

Synthesis and Superswelling Behavior of Carboxymethylcellulose–Poly(sodium acrylate-co-acrylamide) Hydrogel

Mohammad Sadeghi,¹ Hossein Hosseinzadeh²

¹Department of Chemistry, Science Faculty, Islamic Azad University, Arak Branch, Arak, Iran

²Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran, Iran

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ABSTRACT: In this paper, attention is paid to synthesis and swelling behavior of a superabsorbent hydrogel based carboxymethylcellulose (CMC) and polyacrylonitrile (PAN). The physical mixture of CMC and PAN was hydrolyzed in NaOH solution to yield hydrogel, CMC–poly(NaAA-co-AAm). During alkaline hydrolysis, the nitrile groups of PAN were completely converted to a mixture of hydrophilic carboxamide and carboxylate groups followed by *in situ* crosslinking of the grafted PAN chains. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR spectroscopy. The reaction variables affecting the swelling capacity of the hydrogel were systematically optimized to

achieve a hydrogel with swelling capacity as high as possible. Swelling measurements of the synthesized hydrogels in various chloride salt solutions indicated a swelling-loss with increase in the ionic strength of the salt solutions. The pH of the various solutions also affected the swelling of the superabsorbent. Furthermore, the present hydrogels showed a pH-reversible property. Finally, the swelling kinetics of synthesized hydrogels with various absorbent particle sizes was briefly examined. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1142–1151, 2008

Key words: hydrogel; superabsorbent; carboxymethylcellulose; polyacrylonitrile; swelling behavior; crosslinking

INTRODUCTION

In recent years, interest in natural-based superabsorbent hydrogel has increased, mainly due to high hydrophilicity, biocompatibility, nontoxicity, and biodegradability of biopolymers. These materials are defined as crosslinked macromolecular networks that can absorb water or physical fluids up to many times of their own weight in a short time, but are not dissolved when brought into contact with water.¹ The absorbed fluids are hardly removable even under some pressure. Because of excellent characteristics, superabsorbent hydrogels are widely used in many fields, such as agricultural and horticultural, disposable diapers, feminine napkins, pharmaceuticals, and medical applications.^{2–4} This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450,000 tons in 1996.¹ Nowadays, the worldwide production of SAPs is more than one million tons in year. Hence, synthesis and investigation of specific and new superabsorbent hydrogels with high absorbency, mechanical strength, and initial

absorption rate has been the goal of several research groups in the past decades.^{5–8}

Because of their exceptional properties, i.e., biocompatibility, biodegradability, renewability, and nontoxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels. Carboxymethylcellulose (CMC), an anionic water-soluble polysaccharide, is the most modified cellulose, which is used in various fields such as detergent, food, paper, and textile industries. The application potential of CMC has been demonstrated because of its promising characteristics including those of mentioned above.

Most of ionic hydrogels sometimes undergo a volume phase transition in response to a little change in surrounding conditions such as heat, pH, electric field, chemical environments, etc. The hydrogels that respond to external stimuli are often referred to as “intelligent” or “smart” hydrogels. They have important applications in the field of medicine, pharmacy, and biotechnology. 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 (MW) protein drugs.^{9,10}

Free radical graft copolymerization of vinylic monomers onto polysaccharide backbones followed

Correspondence to: M. Sadeghi (m-sadeghi@iau-arak.ac.ir).

by crosslinking of their chains is a well-known method for synthesis of these polysaccharide-based networks. The first industrial superabsorbent hydrogel, hydrolyzed starch-*g*-polyacrylonitrile (HSPAN), was synthesized using this method via ceric-induced graft copolymerization of acrylonitrile onto starch followed by crosslinking alkaline hydrolysis of the nitrile groups of the produced graft copolymer.¹¹ Radical polymerization, however, has several disadvantages. Reproducibility of this method is poor, and there is little control over the grafting process, so that the MW distribution is polydisperse. In addition, the necessity for inert gases, e.g., argon, for preparing of oxygen-free atmosphere and use of toxic and expensive crosslinker agents are another disadvantages of free radical polymerization reactions. These problems have been reviewed in detail elsewhere.¹²

After the development of the HSPAN hydrogel, Fanta et al. indicated by a solubility test that crosslinks were formed during saponification of SPAN, by the reaction of starch alkoxide ions with the nitrile groups of the PAN chains as the initiation reaction of crosslinking.¹³ Therefore, the initially formed oxygen-carbon bonds between starch hydroxyls and nitrile groups of the PAN chains remain as crosslinking sites. For confirming this fact, Fanta et al. treated PAN homopolymers with starch in hot aqueous alkali media.¹³ They demonstrated that PAN saponified in the presence of starch became partially insoluble. Then, Fanta et al. attempted to extend the idea in the case of preparation of superabsorbent hydrogels by saponification of PAN in the presence of polyhydroxy polymers.¹⁴ Finally, Yamaguchi et al. reported the preparation of superabsorbing polymers from mixture of PAN and various saccharide or alcohols.¹⁵

To the best of our knowledge, based on a precise survey of the Chemical Abstracts, there is no published report on the synthesis of a superabsorbing hydrogel via alkaline hydrolysis of CMC-polyacrylonitrile (PAN) physical mixture. Hence, the objectives of this study were to synthesize and investigate the pH-sensitive swelling behavior of a superabsorbent hydrogel made of CMC and PAN.

EXPERIMENTAL

Materials

The polysaccharide, CMC (chemical grade, MW 50,000, DS = 0.50), was purchased from Merck Chemical (Germany). PAN was synthesized through a method mentioned in the literature.¹⁵ Double distilled water was used for the hydrogel preparation and swelling measurements.

