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Partially Hydrolyzed Crosslinked Alginate-*graft*-Polymethacrylamide as a Novel Biopolymer-Based Superabsorbent Hydrogel Having pH-Responsive Properties

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Abstract: In this study, a series of highly swelling hydrogels based on sodium alginate (NaAlg) and polymethacrylamide (PMAM) was prepared through free radical polymerization. The graft copolymerization reaction was performed in a homogeneous medium and in the presence of ammonium persulfate (APS) as an initiator and *N,N'*-methylenebisacrylamide (MBA) as a crosslinker. The crosslinked graft copolymer, alginate-*graft*-polymethacrylamide (Alg-*g*-PMAM), was then partially hydrolyzed by NaOH solution to yield a hydrogel, hydrolyzed alginate-*graft*-polymethacrylamide (H-Alg-*g*-PMAM). During alkaline hydrolysis, the carboxamide groups of Alg-*g*-PMAM were converted into hydrophilic carboxylate anions. Either the Alg-*g*-PMAM or the H-Alg-*g*-PMAM was characterized by FTIR spectroscopy. The effects of the grafting variables (i.e., concentration of MBA, MAM, and APS) and the alkaline hydrolysis conditions (i.e., NaOH concentration, hydrolysis time, and temperature) were optimized systematically to achieve a hydrogel having the maximum swelling capacity. Measurements of the absorbency in various aqueous salt solutions indicated that the swelling capacity decreased upon increasing the ionic strength of the swelling medium. This behavior could be attributed to a charge screening effect for monovalent cations, as well as ionic crosslinking for multivalent cations. Because of the high swelling capacity in salt solutions, however, the hydrogels might be considered as anti-salt superabsorbents. The swelling behavior of the superabsorbing hydrogels was also measured in solutions having values of pH ranging from 1 to 13. Furthermore, the pH reversibility and on/off switching behavior, measured at pH 2.0 and 8.0, suggested that the synthesized hydrogels were excellent candidates for the controlled delivery of bioactive agents. Finally, we performed preliminary investigations of the swelling kinetics of the synthesized hydrogels at various particle sizes.

Keywords: hydrogel, superabsorbent, sodium alginate, swelling behavior, crosslinking.

Introduction

The first superabsorbent polymer (SAP), hydrolyzed starch-*graft*-polyacrylonitrile (HSPAN), which exhibit the ability to highly swell in water, saline or biological fluids and retain a significant fraction of them within their structure, but they do not dissolve in water,[1] was prepared by the U.S. Department of Agriculture, Northern Regional Research Center, in the late 1960s.[2] Since then, synthesis and characterization of SAPs have received significant attention because of their excellent applications in many fields such as hygienic, cosmetics, and agriculture.[3-7]

Hydrogels with swelling and contract in response to external stimuli such as heat, pH, electric field, chemical environments, etc, are often referred to as "intelligent" or "smart" hydrogels. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs.[8-10]

Natural-based superabsorbent hydrogels have attracted much interest from the viewpoint of improving the tissue tolerance of synthetic polymers and the mechanical properties of natural polymers. The presence of the natural parts guarantees biodegradability, biocompatibility, and non-toxicity of the superabsorbing materials. Because of their exceptional properties, polysaccharides are the main part of these biopolymers. One of the best methods for the synthesis of these superabsorbent hydrogels is graft copolymerization

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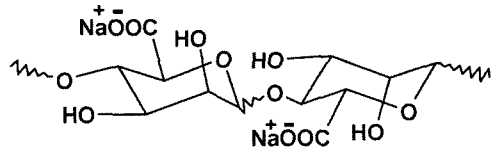


Figure 1. Repeating disaccharide units of sodium alginate (NaAlg).

of vinylic monomers onto polysaccharides.[11-14]

Alginate (Alg) is a collective term for naturally derived polysaccharides, i.e. alginic acid, its salts, and its derivatives. Alginates are composed of (1→4)-linked β-D-mannuronic acid and α-L-guluronic acid in a non-regular, block-wise pattern along the linear chain, which varied in amount and sequential distribution along the polymer chain depending principally upon the seaweed species (Figure 1).[15,16] These polysaccharides are widely used in various applications such as chelating and thickening agents, emulsifiers, stabilizers, encapsulation, swelling and suspending agents, or used to form gels, films, and membranes.[15,17,18] Most studies of alginate chemistry have focused on structural characterization such as conformation, ion selectively or mechanical and rheological properties,[19] but among unique properties of alginates, gelation in the presence of multivalent metal cations is important. However, ionic-crosslinked alginate gels show low absorbencies due to high crosslink density. Therefore, "chemically" crosslinking of alginate salts would be better than "ionic" crosslinking, due to facile control of crosslinking degree and higher crosslink length.

To the best of our knowledge based on a precise survey of the Chemical Abstracts, no report was found on the preparation of a superabsorbing hydrogel through alkaline hydrolysis of Alg-*graft*-polymethacrylamide (PMAM) (Alg-*g*-PMAM). Hence, the objectives of this study were to synthesis and investigate pH-sensitive swelling behavior of a superabsorbent hydrogel made of sodium alginate (NaAlg) and PMAM.

