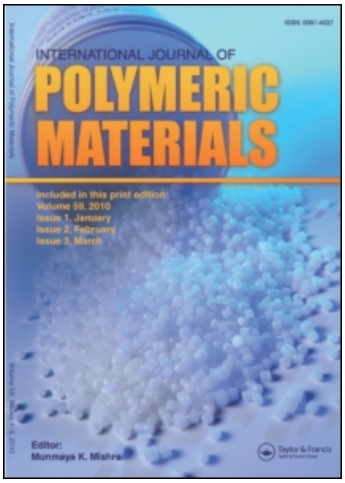

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Synthesis and Swelling Behavior of Acrylamide-Potassium Methacrylate Superabsorbent Copolymers

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A series of acrylamide-potassium methacrylate superabsorbent copolymers were synthesized by simultaneous free radical aqueous polymerization using acrylamide (AAm), potassium methacrylate (KMA), and ammonium persulfate (APS)/N,N,N′,N′-tetramethylethylenediamine (TMEDA) as initiating system in the presence of a crosslinker. The effects of variables such as concentration of hydrophilic monomer (KMA), crosslinker, initiator and activator, and polymerization temperature on swelling capacity have been investigated in detail. In these polymerizations, two different crosslinking agents, namely 1,4-butanediol diacrylate (BDDA) and ethylene glycol dimethacrylate (EGDMA), were employed to study the effect of crosslinker on swelling properties. The swelling kinetic parameters as well as type of water diffusion into the polymer matrix were evaluated at different temperatures for two series of superabsorbent copolymers. The swelling experiments revealed that EGDMA crosslinked superabsorbents have shown higher swelling capacity for all the compositions of AAm/KMA ratio than BDDA crosslinked analogues. Further, the salt sensitivity and de-swelling capacity of the superabsorbent polymers were studied. The pH effect on the swelling ratio of crosslinked copolymers was also investigated.

Keywords: superabsorbent copolymer, simultaneous free radical polymerization, swelling ratio, crosslinker, activator

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INTRODUCTION

Superabsorbents (SAPs) are one of the most promising types of polymers being developed in the area of functional polymers. Superabsorbents are crosslinked networks of hydrophilic polymers absorbing a large amount of water and the absorbed water is hardly removable even under pressure [1]. The hydrophilicity of superabsorbents is attributed to the presence of hydrophilic functional groups such as hydroxyl, carboxyl, and amino groups [2–4]. Because of their excellent characteristics such as lack of toxicity, high swelling capacity in aqueous environment, hydrophilicity, and biocompatibility, these superabsorbents are widely employed in several applications in various fields including agriculture and horticulture, health, bioengineering, pharmaceutical, drug delivery, food industry, and other advanced technologies [2–14]. The superabsorbents were also developed for the adsorption of some cationic dyes, uranyl ions, and bovine serum albumin (BSA) [15–19]. Recently the present authors have reported terpolymers based on acrylamide for agriculture and horticultural applications [20–22]. In many of the aforementioned applications, the water absorbency and water retention are essential. Many authors have contributed significant work to modify the SAPs with a view to enhance their absorbency, gel strength, and absorption rate [20–32].

Porous and composite superabsorbents were developed for higher swelling capacity as well as for reducing the cost of the material [33–38]. Recently, a few series of copolymers were synthesized by simultaneous copolymerization and their swelling and diffusion parameters were investigated [27,30,39–43].

In the authors' previous reports, they have given the details of the preparation of superabsorbent terpolymers by free radical polymerization using ammonium persulfate as initiator at 80°C [20–22]. In that was presented the synthesis of superabsorbent copolymers based on acrylamide for agriculture and horticultural applications as well as the influence of various reaction parameters on the swelling behavior of copolymers [20–22,44–46]. Many reports dealt with the effect of reaction conditions on water absorption and absorption rate [13,39,40,47–48].

This article, reports the preparation of SAPs from acrylamide, potassium methacrylate using ammonium persulfate/TMEDA initiating system in the presence of BDDA or EGDMA crosslinker as well as their swelling and diffusion characteristics at different temperatures. Further, the influence of various reaction parameters on the swelling behavior of SAPs was investigated. The pH and saline sensitivity of superabsorbents were also investigated.

EXPERIMENTAL

Materials

Acrylamide (AAm) and ammonium persulfate (APS) were supplied by S.D. Fine Chem (Bombay, India). Methacrylic acid (MA), 1,4-butanediol diacrylate (BDDA), ethylene glycol dimethacrylate (EGDMA), and N,N,N′,N′-tetramethylethylenediamine (TMEDA) were purchased from Aldrich (Sigma Aldrich Chemicals Private Limited, India). All the chemicals were used as received. Double distilled water was used for all the copolymerization reactions as well as for swelling studies.

Preparation of Potassium Methacrylate (KMA)

Potassium hydroxide (1 mol) solution was prepared in methanol and titrated against methacrylic acid (1 mol) taken in a 500 ml conical flask in methanol. The precipitated solid was filtered and dried in vacuum.

$$CH_2=C(CH_3)COOH + KOH \rightarrow CH_2=C(CH_3)COOK\downarrow + H_2O$$

The IR spectrum of the potassium methacrylate has showed peaks at 1857 cm^{-1} (νC=O of acrylate unit), 2941 cm^{-1} (−CH− stretching of acrylate unit), 1035 and 1234 cm^{-1} (−CO−O− stretching coupling interactions of acrylate units).

SAP Preparation

The AAm-KMA SAPs were prepared employing simultaneous free radical copolymerization by the sequential addition of potassium methacrylate, crosslinker, ammonium persulfate, and TMEDA to the acrylamide solution (1 g/2 ml distilled water) at room temperature under normal atmospheric conditions [43]. The polymerization reactions were carried out in PVC straws (3 mm dia). In a typical polymerization, 1 g (14.06 mM) of acrylamide was dissolved in 2 ml of distilled water. To this solution, 2.01 mM of potassium methacrylate, 0.0075 mM of BDDA crosslinker, 0.065 mM of ammonium persulfate, and 0.685 mM of TMEDA were added one by one. It is observed that the gel was obtained within 10 min. However, the polymerizations were allowed to continue for 24 h. The obtained superabsorbents were cut into pieces of 3–4 mm length and dried in air and then under vacuum to a constant weight and stored in a vacuum desiccator.