Synthesis procedure of the hydrogel

A general one step preparative method for synthesis of CMC-poly(sodium acrylate-co-acrylamide) [CMC-poly(NaAA-co-AAm)] hydrogel was conducted as follows. CMC (0.50–1.50 g) and 35 mL doubly distilled water were added to a three-necked reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm). The reactor was immersed in a thermostated water bath. After complete dissolution of CMC to form a homogeneous solution, required amount of sodium hydroxide (3.0–20.0 wt %) was added to the CMC solution at desired temperature (alkalization temperature, 50–100°C). The mixture was stirred for a certain time period (alkalization times, 30–360 min). Different hydrogels were prepared by varying the amount of PAN (0.50–1.50 g) dispersed in the reaction mixture to saponify for a desired time and temperatures (alkaline time and temperature). During saponification, NH₃ gas 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 addition of 10 wt % aqueous acetic acid solution. Then the gelled product was cut to small pieces and put in methanol (200 mL) for 5 h to remove water. The hardened particles were filtered and dried in oven (50°C, 10 h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

Swelling measurements using tea bag method

The 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 in distilled water (200 mL), desired salt solution (100 mL), or solution with various pHs (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 solution. The equilibrated swelling (ES) was measured twice as grams of water per gram of dry hydrogel using the following equation:

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

where W_1 and W_2 are the weights of dry and swollen gel, respectively.

pH-sensitivity

pH-sensitivity of the hydrogel was determined in terms of swelling and deswelling of the final product

in basic (pH 8.0) and acidic (pH 3.0) solutions, respectively. 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 above-mentioned method.

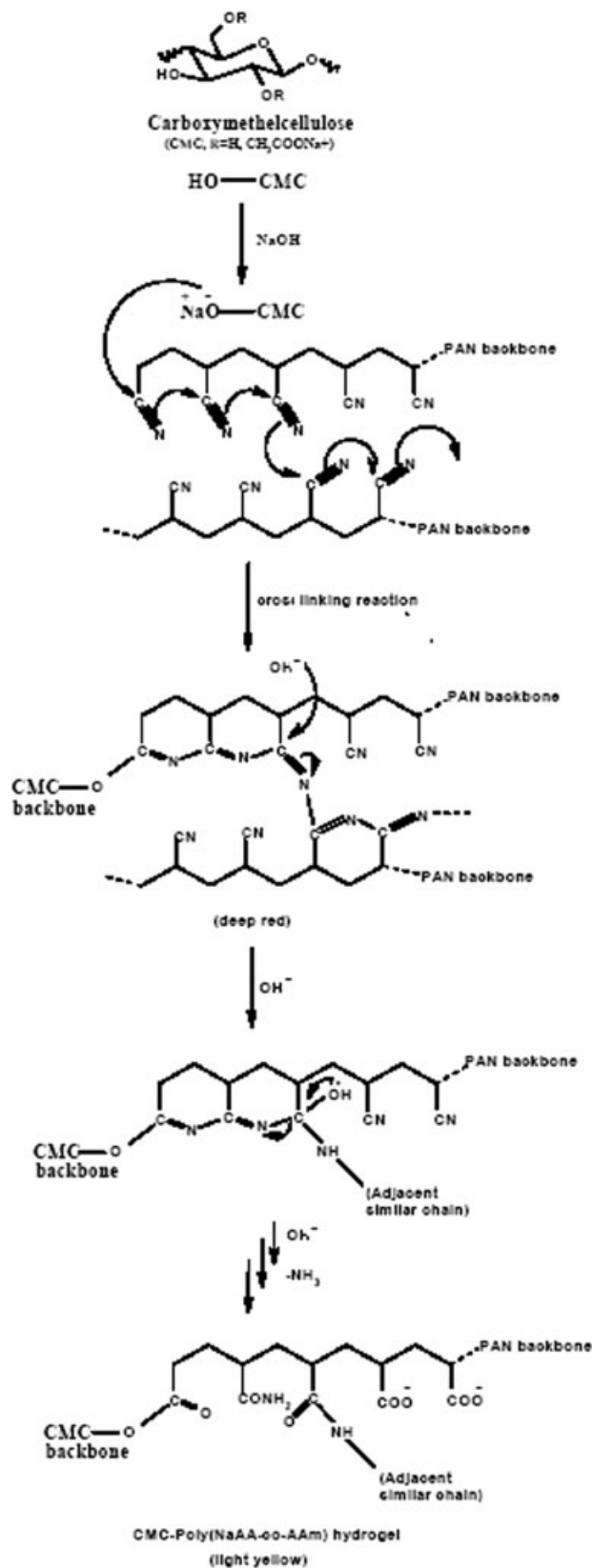
Infrared spectroscopy

The samples were mixed with KBr to make pellets. Spectra were obtained using an ABB Bomem MB-100 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Synthesis and mechanism aspects

Alkaline hydrolysis of the CMC-PAN mixture was carried out using aqueous sodium hydroxide solution. A general reaction mechanism for CMC-poly(NaAA-co-AAm) hydrogel formation is shown in Scheme 1. At the first step, the hydroxyl ions abstract hydrogen from the $-OH$ group of CMC substrate to form corresponding alkoxide anions. Then, these macroalkoxides initiate crosslinking reaction between some adjacent PAN pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, $-C=N-$, conjugated bonds), with dark red color. The intermediate was then saponified using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups. During the alkaline hydrolysis, ammonia was evolved and an orange-red color developed due to conjugated imine formation. This sharp color change was used as an indication to stop the alkaline treatment. As shown in Scheme 1, crosslinking reaction also occurred between some nitrile groups of adjacent PAN pendant. However, incompletely hydrolyzed structures may also give rise to a few crosslinking points resulting in a loosely crosslinked network. It has been reported, in the case of H-SPAN, a maximum conversion of 70% of nitrile to carboxyl groups and the remaining 30% are amide groups.¹⁶ In fact, details of the chemical processes and mechanism involved in H-SPAN synthesis are not yet well understood. For instance, the incomplete hydrolysis is interpreted as being related to steric and polar fac-



Scheme 1 Proposed mechanism for crosslinking during the hydrolysis of nitrile groups of the CMC-PAN mixture to produce the CMC-poly(NaAA-co-AAm) hydrogel.

