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Effect of Potassium Methacrylate Content on Synthesis, Swelling, and Diffusion Characteristics of Acrylamide/Potassium Methacrylate Hydrogels

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Hydrogels based on acrylamide (AAM) and potassium methacrylate (KMA) were synthesized by simultaneous free radical polymerization in aqueous solution using the redox initiator ammonium persulfate (APS) and N,N,N'N'-tetramethylethylenediamine (TMEDA) at room temperature. Eight different compositions of KMA $hydrogels$ were prepared at a fixed concentration of N , N^{\prime} ,-methylenebisacrylamide (MBA) or diallyl phthalate (DP) as crosslinking agents. For all the AAM-KMA hydrogels, the percentage of swelling, swelling kinetics, and diffusion characteristics were investigated. It was found that higher swelling percentage values were obtained for hydrogels crosslinked with DP than for the conventional crosslinker MBA. The de-swelling characteristics of hydrogels were also studied in detail. The power law relationship of hydrogels was evaluated in saline solutions. Hydrogels formation was confirmed by IR spectroscopy. The thermal characteristics of these hydrogels were studied by using differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) and revealed that MBA crosslinked AAM-KMA hydrogels show higher glass transition temperature (Tg) as well as higher decomposition temperatures (Td) than DP crosslinked AAM-KMA hydrogels. It is further confirmed from the studies that the DP crosslinked hydrogels have good swelling as well as de-swelling and salinity characteristics.

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Keywords: superabsorbent polymer (SAP), hydrogel, swelling, de-swelling, thermal decomposition, non-fickian behavior

INTRODUCTION

A superabsorbent polymer or hydrogel can absorb a huge amount of water compared with general absorbing materials, in which the absorbed water is hardly removable even under pressure [1–2]. Because of their excellent characteristics, such as lack of toxicity, high swelling capacity in aqueous environment, hydrophilicity, and biocompatibility, these polymers were found to be useful in many areas, such as soil conditioners for agriculture and horticulture, disposable diapers, water blocking tapes, absorbent pads, gel actuators, drilling fluid additives, polymer crack-blocking materials, feminine napkins, firefighting, extraction of precious metals, extraction of solvents, release of agrochemicals, and so on where both water absorption and water retention is most important [1–10]. Many modifications were carried out in order to enhance their absorbency, gels strength, and absorption rate for hydrogels [3–5,11–20]. Further, pH and temperaturesensitive hydrogels are being employed as novel materials for various applications including controlled drug delivery and immobilized enzyme systems [21–25].

Due to their high importance in various fields, in recent years many authors have modified these hydrogels to increase their absorbency, gel strength, and absorption rates by varying the monomers, crosslinkers, initiating systems and polymerization techniques, and so on [11–12,16,18,26–30]. In this direction the authors have done substantial work on the synthesis of acrylamide-based superabsorbent copolymers [3–5,31–34]. Recently the present authors have reported in detail the effect of the crosslinkers butanediol diacrylate (BDDA) and ethylene glycol dimethacrylate (EGDMA) on the swelling properties of acrylamide-potassium methacrylate hydrogels [35]. In this article the authors report on the synthesis of hydrogels prepared from acrylamide and potassium methacrylate using the crosslinkers MBA and DP in aqueous solution, by using the APS/TMEDA initiating system. The relation between the composition of the copolymer hydrogel and their swelling behavior in water as well as in saline solution is studied. This article also deals with the swelling and diffusion kinetics and de-swelling characteristics. The hydrogel formation and their thermal studies are also studied.

EXPERIMENTAL

Materials

Acrylamide (AAM), methacrylic acid (MA), ammonium persulfate (APS), and N,N'-methylenebisacrylamide (MBA) were supplied by S. D. Fine-Chem Ltd. (Bombay, India). Diallyl phthalate (DP) and N,N,N',N'-tetramethylethylenediamine (TMEDA) were received from Sigma Aldrich Chem. Co. (India). All the chemicals were used as received. Doubly distilled water was used for all the copolymerization reactions as well as for swelling studies. Potassium methacrylate was prepared following the procedure given in Reference [35].

Hydrogel Synthesis

The AAM/KMA hydrogels were prepared by simultaneous free-radical polymerization in aqueous solution [13,35]. The polymerizations were carried out in PVC straws (3 mm dia) at room temperature. The potassium methacrylate, crosslinker, ammonium persulfate, and TMEDA were added in sequence to acrylamide dissolved in 2 ml of distilled water. N,N'-methylenebisacrylamide and diallyl phthalate were employed as crosslinkers in the polymerizations. The gels were cut into pieces of 3–4 mm length and dried in air and then under vacuum. The composition, swelling, and equilibrium swelling of the hydrogels are presented in Table 1.

