

# Modified CMC. V. Synthesis and Super-Swelling Behavior of Hydrolyzed CMC-g-PAN Hydrogel

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**ABSTRACT:** Polyacrylonitrile (PAN) was grafted onto carboxymethyl cellulose (CMC) sodium salt backbones by using ceric ammonium nitrate (CAN) as an initiator. The graft copolymer, CMC-g-PAN, was hydrolyzed by NaOH solution to yield hydrogel, H-CMC-g-PAN. The nitrile groups of CMC-g-PAN were completely converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis, followed by *in situ* crosslinking of the grafted PAN chains. The structure of the products was confirmed by FTIR spectroscopy. The synthetic parameters affecting the swelling capacity of the hydrogel (i.e., CMC-g-PAN add-on value, the hydrolysis time and temperature, and concentration of

NaOH) were systematically optimized to achieve maximum swelling. Absorbency was also measured in various salt solutions. The H-CMC-g-PAN product was recognized to be a smart hydrogel with superswelling properties. Several swelling changes of the hydrogel were observed in lieu of pH variations in a wide range (1–13). Also, the pH reversibility and on-off switching behavior make the hydrogel a good candidate for controlled delivery of bioactive agents. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 877–883, 2007

**Key words:** superabsorbent hydrogel; carboxymethyl cellulose; polyacrylonitrile; graft copolymerization; swelling

## INTRODUCTION

Superabsorbent hydrogels are hydrophilic, three-dimensional networks. They 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.<sup>1</sup> Superabsorbent hydrogels have great advantages over traditional water-absorbing materials such as cotton, pulp, and sponge. They are widely used in sanitary goods such as disposable diapers and hygienic napkins. They are also used in soil conditioning and improving water retention capability of soil in agriculture and horticulture.<sup>2</sup>

Research on superabsorbents was initiated by the development of a starch-based superabsorbent by the U.S. Department of Agriculture, Northern Regional Research Center, in the late 1960s.<sup>3</sup> Since then, modification of natural materials such as starch,<sup>4</sup> cellulose,<sup>5,6</sup> and protein<sup>7</sup> have been utilized to prepare superabsorbents.

Hydrogels responding to external stimuli such as heat, pH, electric field, chemical environments, etc., are often referred to as “intelligent” or “smart” hydrogels. These hydrogels have important applications in the field of medicine, pharmacy, and biotechnology.<sup>8–10</sup> Following a continuous research on modification of carboxymethyl cellulose (CMC) sodium salt,<sup>11–14</sup> in

this article, we report synthesis and characterization of a smart superabsorbing hydrogel from CMC-g-polyacrylonitrile. The effect of the grafting and the subsequent hydrolysis reaction variables on the swelling properties as well as the salt- and pH-sensitivity of the hydrogels were investigated in detail.

## EXPERIMENTAL

### Materials

The polysaccharide used in this work was carboxymethyl cellulose (CMC) with D.S. 0.52. Ceric ammonium nitrate (CAN) was purchased from Merck and was used without purification. It was a freshly prepared 0.1M solution in 1N HNO<sub>3</sub>. Acrylonitrile (AN, Merck) was used after distillation for removing inhibitor. All other chemicals were of analytical grade.

### Graft copolymerization

Graft copolymerization of AN onto CMC was carried out with CAN radical initiator under argon atmosphere.<sup>11</sup> In a 100-mL flask, CMC (0.50 g) was dissolved in 50 mL of degassed distilled water. The flask was placed in a water bath with desired temperature (35–70°C). A given amount of monomer, AN (1.62–4.05 g), was added to the flask and the mixture was stirred for 10 min. Then the initiator solution (7.0 mL) was added to the mixture and continuously stirred for 2 h. The product was then

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worked up with methanol (200 mL) and dried in oven at 50°C for 5 h.

### Homopolymer extraction

The graft copolymer, CMC-g-PAN, was freed from polyacrylonitrile (PAN) homopolymer, by pouring 0.50 g of the product in 50 mL of dimethylformamide solution. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer by filtration of the CMC-g-PAN copolymer, the product was washed with methanol and dried in oven at 50°C to reach a constant weight.