Swelling Measurements

Accurately weighed dry superabsorbent copolymers (40–50 mg) were immersed in 100 ml double distilled water until they reached equilibrium at room temperature. After removing the residual water superficially with filter paper the swollen superabsorbents were weighed. The Swelling ratio (S%) and equilibrium water content percentage (EWC%) of superabsorbents were calculated using the following equations (1) and (2), respectively [14,27,43,49]:

$$S\% = \frac{\text{Weight of swollen gel at time t } (W_s) - \text{Weight of dry gel } (W_d)}{\text{Weight of dry gel } (W_d)} \times 100 \tag{1}$$

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

Swelling Kinetics

To examine the mechanism of the swelling process, several kinetic models were used to test the experimental data. A simple kinetic analysis is the second order equation shown below [14,27,49]:

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

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

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

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 kinetic model, graphs were plotted between t/S and t. The initial rate of swelling (r_i), swelling rate constant (k_S), and the theoretical maximum equilibrium swelling (S_{eq}) values of SAPs were calculated from the slope and intersection of the lines.

Diffusion Process

The dynamics of water sorption process was investigated by monitoring the change in the amounts of water imbibed by the SAP at various periods. In the present diffusion study also, the previous swelling method was followed. For the kinetic analysis the results obtained were utilized only up to 60% of swelling curves [14,27,49].

$$S\% = \frac{W_s - W_d}{W_d} = kt^n \tag{5}$$

where W_s and W_d denote the weight of swollen hydrogel at equilibrium 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, which indicates the water transport mechanism. When $n = 0.5$, the swelling process is Fickian in nature and diffusion controlled, whereas the value of n in between 0.5–1.0 indicates a non Fickian nature of diffusion (anomalous diffusion). If n becomes exactly equal to unity then the diffusion is designed as Case II diffusion. A hypothetical model describing the diffusion pattern of SAP is presented in Figure 1.

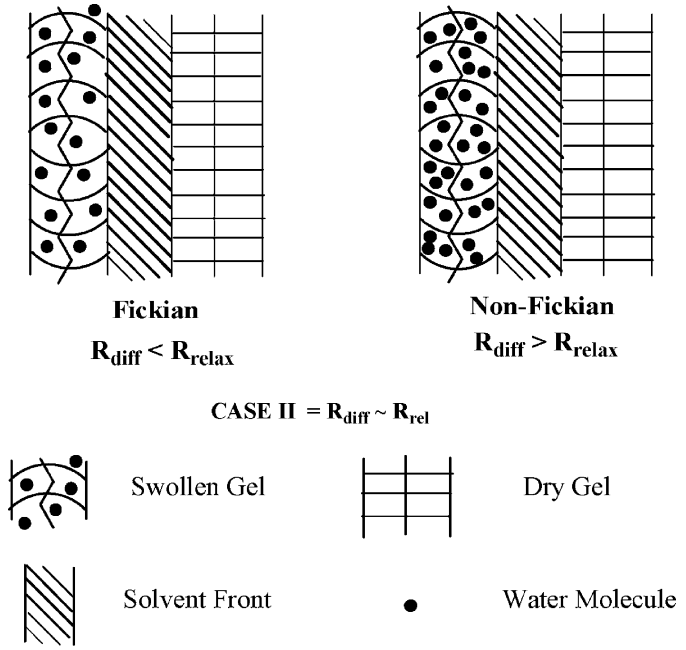

FIGURE 1 A hypothetical model describing swelling of the SAP.

RESULTS AND DISCUSSION

In the present investigation, the acrylamide/potassium methacrylate SAPs were prepared at room temperature using APS/TMEDA initiating system and BDDA or EGDMA as crosslinkers. According to Karadag and Saraydin [43], it is believed that the polymerization process starts with the reaction between APS and TMEDA to form an activated TMEDA molecule containing unpaired valence electrons. These electrons may interact with acrylamide, potassium methacrylate, and/or crosslinkers, thereby initiating the polymerization, co-polymerization, and crosslinking process.

In the free-radical crosslinking copolymerization process, it was noticed that the crosslinking reactions have considerably enhanced the gel effect. This is an auto-acceleration reaction. This gel effect starts right from the beginning of the polymerization process, that is, even at zero conversion. The present copolymerization processes are exothermic in nature and for completion of these processes it took a few minutes for all monomer ratios to copolymerize in gel form. Karadag and Saraydin [43] obtained high water retained hydrogels within one hour through aqueous solution polymerization of concentrated monomers of AAm and crotonic acid. In the present synthetic polymerization reactions, SAPs were obtained faster, within 5–10 min, due to the use of higher concentrations of redox initiator and crosslinker. However, the polymerizations were continued for 24 h to maximize gelation. The gel time (gelation time) increases as the potassium methacrylate comonomer concentration increases. This is due to decrease in the total number of APS, TMEDA molecules that are responsible for initiating the polymerization reaction. The gelation times were also varied by change in the chemical nature of crosslinker.

IR Spectra

The IR spectra of the copolymers have shown the peaks corresponding to the groups present in the copolymer repeating units. The peaks were observed at 3478 cm^{-1} corresponding to the N–H stretching of the acrylamide unit, 1619 cm^{-1} corresponding to the C=O stretching of acrylamide unit, 1640 cm^{-1} corresponding to the C=O stretching of the acrylate unit. In addition to the peaks, peaks are also observed at 1271 cm^{-1}, 1265 cm^{-1} and 1129 cm^{-1} corresponding to C–O–C stretching interactions of ester groups. The above IR analysis indicates that the monomeric units, that is, acrylamide and potassium methacrylate were incorporated in the copolymer chain.

