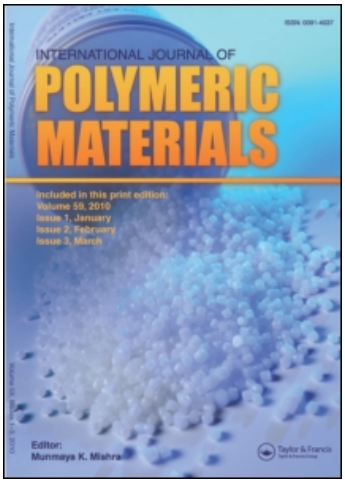

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Swelling and Diffusion Properties of Poly(acrylamide-co-maleic acid) Hydrogels: A Study with Different Crosslinking Agents

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Crosslinked hydrogels comprising acrylamide (AAm) and maleic acid (MA) were synthesized by free radical polymerization in presence of a crosslinker using ammonium persulfate (APS) and N,N,N^1,N^1-tetramethylethylenediamine (TMEDA) as initiator and activator, respectively. The crosslinked hydrogel formation was confirmed by IR analysis. The swelling/de-swelling characteristics were studied in detail for crosslinked poly(acrylamide-co-maleic acid) [poly(AAM-co-MA)] hydrogels containing different amounts of maleic acid. Four different crosslinkers such as 1,2-ethyleneglycol dimethacrylate (EGDMA), 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA), and diallyl phthalate (DP) were utilized to study their influence on the swelling behavior of the hydrogels. The effect of reaction parameters such as the concentration of crosslinker and initiator on swelling capacity of the crosslinked poly(AAm-co-MA) hydrogels was also investigated. Further, the influence of various salts, simulated biological fluids, and pH solutions on the swelling pattern of hydrogels was studied extensively. Phase separation morphology of crosslinked hydrogels was also studied by differential scanning calorimetry. The morphology of crosslinked hydrogels were revealed using scanning electron microscopy (SEM).

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Keywords: diffusion coefficient, equilibrium swelling ratio, hydrogel, phase transition

INTRODUCTION

Attempts were made resulting in the discovery of novel materials such as hydrogels in order to develop sensitive materials for biomedical and biotechnological applications [1]. The hydrogels are network structures of polymeric chains crosslinked to each other and surrounded by an aqueous solution [2–3]. Although there are many natural hydrogels, the synthetic hydrogels show distinctive structural properties due to their structural versatility [4–5]. Because of the characteristic properties of hydrogels such as enormous amounts of water uptake, soft and rubbery nature, hydrophilicity, lack of toxicity, resemblance of a living tissue and biocompatibility, these materials are developed for utilization in environmental, biological, medical, and pharmaceutical applications. Hydrogels derived from poly(acrylamide) have many useful physico-chemical properties and have been investigated for applications as smart polymers. These applications include immobilization of biocatalysts [6], drug delivery systems [7–9], bioseparators [10], and protein adsorption [11–12]. Further, these materials find applicability in the release of agrochemicals [13], release of essential oils [14], extraction of solvents [15], and extraction of specious metals [16–17].

In polyelectrolyte gels, where charges are introduced on the polymeric chains, electrostatic interactions are operating between the chains. Even a small degree of polyelectrolyte character will have influence on the swelling characteristics of the gels, including the extent of collapse and the phase transition [18–19]. In the recent past, Guven et al. [20–21], Raju et al. [22], and Katime and coworkers [23–24] reported a series of hydrogels based on acrylamide and itaconic acid and maleic acid. Bajpai [25] studied the swelling and de-swelling behavior of poly(acrylamide-co-maleic acid) hydrogels. Hydrogels composed of PVP/poly(acrylamide-co-itaconic acid) were reported for oral drug delivery of peptides [26]. Dhara et al. [27] reported a tri-component IPN system composed of poly(acrylamide-co-acrylic acid) [P(AAm-co-AA)] with poly(vinyl alcohol) and used the same for biomedical applications. Super water retainer acrylamide-crotonic acid hydrogels crosslinked by trimethylolpropane triacrylate and 1,4-butanediol dimethacrylate were reportedly used as biocompatible materials [28].

Acrylamide (AAm) along with diprotic acids like maleic acid (MA) and itaconic acids (IA) were employed in the preparation of hydrogels as reported by various authors due to their good compatibility,

versatility, and nontoxicity. Some of the reports indicated that these hydrogels were synthesized by copolymerization using γ-radiations. This method has some drawbacks, as it requires costly equipment. On the other hand, in recent years considerable research work was focused on the synthesis and swelling/diffusion characterization of hydrogels prepared by simultaneous free radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent [28–32].

Because of the wide applicability of acrylamide, maleic acid crosslinked hydrogels, it is necessary to manipulate the physico-chemical characteristics of hydrogels that can be attained by changing the monomers, crosslinkers, initiators, and/or polymerization conditions. In view of this, the present investigation involves the synthesis of crosslinked poly(acrylamide-co-maleic acid) hydrogels by crosslinking with 1,2-ethyleneglycol dimethacrylate (EGDMA), 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA), and diallyl phthalate (DP) as well as an investigation of the influence of various parameters on the swelling behavior because biocompatibility apparently depends on water content.

EXPERIMENTAL

Materials

Acrylamide (AAm), maleic acid (MA), and ammonium persulfate (APS) were supplied by S. D. Fine-Chem Ltd (Mumbai, India). 1,2-ethyleneglycol dimethacrylate (EGDMA), 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA), and diallyl phthalate (DP) and N,N,N′,N′-tetramethylethylenediamine (TMEDA) were received from Aldrich Chemical Company, Inc. (Milwaukee, WI, USA). All the chemicals were used as received. Double distilled water was used for all the copolymerization reactions as well as for swelling studies. Stock solutions of BDDA, EGDMA and DP (1g/100 ml methanol); APS (5g/100 ml dist. water); and TMEDA (1g/100 ml dist. water) were prepared.

Synthesis of Crosslinked Poly(AAm-co-MA) Hydrogels [29]

Crosslinked poly(AAm-co-MA) hydrogels were prepared using the simultaneous free radical copolymerization method. Acrylamide and maleic acid were dissolved in 2 ml of distilled water and mixed using a magnetic bar. Then, the crosslinker (BDDA, EGDMA, HDDA, or DP), and ammonium persulfate were added sequentially to the

reaction mixture. After getting continuous reaction mixture, the activator (TMEDA) was added drop-wise and mixed thoroughly and then the whole reaction mixture was transferred into a 3 mm dia poly(vinyl alcohol) straw, which is used as a polymerization reactor. The polymerization reactor was kept in hot air oven at 50°C for 1 h and the reaction was continued for one day at room temperature in order to get complete gelation of in the hydrogel. In a typical polymerization (BDDA 1), 1 g (14.06 mM) of acrylamide and 0.1 g (0.861 mM) of maleic acid were dissolved in 2 ml of distilled water. To this solution, 1 ml (0.0504 mM) of BDDA crosslinker solution, 1 ml (0.219 mM) of ammonium persulfate, and 1 ml (0.086 mM) of TMEDA were added one by one. The obtained hydrogel was cut into small pieces and dried in air and then under vacuum to a constant weight and stored in a vacuum desiccator. The obtained crude hydrogel pieces were directly used for all studies because there was ≅99% of monomer conversion in all polymerization reactions. The structures of the monomers, crosslinker, initiator, and activators are depicted in Scheme 1. The polymerizations were performed by changing the comonomer concentration from 0.861 to 8.615 mM at a fixed concentration of crosslinker, initiator, and activator. The detailed compositions and designations of the crosslinked hydrogels are listed in Table 1.

pH Solutions Preparation

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. Buffer solution II was prepared by dissolving 38.01 g of trisodium phosphate (M) in 1000 ml distilled water. In order to prepare a specific buffer solution, the two pH solutions (solution I and II) were mixed at different volumes [33].