### Alkaline hydrolysis

The graft copolymer product was hydrolyzed by adding 0.50 g of CMC-g-PAN to 20 mL of NaOH solution in a 50-mL flask immersed in thermostated water bath fitted with a magnetic stirrer and a reflux condenser. The NaOH concentrations of 0.5, 0.7, 1.0, 1.5, 2.0, and 2.5*N*; hydrolysis temperatures of 70, 75, 80, 85, 90, and 95°C; and hydrolysis times of 25, 35, 45, 55, 65, and 75 min were studied. During the hydrolysis, the color of the mixture was changed from deep orange-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 scissored to small pieces and poured in methanol (200 mL) to dewater for 2 h. The hardened particles were filtered and dried in oven (50°C, 10 h).

### Swelling measurements

To determine the swelling capacity of the hydrogel, 0.1 g ( $\pm 0.001$ ) of the hydrolyzed CMC-g-PAN (H-CMC-g-PAN) powder with average particle sizes between 40 and 60 mesh was put into a weighed tea bag, immersed in an excess amount of distilled water (200 mL), salt solution (100 mL), or buffer solution (100 mL), and allowed to soak for 2 h at room temperature. The buffer solutions were composed of hydrochloric acid, potassium chloride (for acidic pHs), potassium dihydrogen phosphate and disodium hydrogen phosphate (for pH 7) and borate, boric acid, hydrochloric acid, and sodium hydroxide (for basic pHs). The weight of the swollen gel containing absorbed liquid was measured after removing the tea bag from water and hanging until no drop drained ( $\sim 15$  min). The equilibrium swelling (ES) was calculated from the following equation:

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

### FTIR analysis

The samples were crushed with KBr to make pellets. Spectra were taken on an ABB Bomem MB-100 FTIR spectrophotometer.

### Grafting parameters

Grafting parameters, i.e., grafting percentage ( $G\%$ ), add-on value ( $Ad\%$ ), and homopolymer content ( $Hp\%$ ) were calculated using the following equations:<sup>15,16</sup>

$$G\% = 100 (W_2 - W_0)/W_0 \quad (2)$$

$$Ad\% = 100 (W_2 - W_0)/W_2 \quad (3)$$

$$Hp\% = 100 (W_1 - W_2)/W_1 \quad (4)$$

where  $W_0$ ,  $W_1$ , and  $W_2$  are the weight of the initial substrate, total product (copolymer and homopolymer), and pure graft copolymer (after DMF extraction), respectively.

