

Preparation of Acrylated Agarose-Based Hydrogels and Investigation of Their Application as Fertilizing Systems

Ali Pourjavadi,¹ Soofieh Sadat Afjeh,¹ Farzad Seidi,¹ Hamid Salimi²

¹Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran, Iran

²Iran Polymer and Petrochemical Institute, Tehran, Iran

Received 11 November 2009; accepted 14 February 2011

DOI 10.1002/app.34341

Published online 17 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, we attempt to synthesize novel acrylated agarose (ACAG)-based hydrogels with three different crosslinking densities. Acrylate groups were inserted onto agarose (AG) backbone through homogeneous reaction of acrylic monomers with AG backbone. Hydrogels were synthesized through radical copolymerization of a mixture of acrylic acid and 2-hydroxyethyl acrylate with ACAG in aqueous solution using ammonium persulfate as an initiator. Infrared spectroscopy (FTIR) was carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was assessed

by scanning electron microscopy. The equilibrium swelling capacities of synthesized hydrogels were evaluated in various conditions. The absorbency under load and dynamic swelling kinetics of the hydrogels were also studied. Finally, the hydrogels were loaded with potassium nitrate and their potential for controlled release of this salt was investigated by conductimetry. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2424–2432, 2011

Key words: acrylic acid (AA); acrylated-agarose; hydrogel; 2-hydroxyethylacrylate (HEA); swelling behavior

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymers that are capable of imbedding large amounts of water or biological fluids usually to equilibrium. The most common hydrogels are polyelectrolyte gels. Their superior swelling abilities originate from the electrostatic repulsion between the charges on the polymer chains and the osmotic imbalance between the interior and exterior of the gels. Hydrogel properties depend strongly on the degree of crosslinking, the chemical composition of the polymer chains, and the interactions of network and surrounding liquid.^{1–3} Because of their unique properties, these materials have become ubiquitous and indispensable materials in many applications in recent years.³

Conventional application of agrochemicals results in ground water contamination. Thus, we need a more controlled application of agrochemicals to reduce amounts of active ingredients without diminishing efficiency. The replacement of conventional agrochemical formulations by controlled release systems not only helps to avoid treatment with excess amounts of active substances but also offers the most suitable tech-

nical solution in special fields of application. In this context, hydrogels may show potential in such applications because of their excellent characteristics.^{4,5}

Synthetic methods have produced numerous hydrogel materials with excellent properties. However, their nonbiodegradability might pose long-term environmental problems and limit their use. As a consequence, various academic and industrial research groups have put considerable amounts of effort and resources toward development of new absorbent materials from natural polymers such as polysaccharides^{6–8} and proteins,^{8,9} which would decompose in landfills.

Agarose (AG) is an alternating copolymer of 3-linked β -D-galactopyranose and 4-linked 3,6-anhydro- α ,L-galactopyranose residues.¹⁰ It has been generally used as a cell immobilization matrix, drug delivery vehicle, or dental impression material because of its gelling ability and biocompatibility.^{11,12} Few chemical modifications on AG have been done and few AG derivatives such as O-acetyl AG,¹³ diethylamino ethyl AG, and carboxymethyl AG¹⁴ synthesized up to now.

According to the basic knowledge of superabsorbent polymer (SAP) hydrogels,³ small amounts of crosslinkers play a major role in modifying the properties of SAPs. In addition to modifying the swelling and mechanical properties, the crosslinker affects the amount of soluble polymer formed during the polymerizations. Recently, some research groups have taken into consideration, the study of the chemical nature of crosslinker^{15–17} and showed that it has a great influence on key parameters such as

This article is dedicated to Prof. M. J. Zohuriaan-Mehr (Iran Polymer and Petrochemical Institute) for his collaboration in development of novel SAP hydrogels for more than two decades.

Correspondence to: A. Pourjavadi (purjavad@sharif.edu).

absorbency under load (AUL),¹⁷ and also temperature and time of the hydrogel drying.¹⁶ In conclusion, crosslinker type and concentration has a great influence on the physical properties of SAPs. Therefore, various crosslinkers should be investigated systematically to achieve hydrogels with improved properties. This new practical research represents deeper physicochemical studies on the structure-property relation in SAP hydrogels.

On the other hand, using external crosslinker (like as *N,N'*-methylene bisacrylamide, MBA) in systems including a polysaccharide, crosslinker, initiator, and monomers results in a product that may be a mixture of homopolymeric (nongrafted) and copolymeric (grafted) networks. Formation of a semi-IPN or IPN network is also possible in some extent.¹⁸ But, with inserting acrylate groups onto the polysaccharide backbone, a macro-crosslinker (modified polysaccharide) is created. As a consequence, a single network is formed only.

Synthesis of novel fertilizing systems with improved properties is the aim of many research groups. In this study, we attempted to synthesize novel acrylated-agarose (ACAG) based hydrogels with different degree of crosslinking through radical graft copolymerization of ACAG with various degree of substitution (DS) with mixture of acrylic acid (AA) and 2-hydroxyethyl acrylate (HEA). According to our previous works on hydrogel hybrids with different AA/HEA weight ratios,¹⁸ with increase of HEA content salt sensitivity is improved in some extent. This is attributed to the existence of nonionizable OH groups. Thus, choosing HEA as one of the hydrogel components is quite reasonable. Swelling properties of the hydrogels in various conditions were studied. Finally, the hydrogel was loaded with potassium nitrate and its potential for controlled release of this salt was investigated by conductimetry.

