

Synthesis of an Alginate–Poly(sodium acrylate-co-acrylamide) Superabsorbent Hydrogel with Low Salt Sensitivity and High pH Sensitivity

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ABSTRACT: This article describes the synthesis and swelling behavior of a superabsorbing hydrogel based on sodium alginate (NaAlg) and polyacrylonitrile (PAN). The physical mixture of NaAlg and PAN was hydrolyzed with a solution of NaOH to yield an alginate–poly(sodium acrylate-co-acrylamide) [Alg–poly(NaAA-co-AAm)] superabsorbent hydrogel. A proposed mechanism for hydrogel formation was suggested, and the structure of the product was established with Fourier transform infrared spectroscopy. The effects of reaction variables were systematically optimized to achieve a hydrogel with a swelling capacity as high as possible. Under the optimized conditions concluded, the maximum capacity of swelling in distilled water was 610 g/g. The absorbency of the synthesized hydrogels was also

measured in various salt solutions. The swelling ratios decreased with an increase in the ionic strength of the salt solutions. In addition, the swelling capacity was determined in solutions with pHs ranging from 1 to 13. The Alg–poly(NaAA-co-AAm) hydrogel exhibited pH responsiveness, so a swelling–deswelling pulsatile behavior was recorded at pHs 2 and 8. This on–off switching behavior made the hydrogel a good candidate for the controlled delivery of bioactive agents. Finally, the swelling kinetics of the hydrogels with various particle sizes were preliminarily investigated as well. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2927–2937, 2006

Key words: synthesis; superabsorbent; alginate

INTRODUCTION

Several studies have been carried out on the synthesis and characterization of superabsorbent polymers (SAPs) since the first SAP was reported by the U.S. Department of Agriculture in 1961.¹ These attractive materials are crosslinked, hydrophilic polymers capable of absorbing large quantities of water, saline, or physiological solutions.² Because of their excellent characteristics, they are widely used in many applications, such as disposable diapers, feminine napkins, and soil for agriculture and horticulture, and they have attracted considerable interest and have been the subject of much research.³ Hydrogels that swell and contract in response to external stimuli such as heat, pH, electric fields, and chemical environments, are often called intelligent or smart hydrogels. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in the site-specific delivery of drugs to specific regions of the gastrointestinal

tract and have been prepared for the delivery of low-molecular-weight protein drugs.^{4–6}

Because of their exceptional properties, that is, biocompatibility, biodegradability, renewability, and nontoxicity, polysaccharides are the main components of natural-based superabsorbent hydrogels. Among polysaccharides, alginates (Alg's) have been considered some of the most promising candidates for the future, primarily because of an attractive combination of availability, price, and performance. *Alginate* is a collective term for naturally derived polysaccharides, that is, alginic acid, its salts, and its derivatives. Alg's are composed of (1→4)-linked β -D-mannuronic acid and α -L-guluronic acid in a nonregular, blockwise pattern along the linear chain, which vary in their amounts and sequential distributions along the polymer chain principally according to the seaweed species.^{7,8} These polysaccharides are widely used in various applications.^{7,9,10}

Free-radical vinyl graft copolymerization onto polysaccharide backbones is a well-known method for the synthesis of natural-based superabsorbent hydrogels.^{11–14} The first industrial superabsorbent hydrogel, hydrolyzed starch-*graft*-polyacrylonitrile (HSPAN), was synthesized with this method.¹ Radical polymer-

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ization, however, has several disadvantages. The reproducibility of this method is poor, and there is little control over the grafting process, so the molecular weight distribution is polydisperse. In addition, the necessity for inert gases (e.g., argon) to prepare an oxygen-free atmosphere and the need for initiators, toxic and/or expensive monomers, and crosslinkers are other disadvantages of free-radical polymerization reactions. These problems have been reviewed in detail.¹⁵ For the first time, Fanta et al.,¹⁶ with a new method, tried to synthesize an HSPAN superabsorbent hydrogel. They hydrolyzed a physical mixture of starch and polyacrylonitrile (PAN). The nitrile groups of PAN were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by *in situ* crosslinking of the grafted PAN chains. The initially formed oxygen-carbon bonds between the starch hydroxyls and nitrile groups of the PAN chains remained crosslinking sites. To confirm this fact, Fanta et al. treated PAN homopolymers with starch in hot aqueous alkali media. They demonstrated that PAN that saponified in the presence of starch became partially insoluble. Then, Fanta and Doane¹⁷ attempted to extend this idea to the preparation of superabsorbent hydrogels by the saponification of PAN in the presence of polyhydroxy polymers. Finally, Yamaguchi et al.¹⁸ reported the preparation of superabsorbing polymers from mixtures of PAN and various saccharides or alcohols.

In a precise survey of *Chemical Abstracts*, we found no report on the preparation of a superabsorbing hydrogel through the alkaline hydrolysis of an Alg-PAN physical mixture. Hence, in this investigation, we paid attention to the synthesis and investigation of a SAP based on sodium alginate (NaAlg) and PAN. The effects of the hydrolysis reaction variables on the swelling properties as well as the salt and pH sensitivity of the hydrogels were investigated in detail.

EXPERIMENTAL

Materials

NaAlg (chemical-grade; molecular weight = 50,000) was purchased from Merck Chemical Co. (Darmstadt, Germany). PAN was synthesized through a method mentioned in the literature.¹⁸ Double-distilled water was used for the hydrogel preparation and swelling measurements.

Hydrogel preparation

A facile one-step preparative method was used for the synthesis of the alginate-poly(sodium acrylate-co-acrylamide) [Alg-poly(NaAA-co-AAm)] hydrogel. The general procedure for the alkaline hydrolysis of the Alg-PAN mixture was as follows. Alg (0.50–1.33

g) was added to a three-necked reactor equipped with a Heidolph RZR 2021 mechanical stirrer (three-blade propeller type; 50–500 rpm) (Schwabach, Germany) and including 35 mL of double-distilled water. The reactor was immersed in a thermostated water bath. After the complete dissolution of Alg to form a homogeneous solution, a certain weight percentage of sodium hydroxide (2.0–20.0 wt %) was added to the solution at the desired temperature (alkalization temperature = 50–90°C). The mixture was allowed to stir for certain times (alkalization time = 15–360 min). Various amounts of PAN (0.50–1.50 g) were dispersed in the reaction mixture to saponify for certain times and temperatures (alkaline time and temperature). During the saponification, NH₃ was evolved, and the color changed from red to light yellow. This discoloration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8.0 by the addition of a 10 wt % aqueous acetic acid solution. Then, the gelled product was cut into small pieces and poured into methanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50°C, 10 h). After being ground, the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

Swelling measurements with the tea bag method

A tea bag (i.e., a 100-mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) with average particle sizes between 40 and 60 mesh (250–350 μm) was immersed entirely in distilled water (200 mL) or a desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min to remove the excess fluid. The equilibrated swelling (ES) was measured twice with the following equation:

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

The accuracy of the measurements was $\pm 3\%$.