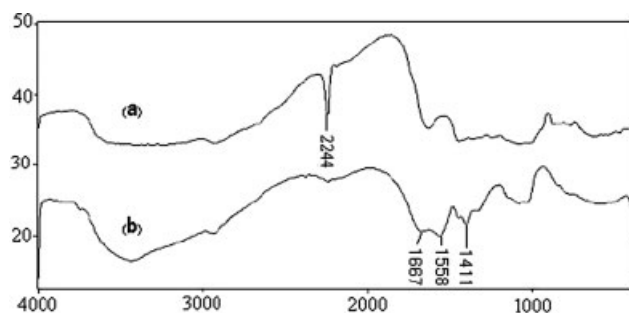


Figure 1 FTIR spectra [transmittance versus wave number (cm^{-1})] of (a) the physical mixture of CMC and PAN and (b) the crosslinked CMC-poly(NaAA-co-AAm) hydrogel.

tors.¹⁷ Weaver et al. suggested that condensation might also occur between carboxyl and amide groups to form imide structures.¹⁸ Therefore, in the case of our hydrogel, CMC-poly(NaAA-co-AAm), we realized that precise control of the ratio is practically impossible.

Spectral characterization

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1(a) is the spectrum of the physical mixture of CMC and PAN. A sharp absorption peak shown at 2244 cm^{-1} is attributed to stretching of $-\text{CN}$ groups of PAN. After alkaline hydrolysis, the absorptions modes at 1667 , 1558 , and 1411 cm^{-1} [Fig. 1(b)] can be attributed to $\text{C}=\text{O}$ stretching in carboxamide functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively.¹⁹ The stretching band of $-\text{NH}$ overlapped with the $-\text{OH}$ stretching band of the CMC 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 an additional evidence of *in situ* "crosslinking reaction" during hydrolyzing nitrile groups, a similar reaction was conducted in absence of the polysaccharide, CMC. Since the resulted product became soluble, the crosslinks really formed between the alkoxide ions of CMC and the nitrile groups of PAN. This fact practically proves that the CMC hydroxyls are involved in the crosslinking. In fact, in absence of CMC no gel is prepared.

Optimization of the reaction conditions

Different variables affecting the ultimate swelling capacity (i.e., alkalization time and temperature, NaOH concentration, PAN/CMC weight ratio, alkaline hydrolysis time and temperature) were opti-

mized to achieve superabsorbents with maximum water absorbing capacity.

Effect of alkalization time

The relationship between the alkalization time of the hydroxyl groups of CMC and water absorbing capacity values was studied by varying the time from 30 to 360 min (Fig. 2). The alkaline hydrolysis conditions were kept constant (8 wt % NaOH, 90°C , 60 min). As shown in the figure, the absorbency is decreased with increasing the alkalization time. This swelling loss can be attributed to some sort of unwanted alkaline degradation of the polysaccharide. This disconnection decreases the main chain MW. Since the swelling capacity is proportionally depended on the MW of the chains in the networks of superabsorbent hydrogels,³ the unwanted disconnection results in the swelling-loss even though it is unextensive. Similar alkaline degradation behaviors were already reported in the case of other polysaccharides.²⁰ In addition, more $-\text{OH}$ groups are converted to corresponding alkoxide anions at longer alkalization times (Scheme 1). Therefore, a higher crosslinked, rigid structure is formed. It is known that a higher degree of crosslinking results in a rigid network that cannot hold a large quantity of fluid.^{1,3,21} Maximum water absorbing capacity (254 g/g) was achieved at the time of 30 min. In fact, with alkalization time lower than 30 min no gel is formed, so that the swollen gel strength is not sufficient to be referred as a "real superabsorbent."

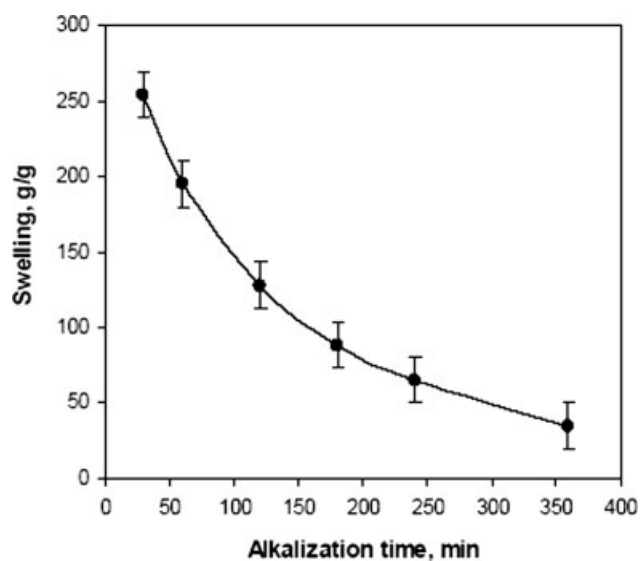


Figure 2 Effect of the alkalization time on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization temperature = 70°C , $[\text{NaOH}] = 8 \text{ wt } \%$, alkaline hydrolysis temperature = 90°C , alkaline hydrolysis time = 60 min, amount of PAN = 1 g, amount of CMC = 1 g).

