDDA crosslinked poly(AAm-KMA-MA) (S_{BD8}) hydrogel.

Thermal Analysis

In order to assess the thermal stability of the poly(AAm-KMA-MA) hydrogel, the TGA experiments were performed in the range of 50–700°C under a nitrogen atmosphere. The results showed that BDDA and EGDMA crosslinked hydrogels have more thermal stability. A representative TGA curve obtained for the terpolymer (S_{8BD}) is presented in Figure 2. The first weight loss below 100°C indicates the loss of water representing the hygroscopic nature of the material as reported by McNeill and Zulfiqar (35). From this step, the amount of moisture present in the hydrogel can be estimated by calculating the amount of weight loss in the TGA curve. The main weight loss step occurs above 275°C with a maximum decomposition rate at 330°C for crosslinked chains of hydrogel. However, the thermogravimetric curves of hydrogels indicates a wider range and shows that the weight loss occurs in many steps. The corresponding TGA results of hydrogels are presented in Table 2.

Swelling Properties

The important key properties of hydrogels depends on the swelling behavior. The swelling behavior of any hydrogel follows an absorption mechanism, which is governed by the diffusion process. The diffusion process relates to the affinity between the polymeric network and the swelling medium. Therefore, it can be expected that the swelling behavior of the poly(AAm-KMA-MA) hydrogel depends on the nature of the polymer network, involving the strength of hydrophilic groups, crosslinking density and elasticity of the copolymer network (13, 14). The swelling behavior also depends on the type of solvent and the characteristics of external solution.

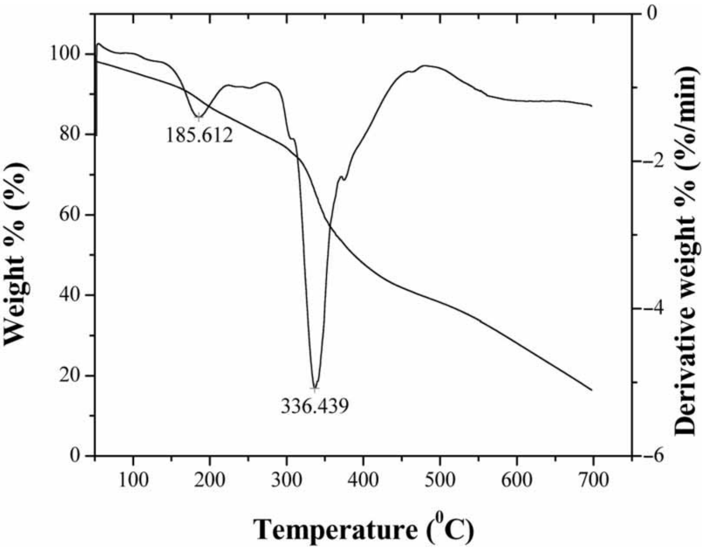

Figure 2. TGA curve of BDDA crosslinked poly(AAm-KMA-MA) (S_{BD8}) hydrogel.

The following three main forces govern the swelling behavior of the superabsorbent: (1) the free energy between the chain networks of the polymers and the external solvent; (2) the electrostatic repulsion (Donnan effect); and (3) the elastic retractile response of the networks. Out of these three forces, the first two promote the swelling behavior and the third one suppresses the swelling phenomena of the hydrogel or superabsorbent polymer.

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 (4) (36);

$$Q^{5/3} = \frac{[(i/2V_uS^{1/2})^2 + (1/2 - X_i)/v_1]}{[V_e/V_0]} \tag{4}$$

where Q, V_e/V_0, $[(1/2) - X_1]/V_i$, V_u, i/V_u and S are the water absorption, the crosslinking density of polymer, the affinity between polymer and external solution, the volume of structural unit, the fixed charge per volume of polymer, and the ionic strength of external solution, respectively. The first and second terms in the numerator belongs to forces 1 and 2 that favors the promotion of the swelling behavior.

The variation in network structure of poly(AAm-KMA-MA) led us to tailor the swelling behavior of the SAP. This can be achieved by changing the reaction parameters, such as concentration of maleic acid, crosslinker (BDDA or EGDMA), initiator and activator.