Experimental

Materials. The polysaccharide, sodium alginate (NaAlg, chemical grade, MW 50,000) was purchased from Merck Chemical Co. (Germany). *N,N'*-methylene bisacrylamide (MBA, Fluka), ammonium persulfate (APS, Fluka), methacrylamide (MAM, Merck), were of analytical grade and were used as received. Double distilled water was used for the hydrogel preparation and swelling measurements.

Graft Copolymerization. The graft copolymerization reactions were carried out using APS as an initiator and MBA as a crosslinker in an aqueous solution. A general procedure was conducted as follows. Alg (1.00 g) was dissolved in 25 mL degassed distillated water in a three-neck reactor equipped with mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm). The reactor was placed in a water bath preset at 70 °C. After complete dissolution of the polysaccharide to form a homogeneous solution, a definite amount of APS solution (0.10-0.4 g in 5 mL H_2O) was added into the mixture and was allowed to stir for 10 min. Then certain amounts of MAM (2.0-5.0 g in 10 mL H_2O) and MBA (0.05-0.25 g in 5 mL H_2O) were simultaneously added to the reaction mixture. After 60 min, the reaction product was allowed to cool to ambient temperature. The obtained hydrogel was then poured into ethanol (200 mL). After complete dewatering for 24 h, the hardened gel particle product were filtered, washed with fresh methanol (2× 50 mL) and dried at 50 °C. After grinding, the powdered hydrogel was stored away from moisture, heat and light.

Alkaline Hydrolysis. The graft copolymer (1.0 g) was saponified using 20.0 mL of NaOH (0.5-8.0 N) in a three-neck flask fitted with a mechanical stirrer and a reflux condenser. The hydrolysis temperatures of 60-120 °C; and hydrolysis times of 15-360 min were studied. The mixture was allowed to cool to room temperature and neutralized to pH 7.0 by addition of 10 wt% aqueous acetic acid solution. Then the product was poured into ethanol (200 mL) to dewater for 10 h. The hardened particles were filtered off, dried in oven (50 °C, 5 h), and kept in a dry and cool place.

Swelling Measurements. A small bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) with average particle sizes between 4,060 mesh (250-350 μm) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The bag was hung up for 15 min in order to remove the excess liquid. The maximum absorbency or equilibrated swelling (ES) was measured twice using the following equation:

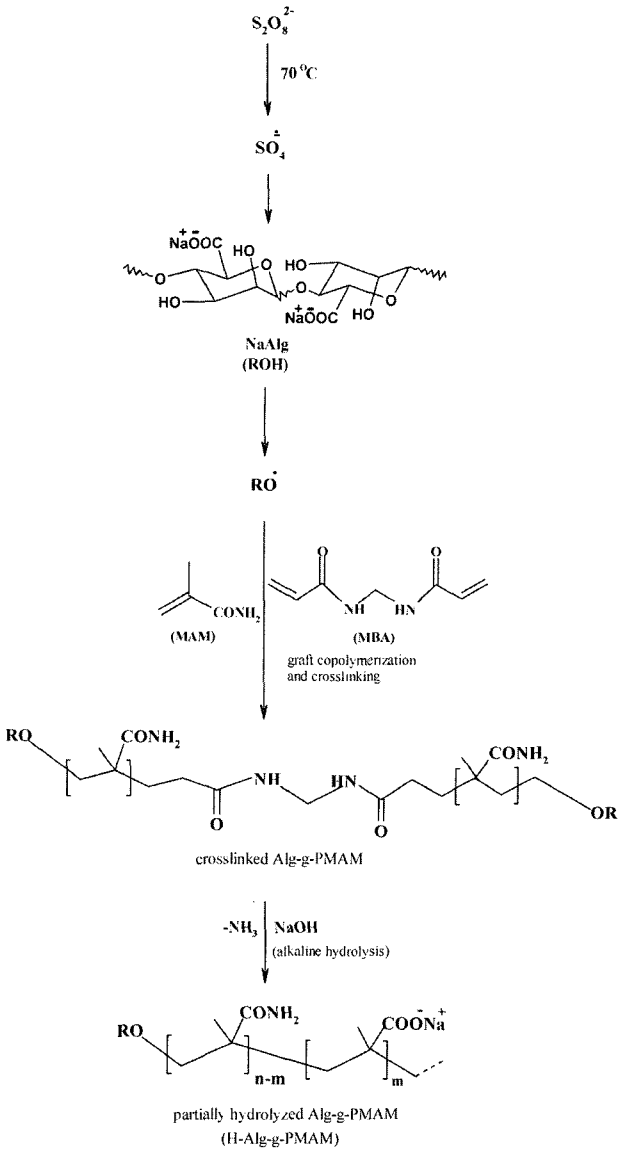
$$ES(g/g) = \frac{\text{weight of swollen gel–weight of dried gel}}{\text{weight of dried gel}} \quad (1)$$

The accuracy of the measurements was ±3%.

Absorbency at Various pHs. Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) aqueous solutions to achieve pH ≥ 6.0 and pH < 6.0, respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ± 0.1). Then, 0.5 g (± 0.001 g) of the dried hydrogel was used for the swelling measurements according to eq. (1).

Swelling Kinetics. For studying the absorbency rate of the hydrogels, certain amount of samples (0.5 ± 0.001 g) with various particle sizes was poured into numbers of weighed tea bags and immersed in distilled water (200 mL) or solution with various pHs (100 mL). At consecutive time intervals, the equilibrium swelling capacity of the hydrogels was measured according to the above mentioned method.