EXPERIMENTAL

Materials

AA (from Merck, Darmstadt, Germany) as ionic monomer was distilled before use. AG was obtained from QUELAB/UK. Ammonium persulfate (APS, from Merck) as a water soluble initiator, HEA (from Fluka, Switzerland), acryloyl chloride (from Merck) were of analytical grade and used without further purification. The solvents (all from Merck) were used as received. All other chemicals were also of analytical grade. Double-distilled water was used for the hydrogel preparation and swelling measurements.

Instrumental analysis

¹H NMR spectra were obtained using a Bruker DPX 500 MHz spectrometer with D₂O as a solvent. The

extent of the esterification was determined from the ¹H NMR spectrum. FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer. Morphology of the dried gel structures was studied by scanning electron microscopy (SEM). Dried superabsorbent powder was coated with a thin layer of gold and was imaged in a SEM instrument (Philips, XL30).

Preparation of ACAG

A total of 2.0 g of dried AG was dissolved in 50 mL *N,N*-dimethylacetamide (DMAc) in 100°C. Then, the reaction flask was cooled to 0°C in an ice-water bath and a suitable amount (0.25, 0.50, and 1 mL) of acryloyl chloride (ACOC) diluted in 5 mL DMAc was slowly added over 10 min with stirring. After completion of the addition, the reaction mixture stirred at 0°C for 1 h and for a further 4 h at room temperature. The product was precipitated and washed thoroughly by acetone, and then dried in air at r.t. The DS was determined by the ¹H NMR spectroscopy.

Hydrogels synthesis

A 200-mL, three-necked, round-bottomed flask, equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 200 rpm) was charged with 35 mL of water and 1 g of ACAG and the mixture stirred for 10 min at r.t until a clear solution was obtained. The reactor was immersed in a thermostated water bath preset at 80°C. Then, 4.0 g of distilled AA [the AA component (4.0 g) has been partially neutralized (30 mol %)] and HEA (1.0 g) dissolved in 10 mL H₂O were added. After 5 min, APS (0.01 g) in 5 mL H₂O was added. After 10–15 min, obtained gel was cooled at room temperature and poured into a non solvent (acetone, 200 mL) and remained for 3 h to dewater. Then, acetone was decanted and the product was cut into small pieces (diameter, ~ 5 mm). Again, 200 mL fresh acetone was added and the hydrogel remained for 48 h. Finally, the filtered gel was dried in an oven at room temperature for 48 h. After grinding, the powdered hydrogel was stored away from moisture, heat, and light.

Swelling measurements

The tea bag (i.e., a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.1 ± 0.001 g) was immersed entirely in 200 mL distilled water or 0.15M of NaCl solution and allowed to soak for 1 h at room temperature. The sample particle sizes were 40–60 meshes (250–400 μm). The tea bag was hung up for 15 min to remove the excess

water. The equilibrium swelling (ES) was calculated according to following equation:

$$\text{ES(g/g)} = (W_2 - W_1)/W_1 \quad (1)$$

where W_1 and W_2 are the weights of dry and swollen gel, respectively. Therefore, the absorbency was calculated three times as grams of water per gram of the dry hydrogel (g/g).

The accuracy of the measurements was about $\pm 5\%$. The standard deviation(s) for a sample of data that are of limited size is given by the following equation:

$$s = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N - 1}} \quad (2)$$

where $(X_i - \bar{X})$ is the deviation from the average of i th measurements and N is the number of replicates of each measurement (for these measurements, $N = 3$).

Absorbency under load

AUL was measured according to a procedure reported earlier.¹⁹ A macroporous sintered glass filter plate (porosity 0, $d = 80$ mm, $h = 7$ mm) was placed in a Petri dish ($d = 118$ mm, $h = 12$ mm), and a weighed, dried hydrogel (0.3 ± 0.01 g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid weight (Teflon, $d = 60$ mm, variable height), which could slip freely in a glass cylinder ($d = 60$ mm, $h = 50$ mm) was used to apply the desired load [applied pressure 0.6 psi (4137 Pa)] to the dry hydrogel sample particles. Then, 0.15M NaCl solution was added so that the liquid level was equal to the height of the sintered glass filter. Whole of the set was covered to prevent surface evaporation and probable change in the saline concentration. After 2 h, the swollen particles were weighed again, and AUL was calculated according to eq. (1).

Swelling kinetics

For studying the rate of absorbency of the hydrogel, certain amount of sample (0.1 ± 0.001 g) with average particle sizes between 40 and 60 mesh (250–400 μm) was poured into a weighed tea bag and immersed in 400-mL distilled water. At consecutive time intervals, the tea bag was taken out from the water, hung up for 2 min to remove the excess solution, and then weighed. The water absorbency of the hydrogel at these time intervals was calculated according to eq. (1).

Absorbency at various values of pH

Individual solutions with acidic and basic values of pH were prepared by dilution of NaOH (pH 13.0)

and HCl (pH 1.0) solutions to achieve $\text{pH} \geq 6.0$ and $\text{pH} \leq 6$, respectively. Then, $0.1 (\pm 0.001)$ g of the dried hydrogel was used for the swelling measurements according to eq. (1).

Loading of KNO_3

The dry gel was put into a solution of KNO_3 and leave to swell for 2 h. The swollen gels were dried at 50°C . The percent loading was calculated by the following equation:

$$\% \text{ Loading} = [(m_1 - m_0)/m_0] * 100$$

where m_1 and m_0 are the weights of loaded gel and dry gel, respectively.