Absorbency at various pHs

Individual solutions with acidic and basic pHs were prepared by the dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions to achieve $\text{pH} \geq 6.0$ and $\text{pH} < 6.0$, respectively. The pH values were precisely checked with a Metrohm 620 pH meter (Switzerland) (accuracy ± 0.1). Then, 0.5 ± 0.001 g of the dried hydrogel was used for the swelling measurements according to eq. (1).

pH sensitivity

The pH sensitivity of the hydrogel was investigated in terms of the swelling and deswelling of the final product in two basic (pH 8.0) and acidic (pH 2.0) solutions, respectively. The swelling capacity of the hydrogels at each pH was measured according to eq. (1) at consecutive time intervals (30 min).

Swelling kinetics

For studying the absorbency rate of the hydrogels, certain amounts of samples (0.5 ± 0.001 g) with various particle sizes were poured into a number of weighed tea bags and immersed in 200 mL of distilled water. At consecutive time intervals, the equilibrium swelling capacity of the hydrogels was measured according to the aforementioned method.

Infrared spectroscopy

Fourier transform infrared (FTIR) spectra of samples were taken in KBr pellets with an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada).

RESULTS AND DISCUSSION

Mechanism of hydrogel formation

A general reaction mechanism for Alg-poly(NaAA-co-AAm) hydrogel formation is shown in Scheme 1. In the first step, hydroxyl groups of the Alg substrate are converted to corresponding alkoxide ions with a sodium hydroxide solution [Scheme 1(a)]. Then, these macroalkoxides initiate a crosslinking reaction between some adjacent PAN pendant chains. This reaction leads to the intermediate formation of naphthyridine cyclic structures (including imine, —C=N— , conjugated bonds) with a deep red color. The intermediate is then hydrolyzed with the residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups [Scheme 1(a,b)], with a resulting color change from red to light yellow. This sharp color change is used as an indication to halt the alkaline treatment. The degree of crosslinking and thus the swelling capacity are strongly dependent on the carboxyl/carboxamide ratio. In fact, the proper ratio between the carboxyl and carboxamide groups is the key property for the swelling of superabsorbing polymers. Therefore, we tried to determine the ratio of the carboxyl groups to the carboxamide groups under different reaction conditions, but we realized that precise control of the ratio is practically impossible. The main reason for this infirmity is the reaction between carboxyl and amide groups to form imide structures.¹⁹ In addition, incompletely hydrolyzed structures may give rise to a few crosslinking points, resulting in a loosely crosslinked network. For HSPAN, a maximum

conversion of 70% of nitrile groups to carboxyl groups has been reported, and the remaining 30% are amide groups.²⁰ In fact, the details of the chemical processes and mechanism involved in HSPAN synthesis are not yet well understood. For instance, the incomplete hydrolysis is interpreted as being related to steric and polar factors.²¹

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1 shows the FTIR spectra of the Alg-PAN physical mixture and the resultant hydrogel, Alg-poly(NaAA-co-AAm). The band observed at 2244 cm^{-1} can be attributed to stretching of the —CN group of PAN [Fig. 1(a)]. The hydrogel comprises an Alg backbone with side chains that carry carboxamide- and carboxylate-functional groups, which are evidenced by three new peaks at 1408, 1557, and 1676 cm^{-1} [Fig. 1(b)]. These peaks can be attributed to C=O stretching in carboxamide-functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively.²² The stretching band of —NH overlaps the —OH stretching band of the Alg portion of the copolymer. As shown in Figure 1(b) and Scheme 1, after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

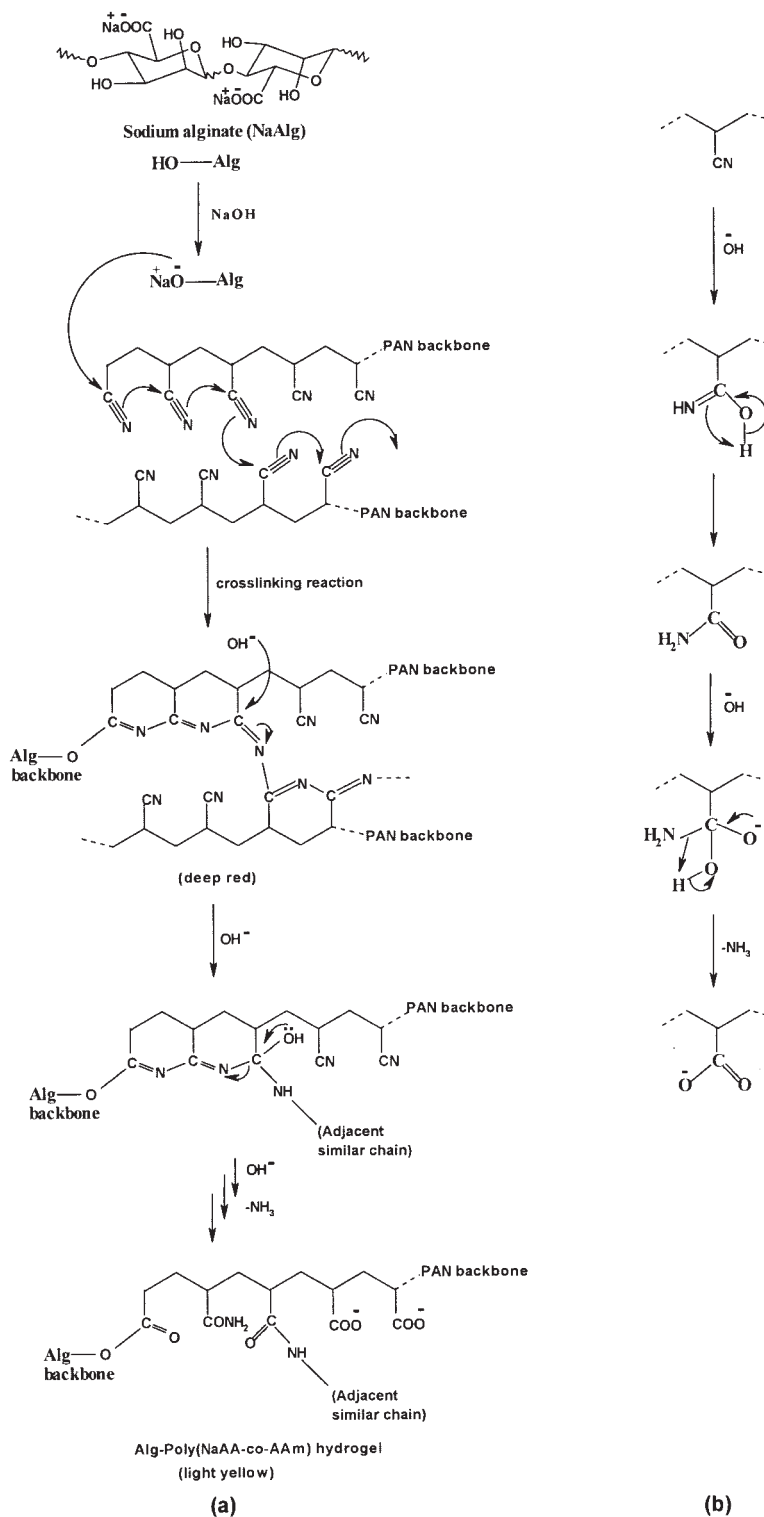
To obtain additional evidence of *in situ* crosslinking during alkaline hydrolysis, a similar reaction was conducted in the absence of the polysaccharide. Because the resultant product became soluble, the crosslinks really formed between the alkoxide ions of Alg and the nitrile groups of PAN. This fact practically proves that Alg hydroxyls are involved in the crosslinking.

