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Effect Of Crosslinker On Swelling Pattern Of Crosslinked Poly(Acrylamide -Sodium Methacrylate) Superabsorbent Copolymers

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ABSTRACT

Crosslinked superabsorbent copolymers composed of acrylamide (AAm) and sodium methacrylate (SMA) were obtained by the free-radical copolymerization using ammonium persulfate (APS)/N,N,N,N-tetramethyl ethylenediamine (TMEDA) initiating system at room temperature in aqueous solution. Different compositions of sodium methacrylate with a fixed concentration of acrylamide and crosslinker were prepared and studied their equilibrium water content (EWC) and , swelling and diffusion kinetic parameters (i.e., initial swelling network constant, swelling rate constant, maximum swelling equilibrium, network structure constant and type of diffusion, etc). The superabsorbent copolymer formation was confirmed by IR spectroscopy. The effect of swelling medium temperature and the influence of salinity on swelling behaviour was investigated. The influence of various reaction parameters, such as, crosslinker, initiator, activator concentrations, and polymerization temperature on the swelling behaviour was investigated in detail. The network structure variation with the variation of crosslinker concentration was studied by SEM analysis. The pH effect and de-swelling behaviour was also studied for the copolymers. Because of higher swelling and water retention capacity of these materials we can find application in agricultural and horticultural applications.

KEYWORDS

Superabsorbent copolymer;
Simultaneous free-radical polymerization;
equilibrium swelling ratio;
Activator;
Crosslinked network structure

INTRODUCTION

Superabsorbent polymers can absorb and hold a large amount of water even under pressure, compared with general absorbing materials[1,2]. These polymers are known as hydrophilic network structured polymers having hydrophilic functional groups such as, hydroxyl, carboxyl, and amines[2,3]. The hydrophilicity, high swelling capacity, lack of toxicity, and biocompatibility prompted these materials used as soil conditioners for agriculture and horticulture, disposable diapers, water blocking tapes, absorbent pads, gel actuators, drilling fluid additives, polymer cracks blocking materials, feminine napkins, firefighting, extraction of precious metals, extraction of solvents, release of agrochemicals, etc[1-11]. Super absorbents were also developed for the adsorption of some cationic dyes, uranyl ions, and serum albumin[12-16]. The pH and temperature-sensitive hydro gels were employed for various applications including controlled drug delivery system and immobilized enzyme systems[17-20]. In most of the above applications, the swelling and water retention properties are most important. The superabsorbent copolymers that are described in the literature were modified with a view to enhance their properties such as improved absorbency, gel strength and absorption rate[1,5-12].

Kiatkamjornwong and Phunchareon[21] reported the synthesis of neutralized poly(acrylic acid-co-acrylamide) superabsorbents and the influence of reaction parameters on water absorbency. W.F. Lee and his coworkers[22-25] have reported the synthesis of crosslinked poly(sodium acrylate-co-hydroxyethyl methacrylate) [poly(SA-co-HEMA)], poly(sodium acrylate-sodium-2-acryalamido-2-methylpropanesul fonate) [poly(SA-co-MPS)], poly[sodium acrylate-co-3,3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate] [poly(SA-co-DMAPS)] and poly (sodium acrylate-co-sulfobetaines) [poly(SA-SBA)]; in presence of N,N′-methylene-bis-acrylamide using 4,4′-azobis(cyanovaleric acid) as initiator and sorbitan monostearate (Span 60) as suspending agent. The terpolymer of 3-trialkyl-4-vinylbenzyl phosphonium chloride, acrylamide, MBA was employed for antibacterial activity as well as adsorption ability for anionic surfactants[26]. The above polymers were synthesized by reverse inverse suspension polymerization.

In contrast to the above method of synthesis, the redox polymerization is also a well suitable method for the preparation of SAPs. A few series of copolymers were synthesized by redox polymerization and also investigated their swelling and diffusion characteristics[27-34]. W.J. Zhou and co-workers[27] have studied the synthesis and swelling properties of copolymers of acrylamide with anionic monomers and crosslinked poly[acrylamide-sodium methallyl sulfonate-acrylic acid], poly(AM-MSAS-AA) gels. S.K.Bajpai et al[28,29] have reported the synthesis and characterization of AAm/Itaconic acid gels for oral drug delivery of peptide and also studied the swelling and de-swelling behaviour of poly(acrylamide-co-maleic acid). E.Karadag et al[30] have reported the synthesis of poly(acrylamide-co-crotonic acid) as well as the swelling behaviour, swelling/diffusion studies of the copolymers. B.Isik[31] have reported the swelling behaviour and diffusion characteristics of acrylamide-acrylic acid hydrogels. J. Chen and Y. Zhao[32] have investigated the relationship between water absorbency and reaction time of neutralized acrylic acid by using potassium persulfate/TMEDA initiating system. The present investigation deals with the preparation of crosslinked poly(acrylamide-co-sodium methacrylate) [poly(AAm-co-SMA) super absorbent copolymers and the investigation of their swelling/diffusion characteristics. It also includes the study of influence of reaction parameters on swelling behaviour of crosslinked superabsorbent copolymers.

EXPERIMENTAL

Materials

Acrylamide (AM), ammonium persulfate (APS), and N,N^1-methylenebisacrylamide (MBA) were procured from S.D. Fine Chem Ltd (India). Methacrylic acid (MA), diallyl phthalate (DP) and N,N,N′,N′-tetramethylethylenediamine (TMEDA) were obtained from Aldrich (Germany). All the chemicals were used as received. Double distilled water was used for all the copolymerization reactions as well as for swelling studies. Sodium methacrylate (SMA) was prepared by neutralization of methacrylic acid with sodium hydroxide.

Synthesis of crosslinked poly(AAm-co-SMA) superabsorbent copolymer[33,34]

The crosslinked poly(AAm-co-SMA) superabsor bent copolymers were prepared by polymerizing 1 g of AAm dissolved in 2 ml of distilled water with various amounts of SMA comonomer using APS/ TMEDA as initiating system in the presence of a crosslinker either DP (0.081 mM) (1 ml of 1.00g/ 100ml methanol) or MBA (0.745 mM) (1 ml of 1.00g/100 ml dist. water). Polymerizations were performed in PVC straws (3 mm dia) at room temperature. The polymerization reactions for all the ratios of monomers gave gels within one hour of reaction time. However, the polymerization reactions were continued upto 24 hrs. The polymer gels obtained were cut into pieces of 3-4 mm length. They were dried in air and then under vacuum, and utilized for swelling and other studies. The complete synthetic details are given in TABLE 1.

Swelling measurements[35,36]

40-50 mg of dry superabsorbent polymer was immersed in a 100 ml beaker containing 50 ml of double distilled water/saline/pH solution/simulated biological solution until they reach equilibrium at room temperature. After attaining the equilibrium swelling, the excess amount of water on the superabsor bent gel was removed superficially with filter and then weighed. The extent of swelling ratio (S_{ex}), the equilibrium swelling ratio (S_{eq}) and the equilibrium water content (EWC%) of the superabsorbents were calculated using the following equations.

$$\text{Extent of swelling ratio (S) (g/g)} = [(M_s - M_d)/M_d] \quad (1)$$
$$(g/g) = [(M_{eq} - M_d)/M_d] \quad (2)$$
$$(\%) = [(M_{eq} - M_d)/M_d] \times 100 \quad (3)$$

where M_s, M_{eq} and M_d denote the weight of the swollen superabsorbent at time t, equilibrium and dry superabsorbent at time 0, respectively.

