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Indu Gupta[a]; Rajiv Singh Tomar[a]; A. K. Nagpal[a]; Reena Singhal[a]
[a] Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur, India

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A Study on Effect of Acrylic Acid Content on Swelling Behavior of Poly(AAm-co-BMA-co-AAc) Hydrogels

INDU GUPTA, RAJIV SINGH TOMAR, A. K. NAGPAL, and REENA SINGHAL

Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur, India

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Poly(acrylamide-co-Nbutylmethacrylate-co-acrylic acid) [poly(AAm-co-NBMA-co-AAc)] hydrogels were prepared by varying the of acrylic acid content four-fold in hydrogel. The effect of acrylic acid content on swelling behavior of the resulting poly(AAm-co-NBMA-co-AAc) hydrogels was studied, and it was found that the equilibrium swelling ratio increased from 54.47 to 127.03 with increasing the acrylic acid content from 20% to 66% in the feed. Detailed swelling kinetics such as swelling ratio, transport exponent 'n', diffusion coefficient 'D' were determined and the effect of pH on equilibrium swelling was studied. The hydrogels were also characterized by FTIR, DSC, SEM analysis, and network parameters such as molecular weight between crosslink (Mc) and crosslink density (q) were determined, explaining the swelling behavior.

Keywords: acrylamide; acrylic acid; N-butyl methacrylate; hydrogels; crosslink density; diffusion coefficient

1 Introduction

Hydrogels have received increasing attention of researchers due to their significance both in theory and application. A hydrogel is a network of hydrophilic polymers that can swell in water and hold a large amount of water by crosslinking polymers chains. Crosslinking can be provided by covalent and hydrogen bonding, Van der Waals interaction, and physical entanglements (1, 2). Hydrogels are one of the most promising types of polymers being used for the development of tissue implant materials, since these polymeric materials do not dissolve in water at physiological temperatures or pH, but swell considerably in aqueous media (3, 4). The idea to use hydrogels as biomaterials dates back to the landmark work of Wichterle and Lim (5), which described the rational design of hydrophilic polymer networks for biological uses including soft contact lenses. The environment-sensitive hydrogels are also called 'intelligent' or 'smart hydrogels', since they exhibit remarkable changes in swelling behavior with changes in physical and chemical stimuli. The physical stimuli include temperature, electric fields, solvent composition, light, pressure, sound and magnetic fields, unlike the chemical or biochemical stimuli including pH, ions, and specific molecular recognition events (6). Smart hydrogels have been used in diverse applications, such as in making artificial muscles (7), chemical valves (8), immobilization of enzymes and cells (9) and concentrating dilute solution in bio-separations (10). Environment–sensitive hydrogels are potential candidates for developing self regulated drug delivery systems. Hydrogels have been attracting much attention in the field of medicine and mechanical engineering, and have been used in the medical device industry as contact lenses, artificial corneas, catheters and electrode sensors. Such a wide range use requires easy manipulation of physical properties, which are attainable with hydrogels by changing the monomer types and/or the polymerization conditions. Since their biocompatibility apparently depends on the water content, characterization of the amount of water taken up in the swollen gel is essential.

Polyacrylamide (PAAM) hydrogels exhibit a very high capability to absorb water; they are permeable to oxygen, and possess good biocompatibility (11). PAAm hydrogels have sufficient hydrophilicity, but are low in hydrolytic stability and tensile strength. Acrylic acid polymers are well noted for their pH sensitivity. They swell to over ten times their dry weight in basic solution and collapse in acidic solution. This behavior is due to electrostatic repulsion between the carboxylic acid polymer side chain, and ions present in the buffer solution. At high pH values, the carboxylate side chains are repelled by the anions in the solution, and minimize charge concentration by expanding. Crosslinked poly(AAc) has been noted for displaying sharp sensitivity

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Address correspondence to: Reena Singhal, Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur 208002, India. E-mail: reena_singhal123@rediffmail.com

to external pH, capable of controlling solvent permeation with the corresponding change in swelling behavior (12).

Though numerous types of comonomers have been synthesized, very few detailed studies on these have been conducted in copolymeric hydrogels. Okano et al. (13) have used IPN formation of acrylamide, N-butyl methacrylate with acrylic acid in order to obtain a temperature sensitive hydrogel for oral drug delivery of Keto profen. Katime *et al.* (14) prepared poly(AAm-co-AAc) (50:50) copolymers by using different amounts of NMBA as a crosslinking agent and 1% (wt) potassium peroxodisulphate as an initiator. They studied the release kinetics of theophylline drug from hydrogels in aqueous media and found that the release mechanism was non-Fickian. G.R. Mahdavinia (15) prepared hydrogels by graft copolymerization of acrylic acid (AAc) on to chitosan, using potassium persulphate (KPS) as a free radical initiator in the presence of methylenebisacrylamide (NN′-MBA) as a crosslinker. The effect of reaction variables, such as NN′-MBA concentration and the AA/AAm ratio on the absorbency capacity was investigated.

Copolymeric pH-sensitive hydrogels consisting of N-vinyl-2-pyrrolidone and acrylic acid were synthesized and their swelling and network parameters were evaluated by S.K. Bajpai (16). These gels exhibited nearly 47.8 ± 4.9% swelling in the medium of pH 1.2, while nearly 2164.6 ± 21.8% swelling was observed in the phosphate buffer medium of 6.8 at 30°C.