Optimization of the reaction conditions

All factors affecting the saponification reaction of the Alg-PAN mixture were systematically optimized to achieve a superabsorbent with maximum water absorbency.

Effect of the alkalization time

Figure 2 depicts the effect of the alkalization time on the swelling ratio. The alkalization time of the hydroxyl groups of NaAlg was varied from 60 to 360 min. The alkaline hydrolysis conditions were kept constant (8 wt % NaOH, 90°C , and 120 min). The absorbency decreased with increasing alkalization time. This swelling loss could be attributed to some sort of unwanted alkaline degradation of the polysaccharide. This disconnection reduced the main-chain molecular weight. Because the swelling capacity proportionally depended on the molecular weight of the chains in the networks of the superabsorbent hydrogels,³ the unwanted disconnection resulted in a swelling loss, even though it was not extensive. Similar alkaline degradation behaviors have already been re-



Scheme 1 Proposed mechanism for (a) crosslinking during the hydrolysis of nitrile groups of the Alg-PAN mixture to produce the Alg-poly(NaAA-co-AAm) hydrogel and (b) the conversion of nitrile groups of PAN chains to carboxamide- and carboxylate-functional groups.

ported for other polysaccharides.²³ In addition, more —OH groups were converted to corresponding alkoxide anions at longer alkalization times (Scheme 1). Therefore, a higher crosslinked, rigid structure was

formed. It is known that a higher degree of crosslinking results in a rigid network that cannot hold a large quantity of fluid.^{2,3,24} The maximum water absorbency (321 g/g) was achieved in 60 min. In fact, with an

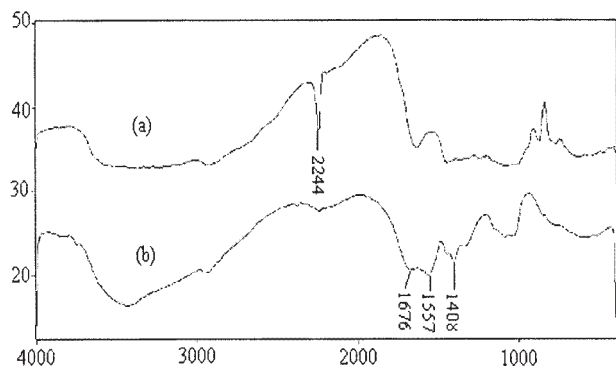


Figure 1 FTIR spectra [transmittance vs wave number (cm^{-1})] of (a) the physical mixture of NaAlg and PAN and (b) the crosslinked Alg-poly(NaAA-co-AAm) hydrogel.

alkalization time lower than 60 min, no gel was prepared, so the swollen gel strength was not sufficient for a real superabsorbent.

Effect of the alkalinization temperature

Figure 3 illustrates the effect of the temperature of the alkalinization reaction on the equilibrium swelling. The alkaline hydrolysis conditions were kept constant, as mentioned previously. The temperature leading to the hydrogel with the highest absorbency (360 g/g) was around 70°C . The temperatures lower and higher than this optimum temperature resulted in reduced swelling capacity. This behavior suggests an incomplete alkalinization reaction at lower temperatures and alka-

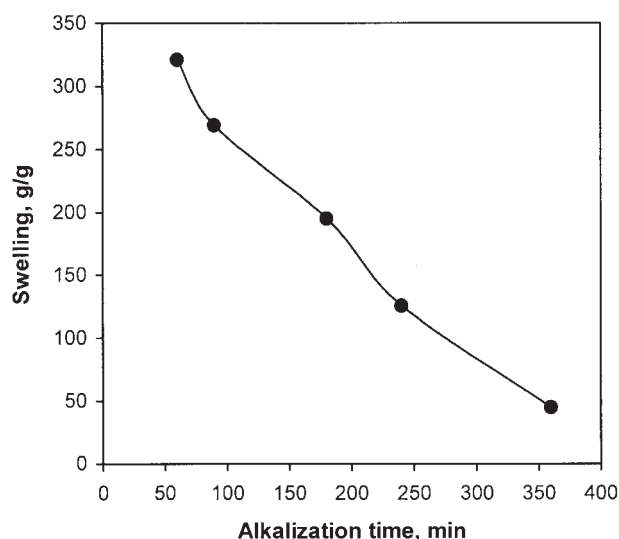


Figure 2 Effect of the alkalinization time on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalinization temperature = 70°C , $[\text{NaOH}] = 8 \text{ wt } \%$, alkaline hydrolysis temperature = 90°C , alkaline hydrolysis time = 120 min, amount of PAN = 1 g, amount of Alg = 1 g).