FTIR Analysis. FTIR spectra of samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FTIR spectrophotometer.



Scheme I. Proposed mechanistic pathway for synthesis of H-Alg-*g*-PMAM hydrogel.

Results and Discussion

Synthesis and Mechanism Aspects. The mechanism for crosslinking graft copolymerization of MAM onto Alg backbones in the presence of APS and MBA is shown in Scheme I. As shown in the scheme, at the first step, the thermally dissociating initiator, i.e. APS, is decomposed under heating (70 °C) to produce sulfate anion-radical. Then the anion-radical abstracts hydrogen from the hydroxyl group of the Alg substrate to form corresponding alkoxy radicals. So, these macroradicals initiate MAM grafting onto Alg backbones led to a graft copolymer so called Alg-*g*-PMAM. In addition, crosslinking reaction was occurred in the presence of a crosslinker, i.e., MBA. The Alg-*g*-PMAM was

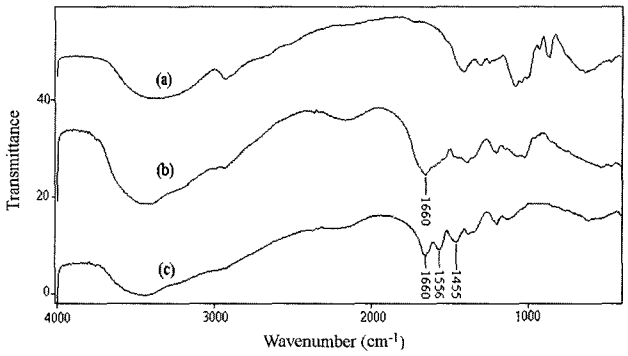


Figure 2. FTIR spectra of Alg (a), Alg-*g*-PMAM (b), and H-Alg-*g*-PMAM (c).

then hydrolyzed with NaOH solution to produce a super swelling hydrogel, H-Alg-*g*-PMAM. During the partially saponification, NH_3 gas was evolved and some of the "non-ionic" carboxamide groups are converted to "ionic" carboxylate salt.

Spectral Characterization. Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 2 shows the FTIR spectra of Alg, Alg-*g*-PMAM, and H-Alg-*g*-PMAM. The graft copolymer, Alg-*g*-PMAM, comprise a Alg backbone with side chains that carry carboxamide functional groups that are evidenced by a new peak at 1660 cm^{-1} (Figure 2(b)). This peak attributed to C=O stretching in carboxamide functional groups of PMAM. The stretching band of -NH overlapped with the -OH stretching band of the Alg portion of the copolymer. After alkaline hydrolysis, the new absorption modes at 1455 and 1556 cm^{-1} can be attributed to symmetric and asymmetric stretching modes of carboxylate groups, respectively (Figure 2(c)).

To obtain an additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. After extracting the homopolymer (PMAM), appreciable amount of synthetic polymer percentage of the graft copolymer (80%) were concluded. The graft copolymer spectrum was very similar to Figure 2(b). Also according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 0.5%. This fact practically proves that all MAM are involved in the polymer network. So, the monomer percent in the network will be very similar to that of the initial feed of reaction.

Optimization of the Reactions Variables. The factors affecting the grafting conditions (i.e. concentration of MBA, MAM, and APS) and the alkaline variables (i.e. concentration of NaOH and hydrolysis time and temperature) as well as the swelling behavior of the resulted pH-responsive superabsorbent hydrogels were investigated.

Effect of MBA Concentration. Figure 3 demonstrates the effect of the crosslinker concentration on swelling capacity of H-Alg-*g*-PMAM product. As shown in Figure 3, the absorbency is decreased with increasing the MBA concen-

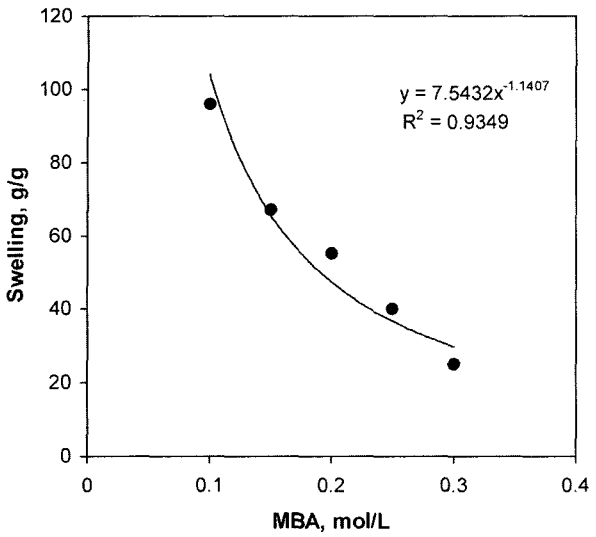


Figure 3. Swelling dependency of H-Alg-*g*-PMAM hydrogel on crosslinker concentration. Grafting conditions: Alg 1.0 g, MAM 0.94 mol/L, APS 0.15 mol/L, 70 °C, 60 min. Alkaline hydrolysis conditions: Alg-*g*-PMAM 1.0 g, NaOH 2.0 N, 80 °C, 60 min.