Determination of KNO_3 release

In a typical release experiment, the loaded gel with known weight (0.1 g, mesh 40–60) was placed in measured volume (200 mL) of distilled water (release medium) and was stirred mildly. The released amount of KNO_3 at different time intervals (Mt) was determined by measuring the conductivity of the release medium using a conductivity meter (Martini Instruments, Mi 170, EC/TDS/NaCl/Temp Meter). This was related to the amount of KNO_3 using a calibration plot.

RESULTS AND DISCUSSION

Spectral characterization of ACAG

The FTIR spectra of the AG and ACAG are shown in Figure 1. ACAG spectrum clearly shows a new absorption peak at 1720 cm^{-1} that can be attributed to C=O stretching. In addition, there is also a distinct absorption band within $3700\text{--}3140 \text{ cm}^{-1}$ corresponding to the hydroxyl group and two small peaks at 893 and 930 cm^{-1} , which is related to the unsubstituted D-galactopyranose unites and the 3,6-anhydro- α -L-galactopyranose unites, respectively.

The ^1H NMR (D_2O , ppm) spectra of AG (a) and ACAG (b) are shown in Figure 2. Appearance of olefinic hydrogens ($-\text{CO}-\text{CH}=\text{CH}_2$) in ^1H NMR spectrum [Fig. 2(b)] at δ 5.9–6.4 region is indicative of the partial modification. The DS was calculated from the integral ratio of δ 5.9–6.4 and that of the signals between 5.0 and 5.3 ppm, which were used as internal standard on the basis of the integral of all the osidic protons. The results are summarized in Table I.

Grafting of AA and HEA onto ACAG

The ACAG was copolymerized with two different monomers (AA and HEA). The reaction route and

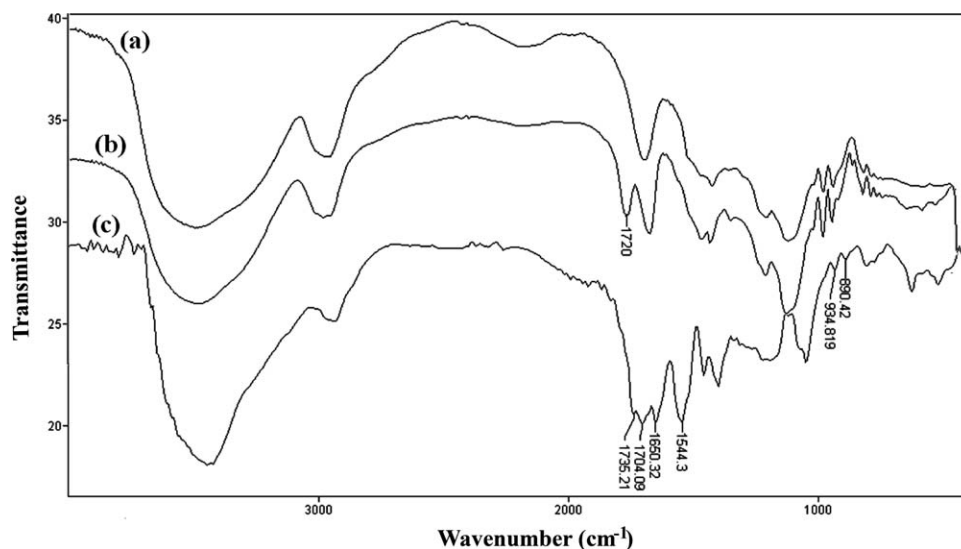


Figure 1 FTIR spectra of (a) AG, (b) ACAG, and (c) ACAG-g-poly(AA-co-HEA).

the chemical structure of the product are shown in Scheme 1. The reaction was conducted under normal atmospheric conditions. In fact, as previously described by Omidian et al.,^{20,21} because of the existence of an inhibition (retardation) period in such systems, which was followed by the onset of rapid, apparently normal polymerization, unrestricted access of the reaction mixture to oxygen, and unrestricted evaporative loss of water complicates the polymerization of the acrylic monomers and the swelling characteristics of the products; however, because of industrial necessity for the process simplicity, this approach has been of interest from the industrial point of view.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. The FTIR

spectra of ACAG and ACAG-g-poly (AA-co-HEA) were shown in Figure 1(b,c). The broad band at 3200–3500 cm^{-1} is due to stretching of hydroxyl groups of ACAG and poly (AA-co-HEA). Spectrum of ACAG-g-poly (AA-co-HEA) [Fig. 1(c)] shows three new peaks at 1705, 1650, and 1544 cm^{-1} , that can be attributed to the stretching of COOH, and asymmetrical and symmetrical stretching of $-\text{COO}^-$ groups, respectively. The peak observed at 1735 cm^{-1} is related to existing ester groups.

Figure 3 shows the SEM pictures of acrylated-agar based hydrogels. As it is obvious, these hydrogels have a highly porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