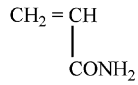
Physiological Fluids Preparation

In order to study the water uptake and water transport phenomena of hydrogels in biological media, different fluids were made from 100 ml distilled water. These solutions 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; D-glucose: 5 g/100 ml.

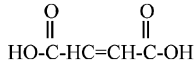
Swelling Measurements

The swelling ratio of the hydrogels was measured in distilled water as per the conventional gravimetric procedure. Pre-weighed dry

Monomers

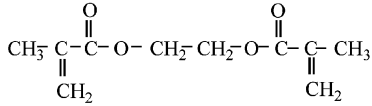


Acrylamide (AAm)

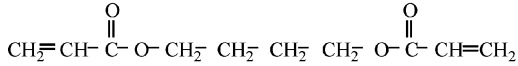


Maleic acid (MA)

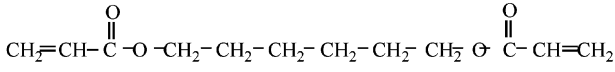
Crosslinkers



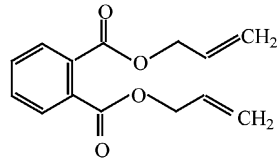
1,2-ethyleneglycol dimethacrylate (EGDMA)



1,4-butanediol diacrylate (BDDA)

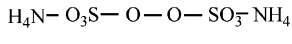


1,6-Hexanediol diacrylate (HDDA)

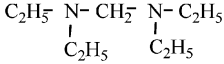


Diallyl phthalate (DP)

Initiator and Activator



Ammonium persulfate (APS)



N,N,N^1,N^1-Tetraethylmethanediamine (TMEDA)

SCHEME 1 Structures of the monomers, crosslinker, initiator, and activators used in polymerization reaction.

hydrogels were immersed in solutions (distilled water, salt, pH, and biological fluids) until they swelled to an equilibrium point. It was noticed that about 2 days were required to reach their swelling equilibrium. The swelling ratio of the hydrogels was measured at different time intervals and the same was calculated using the following

TABLE 1 Composition, Swelling, Diffusion Characteristics and Water Equilibrium Content of Poly(AAm-co-MA) Hydrogels

Crosslinked hydrogel code	Comonomer (mM)	Crosslinker (mM)	Swelling ratio (g/g)	EWC(%)	Swelling kinetics			Swelling exponent n	Diffusion coefficient D [cm^2sec^{-1}]
					S_{eq} (g water/ g gel)	r_i [(g water/ g gel)/min]	k_s [(g gel/g water)/min]		
BDDA crosslinked poly(AAm-co-MA) hydrogels									
BDDA1	0.861	0.0504	11.52	92.01	12.55	0.042	0.00027	0.53	0.34
BDDA2	1.723	0.0504	14.71	93.63	16.56	0.047	0.000173	0.55	0.440
BDDA3	2.584	0.0504	16.13	94.16	19.01	0.030	8.36×10^{-05}	0.68	0.38
BDDA4	3.446	0.0504	**17.72**	94.65	21.93	0.024	5.09×10^{-05}	0.66	0.35
BDDA5	4.307	0.0504	14.57	93.57	17.65	0.027	8.78×10^{-05}	0.68	0.34
BDDA6	5.169	0.0504	13.04	92.87	15.96	0.018	7.45×10^{-05}	0.65	0.27
BDDA7	6.892	0.0504	12.56	92.62	15.83	0.021	8.44×10^{-05}	0.71	0.31
BDDA8	8.615	0.0504	8.25	89.19	9.58	0.010	0.000111	—	0.14
EGDMA crosslinked poly(AAm-co-MA) hydrogels									
EGDMA1	0.861	0.0504	23.39	95.90	29.67	0.057	6.58×10^{-05}	0.63	0.66
EGDMA2	1.723	0.0504	34.94	97.21	50.91	0.053	2.06×10^{-05}	0.79	0.91
EGDMA3	2.584	0.0504	58.20	98.32	101.93	0.079	7.65×10^{-06}	0.88	1.62
EGDMA4	3.446	0.0504	**63.75**	98.45	227.79	0.053	1.02×10^{-06}	0.98	1.57
EGDMA5	4.307	0.0504	60.07	98.36	156.00	0.056	2.31×10^{-06}	0.97	1.53

EGDMA6	5.169	0.0504	68.54	98.56	201.61	0.060	1.5×10^{-06}	1.02	1.79
EGDMA7	6.892	0.0504	38.01	97.43	108.69	0.032	2.74×10^{-06}	0.93	0.91
EGDMA8	8.615	0.0504	37.85	97.42	164.47	0.029	1.07×10^{-06}	0.99	0.92
HDDA crosslinked poly(AAm-co-MA) hydrogels									
HDDA1	0.861	0.0441	10.40	91.23	11.18	0.045	0.000367	0.54	0.33
HDDA2	1.723	0.0441	14.45	93.53	16.98	0.044	0.000156	0.59	0.44
HDDA3	2.584	0.0441	15.26	93.85	18.08	0.046	0.000141	0.64	0.45
HDDA4	3.446	0.0441	**18.40**	94.84	24.66	0.031	5.26×10^{-05}	0.66	0.45
HDDA5	4.307	0.0441	20.87	95.42	30.39	0.033	3.64×10^{-05}	0.74	0.53
HDDA6	5.169	0.0441	14.92	93.72	22.04	0.021	4.35×10^{-05}	0.73	0.35
HDDA7	6.892	0.0441	17.82	94.68	27.97	0.023	3.03×10^{-05}	0.75	0.43
HDDA8	8.615	0.0441	13.40	93.05	18.56	0.017	5.06×10^{-05}	0.68	0.28
DP crosslinked poly(AAm-co-MA) hydrogels									
DP1	0.861	0.0406	9.02	90.02	9.98	0.05	0.000599	0.50	0.35
DP2	1.723	0.0406	10.56	91.35	11.40	0.05	0.00042	0.51	0.36
DP3	2.584	0.0406	12.37	92.52	14.06	0.039	0.000202	0.52	0.35
DP4	3.446	0.0406	14.69	93.62	18.16	0.03	9.64×10^{-05}	0.65	0.39
DP5	4.307	0.0406	15.71	94.01	20.58	0.03	8.17×10^{-05}	0.67	0.43
DP6	5.169	0.0406	11.66	92.10	14.82	0.02	0.000109	0.63	0.30
DP7	6.892	0.0406	9.28	90.27	11.89	0.02	0.000143	0.63	0.24
DP8	8.615	0.0406	8.06	88.96	9.41	0.02	0.000243	0.49	0.20

equation [28–29]:

$$\text{Swelling ratio (S)} = (W_s - W_d)/W_d \quad (1)$$

where W_s is the weight of the swollen gel at a given time, and W_d is the weight of the dry gel. The swelling ratio of hydrogel at equilibrium can be called equilibrium swelling ratio.

