Swelling Behavior and Diffusion Studies of High-Water-Retaining Acrylamide/Potassium Methacrylate Hydrogels

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ABSTRACT: Poly(acrylamide-*co*-potassium methacrylate) hydrogels were prepared by free-radical simultaneous polymerization with aqueous solutions of acrylamide (AAm) and potassium methacrylate (KMA) with a redox initiator. The copolymerization was performed with eight different compositions of KMA at a fixed concentration of oil-soluble crosslinkers, including 1,4-butanediol diacrylate and ethylene glycol dimethacrylate (EGDMA). For every composition of AAm/KMA copolymer, the percentage swelling, swelling equilibrium, and diffusion characteristics were investigated. The copolymers were further studied for deswelling properties. The power law relationships of the hydrogels were evaluated for variation in terms of saline concentration. The AAm/KMA copolymers were confirmed by IR spectroscopy. Thermal studies of hydrogels were performed with differential scanning calorimetry and thermogravimetric analysis. EGDMA was found to be a better crosslinker for obtaining higher swelling and deswelling properties for the AAm/KMA hydrogels. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1153–1164, 2005

Key words: diffusion; hydrogels; swelling

INTRODUCTION

Hydrogels, or superabsorbent polymers (SAPs), are a very important class of materials and are of fundamental and technological interest.[1] Hydrogels are known as loosely crosslinked, three-dimensional networks of hydrophilic, swellable polymers that are capable of absorbing and holding a large amount of water, with the absorbed water is hardly removable even under some pressure.[1,2] Hydrogels have received much attention in various fields, including biotechnology, bioengineering, medicine, pharmaceutics, agriculture, horticulture, the food industry, and other advanced technologies, due to their excellent inherent characteristics, including a lack of toxicity, a high swelling capacity in aqueous environments, hydrophilicity, and biocompatibility.[3–8] These materials have established potential utilization in various biomedical applications, including drug-delivery system, contact lenses, and implants. Further, these materials are also exclusively used in many other applications, such as soil conditioners for agriculture and horticulture, feminine napkins, disposable diapers, water-blocking tapes, absorbent pads, gel actuators, drilling fluid additives, polymer-crack-blocking materials, firefighting, extraction of precious metals, extraction of solvents, and release of agrochemicals.[1,9–20]

Polyelectrolyte-type hydrogels, such as poly(acrylic acid),[21,22] poly(methacrylic acid),[23] poly(acrylamide-*co*-maleic acid),[24] poly(acrylamide-*co*-itaconic acid),[25] poly(acrylamide-*co*-crotonic acid),[26] dextrin–maleic acid,[27] acrylic acid-containing dextran hydrogels,[28] and chitosan/poly(acrylic acid) polyelectrolyte complexes,[29] undergo controllable volume changes in response to small environmental conditions, such as solvent composition, pH, ionic strength, temperature, and electrical stimuli. In fact, pH- and temperature-sensitive hydrogels are being used for an increasing variety of novel applications including site-specific drug delivery, controlled drug-delivery systems, and immobilized enzyme systems.[30,31] Yildiz et al. widely studied *N*-isopropylacrylamide based thermoresponsive hydrogels, such as poly(*N*-isopropylacrylamide-*co*-*N*-hydroxymethylacrylamide),[32] poly(*N*-isopropylacrylamide-*co*-acrylamide),[33] and poly(*N*-isopropylacrylamide-*co*-acrylamide-*co*-hydroxyehtyl methacrylate).[34]

Because of the increasing importance and wide range of usage of hydrogels, or SAPs, they require easy manipulation to attain good physical properties by a change in the monomers and polymerization

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Chemical name	Formula	Abbreviation
Acrylamide	$H_2C{=}CHCONH_2$	AAm
Potassium acrylate	$H_2C{=}C(CH_3)COOK$	KMA
N,N,N',N'-tetramethylethylenediamine	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	TMEDA
1,4-butanediol diacrylate	$[H_2C{=}CHCOOCH_2CH_2]_2$	BDDA
Ethylene glycol dimethacrylate	$[H_2C{=}C(CH_3)COOCH_2]_2$	EGDMA
Ammonium persulfate	$(NH_4)_2S_2O_8$	APS

conditions or processes. Generally, the synthesis of superabsorbent copolymers or hydrogels involves a multiple-step method or simultaneous copolymerization methods. In recent years, a lot of work has focused on the characterization and swelling behavior of hydrogels prepared by simultaneous free-radical copolymerization and crosslinking in the presence of an initiator or initiator pair (redox initiator–oxidizer) and a crosslinker.[35–40] Many studies have also dealt with a one-step polymerization and the gelation of acrylamide (AAm)-based SAPs with free-radical polymerization. In fact, we reported a few series of AAm-based tercopolymers with various comonomers through the use of simultaneous free-radical solution polymerization with various crosslinking agents and ammonium persulfate (APS) as an initiator at 80°C for horticulture and agricultural applications.[9–15]

Many attempts have been made to improve or modify these SAPs to increase their absorbency, gel strength, and absorption rates.[41–45] Flory explained the mechanism of water absorption in a nonionic or ionic network structure for hydrophilic polymers.[46] The kinetics of swelling of poly(sodium acrylate) with a microscope-VTR system and gravimetric and calorimetry techniques were reported by Ogawa et al.[47] Many researchers have also reported on the swelling behavior of the hydrogels. Bajpai studied both the swelling and deswelling behaviors of poly(acrylamide-co-maleic acid).[48] Karadag and coworkers also reported kinetic studies, network structure, and swelling behavior in aqueous salt solutions, apart from the swelling studies of hydrogel carriers for agricultural usage of poly(acrylamide-co-crotonic acid)[49] and the swelling kinetics of AAm/crotonic acid hydrogels.[35] Isik reported the swelling behavior and diffusion characteristics of AAm–acrylic acid hydrogels.[36]

In this study, we prepared hydrogels based on AAm and potassium methacrylate (KMA) with APS and N,N,N',N'-tetramethylethylenediamine (TMEDA) as the initiating system in the presence of multifunctional crosslinkers such as 1,4-butanediol diacrylate (BDDA) and ethylene glycol dimethacrylate (EGDMA). They have shown variation in their swelling behavior as the crosslinker is varied. In this article, we report the synthesis, characterization, swelling and deswelling studies, and the swelling kinetics of the novel superabsorbent copolymers. The swelling and deswelling properties of the copolymers and the power law relationships of saline solutions of the copolymers demonstrated their use as absorbent materials for environmental applications; biological, medical, and pharmaceutical applications; and biomedical materials.

EXPERIMENTAL

Materials

Double-distilled water was used for all of the copolymerization reactions and for swelling studies. AAm, methacrylic acid, APS, and methanol were supplied by S. D. Fine Chemical (Bombay, India). EGDMA, BDDA, and TMEDA were received from Sigma Aldrich Chemical Co. (Milwaukee, WI). All of the chemicals were used as received.