Hydrogels of poly(N-isopropylacrylamide-co-methacrylic acid) were synthesized and investigated as pH and temperature-triggered delivery devices for antithrombotic agents. For hydrogels containing greater than 75 mol% NIPAAM, the pH and temperature sensitivity both influenced the overall swelling behavior of the networks. The hydrogels synthesized in this study were capable of pulsatile streptokinase drug release (17).

Acrylic acid is an important monomer for hydrogel modification (14, 16) especially by copolymerization; and AA**c** also promotes desirable bioadhesive property. In the present work, we have synthesized a series of hydrogels based on poly(AAm-co-NBMA-co-AAc) by varying acrylic acid content from 20% to 60%, i.e., four fold. The aim of the work was to investigate the effect of the acrylic acid content. The effect of the acrylamide content on swelling behavior of poly (AAm-co-NBMA-co-AAc) hydrogels has been investigated in our previous work (18). Detailed swelling studies such as kinetics for swelling percentage, equilibrium swelling, transport exponent ‘n’, diffusion coefficient ‘D’, and the effect of pH on swelling behavior were conducted. The hydrogels were also characterized by Fourier Transform Infrared (FTIR) analysis, Differential Scanning Calorimetry DSC analysis, Scanning Electron Microscopy (SEM) analysis and network parameters, such as average molecular weight between crosslink (Mc) and crosslink density (q) was determined to correlate network property relationship for hydrogels.

2 Experimental

2.1 Materials

Acrylamide (AAm), N-butylmethacrylate (NBMA), N,N′-methylene bisacrylamide (NN′-MBA) and benzoyl peroxide (BPO) were purchased from CDH, New Delhi, India. Dioxane and ammonium per sulphate were obtained from Qualikem Chem., New Delhi, India. Acrylic acid (AAc) and methyl alcohol were obtained from S.D. Fine Chem., New Delhi, India.

Acrylamide was recrystallized with methanol and butylmethacrylate was distilled with a 4% aqueous sodium hydroxide solution before use. Other chemicals were used as received for the synthesis of hydrogels.

2.2 Synthesis of Poly(AAm-co-N BMA-co-AAc) Hydrogel

A series of crosslinked poly(AAm-co-BMA-co-AAc) have been prepared in different ratios by varying the acrylic acid content four fold. For synthesizing a series of hydrogels, the AAm, NBMA and AAc are taken in different ratio: 1:1:0.5, 1:1:1, 1:1:2, 1:1:3, 1:1:4, which were designated as $Ac_{0.5,}$ $A_{1,}$ Ac_2, Ac_3, Ac_4, respectively. The actual feed compositions are given in Table 1. N,N′-methylenebisacrylamide (NMBA) was used as a crosslinker, while benzoyl peroxide (BPO) and ammoniumpersulphate (APS) were used as initiator; and 50% aqueous dioxane solution was used as solvent.

2.3 Polymerization Method

To synthesize the poly(AAm-co-NBMA-co-AAc) hydrogel, initially a solution of acrylamide was prepared in 20 ml of 50% aqueous dioxane. In this solution, NN′-MBA (1% by weight of AAm concentration), and 0.04 gm BPO were added as crosslinker and initiator, respectively. The reaction solution was then stirred with the help of a mechanical stirrer for 30 min at 45°C for complete dissolution. This reaction mixture was then again mixed with AAc containing NN′-MBA (1% by weight of AAc content) and APS. For homogeneity, this reaction mixture was again stirred under nitrogen atmosphere for 30 min at 45°C. The resulting solution was then poured into Petri-dishes, and kept for 2 h in a hot air oven at 60°C for polymerization and subsequent crosslinking. After the completion of reaction in 2 h, the firm hydrogel, in the form of thick sheet was carefully removed from the surface of the Petri-dishes.

In order to remove unreacted monomer, all the hydrogels were immersed into a 50% aqueous dioxane mixture for 4 h for washing. They were again washed with water several times in order to remove traces of solvent. The resultant hydrogel sheets were dried in oven at 50°C up to a constant weight, and then cut into a $15 \times 15\ cm^2$ size. The dried hydrogels were stored in an airtight container till further use.

Table 1. Feed composition of POLY (AAm-co-NBMA-co-AAc) hydrogel prepared by varying AAc content

Hydrogel code	Ratio AAm: NBMA: AAc	Ratio in percentage AAm:NBMA: AAc	Amount of AAm (gm)	Amount of NBMA (ml)	Amount of AAc (ml)	Amount of 1% of AAm NN′-MBA	Amount of 1% of AAc NN′-MBA	Amount of BPO	Amount of APS	Amount of Dioxane/ water
$Ac_{0.5}$	1:1:0.5	40:40:20	1.60	1.60	0.80	0.016	0.008	0.04	0.04	20
A_1	1:1:1	33.33:33.33:33.33	1.33	1.33	1.33	0.013	0.013	0.04	0.04	20
Ac_2	1:1:2	25:25:50	1.00	1.00	2.00	0.010	0.020	0.04	0.04	20
Ac_3	1:1:3	20:20:60	0.80	0.80	2.40	0.008	0.024	0.04	0.04	20
Ac_4	1:1:4	17:17:66	0.68	0.68	2.64	0.006	0.026	0.04	0.04	20

2.4 Swelling Measurements

The degree of swelling was measured by gravimetric measurements. In each experiment preweighed initially dry hydrogel (15×15 mm^2, in dimension) was immersed in 500 ml of distilled water. Afterwards, during swelling, the hydrogel was removed from water at different time intervals and it's surface was quickly blotted free of water by using filter paper. It was weighed, then carefully returned to the swelling medium. The swelling ratio was calculated from Equation (1):

$$\text{Swelling ratio} = \frac{\mathrm{Ws}}{\mathrm{Wd}} \tag{1}$$

The degree of swelling was calculated from Equation (2):

$$\text{Degree of swelling (\%)} = \frac{\mathrm{Ws} - \mathrm{Wd}}{\mathrm{Wd}} \times 100 \tag{2}$$

Where Wd is dry weight of the hydrogel and Ws is the swollen weight of the hydrogel.

