

Swelling and Thermal Characteristics of pH Sensitive Crosslinked Poly(acrylamide-co-calcium methacrylate) Superabsorbent Copolymers

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ABSTRACT: Crosslinked poly(Acrylamide-co-calcium methacrylate) superabsorbent copolymers [Poly(AAm-co-CMA)] were prepared by free-radical copolymerization in aqueous solution of acrylamide (AAm) with calcium methacrylate (CMA) in presence of a crosslinker [*N,N*'-methylenebisacrylamide (MBA), 1,2-ethyleneglycol dimethacrylate (EGDMA), or diallyl phthalate (DP)] using ammonium persulphate-*N,N,N*'*N*'-tetramethylethylenediamine (APS-TMEDA) redox initiator. The influence of relative content of CMA on the swelling ratio of the crosslinked copolymer was examined. The equilibrium swelling ratio (S_{eq}) of crosslinked poly(AAm-co-CMA) superabsorbent copolymers was found in between 13–111 g/g, 14–92 g/g, and 12–33 g/g for superabsorbent copolymers crosslinked by DP, EGDMA, and MBA, respectively. Percentage equilibrium water content (EWC%) of crosslinked superabsorbent copolymers was found in between 92.51 and 99.11%. The cal-

culated theoretical equilibrium swelling ratio (TS_{eq}) and equilibrium swelling ratio (S_{eq}) of these superabsorbent copolymers were in good agreement. Water intake of superabsorbent copolymers crosslinked by DP followed non-Fickian type diffusion, while EGDMA and MBA crosslinked superabsorbent copolymers followed Fickian type diffusion. Further, the influence of pH of the medium on swelling behavior of crosslinked superabsorbent copolymers was also investigated. Thermal stability and morphology of these poly(AAm-co-CMA) superabsorbent copolymers were also studied in detail. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1–12, 2006

Key words: superabsorbent polymer (SAP); hydrogel; calcium methacrylate; swelling ratio; percentage equilibrium water content (EWC%); diffusion; crosslinks

INTRODUCTION

Superabsorbent polymers (SAP)s or hydrogels are three-dimensional crosslinked networks of hydrophilic functional groups of polyelectrolytes, which can absorb large amount of water without dissolving in aqueous media because of their ionic nature and interconnected structural features.¹ The absorbed water can be retained for longer periods, even under pressure.² Superabsorbent polymers have attracted much attention in the area of functional polymers because of their excellent characteristics such as lack of toxicity, high swelling capacity in aqueous environment, hydrophilicity, and biocompatibility.^{1,3–6} The versatile properties of superabsorbents makes them ideally suited to serve as useful materials in various fields, including agriculture and horticulture, health, bio-

engineering, pharmaceutical, drug delivery, food industry, and other advanced technologies.^{7–14}

In recent years, significant research was focused on the swelling behavior of the superabsorbent copolymers prepared by simultaneous free radical copolymerization and crosslinking in the presence of an initiator and a crosslinking agent.^{15–27} Kabiri et al.^{17,18} have reported the preparation of porous acrylic acid based superabsorbent polymers using redox initiator and investigated their swelling and morphological behavior. Zhou et al.^{20,21} have studied the synthesis and swelling properties of copolymers of acrylamide with anionic monomers and crosslinked poly[acrylamide-sodium methallylsulfonate-sodium acrylate], poly(AM-MSAS-AA) gels. Bajpai²² has reported the synthesis and characterization of poly(acrylamide-co-maleic acid). Isýk and kýs^{25,26} have reported the swelling behavior and diffusion characteristics of acrylamide-acrylic acid hydrogels polymerized in presence of poly(ethylene glycol). Karadağ and Saraydin²⁷ have reported the synthesis of poly(acrylamide-co-crotonic acid) as well as the swelling behavior, swelling/diffusion studies of the copolymers.

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TABLE I
The Monomers, Crosslinkers, and the Initiator Used in the Preparation of Crosslinked Poly(AAm-co-CMA) Superabsorbent Copolymers

Name of the chemical	Formula	Abbreviation
Acrylamide	$H_2C=CHCONH_2$	AAm
Calcium methacrylate	$[H_2C=C(CH_3)COO]_2Ca$	CMA
1,2-Ethyleneglycol dimethacrylate	$[H_2C=C(CH_3)COOCH_2]_2$	EGDMA
Diallyl phthalate	$C_6H_4-(COOCH_2CH=CH_2)_2$	DP
<i>N,N'</i> -methylenebisacrylamide	$(H_2C=CHCONH)_2CH_2$	MBA
Ammonium persulfate	$(NH_4)_2S_2O_8$	APS
<i>N,N, N', N'</i> -tetramethylethylenediamine	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	TMEDA

Poly(acrylamide) based superabsorbent copolymers have found to be important materials in agriculture, horticulture, adsorbents, biomedical and pharmaceutical fields. It is widely accepted that the improved absorption capacity or absorption rate can be achieved for acrylamide superabsorbent polymers by incorporation of various hydrophilic units. High polymer chain flexibility as well as the presence of pore or free volume between the SAP networks also enhances the swelling capacity of the superabsorbent polymers. Further, the extent of crosslinking, initial dilution of monomers, pH of the medium, and reaction conditions also decides the resulting superabsorbent polymer swelling capacity. The swelling property of these materials directly measures its utility in environmental applications as an adsorbent and as biomaterial in medical, pharmaceutical, and biological applications. Recently, we reported the synthesis and swelling and diffusion characteristics of poly(acrylamide-co-potassium methacrylate) [poly(AAm-co-KMA)] and poly(acrylamide-co-sodium methacrylate) [poly(AAm-co-NMA)] superabsorbent copolymers using ammonium sulfate/*N,N,N',N'*-tetramethylethylenediamine (APS/TMEDA) redox initiator.^{23,24}

The aim of the present study is to prepare and to disclose the swelling characteristics of poly(acrylamide-co-calcium methacrylate) [poly(AAm-co-CMA)] superabsorbent copolymer. Calcium methacrylate is chosen for this study because of the divalent nature of calcium, which can be linked to two carboxylate groups of methacrylic acid units present in the copolymers. The results obtained are required to correlate with poly(acrylamide-co-potassium methacrylate) and poly(acrylamide-co-sodium methacrylate) superabsorbent copolymers, since these superabsorbent copolymers have found better applications in agriculture and horticultural applications. Moreover, it is of much interest to study the swelling behavior of poly(AAm-co-CMA) superabsorbent copolymers crosslinked with different crosslinking agents. This investigation also deals the influence of pH on swelling behavior of poly(AAm-co-CMA) SAP. Further, their thermal behavior was studied by using differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA).