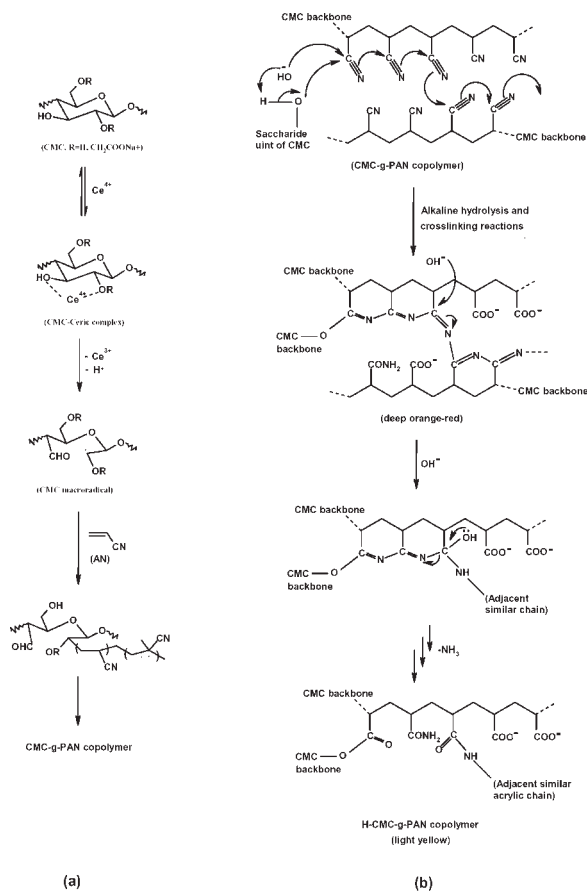
## RESULTS AND DISCUSSION

### Mechanism of hydrogel formation

A general reaction mechanism for AN grafting onto CMC backbones and alkaline hydrolysis of the graft copolymer is shown in Scheme 1. At the first step, a complex between  $Ce^{4+}$  and hydroxyl groups at the C-2 and C-3 positions was formed. This ceric-CMC complex is then dissociated to produce CMC macroradicals that are responsible for the initiation of AN grafting onto polysaccharide backbones<sup>11</sup> [Scheme 1(a)]. The graft copolymer, CMC-g-PAN, was then saponified using aqueous sodium hydroxide solution to produce hydrophilic carboxamide and carboxylate groups [Scheme 1(b)]. During the alkaline hydrolysis, ammonia was evolved and an orange-red color developed because of conjugated imine formation. In the case of hydrolyzed starch-g-PAN (H-SPAN), a maximum conversion of 70% of nitrile to carboxyl groups has been reported and the remaining 30% are amide groups.<sup>17</sup> 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 factors.<sup>18</sup> Weaver et al. suggested that condensation might also occur between carboxyl and amide groups to form imide structures.<sup>19</sup> Therefore, in the case of our hydrogel, H-CMC-g-PAN, we realized that precise control of the ratio is practically impossible. As shown in Scheme 1(b), crosslinking reaction also occurred between some nitrile groups of adjacent PAN pendant.

### Spectral characterization

FTIR spectra of CMC and CMC-g-PAN, before and after alkaline hydrolysis, are shown in Figure 1. Figure 1(b)



**Scheme 1** Proposed mechanism for CMC-g-PAN formation (a) and crosslinking during hydrolyzing nitrile groups of CMC-g-PAN to produce H-CMC-g-PAN hydrogels (b).

is the spectrum of the original CMC-g-PAN. A sharp absorption peak shown at  $2238\text{ cm}^{-1}$  is attributed to stretching of  $-\text{CN}$  groups. After alkaline hydrolysis, the absorption modes at  $1720$  and  $1690\text{ cm}^{-1}$  can be attributed to carbonyl stretching of  $\text{COO}^-\text{Na}^+$  and  $\text{CONH}_2$  groups, respectively, [Fig. 1(c)] that is reconfirmed by a broad band at  $2400\text{--}3600\text{ cm}^{-1}$  due to absorption of the  $\text{N-H}$  stretching of carboxamide group. Moreover,

sharp band of  $-\text{CN}$  groups completely disappeared after hydrolysis.

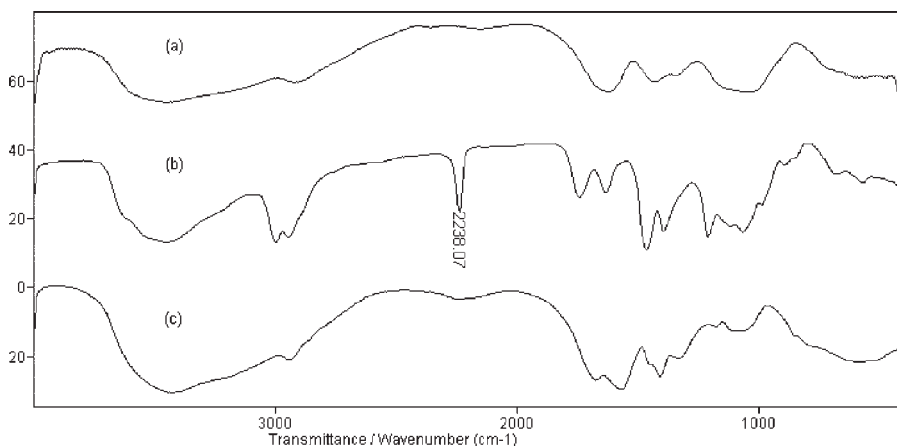
### Swelling dependency on add-on values

To prepare CMC-g-PAN copolymers with different portions of PAN side chains (various add-on values), two series of grafting synthesis were conducted using various temperatures and monomer concentrations (Table I). The individual copolymer samples were hydrolyzed under similar conditions (0.50 g CMC-g-PAN in 20 mL of 1N NaOH for 2 h). As shown in Figure 2, the products resulting from CMC-g-PAN with higher add-on values exhibit higher water- and saline-absorbency, which is attributed to more population of  $\text{CN}$  groups converting to more  $\text{COO}^-$  and  $\text{CONH}_2$  groups (Scheme 1). The linear swelling-Ad relationship is obvious from Figure 2. The swelling difference in water and saline will be explained in Swelling Behavior in Salt Solutions section.