Instruments

The IR spectra of the copolymers were recorded in a Perkin–Elmer IR SUBTECH SPECTRUM ASCII PEDS 1.60 using KBr pellets. Glass transition temperatures of the hydrogels were determined using Perkin–Elmer DSC 7 equipment with aluminum pans and a scan rate of 10°C/min under nitrogen atmosphere. The thermal analysis of hydrogels was performed by using Universal V1.12E Thermogravimetric Analyzer (TGA) with a heating rate of 10° C/min under nitrogen atmosphere.

Swelling Measurements

Pre-weighed dry hydrogels (40–50 mg) were immersed in an excess of doubly distilled water until they reached equilibrium at room temperature. After the residual water was removed superficially with filter paper, the swollen hydrogels were weighed. The equilibrium water

TABLE 1 Polymerization Conditions, Water Absorbency, Swelling (%), EWC and Density Details of Hydrogels

Reaction conditions (mole): MBA series: ammonium persulfate -4.38×10^{-5} ; TMEDA—8.605 \times 10⁻⁵; MBA—7.567 \times 10⁻⁵ and DP series: ammonium persulfate— 4.38×10^{-5} ; TMEDA— 8.605×10^{-5} ; DP—. 567×10^{-5} .

content (EWC) and swelling ratio $(S\%)$ of hydrogels were calculated by using the following expressions (1) and (2), respectively [13–14].

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

Swelling ratio
$$
(S\%) = [(M_s - M_d)/M_d) \times 100
$$
 (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.

RESULTS AND DISCUSSION

Preparation of Hydrogels

Hydrogels are generally produced by either chemical or irradiation techniques. Generally, the hydrogels can be prepared either by multiple step polymerization or by simultaneous polymerization. In recent years, a lot of work was done on synthesis of hydrogels by simultaneous free radical copolymerization using an initiator or initiator pair (redox initiator-oxidizer) and a crosslinker [13–14, 28,30,36–37]. It is known that the presence of initiator or initiating system can affect the structure of crosslinked network and phase behavior of hydrophilic polymers in solution, and also contributes inhomogeneity [28]. In fact, the present authors have reported a few series of acrylamide-based terpolymers using various comonomers by simultaneous free radical solution polymerization using APS as initiator for horticulture and agricultural applications [3–5,31–34].

It is believed that APS/TMEDA initiating system starts the simultaneous free radical polymerization of acrylamide/potassium methacrylate (AAM/KMA) by a reaction between APS and TMEDA to form an activated TMEDA molecule containing unpaired valence electrons. The unpaired valence electrons may interact with acrylamide, potassium methacrylate and/or crosslinkers, thereby initiating the polymerization, copolymerization, and crosslinking processes [13,38]. The present copolymerization processes are exothermic in nature and for the completion of these processes it took only a few minutes to half an hour for any monomeric ratio to obtain the copolymer in the form of a gel. The time taken for the completion of polymerization of these hydrogels is very low due to the employment of higher concentrations of initiator and crosslinker. The values are very low when compared with the acrylamide/crotonic acid (AAM/CA) hydrogels polymerization times as reported by Karadag and Saraydin [13]. The gel time (gelation time or polymerization time) increases as the potassium methacrylate content increases in the copolymer. It is noted that the AAM/KMA hydrogels crosslinked with DP have taken longer gelation times than with MBA and this effect is clearly shown in Figure 1. This may be due to the variation of reactivity of the crosslinker. Furthermore, the obtained gels crosslinked with MBA were hard even at the swollen stage, whereas hydrogels crosslinked with DP were very soft at the equilibrium stage.

IR Analysis

The IR spectra of the hydrogels have shown the peaks corresponding to the groups present in the hydrogel. The peaks were observed at 3463 cm^{-1} corresponding to the N-H stretching of the acrylamide unit, 1617 cm-¹ corresponding to the C=O stretching of acrylamide unit, 1647 cm^{-1} corresponding to the C=O stretching of the acrylate unit. In addition to the above peaks, peaks are also observed at 1249 cm^{-1} and 1129 cm^{-1} corresponding to C-O-C stretching interactions of ester groups. The earlier IR analysis of the samples indicates that

FIGURE 1 Effect of KMA content on gel time. \circ = MBA, \Box = DP.

the monomeric units, that is acrylamide, potassium methacrylate were incorporated in the copolymer backbone [5,39].