Swelling Behavior

The absorption mechanism of crosslinked superabsorbent polymer can be elucidated in terms of swelling behavior, which is caused by diffusion. The diffusion process represents the affinity between polymer networks and external solution. In general the water absorption of superabsorbent polymers depends on the nature of polymer network, involving strength of the hydrophilic groups, crosslinking density, and elasticity of the polymer networks [20–22]. The absorption of solutions reflect a balance among three main forces: (1) the free energy between the chain networks of polymer and external solvent; (2) the electrostatic repulsion (donnan effect); and (3) the elastic retractile response of the networks (elastic swelling) [50]. Out of these three factors forces 1 and 2 promote the swelling behavior whereas force 3 suppress the swelling behavior of the superabsorbent polymer.

Influence of Reaction Parameters on Swelling Behavior

Variations in AAm-KMA superabsorbent copolymer networks can be effected by changing the reaction parameters, such as the concentration of potassium methacrylate (hydrophilic monomer), crosslinker, initiator and activator, leading to changes in their swelling behavior.

Effect of Monomer Concentration

The hydrophilic monomer concentration is one of the most influential factors affecting the polymer swelling behavior [20–22,27,43–47]. In the present study, potassium methacrylate concentration was varied from 0.8 to 4.02 mM in the polymerizations. As the potassium methacrylate content increased in the acrylamide superabsorbent copolymer composition, the swelling ratio increased enormously. The effect of concentration of potassium methacrylate on equilibrium swelling ratio is shown in Figure 2. It is noted that the superabsorbent copolymers crosslinked with EGDMA have shown higher swelling ratio than the BDDA crosslinked superabsorbent copolymers. In both series of these copolymers, it was found that the swelling ratio increases with increasing in potassium methacrylate concentration up to an optimum value and then decreases slowly with further rise in the concentration of potassium methacrylate. The authors' earlier studies have revealed similar effect on the swelling behavior of various SAPs [20–23,27,43–47]. In the present investigation, it is identified that the copolymers containing 2.01 mM of KMA have shown maximum absorbency.

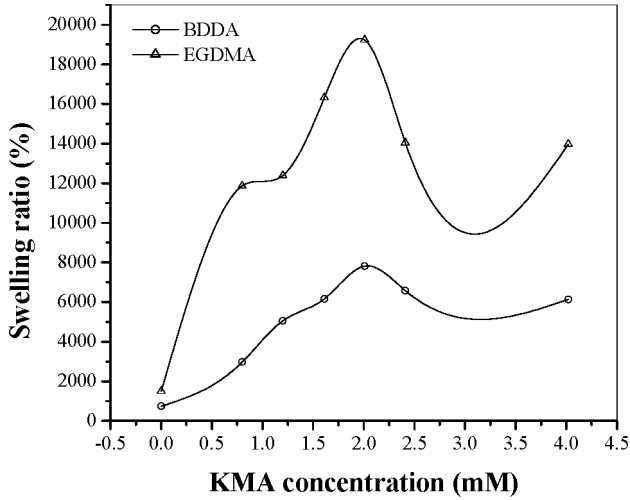

FIGURE 2 Effect of KMA concentration of AAm-KMA SAPs on swelling ratio at [AAm] = 14.06 mM, [BDDA] or [EGDMA] = 0.07 mM, [APS] = 0.219 mM, [TMEDA] = 0.086 mM.

The swelling kinetics and temperature dependency swelling behavior of superabsorbent copolymers in distilled water were studied at 10°C, 20°C, and 45°C and the results are plotted in Figures 3 and 4 for BDDA and EGDMA crosslinked copolymers, respectively. All the superabsorbent copolymers swelled slowly and reached equilibrium by about 20 to 24 h. The swelling ratio increases constantly with increase in temperature. This increase in swelling behavior can be explained due to enhancement of water diffusion and segmental mobility of macromolecular chains with temperature, which ultimately results in a greater degree of swelling.

Swelling kinetics and diffusion characteristics of the superabsorbent copolymers crosslinked with BDDA and EGDMA, at different temperatures were tabulated in Tables 1 and 2, respectively. From Table 1, it is found that the initial swelling rate (r_i) and maximum equilibrium swelling (S_{eq}) of the SAPs crosslinked with BDDA and EGDMA increase as the temperature increases.

Most of the swelling exponent (n) values of SAPs at different swelling temperatures were found in between 0.5–1.00 (Table 2), indicating the diffusion process of water into superabsorbent polymeric networks is non-Fickian type. Only one AAm-KMA copolymer crosslinked by BDDA (KMA-1.20) at swelling temperature, 10°C followed Case II type

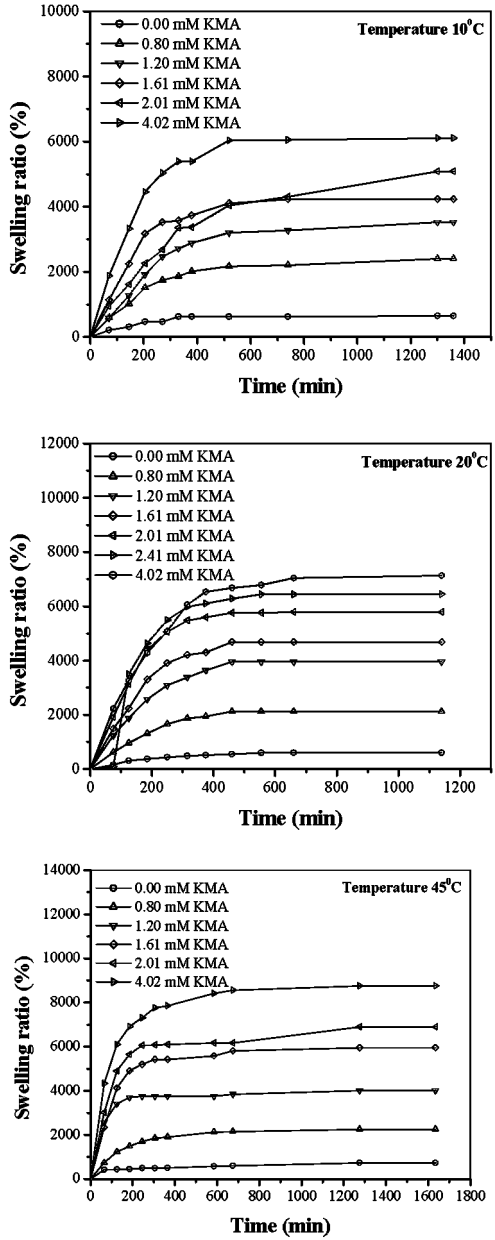

FIGURE 3 Temperature dependency on swelling kinetics of AAm-KMA SAP crosslinked with BDDA containing different KMA contents [AAm] = 14.06 mM, [BDDA] = 0.07 mM, [APS] = 0.219 mM, [TMEDA] = 0.086 mM.