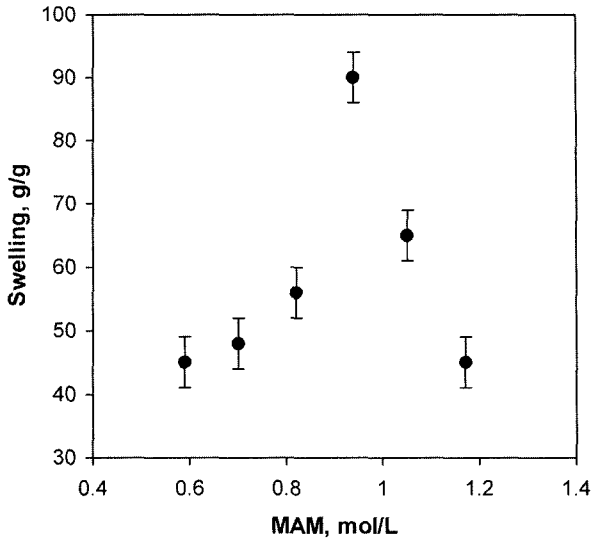


Figure 4. Swelling dependency of H-Alg-*g*-PMAM hydrogel as a function of monomer concentration. Grafting conditions: Alg 1.0 g, MBA 0.1 mol/L, APS 0.15 mol/L, 70 °C, 60 min. Alkaline hydrolysis conditions: Alg-*g*-PMAM 1.0 g, NaOH 2.0 N, 80 °C, 60 min.

tration. More crosslinking concentration causes to the higher crosslinking density and decreases the space between the copolymer chains and consequently, the resulted highly crosslinked rigid structure cannot be expanded and hold a large quantity of water. In fact, in all of hydrogels a small increase in degree of crosslinking causes an appreciable decrease in swelling capacity. Such well-known behavior was reported by pioneering scientists.[9,20,21] Figure 3 exhibits a power law behavior of swelling-[MBA], with K=7.54 and n=1.14 which is obtained from the curve fitted with eq. (2).

$$\text{Swelling capacity} \approx K[\text{MBA}]^{-n} \quad (2)$$

The K and n are constant values for an individual superabsorbent. The n value represents the extent of the sensitivity of the hydrogel to the crosslinker content, while the K value gives an amount useful for comparing the extent of swelling versus fixed crosslinker content. According to Figure 3, maximum swelling (96 g/g) was obtained at 0.1 mol/L of crosslinker concentration so that the hydrogels prepared with MBA concentration lower than 0.1 mol/L do not posses good dimensional stability, therefore the swollen gel strength is not sufficient to refer the hydrogels as "real superabsorbents".

Effect of MAM Concentration. The effect of monomer content on swelling capacity of crosslinked H-Alg-*g*-PMAM was studied by varying MAM concentration from 0.59 to 1.17 mol/L (Figure 4). It is observed that the absorbency is substantially increased with increasing in the MAM concentration and then it is decreased. Initial increment in water absorbency may be attributed to (a) greater availability of monomer molecules in the vicinity of the chain propagating sites of Alg macroradicals, and (b) increase the hydrophilicity of the hydrogel originated from higher MAM content that, in turn, causes a stronger affinity for more absorption of water. The swelling-loss after the maximum may be attributed to (a) preferential homopolymerization over graft copolymerization, (b) increase in viscosity of the medium which restricts the movement of free radicals and monomer molecules, and (c) the enhanced chance of chain transfer to monomer molecules. Such behaviors are reported by other investigators.[22-24]

Effect of APS Concentration. The relationship between the initiator concentration and water absorbency values was studied by varying the APS concentration from 0.09 to 0.35 mol/L (Figure 5). According to Figure 5, the absorbency is increased with increasing the APS concentration from 0.09 up to 0.22 mol/L and then, it is decreased considerably with a further increase in the amount of monomer. The maximum absorbency (197 g/g) is obtained at 0.22 mol/L of the initiator, APS. Initial increment in water absorbency may be attributed to increased number of active free radicals on the Alg backbone. Subsequent decrease in swelling is originated from an increase in terminating step reaction via bimolecular collision which, in turn, causes to enhance crosslinking density. This possible phenomenon is referred to as "self crosslinking" by Chen and Zhao.[25] In addition, the free radical degradation of Alg backbones by sulfate radical-anions is an additional reason for swelling-loss at higher APS concentration. The proposed mechanism for this possibility is reported in the previous work.[26] A similar observation is

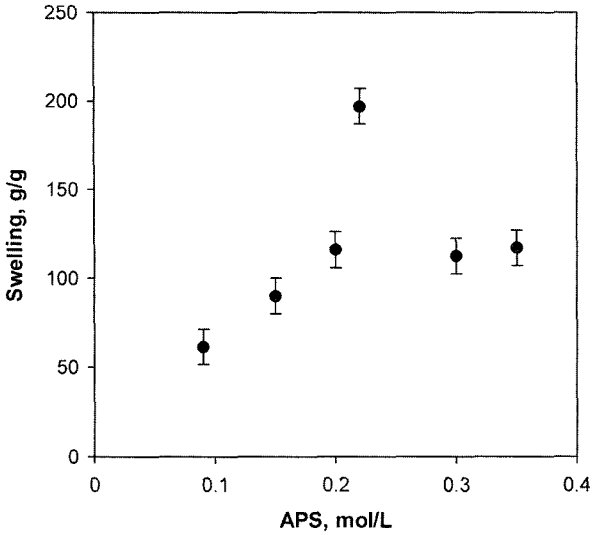


Figure 5. Effect of initiator concentration on swelling capacity of H-Alg-*g*-PMAM superabsorbent hydrogel. Grafting conditions: Alg 1.0 g, MBA 0.1 mol/L, MAM 0.94 mol/L, 70 °C, 60 min. Alkaline hydrolysis conditions: Alg-*g*-PMAM 1.0 g, NaOH 2.0 N, 80 °C, 60 min.