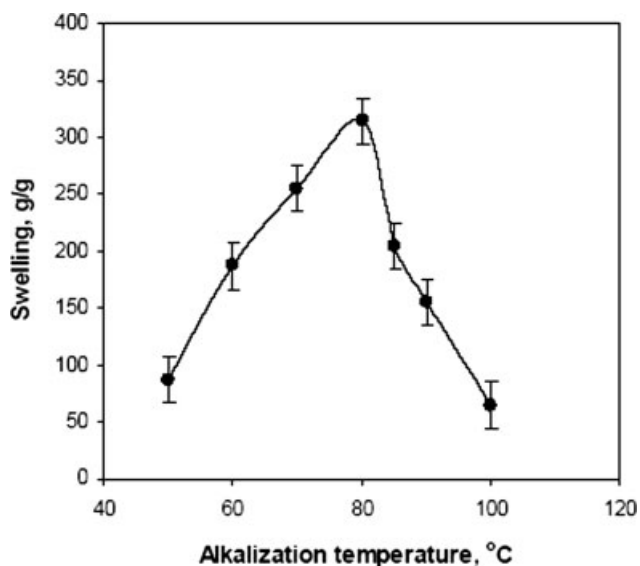


Figure 3 Effect of the alkalization temperature on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 30 min, [NaOH] = 8 wt %, alkaline hydrolysis temperature = 90 °C, alkaline hydrolysis time = 60 min, amount of PAN = 1 g, amount of CMC = 1 g).

Effect of alkalization temperature

The swelling capacity of the hydrogels prepared at different temperatures of alkalization reaction is shown in Figure 3. The alkaline hydrolysis conditions were kept constant as mentioned above. As it is obvious from the figure, the temperature leading the hydrogel with highest absorbency (314 g/g) is around 80°C. The temperatures lower and higher than this optimum temperature resulted in reduced swelling capacity. This behavior suggests the incomplete alkalization reaction at lower temperatures, and alkaline degradation of the polysaccharide at higher temperatures.

Effect of NaOH concentration

Figure 4 demonstrates the effect of NaOH concentration on swelling capacity of CMC-poly(NaAA-co-AAm) hydrogel. Alkaline hydrolysis reaction was carried out at 90°C for 60 min. Maximum swelling capacity (389 g/g) was obtained at 10 wt % of NaOH. Higher or lower than this concentration gives hydrogel with decreased swelling capacity. It is obvious that the higher the reaction time leads to more carboxamide and carboxylate groups generated from alkaline hydrolysis. This behavior was confirmed by faster discoloration at higher NaOH concentration. This accounts for the initial increment in swelling up to a certain amount of sodium hydroxide. The swelling decrease after the maximum

may be attributed to the formation of more cross-links at higher OH^- concentration. A similar observation has been reported by Castel et al. in the case of the hydrolysis of SPAN.²² Additionally, alkaline degradation of the polysaccharide backbone can be another reason of the swelling decrease in highly concentrated alkaline hydrolytic media. Furthermore, the intensive decrease in absorbency can be related to residual (excess) alkaline, which was not removed (e.g., neutralized), after completion of hydrolysis. So, at concentrations higher than 10 wt % of NaOH, the swelling measurement environment of the final product contains higher concentration of Na^+ ions. The sodium hydroxide solutions with concentrations higher than 10 wt % have excess Na^+ . The excess cations shield the carboxylate anions and prevent effective anion-anion repulsion. This phenomenon is often referred to as "charge screening effect."²¹ The diminished repulsion leads to a less expanded networks of the hydrogel being able to uptake and retain lower quantities of the aqueous solution.

Effect of PAN/CMC weight ratio

The effect of PAN/CMC weight ratio on water absorbing capacity was studied by varying the amount of CMC and PAN, while the rest of variables were unchanged (Fig. 5). Maximum swelling (487 g/g) was achieved at the PAN/CMC of 1.5. The

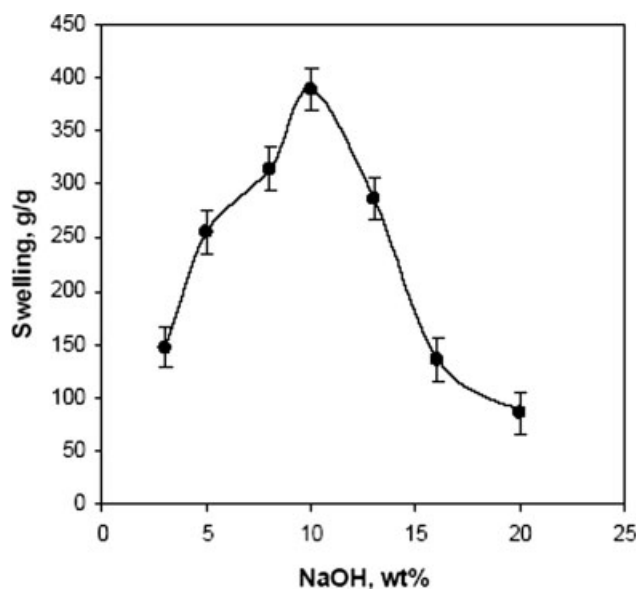


Figure 4 Effect of the NaOH concentration on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 30 min, alkalization temperature = 80 °C, alkaline hydrolysis temperature = 90 °C, alkaline hydrolysis time = 60 min, amount of PAN = 1 g, amount of CMC = 1 g).