Thermal Properties of Hydrogels

The hydrogels were studied by differential scanning calorimeter (DSC) to determine their glass transition temperature (Tg) and melting point (Tm). As shown in Figure 2, the copolymers show two endothermic peaks. Therefore, a phase separation is expected to exist in the hydrogel [39]. The Tg 1 , Tm 1 , Tg 2 , and Tm 2 are 202.35°C, 205.86°C, 236.52°C, and 242.15 C for MBA 4 hydrogel; 202.58 C, 208.20 C, 265.58 C, and 266.82 C for DP 5 hydrogel. In the two series of hydrogels, it is observed that the Tg and Tm values are close to one another. The $Tg¹$ and $Tg²$ are characterized as the Tg of poly(acrylamide) and poly (potassium methacrylate) respectively, where the reference Tg values of their homo poly(acrylamide) and potassium acrylate are 165 C and 194 C [40].

Similar results were also obtained from TGA analysis. The TGA curves of the hydrogels have shown two exothermic peaks and were

FIGURE 2 DSC curves of hydrogels.

identified as their Tg values corresponding to Tg¹ and Tg² 208°C, 259 C for MBA 4 hydrogel; 214 C, 274 C for DP 5 hydrogel. The TGA curves shown in Figure 3 clearly demonstrate that MBA 5 has a larger number of decomposition regions, whereas DP 5 hydrogel has a smaller number of such regions. The onset and peak decomposition temperatures were identified at 346.01°C, 464.30°C for MBA 4 gel and 342.26 C, 462.77 C for DP 5 gel [39]. The maximum decomposition temperature of MBA hydrogel is higher than DP hydrogel due to higher crosslinking in the gel. This may cause the somewhat smaller swelling $(\%)$ of MBA hydrogels.

Hydrogel Swelling and Diffusion Studies

Equilibrium Swelling Percentage (*S%*)

The ionic content in hydrogels is an important controlling factor for swelling of the hydrogel apart from the gel structure and crosslink density. The effect of KMA content in the hydrogel on the swelling in distilled water was investigated for two series of hydrogels and shown in Figures 4. Figure 4a indicates that the equilibrium swelling percentage (%) of MBA series of hydrogels increases from 980 to 8000 as the KMA content increases in the hydrogel and the swelling (%) of hydrogel increases from 980 to 5075 by the addition of just 10% of KMA units in the AAM copolymer hydrogel. It is observed from the Figure 4b, in the DP series of hydrogels, the swelling increases enormously from 671.42 to 23650 as the KMA content increases and it is

FIGURE 3 TGA curves of hydrogels.

further noticed that the swelling $(\%)$ increased up to 14 times by the addition of just 10% of KMA content. The increment in equilibrium swelling percentage values is due to the more hydrophilic nature of the incorporated chemical groups $(-COO-K^+)$ [3-5,11,13]. This is due to induction of electrostatic repulsion forces of the ionic charges of networks [3–5,12–13,18]. A large degree of variation is observed in the equilibrium swelling percentage $(S\%)$ values between the two series of hydrogels. DP crosslinked hydrogels (DP series) were found

FIGURE 4 KMA content effect of hydrogel on swelling ratio. Top (A) MBA. Bottom (B) DP.

to have higher values of equilibrium swelling percentage than any one of the MBA crosslinked hydrogels. This may be due to the difference in the crosslink network formation of their hydrogels. It is also observed that the MBA and DP series hydrogels have shown higher swelling equilibrium values when compared with AAM/CA crosslinked with butanediol methacrylate (BDMA) and trimethylolpropane triacrylate $(TMPTA)$ [13] as well as acrylamide/acrylic acid (AAM/AA) copolymers crosslinked with MBA [14]. This is due to the difference in network formation and gel structure, as well as to the variation in the chemical structure [3–5,11–14].

Percentage Equilibrium Water Content

Another characteristic parameter of hydrogels is the percentage equilibrium water content ($EWC\%$) [13,41] and this is calculated from Eq. 1. The EWC% values were between 99.9949–99.9995 for the MBA series hydrogels and 99.9895–99.9997 for the DP series hydrogels. Because of the very high percentage equilibrium water content values, these hydrogels may behave similar to living tissues containing high amount of fluids. Therefore, these hydrogels may find applicability as biomaterials in the medicine and pharmacy fields.