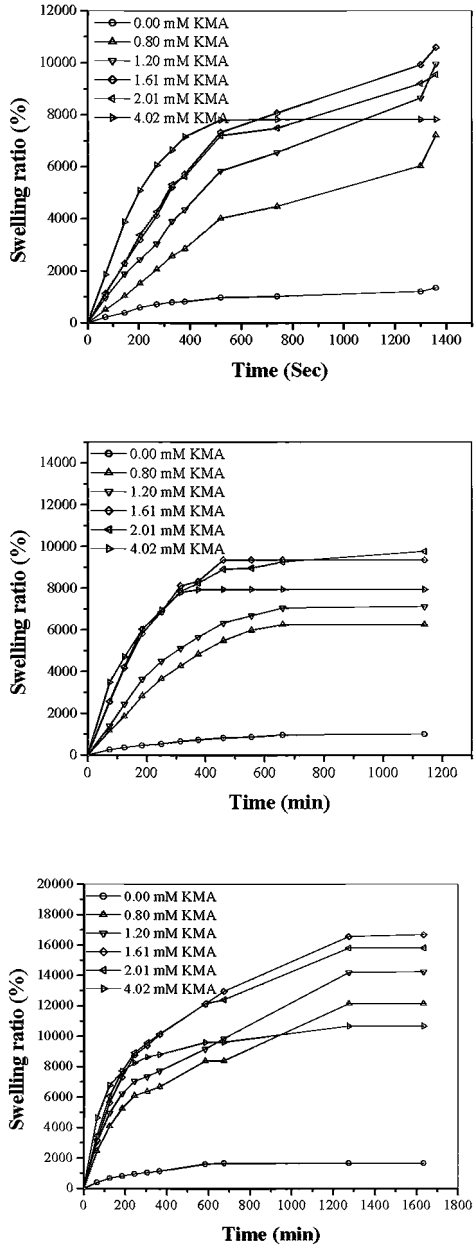

FIGURE 4 Temperature dependency on swelling kinetics of AAm-KMA SAP crosslinked with EGDMA containing different KMA contents [AAm] = 14.06 mM, [EGDMA] = 0.07 mM, [APS] = 0.219 mM, [TMEDA] = 0.086 mM.

TABLE 1 Swelling Kinetics of AAm-KMA Superabsorbent Copolymers at Different Temperatures

AAm-KMA SAP copolymer	Swelling kinetics at 10°C			Swelling kinetics at 20°C			Swelling kinetics at 45°C		
	r_i	k_s	S_{eq}	r_i	k_s	S_{eq}	r_i	k_s	S_{eq}
BDDA crosslinked copolymers containing different KMA concentration									
KMA-0.00	7.633	1.56×10^{-5}	699.30	5.394	1.13×10^{-5}	689.65	6.592	1.11×10^{-5}	769.23
KMA-0.80	18.305	2.58×10^{-6}	2661.28	21.401	3.68×10^{-6}	2410.56	26.809	4.68×10^{-6}	2392.97
KMA-1.20	19.817	1.16×10^{-6}	4116.24	42.698	1.63×10^{-6}	5105.71	165.837	1.00×10^{-5}	4059.34
KMA-1.61	47.778	2.27×10^{-6}	4578.60	56.561	2.08×10^{-6}	5208.82	124.069	3.27×10^{-6}	6154.79
KMA-2.01	21.249	5.70×10^{-7}	6101.54	86.281	2.15×10^{-6}	6325.19	129.198	2.57×10^{-6}	7082.25
KMA-4.02	75.585	1.75×10^{-6}	6560.94	67.980	1.05×10^{-6}	8025.81	189.753	2.32×10^{-6}	9037.17
EGDMA crosslinked copolymers containing different KMA concentration									
KMA-0.00	4.141	1.49×10^{-6}	1667.02	5.363	3.72×10^{-6}	1200.40	7.29	3.36×10^{-6}	1471.98
KMA-0.80	8.418	2.89×10^{-8}	17055.80	29.985	4.60×10^{-7}	8066.72	36.16	2.99×10^{-7}	10994.45
KMA-1.20	14.575	4.50×10^{-8}	17982.73	39.761	5.15×10^{-7}	8779.4	42.10	2.56×10^{-7}	12801.82
KMA-1.61	20.161	6.79×10^{-8}	17221.87	87.489	7.61×10^{-7}	10717.69	53.05	2.29×10^{-7}	15217.50
KMA-2.41	21.621	1.04×10^{-7}	14353.67	80.256	6.59×10^{-7}	11028.24	58.85	3.04×10^{-7}	13894.06
KMA-4.02	60.096	7.56×10^{-7}	8911.306	161.030	2.24×10^{-6}	8475.29	86.58	1.20×10^{-6}	8481.548

Reaction conditions: [AAm] = 14.06 mM, [BDDA] or [EGDMA] = 0.07 mM, [APS] = 0.219 mM, [TMEDA] = 0.086 mM.
r_i—initial swelling rate (g water/g gel)/min).
k_s—swelling rate constant (g gel/g water)/min.
S_{eq}—theoretical maximum swelling equilibrium (g water/g gel).