### Optimization of the alkaline hydrolysis conditions

#### Effect of alkali concentration on swelling

The effect of the alkali concentration on swelling capacity is shown in Figure 3. Alkaline hydrolysis reaction was carried out at  $90^\circ\text{C}$  for 60 min. It was found that the mixture was discolored faster at higher NaOH concentration. In addition, lower absorbency was achieved when a further concentration of the base (higher than 1N) was applied. This can be attributed to the formation of more crosslinks at higher  $\text{OH}^-$  concentration. It is known that a higher degree of crosslinking results in a rigid network that can not hold a large quantity of fluid.<sup>1,2,20,21</sup> A similar observation has been reported by Castel et al.<sup>22</sup> in the case of the hydrolysis of starch-g-PAN. Additionally, alkaline degradation of the polysaccharide backbone can be



**Figure 1** FTIR spectra of (a) CMC, (b) CMC-g-PAN, and (c) H-CMC-g-PAN.

**TABLE I**  
Graft Copolymerization of Acrylonitrile onto CMC:  
Effect of Monomer Concentration and Temperature on  
Grafting Parameters

Reaction variable	Grafting parameter (%)		
	G	Ad	Hp
Monomer <sup>a</sup> (mol/L)			
0.03	11	10	17
0.038	17	15	15.2
0.046	35	26	14.2
0.053	59	37	12.8
0.061	185	65	8.6
0.068	69	41	11.7
0.076	47	32	13.5
Temperature <sup>b</sup> (°C)			
35	10	7	16.9
40	26	15	15.8
45	35	26	16
50	46	48	15.7
55	81	45	14.3
60	108	51	13.4
65	104	42	15.6
70	64	39	15.9

Reaction conditions: CMC, 1% (w/v); CAN, 0.0007 mol/L.

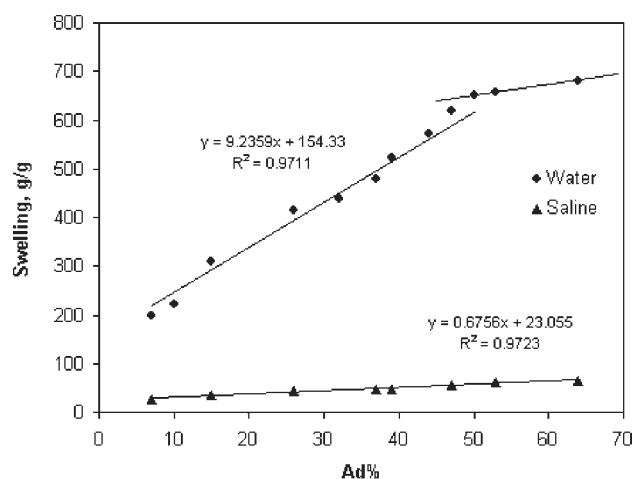
<sup>a</sup> In this series of experiments, reaction temperature was 45°C.

<sup>b</sup> In this series of experiments, monomer concentration was 0.061 mol/L.

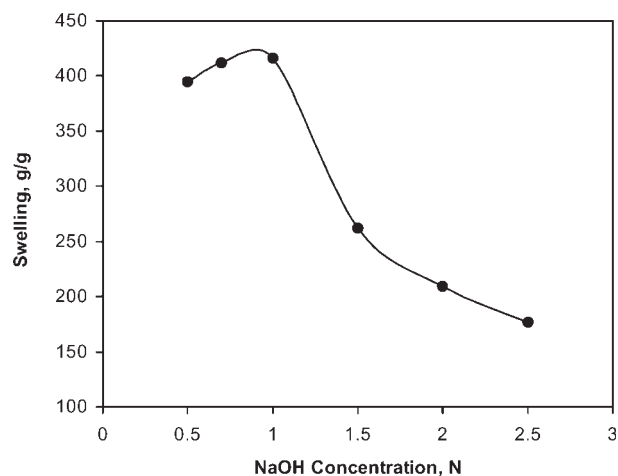
another reason of the swelling decrease in highly concentrated alkaline hydrolytic media. Similar alkaline degradation behaviors were already reported in the case of other polysaccharides.<sup>23,24</sup>

#### Effect of hydrolysis temperature on swelling

Alkaline hydrolysis was carried out at various reaction temperatures (70–95 °C). The mixture was discolored faster at higher temperatures due to the higher



**Figure 2** Swelling dependency of H-CMC-g-PAN hydrogels on add-on (Ad) values of the starting CMC-g-PAN copolymers. Alkaline hydrolysis conditions: CMC-g-PAN, 0.50 g; NaOH, 1N; Temperature, 80°C; time, 2 h.