Effect of MA Concentration

In the present investigation, the influence of maleic acid on the swelling behavior of the tercopolymer was investigated by varying the concentration of maleic acid from 0.00 to 8.41 mM in the feed mixture of the AAm-KMA-MA copolymerizations. Table 1 illustrates the absorbability of copolymers as a function of monomer distribution in the copolymer network and their swelling characteristics. The data clearly indicates that the swelling

Table 1
Swelling characteristics of poly(AAm-KMA-MA) hydrogels

Hydrogel code	Maleic acid (mM)	Equilibrium swelling[a]	Max. equilibrium swelling[b]	Equilibrium water content (EWC)	Initial swelling rate (r_i)	Swelling rate (k_s)	Swelling exponent (n)
S_{BD1}	0.00	42.52	46.46	97.70	0.23	1.10×10^{-5}	0.74
S_{BD2}	1.72	41.66	45.87	97.65	0.27	1.31×10^{-5}	0.89
S_{BD3}	3.44	66.48	77.45	98.51	0.23	3.85×10^{-5}	0.92
S_{BD4}	4.30	43.52	56.98	97.75	0.07	2.42×10^{-5}	0.82
S_{BD5}	5.16	45.46	64.80	97.84	0.07	1.69×10^{-5}	0.84
S_{BD6}	6.89	43.91	73.09	97.77	0.04	0.86×10^{-5}	0.91
S_{BD7}	8.61	29.62	39.33	96.73	0.05	3.26×10^{-5}	0.82
$S_{EG\ 1}$	1.72	41.61	45.22	97.65	0.31	1.53×10^{-5}	0.82
$S_{EG\ 2}$	3.44	73.30	79.36	98.65	0.21	3.47×10^{-5}	0.78
$S_{EG\ 3}$	4.30	95.05	131.92	98.95	0.09	0.54×10^{-5}	0.90
$S_{EG\ 4}$	5.16	78.89	121.95	98.74	0.09	0.63×10^{-5}	0.96
$S_{EG\ 5}$	6.89	70.77	90.41	98.60	0.05	0.64×10^{-5}	0.89
$S_{EG\ 6}$	8.61	45.62	67.24	97.85	0.02	0.62×10^{-5}	0.83

[a] Equilibrium swelling calculated according to Equation 1 experimentally.

[b] Maximum equilibrium swelling calculated theoretically from graphs t/S vs. t.

Reaction conditions: [AAm] = 1 g, [KMA] = 2.5 g, [BDDA] or [EGDMA] = 0.05 mM, [APS] = 0.219 mM, and [TMEDA] = 0.086 mM.

Table 2
TGA results of poly(AAm-KMA-MA) hydrogels

Hydrogel code	Crosslinker concentration (mM)	Maximum decomposition temperature	% wt. loss below 100°C	Temperature corresponding 50% wt. loss	Wt% amount of polymer at 700°C
S_{BD8}	0.012	336.43	4.56	387.76	16.42
S_{BD9}	0.075	335.83	2.68	398.48	11.08
S_{EG8}	0.010	328.58	6.14	373.96	09.82
S_{EG9}	0.075	322.98	5.42	382.57	09.87

Reaction conditions: [AAm] = 1 g, [KMA] = 2.5 g, [APS] = 0.219 mM, and [TMEDA]= 0.086 mM.

increases constantly with an increase of ionic units (MA) in the copolymer backbone up to 3.44 mM. The increase in the number of carboxylate ions along the main chain of hydrogel leads to an increase in the elctrostatic repulsive forces among the COO^- groups resulting in the loosening of the network chains and thus causing an increase of the swelling behavior. However, an excess of ionic units leads to an increase in the solubility of the copolymer at a fixed crosslinker concentration and decreasing the swelling capacity (4, 9–11, 23–27).

The swelling curves of poly(AAm-KMA-MA) hydrogels crosslinked with BDDA and EGDMA are presented in Figure 3(a and b), respectively. In order to examine the mechanism of controlling the swelling process, several kinetic models were used to test the experimental data. An array of different types chemical groups on the AAm polymeric chains (hydroxyl, carboxyl, carbonyl, amide or amine) implies that there are many types of polymer-solvent interactions. Thus, the swelling kinetics of any hydrogel is probably likely to be global. However, a simple kinetic analysis is the second order equation in the form of $dS/dt = k_s\ (S_{max} - S)$, where k_s is the rate constant of swelling and S_{max} is the theoretical equilibrium. After definite integration over the limits $S = 0$ at $t = 0$ and $S = S$ and $t = t$, this equation becomes $t/S = A + Bt$, where A is the reciprocal of initial swelling rate r_i or $1/k_sS^2_{max}$ and B is inverse of the degree of swelling at equilibrium. To test the kinetic models, graphs were drawn between t/S and t. A representative t/S vs. t graph of poly(AAm-KMA-MA) hydrogel crosslinked with BDDA is shown in Figure 4(a). The calculated kinetic parameters for BDDA and EGDMA crosslinked hydrogels are tabulated in Table 1. The results of these kinetic model equilibrium swelling values are in good agreement with the experimental swelling values.