Preparation of KMA

Potassium hydroxide (1 mol) solution was prepared in methanol and titrated against acrylic acid (1 mol) taken in a 500-mL conical flask in methanol. The precipitated solid was filtered and dried *in vacuo*:

$$CH_2{=}CH(CH_3)COOH + KOH$$
$$\rightarrow CH_2{=}CH(CH_3)COOK \downarrow + H_2O$$
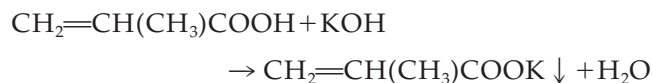
The IR spectrum of the KMA showed peaks at 1857 cm^{-1} (νC$=$O of the acrylate unit), 2941 cm^{-1} (—CH— stretching of the acrylate unit), and 1035 and 1234 cm^{-1} (—CO—O— stretching coupling interactions of the acrylate units).

Preparation of AAm/KMA hydrogels

The AAm/KMA hydrogels initiated by APS/TMEDA were prepared by the mixture of monomer solutions containing 1 g of AAm dissolved in 2 mL of distilled water and with various KMA comonomer compositions in the presence of a crosslinker solution of EGDMA (7.56×10^{-5} mol) or BDDA (7.56×10^{-5} mol). The list of monomers, crosslinkers, and the ini-

TABLE II
TABLE II
Reaction Composition of AAm/KMA Hydrogels Crosslinked with BDDA and EGDMA

Sample	Hydrogel	AAm (g)	KMA (g)	Water absorbency (g/g)	Swelling (%)	EWC %
1	BDDA1	1.0	0.00	7.44	744	99.9879
2	BDDA2	1.0	0.10	29.75	2,975	99.9986
3	BDDA3	1.0	0.15	50.60	5,060	99.9991
4	BDDA4	1.0	0.20	61.66	6,166	99.9990
5	BDDA5	1.0	0.25	78.25	7,828	99.9994
6	BDDA6	1.0	0.30	65.81	6,581	99.9990
7	BDDA7	1.0	0.50	61.35	6,135	99.9984
8	BDDA8	0.0	1.00	90.85	9,085	99.9989
9	EGDMA1	1.0	0.00	19.66	1,966	99.9920
10	EGDMA2	1.0	0.10	118.60	11,860	99.9993
11	EGDMA3	1.0	0.15	123.88	12,388	99.9992
12	EGDMA4	1.0	0.20	163.22	16,322	99.9994
13	EGDMA5	1.0	0.25	192.33	19,233	99.9996
14	EGDMA6	1.0	0.30	144.00	14,400	99.9992
15	EGDMA7	1.0	0.50	140.00	14,000	99.9995
16	EGDMA8	0.0	1.00	179.50	17,950	99.9996

Reaction conditions: samples 1–8: APS = 4.38×10^{-5}; TMEDA = 8.605×10^{-5}; BDDA = 7.567×10^{-5}; samples 9–18: APS = 4.38×10^{-5}; TEMD = 8.605×10^{-5}; EGDMA = 7.567×10^{-5}.

tiator used are given in Table I. The polymerizations were carried out in poly(vinyl chloride) straws (3 mm in diameter) at room temperature. The polymerization reactions were exothermic in nature, and all the ratios of monomers gave gels within 1 h of reaction time. However, the polymerization reactions were conducted for 24 h. The polymer gels obtained were cut into pieces of 3–4 mm in length. They were dried in air and then *in vacuo* and used for swelling and other studies. The conversion of the monomers was confirmed by gravimetric analysis, and it was also further confirmed by the complete incorporation of KMA into the AAm gel matrix. The complete synthetic details are given in Table II.

Swelling measurements

The swelling ratio was measured both in distilled water and in saline solutions. Preweighed dry hydrogels were immersed in solutions at a constant temperature until they swelled to equilibrium. It was confirmed that nearly 24–30 h was enough for the hydrogels to reach maximum equilibrium swelling. After excessive surface water was removed superficially with filter paper, the swollen hydrogels were weighed. The equilibrium water content (EWC) was calculated with the following expression:

$$EWC(\%) = [(M_e - M_d)/M_e] \times 100 \quad (1)$$

where M_e and M_d denote the weight of the swollen gel at equilibrium and the weight of the dry hydrogel at time 0, respectively. The swelling ratio ($S\%$) was cal-

culated as a function of time with the following equation:

$$Swelling\ ratio(\%) = [(M_s - M_d)/M_d] \times 100 \quad (2)$$

where M_s and M_d denote the weight of the swollen stage of the sample at a given time and at time 0, respectively.

IR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA)

The IR spectra of the copolymers were recorded on a PerkinElmer IR Subtech Spectrum ASCII PEDS 1.60 with KBr pellets and scanned from 400 to 4000 cm^{-1}. DSC experiments were performed with PerkinElmer DSC 7 (Serial No. 137380) equipment with aluminum pans under a nitrogen atmosphere at a scanning rate of 10°C/min. Thermal analysis of the copolymers was performed with a Universal V1.12E thermogravimetric analyzer from 50 to 800°C under a nitrogen atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

In this study, the AAm/KMA SAPs were prepared with a APS/TMEDA initiating system and BDDA or EGDMA as a crosslinker at room temperature. According to Karadag and coworkers,[35,38] the polymerization process starts with the reaction between APS and TMEDA to form an activated TMEDA molecule containing unpaired valence electrons. The unpaired valence electrons may interact with AAm, KMA,
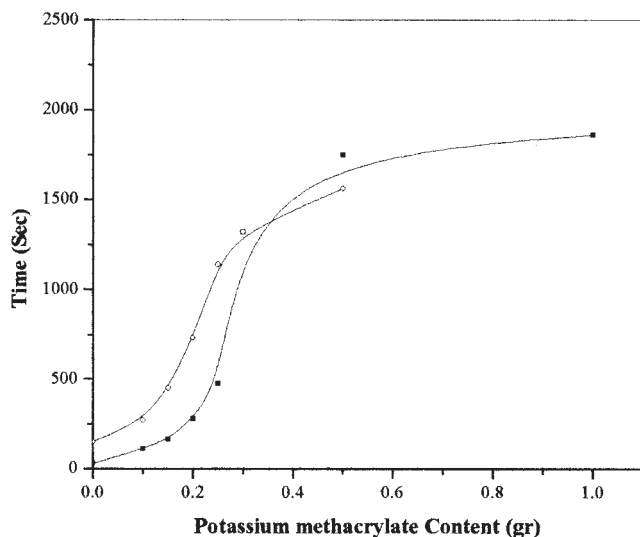
Figure 1 Representative graph of KMA content versus polymerization time for AAm/KMA hydrogel synthesis with (●) BDDA and (○) EGDMA crosslinkers.