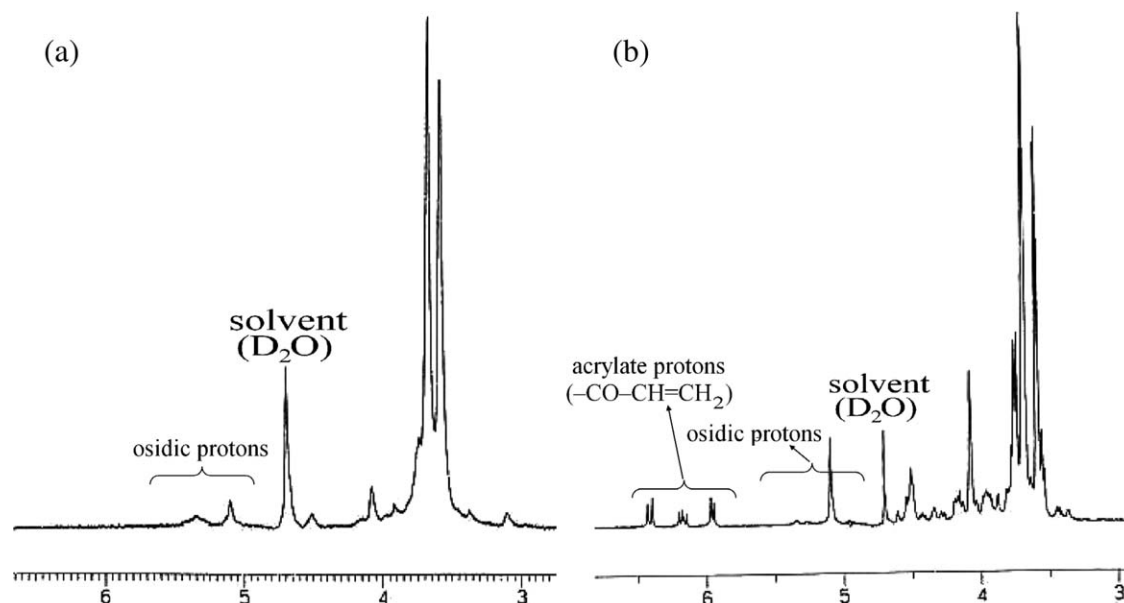


Figure 2 ^1H NMR spectra of (a) AG and (b) ACAG.

TABLE I
Substitution Degree (DS) at Different ACOCl/Glucosidic Unit Ratios

Sample	Agarose (g)	ACOCL (mL)	DS
1	2.0	0.25	0.22
2	2.0	0.50	0.50
3	2.0	1	0.80

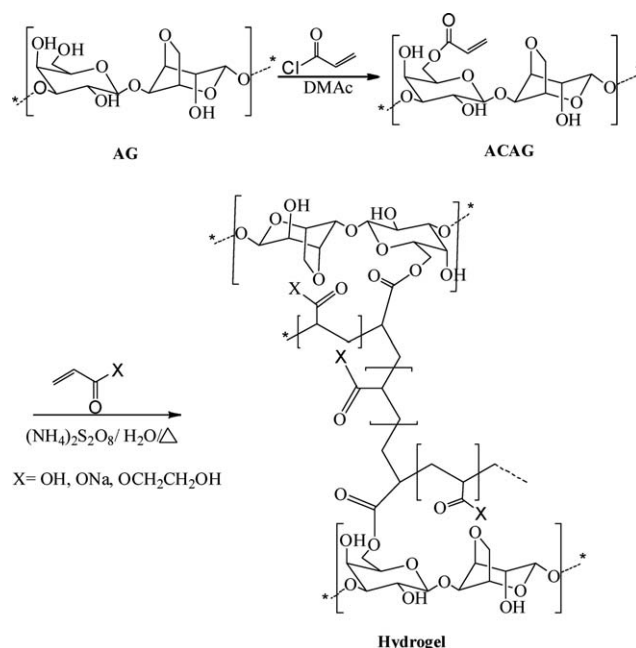
Effect of the DS of ACAG on the hydrogel swelling

During graft copolymerization process, existing acrylate groups on the AG backbone result in crosslinking of polymer chains. In other words, ACAG acts as a macrocrosslinker. Thus, with increasing the acrylate groups on the AG backbone, crosslinking density is increased too.

Second column of Table II shows the swelling ratio as a function of DS in distilled water. As it is obvious, maximum absorbency is achieved at the lowest of DS. In general, absorbency values are increased with a decrease in crosslinking density.²² Increasing the crosslinking agent and subsequently, the crosslinking density results in a highly cross-linked, rigid structure that cannot be expanded to hold a large quantity of water.

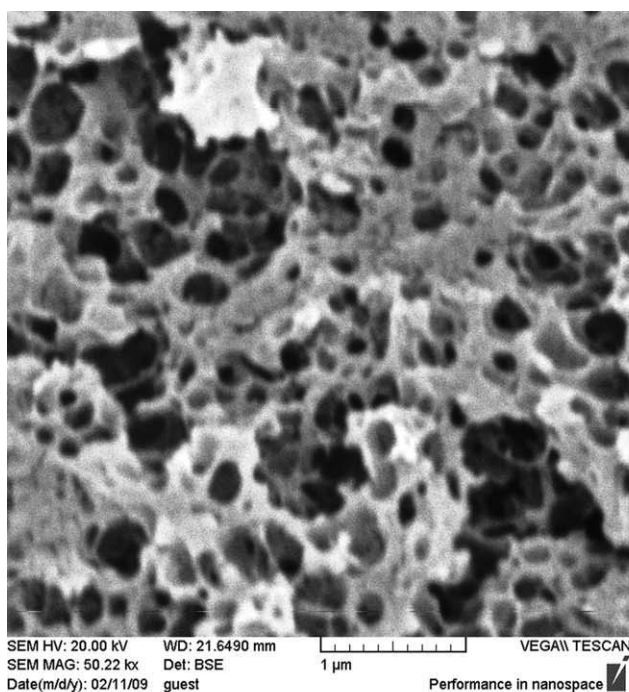
Absorbency under load

The AUL is an effective factor to investigate the swollen gel strength, which is usually given in the