2.5 Data Analysis

2.5.1 Dynamic Swelling Study

The dried hydrogel was immersed in an excess of distilled water at 25°C. The amount of water absorbed at a particular time 't' was designated by 'Mt' of the hydrogel and is a function of time 't' (19). The equilibrium absorption at an infinitely long time, which was designated by 'M_∞', is taken as weight of hydrogel after equilibrium has been achieved. Equation (3) expresses the relation between '$\mathrm{Mt}/\mathrm{M}_\infty$' can be used to calculate the characteristic constant K and transport exponent 'n' for $\mathrm{Mt}/\mathrm{M}_\infty \leq 0.6$

$$\mathrm{M_t}/\mathrm{M}_\infty = \mathrm{Kt^n} \tag{3}$$

Where 'K' is a characteristic constant of the gel, and 'n' is a characteristic exponent of the mode of transport for the penetrant. For a slab geometry when $n = 0.5$, the swelling process is diffusion controlled and was termed "Fickian" or case I transport. Transport was assumed to be Relaxation controlled (Case II) when $n = 1$; when the exponent 'n' was between 0.50 and 1.0, the transport was termed Anomalous. An observation of $n > 1$ is termed as "Super case". The rate of approach to equilibrium can be characterized by diffusion coefficient 'D', which can be calculated for planar geometry from the following Equation (4) (20):

$$\mathrm{M_t}/\mathrm{M}_\infty = (4/\pi^{\mathrm{n}})(\mathrm{Dt}/\mathrm{L}_0^2)^{\mathrm{n}} \tag{4}$$

Where 't' is the time and 'L_0' is the initial thickness of the dried sample. The value of 'n' and 'K' were calculated from the slope, and the intercept of the plot of "log ($\mathrm{M_t}/\mathrm{M}_\infty$) against log (t)."

2.5.2 Network Parameters

Network parameters characterizing the crosslinked polymers are average molecular weight between crosslink 'Mc', which is directly related to the crosslink density. The magnitude of Mc significantly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine Mc for a perfect network, according to the theory of Flory and Rehner (21).

$$\mathrm{Mc} = -\mathrm{V_1 d} \quad \frac{(\mathrm{Vs}^{1/3} - \mathrm{Vs}/2)}{[\ln(1 - \mathrm{Vs}) + \mathrm{Vs} + \chi \mathrm{Vs}^2]} \tag{6}$$

Where 'Mc' is the number average molecular weight of the polymer chain between crosslinks. $\mathrm{V_1}$ is the molar volume of the solvent (water), and the molar volume of water at 25°C is 18 cm^3. The VS is the volume fraction of polymer in the swollen hydrogel, which is reciprocal of the swelling ratio (22).

The Flory-Huggins interaction parameter 'χ' between the solvent and the polymer were already calculated for different hydrogels according to Wei Xue et al. (23) and polymer density (d) for various hydrogels were already calculated by direct measurements of dimensions of the hydrogel using a caliper (24). The swelling ratio ϕ is reciprocal of volume fraction of swollen gel. Here, the crosslink density q is defined as the mole fraction of crosslinked units.

$$\mathrm{q} = \frac{\mathrm{M_o}}{\mathrm{Mc}} \tag{7}$$

Where '$\mathrm{M_o}$' is the molecular weight of the polymer repeat unit and can be calculated by following equation:

$$\mathrm{M_o} = \frac{\mathrm{n_{AAm}} \times \mathrm{M_{AAm}} + \mathrm{n_{AAc}} \times \mathrm{M_{AAc}} + \mathrm{n_{BMA}} \times \mathrm{M_{BMA}} + \mathrm{n_{CL}} \times \mathrm{M_{CL}}}{\mathrm{n_{AAm}} + \mathrm{n_{AAc}} + \mathrm{n_{BMA}} + \mathrm{n_{CL}}} \tag{8}$$

Where $\mathrm{n_{AAm}}$, $\mathrm{n_{AAc}}$, $\mathrm{n_{BMA}}$ are mole number of AAm, AAc, NBMA and crosslinker and $\mathrm{M_{AAm}}$, $\mathrm{M_{AAc}}$, $\mathrm{M_{BMA}}$ and $\mathrm{Mc_L}$ are the molecular weight of the AAm, AAc, NBMA and crosslinker N,N′MBA, respectively.

2.6 Characterization

2.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of various hydrogels were recorded using a Nicolet 400D spectrophotometer in solid potassium bromide pellet form after completely drying the hydrogels in a vacuum at 60°C for 8 h.

2.6.2 Elemental Analysis

Elemental analysis for Carbon, Hydrogen and Nitrogen was performed on an Elemental Analyzer (Elemental Vario EL III Carlo Erba 1108).

2.6.3 Differential Scanning Calorimeter (DSC)

DSC was carried out using a Perkin-Elmer (Pyris Diamond) differential scanning calorimeter under the nitrogen atmosphere at a heating rate of 5°C/min. from 80 to 200°C.