EXPERIMENTAL

Materials

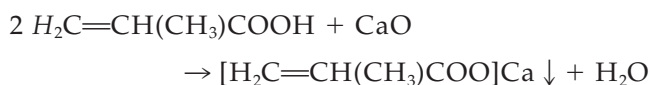
Acrylamide (AAm) and ammonium persulfate (APS) were obtained from S.D. Fine Chemicals (Mumbai, India). Methacrylic acid (MA), *N,N'*-methylenebisacrylamide (MBA), 1,2-ethyleneglycol dimethacrylate (EGDMA), diallyl phthalate (DP), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (Aldrich, Milwaukee, WI) were purchased from Sigma-Aldrich (Secunderabad, India). All the chemicals were used without further purification. Double distilled water was used for all the copolymerization reactions as well as for swelling studies. The chemicals used in the polymerization were presented in Table I.

Stock solutions

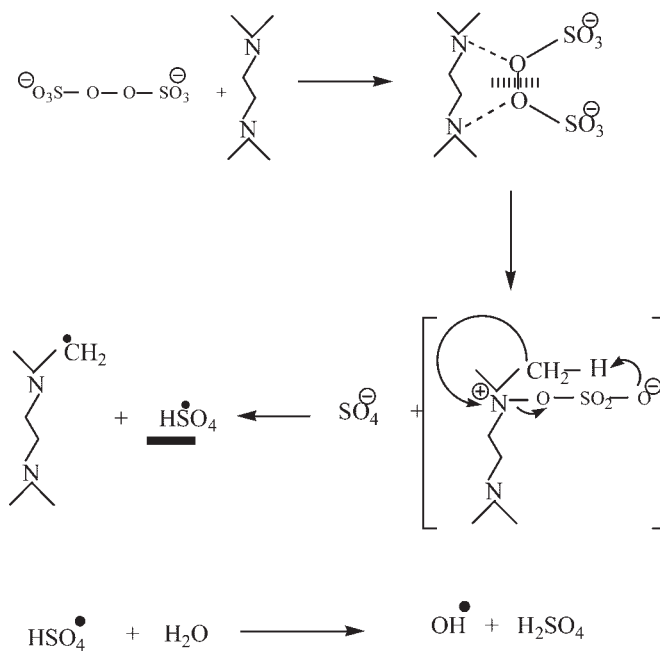
MBA (1 g/100 mL water), TMEDA solution (1 g/100 mL water), DP solution (1 g/100 mL methanol), EGDMA solution (1 g/100 mL methanol), buffer solution I (12.3 g of anhydrous boric acid + 10.51 g of citric acid in 1000 mL water, buffer solution II (38.01 g of trisodium phosphate in 1000 mL water), saline water (0.9 g NaCl/100 mL), synthetic urine [(0.8 g NaCl + 0.10 g MgSO₄ + 2.0 g urea + 0.06 g CaCl₂)/(100 mL water)], urea (5 g/100 mL water), and D-glucose (5 g/100 mL) were prepared.

Preparation of calcium methacrylate

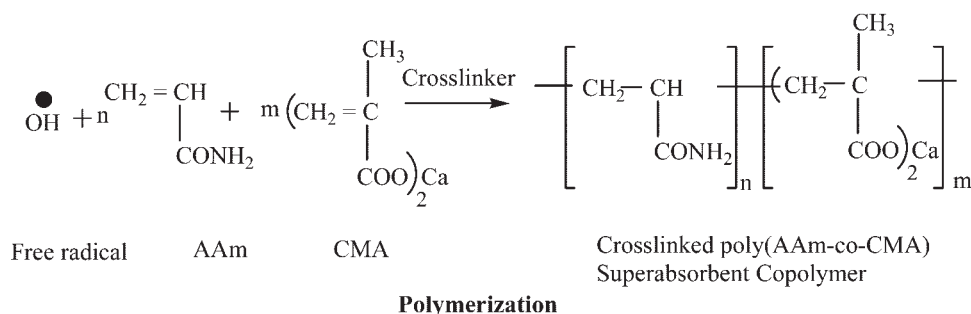
Calcium oxide (0.5 mol) was dispersed in methanol. Methacrylic acid (0.1 mol) was taken in a conical flask in dry ether and titrated with the calcium oxide suspension. A white solid was separated out. The product was filtered under vacuum and dried in a vacuum desiccator.



IR (KBr disk): 1710 cm⁻¹, C=O acrylate unit; 2820 cm⁻¹, —CH— stretching of acrylate unit; 1232 and



Freeradical formation with APS/TMEDA



Scheme 1 Preparation of crosslinked poly(AAm-co-CMA) superabsorbent copolymer.

1127 cm^{-1} , C—O—C coupling interaction of ester groups.

Preparation of crosslinked poly(AAm-co-CMA) superabsorbent copolymers

Poly(AAm-co-CMA) superabsorbent copolymers were prepared by simultaneous copolymerization and crosslinking of acrylamide with calcium methacrylate in the presence of a crosslinker.

To prepare crosslinked poly(AAm-co-CMA) superabsorbent copolymer, 1 g (14.06 mM) of acrylamide was dissolved in 2 mL of distilled water, and then 0.399, 0.079, 1.198, 1.597, 1.997, 3.994, and 8.00 mM of calcium methacrylate were added to the aqueous solutions of acrylamide. To these solutions, 2 mL (0.0812 mM) of DP solution, 1 mL (0.219 mM) of ammonium persulphate, and 1 mL of (0.086 mM)

TMEDA solutions were sequentially added to obtain DP1, DP2, DP3, DP4, DP5, DP6, and DP7 superabsorbent copolymers, respectively. The whole reaction was performed in a 50 mL beaker at room temperature $[(30 \pm 1)^\circ\text{C}]$. Soon after the addition of TMEDA, the superabsorbent copolymers were formed in the gel form. However, the polymerizations were allowed to proceed for 24 h so as to complete the polymerization reaction and the obtained gels were kept in distilled water for a day to leach out the unreacted monomers/crosslinker/APS/TMEDA. The obtained SAPs were cut into 1 mm squares. These SAPs were used for the swelling experiments. The schematic representation of the crosslinked poly(AAm-co-CMA) superabsorbent copolymer (random copolymer) is depicted in Scheme 1. The monomers, crosslinkers, and initiator used in