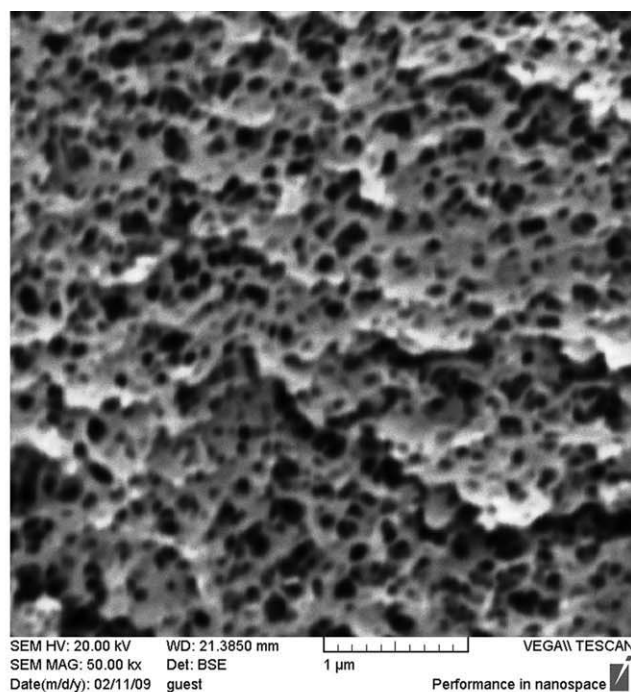


Scheme 1 Proposed reaction scheme for synthesis of ACAG-based hydrogels.

patent literature and technical data sheets offered by industrial hydrogel manufacturers. The AUL values of hydrogel samples are determined by using an AUL tester according to a procedure reported earlier.¹⁹ Figure 4 represents the AUL values of the hydrogels in saline solution (NaCl 0.15M) at r.t



(a)



(b)

Figure 3 SEM photographs of ACAG-g-poly(AA-co-HEA) hydrogel with DS = 0.22 (a) and DS = 0.50 (b). Surfaces were taken at a magnification of $\times 50,000$.

TABLE II
A Comparison between Strength of Hydrogels According to their Decreased Swelling under Loads

DS	Swelling in water (g/g)	AUL ^a	Ratio of AUL to swelling in water (%)
0.22	283	28.5	10.1
0.50	142	28	19.7
0.80	77	21.2	27.5

^a Under 0.6 psi in 0.15M NaCl solution after 30 min.

under the desired load [applied pressure 0.6 psi (4137 Pa)].

With applying the pressure (0.6 psi), the water absorbency of all three hydrogels decreased. Amount of decrement percentage is presented in Table II. With an increase of DS value, difference between values of AUL and that of free absorbency was decreased. Therefore, it can be concluded that with increasing the DS value, the mechanical strength of the hydrogel also rather increases.

Swelling kinetics

Figure 5 shows the dynamic swelling behavior of three hydrogel samples with certain particle sizes (40–60 mesh) in distilled water. Initially, the rate of water uptake sharply increases and then begins to level off. The initial swelling rate can be calculated using Voigt-based equation [eq. (3)].²³

$$S_t = S_e(1 - e^{-t/\tau}) \tag{3}$$

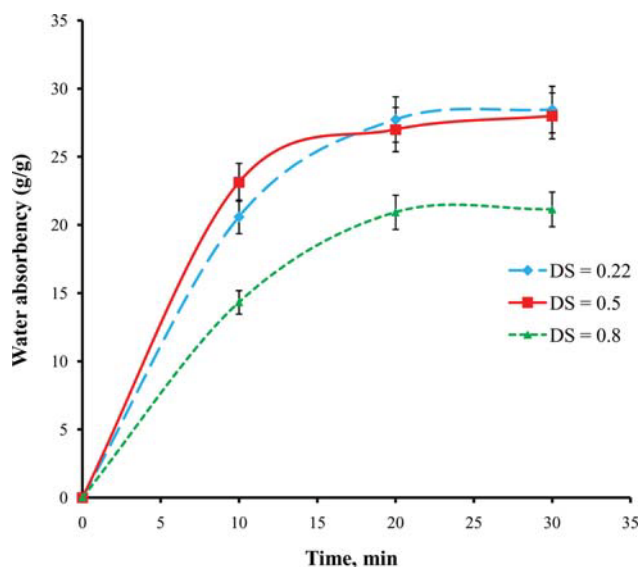


Figure 4 Time dependence of the AUL values for synthesized hydrogels swollen in 0.15M NaCl solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

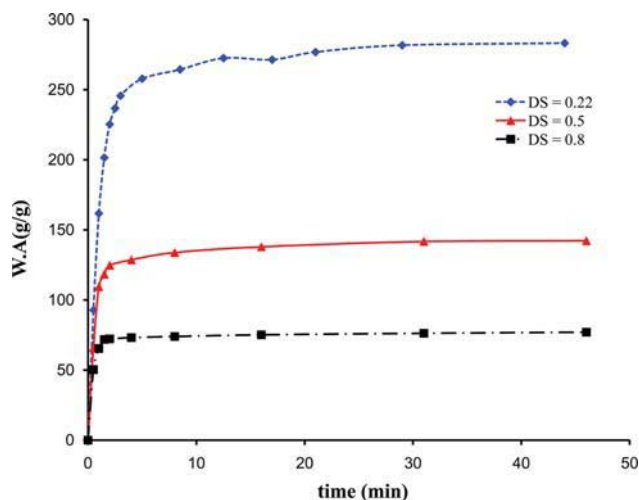


Figure 5 Representative swelling kinetics of synthesized hydrogels with various DS and certain particle sizes (40–60 mesh) in distilled water. W.A. stands for water absorbency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where S_t (g/g) is swelling at time t , S_e (power parameter, g/g) is ES; t (s) is time for swelling S_t , and τ (s) stands for the “rate parameter.”