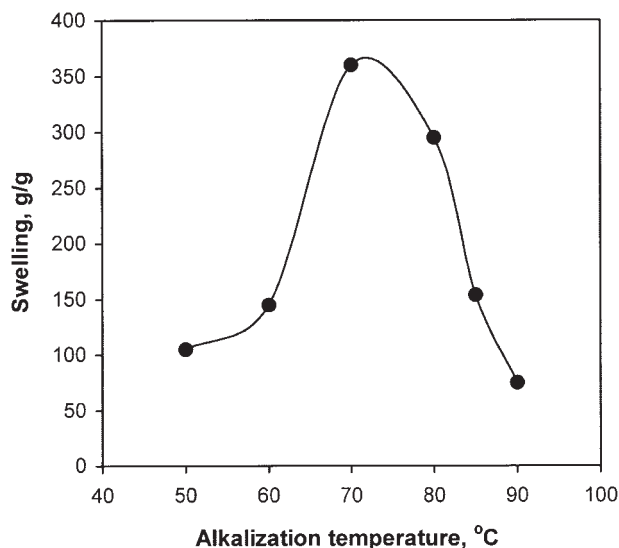


Figure 3 Effect of the alkalinization temperature on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalinization time = 60 min, $[\text{NaOH}] = 8 \text{ wt } \%$, alkaline hydrolysis temperature = 90°C , alkaline hydrolysis time = 120 min, amount of PAN = 1 g, amount of Alg = 1 g).

line degradation of the polysaccharide at higher temperatures.

Effect of the NaOH concentration

The effect of the concentration of NaOH on the water absorbency for the Alg-poly(NaAA-co-AAm) hydrogel is shown in Figure 4. The alkaline hydrolysis temperature and time were kept constant (70°C and 60 min, respectively). A higher NaOH concentration led to more carboxamide and carboxylate groups. The concentrations of NaOH higher than 10 wt %, however, led to low-swelling superabsorbents. This swelling loss could be related to residual (excess) alkaline, which was not removed (e.g., neutralized), after the completion of hydrolysis. The excess cations shielded the carboxylate anions, so the main anion-anion repulsive forces were eliminated and less expanded networks of the hydrogel were able to uptake and retain lower quantities of the aqueous solution. This phenomenon is often called a charge-screening effect.²⁴ In addition, a higher crosslinked structure formed at a higher OH^- concentration. A similar observation was reported by Castel et al.²⁵ for the hydrolysis of starch-g-PAN. Furthermore, the alkaline degradation of the polysaccharide part of the network could be another reason for the swelling decrease in highly concentrated alkaline hydrolytic media.

Effect of the PAN/Alg weight ratio

Different superabsorbent hydrogels with various PAN/Alg weight ratios were synthesized through

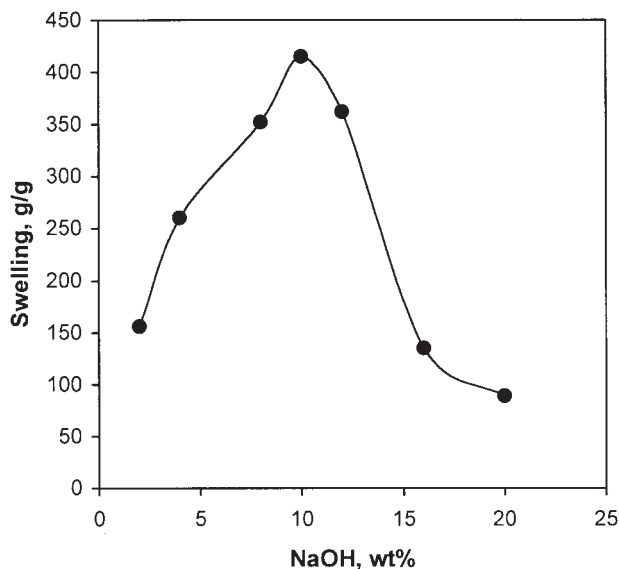


Figure 4 Effect of the NaOH concentration on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 60 min, alkalization temperature = 70°C, alkaline hydrolysis temperature = 90°C, alkaline hydrolysis time = 120 min, amount of PAN = 1 g, amount of Alg = 1 g).

changes in the amounts of PAN (0.50–1.50 g) and Alg (0.50–1.33 g). The results are shown in Figure 5. More PAN led to more carboxamide and carboxylate groups generated from alkaline hydrolysis. However, lower absorbency was achieved when a greater amount of PAN (>1.20 g) was applied. This could be attributed

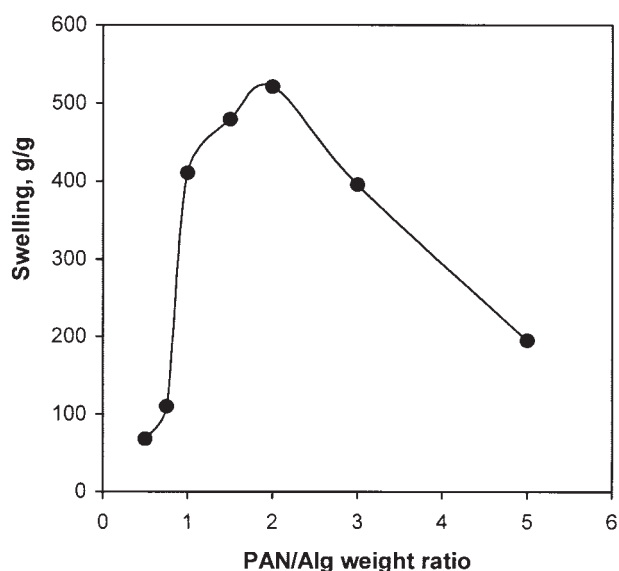


Figure 5 Effect of the PAN/Alg weight ratio on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 60 min, alkalization temperature = 70°C, [NaOH] = 10 wt %, alkaline hydrolysis temperature = 90°C, alkaline hydrolysis time = 120 min).

to the formation of more crosslinks at higher PAN amounts. According to Figure 6, the maximum swelling capacity (521 g/g) was achieved with 1.2 g of PAN.