In order to study the nature of diffusion, $F = k\ t^n$ equation is used; where F is the fractional uptake at time t, k is a constant indicating the characteristic of the macromolecular network system and the penetrant, and n is the diffusional exponent, indicating the type of transport mechanism. This equation is valid for the first 60% of the fractional uptake. Depending on the n value, the nature of transport mechanism can be decided. For Fickian transport ($n = 1/2$), Case II ($n = 1$) and for Anomalous transport (non-fickian diffusion) the value is in between Fickian and Case II ($1 < n > 1/2$).

For BDDA crosslinked hydrogels, a graph is plotted between ln F and ln t and the same is presented in Figure 4(b). The exponent values are found in between 1/2 and 1, indicating the non-Fickian diffusion (Anomalous transport) nature of these hydrogels.

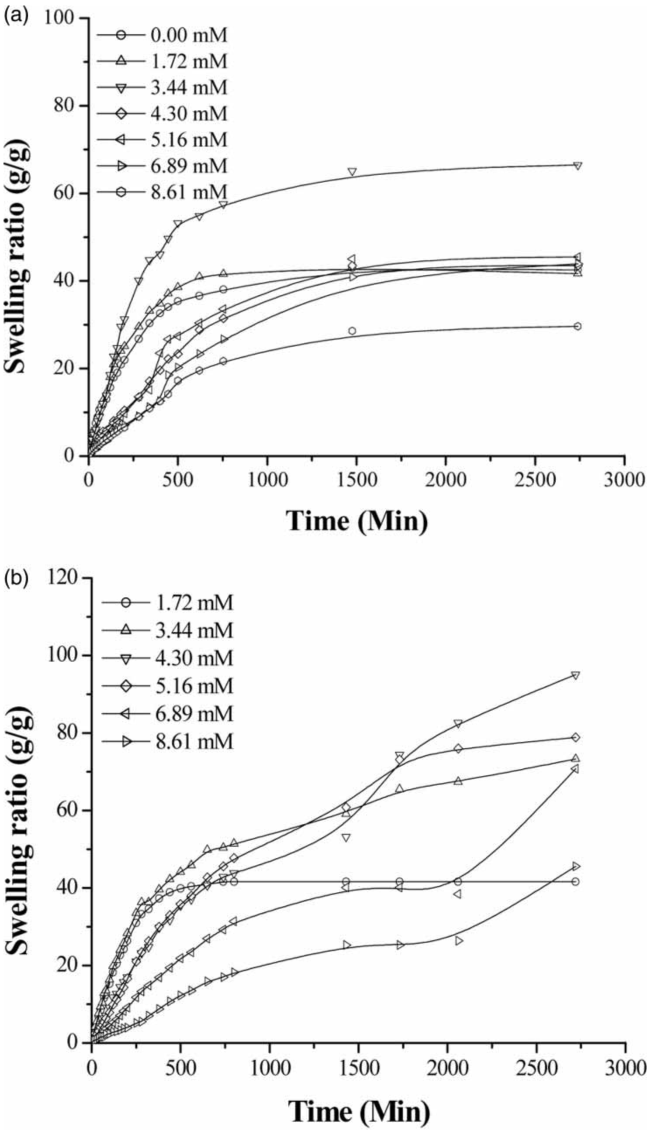

Figure 3. Swelling curves of (a) BDDA crosslinked and (b) EGDMA crosslinked hydrogels with different MA concentrations for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [BDDA] or [EGDMA] = 0.050 mM, [APS] = 0.324 mM, and [TMEDA] = 0.086 mM.

Effect of Crosslinker

The concentration of crosslinker and the type of crosslinking agent directly affects the network structure and thereby influencing the swelling behavior of the superabsorbent polymer (9–14, 21, 32). To estimate the influence of crosslinkers on the swelling behavior of poly(AAm-KMA-MA) hydrogels, two different crosslinkers namely BDDA and EGDMA were employed in the present investigation. The concentration of these crosslinkers in the polymerization reaction was varied from 0.0100 to 0.0756 mM. The