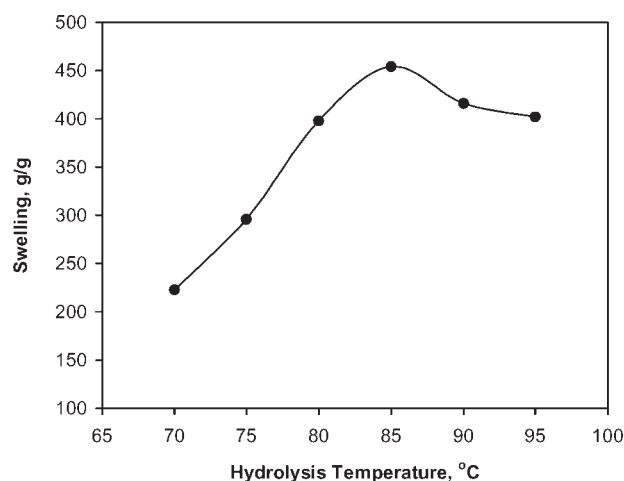


**Figure 3** Effect of NaOH concentration on the swelling capacity of H-CMC-g-PAN superabsorbent hydrogel (the hydrogel was prepared from the CMC-g-PAN with add-on 65%). Reaction conditions: hydrolysis temperature, 90°C; hydrolysis time, 60 min.

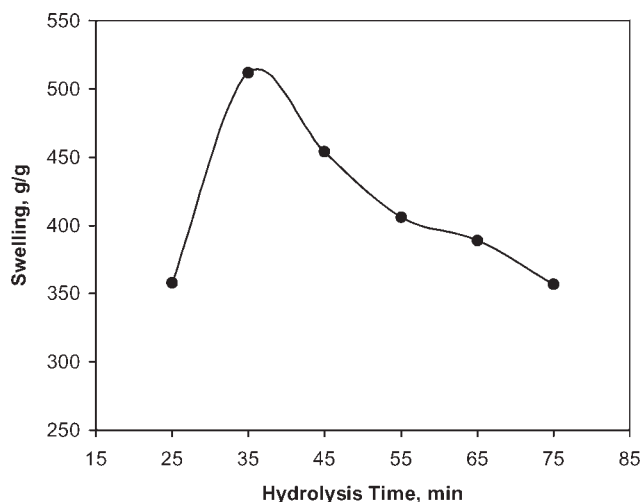
rates of hydrolysis reaction. The highest swelling capacity was obtained at 85°C, so that the temperatures lower and higher than this optimum temperature resulted in reduced swelling capacity (Fig. 4). This behavior suggests the incomplete hydrolysis reaction at lower temperatures, more crosslink formation, and alkaline degradation of the polysaccharide part of the hydrogel at higher temperatures.

#### Effect of hydrolysis time on swelling

Figure 5 presents the relationship between the reaction time and swelling capacity. It is obvious that the higher



**Figure 4** Effect of hydrolysis temperature on the swelling capacity of H-CMC-g-PAN superabsorbent hydrogel (the hydrogel was prepared from the CMC-g-PAN with add-on 65%). Reaction conditions: NaOH, 1N; hydrolysis time, 60 min.