crosslinker. However, the polymerizations were continued for 24 h to obtain good gelation. The gel time (gelation time or polymerization time) increased as the KMA comonomer content increased. This was due to a decrease in the total number of APS and TMEDA molecules, which were responsible for initiating the polymerization reaction. Moreover, the gelation times were varied as the chemical nature of the crosslinker changed. This effect is clearly shown in Figure 1. The AAm/KMA hydrogels crosslinked with EGDMA took higher gelation times than those crosslinked with BDDA. This may have been due to the structural variation of the crosslinker and reactivity. The AAm/KMA crosslinked copolymers obtained with EGDMA and BDDA as crosslinking agents were transparent in nature. EGDMA-crosslinked hydrogels were smooth and elastic in nature in the swollen stage, and BDDA-crosslinked hydrogels were very stiff and nonelastic in nature.

and/or the crosslinker, thereby initiating the polymerization, copolymerization, and crosslinking processes.

In the free-radical crosslinking copolymerization process, the crosslinking reactions considerably enhance the gel effect.[40] This is an autoacceleration reaction. This gel effect starts right from the beginning of the polymerization process, that is, even at zero conversion.[50–51] This copolymerization processes are exothermic in nature, and for the completion of these processes, it took a few minutes to half an hour only at any monomeric ratio to obtain the gel form. Karadag and Saraydin obtained high-water-retaining hydrogels within 1 h through the aqueous solution polymerization of concentrated monomers of AAm and crotonic acid.[35] However, in our synthetic polymerization reactions, it took shorter times (<30 min) because we used higher concentrations of the redox initiator and

IR analysis

The IR spectra of the copolymers showed peaks corresponding to the groups present in the copolymer repeating units. Peaks were observed at 3478 cm^{-1} corresponding to the N—H stretching of the AAm unit, at 1619 cm^{-1} corresponding to the C=O stretching of AAm unit, and at 1640 cm^{-1} corresponding to the C=O stretching of the acrylate unit. In addition to the previous peaks, peaks were also observed at 1271, 1265, and 1129 cm^{-1} corresponding to C—O—C stretching interactions of ester groups. The previous IR analysis of the samples indicated that the monomeric units, that is, AAm and KMA, were incorporated in the copolymer backbone. Figure 2 represents the IR spectrum of the EGDMA 5 hydrogel with a higher water absorbency.
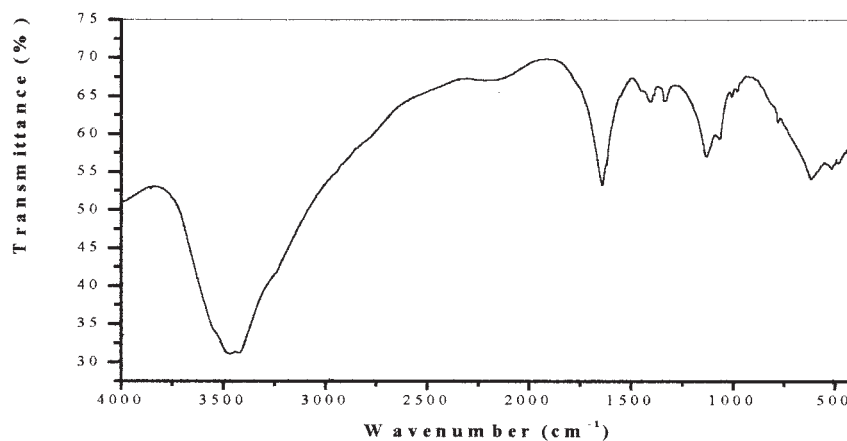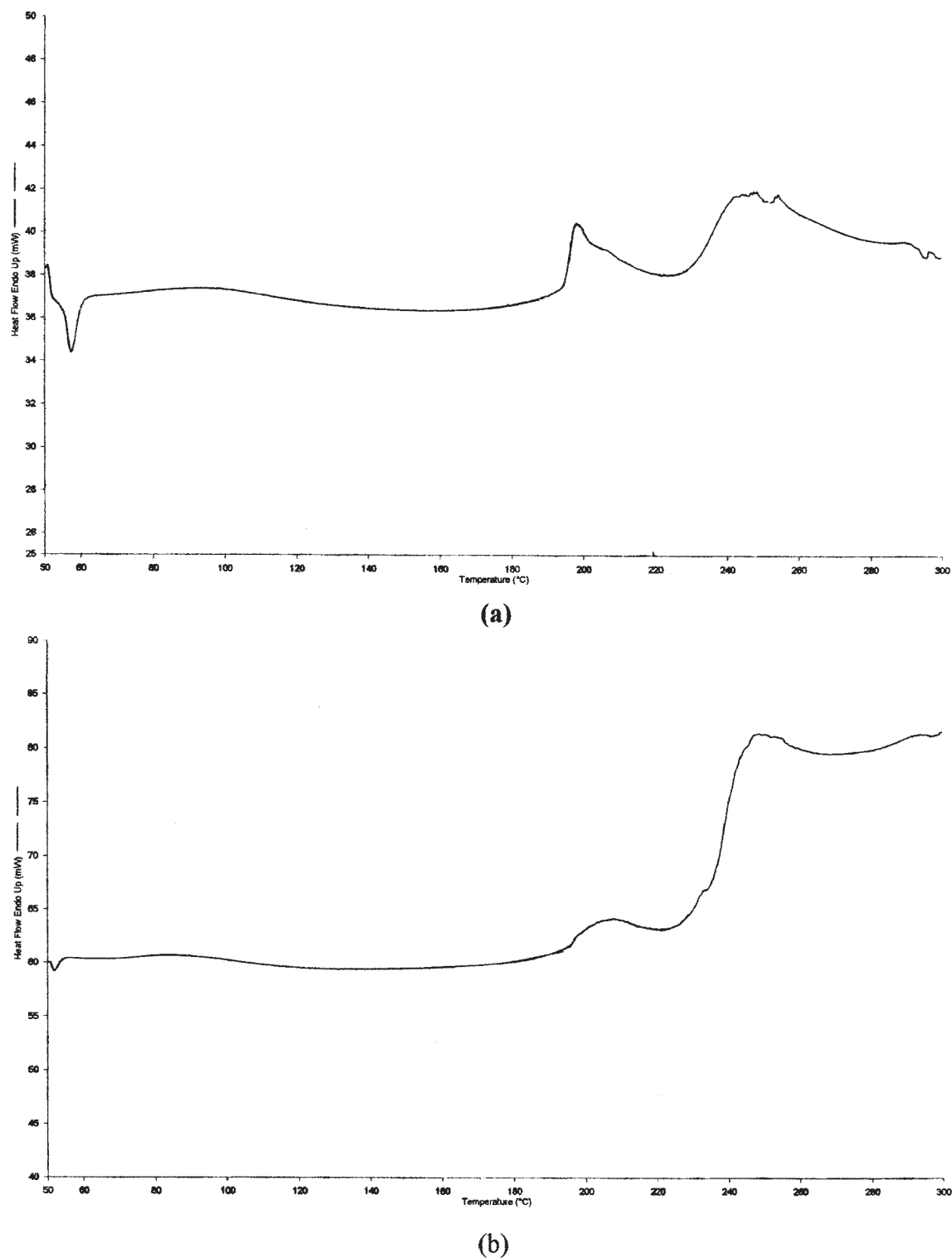

Figure 2 IR spectrum of the EGDMA 5 AAm/KMA hydrogel.