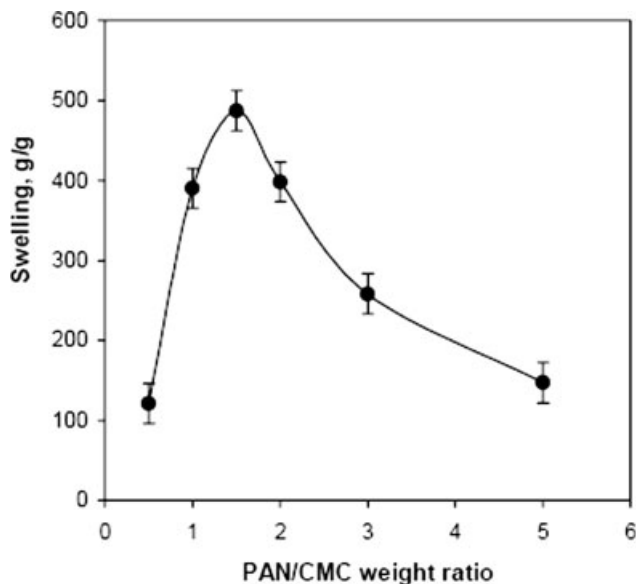


Figure 5 Effect of the PAN/CMC weight ratio on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 30 min, alkalization temperature = 80 °C, [NaOH] = 10 wt %, alkaline hydrolysis temperature = 90 °C, alkaline hydrolysis time = 60 min).

initial increase in water absorbing capacity could be originated from the more carboxamide and carboxylate groups generated from alkaline hydrolysis of PAN. The swelling loss at higher PAN amount can

be explained by the formation of a higher cross-linked, rigid structure.

Effect of alkaline hydrolysis temperature

In this series of experiments, the effect of concentration of the alkaline hydrolysis temperature on water absorbing capacity was investigated. As indicated in Figure 6, the maximum absorbency (491 g/g) is achieved at 90°C. Higher temperature favors the kinetics of alkaline hydrolysis up to ~90°C. The temperatures higher than this value, however, lead to low-swelling superabsorbents. This swelling-loss may be attributed to more crosslink formation and alkaline degradation of the polysaccharide part of the hydrogel occurred at high temperatures. Similar observation has been reported by Lim et al. in the case of the hydrogels of sodium starch sulfate-g-PAN.²³

Effect of alkaline hydrolysis time

The relationship between the time of hydrolysis of PAN (the time after the addition of PAN to the mixture) and water absorbing capacity values was studied by varying the hydrolysis time from 20 to 180 min. As it is obvious from Figure 7, the absorbency is increased with increase in the alkaline hydrolysis time up to 90 min (559 g/g) and then, decreased with a further increase in time of alkaline

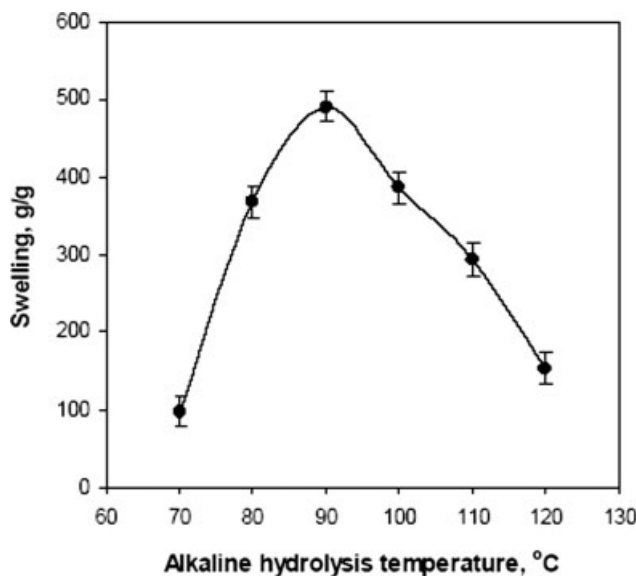


Figure 6 Effect of the alkaline hydrolysis temperature on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 30 min, alkalization temperature = 80 °C, [NaOH] = 10 wt %, alkaline hydrolysis time = 60 min, amount of PAN = 1.20 g, amount of CMC = 0.80 g).

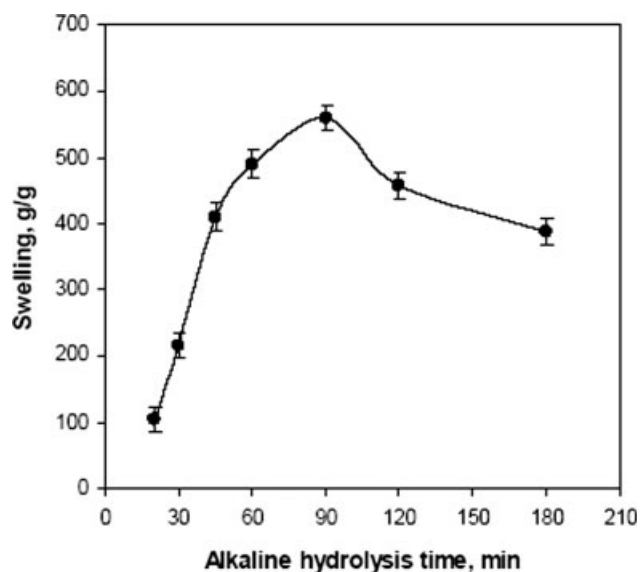


Figure 7 Effect of the alkaline hydrolysis time on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel (reaction conditions: alkalization time = 30 min, alkalization temperature = 80 °C, [NaOH] = 10 wt %, alkaline hydrolysis temperature = 90 °C, amount of PAN = 1.20 g, amount of CMC = 0.80 g).