TABLE 2 Diffusion Characteristics of AAm-KMA Superabsorbent Copolymers

AAm-KMA SAP copolymer	Diffusion characteristics at 10°C		Diffusion characteristics at 20°C		Diffusion characteristics at 45°C	
	Swelling constant (k)	Swelling exponent (n)	Swelling constant (k)	Swelling exponent (n)	Swelling constant (k)	Swelling exponent (n)
BDDA crosslinked copolymers containing KMA concentration						
KMA-0.00	9.79	0.71	2.34	0.98	299.54	0.07
KMA-0.80	15.44	0.85	16.77	0.83	42.64	0.68
KMA-1.20	5.30	1.00	37.06	0.81	589.96	0.35
KMA-1.61	19.99	0.95	33.84	0.87	118.27	0.72
KMA-2.01	30.25	0.80	35.19	0.92	236.17	0.61
KMA-4.02	62.13	0.80	97.65	0.72	661.09	0.45
EGDMA crosslinked copolymers containing KMA concentration						
KMA-0.00	9.69	0.75	16.88	0.63	33.88	0.60
KMA-0.80	8.73	0.96	21.74	0.92	283.23	0.54
KMA-1.20	27.91	0.84	20.40	0.98	452.77	0.48
KMA-1.61	21.59	0.93	73.22	0.83	202.02	0.67
KMA-2.41	21.24	0.94	45.50	0.93	229.94	0.66
KMA-4.02	33.71	0.94	260.92	0.60	772.46	0.43

of diffusion. Such types of copolymers were found to have better applicability in pharmacy.

Effect of Crosslinking Agent Type and Concentration

In general, any crosslinking agent contains two or more double bonds, which participate in the free radical polymerization with the acrylate monomers and form permanent crosslinks between the polymeric chains. The nature of crosslinking agent is an important factor that directly affects the swelling behavior of superabsorbent polymer [20–23,27,33,37,44–47]. Figure 2 shows the swelling ratio of the superabsorbent polymers crosslinked by BDDA and EGDMA at room temperature in distilled water. It is observed that the copolymer crosslinked with EGDMA had higher swelling ratio than the BDDA crosslinked copolymer. This is due to the difference in the formation of crosslinks between the polymeric chains.

To verify the effect of concentration of crosslinker on the swelling behavior of AAm-KMA SAP, BDDA concentration was varied between 0.0025–0.050 mM and EGDMA concentration was varied from 0.054 to 0.438 mM in the polymerizations. Figures 5 and 6 show the swelling ratio of the superabsorbent copolymers as a function of BDDA and EGDMA crosslinker concentration, respectively. In general, the swelling behavior varies as the crosslinker concentration varies. The

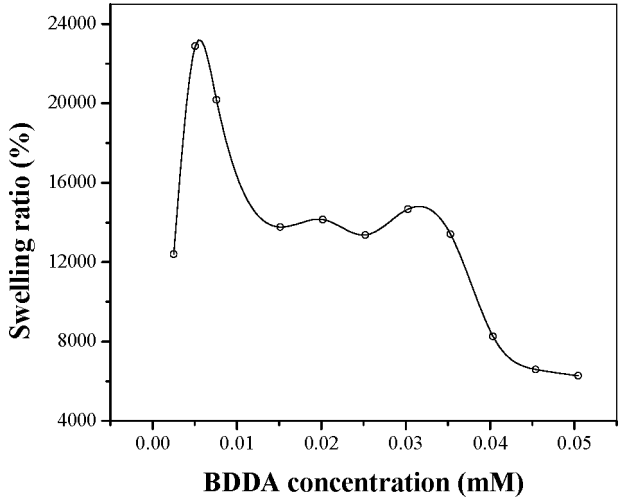

FIGURE 5 Influence of crosslinker concentration on swelling ratio of AAm-KMA SAP at 14.6 mM, [KMA] = 2.01 mM, [APS] = 0.219, [TMEDA] = 0.086 mM.

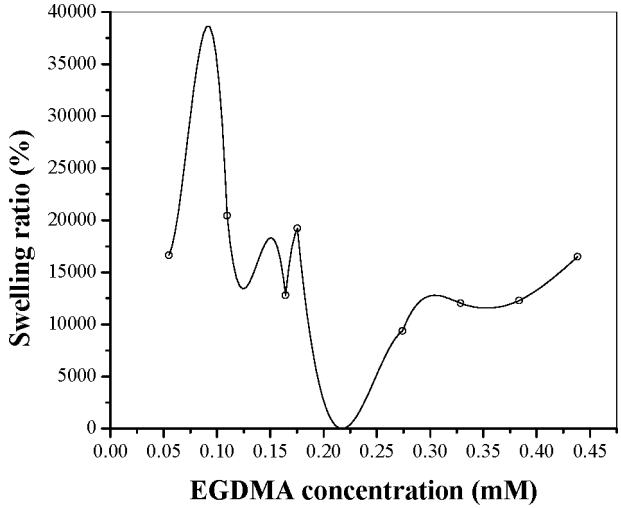

FIGURE 6 Influence of crosslinker concentration on swelling ratio of AAm-KMA SAP at [AAm] = 14.6 mM, [KMA] = 2.01 mM, [APS] = 0.219, [TMEDA] = 0.086 mM.

results in the present investigation suggest that at one particular concentration of crosslinker the swelling ratio of SAP had an optimum value indicating the presence of perfect network structure in the polymeric chains at this concentration. Further increase in the concentration of crosslinker reduced the swelling ratio and this is due to higher crosslink density reducing the space between the polymer chains thereby suppressing the swelling of the superabsorbent [20–22]. The optimum concentration of crosslinker for highest swelling ratio is found at 0.0075 mM (S% = 20173) and 0.109 mM (S% = 20436) for BDDA and EGDMA crosslinkers, respectively.

Effect of Initiator and Activator

It is well known that the amount of initiator or initiating system can affect the crosslink network structure and phase behavior of hydrophilic polymers [20–22,27,43–47]. They also contribute to the inhomogeneity in the polymer system. In the present investigation, the polymerization of AAm and KMA starts with the reaction between APS and TMEDA and then simultaneously initiating free radical polymerization between the monomers and crosslinking agents. [27,43]. In recent years, redox initiators have been employed to obtain polymers and various authors have reported the use of these initiators for the

polymerization of acrylamide/acrylic acid [27], starch/acrylamide/kaolinite [36], acrylamide/crotonic acid [43], poly(vinyl alcohol)/isopropylacrylamide (IPN) [51] and N-isopropylacrylamide [52].