2.6.4 Scanning Electron Microscopy (SEM)

The morphology of a synthesized poly(AAm-co-NBMA-co-AAc) hydrogels surface was examined under a Scanning Electron Microscope (SEM). Dried poly(AAm-co-NBMA-co-AAc) hydrogels, coated with a thin layer of pure gold, is a 5150-sputter coater, and imaged in a SEM (LEO Electron Microscopy Ltd., England).

3 Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy

The FTIR spectra of various synthesized poly(AAm-co-NBMA-co-AAc) hydrogels $Ac_{0.5}$ to Ac_4 were recorded; and found to be the same for various peaks corresponding to AAm, NBMA, and AAc for all the composition of hydrogels. Figure 1 represents the FTIR of (a) crosslinked polyacrylic acid, (b) crosslinked poly(AAm-co-NBMA) and, (c) poly(AAm-co-NBMA-co-AAc) ($Ac_{0.5}$). In Figure 1, the peak for C═O bond of PAAc was observed at 1724.54 cm^{-1}. The FTIR (Figure 1(b)) spectrum of PAAM showed strong absorption peaks at 1662.57 cm^{-1}, which was due to C-N stretching. In addition to the above, a strong peak was observed at 2170.14 cm^{-1} corresponding to C═O stretching of the methyl ester of NBMA units. A strong peak was also observed at 2371.86 cm^{-1} corresponding to C-H stretching of hydrocarbon. The FTIR (Figure 1(c)) spectrum of the $Ac_{0.5}$ hydrogel showed the peak corresponding to the functional groups attached to the monomeric units. Peaks were observed at 1630 cm^{-1} corresponding to C═O group of PAAc and at 1592 cm^{-1} corresponding to $-CONH_2$ group of AAm. A strong peak was also observed at 1362.50 cm^{-1} corresponding to C═O stretching of the methyl ester of NBMA units. The FTIR analysis indicated that all monomer units (AAm, NBMA, AAc) were incorporated into the hydrogel.

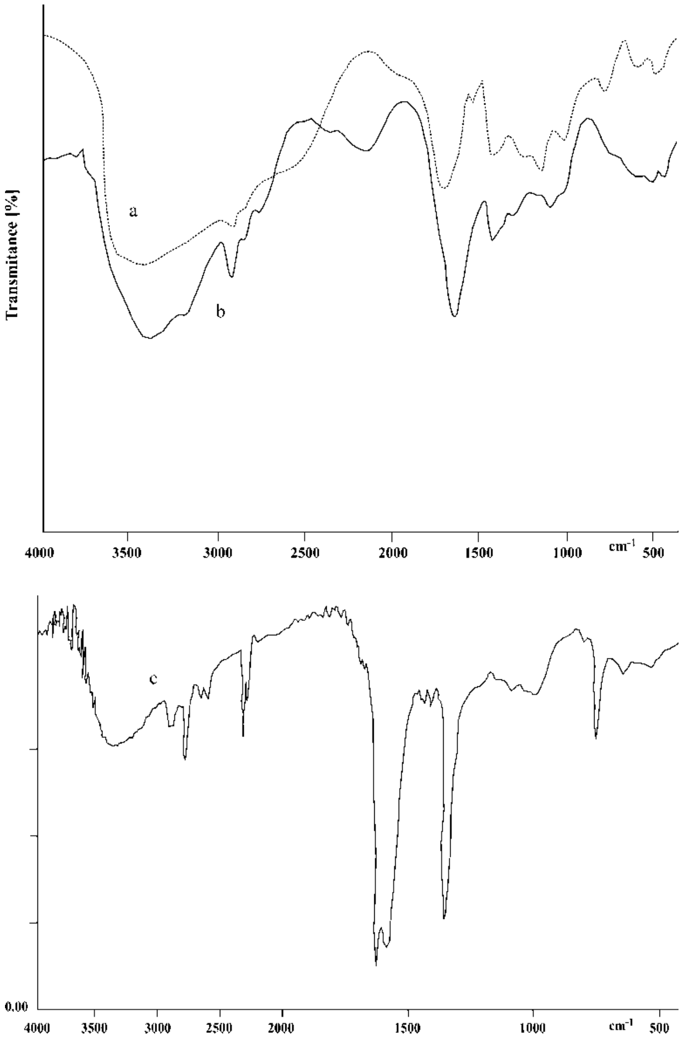

Fig. 1. FTIR spectra of (a) crosslinked poly(AAc), (b) crosslinked Poly(AAm-co-NBMA). (c) FTIR spectrum of poly (AAm-co-NBMA-co-AAc) Hydrogel ($Ac_{0.5}$).

3.2 Elemental Analysis

The nitrogen content of poly(AAm-co-NBMA-co-AAc) hydrogels prepared by varying the acrylic acid was analyzed by Elemental Analysis and on its basis, the percentage of nitrogen, which was later used in calculating acrylamide content present in the hydrogels was determined. The results are given in the Table 2. It can be seen that the nitrogen content present in the hydrogel was decreased from 9.56% to 2.78%; when the acrylic acid content was increased from 20% to 66% in the feed. The elemental analysis results of synthesized hydrogels also clearly indicates that the combined percentages of acrylic acid and NBMA in them were increased from 51.52% to 85.90%. These values are quite similar to the combined percentages of AAc and NBMA taken in the feed in Table 2.