Preparation of buffer solutions

Buffer solution 1 was prepared by dissolving 12.3 gms of anhydrous boric acid (0.20M) and 10.51 gms of citric acid (0.05M) in 1000 ml distilled water and buffer solution 2 was prepared by dissolving 38.01 gms of tri-sodium phosphate in 1000 ml distilled water. In order to prepare a specific pH buffer solutions 1 and 2 were mixed in different volumes based

TABLE 1: Influence of SMA content on the swelling behaviour of AAM-NMA superabsorbent copolymer[a]

Polymer Code	Crosslinker DP or MBA	Sodium methacrylate	Equilibrium swelling ratio (g/g)[b]	Equilibrium water content (EWC%)	Swelling kinetics			Diffusion characteristic
					Equilibrium swelling ratio (S_{eq})	Initial swelling rate (k_i)	Swelling rate constant(k_s)	Swelling exponent (n)
DP1	0.081	0.462	49	99.86	69.01	0.108	515.18	0.87
DP2	0.081	0.926	94	99.93	141.04	0.233	4635.77	1.04
DP3	0.081	1.387	119	99.94	150.15	0.403	9092.22	0.89
DP4	0.081	1.850	149	99.94	217.39	0.334	15780.29	1.00
DP5	0.081	2.313	227	99.97	359.71	0.427	55281.70	1.00
DP6	0.081	4.626	268	99.97	375.93	0.588	83057.58	0.96
DP7	0.081	9.262	325	99.98	380.22	1.98	286715.50	0.93
MBA1	0.745	0.925	41	99.81	46.46	0.111	240.88	0.34
MBA2	0.745	1.387	47	99.87	56.72	0.228	736.11	0.31
MBA3	0.745	1.850	49	99.87	56.08	0.301	948.94	0.49
MBA4	0.745	2.313	60	99.88	70.02	0.284	1395.88	0.29
MBA5	0.745	4.626	60	99.90	66.35	0.560	2470.03	0.50
MBA6	0.745	9.262	81	99.92	88.26	0.763	5945.69	0.52

[a]Reaction conditions: Acrylamide = 14.068 mM; DP = 0.081 mM; MBA = 0.745 mM; APS = 0.0219 mM; TMEDA = 0.04302 mM Temperature = 25^{0}C; [b]Experimental equilibrium swelling ratio; (Seq) (g gal/g water)/ min ; (k_i)(g water/g gel)/min ; (k_s) (g water/g gel);

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on Shugar and Dean[37].

Preparation of physiological solutions

To evaluate the water uptake phenomena of cross linked poly(AAm-co-SMA) superabsorbent copolymers in biological media, different solutions were made in 100 ml of distilled water[36]. 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; Urea: 5 g / 100 ml; and D-glucose: 5 g /100 ml.

Instrumentation

The IR spectra of dry powdered superabsorbent copolymers were carried out on a Perkin-Elmer Spectrophotometer ASCII (Perkin Elmer Cetus Instruments, Norwalk, CT). The crosslinked poly(AAm-co-SMA) superabsorbent copolymers were coated with a thin layer of palladium gold alloy and their structural and morphological variations were observed by using a JOEL JSM 840A (Japan) scanning electron microscope (SEM). The thermal analysis of crosslinked SAPs was investigated using a Universal V1 12E thermogravimetric analyzer (TGA). The temperature range covered in this study was 50–700°C with a heating rate of 20°C/min and 50 ml/min of nitrogen flow.

RESULTS AND DISCUSSION

IR Spectra

The IR spectra of crosslinked poly(AAm-co-SMA) showed peaks at 3475 cm^{-1} corresponding to the N-H stretching of the acrylamide unit, 1685 and 1663 cm^{-1} corresponding to the C=O of the acrylate units of sodium methacrylate, acrylamide unit and crosslinkers (MBA and DP), 1239 and 1172 cm^{-1} corresponding to C-O-C stretching coupling interactions of ester groups[5-7]. The IR analysis confirms the presence of all the monomeric units and crosslinker units, i.e., acrylamide, sodium methacrylate and diallyl phthalate or N,N[1]-methylene-bis-acrylamide in the crosslinked copolymer.

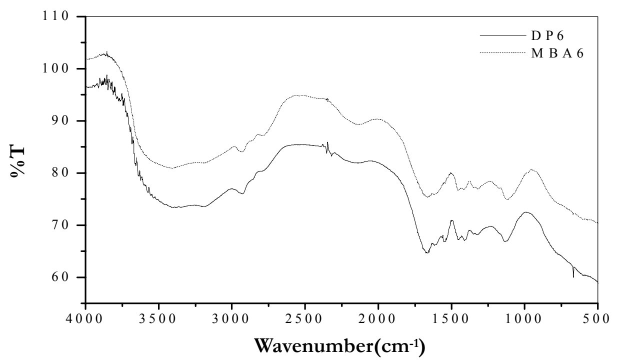

Figure 1: IR Spectra of crosslinked poly(AAm-co-SMA) superabsorbent copolymers

Thermal Analysis

To investigate the thermal stability of crosslinked poly(AAm-co-SMA) superabsorbent copolymers, the TGA experiments were performed in the temperature range of 50-700°C under nitrogen atmosphere. The TGA thermograms of DP crosslinked poly (AAm-co-SMA) superabsorbent copolymers DP6 and DP7 are presented in figure 2. Low weight loss