To find the rate (τ) and power (S_e) parameters for superabsorbent samples, the data obtained from swelling of the hydrogels at consecutive time intervals were fitted into eq. (3) using Origin 6.1 software. The results are summarized in Table III. The values of swelling rate (SR, g/g s) for the individual samples were determined from the following equation^{18,24–27}:

$$SR = S_{m\tau} \tau_{min} \tag{4}$$

where $S_{m\tau}$ stands for swelling at the time related to the minimum rate parameter τ_{min} (s) (28 s in this case) obtained from superabsorbents from a set of similar experiments (Table III).

The SR are found to be 3.2, 2.3, and 1.7 g/g s for hydrogels with DS = 0.22, 0.5, and 0.80, respectively. In fact, in larger DS, the crosslinking density increases. Higher crosslinker density results in lower rate of swelling. This observation is reasonable, because water cannot easily and rapidly diffuse into a hydrogel network having high density of crosslinking.^{24,27}

TABLE III
Values of τ (s), S_e (g/g), $S_{m\tau}$ (g/g), and SR (g/g s) for Synthesized Hydrogels ($\tau_{min} = 28$ s)

DS	τ (s)	S_e (g/g)	$S_{m\tau}$ (g/g)	SR (g/g s)
0.22	70	272.7	89	3.2
0.5	43	136.6	65	2.3
0.80	28	74.7	47	1.7

Equilibrium swelling at various pH solutions

Ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pH values. Since the swelling capacity of all "ionic" hydrogels is appreciably decreased by addition of counter ions to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH = 13.0) and HCl (pH = 1.0) solutions were diluted with distilled water to reach desired basic and acidic pH values, respectively.

Figure 6 shows the effect of pH on the swelling ratio of the hydrogel. The results clearly indicate that the hydrogel exhibits extremely low degree of swelling in the media with low pH (pH < 3), whereas the gel demonstrates extensive swelling in the swelling media of pH ~ 8–9. The low swelling in the media with low pH may be attributed to the fact that the -COOH groups present along the macromolecular chains in the matrix remain almost unionized, thus resulting into almost nil osmotic swelling pressure as there are no mobile/counter ions present inside the gel matrix. In addition, there occur H-bonding interactions among the carboxylic groups within the matrix, thus providing a compact H-bonded structure to the hydrogel, which ultimately restricts the movements of polymeric segments and highly discourage the solvent entrance. However, when the gel is put in the medium of pH ~ 8–9, the ionization of -COOH groups not only increases the osmotic swelling pressure but it also results in relaxation of polymeric chains due to repulsion among similarly charged -COO^- groups along the macromolecular chains. This causes extensive swelling of the hydrogel as indicated by higher water uptake value of the gel. The swelling-loss in the highly basic solutions may be attributed to the "charge screening effect" of excess Na^+ in the swelling media, which, in turn, shields the carboxylate anions and prevents effective anion–anion repulsion.²⁸

Release study of KNO_3

The release of an active agent from swellable polymeric matrix is an important aspect of hydrogel. The release of solute from loaded hydrogel involves the sorption of water into the matrix and simultaneous release of solute via diffusion.²⁹ The concentration difference of solute between medium and hydrogels drives the solute out of the loaded hydrogel, but the special space arrangements of functional groups constructed by hydrogen bonds hinder solute to migrate out. The release kinetics of a loaded hydrogel is closely related to its water sorption kinetics, that is, initially, the rate of release sharply increases and then begins to level off. As a result, a highly swelling hydrogel should release a greater amount of solute entrapped within the gel.

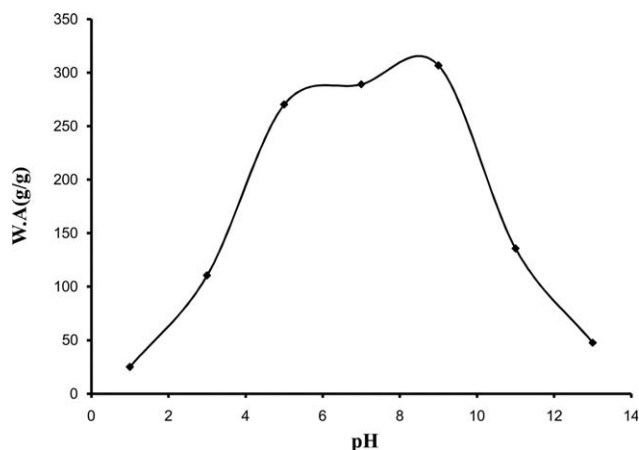


Figure 6 Effect of pH of solutions on swelling capacity of the hydrogel (DS = 0.22). W.A. stands for water absorptency.

In this study, effect of various parameters such as pH, DS, and loading percent on the release rate were investigated. In all cases, amount of release for 0.1 g of loaded or unloaded hydrogel were calculated and reported.

Loading percent

When the use of hydrogels as the carrier of active compounds is intended, effect of loading percent on the solute release rate is one of the important phenomena that should be considered. For this purpose, the hydrogel sample with DS = 0.22 was equilibrated with KNO_3 solutions of varying concentrations (0.3, 0.6, and 0.9M) for 2 h. The dry loaded hydrogel was mildly stirred in the release medium and the progress of the release process was monitored conductometrically. Also, the conductivity of swelling medium for 0.1 g of unloaded hydrogel was determined. At consecutive time intervals, the conductivity of solution was measured and these values were detracted from the conductivity values of the release medium of loaded hydrogel at each time. After 3 h, the increment in conductivity of this solution was only ~ 22 μs (equals to ~ 8 mg KNO_3). As it is obvious from Figure 7, conductivity of the hydrogel without KNO_3 is very low and has no important effect onto the final conductivity of the medium.