Effect of the alkaline hydrolysis temperature

The relationship between the alkaline hydrolysis temperature and water absorbency values was studied through the variation of the hydrolysis temperature from 50 to 120°C (Fig. 6). A higher temperature favored the kinetics of alkaline hydrolysis up to 100°C. This behavior was confirmed by faster discoloration at higher temperatures. The temperatures higher than this value, however, resulted in reduced swelling. This may be attributed to the formation of more crosslinks and alkaline degradation of the polysaccharide chains of the hydrogel at higher temperatures (>100°C). A similar observation was reported by Lim et al.²¹ for hydrogels of sodium starch sulfate-g-polyacrylonitrile.

Effect of the alkaline hydrolysis time

Figure 7 shows the effect of the alkaline hydrolysis time on the swelling capacity. The reaction period (the time after the addition of PAN to the mixture) was varied from 15 to 180 min. According to the figure, the water absorbency intensely increased versus time up to 90 min and then gradually decreased. When the hydrolysis time was increased up to 90 min, more carboxamide and carboxylate groups were generated

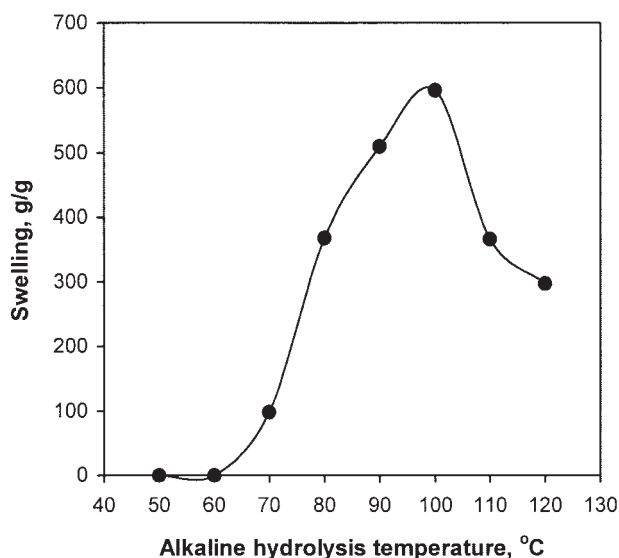


Figure 6 Effect of the alkaline hydrolysis temperature on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 60 min, alkalization temperature = 70°C, [NaOH] = 10 wt %, alkaline hydrolysis time = 120 min, amount of PAN = 1.33 g, amount of Alg = 0.67 g).

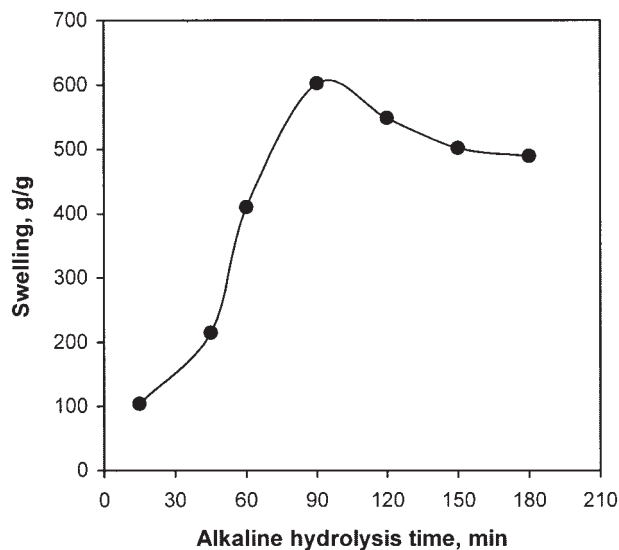


Figure 7 Effect of the alkaline hydrolysis time on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 60 min, alkalization temperature = 70°C, [NaOH] = 10 wt %, alkaline hydrolysis temperature = 100°C, amount of PAN = 1.33 g, amount of Alg = 0.67 g).

from the alkaline hydrolysis of nitrile groups. Intensive electrostatic repulsion of the anions led to higher swelling of the hydrogel. It is obvious that with the reaction time further increasing, more crosslinked structures were formed. In addition, the degradation of the hydrogel, especially the polysaccharide part, under relatively alkaline conditions at 100°C may be another possible reason for the decreased swelling capacity versus higher reaction times.

Effect of the postneutralization pH

In this series of experiments, after the alkaline hydrolysis, excess NaOH was neutralized by an acetic acid solution to a desired pH value (Fig. 8). Without the postneutralization stage (pH ≈ 13), the decreased absorbency was related to the screening effect of excess Na⁺ ions in the swelling media (this effect was described in previous sections). Therefore, the diminished repulsion forces between carboxylate groups led to decreased absorbencies. According to Figure 8, the best pH adjusted after hydrolysis was 7.0. This behavior has also been observed for commercial acrylic acid based SAPs as standard crosslinked polyelectrolytes.²⁶

Effect of the stirring speed

The water absorbency of the product, Alg-poly(NaAA-co-AAm), was affected by the stirring speed of the mechanical stirrer (Fig. 9). The influence of the speed of stirring of the mixture on the final swelling of the hydrogel was varied from 50 to 500 rpm. The water absor-

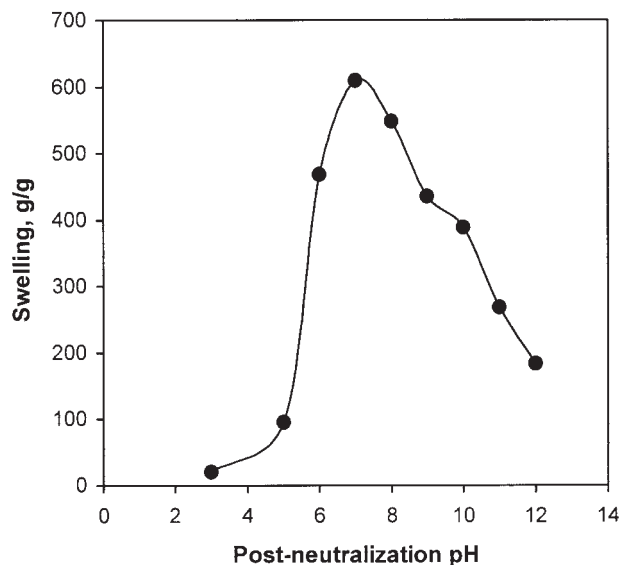


Figure 8 Effect of the postneutralization pH on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 60 min, alkalization temperature = 70°C, [NaOH] = 10 wt %, alkaline hydrolysis temperature = 100°C, alkaline hydrolysis time = 90 min, amount of PAN = 1.33 g, amount of Alg = 0.67 g).