Figure 3 DSC curves of AAm/KMA hydrogels crosslinked with (a) BDDA and (b) EGDMA.

DSC and TGA

The thermal analysis of the AAm/KMA copolymers was investigated by DSC to obtain the glass-transition temperature (T_g) and decomposition temperature of the copolymers. As shown in Figure 3, the copolymers showed two endothermic peaks. Because the phase separation was anticipated to exist in the AAm/KMA copolymers, accordingly, they exhibited two glass-transition temperatures $(T_g^1$ and $T_g^2)$.[52] T_g^1 and T_g^2 were characteristic of the corresponding T_g values of their homopolymers, polyacrylamide and poly(potassium methacrylate), respectively. T_g values are found

at 198 and 247°C and 217 and 251°C for the copolymers crosslinked with BDDA and EGDMA, respectively. Similar results were also obtained in their TGAs. The TGA curves of the copolymers showed two exothermic peaks that were identified as their T_g values, corresponding to $T_g{}^1$ and $T_g{}^2$ (216 and 278°C for the EGDMA-crosslinked copolymer and 212 and 281°C for the BDDA-crosslinked copolymer). Their thermal stability was evaluated from the TGA. From the TGA curve as presented in Figure 4 (from 300 to 500°C), the BDDA-crosslinked AAm/KMA copolymer showed a higher number of decomposition regions, whereas the EGDMA-crosslinked copolymer showed a lower number of decomposition regions. The maximum peak decomposition temperature was identified at 464.75 and 456.75°C for the BDDA- and EGDMA-crosslinked AAm/KMA hydrogels, respectively. The maximum peak decomposition temperature value indicated the crosslinking nature of the copolymers. As the number of crosslinks increased in the copolymer, the peak temperatures increased. Further, this crosslinking nature was also responsible for the higher absorption properties.

Swelling and diffusion studies

A fundamental and well-accepted property of hydrogels, or SAPs, is their swelling behavior in aqueous, salt, and water-soluble organic solutions.[4–15] The swelling measurements are the main characteristic parameters for any hydrogel. Therefore, the swelling behavior of AAm/KMA hydrogels was studied in detail in this investigation.

In hydrogels, the copolymer ionic content is an important controlling factor for the swelling of the hydrogel apart from the gel structure. The effect of the AAm/KMA molar ratio on the swelling curve of the hydrogels was studied by the variation of the KMA comonomer. In all of the polymerizations, the AAm amount was fixed to 1 g/2 mL. The AAm/KMA hydrogels crosslinked by BDDA and EGDMA swelling isotherms are presented in Figure 5. As shown in the swelling curves, the swelling capacity of the hydrogels increased up to a certain time and remained almost constant after that. When the swelling reached a constant value for the hydrogels, that constant value was taken as the equilibrium swelling percentage ($S\%$ = Equilibrium swelling). Table II shows that higher $S\%$ values were obtained when the KMA content was increased in the copolymeric chains. The increment in $S\%$ values was due to the more hydrophilic nature of the incorporated chemical groups (—COO$^-$K$^+$).[4–15] This was due to induction of electrostatic repulsion forces of the ionic charges of networks.[4–15]

The equilibrium swelling percentage ($S\%$) value of the EGDMA-crosslinked copolymer of AAm increased from 1966 to 11,860 by the addition of just 10% of

KMA units in the polymeric structure, and this behavior continued as the insertion of KMA in the AAm copolymeric structure increased up to 25%. $S\%$ was as high as 19,233 for AAm copolymer containing 25% KMA. Further increases in the amount of KMA in the AAm copolymer did not increase the swelling equilibrium values; instead, there was a slight decrement in the values. However, the pure KMA polymer crosslinked with EGDMA had a higher water absorbency at the beginning, but this behavior decreased at the end and showed a lower swelling equilibrium value than the AAm/KMA (1:0.25) copolymer (Tables II and III). This may have been due to the formation of some amounts of soluble matter in the KMA crosslinked copolymer. The same behavior was also found in the equilibrium values of AAm/KMA copolymers crosslinked with BDDA. A high swelling equilibrium percentage was found for the AAm/KMA copolymer obtained with a molar ratio of 1:0.25. In the case of the KMA polymer crosslinked with BDDA, this copolymer had higher swelling equilibrium values than any of the AAm/KMA copolymers. This can be explained by the fact that the BDDA crosslinker may have given a KMA copolymer without any soluble matter due to its higher crosslinking reaction behavior than the EGDMA.

One novel observation made in this study was a high value of variation in $S\%$ of the AAm/KMA copolymers prepared in the presence of different crosslinkers.[9–15] This was mainly due to the difference in the crosslink network formation and the free-radical polymerization method used in this investigation. Further, the copolymers of AAm/KMA obtained by crosslinking with BDDA and EGDMA showed higher swelling equilibrium values when compared with AAm/CA crosslinked with 1,4-butanediol dimethacrylate (BDMA) and Trimethylolpropane triacrylate (TMPTA)[35] and AAm/AA copolymers crosslinked with N,N^1-methylenebisacrylamide (MBA).[36] This may have been strictly due to the difference in network formation or gel structure[52] and to the variation of the chemical structure, which was responsible for the hydrophilicity.[9–15,35,36]