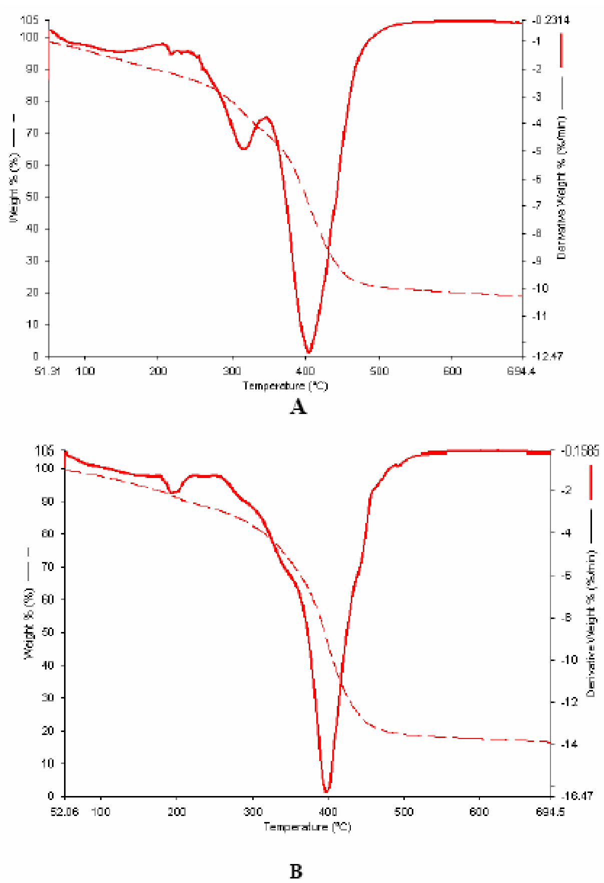

Figure 2: TGA curves of crosslinked poly(AAm-co-SMA) SAPs A. DP6 and B. DP7

below 100°C indicates the loss of water representing the hygroscopic nature of the material. From this analysis, McNeill and Zulfiqar[26] reported the estimation of moisture content present in the superabsor bent copolymers. In the DTA curve of the present samples, major weight loss occurred around 400°C. The maximum decomposition temperature increased from 398 to 404°C as the SMA content in the copolymer decreased from 9.262 to 4.626 mM. This behaviour can be explained on the basis of amount of crosslink density. An increase of SMA concentration in the copolymer at a fixed crosslinker concentration gave lower crosslinked dense structure resulting in less peak decomposition temperature. Further, it is also identified that the highly cross linking behaviour is responsible for higher thermal stability since SAPDP6 was degraded to 88 wt% where as SAPDP7 degraded to 83 wt% only.

Influence of parameters on swelling behavior

The swelling behaviour of any superabsorbent polymer varies with changes in the strength of the hydrophilic groups, crosslinking density, polymer network behaviour, elasticity of the polymer networks, type of solvent and the strength of the external solution as well as the characteristics of the external solution etc[31,38]. The swelling capacity and elastic modulus ate the key properties of the superabsorbent gels. These properties are related to the cross-link density of the net works of the gel. Flory's elastic theory as a function of crosslink density can be applied to evaluate the swelling capacity of any crosslinked polymer as expressed in the following equation[39].

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

where Q, V_e/V_o, $[(1\text{-}2)\text{-}X_1]/V_1$, V_u, i/V_u and S are the water absorption, the crosslinking density of polymer, the affinity between polymer and external solution, the volume of structural unit, the fixed charge per volume of polymer, and the ionic strength of external solution, respectively. The first and second terms in the numerator favours the promotion of swelling behaviour.

In the present investigation, to improve the swelling capacity of the crosslinked poly(AAm-co-SMA) superabsorbent copolymer, various reaction parameters were changed including the concentration of co-monomer (SMA), crosslinker (DP or MBA), initiator (APS), the activator (TMEDA) and the results of influence of these reaction parameters on swelling capacity are presented in detail below.

1. Effect of monomer concentration

TABLE 1 illustrates the equilibrium swelling ratio, swelling and diffusion characteristics of crosslinked poly(AAm-co-SMA) superabsorbent copolymers as a function of monomeric units present in the copolymer network. The hydrophilic monomer (sodium methacrylate) concentration is the influencing factor affecting the swelling properties of the superabsorbent copolymer. The crosslinked poly(AAm-co-SMA) superabsorbent copolymers swelled slowly and reached the equilibrium in about 20-24 hrs. The equilibrium swelling ratio ranged from 49 to 325 g/g for copolymers crosslinked with DP (Figure 3A) and 41 to 81 g/g for copolymers crosslinked with MBA (Figure 4A). With increase of sodium methacrylate units (-COONa) in the copolymer backbone the swelling ratio increased. This is due to the hydrophilic character of the sodium methacrylate (SMA). It is observed that DP crosslinked superabsorbents poly(AAm-co-SMA)s have higher equilibrium swelling ratio than the MBA crosslinked superabsorbent copolymers. This can be explained on the basis of different network formation in the copolymer as well as creation of porosity in DP crosslinked poly(AAm-co-SMA) superabsor bent copolymers due to the presence of methanol as porogen. The swelling behaviour of the crosslinked poly(AAm-co-SMA) superabsorbent copolymers on temperature dependency was investigated in a temperature range from 10°C to 45°C and the results are shown in figure 5. The crosslinked superabsorbent copolymers have swelled rapidly to a maximum extent and reached the equilibrium in a short time at 45°C when compared to at lower temperatures. For both series of superabsorbent copolymers, the highest swelling ratios are observed at 45°C. The reason to increase in the swelling ratio at higher temperatures is due to higher diffusion rate which increases

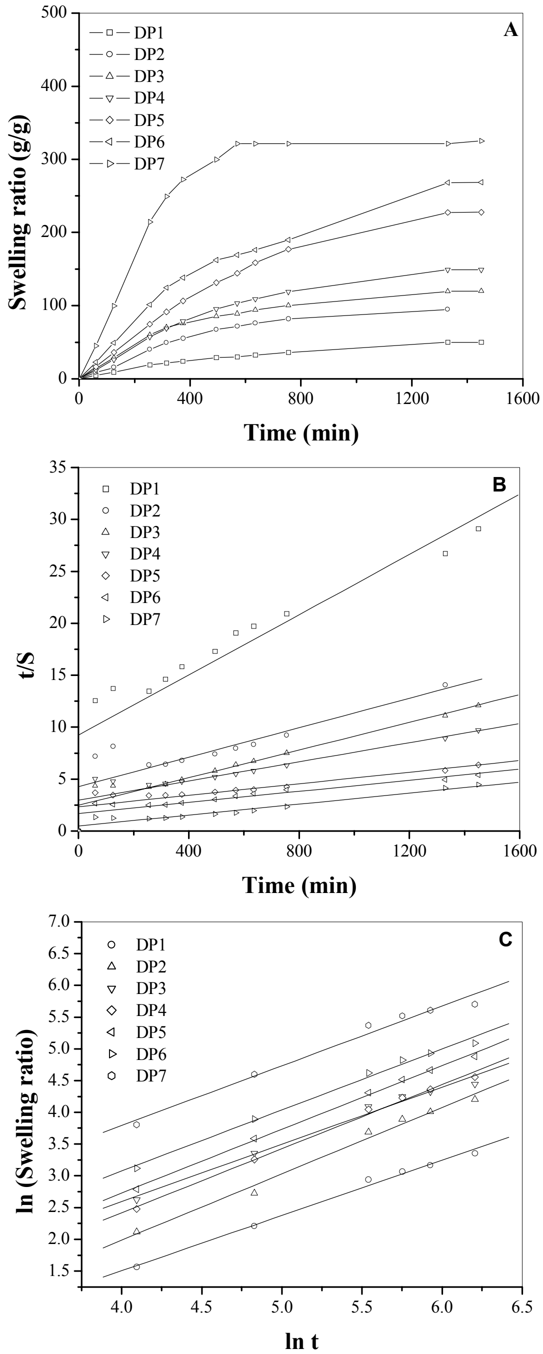

Figure 3: (A) Swelling isotherms; (B) t/S and t graph; and (C) ln F and ln t graphs of poly (AAm-co-SMA) SAPs crosslinked with DP