hydrolysis of AN groups. The increase in the alkaline hydrolysis time results in higher extent of the reactions between nitrile groups including those of adjacent pendant PAN of the neighboring polymer chains. Therefore, the increase in the reaction time leads to more carboxamide and carboxylate groups; hence, increased carboxylate anions resulting in absorbency enhancement. Intensive electrostatic repulsion of the anions leads to higher swelling of hydrogel. Thereafter, decreasing the absorbency may be attributed to unwanted degradation of the hydrogel under relatively alkaline conditions (10 wt % NaOH, 90°C).

Swelling behavior in salt solutions

The swelling capacity of superabsorbent hydrogels could be significantly affected by various factors of the external solutions such as its valencies and salt concentration. The presence of ions in the swelling medium has a profound effect on the absorbency behavior of the superabsorbent hydrogels. Many theories were reported in the case of swelling behavior of ionic hydrogels in saline solutions. The simplest one of the theories is Donnan equilibrium theory. This theory attributes the electrostatic interactions (ion swelling pressure) to the difference between the osmotic pressure of freely mobile ions in the gel and in the outer solutions. The osmotic pressure is the driving force for swelling of superabsorbents. Increasing the ionic mobile ion concentration difference between the polymer gel and external medium which, in turn, reduces the gel volume, i.e., the gel shrinks and swelling capacity decreases (charge screening effect). In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciably decrease in swelling capacity. For example, Castel et al. reported that calcium ion can drastically decrease the swelling capacity for a hydrolyzed SPAN, due to the complexing ability of the carboxylate group to include the formation of intra- and intermolecular complexes.²²

The effect of charge of cation on swelling can be concluded from Figure 8. With increasing the charge of cation, degree of ionic crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency of the synthesized hydrogel is in the order of NaCl > CaCl₂ > AlCl₃. Figure 8 also shows the swelling capacity of the hydrogel [CMC-poly(NaAA-co-AAm)] as a function of the salt concentration for NaCl, CaCl₂, and AlCl₃ solutions. These results reveal that the swelling ratio decreases as the salt concentration of the medium increases. The known relationship between swelling and con-

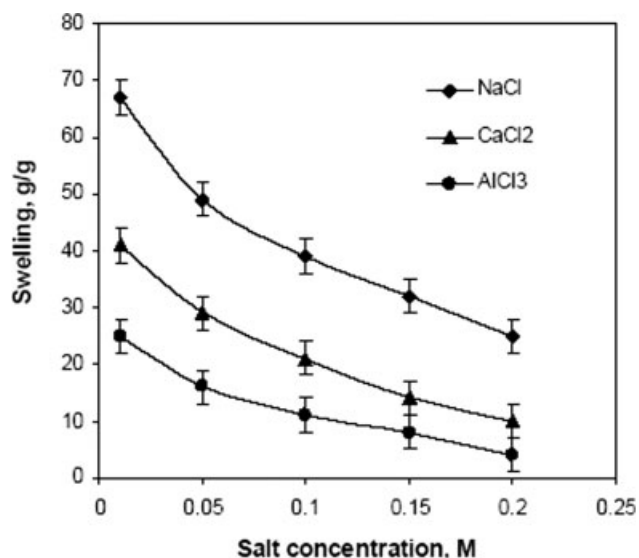


Figure 8 Swelling capacity variation of the CMC-poly(NaAA-co-AAm) superabsorbent in saline solutions with various concentrations.

centration of salt solution is stated as following equation:²¹

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

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. While the k values are almost the same (~ 8) for the swelling in various salt solutions, the n values are totally different (Table I). As given in Table I, the n values proportionally increase with the cation valency enhancement. These results imply that the effect of the ionic crosslinking acts as more effective factor against swelling rather than the charge screening effect of the cation.

The results shown in Figure 9 indicate that the absorbency for the CMC-poly(NaAA-co-AAm) hydrogels in various salt solutions decreased with the increasing ionic strength of the salt solution. The effect of the ionic strength on water absorbing capacity has been determined using the relation suggested by Hermans:²⁴

$$Q_{(\text{eq})}^{5/3} = A + B I^2 / I \quad (3)$$

where $Q_{(\text{eq})}$ is the equilibrium water absorbing capacity, I is the ionic strength of the external solution, and A and B are the empirical parameters. At low ionic strengths, the concentration of bond charges within the hydrogel network exceeds the concentration of salt in the external solutions; a large ion-swelling pressure causes the hydrogel to expand, thereby lowering the concentration of ions within the hydrogel. As the external salt concentration rises,

TABLE I
***k* and *n* Values^a for the CMC-poly(NaAA-co-AAm) Hydrogel**

Swelling medium	<i>k</i>	<i>n</i>
NaCl	8.3	0.38
CaCl ₂	8.2	0.48
AlCl ₃	8.4	0.53

^a Obtained from curve fitting (Fig. 8).

the difference between the internal and external ion concentration decreases and the hydrogel deswells. The hydrogel continues to deswell with increasing external salt concentration until the mobile-ion concentrations inside and outside are approximately equal. These phenomena can also be explained on the basis of repulsion between fixed charged groups on the hydrogel. As ionic strength increases, repulsion is shielded and the hydrogel deswell (charge screening effect).