The equilibrium water content (EWC) of the hydrogels was calculated using the equation [28–29]:

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

where W_e denotes the weight of the swollen gel at equilibrium. The swelling experiments were repeated three times and average values were taken for the studies.

Characterization

IR spectra of poly(acrylamide) and poly(acrylamide-co-maleic acid) were recorded on Nicolet 750 FTIR spectrophotometer using KBr pellet. Thermal transition measurements were performed for swollen hydrogels with Differential Scanning Calorimeter (Rheometric Scientific, Model DSC SP, United Kingdom) under nitrogen atmosphere and a heating rate of 2°C/min.

RESULTS AND DISCUSSIONS

Synthesis of Crosslinked Poly(AAm-co-MA) Hydrogels

In the present investigation, the polymerization reactions of acrylamide and maleic acid with a crosslinker (BDDA, EGDMA, HDDA, or DP) were carried out in the presence of redox initiating system APS/TMEDA in 2 ml of distilled water. APS and TMEDA react with each other and form an activated TMEDA molecule containing unpaired valence electrons. The unpaired valence electrons may interact with acrylamide, maleic acid, and/or the crosslinker, and are responsible for initiation of polymerization, copolymerization, and crosslinking processes [28–29].

IR Analysis

The IR spectrum of polyacrylamide gel crosslinked by BDDA had showed peaks characteristic of the acrylamide repeating units in the region of 3500–3400 cm^{-1} characteristic of N-H stretching vibrations, between 1652 and 1600 cm^{-1} characteristic of carbonyl stretching

vibrations and amide II band of N-H bending vibrations. In addition to this, another peak was observed at 1323 cm^{-1} characteristic of amide III band corresponding to C-N stretching mixed with N-H bending. In the case of copolymers of acrylamide and maleic acid crosslinked with various crosslinking agents like BDDA, EGDMA, HDDA, and DP, the IR spectra showed characteristic peaks of maleic acid repeating unit in addition to the characteristic peaks of the acrylamide unit. The peaks corresponding to carboxyl groups of maleic acid have overlapped with N-H stretching frequency in the region 3000 cm^{-1}. There are small humps around 1720–1710 cm^{-1} characteristic of the carbonyl group of maleic acid. In addition to this, other characteristic peaks related to OH group of the carboxyl group are observed at 1455, 1149, and 1118 cm^{-1} indicating the incorporation of maleic acid units in the copolymer chains. Thus the IR spectra confirms the presence of two repeating units, that is, the acrylamide and maleic acid in the copolymer structure. Representative IR spectra of polyacrylamide and poly(acrylamide-co-maleic acid) are presented in Figure 1.

Effect of Maleic Acid Content

In general the concentration of the co-monomer in the reaction solution affects the properties of the resulting polymer or copolymer, the kinetics of the reaction, and the economics of the process. Table 1 demonstrates the equilibrium swelling ratio of poly(acrylamide-co-maleic acid) hydrogels as a function of maleic acid. The results are quite interesting, as the maleic acid content increases up to a certain level their equilibrium swelling ratio also increases. But, with further increase of maleic acid content in the copolymer reaction mixture leads to decrement in equilibrium swelling ratio. BDDA crosslinked poly(AAm-co-MA) hydrogels showed improved equilibrium swelling ratio from 11.52 g/g to 17.72 g/g with increase of maleic acid content from 0.86 mM to 3.44 mM. Similarly, poly(AAm-co-MA) hydrogels crosslinked with HDDA, EGDMA, and DP showed improved equilibrium swelling behavior from 10.40 g/g to 20.85 g/g; 2.39 g/g to 68.54 g/g; 9.02 g/g to 15.71 g/g; with increase of maleic acid contents from 0.86 mM to 4.30 mM; 0.86 mM to 5.16 mM; 0.86 to 4.30 mM; respectively. It is clearly noticed that with further increase of maleic acid content in all the copolymerization reaction mixtures, a lowering in the equilibrium swelling ratio values was observed. The results are contrary to the normal existing swelling behaviour of maleic acid copolymer hydrogels, according to which the increase in acid content should increase the equilibrium swelling ratio. With lower contents of maleic acid in the hydrogels, their equilibrium swelling ratio

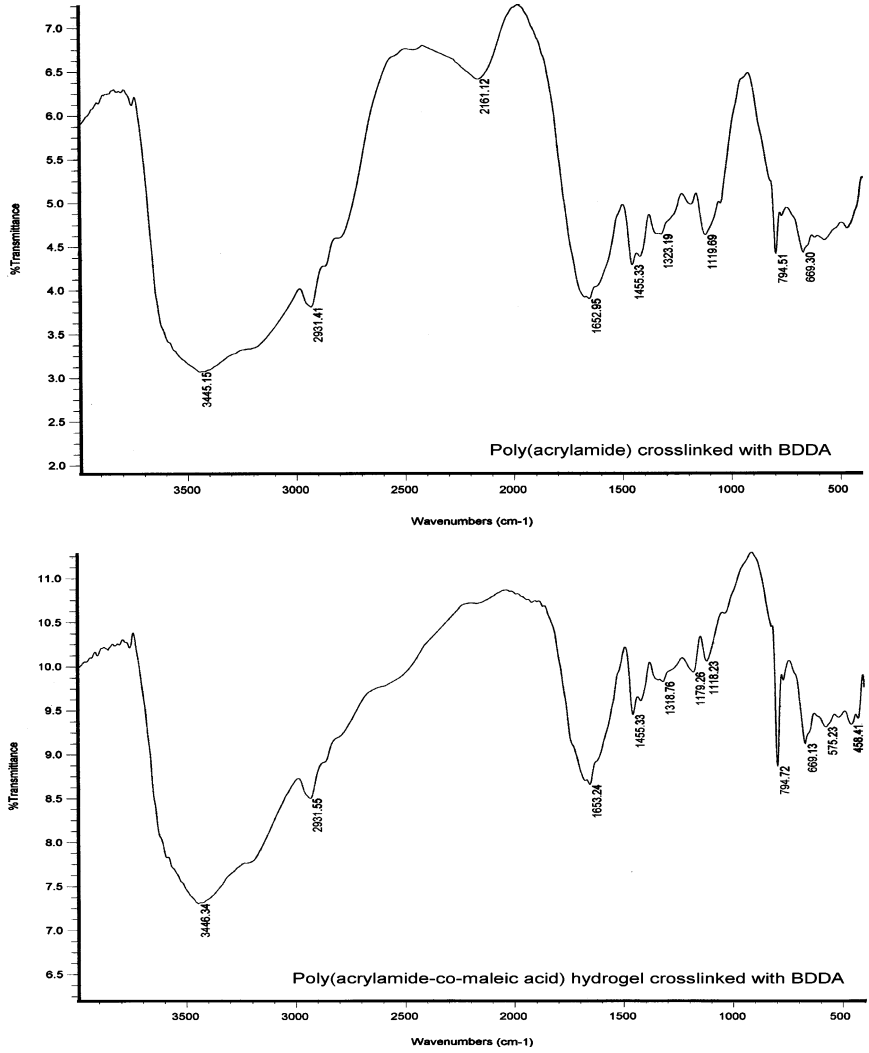


FIGURE 1 IR spectra of polyacrylamide and poly(acrylamide-co-maleic acid) crosslinked with BDDA.