TABLE II
Swelling Ratio And Equilibrium Water Content Data of Crosslinked Poly(AAm-co-CMA) Superabsorbent Copolymers

S. No.	Calcium methacrylate (mM)	Swelling ratio at equilibrium, S_{eq} (g/g)			Percentage equilibrium water content, EWC% (%)		
		EGDMA ^a	DP ^b	MBA ^c	EGDMA ^a	DP ^b	MBA ^c
1	0.399	14	13	12	93.60	92.90	92.51
2	0.079	38	25	20	97.47	96.21	95.31
3	1.198	63	43	24	98.44	97.67	96.02
4	1.597	77	65	27	98.72	98.50	96.50
5	1.997	92	77	33	98.92	98.71	97.02
6	3.994	51	54	32	98.08	98.18	96.98
7	8.000	–	111	–	–	99.11	–

Reaction conditions: Acrylamide, 14.06 mM; APS, 0.219 mM; TMEDA, 0.086 mM. S. No. in table indicate the number of superabsorbent copolymer code (e.g., S. No. 1 in DP series = DP 1).

^aEGDMA crosslinked poly(AAm-co-CMA) superabsorbent copolymers.

^bDP crosslinked poly(AAm-co-CMA) superabsorbent copolymers.

^cMBA crosslinked poly(AAm-co-CMA) superabsorbent copolymers.

the preparation of crosslinked superabsorbent copolymers are tabulated in Table I.

To investigate the effect of crosslinker on the preparation of crosslinked poly(AAm-co-CMA) superabsorbent copolymer, two other crosslinking agents namely, 1.5 mL (0.0756 mM) of EGDMA or 1.2 mL (0.0777 mM) of MBA solutions were employed instead of diallyl phthalate. The effect of calcium methacrylate on swelling behavior of crosslinked poly(AAM-co-CMA) superabsorbent copolymers for different crosslinker series are presented in Table II.

Swelling studies

The weight of crosslinked dry and swollen hydrogels was measured using an electronic balance with an accuracy of ± 0.1 mg (Adventurer; Ohaus Corp., NJ). Preweighted (≈ 50 mg) dry gels were immersed in 100 mL swelling medium at room temperature and these hydrogels were removed periodically from the swelling medium and after wiping out the excess surface water the gels were weighed. The swelling studies were monitored until the gels swollen to equilibrium stage. (Equilibrium swelling, S_{eq}). The fractional weight (periodical) change was transformed either in swelling factor or swelling ratio (S) or in percentage equilibrium water content (EWC%) using the empirical formula as given below^{23–27}

$$\text{Swelling ratio}(S) = \frac{W_t - W_0}{W_0} \quad (1)$$

Equilibrium water content (EWC) (%)

$$= \frac{W_{eq} - W_0}{W_{eq}} \times 100 \quad (2)$$

where W_0 , W_t , W_{eq} are weight of gel at time zero, t , and equilibrium stage, respectively. The swelling ratio at equilibrium stage can be termed as equilibrium swelling ratio (S_{eq}). The swelling measurements were made thrice and the average data was used for the presentation as well as for calculations.

Analysis of polymers

The IR spectra of dry superabsorbent hydrogels were carried out on a Perkin–Elmer Spectrophotometer ASCII (PerkinElmer Cetus Instruments, Norwalk, CT). Thermal analysis of the superabsorbent copolymers were determined using Differential scanning calorimetry (DSC, METLER TOLEDO STARE System) and Thermogravimetric analyzer (METLER TOLEDO STARE System) with a scan rate of 20°C/min under nitrogen flow (30 mL/min). The dry gels were coated with a thin layer of palladium gold alloy and their structural and morphological variations were observed using a JEOL JSM 840A (Tokyo, Japan) scanning electron microscope (SEM).

RESULTS AND DISCUSSIONS

Preparation of crosslinked poly(AAm-co-CMA) SAP

An extensive research work was carried out by various authors with regard to the swelling characteristics of the superabsorbent copolymers or superabsorbent polymers (SAP)s. Most of the reports were observed based on sodium acrylate (NA), potassium acrylate (KA), sodium methacrylate (SMA), and potassium methacrylate (KMA) with acrylamide SAPs.^{11–33} Karadag and Saraydin²⁷ reported the copolymerization of AAm with anionic comonomers such as itaconic acid (IA), maleic acid (MA), crotonic acid (CA),

and succinic acid (SA) using γ -irradiation.^{28–31} The copolymerization of AAm with potassium methacrylate and sodium methacrylate was studied by simultaneous aqueous free radical solution polymerization, using different crosslinkers and APS/TMEDA as initiating system.^{23,24}

In the present investigation, calcium methacrylate used as comonomer in the polymerization of acrylamide using APS/TMEDA initiating system in presence of a crosslinker. To study the variation in swelling property of crosslinked poly(AAm-co-CMA) superabsorbent copolymer, different amounts of CMA was used for the polymerizations. Further, their swelling behavior was also verified by changing the crosslinker in the polymerizations.

It is believed that the polymerization process starts with the reaction between APS and TMEDA to form an activated TMEDA molecule containing unpaired valence electron (free-radical). The unpaired valence electron may combine with acrylamide, calcium methacrylate, or crosslinkers; in this process the unpaired electron was transferred to the monomeric units, thereby starts the initiation of the polymerization, copolymerization, and crosslinking processes, simultaneously. The polymer (AAm) or copolymer [poly(AAm-co-CMA)] continue to grow, with the active center being continually shifted to the free end of the chain. Crosslinker molecules were also incorporated into the polymeric chains simultaneously, forming permanent link between them.^{32–34} The schematic representation of the polymerization process of superabsorbent polymer is depicted in Scheme 1.

The AAm/CMA polymerization process took only 10–15 min to obtain the gels. However, for all polymerizations, the reactions were allowed to proceed for 24 h to get complete gelation of the polymers. The obtained crosslinked SAPs were colorless and few of them were semitransparent. They were elastic, very soft, and with slippery surfaces. It was further noticed that there was no difference in the external appearance of SAPs even by changing the crosslinker. But, MBA crosslinked SAPs showed somewhat a stiff nature when compared with the other samples.