3.3 Differential Scanning Calorimeter (DSC) Analysis

The DSC scans of poly(AAm-co-NBMA-co-AAc) hydrogels ($Ac_{0.5}$, Ac_1, Ac_2, Ac_3, Ac_4) having different amount of AAc content are shown in Figure 2. The glass transition temperature 'Tg' values of the hydrogel, having different amounts of AAc, as observed by the DSC scans, are given in Table 3. The percentage of AAc present in the hydrogels increases the glass transition temperature significantly due to its highly ionic nature. From Table 3, it is clear that as the amount of AAc increased; the value of Tg increases correspondingly. DSC thermogram (Figure 2) shows that Tg increased from 125.98°C to 160.53°C with an increase in AAc content of the hydrogels in feed from 20% to 66% for $A_{0.5}$ to A_4 hydrogels.

3.4 Effect of Acrylic Acid Content

In the present investigation, acrylamide hydrogels swelling were improved upon by incorporation of AAc; but in order

Table 2. Percentage of AAm and (AAc + NBMA) content present in Poly(AAm-co-NBMA-co-AAc) hydrogels prepared by varying acrylic acid content, determined by elemental analysis

Hydrogel code	Elemental analysis (%) C	H	N	Percentage of AAm content taken in feed	Percentage of AAm content in hydrogel calculated by elemental analysis	Total percentage of AAc and NBMA component taken in feed	Total percentage of AAc and NBMA content in hydrogel calculated by elemental analysis
$Ac_{0.5}$	46.24	6.76	9.56	40	48.48	$20 + 40 = 60$	51.52
A_1	47.37	6.53	6.68	33.33	33.87	$33.33 + 33.33 = 66.66$	66.13
Ac_2	48.40	6.33	4.10	25	20.79	$50 + 25 = 75$	79.21
Ac_3	47.34	5.98	2.78	20	15.11	$60 + 20 = 80$	84.88
Ac_4	42.36	5.80	2.98	17	14.09	$66 + 17 = 83$	85.90

to prevent hydrogel solubilization at a high AAc content and also for better mechanical strength of resulting hydrogels, NBMA was also incorporated as a comonomer. By incorporating an ionic monomer into the hydrogel, it is expected that it will improve the swelling significantly. In the present work, we investigated the influence of the acrylic acid content, which was varied as a commoner four fold, i.e., from 20% to 66% in the feed, while keeping acrylamide and N-butyl methacrylate quantities constant. The swelling ratio of poly(AAm-co-NBMA-co-AAc) hydrogels having acrylic acid content 20%, 33.33%, 50%, 60% and 66% in the feed; (were designated as $Ac_{0.5}$, A_1, Ac_2, Ac_3 and Ac_4, respectively) are shown in Table 4 and Figure 3. From Figure 3, it is clear that the equilibrium swelling ratio of hydrogels, gradually increased with an increase in acrylic acid content for hydrogel $Ac_{0.5}$ to Ac_4. It is also apparent from the data that initially there was a moderate increase in equilibrium swelling ratio from 54.47 to 62.88 for $Ac_{0.5}$ to A_1 hydrogels having AAc content 20% to 33.33% in feed. The equilibrium swelling ratio was further increased nominally from 62.88 to 66.07 for A_1 to Ac_2 hydrogels; as the concentration of AAc increased from 33.33% to 50% in feed, the equilibrium swelling ratio increased from 66.07 to 73.93; for Ac_2 to Ac_3 hydrogels having a 50-60% AAc content in the hydrogel feed. However, there was a drastic increase in equilibrium swelling ratio from 73.93 to 127.03 for Ac_3 to Ac_4 hydrogels, which have 60–66% acrylic acid content in the feed. The increase in swelling ratio with increasing acrylic acid content can be explained by the fact that the presence of acrylic acid makes the hydrogel more ionic, and increased the H^+ ion concentration inside the hydrogel. The increase in AAc content created an ion swelling pressure, which increased the degree of swelling of resulting hydrogels. The crosslink density of hydrogels also significantly affected the swelling behavior of these hydrogels. It was found that as the crosslink density decreased from 1.09×10^{-6} to 3.80×10^{-8} for $Ac_{0.5}$ to Ac_4 hydrogels, the swelling ratio increased considerably from 54.47 to 127.03 correspondingly. A nearly similar phenomenon was also obtained by Zhou et al. (25), when they studied the copolymeric hydrogels based on acrylamide (AAm), sodium methallylsulphonate (MSAS), sodium acrylate (SA) and N,N′-methylenebisacrylamide (N,N′-MBA) in an aqueous solution, using potassium persulphate (KPS) and N,N,N′,N′,-tetra methylenediamine (TMEDA) as initiator. They observed that the mol/L, and reached its maximum, a concentration of 0.10 mol/L.

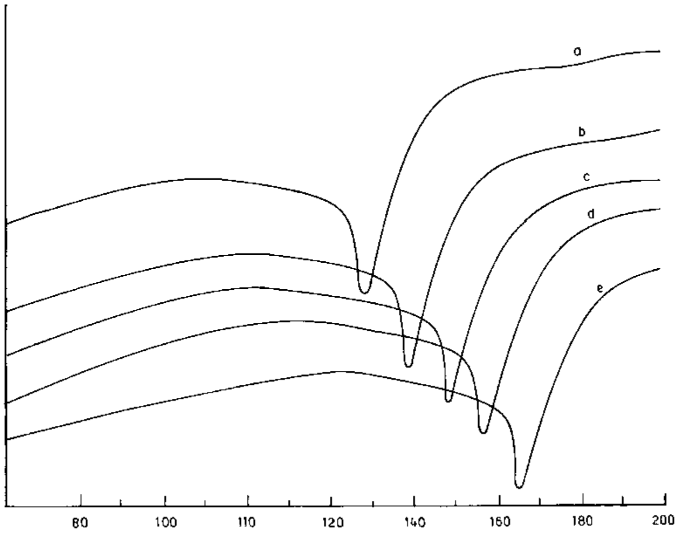

Fig. 2. DSC Thermograms of (a) $Ac_{0.5}$, (b) Ac_1, (c) Ac_2, (d) Ac_3, (e) Ac_4 Hydrogels.