increases due to the ionization of carboxylic groups (-COOH) in the hydrogel matrix, which in turn increases the osmotic swelling pressure. When the maleic acid content further increased, the equilibrium swelling ratio decreases slightly due to unionized maleic acid or due to the presence of excess of ionic units (-COOH) leading to an increase in the solubility of the copolymer at a fixed crosslinker concentration in

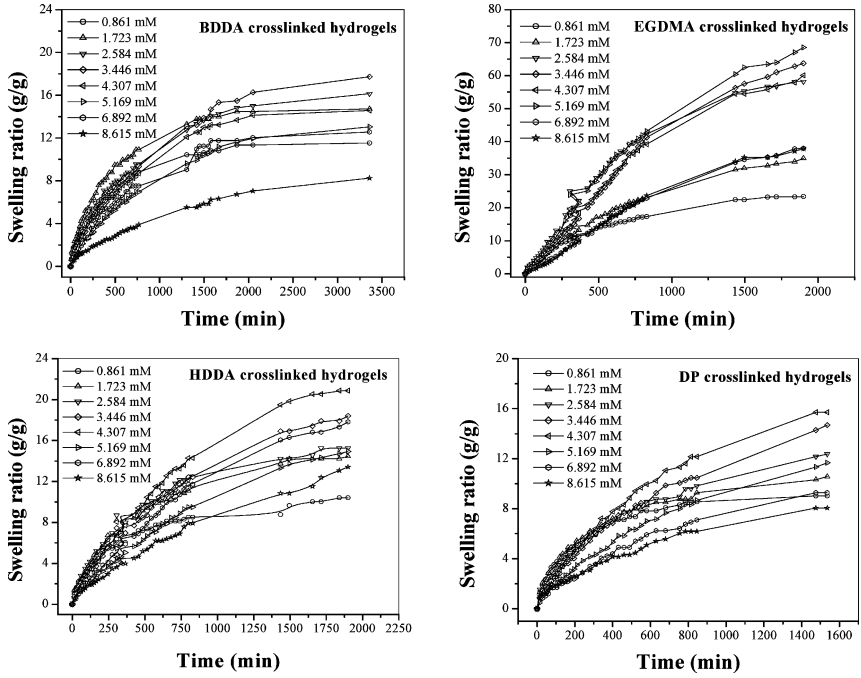


FIGURE 2 Swelling behavior of crosslinked poly(AAm-co-MA) hydrogels.

the swelling medium. The swelling behavior of crosslinked poly(AAm-co-MA) hydrogels are depicted in Figure 2.

Swelling and Diffusion Analysis

The swelling and shrinking properties of hydrogels are currently being exploited in a number of applications including control of microfluidic flow, development of muscle-like actuators, filtration/separation, and drug delivery.

The mechanism of swelling process can be tested by simple kinetic analysis using the second order equation as shown below [34–35]:

$$\frac{ds}{dt} = k_S(S_{eq} - S)^2 \tag{3}$$

where, S_{eq} and k_S denote the degree of swelling at equilibrium and swelling rate constant, respectively. The integration of the Eq. (3) over the limits $S = S_0$ at $t = t_0$ and $S = S$ at $t = t$, gives the following equation:

$$\frac{t}{S} = A + Bt \tag{4}$$

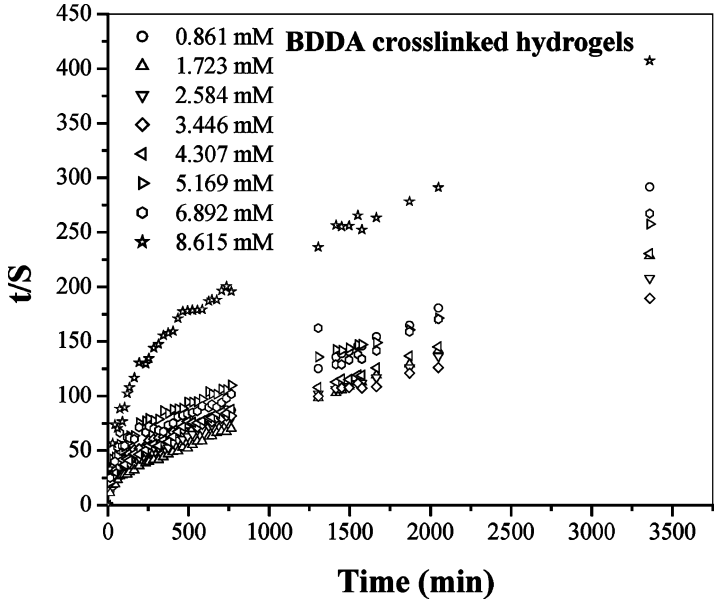


FIGURE 3 Swelling rate curves of poly(AAm-co-MA) hydrogels crosslinked with BDDA.

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 SAP, and k_s is the swelling rate constant. This relation represents the second order kinetics. To examine the swelling kinetic parameters, such as initial swelling rate (r_i), maximum equilibrium swelling ratio (S_{eq}) and swelling rate constant (k_s), for superabsorbent hydrogels, graphs were drawn t/S vs. t and a representative graph is shown in Figure 3.

The above parameters were calculated as per the equations reported in the literature [29,34–35]. The swelling characteristics of all the hydrogels for different amounts of maleic acid are given in Table 1. Table 1 illustrates that the maximum equilibrium swelling ratio values calculated theoretically are in good agreement with equilibrium swelling ratio values obtained experimental. The initial swelling rate and swelling rate constant values vary with maleic acid content for all the copolymer hydrogels crosslinked by BDDA, EGDMA, HDDA, and DP.

Highly water swollen polymers/hydrogels were considered as promising materials in agricultural engineering, biotechnology, biomedicine, and environmental applications and in this direction the analysis of the mechanism of water diffusion in hydrogels has received considerable attention in recent years. When hydrogels are brought in

contact with water the water diffuses into the networks of the gels interior and causes the gel to swell. This results in an increase in the segmental mobility of polymeric chains and therefore increases the distance between the polymeric chains. The dynamics of water sorption process was studied by monitoring the water imbibed by the hydrogel at different time intervals. For diffusion kinetic analysis, the swelling results obtained were utilized only up to 60% of the swelling curves [36–37].

$$\text{Swelling ratio (S)} = ((W_s - W_d)/W_d) = kt^n \quad (5)$$

where W_s and W_d denote weight of swollen hydrogel at time t and weight of 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 that indicates the water transport mechanism.