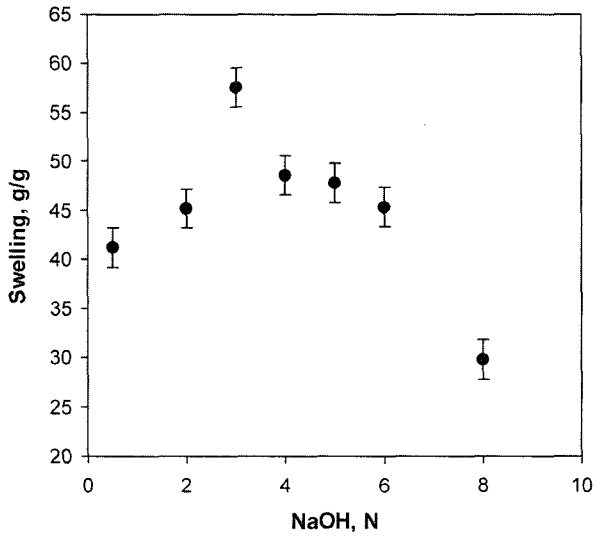


Figure 6. Influence of NaOH concentration on swelling capacity of H-Alg-*g*-PMAM superabsorbent hydrogel. Grafting conditions: Alg 1.0 g, MBA 0.1 mol/L, MAM 0.94 mol/L, APS 0.22 mol/L, 70 °C, 60 min. Alkaline hydrolysis conditions: Alg-*g*-PMAM 1.0 g, 80 °C, 60 min.

recently reported by Hsu *et al.* in the case of degradation of chitosan with potassium persulfate.[27]

Effect of NaOH Concentration. In this series of experiments, swelling capacity of the final hydrogel, H-Alg-*g*-PMAM, was studied as a function of NaOH concentration (Figure 6). It is observed that the absorbency is increased substantially with increasing the NaOH concentration from

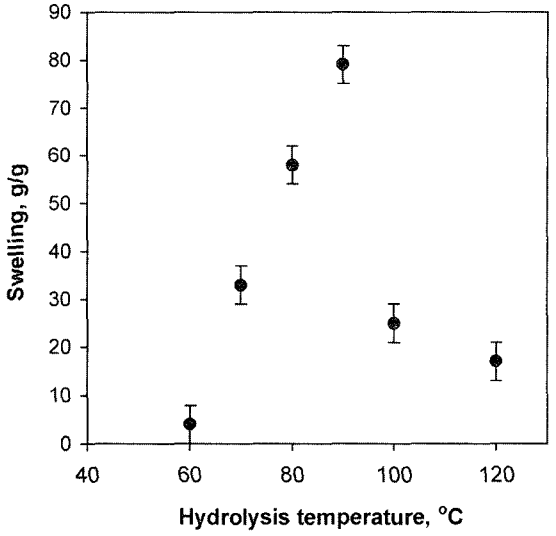


Figure 7. Effect of hydrolysis temperature on swelling capacity of H-Alg-*g*-PMAM superabsorbent hydrogel. Grafting conditions: Alg 1.0 g, MBA 0.1 mol/L, MAM 0.94 mol/L, APS 0.22 mol/L, 70 °C, 60 min.

0.5 to 3.0 N and then it is decreased. Initial increase in swelling values is due to enhancement of the repulsive action of the increasing carboxylate anions. The swelling loss after the maximum can be attributed to residual alkaline, after completion of alkaline hydrolysis. The excess cations shield the carboxylate anions and prevent effective anion-anion repulsion (screening/shielding effect). Additionally, "alkaline degradation" of the polysaccharide backbone can be another reason of the swelling decrease in highly concentrated alkaline hydrolytic media. The proposed mechanism for this alkaline degradation is reported in the previous work.[28] Similar alkaline degradation behaviors were already reported in the case of other polysaccharides.[29]

Effect of Hydrolysis Temperature. Figure 7 demonstrates the effect of hydrolysis temperature on swelling capacity of H-Alg-*g*-PMAM product. The absorbency is increased versus increasing the hydrolysis temperature from 60 up to 90 °C and then, it is decreased with a further increase in hydrolysis temperature. By increasing the hydrolysis temperature up to 90 °C, the kinetics of alkaline hydrolysis increased which, in turn, results in carboxylate anions increment and consequently absorbency enhancement. Thereafter, decreasing the swelling capacity may be attributed to alkaline degradation of the Alg part of the hydrogel.