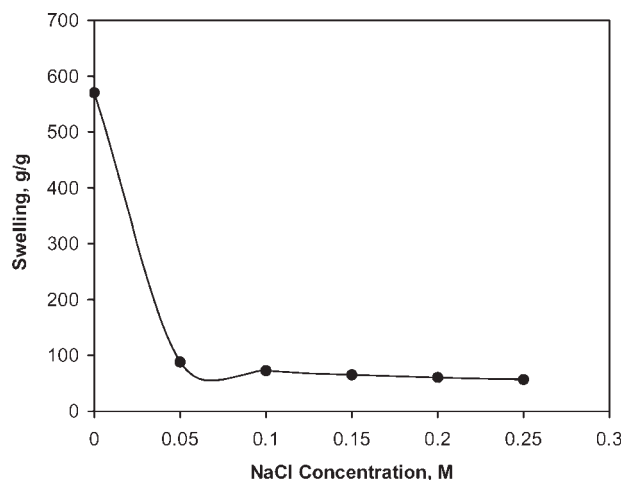
**Figure 5** Effect of hydrolysis time on the swelling capacity of H-CMC-g-PAN superabsorbent hydrogel (the hydrogel was prepared from the CMC-g-PAN with add-on 65%). Reaction conditions: NaOH, 1N; hydrolysis temperature, 85°C.

reaction time leads to more carboxamide and carboxylate groups generated from alkaline hydrolysis. As shown in Figure 5, swelling capacity is decreased with further increase in hydrolysis time after 35 min. The lower absorbency at longer hydrolysis times can be explained by the formation of a higher crosslinked, rigid structure. In addition, degradation of the hydrogel, especially the polysaccharide part,<sup>23,24</sup> under relatively alkaline conditions at 85°C may be another possible reason for the decreased swelling capacity versus higher reaction times.

#### Swelling behavior in salt solutions

The swelling behavior of the “ionic” hydrogel, H-CMC-g-PAN, could be significantly affected by various factors of the external solution, such as its pH and ionic strength. The swelling of our “anionic” hydrogels in saline solutions was appreciably decreased when compared with the values measured in deionized water (Fig. 2), because the repulsive anionic sites (carboxylate groups) on the polymeric chain were shielded by the counter ions (cations). Therefore, the swelling values decreased with an increase in the ionic strength of the solution.<sup>20,21</sup>

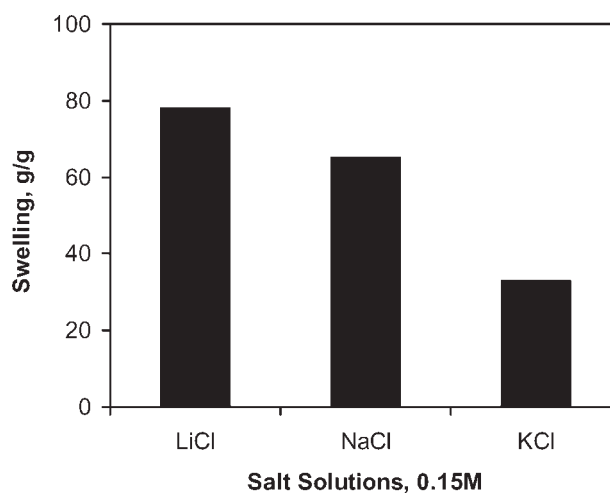
Figure 6 illustrates the effect of the various concentrations of NaCl solution on swelling capacity of the synthesized hydrogels. The figure indicates that changing the NaCl concentration higher than ~0.1M has no significant influence on absorbency of the hydrogel. The effect of different cations with a common anion (Cl<sup>-</sup>) on the absorbency of the hydrogel was also investigated. Results are shown in Figures 7 and 8. The swelling capacity decreases in the order Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> in the same concentration (0.15M)



**Figure 6** Effect of concentration of NaCl solution on swelling capacity of the hydrogel prepared from the copolymer with add-on 65%. Reaction conditions: CMC-g-PAN, 0.50 g; NaOH, 1N; temperature, 85°C; time, 35 min.