In order to examine the swelling exponent (n) by using Eq. (5) up to 60% of the swelling ratio values, are utilized graphs were plotted of ln S vs. ln t and a representative graph is shown in Figure 4. The swelling exponent was calculated from the slope of the lines of ln S−ln t plots. In the present study, hydrogels prepared with different amounts of maleic acid have shown n values fluctuating between 0.5–1.0,

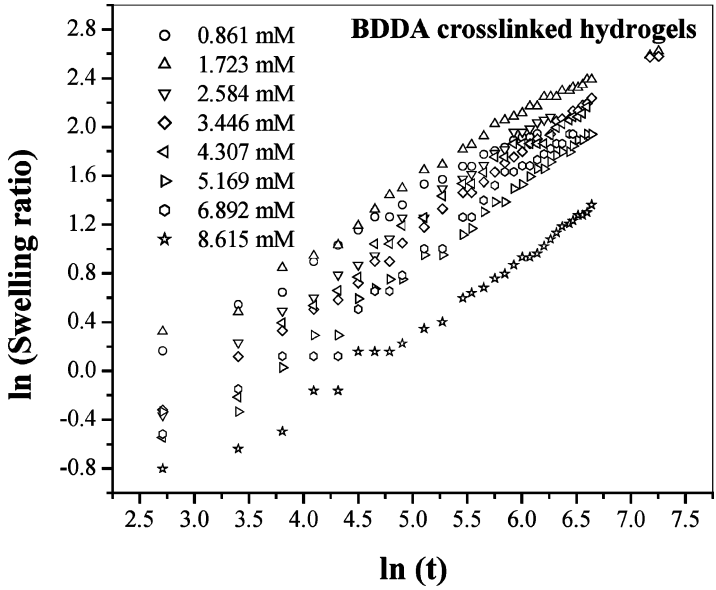


FIGURE 4 Swelling kinetic curves of poly(AAm-co-MA) hydrogels crosslinked with BDDA.

indicating anomalous type of swelling. The hydrogels crosslinked with BDDA, EGDMA, HDDA, and DP had exponent values between 0.53–0.71; 0.63–1.02; 0.54–0.75; 0.49–0.67, respectively; indicating for most of the hydrogels the rate of diffusion of water into the hydrogel is equal to chain relaxation ($R_{diff} \sim R_{relax}$).

The diffusion phenomena of water into hydrogel is of much importance in many areas of applications. In order to analyze the diffusion phenomena of the crosslinked poly(AAm-co-MA) hydrogels, the swelling curves of hydrogels were taken into account. Diffusion coefficient of hydrogels can be calculated by using short time approximation method, which is valid only for the first 60% of the swelling. According to this method, diffusion coefficients of the hydrogels can be calculated using the following equation [34,38]:

$$\text{Swelling ratio} = 4[D/\pi r^2]^{1/2}(t)^{1/2} \tag{6}$$

where D and r indicate diffusion coefficient of hydrogel and radius of hydrogel. To calculate the diffusion coefficient of hydrogel, F vs. $t^{1/2}$ graphs were plotted. From these graphs, the diffusion coefficient of hydrogels was calculated from the slope of the lines and the results are tabulated in Table 1. Table 1 clearly indicating that EGDMA

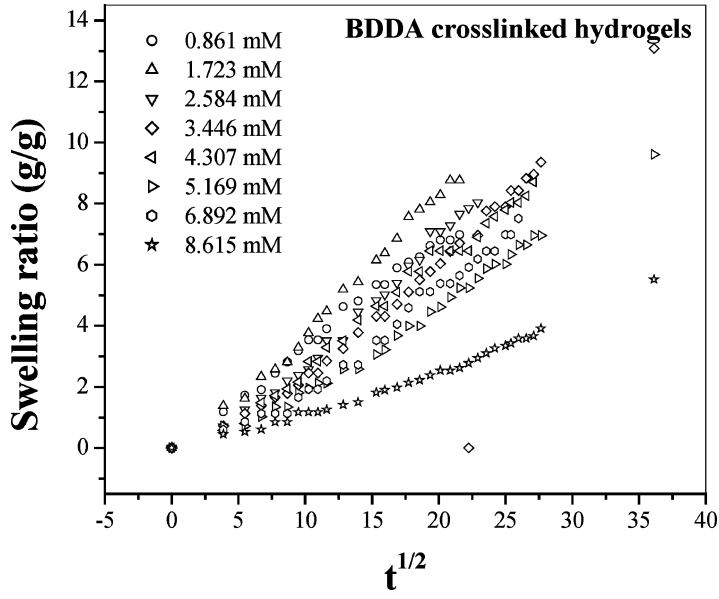


FIGURE 5 Diffusion curves of poly(AAm-co-MA) hydrogels crosslinked with BDDA.

crosslinked poly(AAm-co-MA) hydrogels have higher diffusion coefficient values than other crosslinked hydrogels. This behavior is quite natural and that is why EGDMA crosslinked hydrogels showed higher equilibrium swelling ratio values. A representative graph F vs. $t^{1/2}$ is depicted in Figure 5.

Effect of Crosslinker

Even small amounts of crosslinkers play a prominent role in modifying the properties of hydrogels [39–40]. In general di- and tri-functional crosslinkers are employed. The nature of the crosslinker and the concentration of crosslinker not only modify the swelling and mechanical properties of hydrogels but also influence the amount of soluble polymer formed during polymerization reaction. The solubility, reactivity, and steric hindrance of a given crosslinker determine their efficiency. Most of the hydrogels were effectively synthesized using N,N^1-methylene-bis-acrylamide (MBA) as crosslinker. Recently, a series of copolymers based on acrylamide and potassium/sodium methacrylate hydrogels were reported [29,41] using different crosslinking agents. Literature on acrylamide-maleic acid hydrogels revealed that MBA was widely used as crosslinking agent in the preparation of hydrogels. Thus it is realized that it is necessary to study the contribution of different crosslinkers in controlling the swelling behavior of the hydrogels. Therefore, the effect of the different types of crosslinkers on the swelling behavior of poly(acrylamide-co-maleic acid) hydrogels were investigated. They are 1,2-ehtyleneglycol dimethacrylate (EGDMA), 1,4-butanediol diacrylate (BDDA), 1,6-hexanediol diacrylate (HDDA), and diallyl phthalate.

The influence of various crosslinkers on swelling phenomena of poly(acrylamide-co-maleic acid) hydrogels is depicted in Figure 6. It is clearly observed from the Figure 6 that at lower concentration of BDDA, HDDA, and DP the equilibrium swelling ratio is high and with increases crosslinker concentration the swelling diminishes. This behavior can be explained on the basis of formation of networks in the copolymer chains. At lower crosslinker concentrations the formed copolymer has lower crosslink density, whereas at higher crosslinker concentrations the formed gel has higher crosslink density causing decrease in the space between the polymer chains thereby suppressing the swelling ratio of the hydrogel. Drastic reduction in swelling ratio is observed only in the case of DP crosslinked poly(AAm-co-MA) hydrogels. In contrast to this, EGDMA crosslinked hydrogels showed increase the equilibrium swelling ratio from 54.84 to 101.74 g/g as the concentration of EGDMA varied from 0.01008 to 0.03024 mM.

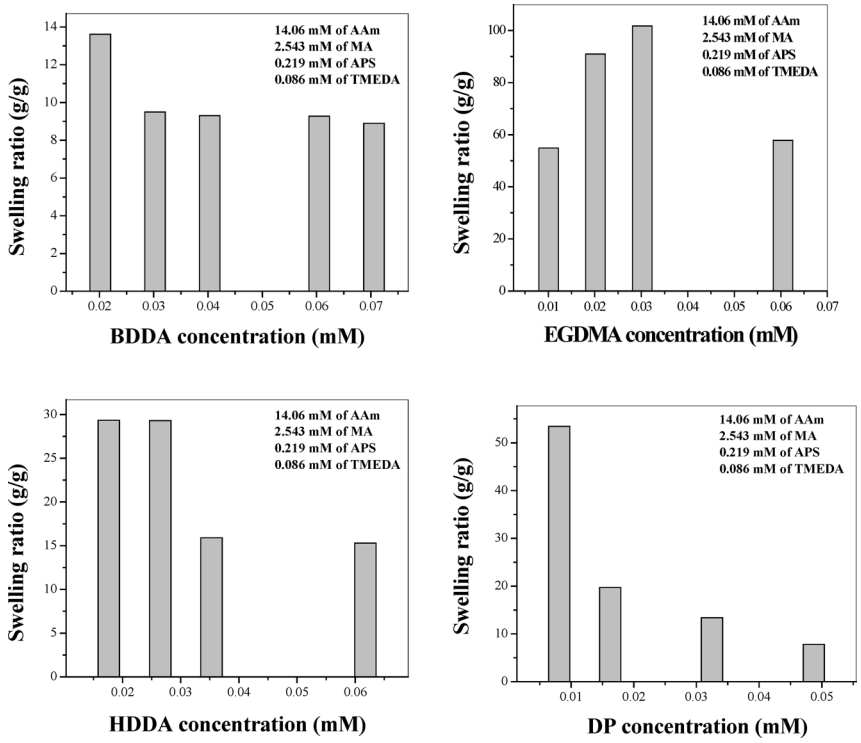


FIGURE 6 Influence of crosslinker concentration on swelling behavior of crosslinked poly(AAm-co-MA) hydrogels.