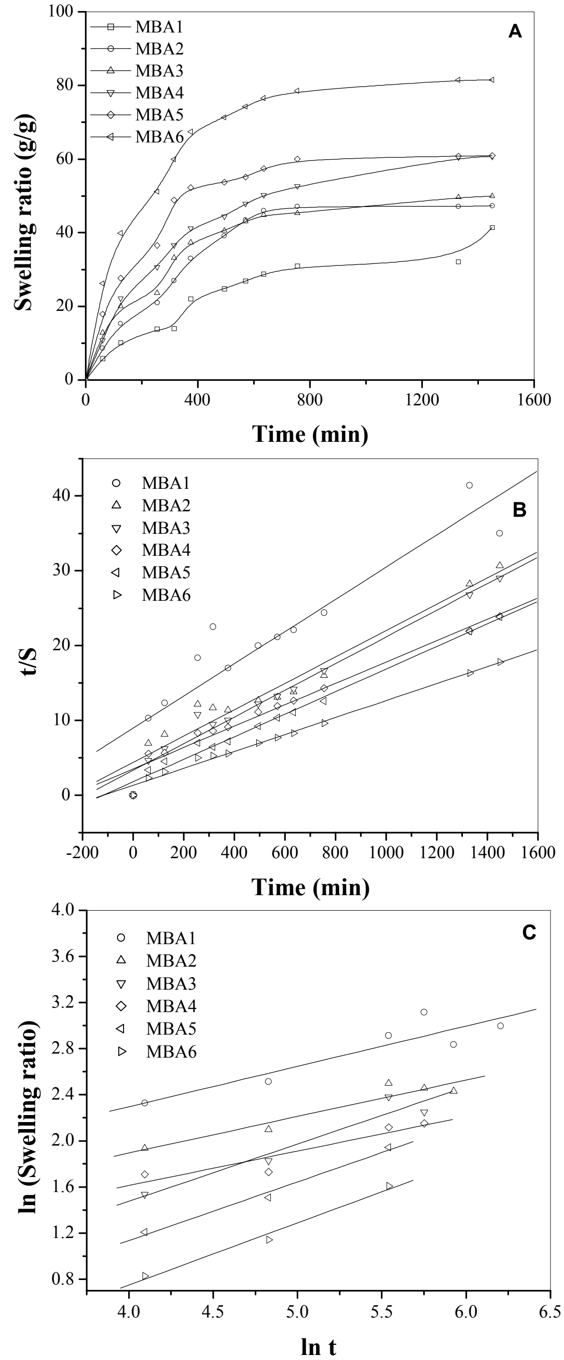

Figure 4: (A) Swelling isotherms; (B) t/S and t graph; and (C) ln F and ln t graphs of poly(AAm-co-SMA) SAPs crosslinked with MBA

with increasing temperature. In most of the cases, the swelling ratio was found to be lower at 25°C At this temperature, the abnormal swelling changes are received. The crosslinked poly(AAm-co-SMA) superabsorbent copolymers have exhibited the temperature dependence swelling behaviour due to the presence of association/dissociation process of hydrogen bonding by the hydrophilic groups present in the copolymer.

Swelling and diffusion characteristics[31,33-35]

The swelling and diffusion characteristics of the crosslinked poly(AAm-co-SMA) superabsorbent copolymers were determined using the swelling curves of the copolymers. To investigate the mechanism of swelling processes or extensive swelling process, a simple kinetic analysis of second order equation is used in the form of $dS/dt = k_S (Seq-S)^2$, where, Seq and k_S denotes the degree of swelling at equilibrium, and swelling rate constant, respectively. The integration of the above equation over the limits $S=S_0$ at time $t=t_0$ and S=Seq at equilibrium at time $t=t_{eq}$, gives the following equation; t/S=A+Bt; where $A=(1/k\ S^2eq)$ is the reciprocal of the initial swelling rate (r_i), B = 1/Seq is the inverse of the maximum or equilibrium swelling, and ks is the swelling rate constant. Figures 3 A and 4 A shows the swelling isotherms of poly(AAm-co-SMA) superabsorbent copolymers crosslinked with DP and MBA. In order to examine the above kinetic model, graphs were plotted between t/S and t and the same are presented in the form of figures 3 B and 4 B for DP and MBA crosslinked poly(AAm-co-SMA) superabsorbent copolymers, respectively. The initial rate of swelling (r_i), swelling rate constant (k_s), and the theoretical equilibrium swelling (Seq) values of hydrogels are calculated from the slope and intersection of the lines and the results were tabulated in TABLE 1.

When a solid polymer is brought into contact with a penetrating liquid, the penetrant diffuses into the polymer leading to swell. The concentration gradient-controlled diffusion and relaxation controlled swelling contributes to the rate and extent of penetrant sorption into the polymer. To analyze the sorption mechanism, the diffusion phenomena of the copolymers is analyzed using the equation, $F_{swp} = (M_s - M_d)/M_d = kt^n$, where F_{swp} is the fractional uptake of water at time t, k is a constant incorporating the characteristic of the macromolecular network system and the penetrant, and n is the diffusional exponent, indicating the type of transport mechanism. This equation is valid for the first 60% of the swelling isotherms. For Fickian transport (n= ½), Case II (n=1) and for Anomalous transport (non-Fickian diffusion) the value is in between Fickian and Case II (1 < n > ½). The graphs are plotted between ln F and ln t for poly(AAm-co-SMA) superabsorbent copolymers crosslinked with DP and MBA and the same are depicted in figures 3 C and 4 C, respectively. The exponent values for poly(AAm-co-SMA) crosslinked with DP are found in between 0.87 – 1.04, indicating the non-Fickian and super Case II diffusion and for poly(AAm-co-SMA) crosslinked with MBA are found in between 0.29-0.54, indicating the Fickian diffusion.