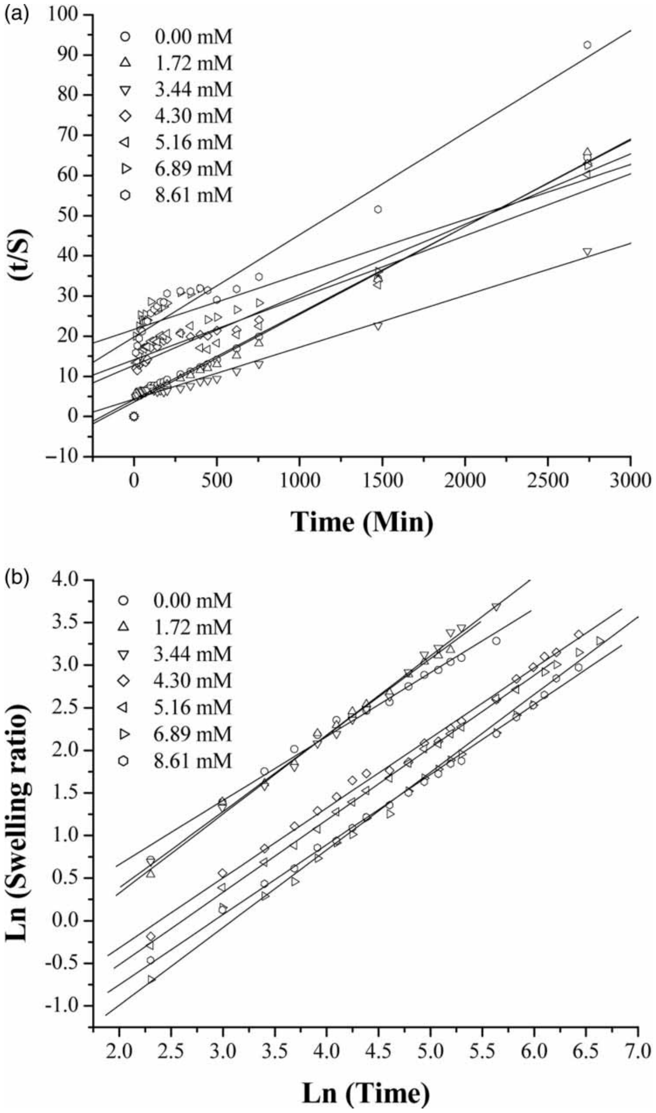

Figure 4. (a) Second order swelling kinetics and (b) ln F and ln t of BDDA crosslinked hydrogels with different MA concentrations for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [BDDA] or [EGDMA] = 0.050 mM, [APS] = 0.324 mM, and [TMEDA] = 0.086 mM.

results are shown in Figures 5 and 6 for hydrogels crosslinked with BDDA and EGDMA, respectively. The figures clearly demonstrate that as the concentration of the crosslinker increases, the swelling ratio of hydrogels decreases considerably. This is due to an increase in crosslink density, which decreases the space between the polymer chains, thereby suppressing the swelling ratio of the poly(AAm-KMA-MA) hydrogels. Furthermore, it is also observed that BDDA crosslinked hydrogels influenced, to a great extent, the swelling behavior, whereas EGDMA crosslinked hydrogels did not show much difference in their swelling behavior. This is due to a difference in the network structure

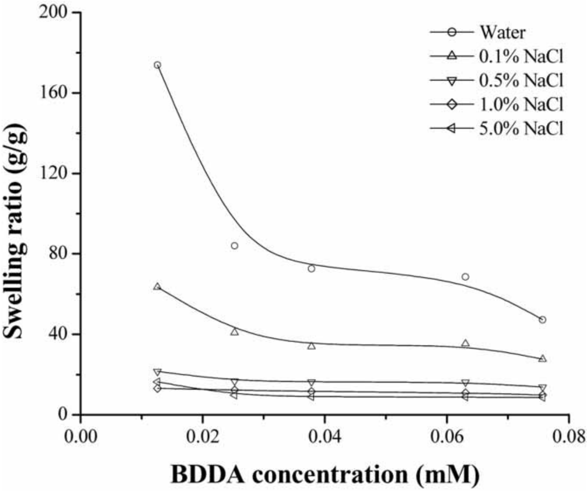

Figure 5. Swelling behavior of BDDA crosslinked poly(AAm-KMA-MA) hydrogels with different concentrations of BDDA for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM, [APS] = 0.324 mM, [TMEDA] = 0.086 mM.

formation of hydrogels. Figures 5 and 6 show the swelling behavior of hydrogels in different % of NaCl solutions.

The difference in the morphology of hydrogels with a change of crosslinker (BDDA) concentration was verified by SEM analysis and the SEM photographs are presented in Figure 7. The cross-sectional views of scanning electron microscopic images of these hydrogels displays a close crosslinked network structure as the concentration of crosslinker increases in the reaction feed, indicating higher crosslink density. Figure 7 (d), shows a fine crosslink network structure indicating no free-space (no porosity) and thereby supporting the lower swelling behavior.

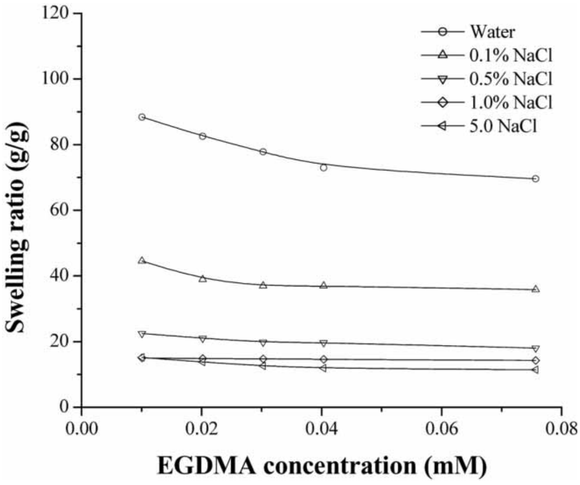

Figure 6. Swelling behavior of EGDMA crosslinked poly(AAm-KMA-MA) hydrogels with different concentrations of EGDMA for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 1.77 mM for EGDMA [APS] = 0.324 mM, [TMEDA] = 0.086 mM.

