

# Synthesis, Characterization, and Swelling Behavior of Alginate-*g*-Poly(sodium acrylate)/Kaolin Superabsorbent Hydrogel Composites

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**ABSTRACT:** A novel superabsorbent composite based on sodium alginate and the inorganic clay kaolin was synthesized via the graft copolymerization of acrylic acid (AA) in an aqueous medium with methylene bisacrylamide (MBA) as a crosslinking agent and ammonium persulfate (APS) as an initiator. The effects of reaction variables, such as the MBA, AA, and APS concentrations and the alginate/kaolin weight ratio, on the water absorbency of the composite were systematically optimized. Evidence of grafting and kaolin interactions was obtained by a comparison of the

Fourier transform infrared spectra of the initial substrates with that of the superabsorbent composite, and the hydrogel structure was confirmed with scanning electron microscopy. The results indicated that with an increasing alginate/kaolin weight ratio, the swelling capacity and gel content increased. The effects of various salt media were also studied, along with the swelling kinetics. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2631–2639, 2007

**Key words:** composites; hydrogels; swelling; synthesis

## INTRODUCTION

Superabsorbent hydrogels are slightly crosslinked networks that can absorb a large amount of water and aqueous fluids in a short time and retain water under pressure. They are widely used in many fields, such as medicine for drug delivery systems,<sup>1–3</sup> agriculture and horticulture,<sup>4,5</sup> sealing composites,<sup>6</sup> biosensors,<sup>7,8</sup> artificial snow,<sup>9</sup> and drilling fluid additives.<sup>10</sup> Various methods have been tried to improve the absorbing properties and to expand the application fields of superabsorbent hydrogels.<sup>11</sup> Recently, much attention has been paid to inorganic materials for the preparation of superabsorbent composites, such as montmorillonite,<sup>12,13</sup> attapulgite,<sup>14,15</sup> kaolin,<sup>16,17</sup> mica,<sup>18,19</sup> bentonite, and sercite.<sup>20,21</sup> Mineral powders are hydrated layered aluminosilicates with reactive —OH groups on the surface. The interaction of mineral powders with the reactive sites of natural polymers and monomers results in a superabsorbent composite. The incorporation of these clays not only reduces production costs but also improves the properties (e.g., swelling ability, gel strength, and mechanical and thermal stability) of superabsorbents and accelerates the generation of new materials for special applications.<sup>22,23</sup> A kaolin powder can disperse to some extent in water

and crosslink with acrylic acid (AA) and sodium alginate (Na-Alg). A schematic illustration of kaolin is shown in Scheme 1(a). Polysaccharides constitute the majority of the natural-based superabsorbent hydrogels because of their exceptional properties, that is, biocompatibility, biodegradability, renewability, and nontoxicity. In particular, Na-Alg is a renewable and biodegradable natural polymer that is used in a variety of commercial applications because of its capacity for gelatinization. Alginates are linear anionic polysaccharides of (1,4)-linked  $\alpha$ -L-guluronate (G units) and  $\beta$ -D-mannuronic acid (M units) residues. The structure of alginates can therefore be represented schematically, as shown in Scheme 1(b). Alginates and their derivatives are widely used in food, cosmetic, and pharmaceutical industries.<sup>24,25</sup>

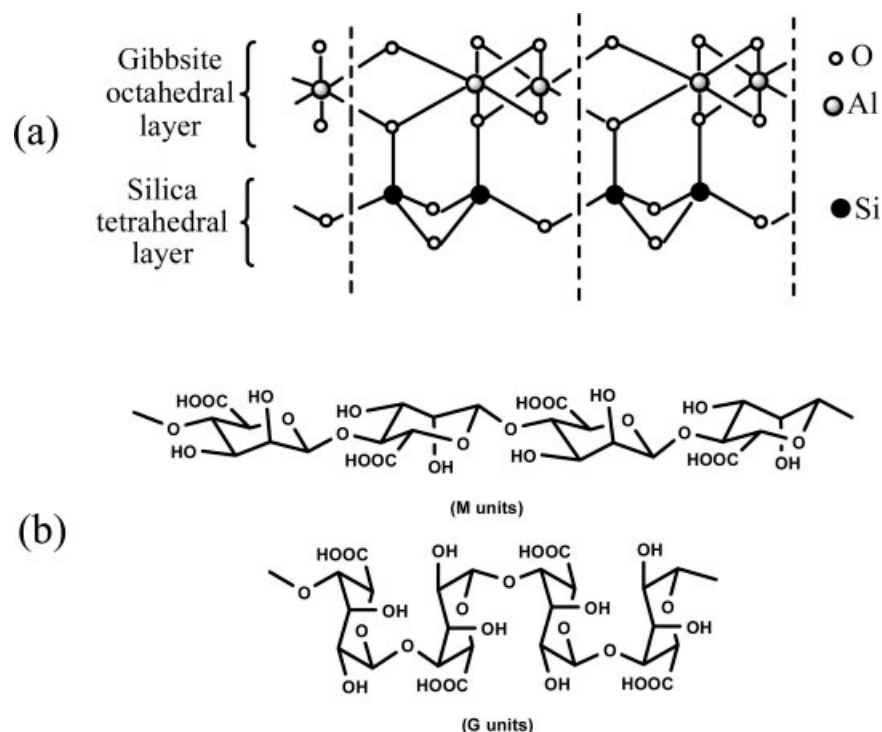
In this study, a novel alginate-*graft*-poly(sodium acrylate)/kaolin superabsorbent hydrogel with a water absorbency about 400 times its weight was synthesized. The influence of the mineral powder, crosslinker, and initiator as well as the polymerization process on the resulting absorbent properties is discussed. Also, we determined the absorbency under load (AUL) of the superabsorbent composite hydrogel.