Further increase in the EGDMA concentration decreased the swelling ratio (Figure 6).

Effect of Initiator

The polymerization was initiated by free radicals in the aqueous phase using thermally decomposable initiators, redox initiators, or combinations. It is well known that initiator or initiating system has direct influence on the physical properties of hydrogels because it affects the crosslinking network structure as well as phase behavior. Redox systems for the crosslinking copolymerizations include couples of persulfate/bisulfite, persulfate/thiosulfate, persulfate/ascorbate, hydrogen peroxide/ascorbate, persulfate/TMEDA, and so on. They are also responsible for the inhomogeneity in the hydrogel system.

In the present investigation, ammonium persulfate and TMEDA were employed as initiator and activator, respectively. The effect of

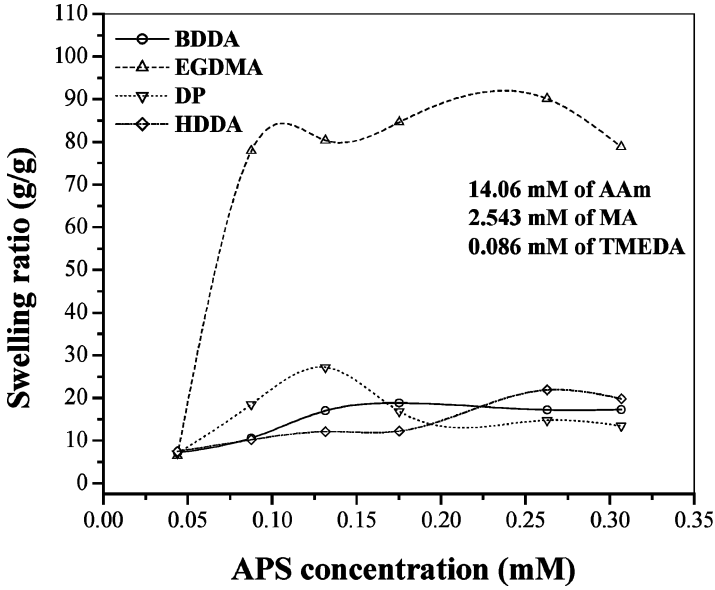


FIGURE 7 Influence of APS concentration on swelling behavior of crosslinked poly(AAm-co-MA) hydrogels.

concentration of ammonium persulfate on equilibrium swelling ratio of poly(AAm-MA) hydrogel was studied and the results are presented in Figure 7. The equilibrium swelling ratio of EGDMA crosslinked poly-(AAm-co-MA) hydrogel increases as APS concentration proceeds from 0.04382 mM to 0.17528 mM and decreases slowly with further increase in the concentration of ammonium persulfate. Other crosslinked series of hydrogels also showed similar swelling pattern. The maximum equilibrium swelling ratio was observed at 0.17 mM, 0.13 mM, 0.17 mM of ammonium persulfate in the poly(AAm-co-MA) hydrogels crosslinked with BDDA, DP, HDDA, respectively. At lower concentrations of ammonium persulfate, the number of free radicals produced is comparatively smaller giving lesser crosslinking density to the network, thereby decreasing the absorbing capacity of the gel.

Effect of Salts on Swelling Behavior

The concentration of salt and its charge valencies also affect the swelling of any hydrogel or SAP. The presence of a salt and its charge valencies causes a change in the hydrogel network structure, influencing the swelling behavior of hydrogels, the mechanical properties and diffusion coefficient of the gel.

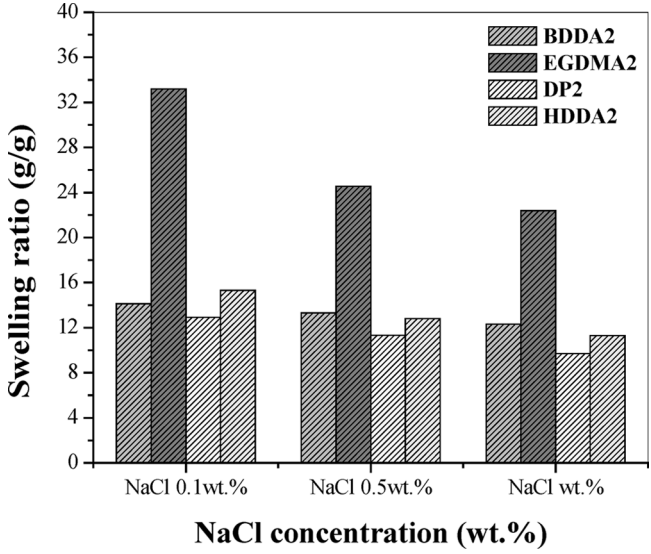


FIGURE 8 Influence of NaCl concentration on swelling behavior of crosslinked poly(AAm-co-MA) hydrogels.

In the present investigation, the effect of NaCl concentration in aqueous solution on the equilibrium swelling ratio was studied for the poly(AAm-co-MA) hydrogels crosslinked by BDDA, EGDMA, HDDA, and DP. Figure 8 shows the equilibrium swelling ratios of the hydrogels in various aqueous NaCl solutions. From Figure 8, it is clearly seen that the equilibrium swelling ratios decreased with increasing NaCl concentration. 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. According to Eq. (7), it is quite acceptable that an increase of the movable counter-ions of a solution may lead to decrease in the osmotic pressure within the gel [42], causing the gel to shrink.

$$\pi_{\text{ion}} = \text{RT}\Sigma_{\text{i}}(\text{C}_{\text{i}}^{\text{g}} - \text{C}_{\text{i}}^{\text{s}}) \tag{7}$$

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 in aqueous medium on the equilibrium swelling ratio of hydrogels, the halide anions of potassium (KCl, KBr, and KI) and chloride salt of K^+, Ca^{2+}, and Fe^{3+} were added, respectively, to the swelling medium. Figures 9 and 10, shows the equilibrium swelling capacity of hydrogels

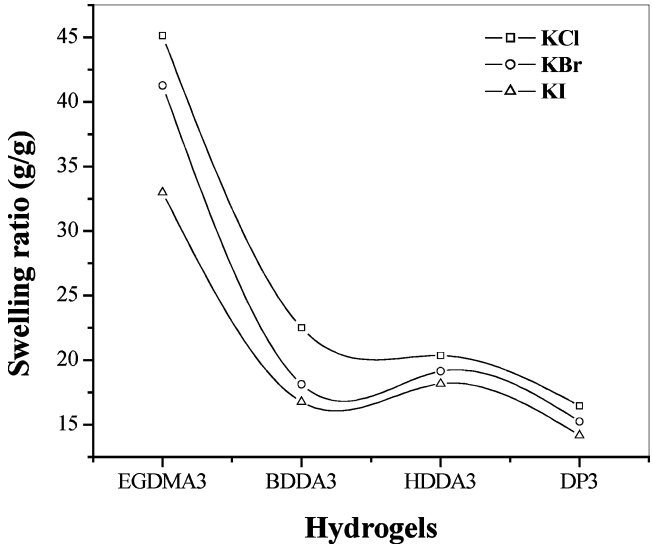


FIGURE 9 Influence of halide anions of potassium (0.01 M) solution on swelling behavior of poly(AAm-co-MA) hydrogels.