The percentage equilibrium water content (EWC%)[53,54] was another parameter of the hydrogel characteristics, and this was calculated from eq. (1). The EWC values for the AAm/KMA hydrogels crosslinked with EGDMA and BDDA were high when compared with the AAm/CA hydrogels. The values for AAm/KMA hydrogels were between 99.9920 and 99.9996 and 99.9879 and 99.9994 when crosslinked with EGDMA and BDDA, respectively. Because of their higher EWC% values, these copolymers may behave similar to living tissues containing a high amount of fluids. Therefore, these crosslinked hydrogels may find an application in medicine and pharmacy as novel biomaterials.
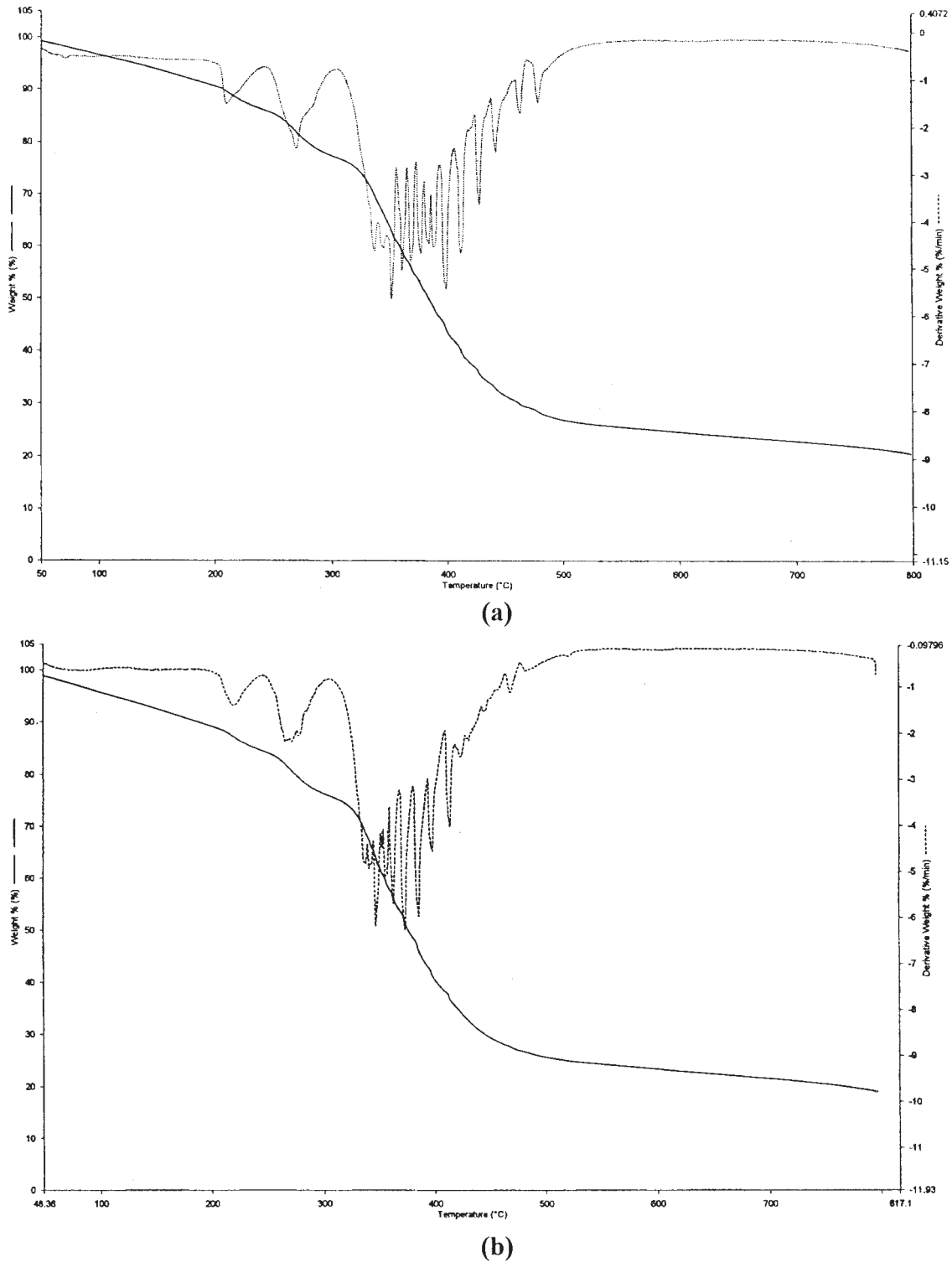
Figure 4   TGA thermograms of AAm/KMA hydrogels crosslinked with (a) BDDA and (b) EGDMA.

To evaluate the mechanism of swelling processes or extensive swelling, a simple kinetic analysis was followed with a second-order equation[55,56] as shown next:
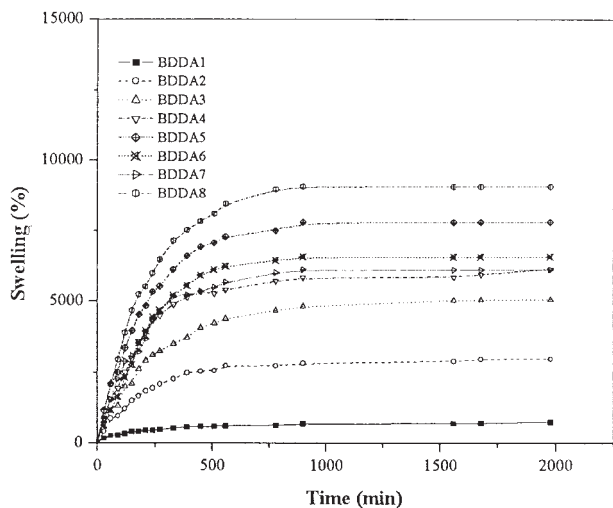
$$dS/dt = k_s(S_{eq} - S)^2 \qquad (3)$$

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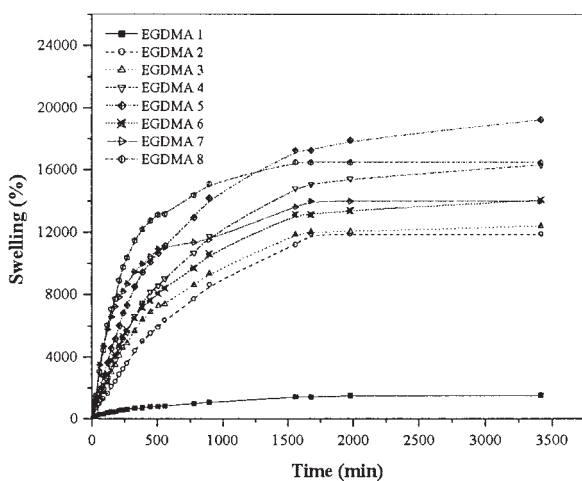
The integration of this equation over the limits S (swelling) $= S_0$ at time $t = t_0$ and $S = S$ at equilibrium at time $t = t$, gives the following equation:

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

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

(a)

(b)

Figure 5 Swelling isotherms of AAm/KMA hydrogels prepared with (a) BDDA and (b) EGDMA crosslinkers.