Salinity effect on swelling ratio

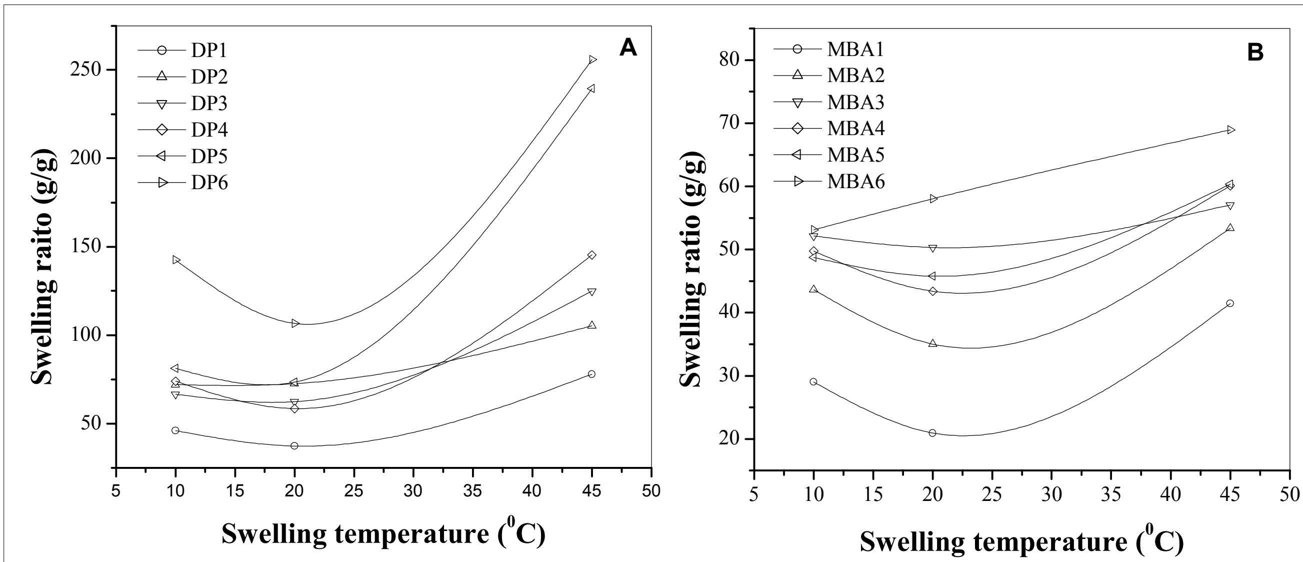

Figure 5: Temperature dependency of swelling behaviour of poly(AAm-co-SMA) copolymers crosslinked with (A) DP and (B) MBA

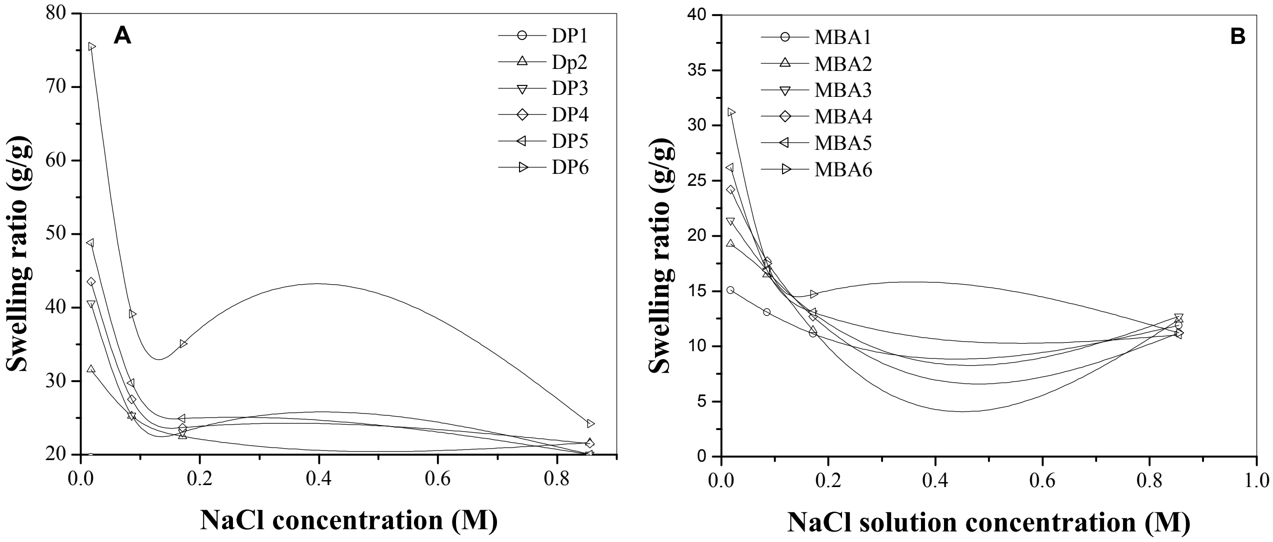

Figure 6: Influence of NaCl solution concentration on swelling behaviour of poly(AAm-co-SMA) copolymers crosslinked with (A) DP and (B) MBA

The factors of external solution such as charge valencies and salt concentrations greatly influence the swelling behaviour of the superabsorbent polymers. The effect of salinity on the swelling phenomena of various polymers, poly(sodium acrylate-sodium 2- acrylamido-2-methyl propane sulfonate), poly(SA-NaAMPS), poly(sodiumacrylate-hydroxyl ethyl methacrylate), poly(SA-HEMA), poly[sodium acrylate-3,3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate] poly(SA-DMAPS) copolymers was reported[22-25]. In the present investigation, the influence of different concentrations of sodium chloride solution on swelling behaviour of crosslinked poly(AAm-co-SMA) superabsorbent copolymers was investigated. Figure 6 shows the swelling behaviour of crosslinked poly(AAm-co-SMA) superabsorbent copolymers as a function of concentration of sodium chloride solution. It is clearly seen form the figure 6, the swelling ratio of the crosslinked superabsorbent copolymers decreased in salt solution as ionic concentration of the salt solution increases. This is due to the decrement in the expansion of the gel network due to repulsive forces of counter ions on the polymeric chain shielded by the bound ionic charges. Therefore, the osmotic pressure difference between the gel network and the external solution decreases with an increase in the ionic strength of the saline concentration.

The dimensionless factor (α) is the ratio of absorption at a given salinity to salt free water[40]. This factor is a measure for the salt sensitivity of the superabsorbent polymers. The α values for different saline concentrations are given in TABLE 2, for poly (AAm-co-SMA) superabsorbent copolymers crosslinked with DP and MBA.

TABLE 2: Dependency of dimensionless swelling factor (α), on the monomer content at various saline concentrations

Polymer code	Dimensionless factor (α)			Polymer code	Dimensionless factor (α)		
	$(\alpha)_{0.0171}$	$(\alpha)_{0.0855}$	$(\alpha)_{0.171}$		$(\alpha)_{0.0171}$	$(\alpha)_{0.0855}$	$(\alpha)_{0.171}$
DP1	0.395	0.376	0.366	MBA1	0.464	0.398	0.276
DP2	0.334	0.267	0.238	MBA2	0.452	0.356	0.274
DP3	0.339	0.211	0.193	MBA3	0.484	0.354	0.254
DP4	0.292	0.184	0.159	MBA4	0.432	0.278	0.215
DP5	0.214	0.130	0.109	MBA5	0.511	0.287	0.241
DP6	0.282	0.146	0.130	MBA6	0.573	0.332	0.239