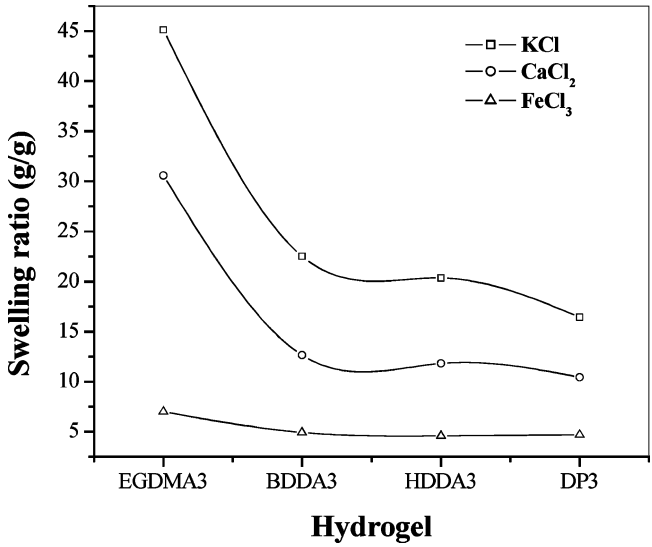


FIGURE 10 Chloride salt of K^+, Ca^{2+}, and Fe^{3+} (0.01 M) solution on swelling behavior of poly(AAm-co-MA) hydrogels.

with added anions and cations in the swelling medium. The results clearly indicates that the equilibrium swelling ratio of all hydrogels decreases with increase of the size of ions present in the swelling medium. The order of swelling behavior is $K^+ > Ca^{2+} > Fe^{3+}$ and $Cl^- > Br^- > I^-$. Similar type of results was also revealed by Lee et al. [43–45].

Effect of pH on Swelling Behavior

The water imbibing capacity is not only affected by the chemical architecture of network such as chain flexibility, crosslinking density, hydrophilic functional groups, osmotic potentials, and free volume but also by temperature, pH, ionic strength, and simulated biological fluids. Among them, temperature and pH sensitivity of hydrogels have gained much importance in the various applications in the biomedical field. In the case of pH-dependent drug delivery systems, many researchers have focused on the swelling properties of hydrogels. Thus, the aim of the present investigation is to study the influence of pH on swelling behavior of the poly(AAm-co-MA) hydrogels. Table 2 gives pH sensitivity equilibrium results of poly(AAM-co-MA) hydrogels, which illustrates the dependence of swelling of hydrogels to in all pH solutions ranging from 2 to 12. From Table 2, it is observed that reasonable swelling sensitivity of the hydrogels is present at all pH. The swelling of the hydrogel was found to increase from pH 2 to 11. At low pH, the H^+ ions in the external medium suppress the ionization of the maleic acid and ultimately the flexibility of the hydrogel chains is low. As the pH increases, the maleic acid ionizes and attracts cations into the gel network to replace the H^+ ions. This, in turn, increases the concentration of mobile ions inside the gel matrix, which increases the ion swelling pressure and therefore higher equilibrium

TABLE 2 Influence of pH Solutions on Swelling Behavior of Crosslinked Poly(AAm-co-MA) Hydrogels

pH of the swelling medium	BDDA3	EGDMA3	HDDA3	DP3
2	8.22	15.84	7.19	8.31
3	10.14	23.51	9.16	7.57
5	14.70	33.29	14.11	13.38
7	16.21	35.82	15.61	16.03
9	20.13	51.70	20.62	16.03
11	Dissolved	Dissolved	Dissolved	19.08
12	Dissolved	Dissolved	Dissolved	Viscous

swelling ratios are obtained. It is observed that at very high pH swelling medium all crosslinked poly(AAm-co-MA) hydrogels dissolved or formed as highly viscous gels, indicating the possibility of hydrolysis.

Effect of Simulated Biological Fluids on Swelling Behavior

The swelling of hydrogel is the net result of osmotic and the restoring elastic pressure. It is widely accepted that the presence of solute in the surrounding aqueous medium is capable to alter the swelling behavior of hydrogels. To find out the effect of various simulated biological solutions on swelling behavior of poly(AAm-co-MA) hydrogel four different biological fluids were employed. As shown in Figure 11, solute-dependent swelling behavior with changing biological solutions is observed. The results clearly demonstrate that poly(AAm-co-MA) hydrogels crosslinked by BDDA, EGDMA, HDDA, and DP show the highest equilibrium swelling ratio values in urea solution than other biological solutions. This behavior could be explained on the basis of formation of hydrogen bonds between the polymeric chains solute and hence a possibility to hold larger amounts of water within the three-dimensional networks of hydrogel. The order of equilibrium swelling capacity for all hydrogels in different biological fluids follows

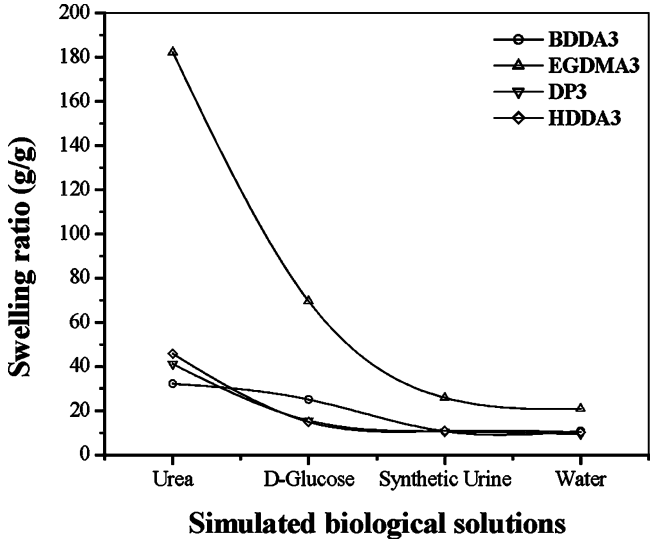


FIGURE 11 Influence of simulated biological fluids on swelling behavior of crosslinked poly(AAm-co-MA) hydrogels.

as, urea > glucose > synthetic urine > saline water. Further, their equilibrium swelling ratio in all biological solutions is low when compared to water as swelling medium. This is due to increase of various ionic species concentration in the swelling medium.

Summary of the Swelling Behavior of the Hydrogels

The swelling studies of the hydrogels revealed that poly(AAm-co-MA) hydrogels showed similar variation in their swelling capacity when the monomeric compositions are about the same. EGDMA crosslinker hydrogels showed higher swelling capacity than any other crosslinked hydrogels. This is due to the structure and reactivity of the crosslinker. This crosslinker gives a fine network that is capable of holding large amounts of water within the crosslinked networks, whereas 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, and diallyl phthalate crosslinkers give hydrogels with loosely crosslinked networks that may not have the same holding capacity of water molecules.