the initial swelling rate (r_i) of the hydrogel, and k_s is the swelling rate constant. This relation represents second-order kinetics. To examine this kinetic model, graphs were plotted of t/S versus t, and these are shown in Figure 6 for AAm/KMA crosslinked with BDDA and EGDMA. The swelling kinetics of the copolymers varied as the nature of the chemical groups (e.g., hydroxyl, carboxyl, carbonyl, amide, and amine) changed in the AAm copolymer chains. This was mainly due to the many types of polymer–solvent interactions.[4–8,35,36,57] r_i, k_S, and the theoretical equilibrium swelling (S_{eq}) values of the hydrogels were calculated from the slope and intersection of the lines, as shown in Figure 6. The calculated values are presented in Table III. The calculated theoretical equilib-

rium swelling values (S_{eq})of the hydrogels were in good agreement with the results obtained by the equilibrium swelling ($S\%$) of the AAm/KMA copolymers. From the swelling studies, we concluded that the swelling phenomena of the copolymeric hydrogels were directly related to the density of crosslinking networks[35,36,52] and the chemical repeating units present in the copolymers.[4–15,35,36]

SAPs, or hydrogels, which are considered as important materials in the fields of agriculture, biomedicine, pharmaceutics, and environmental engineering; it became necessary to know the diffusion mechanism of water in the polymeric chains. The diffusion of water takes place when the SAPs, or hydrogels, are brought in contact with water, and this happens by the migration of water into the free existing spaces between the polymeric chains.[58,59] The migration of water can be varied by changing the crosslink network formation in the copolymer. Crosslink network formation represents the free space or segmental motion of the polymeric chains. The increase in the segmental motion or free space within the polymeric system results in the increment in the diffusion of water due to an increase in the distance of separation between the polymeric chains. To evaluate the diffusion phenomena of AAm/KMA copolymers, eq. (5) was followed for up to 60% of swelling curves:[59,60]

$$F_{swp} = M_s - M_d/M_d = kt^n \tag{5}$$

where M_s and M_d denote the weight of the swollen hydrogel at equilibrium and the weight of the 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, a number used to determine

TABLE III
Swelling Parameters of AAm/KMA Hydrogels Crosslinked by BDDA and EGDMA

| Hydrogel	r_i[a]	k_s[b]	S_{eq}[c]
BDDA2	21.52853	2.07×10^{-6}	3.22×10^3
BDDA3	29.45508	9.28×10^{-7}	5.63×10^3
BDDA4	47.01457	1.09×10^{-7}	6.56×10^3
BDDA5	61.34969	8.41×10^{-7}	8.54×10^3
BDDA6	39.55696	7.12×10^{-7}	7.45×10^3
BDDA7	49.45598	1.11×10^{-6}	6.69×10^3
BDDA8	66.9344	6.70×10^{-7}	9.99×10^3
EGDMA2	18.89288	7.58×10^{-8}	1.58×10^4
EGDMA3	27.79322	1.26×10^{-7}	1.48×10^4
EGDMA4	29.29974	7.14×10^{-8}	2.03×10^4
EGDMA5	41.80602	8.32×10^{-8}	2.24×10^4
EGDMA6	34.07155	1.29×10^{-7}	1.63×10^4
EGDMA7	79.80846	3.59×10^{-7}	1.49×10^4
EGDMA8	84.45946	2.61×10^{-7}	1.80×10^4

[a] (g of water/g of hydrogel)/min.
[b] (g of hydrogel/g of water)/min.
[c] g of water/g of hydrogel.
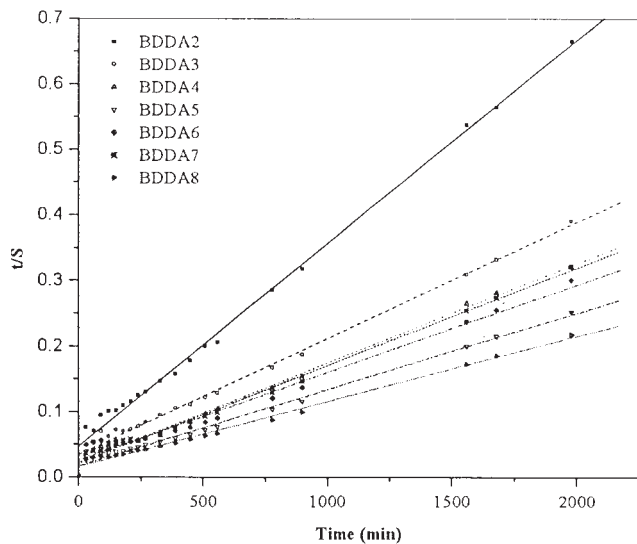
(a)
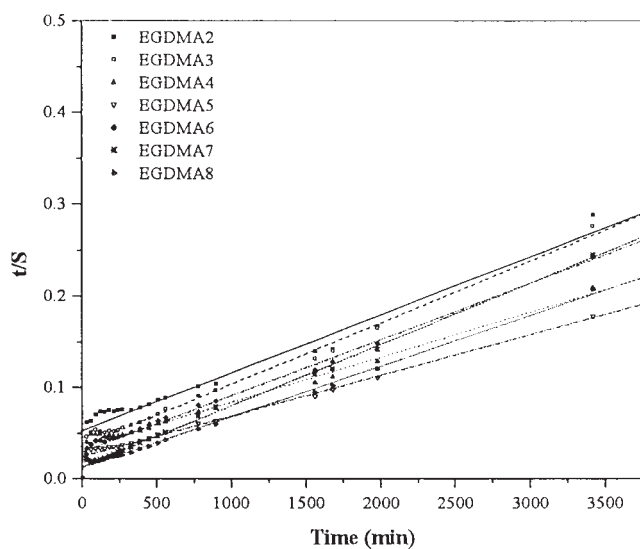
(b)

Figure 6 Swelling rate curves of AAm/KMA hydrogels prepared with (a) BDDA and (b) EGDMA crosslinkers.

the type of diffusion. For cylindrical shaped hydrogels, the n in which the rate of penetrant diffusion is rate-limiting is equal to 0.5. If during the swelling, non-Fickian diffusion occurs, the n values will be between 0.5–1.0.