Effect of Hydrolysis Time. The effect of hydrolysis time on swelling capacity of crosslinked H-Alg-*g*-PMAM was studied by varying the hydrolysis time from 15 to 360 (Figure 8). As shown in the figure, the absorbency is increased with increasing the hydrolysis time up to 60 min and then it is substantially decreased. The initial increasing in swelling value can be attributed to increase carboxylate-to-carboxa-

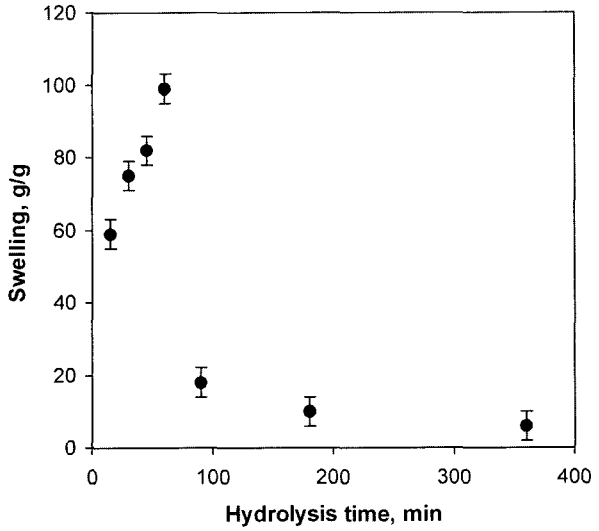


Figure 8. Effect of hydrolysis time on swelling capacity of H-Alg-*g*-PMAM superabsorbent hydrogel. Grafting conditions: Alg 1.0 g, MBA 0.1 mol/L, MAM 0.94 mol/L, APS 0.22 mol/L, 70 °C, 60 min. Alkaline hydrolysis conditions: Alg-*g*-PMAM 1.0 g, NaOH 3.0 N, 90 °C.

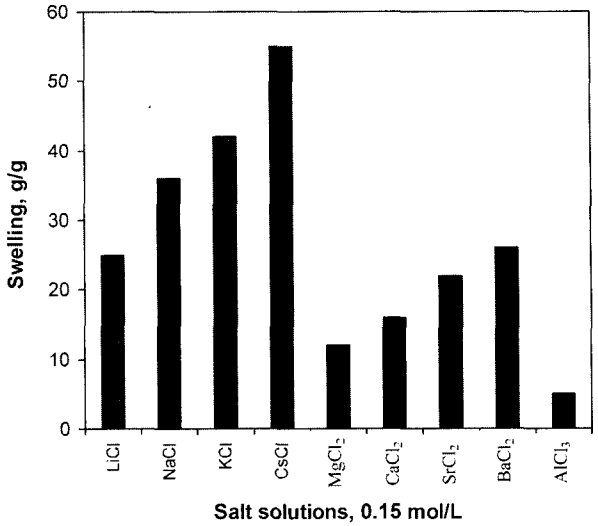


Figure 9. Swelling capacity of the hydrogel, H-Alg-*g*-PMAM, in different chloride salt solutions (0.1 5M).

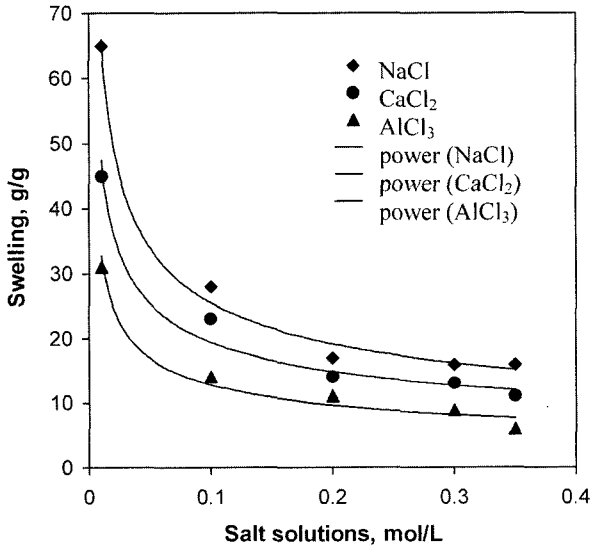


Figure 10. Swelling capacity variation of H-Alg-*g*-PMAM superabsorbent in saline solutions with various concentrations.

mide ratio values. Intensive electrostatic repulsion of the anions leads to higher swelling of the hydrogel. The swelling-loss after the optimum time (60 min) may be attributed to degradation of the Alg part of the hydrogel under relatively alkaline conditions (3.0 N NaOH, 90 °C).

Effect of Salinity on Swelling Capacity. The swelling ratio is mainly related to the characteristics of the external solution, i.e. the charge number and ionic strength, as well as the nature of polymer, i.e. the elasticity of the network, the presence of hydrophilic functional groups, and the extent of crosslinking density. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing to the swelling values in distilled water. This well-known undesired swelling-loss is often attributed to a "charge screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion.[21] Therefore, the osmotic pressure resulted from the mobile ion concentration difference between the gel and aqueous phases decreased and consequently the absorbency amounts decreased. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciably decrease in swelling capacity. It is obvious that swelling decrease is strongly depended on the "type" and "concentration" of salt added to the swelling medium. The effect of cation type (cations with different radius and charge) on swelling behavior is shown in Figure 9. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency for H-Alg-*g*-PMAM hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations. The effect of cation radius on swelling, may also been observed from Figure 9. As reported by Pass *et al.*,[30] the carboxylate anion interacts with small cations, e.g. Li^+, stronger than with large cations, e.g. Cs^+. The stronger interactions of carboxylate-small cation have been observed using measurement of activating coefficients of various cations in several salt solutions. As a result, the water absorbency in monovalent and divalent cations salt solutions is in the order of CsCl > KCl > NaCl > LiCl and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$, respectively.