IR analysis

The IR spectra of the crosslinked poly(AAm-co-CMA) superabsorbent copolymers showed the peaks corresponding to the functional groups of the monomers in the polymeric chains. A broad peak was observed between 3570 and 3050 cm^{-1} corresponding to hydrogen bonded (bridged) N—H stretching due to acrylamide/MBA; other peaks observed at 1720 cm^{-1} corresponding to the $\nu\text{C}=\text{O}$ of the acrylate unit of sodium methacrylate/crosslinker (EGDMA or DP); 1665 cm^{-1} corresponding to the $\nu\text{C}=\text{O}$ group of acrylamide/MBA units; and 1124 cm^{-1} corresponding to

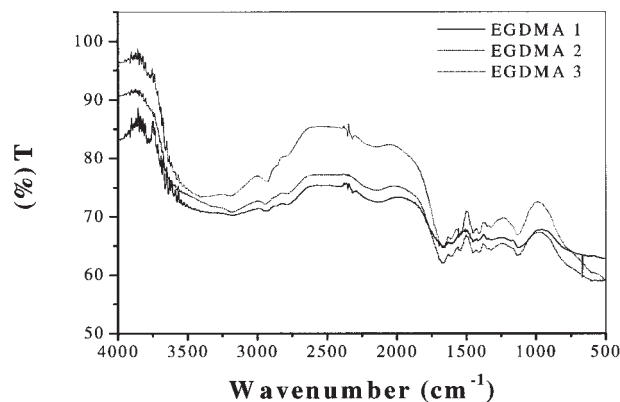


Figure 1 IR spectra of EGDMA crosslinked poly(AAm-co-CMA) hydrogels.

C—O—C stretching peaks of ester groups. Therefore, the IR analysis literally demonstrates the incorporation of acrylamide, calcium methacrylate, and crosslinker units into the copolymer chain. Representative IR spectra of poly(AAm-co-CMA) copolymers crosslinked with EGDMA are shown in Figure 1.

Influence of CMA content on swelling characteristics of poly(AAm-co-CMA) superabsorbent copolymer

Water absorbency of superabsorbent copolymers or superabsorbent polymers (SAPs) can be expressed as a function of crosslinking density through Flory's elastic theory of dilute polymer solutions as represented by the following equation³⁵

$$Q^{5/3} = \frac{[(i/2V_u S^{1/2})^2 + (1/2 - X_i)/v_1]}{[V/V_0]} \quad (3)$$

where Q , V_e/V_0 , $[(1/2) - X_1]/V_1$, V_u , i/V_w , and S are the swelling capacity or 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. Therefore, Q is a function of the ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water. The first and second terms in the numerator belonging to forces 1. Free energy between chain networks of the polymers and external solvent, and 2. Electrostatic repulsion (Donnan effect) favor the promotion of swelling behavior.

In the present study, the influence of ionic monomer, namely calcium methacrylate, on the swelling behavior of crosslinked poly(AAm-co-CMA) superabsorbent copolymer was studied by varying the concentration of calcium methacrylate from 0.399 to 7.989 mM in the feed mixture of the superabsorbent copol-

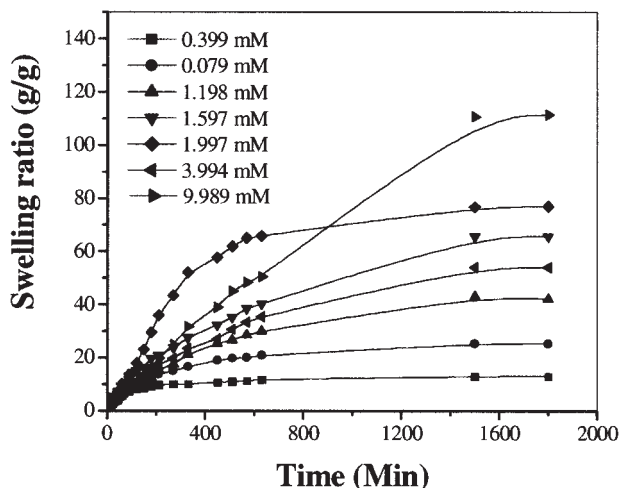


Figure 2 Swelling behavior of poly(AAm-co-CMA) superabsorbent copolymers crosslinked with DP.

mer. The swelling results as a function of CMA content is tabulated in Table II.

Figures 2-4 illustrate the swelling behavior of hydrogels crosslinked with DP, EGDMA, and MBA, respectively. In all the crosslinked hydrogels, it can be seen that swelling ratio (S) increases with time until a certain point, where it becomes constant. At a stage where there is no change in the weight of the gel with time, the swelling ratio of the hydrogel may be called "equilibrium swelling ratio or equilibrium swelling" (S_{eq}). The values of swelling ratio of crosslinked poly(AAm-co-CMA) superabsorbent copolymers are used for the calculation of swelling characteristics and to investigate the type of diffusion of water into gel networks. Most of the crosslinked poly(AAm-co-CMA) superabsorbent copolymers took 1750 min to obtain equilibrium swelling.

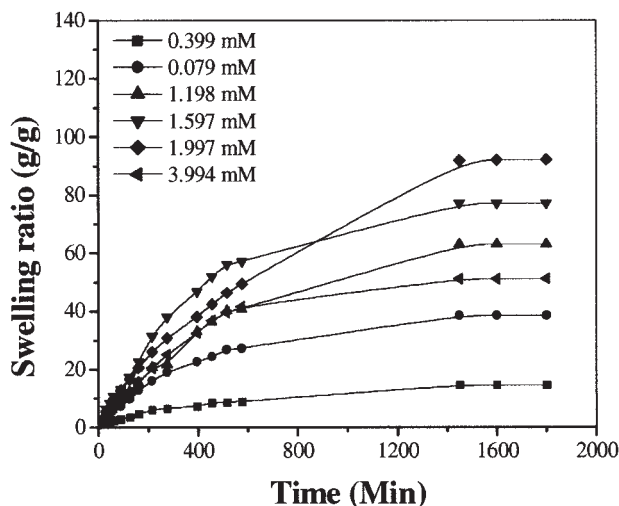


Figure 3 Swelling behavior of poly(AAm-co-CMA) superabsorbent copolymers crosslinked with EGDMA.

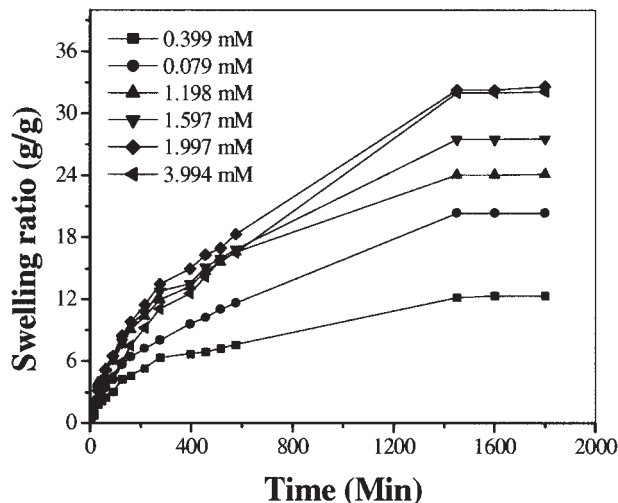


Figure 4 Swelling behavior of poly(AAm-co-CMA) superabsorbent copolymers crosslinked with MBA.