Table 3. Glass transition temperature of poly(AAm-co-NBMA-co-AAc) hydrogels having varying acrylic acid content obtained by dsc thermograms

Hydrogel code	Percentage of AAc content in feed composition	Glass transition temperature (Tg) of AAc obtained from DSC (°C)
$Ac_{0.5}$	20	125.98
A_1	33.33	135.38
Ac_2	50	148.12
Ac_3	60	157.43
Ac_4	66	163.27

Table 4. Swelling behavior and diffusion parameter of poly(AAm-co-NBMA-co-AAc) hydrogels prepared by variation of acrylic acid.

Hydrogel code	Swelling ratio ‘Φ’	Swelling exponent ‘n’	K	Diffusion coefficient
$Ac_{0.5}$	54.47	1.00	−1.75	2.72×10^{-2}
A_1	62.88	0.94	−1.80	1.08×10^{-3}
Ac_2	66.07	1.12	−2.10	6.6×10^{-4}
Ac_3	73.97	1.00	−1.58	1.00×10^{-3}
Ac_4	127.03	1.00	−1.99	5.36×10^{-4}

However a further increase of AAc concentration leads to a decrease in absorbency, which was still as high as 105 times.

In order to get an insight into the swelling mechanism for hydrogels $Ac_{0.5}$, A_1, Ac_2, Ac_3 and Ac_4; the dynamic water absorption experiments were performed. The data was analyzed in terms of swelling exponent ‘n’, diffusion coefficient ‘D’ and rate constant ‘K’ and the results were shown in Table 4. Table 4 showed that the value of the swelling exponent ‘n’ lies in the range of 0.94 to 1.12 for the hydrogels so it can be taken nearly ‘1’. Therefore, it can be studied that all hydrogels exhibit relaxation controlled to “Supercase” release mechanism. The value of diffusion coefficient ‘D’ lies in the range of 2.72×10^{-2} to 5.36×10^{-4} for $Ac_{0.5}$ to Ac_4 hydrogels.

S.K. Bajpai (16) had also reported similar ‘n’ values for copolymeric hydrogels based on N-vinyl-2-pyrrolidone-co-acrylic acid containing different amounts of crosslinker. They found that the value of ‘n’ lies in the range of 0.77 to 0.98.

3.5 Network Parameters Study

The network parameters were determined for hydrogels $Ac_{0.5}$ to Ac_4 having a varying acrylic acid content and are shown in Table 5. Table 5 shows the values of swelling ratio, polymer volume fraction in swollen gel, interaction parameter between the polymer and solvent ‘χ’, average molecular weight between crosslink ‘Mc’ and crosslink density ‘q’. The crosslink density is one of the most significant structural parameters for a family of hydrogel, which can drastically alter the swelling ratio (26). It is clear from Table 5 that the crosslink density for $Ac_{0.5}$ to Ac_1 hydrogels was slightly increased from 1.09×10^{-6} to 1.86×10^{-6}. It was a minor increase in the crosslink density, however, the equilibrium swelling ratio increased from 54.47 to 62.88. To explain the above increased swelling behavior; hydrogels ($Ac_{0.5}$, A_1 and Ac_4) were characterized by Scanning Electron Microscopy (SEM) before Figure 4 (a_1, b_1, c_1) and after swelling Figure 4 (a_2, b_2, c_2), respectively: Figure $4a_1$, shows a smooth surface with some bead-like formations, while Figure $4a_2$ shows that after swelling more beads-like formations appeared, Figure $4b_1$, shows a smooth, with some small granules-like, structure. The roughness is increased with a cracks-like structure (Figure $4b_2$), so more space is available for water penetration which leads to increased swelling of A_1 hydrogel compared to $Ac_{0.5}$ hydrogel, Furthermore, the crosslink density was decreased from 1.86×10^{-6} to 3.5×10^{-7} which leads to an increase in equilibrium swelling ratio nominally from 62.88 to 66.07 for A_1 to Ac_2 hydrogels. Afterwards, the crosslink density was decreased from 1.48×10^{-7} to 3.80×10^{-8}, which lead to a drastic increase in equilibrium swelling ratio from 73.93 to 127.03 for Ac_3 to Ac_4 hydrogels. This drastic change in equilibrium swelling ratio could be explained by SEM of Ac_4 hydrogel before swelling (Figure $4c_1$) and after swelling (Figure $4c_2$). Before swelling, (Figure $4c_1$) a crack-like structure appears on the surface of hydrogels (Figure $4c_1$), through which the water enters by diffusion into the surface; as well as from direct penetration through these cracks, resulting in a drastic increase in swelling. After swelling (Figure $4c_2$), these crack-like structures, which increased in number on the hydrogel surface, may be due to a heavy water content at equilibrium swelling. The overall conclusion is that swelling of these hydrogels depends upon concentration of acrylic acid, as well on the as crosslink density and the surface morphology of the hydrogels.