bency was considerably increased when the speed of the propeller-type stirrer was increased from 50 to 250 rpm and then increased very gradually. The sudden swelling enhancement emphasized the remarkable effect of the stirring efficiency on the final product properties. In such

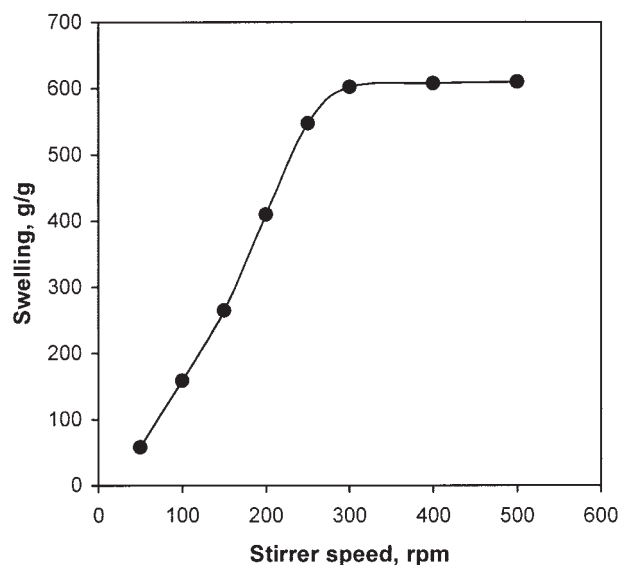


Figure 9 Effect of the stirrer speed on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 60 min, alkalization temperature = 70°C, [NaOH] = 10 wt %, alkaline hydrolysis temperature = 100°C, alkaline hydrolysis time = 90 min, amount of PAN = 1.33 g, amount of Alg = 0.67 g, postneutralization pH = 7).

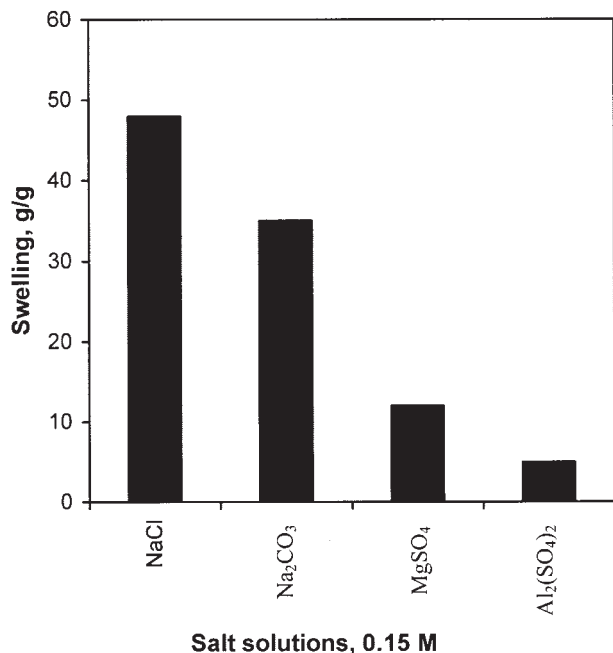


Figure 10 Effect of the ionic strength of salt solutions on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel.

viscous heterogeneous media, effective stirring is required to achieve effective mixing and mass transfer. However, at high rpm values, shear forces may also act to degrade macromolecular chains, leading to decreased molecular weight and subsequent loss of swelling. Therefore, at higher stirring rates, shear degradation neutralizes the enhancing effect of a high speed of mixing. Similar behavior was observed in our previous work.²⁷

Effect of the salinity on the swelling capacity

The swelling ratio is mainly related to the characteristics of the external solution, that is, the charge number and ionic strength, as well as the nature of the polymer, that is, the elasticity of the network, the presence of hydrophilic functional groups, and the extent of crosslinking density.

In this series of experiments, the swelling capacity was measured in various salt solutions (Figs. 10–12). Generally, the swelling ability of anionic hydrogels in various salt solutions is appreciably decreased in comparison with 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 nonperfect anion–anion electrostatic repulsion.²⁴ Therefore, according to the Donnan membrane equilibrium theory, the osmotic pressure resulting from the mobile ion concentration difference between the gel and aqueous phases decreased, and consequently, the absorbency decreased. In addition,

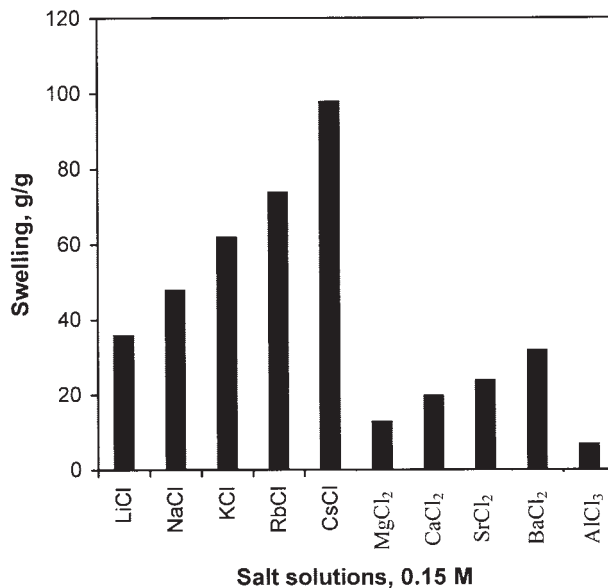


Figure 11 Swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel in different chloride salt solutions (0.15M).

in the case of salt solutions with multivalent cations, ionic crosslinking at the surfaces of the particles caused an appreciable reduction in the swelling capacity.

The results shown in Figure 10 indicate that the absorbency for the Alg-poly(NaAA-co-AAm) hydrogels in various salt solutions decreased with the increasing ionic strength of the salt solution. As mentioned previously, this could be attributed to the cations in the water, which neutralized the carboxylate groups in the hydrogel network.