The equilibrium swelling ratio (S) increases from 12 to 111 g/g with increase of calcium methacrylate concentration from 0.399 to 7.989 mM for poly(AAm-co-CMA) superabsorbent copolymers crosslinked with DP (Fig. 2). This improved swelling behavior can be attributed only to increase in the CMA concentration in the copolymer. Thus, the concentration of fixed charges, i.e., i/V_u increases within the gel matrix and as predicted from eq. (3), the swelling ratio increases. Another possible explanation is that with increase of the number of carboxylate ions (COO^-) along the poly(AAm-co-CMA) chains, the resulting electrostatic repulsive forces among the COO^- groups become operative and causes to loosen the network chains and ultimately responsible for the increase of swelling capacity or sorption.

The poly(AAm-co-CMA) superabsorbent copolymers crosslinked with EGDMA and MBA as shown in Figures 3 and 4 also represented similar behavior as mentioned already. As CMA concentration increased from 0.399 to 1.997 mM, the equilibrium swelling behavior of copolymers increased from 14 to 92 g/g and 12 to 32 g/g for EGDMA and MBA crosslinked copolymers, respectively. A sudden fall in the swelling capacity is observed in the case of EGDMA crosslinked copolymer and a slight fall is noticed in the case of MBA crosslinked copolymer above 1.997 mM of calcium methacrylate concentration. This can be explained on the basis of increase in the number of poly(calcium methacrylate) chains, as the CMA concentration is increased beyond 1.997 mM thereby resulting in the formation of uncrosslinked or soluble polymer chains in the hydrogel matrix, which ultimately may results in the lowering of the swelling capacity.¹⁰⁻¹³ Further, a difference in the swelling behavior of hydrogel is noticed because of the presence

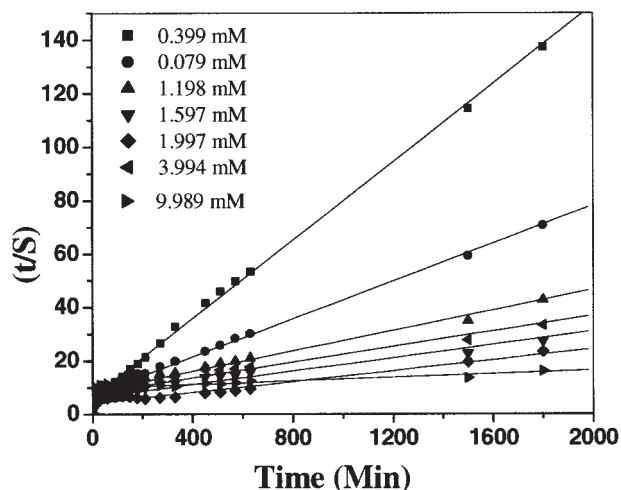


Figure 5 Swelling rate curves of DP crosslinked superabsorbent copolymers.

of different kind of network formation within the gel, which is caused by the nature of crosslinker.^{23,24}

But in the case of DP crosslinked hydrogel, the swelling capacity is continuously increased and this is due to the presence of highly elastic nature of the crosslinked gel. The main reasons for getting higher swelling absorbency for DP crosslinked superabsorbent copolymers were given in detail in our previous reports.^{23,24}

Percentage equilibrium water content (EWC%) is an important swelling characteristic of any hydrogel that

can be measured by using eq. (2). This characteristic also changed by varying the CMA content in the hydrogel. The hydrogels having higher EWC values shows higher swelling capacity. In the present investigation, all the hydrogels showed EWC values greater than 90%. The EWC values were found in between 92.90–99.10%, 93.60–98.92% and 92.51–97.02% for DP, EGMDA and MBA crosslinked hydrogels, respectively.

The hydrogels having equilibrium water content greater than 60% may exhibit resemblance with the fluid contents present in the living tissues. Therefore, these hydrogels may find better applicability in the fields of medicine, pharmacy, and in drug delivery as biomaterials.

Swelling and diffusion parameters

The swelling curves of crosslinked hydrogels are used for the calculation of certain swelling characteristics including, initial swelling rate (r_i), swelling rate constant (k_s), and theoretical equilibrium swelling (TS_{eq}). For estimating the swelling characteristics of poly(AAm-co-CMA) hydrogels, the following equation used:³⁶

$$t/S = A + Bt \quad (4)$$

where $B = 1/S_{eq}$ is the reverse of the equilibrium swelling, $A = 1/(k_s S_{eq}^2)$ is the reciprocal of the initial

TABLE III
Swelling Parameters of Crosslinked Poly(AAm-co-CMA) Superabsorbent Copolymers

	Initial swelling rate (r_i) [(g water/g hydrogel)/min]	Theoretical equilibrium swelling (TS_{eq}) [(g water/g hydrogel)]	Swelling rate constant (k_s) [(g hydrogel/g water)/min]
EGDMA	0.0458	17.45	1.50×10^{-5}
	0.1317	46.23	6.16×10^{-5}
	0.1429	84.96	1.98×10^{-5}
	0.2280	97.27	2.41×10^{-5}
	0.1719	129.53	1.02×10^{-5}
	0.1551	64.85	3.69×10^{-5}
	–	–	–
DP	0.1535	13.65	0.82×10^{-5}
	0.1361	28.20	1.71×10^{-5}
	0.1183	52.32	4.32×10^{-5}
	0.1626	80.00	2.54×10^{-5}
	0.2481	97.84	2.59×10^{-5}
	0.1274	68.58	2.71×10^{-5}
	0.1021	96.73	1.16×10^{-6}
MBA	0.0459	14.10	2.31×10^{-5}
	0.0574	24.56	9.51×10^{-5}
	0.0962	27.55	1.27×10^{-5}
	0.0878	32.58	8.27×10^{-5}
	0.0865	39.74	5.48×10^{-5}
	0.0636	43.17	3.41×10^{-5}
	–	–	–