Figure 10 illustrates a reverse and power law relationship between concentration of salt solutions (NaCl, $CaCl_2$, and $AlCl_3$) and swelling capacity of the hydrogel, H-Alg-*g*-MAM.

Again, charge screening effect and ionic crosslinking are the main explanations for the intense loss of swelling. The known relationship between swelling and concentration of salt solution is stated as following equation[21]:

$$\text{Swelling} = k\,[\text{salt}]^{-n} \quad (3)$$

where k and n are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity. Figure 10 indicates that changing of the salt concentrations higher than ~0.2 M has no appreciable influence on superabsorbency of the superabsorbent. As given in Table I, the k values are almost the same (~8) for the swelling in various salt solutions. The n values are proportionally changes with the cation valency enhancement. Here, the effect of the ionic crosslinking acts as more effective factor against swelling rather than the charge screening effect of the cation.

Swelling capacity of the synthesized hydrogel, H-Alg-*g*-PMAM, in distilled water and various salt solutions comparison with other superabsorbents is shown in Table II. As shown in the table, the H-Alg-*g*-PMAM hydrogel has more swelling ratio than some other superabsorbents, especially full-synthetic counterparts. However, because of the existence of the hydrophilic and anti-salt sulfate groups, the absorbency value of the hydrogels such as H-κC-*g*-PMAM is more than the synthesized hydrogel in this work (kappa-carrageenan, κC , is a linear sulfated polysaccharide prepared by alkaline extraction from red seaweeds). It is necessary to mentioned that the synthesized hydrogel comparison with full-synthetic superabsorbents has the advantages of biocompatibility, biodegradability, and non-toxicity of the superabsorbing materials.

Table I. Values *k* and *n* (as obtained from the curve fitting, Figure 10) for the Optimally Prepared Superabsorbent Hydrogel, H-Alg-*g*-PMAM

Swelling Medium	*k*	*n*
NaCl	8.2	0.41
$CaCl_2$	8.3	0.52
$AlCl_3$	8.4	0.65

Equilibrium Swelling at Various pH Solutions. Ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, equilibrium swelling for H-Alg-*g*-PMAM hydrogel was measured in different pH solutions ranged from 1.0 to 13.0 (Figure 11). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by addition of counter ions (cations) 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 pHs, respectively. Maximum swelling (58 g/g) was obtained at pH 8. In acidic media, the most of

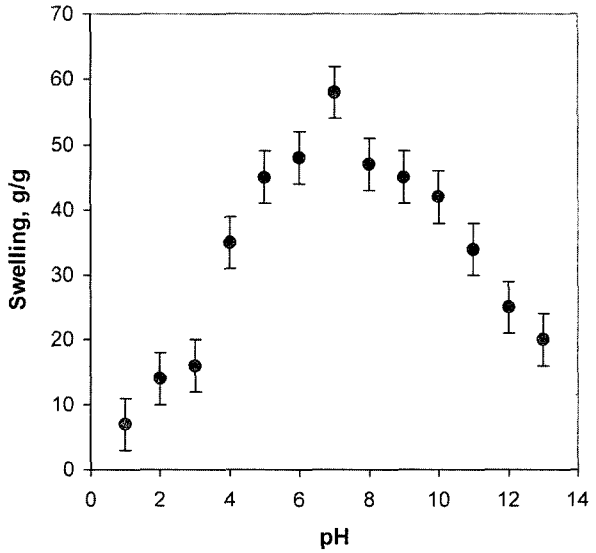


Figure 11. Effect of pH of solutions on swelling capacity of H-Alg-*g*-PMAM hydrogel.

Table II. A Comparison between the Equilibrium Swelling Capacity of H-Alg-*g*-PMAM Hydrogel and Other Counterparts in Distilled Water and Various Salt Solutions (0.15 M)

Swelling Medium	Superabsorbent Hydrogel					
	H-Alg-*g*-PMAM[a]	H-κC-*g*-PMAM[b]	κC-*g*-AMPS[c]	H-CMC-*g*-PAN[d]	Crosslinked PAAm[e]	Crosslinked PAANa[f]
H_2O	197	435	95	180	61	152
NaCl	36	85	83	27	8	10
$CaCl_2$	12	16	40	5	4	3
$AlCl_3$	5	7	10	3	2	1

[a]Prepared in this work under optimized conditions (MBA 0. 1mol/L, MAM 0.9 4mol/L, APS 0.2 2mol/L, NaOH 3.0 N, hydrolysis time 6 0min, and hydrolysis temperature 90°C). [b-f]Prepared in the previous works[42-45] under conditions similar to that of employed in the present work (κC: kappa-carrageenan, AMPS: 2-acrylamido-2-methylpropanesulfonic acid, CMC: carboxymethylcellulose, PAN: polyacrylonitrile, PAAm: polyacrylamide, PAANa: polyacrylic acid sodium salt).