The release results (Fig. 7 and Table IV) indicate that the amount of released KNO_3 increases with increasing loading percent of the hydrogel. The results are reasonable, because larger the initial load, the faster is the movement of the solvent front penetrating the surface of the loaded hydrogel.³⁰ A larger loading of the hydrogel may also facilitate the relaxation of macromolecular chains that can be attributed to the electrostatic repulsion between -COO^-

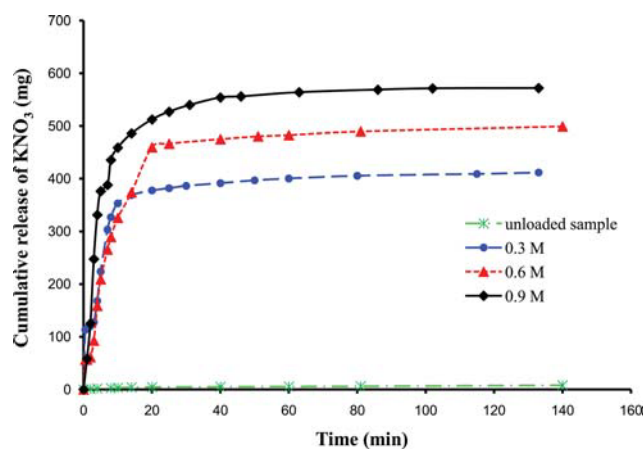


Figure 7 Influence of loading on the release rate of KNO_3 from hydrogel with $\text{DS} = 0.22$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and NO_3^- groups.³¹ Similar results have been reported in similar previous studies.³²

Degree of substitution

The crosslink density of a hydrogel intimately affects the degree of the swelling, and consequently, the release behavior of the hydrogel. In this study, the effect of DS on the release rate of KNO_3 has been investigated by measuring the conductivity of solution at consecutive time intervals. There is a consistency between the results and swelling behavior values (Fig. 8). According to Figure 8 and Table IV, a maximum release is observed at $\text{DS} = 0.22$. Moreover, with increasing DS, the released amount decreases. The results are quite reasonable. In fact, the release of a solute is more difficult in the case of a densely crosslinked network in comparison to a loosely crosslinked ones.

pH

For studying the effect of pH on the release rate, the optimum hydrogel sample was equilibrated with 0.9M KNO_3 solution for 1 h. Then, the amount of

TABLE IV
Loading Condition, Loading Percent, and Release Percent after 3 h

DS	Molarity of KNO_3 in loading medium (M)	% Load	% Release after 3 h	Amount of released KNO_3 (mg) for 0.1 g of loaded hydrogel
0.22	0.3	95	43	40.8
0.22	0.6	100	50	50
0.22	0.9	115	52	59.8
0.5	0.3	83.3	45	37.3
0.80	0.3	67	54	36.2

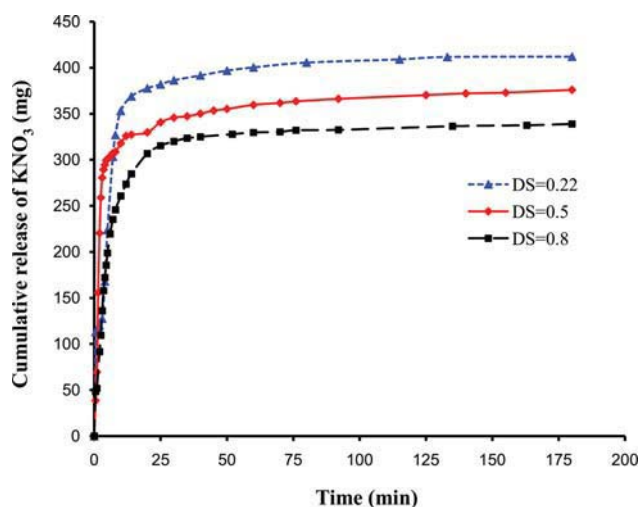


Figure 8 DS effect on the release rate of KNO_3 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

released KNO_3 in phosphate buffer solutions with three different pH (concentration of phosphate buffer was 10 mM) was determined by measuring the conductivity of the release medium.

The results are shown in Figure 9. The initial burst release may be attributed to the release of potassium nitrates loaded near the surfaces of the hydrogel. This figure clearly indicates that the release rate in highly basic or acidic solutions is low. In $\text{pH} = 8$, however, release rate is relatively high. As a matter of fact, the active agent in the hydrogel is released as a result of the hydrogel volume change. According to the Figure 6, the swelling of hydrogel in $\text{pH} \sim 8$ is greater than that of in more acidic or basic solutions and according to the Figure 9, maximum release is in $\text{pH} = 8$. This result indicates that the higher swelling ratios of the hydrogel create larger