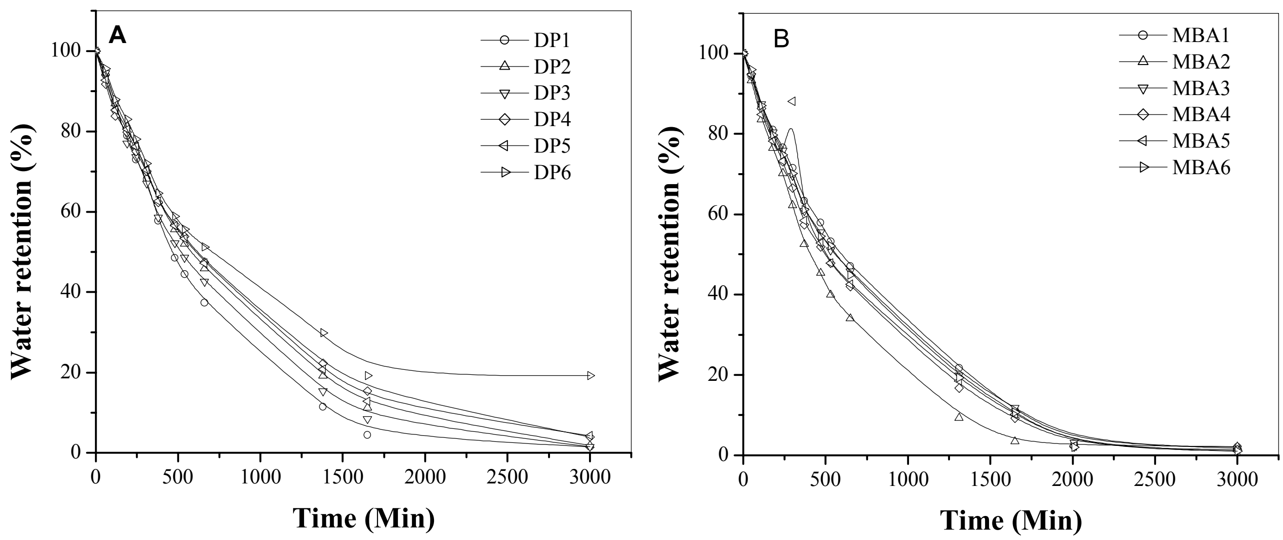

Figure 7: Water retention capacity of poly(AAm-co-SMA) copolymers crosslinked with (A) DP and (B) MBA

Water retention capacity

Water retention capacity property of SAPs prompted to use them as horticulture and agricultural materials and also as soil conditioners[5-7]. To study the water retention capacity of the crosslinked poly(AAm-co-SMA) superabsorbent copolymers, the de-welling experiments were performed. Around 2.5 g of swollen crosslinked superabsorbents were taken on aluminum foil sheet and weight loss of water in swollen gels were estimated at different time intervals gravimetrically. The water retention curves of crosslinked poly(AAm-co-SMA) superabsorbent copolymers are presented in figure 7. A large variation was observed in their de-swelling behaviour of the DP crosslinked poly(AAm-co-SMA) superabsorbent copolymers. The de-swelling behaviour was reduced or the water retention capacity was improved. The MBA crosslinked copolymer showed similar de-dwelling performance for all the co-monomer ratios. De-swelling studies indicates that the DP crosslinked copolymers have higher water retention capacity than the MBA crosslinked copolymers. From figure 7, it was confirmed that DP crosslinked copolymer have high water retention capacity of 1.5 to 19% where as MBA crosslinked copolymers have lower water retention capacity of 1 to 2 %. These results suggests that DP crosslinked poly(AAm-co-SMA) superabsorbents copolymers may find an application in agriculture and horticultural fields.

2. Effect of crosslinking agent type and concentration

The concentration of crosslinker is responsible in the formation of three dimensional network structures permanently in the crosslinked superabsorbent polymers in the polymerization process. Further, it is also a promising factor, which affect directly the swelling ratio of the SAP. TABLE 3, illustrates the reaction conditions of crosslinked poly(AAm-co-SMA) superabsorbent copolymers. Figure 8 shows the swelling ratio of the crosslinked poly(AAm-co-SMA) superabsorbent copolymer as a function of crosslinker concentration. It is observed that the

TABLE 3: Reaction conditions of crosslinked poly (AAm-co-SMA) superabsorbent copolymers

Polymer code	Crosslinker DP or MBA	APS (mM)	TMEDA (mM)
DPC1	Variation	0.0219	0.04302
MBAC1	Variation	0.0219	0.04302
DPAPS1	0.0568	Variation	0.04302
MBAAPS1	0.0454	Variation	0.04302
DPTMEDA1	0.0568	0.0876	Variation
MBATMEDA1	0.0454	0.0438	Variation
DPTEM1	0.0568	0.0876	0.0860
MBATEM1	0.0454	0.0438	0.0602

Acrylamide = 14.068 mM; SMA = 9.262 mM

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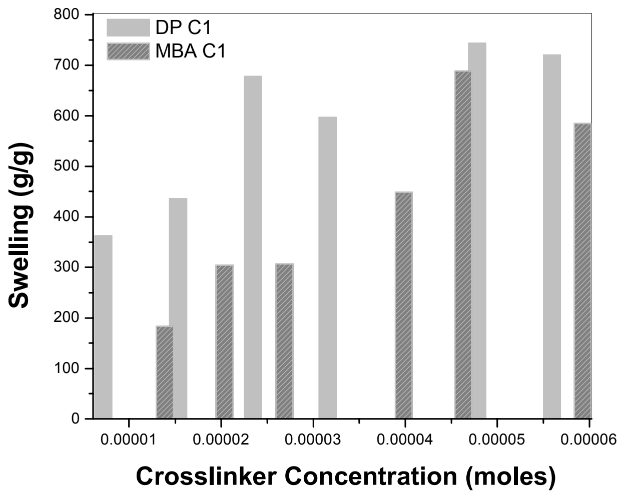

Figure 8: Influence of crosslinker concentration on swelling behaviour of poly(AAm-co-SMA) crosslinked copolymers

swelling ratio increases as DP and MBA concentration increases up to a particular concentration and further increase of crosslinker concentration slightly decreases the swelling ratio. The similar effect of crosslinker concentration on swelling behaviour of superabsorbent copolymer was reported in our previous studies[5-7]. The scanning electron microscopy (SEM) of crosslinked poly(AAm-co-SMA) showed differences in their network structure formation. The microstructure of the DP crosslinked poly(AAm-co-SMA) (Figure 9A) shows the presence of porosity in the copolymer network structure. This porosity is obtained due to the employment of DP crosslinker in methanol solution. The porosity creation is not observed if higher crosslinker concentration is used due to the formation of a regular fine-network structure (Figure 9B and 9C). The micrographs of MBA crosslinked poly(AAm-co-SMA) superabsorbent copolymers showed no free spaces between the networks formed at higher concentration of crosslinker (Figure 10B) whereas more voids are observed in the networks formed at lower crosslinker concentration (Figure 10A).