The swelling behavior of AAm-KMA superabsorbent copolymers as a function of initiator concentration is presented in Figures 7 and 8. It is noticed that as APS concentration increases the swelling ratios of BDDA crosslinked copolymers increases correspondingly from 0.021 to 0.065 mM and then decreases up to 0.131 mM. A further increase in the concentration of APS increases the swelling ratio. Similar behavior is also observed with EGDMA crosslinked copolymers when the concentration of APS varied increased from 0.054 to 0.16 mM and then decreased up to 0.219 mM. A further increase in the concentration of APS increases the swelling ratio.

The influence of activator (N,N,N′,N′-tetramethylethylenediamine) concentration on the swelling behavior of SAPs was also studied in detail. The results are presented in Figures 9 and 10. The results indicated that the swelling ratio of the superabsorbent copolymers was influenced to a great extent by the concentration of the activator. It is noticed that the BDDA crosslinked superabsorbent copolymers had increased the swelling ratio from 16537 to 63233% by changing the activator concentration from 0.086 mM to 0.688 mM. A further increment in the concentration of the activator decreases the swelling

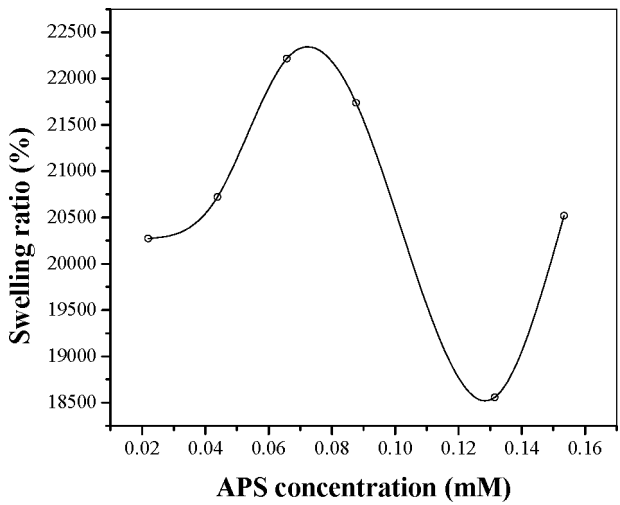

FIGURE 7 Influence of APS concentration on swelling ratio of AAm-KMA SAP at [AAm] = 14.6 mM, [KMA] = 2.01 mM, [BDDA] = 0.0075 mM, [TMEDA] = 0.086 mM.

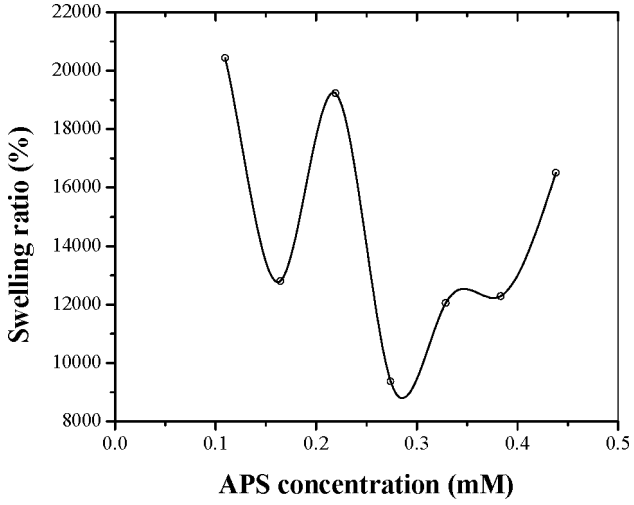

FIGURE 8 Influence of APS concentration on swelling ratio of AAm-KMA SAP at [AAm] = 14.6 mM, [KMA] = 2.01 mM, [EGDMA] = 0.109 mM, [TMEDA] = 0.086 mM.

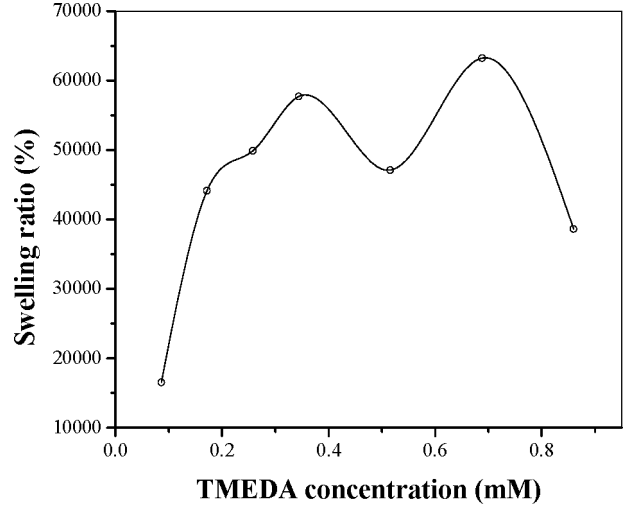

FIGURE 9 Influence of TMEDA concentration on swelling ratio of AAm-KMA SAP at [AAm] = 14.6 mM, [KMA] = 2.01 mM, [BDDA] = 0.0075 mM, [APS] = 0.065 mM.

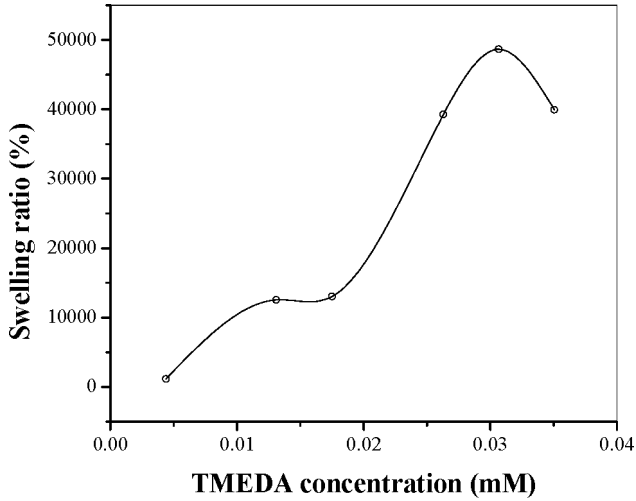

FIGURE 10 Influence of TMEDA concentration on swelling ratio of AAm-KMA SAP at [AAm] = 14.6 mM, [KMA] = 2.01 mM, [EGDMA] = 0.109 mM, [APS] = 0.109 mM.

ratio of the copolymer. In the EGDMA series too, as mentioned before the increase in the concentration of TMEDA favors an increased swelling ratio.