Swelling Kinetics and Diffusion Kinetics

The mechanism of swelling processes of hydrogels was studied by using the equation [13–14,42] shown below:

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

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

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

where $B = 1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A = (1/k_S S_{eq}^2)$ is the reciprocal of the initial swelling rate of the hydrogel, and k_s is the swelling rate constant. This relationship represents a second order kinetics. To examine the aforementioned kinetic model, graphs were plotted of t/S versus t and they are shown in Figure 5a and b for MBA and DP series of hydrogels, respectively. The swelling kinetics of the hydrogels have varied as the nature of chemical groups (hydroxyl, carboxyl, carbonyl, amide, and amine, etc.) changes in the AAM copolymer chains. This is mainly due to many types of polymer–solvent interactions. The initial rate of swelling (r_i) , swelling rate constant (k_S) , and the theoretical equilibrium swelling (S_{eq}) values of hydrogels were calculated from the slope and intersection of the lines in Figure 5a and b. The calculated values are presented in Table 2. The obtained equilibrium swelling values of the hydrogels and the calculated theoretical equilibrium swelling values of the hydrogels are in good agreement. The swelling kinetics indicate that the swelling phenomena of the hydrogels are directly related to the chemical repeating units present in the hydrogel as well as the crosslink network density of the hydrogels [14].

It is also necessary to study the diffusion mechanism of water into the polymer matrix due to the importance of the diffusion of water in many applications including agriculture, biomedical, pharmaceutical,

FIGURE 5 Swelling rate curves (a) MBA series (b) DP series hydrogels.

and environmental engineering [13]. Diffusion of water takes place by the migration of water into the free existing spaces between the polymeric chains, when the hydrogels are brought in contact with water. As the segmental motion or free space within the polymeric system increases, the diffusion of water also increases. To evaluate the diffusion phenomena of hydrogels, the swelling data of hydrogels were fit into the following equation up to 60% of swelling [13–14,43].

$$
F_{swp}=M_s-M_d/M_d=kt^n\qquad \qquad (5)
$$

	Swelling rate parameters			Diffusion parameters	
Hydrogel	Initial swelling rate $(ii)^a$	Swelling rate constant $(k_{\rm s})^b$	Swelling equilibrium $(S_{eq})^c$	Swelling constant (k)	Swelling exponent (n)
MBA1				42.14	0.52
MBA ₂	13.74	3.45×10^{-7}	6.31×10^{3}	44.53	0.68
MBA3	41.99	1.48×10^{-6}	5.31×10^3	141.1	0.62
MBA4	56.40	7.60×10^{-7}	8.61×10^{3}	92.24	0.81
MBA5	63.69	1.75×10^{-6}	6.03×10^3	66.06	0.84
MBA6	39.98	1.01×10^{-6}	6.29×10^3	84.39	0.76
MBA7	74.12	3.05×10^{-6}	4.92×10^3	103.76	0.73
MBA8	48.85	3.64×10^{-5}	1.16×10^3	431.8	0.12
DP ₁				25.00	0.51
DP2	8.49	1.29×10^{-8}	2.56×10^4	15.14	0.86
DP ₃	33.03	1.34×10^{-7}	1.57×10^4	31.04	0.91
DP4	23.75	1.37×10^{-8}	4.17×10^{4}	18.40	1.00
DP5	24.10	4.72×10^{-9}	7.15×10^4	20.50	0.99
DP ₆	24.74	2.20×10^{-8}	3.36×10^4	24.51	0.96
DP7	52.68	6.75×10^{-8}	2.79×10^4	63.76	0.89

TABLE 2 Swelling and Diffusion Parameters of MBA and DP Series of Hydrogels

 α (g water/g hydrogel)/min; α (g hydrogel/g water)/min; α (g water/g hydrogel).

where M_s and M_d denote the weight of swollen hydrogel at equilibrium and weight of dried hydrogel at time $t = 0$ respectively; k is a swelling constant related to the structure of the network; and n is the swelling exponent, a number used to determine the type of diffusion. To determine the swelling exponents (n) and swelling constant (k), graphs were plotted of ln F_{swp} versus lnt and straight lines were obstained as shown in Figure 6a and b. The swelling exponents were calculated from the slope of the lines of ln F_{swp} - ln t plots. The values of n are presented in Table 2 as function of the comonomer (KMA). The swelling exponent values (n) were between 0.12–0.84 and 0.51–1.00 for MBA series and DP series of hydrogels, respectively. In the MBA series, pure KMA hydrogel has shown lower n value than any of AAM/KMA copolymers and as the KMA content increased from $0 g$ to $0.5 g$ in the copolymer hydrogel the n value has increased from 0.52 to 0.84. At further increase in KMA content, the n values slightly decreased. Similarly, the DP series of hydrogels have also followed the same behavior, that is, increase in the KMA content in the hydrogel increased the n values to certain extent and then decreased slightly. From the diffusion exponent values (n) of the hydrogels, it can be concluded that the diffusion of water into the hydrogels is non-fickian in character [13–14,44–45].

FIGURE 6 Diffusion curves of (a) MBA series and (b) DP series hydrogels.