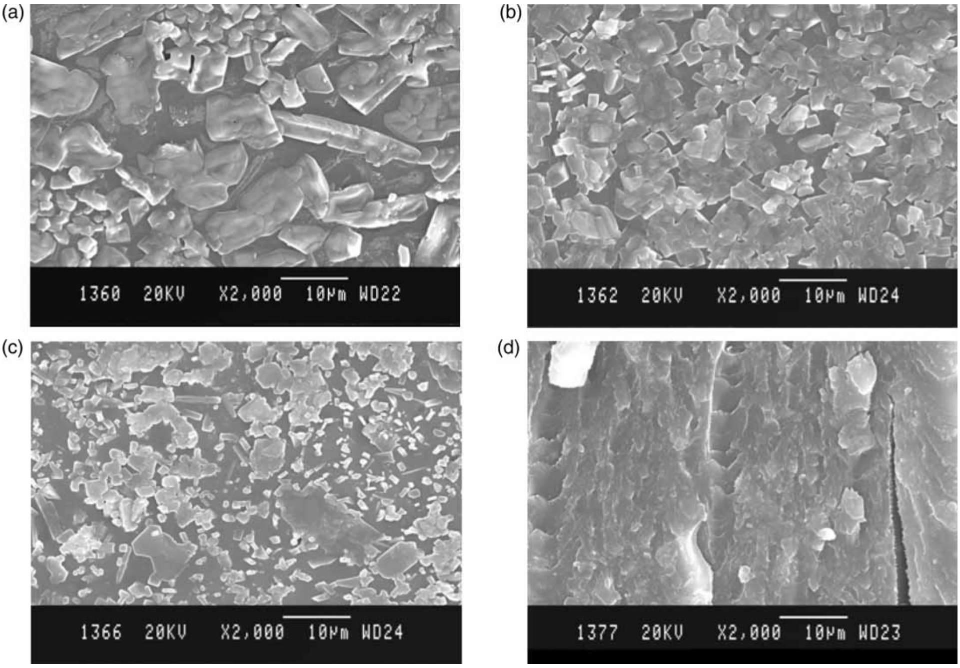

Figure 7. SEM photographs of BDDA crosslinked poly(AAm-KMA-MA) hydrogels (a) 0.012 mM, (b) 0.025 mM, (c) 0.037 mM, and (d) 0.075 mM of BDDA for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM, [APS] = 0.324 mM, and [TMEDA] = 0.086 mM.

Effect of Initiator and Activator

In the process of crosslinking redox-polymerization, the initiator and activator also influences the degree and molecular weight between two crosslinking points. The lower initiator concentration results in a decrease of crosslinking degree and conversion, whereas the molecular weight of the polymer increases with a decreasing of initiator concentration based on the principle of kinetic chain length (21, 37). In the present study, ammonium persulfate was employed as an initiator. The initiator concentration was varied from 0.0657 to 0.2629 mM in the AAm-KMA-MA hydrogel copolymerization reactions. The influence of the initiator concentration on the swelling behavior of hydrogel is shown in Figure 8. The swelling ratio of AAm-KMA-MA SAP increases as APS concentration proceeds from 0.06573–0.2629 mM for BDDA and EGDMA crosslinked hydrogels and then decreases with a further increase in the concentration of APS. This is due to the production of more radicals as the concentration of APS increases.

The different chain lengths produced in the hydrogels by varying the concentrations of APS and TMEDA may give sufficient three-dimensional network structure to the SAP thereby increasing the swelling ratio. In the case of BDDA and EGDMA crosslinked hydrogels higher swelling ratio is observed at 0.0505 mM and 0.0252 mM of TMEDA concentration respectively. The influence of TMEDA concentration on the swelling behavior of hydrogels is depicted in Figure 9.