Effect of Polymerization Temperature

To study the effect of polymerization temperature on the swelling property of the superabsorbent copolymers, the polymerization reactions were conducted at different temperatures ranging from 10°C to 45°C. The superabsorbent copolymers prepared at higher temperature have shown high swelling capacity. The highest swelling ratios of 40200 and 48000% were observed in BDDA and EGDMA crosslinked copolymers respectively, polymerized at 45°C. The effect of polymerization temperature on the swelling ratio of SAPs is shown in Figure 11.

Influence of External Stimuli on Swelling Behavior

Over the last two decades, important characteristics have been noticed in the SAPs/Hydrogels response to changes in the environmental conditions such as temperature, pH, electric filed, solvent quality, light intensity and wavelength, pressure, ionic strength, nature of ion in swelling medium, and specific chemical triggers such as glucose and biofluids. In order to find such changes in their swelling behavior,

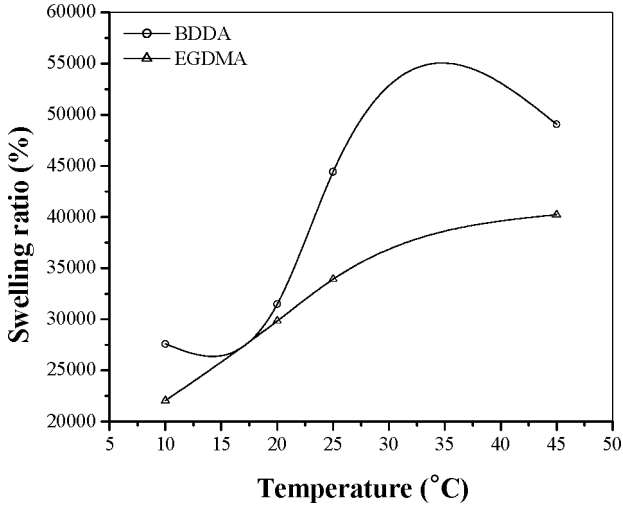

FIGURE 11 Influence of polymerization temperature on swelling ratio of the SAP **SAP crosslinked with BDDA**: [AAm] = 14.6 mM, [KMA] = 2.01 mM, [BDDA] = 0.0075 mM, [APS] = 0.065 mM, [TMEDA] = 0.068 mM; **SAP crosslinked with EGDMA**: [AAm] = 14.6 mM, [KMA] = 2.01 mM, [EGDMA] = 0.109 mM, [APS] = 0.10 mM, [TMEDA] = 0.306 mM.

the authors have investigated the effect of salts and pH on the swelling behavior of AAm-KMA SAPs.

Effect of Salts

The salt concentration as well as the charge valencies significantly affect the swelling behavior of the absorbent [39–40]. The effect of salt solutions on the swelling behavior was studied by many authors [39–40,53–54]. The presence of a salt greatly affects the swelling behavior due to change in the mechanical properties of the gel matrix, which is responsible for different diffusion coefficients of drug release. The possible consequence of salt ions in the swelling medium is to change the osmotic pressure due to the difference in ionic concentration of the SAP interior and the external solution. Donnan equilibrium theory contributes to the determination of osmotic pressure π_{ion}, which reveals the extent of swelling as given by the following equation:

$$\pi_{ion} = RT \sum_i (C_i^g - C_i^s)$$

where C_i is the mobile ion concentration of species i and superscripts "g" and "s" represent gel and solution phases, respectively.

In the present investigation, the effect of different concentrations of sodium chloride solution on the swelling behaviour of AAm-KMA superabsorbent polymers was studied. Figures 12 and 13 illustrate the swelling ratio of AAm-KMA superabsorbent copolymers as a function of crosslinker concentration in different concentrations of saline solutions. The figures demonstrate that the swelling ratio of SAPs decreased in salt solutions as ionic concentration of the salt solution increases. This is because of decrement in the expansion of the gel network due to repulsive forces of counter ions on the polymeric chain shielded by the bound ionic charge. Therefore the osmatic pressure difference between the gel network and the external solution decreased with an increase in the ionic strength of the saline concentration. Similar results were also found in the case of poly(sodium acrylate-sodium 2-acrylamido-2-methyl propane sulfonate), poly(SA-NaAMPS), poly(sodiumacrylate-hydroxylethyl methacrylate), poly(SA-HEMA), poly[sodium acrylate-3,3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate] poly(SA-DMAPS) copolymers [53–56].

The salt sensitivity was evaluated by a dimensionless factor, (α). The dimensionless factor (α) is the ratio of absorption at a given salinity to salt free water [48]. The α values for different saline concentrations are given in Table 3. The results indicate that the sensitivity of absorbance to changes in salinity is lowered, as the crosslinker concentration decreases.

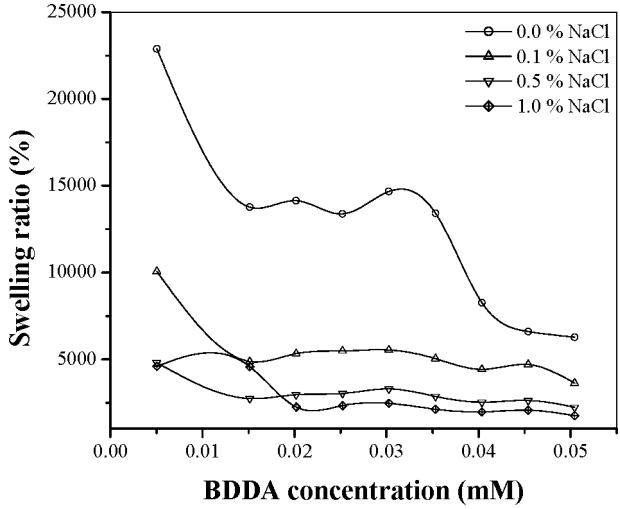

FIGURE 12 Swelling ratio of AAm-KMA SAPs as a function of BDDA concentration in different concentrations of saline solutions.