Effect of pH on equilibrium swelling

Most of the ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, the equilibrium swelling for the synthesized hydrogels was measured in different pH solutions ranged from 1.0 to 12.0 (Fig. 10). The swelling capacity of all "anionic" hydrogels

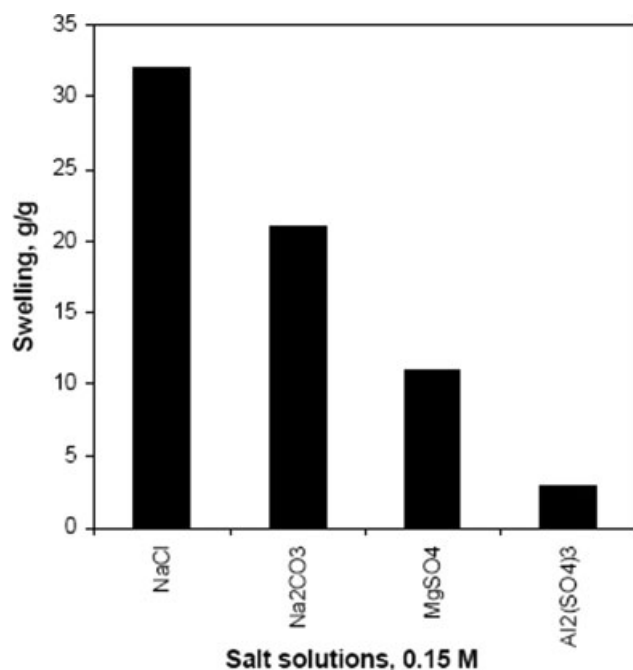


Figure 9 Effect of the ionic strength of salt solutions on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel.

is appreciably decreased by addition of counter ions (cations) to the swelling medium. No buffer solutions were used and stock NaOH (pH 12.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (107 g/g) was obtained at pH 8. Under acidic pHs (≤ 3), most of the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently the swelling decreased. However, some sort of attractive interactions (H—O and H—N hydrogen bonding) lead to decreased absorbencies. On further increase in the pH (3–8) the swelling capacity surprisingly improved. This can be attributed to the fact that with increasing pH of the external solution, the carboxylic acid groups of the hydrogel are converted to carboxylate anions. This obviously results in an expansion of the network chains causing to an increase in absorbency amount. The reason of the swelling-loss for the highly basic solutions (pH > 8) is "charge screening effect" of excess Na⁺ in the swelling media, which shields the carboxylate anions and prevents effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems.^{25–28}

pH-responsiveness behavior of hydrogel

Since the present hydrogels show different swelling behaviors in acidic and basic pH solutions, we investigated the reversible swelling-deswelling behavior of these hydrogels in 0.01M solutions at pH 3.0 and 8.0 (Fig. 11). At pH 8.0, the hydrogel swells because of anion-anion repulsive electrostatic forces, while at

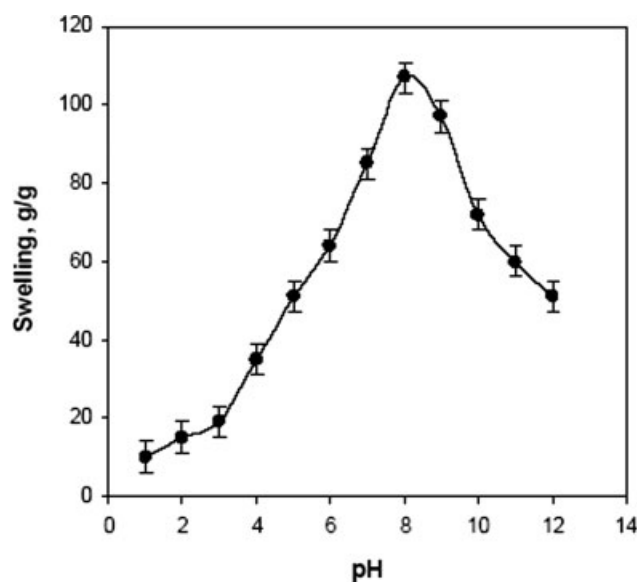


Figure 10 Effect of the pH of solutions on the swelling capacity of the CMC-poly(NaAA-co-AAm) hydrogel.

pH 3.0, it shrinks within a few minutes because of protonation of the carboxylate anions. This swelling–deswelling behavior of the hydrogels makes them as suitable candidate for designing drug-delivery systems. Such on–off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels.^{29–31}

Swelling kinetics

In practical applications, a higher swelling rate is required as well as a higher swelling capacity. It is well known that the swelling kinetics for the absorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area, and composition of polymer. The influences of these parameters on the swelling capacity have been investigated by various workers.^{32,33} For example, the dependency of water absorbing capacity of SAPs on particle size investigated by Omidian et al.³⁴ Results indicated that as the particle size became smaller, the rate of absorption increased. This may be attributed to an increase in surface area with decreasing particle size of samples. Results in Figure 12, which show that the dynamic swelling behavior of the superabsorbent hydrogel with various particle sizes in water, confirm this fact. According to the figure, the rate of water absorbing capacity sharply increases and then begins to level off. For preliminary study of swelling kinetics, a “Voigt-based model” may be used for fitting the swelling data (eq. 4).³⁵