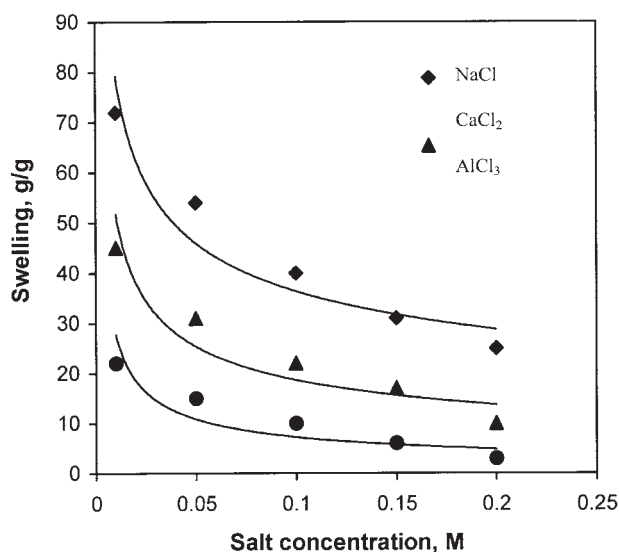


Figure 12 Swelling capacity variation of the Alg-poly(NaAA-co-AAm) superabsorbent in saline solutions with various concentrations.

TABLE I
k and *n* Values^a for the Partially Neutralized
 Collagen-g-PAA Hydrogel

Swelling medium	<i>k</i>	<i>n</i>
NaCl	6.3	0.34
CaCl ₂	6.2	0.44
AlCl ₃	6.4	0.58

^a Obtained from curve fitting (Fig. 12).

The effect of the cation type (cations with different radii and charges) on the swelling behavior is shown in Figure 11. With an increasing cation charge, the degree of crosslinking increased, and swelling consequently decreased. Therefore, the absorbency for the Alg-poly(NaAA-co-AAm) hydrogel in the studied salt solutions was in the following order: monovalent cations > divalent cations > trivalent cations. The effect of the cation radius on the swelling can also be observed in Figure 11. A smaller cationic radius led to lower water absorbency. This was because the smaller the cationic radius was, the stronger the binding ability was of the cation with the carboxylate groups; that is, the hydration ability was weakened, and this led to the water absorbency decrease. As reported by Pass et al.,²⁸ the carboxylate anion interacted with small cations (e.g., Li⁺) more strongly than with large cations (e.g., Cs⁺). The stronger interactions of the carboxylate and small cations were observed with the measurement of the activating coefficients of various cations in several salt solutions. As a result, the water absorbency in monovalent and divalent cation salt solutions was in the order of CsCl > RbCl > KCl > NaCl > LiCl and Ba²⁺ > Sr²⁺ > Ca²⁺ > Mg²⁺, respectively. The swelling capacity of the hydrogels was also measured in various salt solutions (NaCl, CaCl₂, and AlCl₃) with different concentrations. Figure 12 illustrates a reverse relationship between the concentration of the salt solutions and the swelling capacity of the hydrogel. Again, a charge-screening effect and ionic crosslinking were the main explanations for the intense loss of swelling. The known relationship between the swelling and concentration of a salt solution can be stated as follows:²⁴

$$\text{Swelling} = k[\text{Salt}]^{-n} \quad (2)$$

where *k* and *n* are constant values for an individual superabsorbent. The *k* value is the swelling at a high salt concentration, and the *n* value is a measure of the salt sensitivity. Figure 12 indicates that making the salt concentrations higher than ~0.15M had no appreciable influence on the superabsorbency of the superabsorbent. In the other words, the trend of monovalent cations > divalent cations > trivalent cations was observed in the dilute salt solutions. As shown in

Table I, the *k* values were almost the same (~6) for the swelling in various salt solutions. The *n* values proportionally changed with the cation valence enhancement. Here, the ionic crosslinking was a more effective factor against swelling than the charge-screening effect of the cation.

pH-dependent swelling

Most ionic hydrogels are pH-sensitive, and so the pH of the swelling medium has direct control over the degree of absorbency capacity of the network. Therefore, the equilibrium swelling of the Alg-poly(NaAA-co-AAm) hydrogel was measured in solutions with various pHs ranging from 1 to 13 (Fig. 13). Because the swelling capacity of all anionic hydrogels is appreciably reduced by the addition of counterions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 13.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (99 g/g) was obtained at pH 8. In the pH region from 1 to 3, most carboxylate groups were in the form of —COOH, and the low swelling values of the hydrogels could be attributed to the presence of nonionic hydrophilic COOH and —OH groups in the hydrogel network. The swelling ratio increased rapidly as the pH of the solutions was increased from 4 to 8. At higher pHs (4–8), some carboxylate groups were ionized, and the electrostatic repulsion between COO[−] groups caused an enhancement of the swelling capacity. The reason for the swelling loss of the highly basic solutions (pH > 8) was the charge-screening effect of excess Na⁺ in the swelling media, which shielded the carboxylate anions and prevented effec-

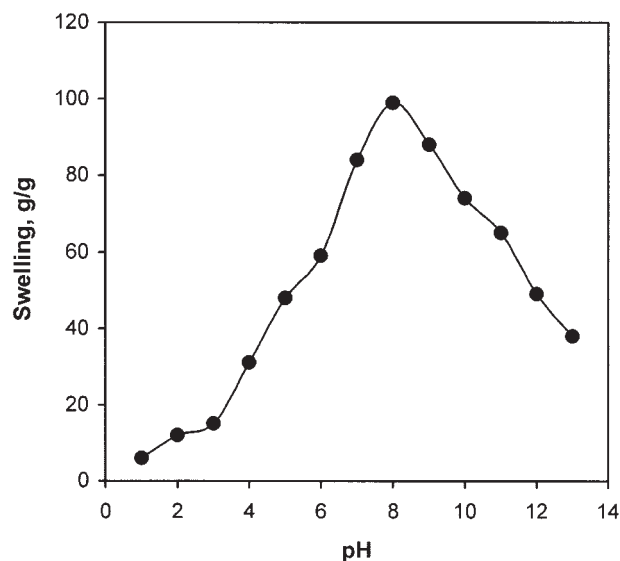


Figure 13 Effect of the pH of solutions on the swelling capacity of the Alg-poly(NaAA-co-AAm) hydrogel.