Thermal Transition of Hydrogels

The differential calorimetry measurements clearly show the transition domain of the copolymers to the between 70°C and 80°C. These Transitions are the glass transition temperature of crosslinked poly(AAm-co-MA) hydrogels. Different transition temperatures were observed for crosslinked hydrogels due to the presence of different polymer network structures. This network structure variation rose only due to the employment of different type of crosslinking agents in the polymerization. Table 3 gives the transition temperature of the poly(AAm-co-MA) hydrogels. A representative DSC thermogram is presented in Figure 12.

SEM Studies

The morphological variation in poly(acrylamide-co-maleic acid) hydrogels directly relate to swelling capacity of the hydrogels, because

TABLE 3 Transition Temperature of Poly(AAm-co-MA) Hydrogels

Hydrogel code	Transition temperature (°C)
BDDA3	72
EGDMA3	81
HDDA3	73
DP3	77

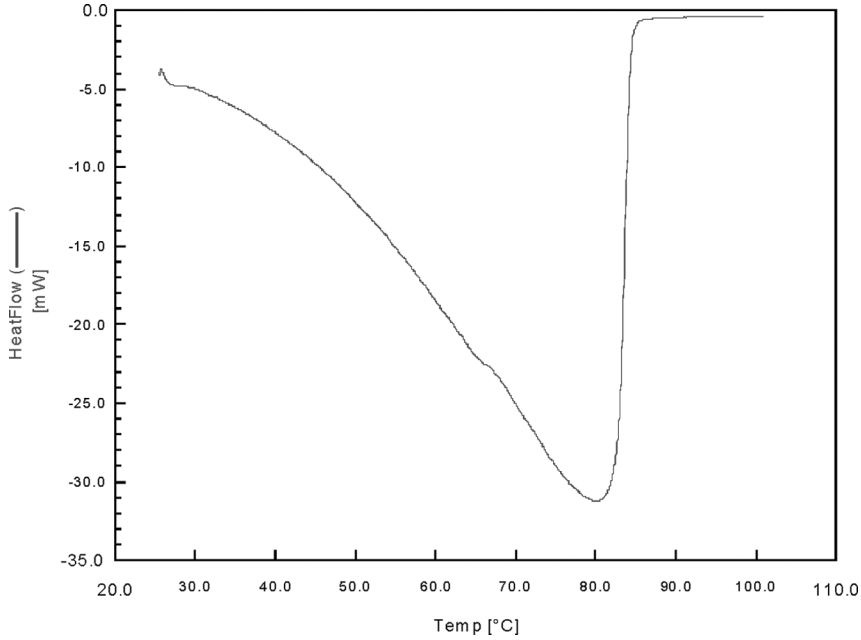


FIGURE 12 DSC thermogram of EGDMA3 hydrogel.

this represents the porosity or crosslinking behavior. In the present study, SEM photographs of cross-sectional area of poly(AAm-co-MA) hydrogels are depicted in Figure 13. It is clearly observed that EGDMA 4 contains low crosslink density (Figure 13B). On the other hand, highly crosslinked network structures are observed in the case of BDDA 4 (Figure 13A) and HDDA (Figure 13C), which, in turn, indicates a lower swelling capacity than EGDMA 4. The higher swelling capacity for EGDMA 4 is attained due to the presence of available pore volume (less crosslink junctions), which in turn accommodate larger amounts of water molecules within the hydrogel networks.

CONCLUSION

Chemically crosslinked poly(AAm-co-MA) hydrogels were prepared by the copolymerization of acrylamide with maleic acid comonomer using APS/TMEDA as initiating system in presence of a crosslinker. The influence of maleic acid content on swelling, diffusion characteristics was studied in detail. Swelling results indicate that EGDMA crosslinked hydrogels have higher absorption capacity than other poly-(AAM-co-MA) hydrogels crosslinked with BDDA, DP, and HDDA. All

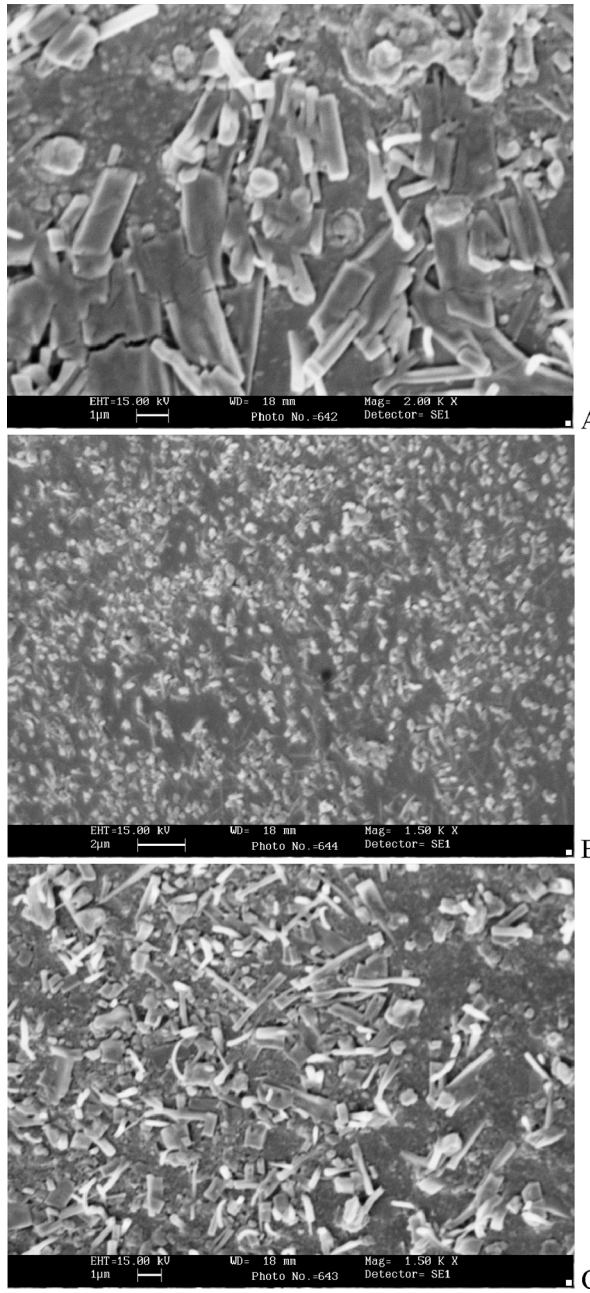


FIGURE 13 SEM photographs of (A) BDDA 4 (17.72 g/g); (B) EGDMA 4 (63.75 g/g) and (C) HDDA 4 (18.40 g/g).

crosslinked hydrogels followed a non-fickian diffusion behavior. The influence of crosslinker (BDDA, EGDMA, HDDA, and DP) and initiator (APS) concentration on swelling pattern was investigated. The cationic and anionic salts, simulated biological fluids, and pH-dependent swelling behavior of poly(AAm-co-MA) hydrogels was also investigated. The structural variation in the crosslinked hydrogels was analyzed using SEM. The crosslinked hydrogels developed in the present investigation may find applicability in various biomedical applications due to their high water equilibrium contents.

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