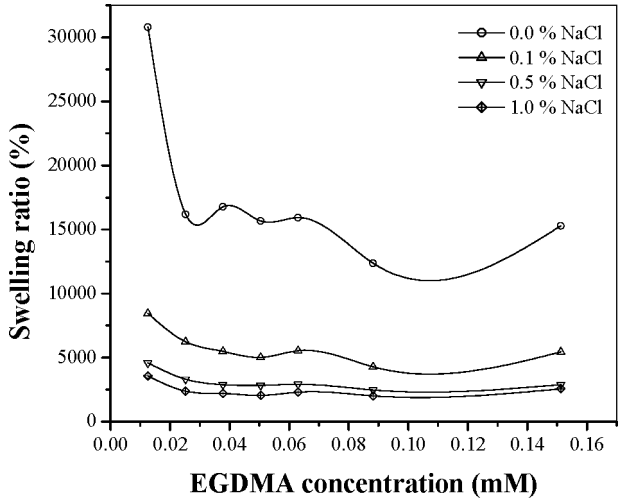

FIGURE 13 Swelling ratio of AAm-KMA SAPs as a function of EGDMA concentration in different concentrations of saline solutions.

TABLE 3 Dependency of Dimensionless Swelling Factor (α), on the Crosslinker Concentration

Crosslinker concentration (mM)	Dimensionless factor (α)		
	$\alpha_{0.1\%}$	$\alpha_{0.5\%}$	$\alpha_{1.0\%}$
BDDA			
0.005	0.439	0.210	0.200
0.015	0.353	0.198	0.332
0.020	0.377	0.209	0.159
0.025	0.410	0.227	0.174
0.030	0.377	0.224	0.168
0.035	0.375	0.213	0.158
0.040	0.534	0.306	0.238
0.045	0.712	0.398	0.314
0.050	0.579	0.357	0.279
EGDMA			
0.012	0.116	0.149	0.274
0.025	0.146	0.205	0.385
0.037	0.130	0.170	0.326
0.050	0.130	0.180	0.320
0.063	0.144	0.182	0.348
0.088	0.163	0.199	0.346
0.151	0.167	0.189	0.356

TABLE 4 Influence of pH Solution (2–12) on the Swelling Ratio of the Copolymers

Desired pH	Solution 1 ml	Solution 2 ml	Ionic strength (mol ion dm^{-3})	Swelling ratio of BDDA copolymer[a] (%)	Swelling ratio of EGDMA copolymer[b] (%)
2	97.50	2.50	0.1866	223	1593
3	88.00	12.00	0.1762	244	1945
5	67.00	33.00	0.1521	3143	4082
7	49.50	50.50	0.1243	4869	6410
11	22.00	78.00	0.0886	3775	1900
12	8.50	91.50	0.0711	3462	1989

[a]Reaction conditions: [AAm] = 14.6 mM, [KMA] = 2.01 mM, [BDDA] = 0.0075 mM, [APS] = 0.065 mM, [TMEDA] = 0.068 mM.

[b]Reaction conditions: [AAm] = 14.6 mM, [KMA] = 2.01 mM, [EGDMA] = 0.109 mM, [APS] = 0.10 mM, [TMEDA] = 0.306 mM.

Effect of pH

Buffer solution 1 was prepared by mixing 12.3 g anhydrous boric acid (0.20*M*) and 10.51 g citric acid (0.05*M*) in 1000 ml distilled water, and buffer solution 2 was prepared from 38.01 g of tri-sodium phosphate in 1000 ml distilled water. In order to prepare a specific buffer solution (pH) solutions 1 and 2 were mixed at different volumes based on Shugar and Dean [57]. Table 4 gives different buffer solutions along with their ionic strength as well as influence of pH solution (2–12) on the swelling ratio of the copolymers. From this table it is clear that the swelling behavior of the copolymers is dependent on the pH. The swelling behavior of the copolymers was found to increase slightly from pH 2 to 3, gradual increment at pH 4 and 5, but further increment of pH decreased the swelling ratio. The swelling ratio in higher proportion of phosphate buffer is greater than the swelling in a citrate buffer.

CONCLUSIONS

The AAm-KMA superabsorbent copolymers prepared in this investigation are hydrophilic, ionizible, and pH sensitive, showing enormous water absorbency. The effect of crosslinker type on the swelling behavior of SAPs was studied by choosing BDDA and EGDMA crosslinkers. The swelling and diffusion characteristics of the SAPs were investigated at different temperatures. These copolymers have followed a non-Fickian diffusion. The effect of variables such as concentration of crosslinker, monomer, initiator, activator, and polymerization

temperature on the swelling capacity has been investigated. Further, the stimuli responsiveness was also studied. The maximum absorbencies (swelling ratios) for BDDA crosslinked AAm-KMA SAP at [AAm] = 14.6 mM, [KMA] = 2.01 mM, [BDDA] = 0.0075 mM, [APS] = 0.065 mM, [TMEDA] = 0.068 mM was found to be 63233% and for EGDMA crosslinked AAm-KMA SAP as 48677% at [AAm] = 14.6 mM, mM, [KMA] = 2.01 mM, [EGDMA] = 0.109 mM, [APS] = 0.10 mM, [TMEDA] = 0.306 mM. Finally, from all of the earlier experimental results the optimized reaction conditions were found for BDDA and EGDMA crosslinked superabsorbent copolymers, and at these reaction conditions the swelling ratios of the copolymers were found to be slightly higher than the authors' earlier reports.

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