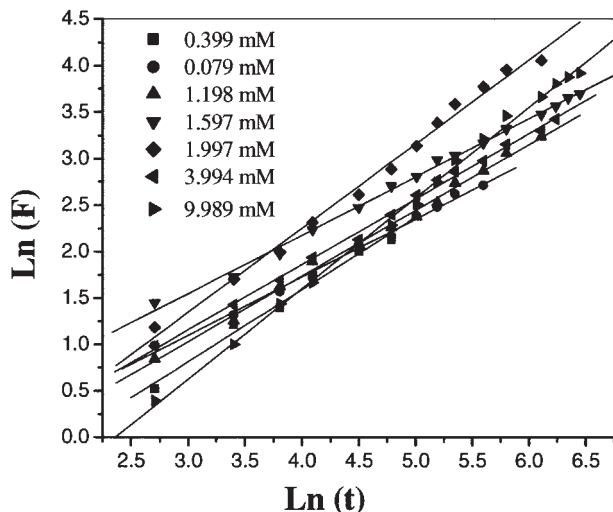


Figure 6 Swelling kinetic curves of DP crosslinked superabsorbent copolymers.

swelling rate of the gel, and k_s is the swelling rate constant. To examine the kinetic analysis for the crosslinked hydrogels, t/S versus t graphs were drawn and these graphs showed linear regression for the swelling curves obtained by means of eq. (4) for crosslinked poly(AAm-co-CMA) hydrogels. A representative t/S versus t graph for DP crosslinked poly(AAm-co-CMA) hydrogel is illustrated in Figure 5. The initial rate of swelling (r_i), swelling rate constant (k_s), and theoretical equilibrium swelling (TS_{eq}) of the hydrogels were calculated from the slope and intersection of the lines and the calculated results are tabulated in Table III.

Table III clearly indicates that the values of the theoretical equilibrium swelling (TS_{eq}) of the hydrogels are in good agreement with the experimental equilibrium swelling (S_{eq}) values of hydrogels. A similar behavior was noticed in the theoretical equilibrium swelling values with the experimental equilibrium swelling ratio values in our previous investigations for acrylamide-potassium methacrylate superabsorbent polymers,²³ acrylamide-sodium methacrylate superabsorbent polymers,²⁴ and semi-interpenetrating networks polymers composed of poly(vinyl alcohol).³⁷ Theoretical equilibrium swelling values are found in between 13.65–96.73; 17.45–129.53; 14.10–43.17 for DP, EGDMA and MBA crosslinked poly(AAm-co-CMA) superabsorbent copolymers, respectively. The initial swelling rate (r_i) values for DP, EGDMA and MBA crosslinked superabsorbent copolymers are found in the range of 0.1021–0.2481; 0.0458–0.2280; 0.0459–0.0962, respectively. The theoretical equilibrium swelling (TS_{eq}), initial swelling rate (r_i) and swelling rate constant (k_s) values of MBA crosslinked poly(AAm-co-CMA) superabsorbent copolymers have shown very lower swelling than EGDMA and DP crosslinked poly(AAm-co-CMA) superabsorbent copol-

ymers at all CMA concentrations. This lower swelling characteristic values for MBA crosslinked superabsorbent copolymers indicates their lower swelling capacity. These results are only possible due to higher crosslinking density within MBA crosslinked polymeric chains, which is directly related to swelling process.

To analyze the type of diffusion of water into superabsorbent copolymers, the swelling results obtained were utilized upto 60% of the swelling curves. The following equation was used to determine the nature of diffusion of water into hydrogels.³⁸

$$F = W_s - W_d / W_d = kt^n \quad (5)$$

where F , W_s , and W_d denote swelling ratio at time t , the weight of swollen superabsorbent polymer 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 type of water transport mechanism or type of diffusion. If $n < 0.50$ diffusion is of Fickian nature and if n is in between 0.50–1.0 the diffusion is non-Fickian type.

To evaluate the type of diffusion for the crosslinked poly(AAm-co-CMA) superabsorbent copolymers, graphs were plotted $\ln F$ versus $\ln t$ to yield straight lines. A representative graph is shown in Figure 6. The n values are obtained from the slope of the straight lines and the values are listed in Table IV. It can be observed from Table IV that n takes values in between 0.62 and 0.97 for DP crosslinked superabsorbent copolymers, thereby indicating the diffusion of water into the gels is of non-Fickian type. However EGDMA and MBA crosslinked poly(AAm-co-CMA) superabsorbent copolymers have n values in between 0.17–0.39 and 0.31–0.45, respectively, representing their Fickian diffusion phenomena.

pH sensitivity of hydrogels

The characteristic phenomena of pH sensitive hydrogels are the dynamic swelling corresponding to differ-

TABLE IV
Swelling Exponent Data of Crosslinked Poly(AAm-co-CMA) Superabsorbent Copolymers

S. No.	Swelling exponent (n)		
	EGDMA	DP	MBA
1	0.39	0.77	0.40
2	0.31	0.62	0.38
3	0.19	0.70	0.45
4	0.17	0.62	0.37
5	0.22	0.90	0.35
6	0.17	0.70	0.31
7	–	0.97	–

TABLE V
Swelling Ratio of Crosslinked SAPs in Different pH Solutions

pH	Swelling ratio (S)		
	DP	MBA	EGDMA
2	15.52	–	–
3	9.76	7.36	13.33
5	10.15	9.16	15.12
7	22.57	16.81	26.27
9	25.46	17.23	32.61
11	36.40	17.33	52.00

ent pH of the swelling medium. For instance, the dimensional change in hydrogels is only due to ionization transfer from the surrounding swelling media by acid or base groups contained in the gel matrix.^{39–42} The acid or base character of the swelling medium causes the gels to swell or shrink, but the gel normally keeps its overall geometry. Many of the applications of hydrogels in biotechnology, pharmaceuticals, controlled drug-delivery, and environmental fields are closely related to water or solute transport properties of the hydrogels.^{39–42} Therefore the present study is aimed to investigate the influence of pH sensitivity of crosslinked poly(AAm-co-CMA) hydrogels. The dependence of swelling behavior in pH solutions ranging from 2 to 12 is evaluated in detail. The hydrogels reached equilibrium swelling in about 1600 min in all the cases. Table V clearly demonstrates the pH sensitivity if hydrogels crosslinked by DP and indicates a uniform increase in their swelling capacity as the medium pH increases from 2 to 12. Similar increase in the nature of swelling capacity of the hydrogels crosslinked by MBA and EGDMA is also noticed, as shown in Table V. As the medium pH increases, the CMA ionizes and attracts the cations into the gel to replace the H⁺ ions. This effectively raises the concentration of mobile ions inside the gel and thereby the ion swelling pressure increases, which is responsible for higher swelling capacity of the gel. Further, the

results also indicate that the swelling capacity of IPNs is far below in all the pH solutions when compared in distilled water.