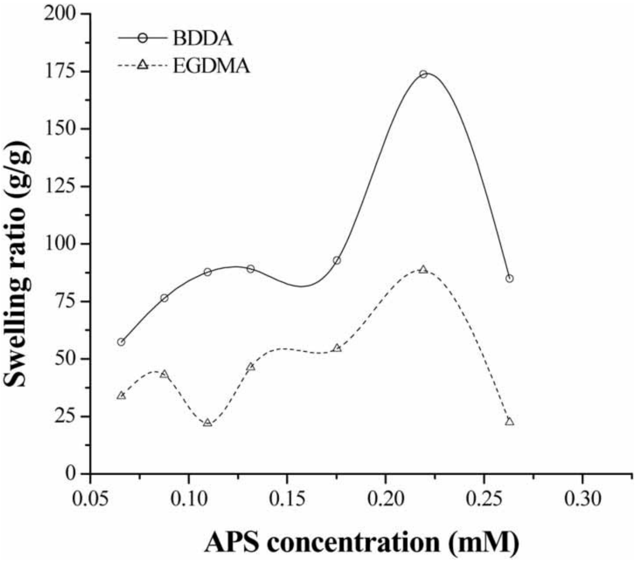

Figure 8. Swelling behavior of –O–BDDA and · △ · EGDMA crosslinked poly(AAm-KMA-MA) hydrogels with different concentrations of APS for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM for BDDA or 1.77 mM for EGDMA, and [TMEDA] = 0.086 mM.

Influence of External Stimuli on Swelling Behavior

Over the last two decades, important characteristics were noticed in the behavior of SAPs/ Hydrogels with regard to a change in specific environmental parameters, such as,

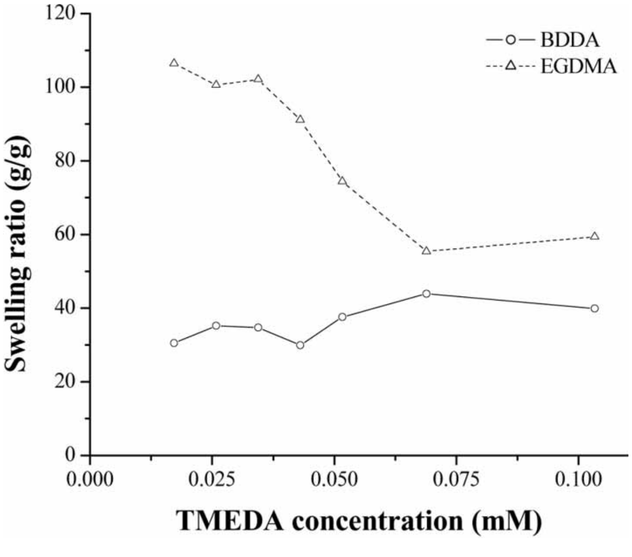

Figure 9. Swelling behavior of –O–BDDA and · △· EGDMA crosslinked poly(AAm-KMA-MA) hydrogels with different concentrations of TMEDA for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM for BDDA or 1.77 mM for EGDMA, and [APS] = 0.043 mM

temperature, pH, electric filed, solvent quality, light intensity and wavelength, pressure, ionic strength, etc., and they were studied in detail.

Effect of pH

The main principle involved in drug delivery is pH controlled swelling of gel, which normally results in a variation in the relaxation rate of network chains of gel by changing the pH of the medium. In order to study the effect of pH of the medium on the swelling capacity of AAm-KMA-MA hydrogels, different pH swelling mediums in the range 2 to 12 were employed. The results are depicted in Figure 10, and show an increase in the swelling ratio with an increase of swelling medium from pH 2 to 11, while falling drastically beyond the pH 11 swelling medium. On the other hand, there is a decrease in the swelling at pH 12 with an increase of swelling time. This is due to a dissolution of gel in the swelling medium. The highest swelling ratio was observed only at a pH 11 swelling medium. This can be attributed due to lower ionic strength of the buffer solution.

Effect of Simulated Biofluids

Swelling is a net result of osmotic and restoring elastic pressure. The presence of solute in the surrounding aqueous medium is capable of tilting this balance resulting in the variation of swelling behavior. To study the influence of simulated biofluids on the swelling behavior of the hydrogel, different biofluids were employed and the swelling results are presented in Figure 11. The results demonstrate that lower swelling ratio values are for all the simulated biofluids when compared to water as the swelling medium. This nature can be explained on the basis of increase of various ionic species concentration