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

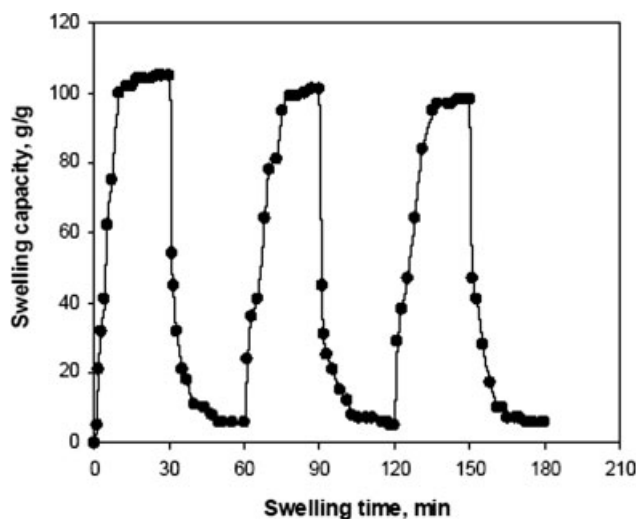


Figure 11 On–off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 3.0) of the CMC–poly(NaAA–co–AAm) hydrogel. The time interval between the pH changes was 30 min.

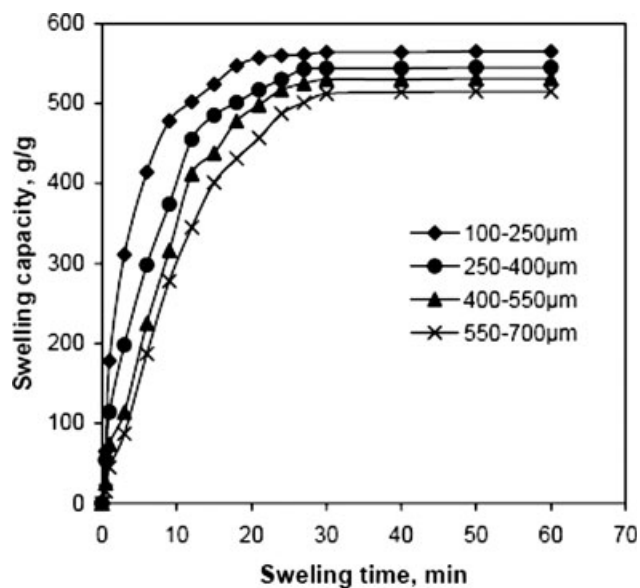


Figure 12 Representative swelling kinetics of the CMC–poly(NaAA–co–AAm) superabsorbent hydrogel with various particle sizes.

where S_t is the swelling at time t , S_e is the equilibrium swelling (power parameter), and τ is the rate parameter. The τ value is a measure of swelling rate (i.e., the lower the τ value, the higher the rate of swelling). The rate parameter is calculated by plotting $\ln(1 - S_t/S_e)$ versus time (t), using eq. (4) with slight modification. The slope of the straight line fitted (slope = $-1/\tau$) gives the rate parameter. The rate parameters for superabsorbent are found to be 4.2, 8.4, 10.5, and 11.3 min for superabsorbent with particle sizes of 100–250, 250–400, 400–550, and 550–700 μm , respectively. From the τ value, it can be inferred that the swelling of the superabsorbent with 100–250 μm particle sizes is faster than that of other counterparts.

CONCLUSIONS

A novel superabsorbent hydrogel was synthesized in an aqueous solution by alkaline hydrolysis of the physical mixture of CMC and PAN. The reaction of CMC alkoxide anions with nitrile groups of PAN, forms crosslinking points and results in a three-dimensional network. The reaction conditions were attempted to be optimized for obtaining hydrogels with higher swelling values. So, the maximum water absorbing capacity (559 g/g) was achieved under the optimum conditions that found to be: alkalization time 30 min, alkalization temperature 80°C, NaOH 10 wt %, PAN/CMC weight ratio 1.5, alkaline hydrolysis temperature 90°C, and alkaline hydrolysis time 90 min. Swelling measurement in various salt

solutions shows a swelling-loss, in comparison with distilled water. This behavior can be attributed to charge screening effect and ionic crosslinking for mono- and multivalent cations, respectively. In addition, the swelling of hydrogels in solutions with various pHs exhibited high sensitivity to pH; hence, the pH reversibility and on-off switching behavior makes the intelligent hydrogel as a good candidate for considering as potential carriers for bioactive agents, e.g., drugs. The swelling kinetics for the superabsorbent hydrogels showed high dependency of absorbency rate on particle size of the absorbents. The rate of water uptake increased with decreasing the particle size of the hydrogels. This can be attributed to high surface availability of small particle size of superabsorbing polymers when brought into contact with water.

The synthetic approach used in this research to prepare the superabsorbent hydrogel has several advantages:

- The practical one-step method for hydrogel synthesis is relatively simple and easy in comparison with free radical graft copolymerization method.
- The dark red–yellow color change provides a visual indication for recognizing the reaction completion.
- No petrochemical monomer is needed. So, the process is not involved with problems originating from the monomer (e.g., the monomer toxicity and the residual monomer).
- No initiator and expensive crosslinking agent is used. Therefore, this practical approach may be preferred to as a relatively “green process.”
- This facial and convenient preparative method conducted under normal atmospheric conditions in a short period of time. Because this method is not involved radical polymerization, the expensive inert gases, e.g., argon, are not needed to remove molecular oxygen that is a radical scavenger in radical graft copolymerization reactions.
- Biopolymeric convenient material, i.e., CMC, is used to yield superswelling biomaterials with potential bioactivity and biocompatibility.

In general, for synthesis of polysaccharide-based superabsorbent hydrogels, alkaline hydrolysis of the physical mixture of PAN and a polysaccharide has several advantages over free radical graft copolymerization of vinylic monomers onto a polysaccharide backbone.

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