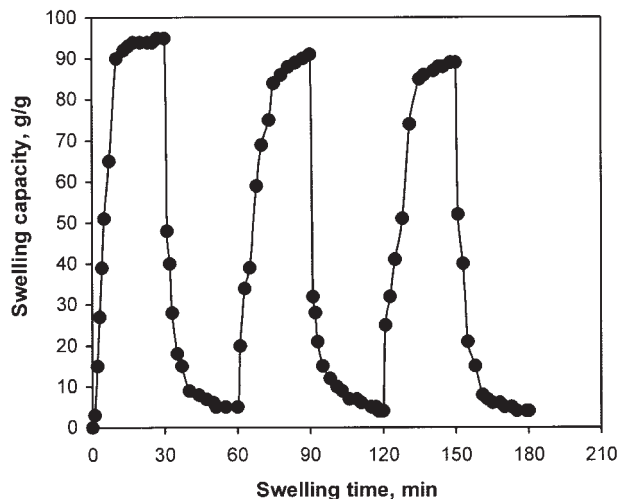


Figure 14 On-off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of the Alg-poly(NaAA-co-AAm) hydrogel. The time interval between the pH changes was 30 min.

tive anion-anion repulsion. Similar swelling pH dependence has been reported for other hydrogel systems.^{29–32}

pH reversibility for the Alg-poly(NaAA-co-AAm) hydrogel

Because these hydrogels showed different swelling behaviors in various pH solutions, we investigated the pH reversibility of these hydrogels in 0.01M solutions with pH 2 and pH 8 (Fig. 14). At pH 8.0, the hydrogel swelled up to 95 g/g because of anion-anion repulsive electrostatic forces, whereas at pH 2.0, it shrank within a few minutes because of protonation of the carboxylate groups. This sharp swelling-deswelling behavior of the hydrogels makes them suitable candidates for controlled drug delivery systems. On-off switching behavior such as reversible swelling and deswelling has been reported for other ionic hydrogels.^{33–36}

Kinetics of swelling

In practical applications, not only is a higher swelling capacity required, but a higher swelling rate is also needed. Buchholz³⁷ suggested that the swelling kinetics for superabsorbents are significantly influenced by factors such as the swelling capacity, size distribution of powder particles, specific size area, and composition of the polymer. Figure 15 presents the dynamic swelling behavior of Alg-poly(NaAA-co-AAm) superabsorbent samples with various particle sizes in water. Initially, the rate of water uptake sharply increased, and then it began to level off. The time required to reach the equilibrium swelling capacity was achieved after ~20 min. According to the Voigt-based

model, the swelling rate can be described by the following equation:³⁸

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

where S_t (g/g) is the swelling at time t (min), S_e is the equilibrium swelling (power parameter; g/g), and τ (min) is the rate parameter. To calculate τ , using the formula and a little rearrangement, we plotted $\ln[1 - (S_t - S_e)]$ versus time t . The slope of the straight line (slope = $-1/\tau$) gave τ . For example, in the case of hydrogels with particle sizes of 100–250 μm , the τ value was 5.3 min. This means that this hydrogel took 5.3 min to absorb 0.63 of its equilibrium capacity of swelling. Because the τ value is a measure of the swelling rate (i.e., the lower the τ value, the higher the rate of swelling), it can be used for comparative evaluation of the rate of water absorbency of hydrogels. The τ values were 5.3, 8.4, 10.1, and 11.4 min for the superabsorbents with particle sizes of 100–250, 250–400, 400–550, and 550–700 μm , respectively. As the size of the sample decreased, the time taken for the maximum absorbency (i.e., τ) for the hydrogel also decreased.³⁹ This could be attributed to an increase in the surface area with the decreasing particle size of the hydrogel.

CONCLUSIONS

In this study, we prepared a superabsorbent hydrogel, Alg-poly(NaAA-co-AAm), by the alkaline hydrolysis of an Alg-PAN physical mixture. The reaction of the alginate alkoxide anions with nitrile groups of PAN formed crosslinking points and resulted in a three-

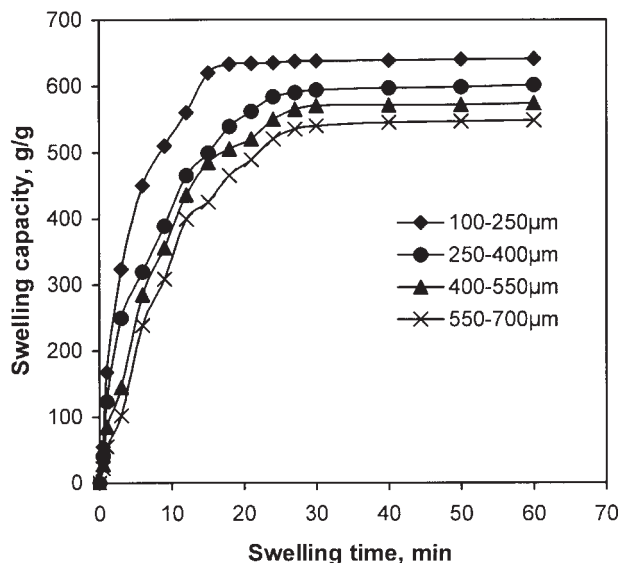


Figure 15 Representative swelling kinetics of the Alg-poly(NaAA-co-AAm) superabsorbent hydrogel with various particle sizes.

dimensional network. Because a polymerization reaction was not involved, there was no need for initiators, toxic and/or expensive monomers, and crosslinkers. Therefore, problems such as polymerization control, conversion loss, and residual monomer were eliminated. Indeed, because no toxic material was used for the synthesis, this practical approach may be considered a relatively green process. In addition, this one-step preparative method was conducted under normal atmospheric conditions in a short period. The dark red/yellow color change provided a visual indication for recognizing the reaction completion. We attempted to optimize the reaction conditions to obtain hydrogels with higher swelling values. Therefore, the maximum water absorbency (610 g/g) was achieved under the following optimum conditions: an alkalization time of 60 min, an alkalization temperature of 70°C, a NaOH concentration of 10 wt %, a PAN/Alg weight ratio of 2, an alkaline hydrolysis temperature of 100°C, an alkaline hydrolysis time of 90 min, a postneutralization pH of 7, and a stirrer speed of 250 rpm. The swelling measurements of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in CsCl, RbCl, and KCl solutions. However, the swelling loss in salt solutions, in comparison with distilled water, could be attributed to a charge-screening effect and ionic crosslinking for mono- and multivalent cations, respectively. Also, the superabsorbent hydrogels exhibited high sensitivity to pH, so several swelling changes of the hydrogel were observed in lieu of pH variations in a wide range (1–13). Furthermore, the reversible swelling–deswelling behavior in solutions with acidic and basic pHs made the hydrogels suitable candidates for controlled drug delivery systems. Finally, the dynamic swelling kinetics of the hydrogels showed that the rate of absorbency increased with the decreasing particle size of the superabsorbing samples.

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