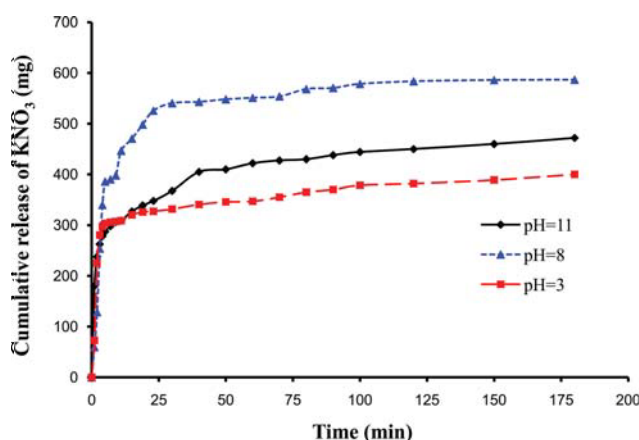


Figure 9 Effect of pH on KNO_3 release ($\text{DS} = 0.22$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface areas to diffuse the KNO_3 . Similar results have been reported in similar previous studies.³²

CONCLUSIONS

The ACAG with three different DS was synthesized by esterification of the hydroxyl groups of AG with the acryloyl chloride and characterized by FTIR and ^1H NMR. AG-based hydrogels were prepared by simultaneous graft copolymerization of AA and HEA onto ACAG. Effect of DS on the water absorbency, AUL and dynamic swelling kinetics of hydrogels were investigated. The results revealed that at high DS, water absorbency is decreased. AUL values indicated that the strength of hydrogel is increased at larger DS. Finally, the potassium nitrate loaded dry hydrogel swells in aqueous medium and releases the salt entrapped within its matrix. The release results correlate well with the swelling results. However, releasing around 50% of the loaded compound after 3 h (Table IV) may be a drawback for the application of these new hydrogels as fertilizing systems. As the present work is a preliminary study, further investigations should be conducted to improve their properties in the future.

References

1. Yoshihito, O.; Alexei, R. K. *Polymer Gels and Networks*; Marcel Dekker: New York, 2005.
2. Peppas, N. A.; Mikos, A. G. In *Hydrogels in Medicine and Pharmacy*, vol.1; Peppas, N. A., Ed.; CRC Press: Boca Raton, FL, 1986.
3. Buchholz, F. L.; Graham, A. T.; *Modern Superabsorbent Polymer Technology*; Wiley-VCH: New York, 1998.
4. Hüttermann, A.; Oriquiriza, L. J. B.; Agaba, H. *Clean* 2009, 37, 517.
5. Brown, R. P. *Polymers in Agriculture and Horticulture*; Rapra Review Reports, vol. 15, Nu. 2. 2004.
6. Athawale, V. D.; Lele, V. *Starch/Stärke* 2001, 53, 7.
7. Dutkiewicz, J. K. *J Biomed Mater Res (Appl Biomater)* 2002, 63, 373.
8. Ichikawa, T.; Nakajima, T. *Polymeric Materials Encyclopedia*, vol.10; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996, pp 8051-8059.
9. Zohuriaan-Mehr, M. J.; Pourjavadi, A.; Salimi, H.; Kurdtabar, M. *Polym Adv Technol* 2009, 20, 655.
10. Dumitriu, S. *Polysaccharides: Structural Diversity and Functional Versatility*; Marcel Dekker: New York, 2005.
11. Uludag, H.; de Vos, P.; Tresco, P. A. *Adv Drug Deliv Rev* 2000, 42, 29.
12. Wang, N.; Wu, X. S. *Int J Pharm* 1998, 166, 1.
13. Garcia, R. B.; Vidal, R. R. L.; Rinaudo, M. *Polímeros* 2000, 10, 155.
14. Paliwal, S. K.; Nadler, T. K.; Varady, L.; Regnier, F. E. *U.S. Pat.* 5,756,717 (1998).
15. Metz, N.; Theato, P. *Macromolecules* 2009, 42, 37.
16. Kabiri, K.; Mirzadeh, H.; Zohuriaan-Mehr, M. J. *J Appl Polym Sci* 2008, 110, 3420.
17. Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad-Langroudi, A.; Kabiri, K. *J Appl Polym Sci* 2009, 113, 3676.
18. Salimi, H.; Pourjavadi, A.; Seidi, F.; Eftekhari Jahromi, P.; Solayman, R. *J Appl Polym Sci* 2010, 117, 3228.
19. Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad-Langroudi, A.; Kabiri, K. *Polym Test* 2006, 25, 470.
20. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. G. *Polymer* 1998, 39, 3459.
21. Omidian, H.; Zohuriaan-Mehr, M. J. *Polymer* 2002, 43, 269.
22. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: New York, 1953.
23. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. *Polymer* 1998, 39, 6697.
24. Zohuriaan-Mehr, M. J.; Motazedi, Z.; Kabiri, K.; Ershad-Langroudi, A.; Allahdadi, I. *J Appl Polym Sci* 2006, 102, 5667.
25. Pourjavadi, A.; Salimi, H. *Ind Eng Chem Res* 2008, 47, 9206.
26. Kabiri, K.; Zohuriaan-Mehr, M. J. *Macromol Mater Eng* 2004, 289, 653.
27. Kabiri, K.; Zohuriaan-Mehr, M. J. *Iran Polym J* 2004, 13, 423.
28. Lee, W. F.; Wu, R. J. *J Appl Polym Sci* 1996, 62, 1099.
29. Hopfenberg, H. B.; Hsu, K. C. *Polym Eng Sci* 1978, 18, 1186.
30. Kim, S. W.; Bae, Y. H.; Okano, T. *Pharm Res* 1992, 9, 283.
31. Wang, H.; Wang, Z.; Zhu, B. *React Funct Polym* 2007, 67, 225.
32. Pourjavadi, A.; Farhadpour, B.; Seidi, F. *J Polym Res* 2009, 16, 655.