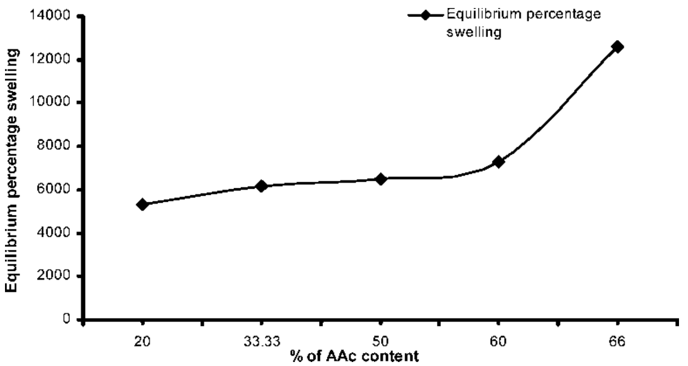

Fig. 3. Effect of % AAc content on equilibrium percentage swelling of hydrogels.

3.6 Effect of pH

The equilibrium percentage swelling of various poly(AAm-co-NBMA-co-AAc) hydrogels prepared by varying acrylic acid content were also studied in a swelling medium having different pH (2, 5, 7 and 10) made by HCl and NaOH; and the results are shown in Figure 5. It is clear from Figure 5 that for the $Ac_{0.5}$ hydrogel, the percentage of equilibrium swelling increased drastically from 69.2% to 2966%, when the pH was increased from 2 to 5. The equilibrium percentage swelling then increased from 2966% to 5341% when pH was further raised from 5 to 7. The equilibrium percentage swelling then further increased drastically from 5341% to 8575% as the pH was raised further 7 to 10. For A_1 hydrogel, the percentage of equilibrium swelling increased

Table 5. Determination of network parameter of poly(AAm-co-NBMA-co-AAc) hydrogels prepared by variation of acrylic acid

Hydrogel code	Swelling ratio 'Φ'	Polymer volume fraction in swollen gel 'Vs'	Interaction parameter between polymer and solvent 'χ'	Average molecular weight between crosslink 'Mc'	Crosslink density 'q'
$Ac_{0.5}$	54.47	0.01836	0.506	8.17×10^{7}	1.09×10^{-6}
A_1	62.88	0.01616	0.505	4.86×10^{7}	1.86×10^{-6}
Ac_2	66.07	0.01514	0.505	2.34×10^{8}	3.5×10^{-7}
Ac_3	73.93	0.01352	0.505	5.37×10^{8}	1.48×10^{-7}
Ac_4	127.03	0.00787	0.503	2.07×10^{9}	3.80×10^{-8}

drastically from 150% to 3580%, as the pH was raised from 2 to 5. The equilibrium percentage swelling further increased from 3580% to 6188% when pH was raised further from 5 to 7. The equilibrium percentage swelling was again increased from 6188% to 9100% when the pH of the swelling medium was raised from pH 7 to 10. In the same fashion, for Ac_2 hydrogels, the percentage equilibrium swelling increased heavily from 160% to 10275%, when the pH was raised from pH 2 to 10. Further equilibrium percentage swelling increased from 190% to 12042.8% from pH 2 to 10 for Ac_3 hydrogels. For Ac_4 hydrogels, from pH 2 to 10, the percentage equilibrium swelling increased from 225% to 13, 150%. It was observed that the equilibrium percentage swelling increased gradually with an increase in pH of the swelling medium for all types of hydrogels. Thus, the variation of swelling of hydrogels with increasing pH can be divided into three steps. In first step, there was a rapid increase in equilibrium percentage swelling (from pH 2 to 5) as the swelling increases nearly 40 times. Then, in the second step, there was a mild increase in equilibrium percentage swelling as it increased nearly twice (from pH 5 to 7). Furthermore, in the third step, there was a nominal increase in equilibrium percentage swelling as it increased nearly one and half times as the pH was raised from pH 7 to 10. The minimum swelling occurred in the highly acidic swelling medium having pH 2, which may be attributed to the fact that the -COOH groups present along the macromolecular chains in the hydrogel remain almost unionized (since