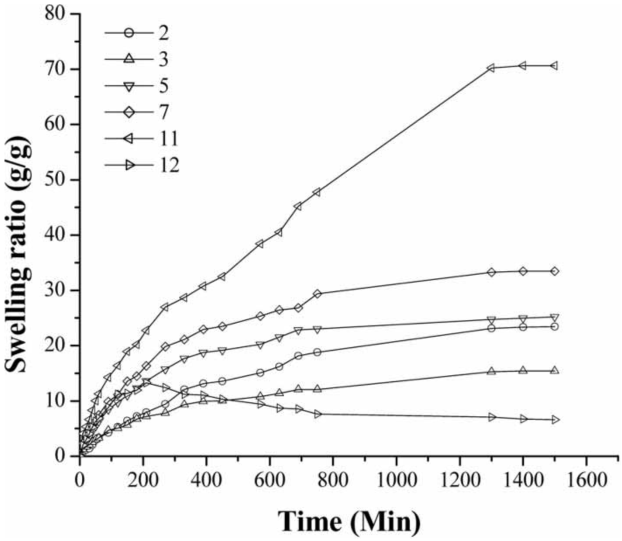

Figure 10. Effect of pH on swelling behavior of BDDA crosslinked poly(AAm-KMA-MA) hydrogels for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM, [BDDA] = 0.012 mM, [APS] = 0.043 mM, and [TMEDA] = 0.086 Mm.

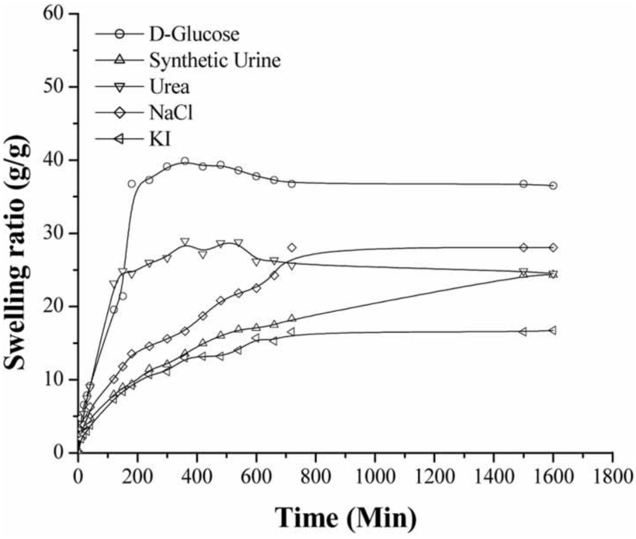

Figure 11. Effect of simulated biological fluids on swelling behavior of BDDA crosslinked poly (AAm-KMA-MA) hydrogels for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM, [BDDA] = 0.012 mM, [APS] = 0.043 mM, and [TMEDA] = 0.086 mM

in the swelling medium and thereby lowering the swelling ratio. It is also observed that the swelling ratio is high for D-glucose solution where as it is very low for potassium iodide solution, among the five simulated biofluids.

Effect of Salts

The concentration of salt and its charge valencies significantly affect the swelling behavior of any hydrogel or SAP. The presence of a salt can affect the swelling behavior of SAP, due to change in the gel matrix, which is responsible for mechanical properties of the gel and diffusion coefficients of drug release. The possible consequences of salt ions in the swelling medium is to vary the osmotic pressure due to difference in the ionic concentration of interior of the gel and the external solution. The Donnan equilibrium theory is generally used to determine the osmotic pressure π_{ion}, which indirectly reveals the swelling behavior of any gel as given by the following 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 investigate the effect of anions and cations on the swelling ratio, the halide anions of potassium and chloride salts of K^+, Ca^{2+} and Fe^{3+} were added respectively to the swelling medium. For anions and cations, the results are depicted in Figures 12 and 13. The results clearly demonstrate that the swelling ratio of the hydrogel decreases with increasing ionic concentration and followed the order of swelling i.e., $Cl^- > Br^- > I^-$ (anions) and $K^+ > Ca^{2+} > Fe^{3+}$ (cations). The results are acceptable, since an increase of concentration causes the value of the term $(C_i^g - C_i^s)$ to have lower values, which causes the degree of swelling lower. A similar type of results were also published by Bajpai et al. (12) and W.-F. Lee et al. (23–26).

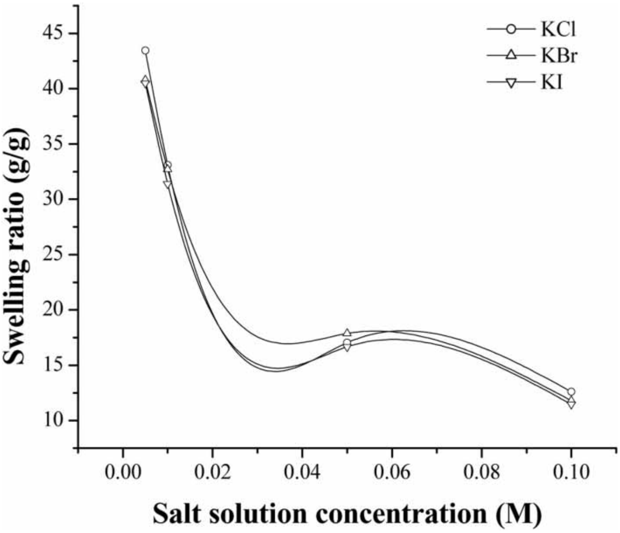

Figure 12. Effect of addition of anions of potassium on swelling behavior of BDDA crosslinked poly(AAm-KMA-MA) hydrogels for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM, [BDDA] = 0.012 mM [APS] = 0.043 mM, and [TMEDA] = 0.086 mM