To estimate n and k with the previous equation up to 60% of the swelling, graphs were plotted of $\ln F_{swp}$ versus $\ln t$ and obtained as straight lines, as shown in Figure 7. The n values were calculated from the slope of the lines of the $\ln F_{swp}$ versus $\ln t$ plots.[59,60] The values of n are presented in Table IV as a function of the comonomer (KMA). The calculated n values were

between 0.54529 and 0.94501 and 0.62941 and 1.00 for the BDDA- and EGDMA-crosslinked AAm/KMA copolymers, respectively. Hence, the diffusion of water into the gels was taken to be non-Fickian in character. In this diffusion, diffusion and relaxation can be said to be isochronal effective.[59,60]

Salinity

Salinity has a well-known influence on the swelling properties of hydrogels. The swelling behavior of the synthesized hydrogels of AAm and KMA monomers
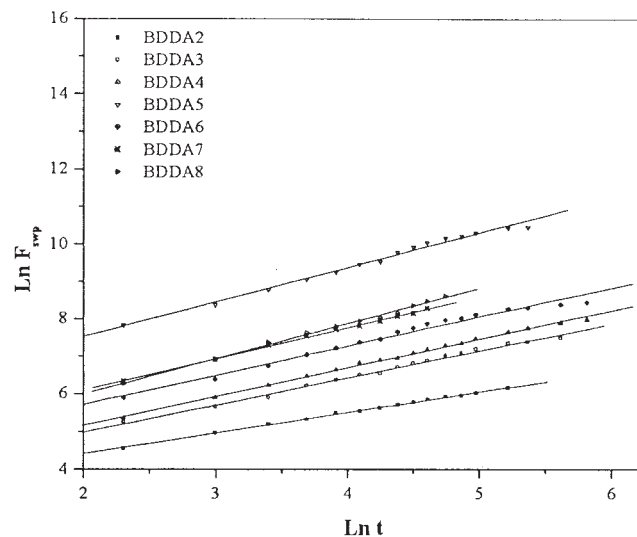
(a)
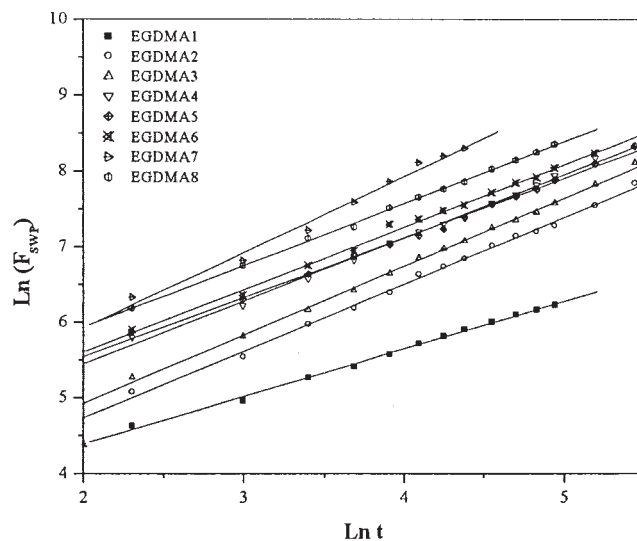
(b)

Figure 7 Diffusion kinetics of AAm/KMA hydrogels crosslinked with (a) BDDA and (b) EGDMA.

TABLE IV
Diffusion Parameters of the AAm/KMA Hydrogels

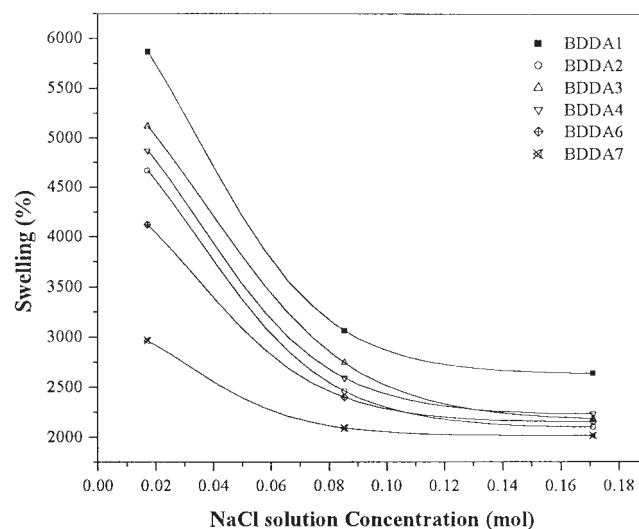| Hydrogel	k	n
BDDA2	27.85	0.54529
BDDA3	34.09	0.72425
BDDA4	37.59	0.76757
BDDA5	28.98	0.92750
BDDA6	63.73	0.78088
BDDA7	84.06	0.83399
BDDA8	60.29	0.94501
EGDMA1	22.80	0.62941
EGDMA2	19.21	0.88609
EGDMA3	22.45	0.90666
EGDMA4	43.45	0.83569
EGDMA5	52.31	0.78978
EGDMA6	52.07	0.82597
EGDMA7	50.15	1.00000
EGDMA8	73.15	0.81916

with BDDA and EGDMA crosslinkers were tested for three different sodium chloride solutions. The swelling capacity decreased as the sodium chloride concentration increased. Swelling studies for different saline concentrations were plotted, and these are presented in the form of a graph shown in Figure 8. The power law relationship was found for the dependence of the ultimate swelling ratio of the hydrogel on the saline concentration. The power law constants are presented in Table V.

Another aspect of the swelling in saline media is salt sensitivity, which may be evaluated by a dimensionless factor (α). α is defined as the ratio of the absorption in a given salinity to swelling in salt free water.[61] The α values for three saline concentrations are given in Table VI. The results indicate that the sensitivity of absorbance to changes in salinity decreased as the KMA content increased in the copolymer chain. This behavior was expected due to the increase in the KMA content in the copolymer chains, which expanded to its fullest extent, just as salinity did.[62]

Deswelling or water-retention capacity of SAPs

To understand the water retention of the AAm/KMA hydrogels synthesized by the redox free-radical polymerization with BDDA and EGDMA crosslinkers, the water-retention properties of the copolymers were carried out by deswelling experiments at room temperature.[9–15] Equal weights of swollen copolymer gels were taken in a watch glass, and the weight loss of water of the swollen gels was estimated by gravimetric analysis at different time intervals. A large variation in the deswelling behavior of EGDMA- and BDDA-crosslinked AAm/KMA hydrogels was observed. The deswelling studies indicated that the BDDA-crosslinked hydrogels had higher losses of water content with lower times than did the EGDMA-

crosslinked hydrogels. The deswelling curves of the AAm/KMA copolymers are illustrated in Figure 9. The BDDA crosslinked copolymers had 3.88–10.52 in its gel weight percentage within 2400 min, indicating a higher deswelling capacity, that is, a lower water-retention capacity, of these copolymers. In contrast, there were higher gel weight percentages for EGDMA-crosslinked hydrogels. This nature was easily identified when we saw the gels, where the copolymers still had 20% of the water content around the gels even after 4560 min. From these results, we concluded that the deswelling rates were slow and water-retention capacity was high for the hydrogel crosslinked by EGDMA.