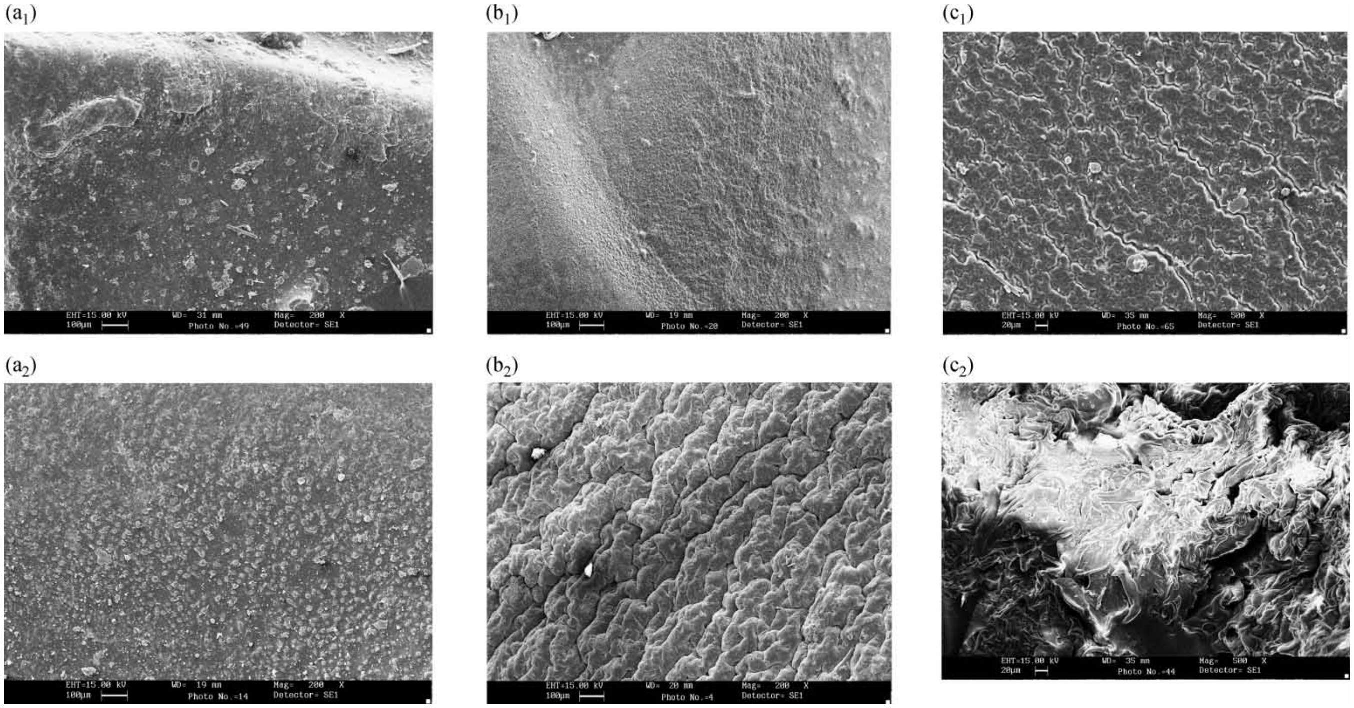

Fig. 4. (a_1) SEM of Poly (AAm-co-NBMA-co-AAc) hydrogel ($Ac_{0.5}$) before swelling; (a_2) SEM of Poly (AAm-co-NBMA-co-AAc) hydrogel ($Ac_{0.5}$) after swelling; (b_1) SEM of Poly (AAm-co-NBMA-co-AAc) hydrogel (Ac_1) before swelling; (b_2) SEM of Poly (AAm-co-NBMA-co-AAc) hydrogel (Ac_2) after swelling; (c_1) SEM of Poly (AAm-co-NBMA-co-AAc) hydrogel (Ac_4) before swelling; (c_2) SEM of Poly (AAm-co-NBMA-co-AAc) hydrogel (Ac_4) after swelling.

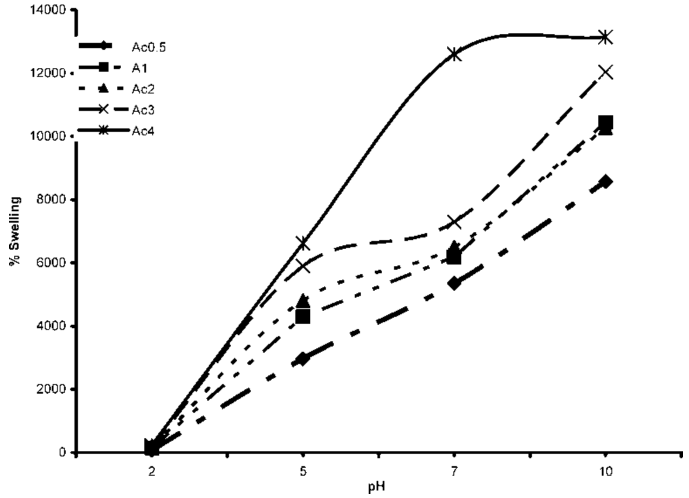

Fig. 5. Effect of different pH solutions (as a swelling medium) on equilibrium percentage swelling of poly(AAM-co-NBMA-AAc) hydrogels having different percentage of AAc content.

pKa of acrylic acid is 4.7) (15), thus resulting into almost zero osmotic swelling pressure as there are no mobile/counter ions present inside the hydrogel (27). It was observed that as the pH of selling medium was increased from pH 2 to 7 (i.e., above the pKa value 4.7 of acrylic acid); the degree of ionization in acrylic acid and acrylamide increased to give COO$^-$ and NH$_3$ ion that resulted in a more hydrophilic polymer network and contributed to this higher water uptake. Moreover, hydrogen-bonding interactions occurred among the carboxylic groups present within the hydrogel; thus providing a compact hydrogen-bonded structure to the hydrogel (28). The protonation of amine and carboxylic groups takes place at pH, i.e., $2 < \mathrm{pH} > 4.7$, and NH$_2$ groups are converted to NH$_3^+$. But at pH < 4.7, the carboxylic functional groups are converted to carboxylate ions. Either protonated (NH$_3^+$) or deprotonated (COO$^-$) groups increase charge density on the polymer causing an enhancement of the osmotic pressure inside the gel particles, because of the NH$_3^+$ – NH$_3^+$ or COO$^-$ – COO$^-$ electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the hydrogel (15).

4 Conclusions

From the study, it can be concluded that the swelling ratio increased nearly 2.5 times as the acrylic acid content in crosslinked hydrogels of poly(AAm-co-NBMA-co-AAc) increased up to 3 times. The transport mechanism for various hydrogels was anomalous, zero order, and super case; depending upon hydrogel composition. The hydrogels synthesized in the study also exhibited pH sensitive nature, as the swelling ratio increased drastically when the pH was raised from 2 to 10. It can be concluded that hydrogel composition, ionization equilibrium, and polymer and morphology play a very important role in controlling the swelling properties of ionizable hydrogels.

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