Thermal properties

Differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA) were employed to evaluate the thermal properties viz., the glass transition temperature (T_g), the decomposition temperature (T_d), and weight loss pattern of the hydrogels. Thermal stability of the hydrogels is very important since these materials are employed as water retention materials for water management in agriculture and horticulture applications.^{11–13}

The glass transition temperatures (T_g) determined for hydrogels by DSC is listed in Table VI. The T_g values obtained for the MBA hydrogels prepared with different CMA concentrations, are in between 165 and 168°C and 230–236°C due to the characteristic of the corresponding T_g values of their homo-polymers, poly(acrylamide), and poly(calcium methacrylate), respectively. In the case of EGDMA crosslinked hydrogels the T_g values obtained are in between 161 and 162°C and 224–231°C. It is clearly observed from Table VI that the decomposition temperature (T_d) decreased as the CMA content increased. This behavior is quite acceptable because, at a fixed concentration of crosslinker with the increase of monomer concentration will give loosely crosslinked networks to the hydrogels and thereby lowering their decomposition temperature.

Thermogravimetry of the crosslinked hydrogels using different amounts of CMA reveals variation in their thermal stability. Thermal decomposition behavior depends on the macromolecular characteristics of hydrogels and the type of crosslinking density. The DTG–TG curves of MBA and EGDMA crosslinked hydrogels showed two glasstransition peaks to support the results obtained in DSC study. These T_g values are tabulated in detail in Table VI. The peak decomposition temperature is noticed above 340°C for all the hydrogels. But, these de-

TABLE VI
DSC and TGA Analysis of Crosslinked Poly(AAm-co-CMA) Superabsorbent Copolymers

Polymer	DSC			TGA			
	T_g^1 (°C)	T_g^2 (°C)	Decomposition temperature, T_d (°C)	T_g^1 (°C)	T_g^2 (°C)	Decomposition temperature, T_d (°C)	Moisture content (%)
MBA 1	165	230	303	202	284	393	1.50
MBA 4	165	232	298	210	250	342	3.00
MBA 6	168	236	283	219s	248	340	3.70
EGDMA 1	161	224	405	212	283	394	1.04
EGDMA 4	161	227	369	214	251	345	3.62
EGDMA 6	162	231	363	–	250	343	2.90

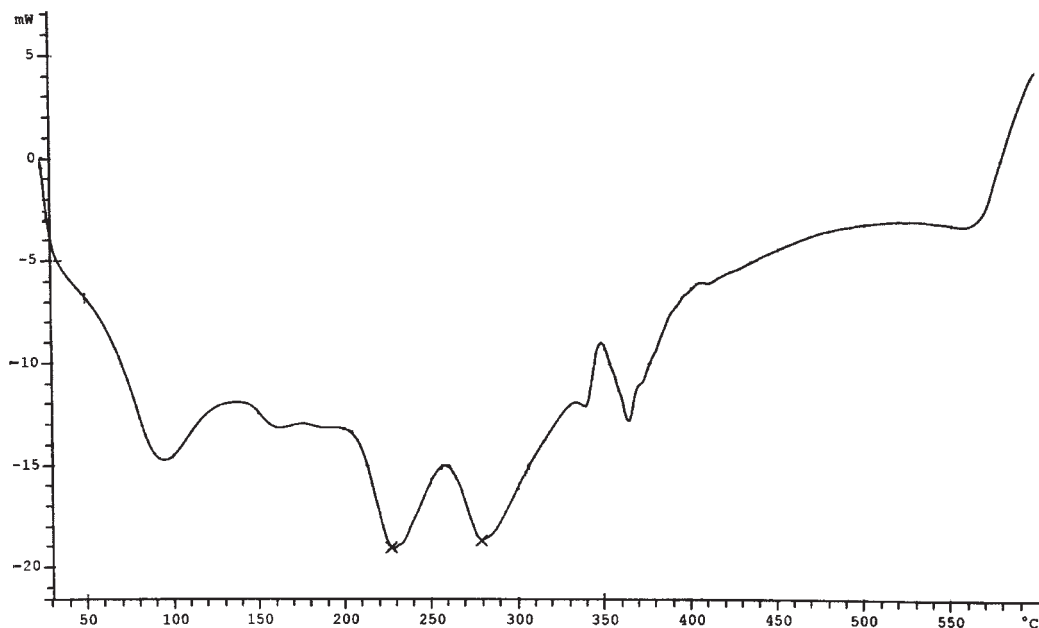


Figure 7 DSC thermogram of EGDMA 4.

composition temperatures decreased with increase of CMA content in the hydrogels. The same results are also obtained in the DSC analysis of these hydrogels. Our earlier report on poly(acrylamide-*co*-potassium methacrylate) hydrogels crosslinked with BDDA and EGDMA also supports for the presence of two glass transition temperatures in the DSC and TGA studies due to the phase separation behavior of hydrogels.^{23,43} The poly(AAm-*co*-CMA) hydrogels showed a broad decomposition pattern as that of acrylamide-potassium methacrylate hydrogels.²³ The moisture content present

in the hydrogels, as determined by Thermogravimetry analysis, also represent their swelling ability. The higher moisture absorbed by the hydrogels in turn indicates their higher swelling capacity. Representative DSC and DTG-TG thermograms are presented in Figures 7 and 8, respectively.