(a)
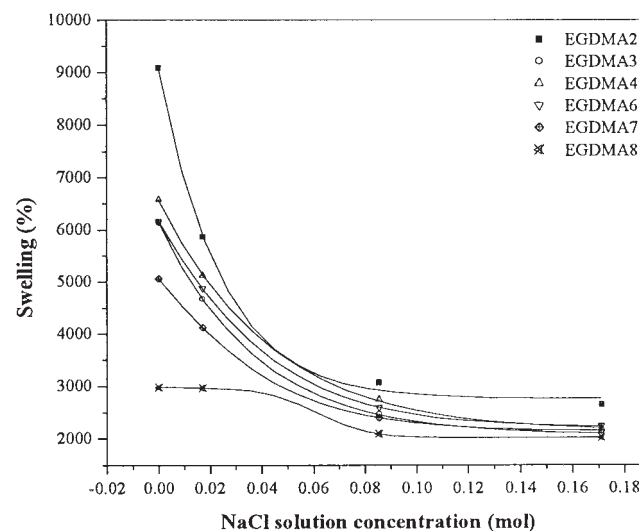
(b)

Figure 8 Swelling graph of AAm/KMA hydrogels crosslinked with (a) BDDA and (b) EGDMA.

TABLE V
Power Law Constants for the Swelling Dependency of Different Samples on the Salt Concentration (0–0.1711 mol)

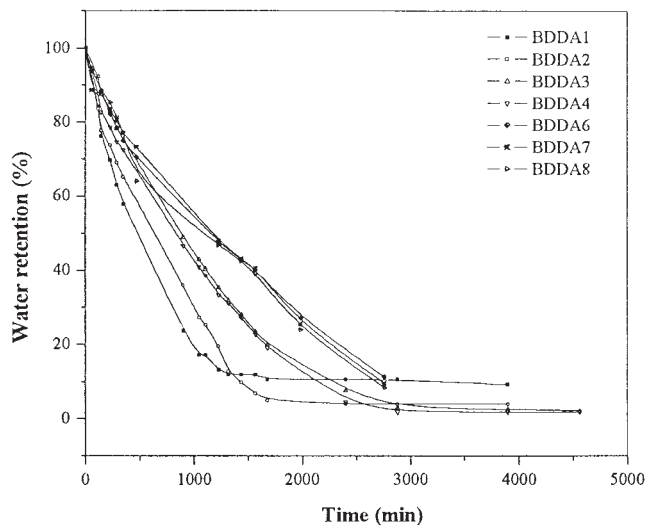| Hydrogel	k	n
BDDA1	600.31	0.03936
BDDA2	463.33	0.22339
BDDA3	628.43	0.28404
BDDA4	679.71	0.31921
BDDA6	730.24	0.33439
BDDA7	919.74	0.3526
EGDMA2	1347.8	0.35741
EGDMA3	1078.37	0.35644
EGDMA4	1115.73	0.37321
EGDMA6	1159.87	0.34901
EGDMA7	1235.98	0.29192
EGDMA8	1422.89	0.17685

Water-retention capacity of SAPs in soil

The main application of SAPs is for agricultural and horticultural purposes, for effective use of water, especially in dry and desert regions.[9–15] These SAPs can be used to transform dry and desert regions into fertile green lands. In this connection, the water-retention capacity of the prepared SAPs was preliminarily investigated experimentally in two different soils, instead of in growing plants. From the water-retention studies, we concluded that the water storage in the soil was high in the presence of AAm/KMA SAPs. This type of behavior is particularly useful for growing plants in dry and desert regions to convert them into green and fertile lands.

CONCLUSIONS

Hydrogels based on AAm and KMA were prepared by simultaneous free-radical polymerization with a AP/TMEDA initiating system and multifunctional crosslinkers (BDDA and EGDMA). The hydrogels prepared were characterized in terms of maximum $S\%$,

TABLE VI
Dependency of α on the AAm/KMA Hydrogels

Hydrogel	$\alpha_{0.017\%}$	$\alpha_{0.085\%}$	$\alpha_{0.171\%}$
BDDA1	0.92224	0.899504	0.856891
BDDA2	0.415532	0.212023	0.273395
BDDA3	0.402932	0.232593	0.215509
BDDA4	0.407884	0.233977	0.198116
BDDA6	0.440225	0.238059	0.208676
BDDA7	0.633552	0.348806	0.283857
EGDMA2	0.250071	0.176319	0.169757
EGDMA3	0.33268	0.193486	0.173661
EGDMA4	0.298724	0.158886	0.136623
EGDMA6	0.355546	0.190575	0.151622
EGDMA7	0.333608	0.175609	0.149918
EGDMA8	0.326963	0.170785	0.146879

(a)
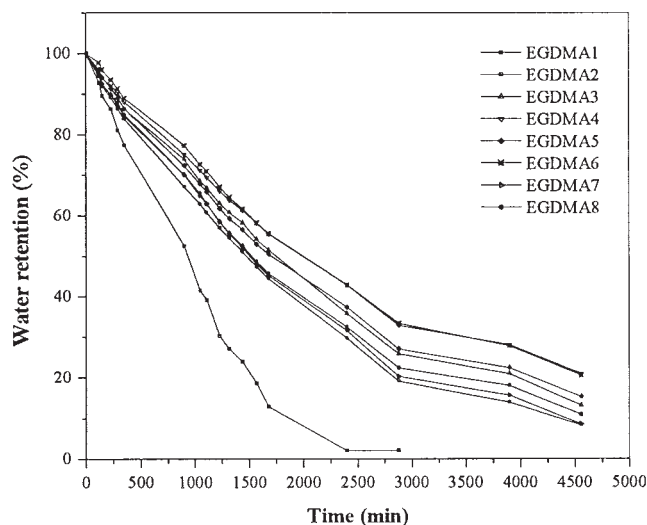
(b)

Figure 9 Water retention capacity of AAm/KMA hydrogels crosslinked with (a) BDDA and (b) EGDMA.

EWC, swelling, and diffusion. All of the hydrogels swelled rapidly and reached equilibrium within 24–30 h. BDDA 5 and EGDMA 5 hydrogels showed very high $S\%$ values of 7828 and 19,233 in their AAm/KMA hydrogel copolymer series and also showed high EWC values of 99.9994 and 99.9996, respectively. However, homo-KMA hydrogels had higher values than AAm/KMA hydrogels due to the more hydrophilic nature of groups in their polymeric chains. The hydrogel formation was confirmed by IR spectroscopy, and the thermal properties were studied with DSC and TGA. The deswelling properties were also investigated, and we found that BDDA-crosslinked

AAm/KMA hydrogels had higher deswelling natures than EGDMA-crosslinked AAm/KMA hydrogels. The power law relation was tested in saline solutions. Hydrogels were tested for soil moisture, and we found that these materials would be very useful as soil conditioners to convert desert or dry lands into green and fertile lands.

The obtained results from the deswelling and swelling studies of these hydrogels indicates that they will act as high water retainers for carrying various substances in aquatic fields, such as in agricultural, pharmaceutical, biomedical, and environmental applications.

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