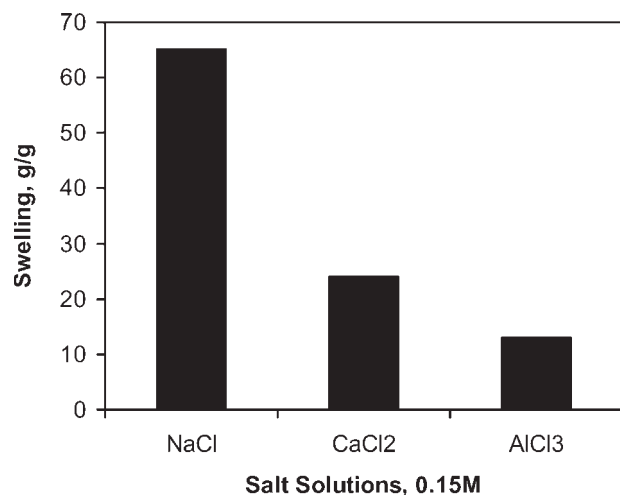
(Fig. 7). This result is due to their cationic radius or their hydration force. The hydration radius grows as a result of the small cation that is surrounded by more molecules of water; therefore its bonding ability to the carboxylate group will be weaker.<sup>25,26</sup> The cation with a larger radius therefore tends to enter the network and bind easily with the carboxylate groups. Decreased swelling capacity was also observed with an increase in the charge of the cation (Na<sup>+</sup> > Ca<sup>2+</sup> > Al<sup>3+</sup>) (Fig. 8). This can be attributed to the higher complexing ability arising from the coordination of the multivalent cations with H-CMC-g-PAN carboxylate groups. This “ionic crosslinking” makes the hydrogel to be hard so that it can not swell well.

Figure 9 shows the salt-sensitivity of the H-CMC-g-PAN hydrogel calculated as a dimensionless factor (*f*):



**Figure 7** Swelling capacity of the hydrogel (prepared from the CMC-g-PAN with add-on 65%) in chloride salt solutions (0.15M) with different sizes of cations.

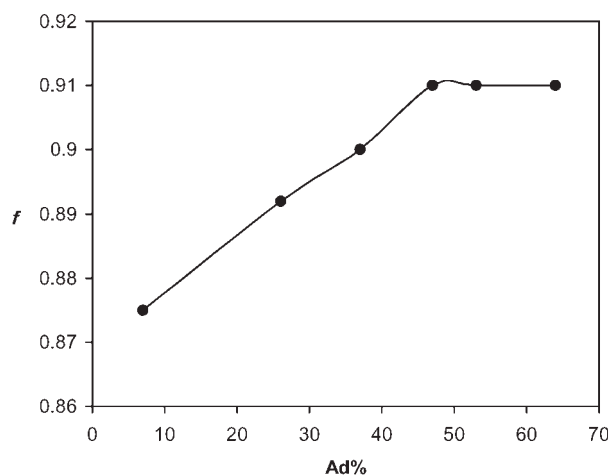




**Figure 8** Swelling capacity of the hydrogel (prepared from the CMC-g-PAN with add-on 65%) in chloride salt solutions (0.15M) with different charges of cations.

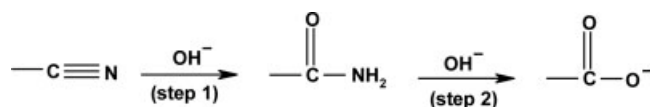
$$f = 1 - \frac{[(\text{Swelling in saline solution})]}{[(\text{Swelling in deionized water})]} \quad (5)$$

According to the figure, the  $f$  value is proportionally increased with add-on (Ad) value of the original CMC-g-PAN graft copolymer up to around Ad 48% and then it is leveled off. The initial enhancement of the salt-sensitivity is obviously related to the increase in anionic groups that are very sensitive to the environmental ionic strength. After a certain amount (Ad 48%), the population of the carboxylate anions exhibits no effect on the salt-sensitivity factor. This behavior is most probably due to insufficient concentration of  $\text{OH}^-$  (fixed NaOH concentration 1N) in the alkaline hydrolysis when the concentration of the CN groups is higher than the specified amount. So,



**Figure 9** Influence of add-on (Ad) values of the original CMC-g-PAN copolymers on the saline-sensitivity of the hydrogels obtained from the alkaline hydrolysis of the copolymers.

most of the nitrile groups are hydrolyzed only one step to produce nonionic (non-salt-sensitive) amide groups rather than anionic (salt-sensitive) carboxylates that are formed after a subsequent (second step) hydrolysis:

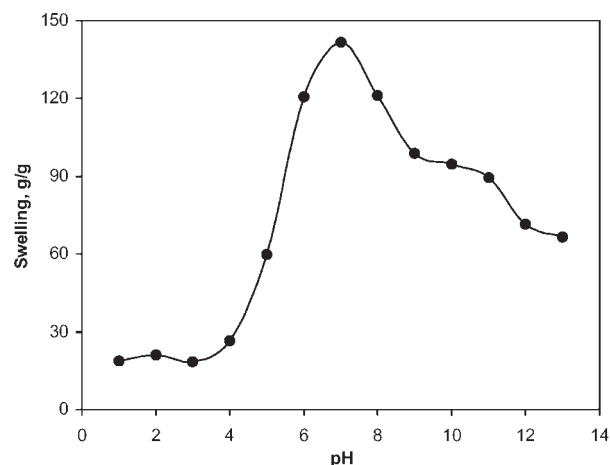


This apparent independency is also shown in Figure 2, in the case of swelling in water (3 last empirical points).

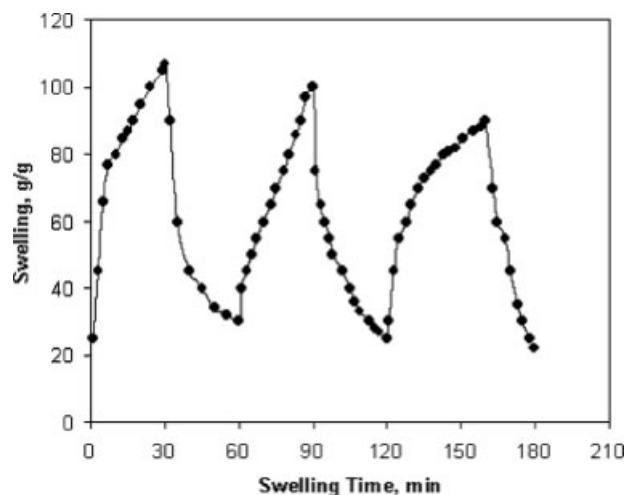
#### Effect of pH on swelling behavior

The swelling behavior of H-CMC-g-PAN hydrogel was investigated in various buffer solutions with pH that ranged from 1 to 13 (Fig. 10). The swelling capacity is decreased in acidic pHs. The remarkable decrease in swelling is due to the interaction of  $\text{H}^+$  ions with carboxylate groups. So, a decreased repulsion of anionic groups leads to a decreased swelling capacity. At higher pHs (5–8), some of carboxylate groups are ionized and the electrostatic repulsion between  $\text{COO}^-$  groups causes an enhancement of the swelling capacity. The decreased absorbency at higher basic pHs (pHs > 8) is related to “screening effect” of excess cations in the swelling media. (This effect was also observed in previous sections.)

Figure 11 shows the reversible swelling–deswelling behavior of the hydrogel in pH 2 and 8. At pH 8, the hydrogel swells because of anion–anion repulsive electrostatic forces, while at pH 2, it shrinks within a few minutes because of “screening effect” of excess cations. The figure demonstrates that the hydrogel is highly pH-responsive and it may be a suitable candidate for controlled drug delivery systems.



**Figure 10** Effect of buffered pH on swelling capacity of the H-CMC-g-PAN hydrogel prepared from CMC-g-PAN copolymer with add-on 65%.



**Figure 11** pH-reversibility (on-off switching) behavior of the H-CMC-g-PAN hydrogel prepared from the CMC-g-PAN with add-on 65% in pH 8 (swelling) and pH 2 (deswelling). The time interval between the pH changes was 30 min.

## CONCLUSIONS

A novel superabsorbent hydrogel, H-CMC-g-PAN, was prepared by graft copolymerization of AN onto CMC, followed by alkaline hydrolysis of the CMC-g-PAN graft copolymer. The swelling capacity of the synthesized hydrogel was affected by the grafting percent of PAN onto the CMC substrate, NaOH concentration, hydrolysis temperature, and hydrolysis time. Therefore, the maximum swelling capacity (512 g/g) was achieved under the optimum alkaline hydrolysis conditions, which were found to be as follows: NaOH concentration, 1N; hydrolysis temperature, 85°C; and hydrolysis time, 35 min. Also, the superabsorbent swelling exhibited a high sensitivity to the pH and ionic strength of solutions. In addition, pH-reversibility behavior of the hydrogel might be a key factor to its possible application in many technologies, such as controlled delivery of drugs.

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