SEM studies

Morphology of the hydrogels is an important investigating factor because the network structure of the

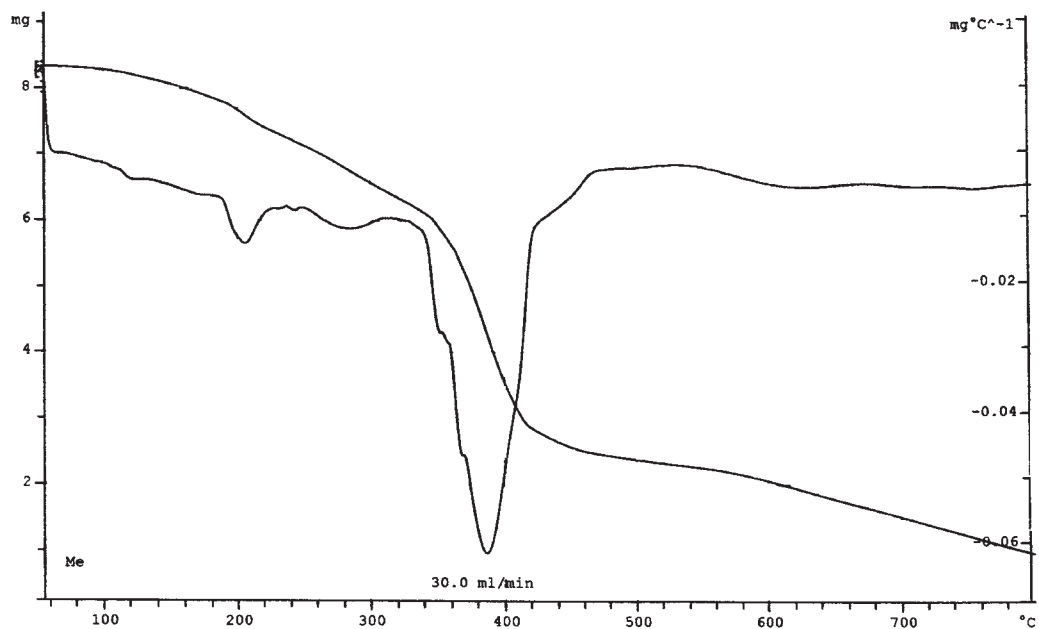


Figure 8 DTG-TG thermogram of EGDMA 1.

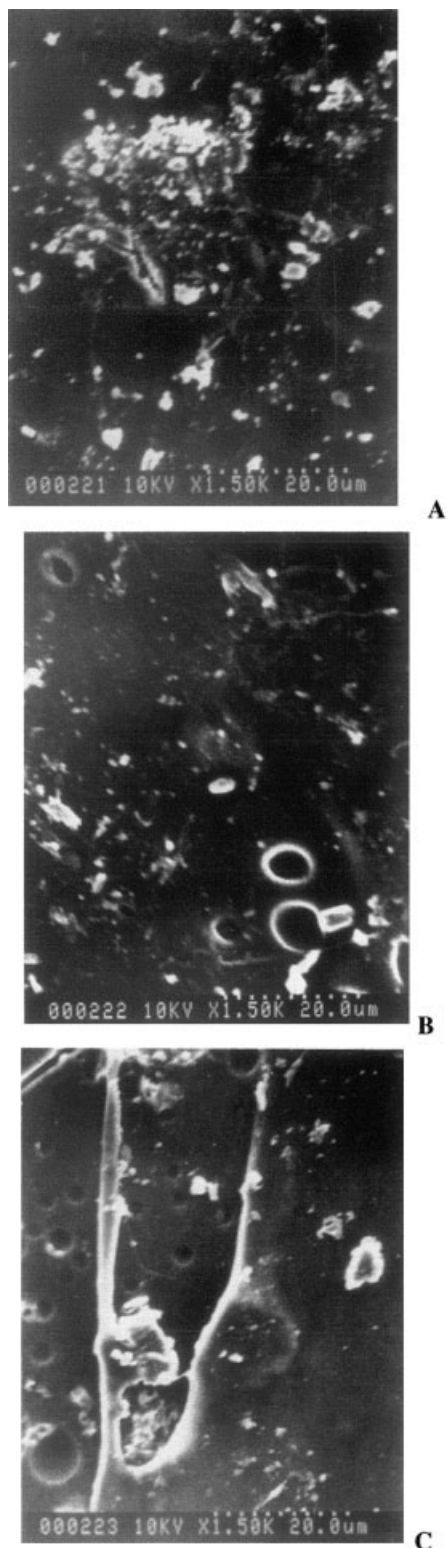


Figure 9 SEM photographs of (A) DP 1, (B) DP 3, and (C) DP 6 superabsorbent copolymers.

hydrogels is responsible for their swelling behavior. In this direction, the authors have recorded the SEM photographs for DP crosslinked hydrogels containing different amounts of CMA and the same are presented

in Figure 9. In these SEMs, it is clearly observed that there were few porous units in their network structure. However the MBA and EGDMA crosslinked hydrogels showed plain surface and have no porosity, as shown in Figure 10. The figure clearly represents for lower swelling capacities to the MBA and EGDMA crosslinked hydrogels because of their highly rigid type structure.

CONCLUSIONS

In this investigation, poly(AAm-co-CMA) superabsorbent copolymers were prepared by free radical polymerization in aqueous solution. Three different difunctional crosslinkers, such as EGDMA, DP, and MBA, were used in the polymerizations. Superabsorbent copolymers completely swollen in water took about 1750 min. Very high equilibrium swelling ratio of superabsorbent copolymer was found for DP crosslinked superabsorbent copolymers while MBA and EGDMA crosslinked superabsorbents showed lower values. This behavior is obtained for DP crosslinked superabsorbent copolymers due to elastic network formation in the gels. The equilibrium water content of these copolymers were found in the range of 92.51–99.11%. Further, the swelling (initial swelling rate, swelling rate constant, and equilibrium swelling) and type of diffusion of poly(AAm-co-CMA) superabsorbents were determined. Thermal stability of these copolymers were also shown in detail and moisture content in turn represent their swelling behavior. The morphological studies of poly(AAm-co-CMA) demonstrates that DP crosslinked copolymers showed loosely crosslinked network behavior whereas MBA or EGDMA crosslinked products are highly crosslinked in nature. Their pH dependence swelling property was also tested.

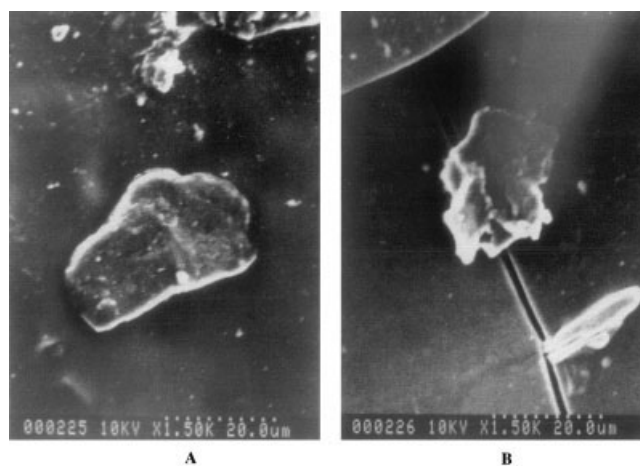


Figure 10 SEM photographs of (A) EGDMA 1 and (B) MBA 1 superabsorbent copolymers.

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