Temperature Effect

The hydrogels swelled rapidly to a maximum extent at higher temperatures and reached the equilibrium in less time when compared to lower temperatures. For BDDA and EGDMA crosslinked hydrogels, the highest swelling ratio is obtained at 50°C and the lowest at 10°C, (Figure 14). The reason for an increase of swelling behavior at higher

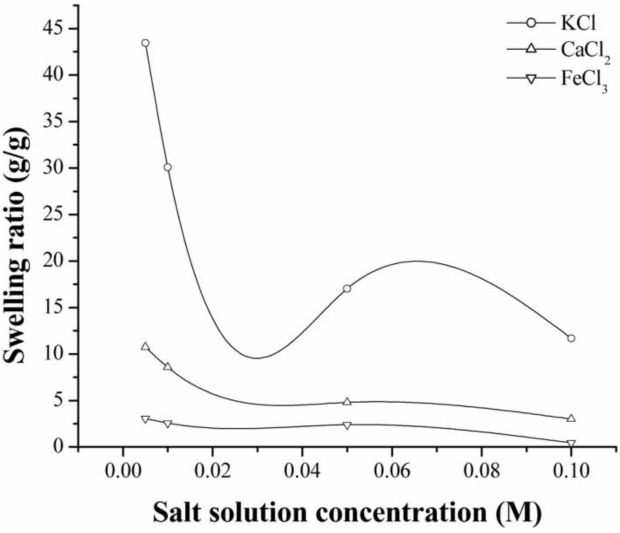

Figure 13. Effect of addition of cations of chloride on swelling behavior of BDDA crosslinked poly(AAm-KMA-MA) hydrogels for a defined composition of [AAm] = 1.00 g, [KMA] = 0.25 g, [MA] = 3.44 mM, [BDDA] = 0.012 mM [APS] = 0.043 mM, and [TMEDA] = 0.086 mM

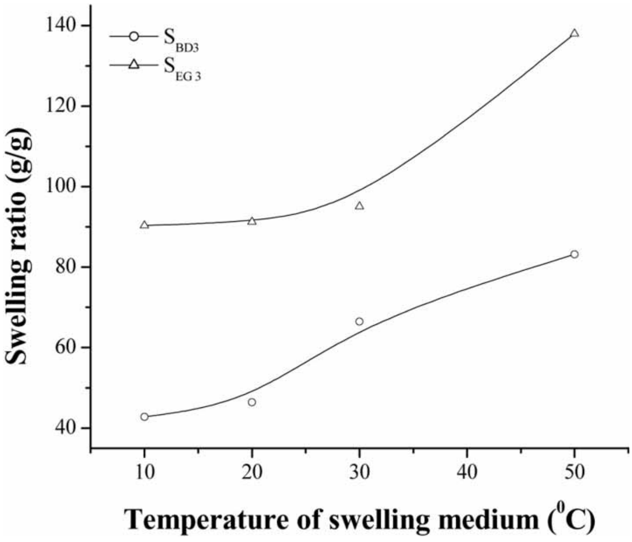

Figure 14. Effect of swelling medium temperature on swelling behavior of poly(AAm-KMA-MA) hydrogels

temperatures may be due to a fast diffusion process since the diffusion process is a function of temperature and increases with increasing temperature (12).

Conclusions

Poly(AAm-KMA-MA) hydrogels crosslinked with BDDA showed ionizable, hydrophilic, and stimuli responsiveness. The swelling capacity of these superabsorbent hydrogels was studied in detail by varying the maleic acid concentration and for these hydrogels, the swelling network and diffusion parameters were also reported. The water transport of hydrogels followed the non-Fickian type. The effect of various reaction parameters such as concentration of BDDA or EGDMA, APS, and TEMDA in the polymerization feed, on the swelling capacity of the hydrogels was investigated. As the crosslinker concentration increases the swelling ratio of the hydrogels decreases and their morphologies were verified with SEM. TGA results indicates that the hydrogels crosslinked with BDDA and EGDMA showed higher thermal stability. The salt sensitivity of the porous hydrogels was investigated, and the results indicate that with an increase of ionic concentration, their swelling capacity decreases. The order of salt effect on the swelling capacity of hydrogels follows, for halide anions of potassium $Cl^- > Br^- > I^-$ and for chloride salts of cations $K^+ > Ca^{2+} > Fe^{3+}$. Furthermore, the influence of pH and simulated biological fluids on the swelling behavior was also studied.

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