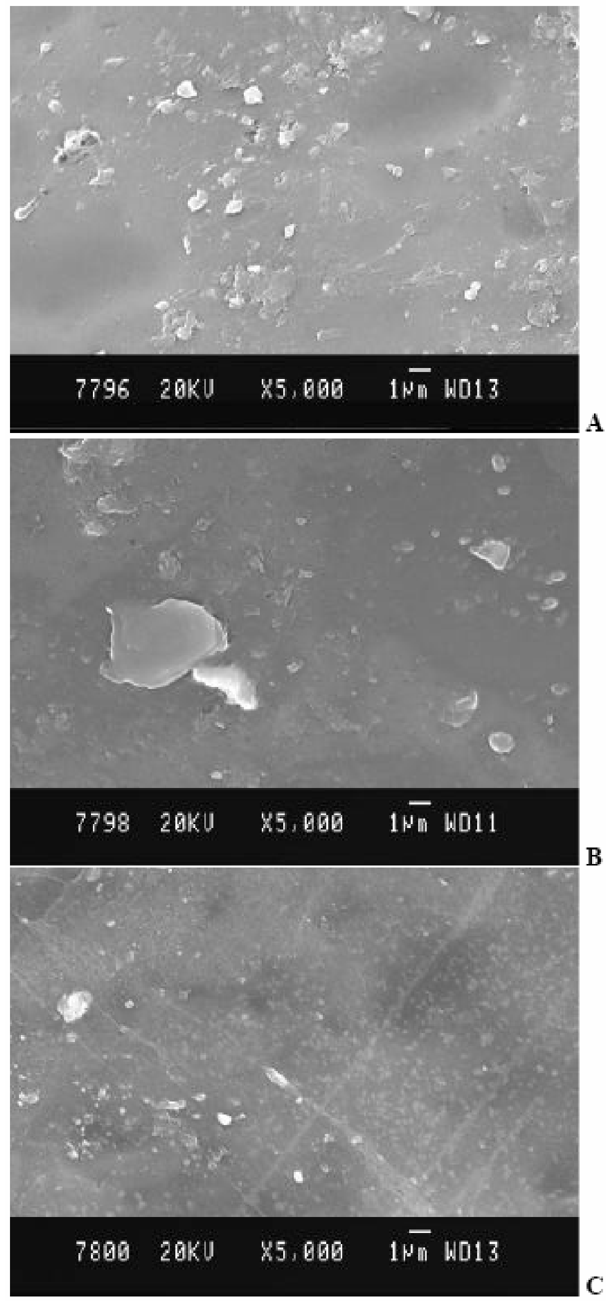

Figure 9: SEM micrographs of poly(AAM-co-SMA) superabsorbent copolymers crosslinked with (A) 0.0081 mM; (B) 0.0243 mM; and (C) 0.048 mM of DP

3. Effect of initiator and activator

The initiator concentration shows significant influence on both the polymerization rate and the molecular weight of the polymer. In the simultaneous crosslinking copolymerization reactions, the initiator not only affect the degree of crosslinking and molecular weight between two crosslinking points but also contributes for inhomogeneity in the copolymer system. In the present study, copolymerization between AAm and SMA starts with the reaction between APS and TMEDA and then follows simulta-

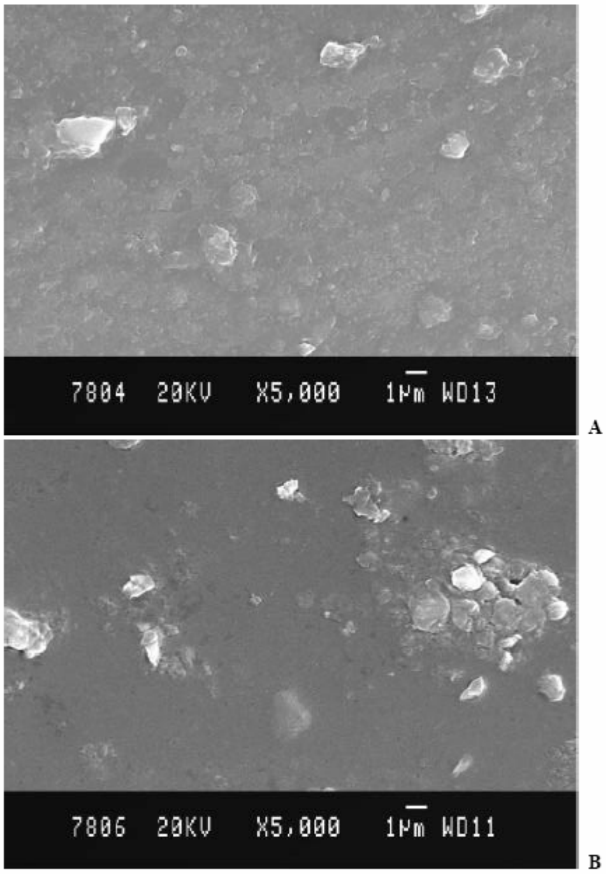

Figure 10: SEM micrographs of poly(AAM-co-SMA) superabsorbent copolymers crosslinked with (A) 0.0129 mM; and (B) 0.0259 mM of MBA

neous free radical addition polymerization as well as the crosslinking reactions simultaneously. Similar type of work was reported recently by various authors in the preparation of polymers or copolymers based on acrylamide and acrylic acid[31]; starch, acryla mide, and kaolinite[41]; acrylamide and crotonic acid [30]; poly(vinyl alcohol) and N-isopropylacrylamide; and N-isopropylacrylamide[42]. Figure 11 shows the influence of APS concentration on the swelling behaviour. The results indicates that the poly(AAm-co-SMA) showed higher swelling ratio at low concentration of APS (0.0438 mM). Further increase in the concentration of APS leads to decrease in the swelling ratio of crosslinked poly(AAm-co-SMA) superabsorbent copolymers.

The influence of activator N,N,N′,N′-tetramethyl ethylenediamine concentration on the swelling ratio of SAPs was also studied and the results obtained is

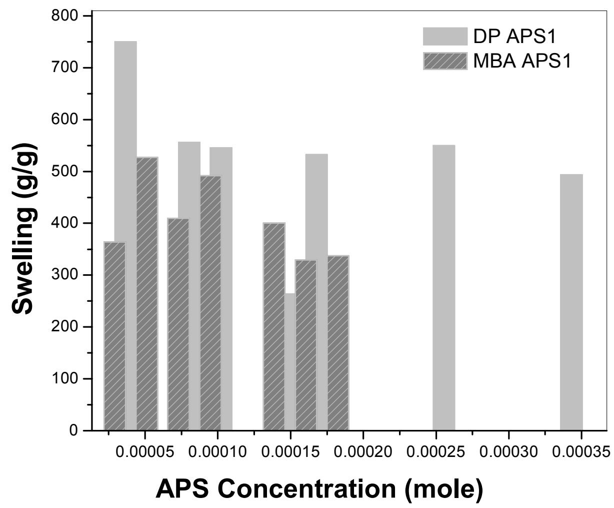

Figure 11: Effect of APS concentration on swelling behaviour of crosslinked poly(AAm-co-SMA) copolymers

showed in figure 12. From figure 12, it is observed that the swelling ratio of the crosslinked superabsor bent copolymers varied significantly as TMEDA concentration varied. As increase of activator concentration from 0.0172 to 0.0861 mM, increases the swelling ratio of DP crosslinked poly(AAm-co-SMA) copolymers from 362 to 743 g/g and further increase of activator concentration drastically decreases the swelling ratio. Similarly, the swelling ratio of MBA crosslinked copolymers increased as the TMEDA concentration varied from 0.0172 to 0.060 mM and

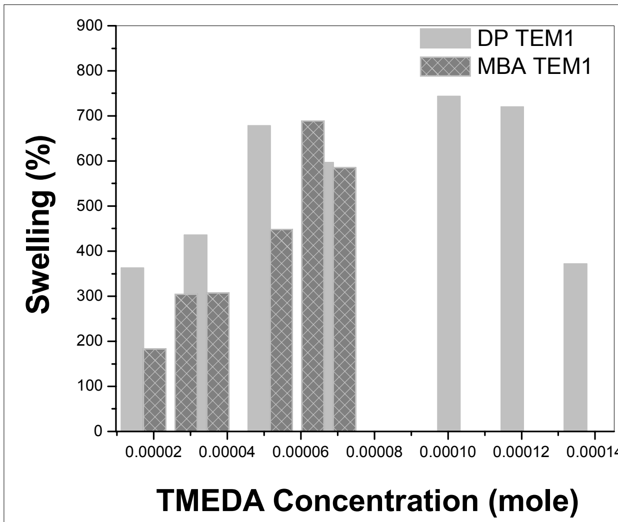

Figure 12: Effect of TMEDA concentration on swelling behaviour of crosslinked poly(AAm-co-SMA) copolymers

slightly decreased with further increase of TEMDA concentration.