Effect of Salt Solution on Hydrogel Swelling Behavior

Several factors of external solution, such as salt concentration and charge valencies, significantly affect the swelling behavior of the absorbents. Many authors have investigated the effect of various salt solutions of different concentrations on the swelling behavior of many series of copolymers [3–5,46–49]. The effect of salt solution on the swelling behavior of AAM/KMA hydrogel is investigated in this present study. Figure 7 shows the equilibrium swelling of AAM/KMA hydrogels as a function of NaCl concentration. These figures illustrate

FIGURE 7 Swelling behavior in NaCl solutions of (a) MBA series and (b) DP series hydrogels.

that the swelling $(\%)$ in salt solution decreases as ionic concentration of the salt solution increases. This is because the expansion of the gel network decreases due to repulsive forces of counter ions on the polymeric chain shielded by the bound ionic charge [46,48]. Therefore the osmatic pressure difference between the gel network and the external solution decreases with an increase in the ionic strength of the saline solution. Similar results were also reported by many researchers with various hydrogels, including poly(sodium acrylate-sodium 2-acrylamido-2-methyl propane sulfonate), poly(SA-NaAMPS);

	Power law constants		Dimensionless swelling factor (α)		
Hydrogel	k	n	$\alpha_{0.017}$	$\alpha_{0.085}$	$\alpha_{0.171}$
MBA ₂	782.61	0.214	0.371	0.257	0.227
MBA3	697.95	0.330	0.540	0.306	0.255
MBA5	784.60	0.327	0.524	0.524	0.247
MBA6	771.04	0.324	0.496	0.302	0.233
MBA7	868.84	0.290	0.612	0.361	0.319
M _B A ₈	925.57	0.005	0.835	0.832	0.807
DP ₁	496.28	0.161	0.950	1.000	1.000
D _{P2}	1594.85	0.179	0.385	0.672	0.258
DP ₃	1688.70	0.243	0.425	0.276	0.245
DP4	1693.46	0.312	0.328	0.194	0.161
DP ₅	2056.99	0.260	0.250	0.164	0.137
D _{P6}	1646.17	0.342	0.341	0.185	0.158

TABLE 3 Power Law Constants for Swelling Dependency of Different Samples on Saline Concentration and Dimensionless Swelling Factor on the Crosslinker Concentration

poly(sodiumacrylate-hydroxylethyl methacrylate), poly(SA-HEMA); poly[sodium acrylate-3,3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate] poly(SA-DMAPS) copolymers; and also including the authors' previous reports [46–49].

The aspect of the swelling in saline media due to salt sensitivity can be evaluated by a dimensionless factor (α) . The dimensionless factor α , is the ratio of absorption at a given salinity to swelling in salt free water [50]. The α values for three saline concentrations are given in Table 3. The results indicate that the sensitivity of absorbance to changes in salinity decreases as the crosslinker concentration decreases or KMA content increases in the hydrogel. A power law relation was determined for the dependency of the ultimate swelling on the saline concentration [17] and the power law constants are presented in Table 3. In both series of hydrogels, the exponent decreases with increment of salinity concentration. The constants attain lower values as the crosslinker concentration decreases or higher amounts of KMA are present in the hydrogels.

Water Retention Capacity

To determine the water retention capacity of the AAM/KMA hydrogels, the copolymers have undergone de-swelling experiments at room temperature [3–5,31–34]. 5–6 g of swollen hydrogels were taken on a aluminum foil sheet and the weight loss of water in the gels was

FIGURE 8 Water retention curves of (a) DP and (b) MBA series hydrogels.

estimated at different intervals by gravimetric method. A large variation was observed in the de-swelling behavior of the two series of hydrogels. The water retention de-swelling curves of the AAM/KMA copolymers are shown in Figure 8. De-swelling results indicate that the MBA crosslinked hydrogels have higher de-swelling capacity than the DP series of hydrogels. On the other hand, the DP series also has good water retention capacity. This nature is easily confirmed from Figure 8, where the DP series of hydrogels contain about 8.72 to 20.04 gel wt% even after 1840 min, whereas in the case of MBA hydrogel series the gel wt% is 8.49 or less at 1690 min. Furthermore, some hydrogels have lost all the water.

The superabsorbent hydrogels are highly valuable materials in agricultural and horticultural fields, to transform dry and desert regions into fertile green lands [3–5,31–34]. For this reason, the hydrogels were examined for water retention in two different soils, instead of growing plants. The water retention studies indicated that the water storage in the soil is high in the presence of AAM/KMA hydrogels when compared to blanks without hydrogels. This type of behavior is particularly useful for growing plants in dry and desert regions.

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