carboxylate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio. At higher pHs (5-8), some of carboxylate groups are ionized and the electrostatic repulsion between COO^- groups causes an enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions is "charge screening effect" of excess Na^+ in the swelling media which shield the carboxylate anions and prevent effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems.[31-34]

pH-Responsiveness Behavior of the Hydrogel. The pH-dependent swelling reversibility of the hydrolyzed hydrogel, H-Alg-*g*-PMAM, was examined in two acidic and basic buffered solutions. Figure 12 shows the reversible swelling-deswelling behavior of the hydrogel at pHs 2.0 and 8.0. At pH 8.0, the hydrogel swells due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to "screening effect" of excess cations. This sudden and sharp swelling-deswelling behavior at different pH values makes the system to be highly pH-responsive and consequently it may be a suitable candidate for designing controlled drug delivery systems. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems.[35-38]

Kinetics of Swelling. In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Buchholz has suggested that the swelling kinetics for the superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer.[39] Figure 13 represents the dynamic swelling behavior of H-Alg-*g*-PMAM superabsorbent samples with various particle sizes in water. Initially, the rate of water uptake sharply

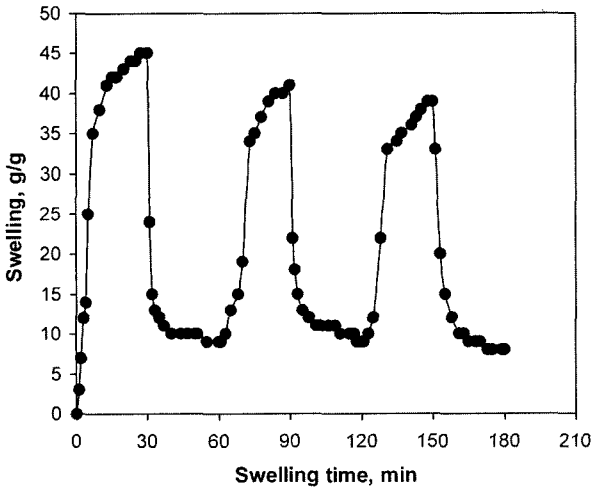


Figure 12. On-off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of H-Alg-*g*-PMAM hydrogel. The time interval between the pH changes was 30 min.

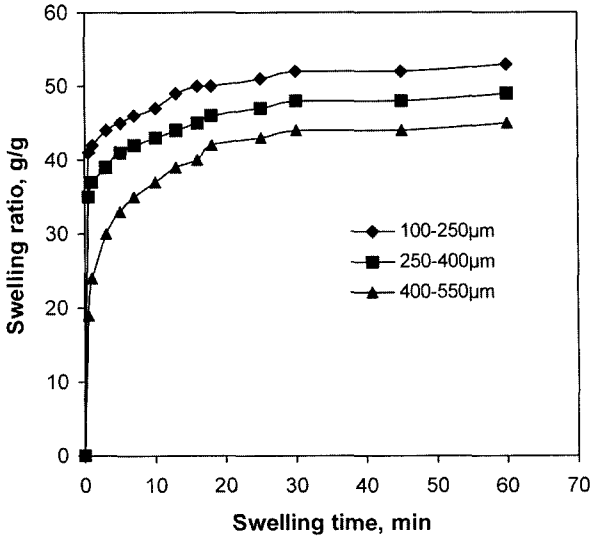


Figure 13. Representative swelling kinetics of H-Alg-*g*-PMAM superabsorbent hydrogel with various particle sizes.

increases and then begins to level off. The time required to reach the equilibrium swelling capacity was achieved after ~20 min. A power law behavior is obvious from Figure 13. The data may be well fitted with a Voigt-based equation (eq. (4))[40]:

$$S_t = S_e (1 - e^{t/\tau}) \quad (4)$$

where S_t (g/g) is swelling at time t, S_e is equilibrium swelling (power parameter, g/g), t is time (min) for swelling S_t, and τ (min) stand for the "rate parameter". The rate parameters for superabsorbent are found to be 0.5, 1.5, 3.2 min for superabsorbent with particle sizes of 100-250, 250-400 and 400-550 μm, respectively. It is well-known that the swelling kinetics for the superabsorbent polymers is significantly influenced by particle size of the absorbents.[41] With a lower the particle size, a higher rate of water uptake is observed. An increase in the rate of absorption would be expected from the increase in surface area with decreasing particle size of hydrogel.

Conclusions

In this work, we prepared a novel superabsorbent hydrogel, H-Alg-*g*-PMAM, by graft copolymerization of MAM onto Alg backbones followed by alkaline hydrolysis of the graft copolymer, Alg-*g*-PMAM. The synthesis of superabsorbent hydrogel was optimized by varying the reaction parameters affecting the ultimate swelling capacity of the final product. The maximum water absorbency (197 g/g) was achieved under the optimum conditions that found to be MBA 0.1 mol/L, MAM 0.94 mol/L, APS 0.22 mol/L, concentration of NaOH 3.0 N, hydrolysis time 60 min, and

hydrolysis temperature 90 °C. Swelling capacity of H-Alg-*g*-PMAM hydrogel in various salt solutions, especially in CsCl and KCl solutions is appreciable. However, swelling-loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. Also the superabsorbent hydrogels exhibited high swelling capacity at basic pHs as well as reversible pH-responsiveness property. Therefore, this natural-based superabsorbent intelligently responding to pH may be considered as an excellent candidate to design novel drug delivery systems.

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