4. Effect of pH on the swelling ratio of SAPs

Figure 13 reveals the influence of pH on the swelling behaviour of crosslinked poly(AAm-co-SMA) superabsorbent copolymers. From this it is noticed that the swelling ratio increased from pH 2 to 7 and then decreased with further increase of pH of the 14 solution. The swelling ratio of both co-polymers crosslinked by MBA and DP showed maximum at pH 7. In the case of DP crosslinked copolymers, the superabsorbent dissolved partially at pH 12.

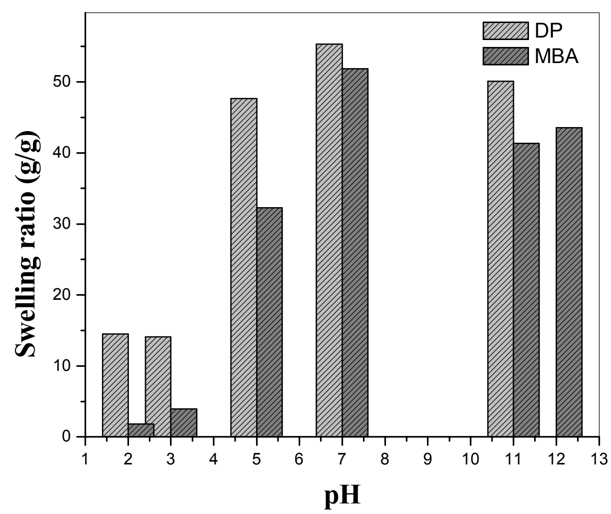

Figure 13: Influence of pH on swelling behaviour of crosslinked poly(AAm-co-SMA) copolymers

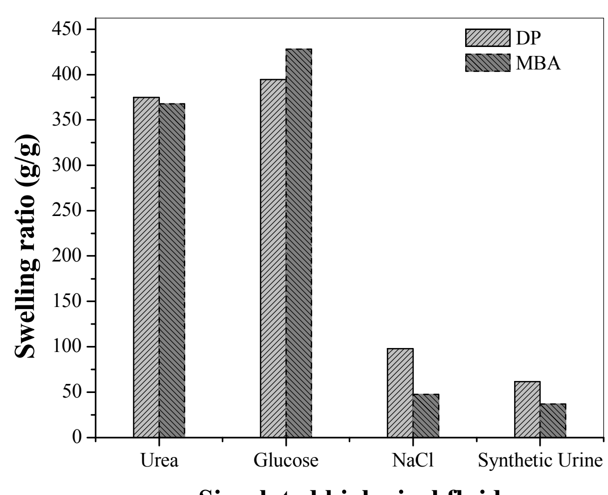

Figure 14: Influence of pH on swelling behaviour of crosslinked poly(AAm-co-SMA) copolymers

5. Effect of simulated biological fluids

It is well accepted that the swelling is the net result of osmotic and the restoring elastic pressures. The presence of solute in the surrounding aqueous medium is capable of tilting this balance resulting in variations in the swelling phenomena. In order to study the effect of simulated biological fluids on the swelling behaviour of crosslinked poly(AAm-co-SMA) superabsorbent copolymers, four different biological fluids were employed and the results are presented in figure 14. The results indicate lower swelling ratio values in all biological fluids when compared to water as swelling medium. This nature is attributed due to the presence of more number of ionic species in the swelling medium. It is identified that the swelling ratio is very high in glucose and urea solutions and very low in synthetic urine and sodium chloride solutions. Further it is also found that the DP crosslinked poly(AAm-co-SMA) superabsorbents were very smooth in the swollen state.

6. Influence of polymerization temperature on swelling ratio

To study the effect of polymerization temperature on the swelling property of the poly(AAm-co-SMA) superabsorbent copolymers, the polymeriza-

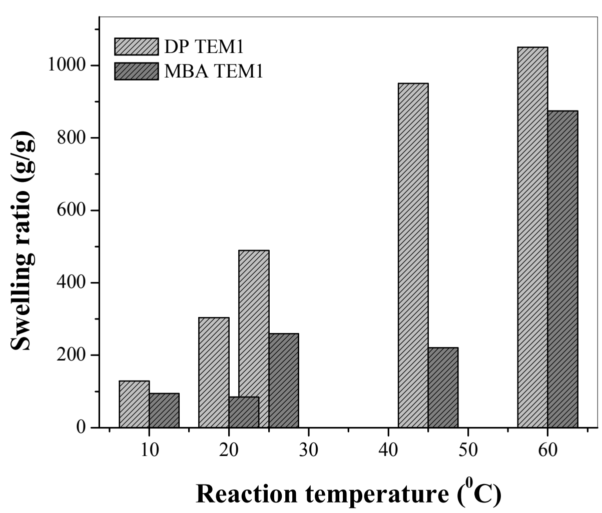

Figure 15: Influence of reaction temperature on swelling behaviour of crosslinked poly(AAm-co-SMA) copolymers

tion reactions were conducted at different temperatures ranging from 10 to 60^{0}C. The crosslinked poly(AAm-co-SMA) superabsorbent copolymers prepared at higher temperature have shown high swelling capacity. The higher swelling ratios of 1050 g/g and 874 g/g were observed in DP and MBA crosslinked copolymers respectively at 60^{0}C. The effect of polymerization temperature on the swelling ratio of crosslinked poly(AAm-co-SMA)s is shown in figure 15.

CONCLUSION

The crosslinked superabsorbent copolymers composed of acrylamide and sodium methacrylate were prepared using DP and MBA as crosslinkers and APS/TMEDA as initiating system. The influence of various reaction parameters, such as, concentration of co-monomer (SMA), crosslinker, initiator and activator; as well as polymerization temperature, on the swelling behaviour of the crosslinked poly(AAm-co-SMA) superabsorbent copolymers was investigated. Further their swelling behaviour was evaluated as a function of temperature, salinity, pH, and simulated bio-fluids. The swelling/diffusion characteristics were determined for DP and MBA cross linked poly(AAm-co-SMA) SAPs containing different amounts of co-monomer. Moreover, the water retention capacity of the crosslinked poly(AAm-co-SMA) superabsorbent copolymers was also investigated.

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