## EXPERIMENTAL

### Materials

The polysaccharide Na-Alg was purchased from Merck (Darmstadt, Germany) and used without further purifi-

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**Scheme 1** Schematic structures of (a) kaolin and (b) repeating polysaccharide units of Na-Alg.

cation. AA (Merck) was used after vacuum distillation. Methylene bisacrylamide (MBA; Fluka, Switzerland), ammonium persulfate (APS; Merck), and kaolin (Khorassan Co., Iran; KPS-grade, particle size <5 Dm) were used as received. All other chemicals were analytical-grade.

### Superabsorbent composite synthesis

A series of superabsorbent composites were prepared through the graft copolymerization of AA onto alginate in the presence of powdery kaolin with MBA as a crosslinking agent and APS as an initiator. Typically, various amounts of Na-Alg (0.25–1.75 g) were added to 35 mL of degassed distilled water in a 1-L reactor equipped with a mechanical stirrer (a three-blade-propeller type, RZR 2021, Heidolph, Germany). The reactor was placed in a thermostated water bath to control the reaction temperature at 80°C. After the complete dissolution of Na-Alg, various amounts of kaolin powder (1.75–0.25 g) were added to the Na-Alg solution and stirred (200 rpm) for 10 min. Then, AA [1.0–5.0 g, completely neutralized with sodium hydroxide (NaOH)], MBA (0.05–0.2 g, dissolved in 5 mL of water), and the APS initiator (0.05–0.4 g, dissolved in 5 mL of water) were added simultaneously to the reactor. All the reactions were carried out at 80°C under atmospheric conditions, and the reaction mixture was continuously stirred (330 rpm) for 1 h. At the end of the propagation reaction, the gel product was poured into ethanol (300 mL) and allowed to dewater

for 48 h. Then, the product was cut into small pieces, washed several times with ethanol, and filtered. The resulting products were dried in an oven at 50°C for 24 h. After grinding, the powdered superabsorbent composite was stored away from moisture, heat, and light. All samples had a particle size in the range of 40–60 mesh.

### Swelling measurements

The equilibrium swelling (g/g) was measured according to a conventional tea-bag method.<sup>26</sup> The tea bag (100-mesh nylon screen), containing an accurately weighed powdered sample ( $0.5 \pm 0.001$  g), was immersed entirely in 200 mL of distilled water and allowed to soak for 2 h at room temperature. The sample particle size was 40–60 mesh (250–400 μm). The tea bag was hung up for 15 min to remove the excess solution. The equilibrium swelling (ES) was calculated three times according to eq. (1):

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

Therefore, the absorbency was calculated three times as grams of water per gram of the dry hydrogel (g/g). The accuracy of the measurements was about  $\pm 3\%$ . The standard deviation (s) for a sample of

data that are of limited size is given by the following equation:

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

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

### Measurement of AUL

A macroporous sintered glass filter plate (porosity = 0, diameter = 80 mm, height = 7 mm) was placed in a Petri dish (diameter = 118 mm, height = 12 mm), and a weighted, dried hydrogel sample ( $0.9 \pm 0.01$  g) was uniformly placed on the surface of polyester gauze located on the sintered glass. A cylindrical, solid load (Teflon, diameter = 60 mm, variable height) was put on the dry hydrogel particles, although it could be freely slipped in a glass cylinder (diameter = 60 mm, height = 50 mm). The desired load (applied pressure = 0.3 psi) was placed on the hydrogel sample (shown later in Fig. 11). Then, a 0.9% saline solution was added so that the liquid level was equal to the height of the sintered glass filter. The whole set was covered to prevent surface evaporation and probable changes in the saline concentration. After 60 min, the swollen particles were weighed again, and AUL was calculated with eq. (1).

### Gel and sol content determination

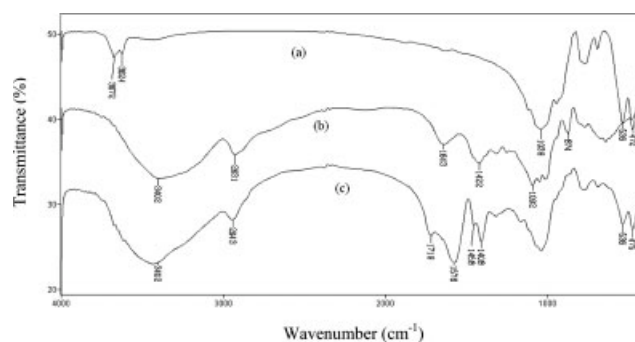
The weighed crude product particles were dispersed in distilled water to swell completely. The hydrogel washed with distilled water frequently and then filtered, dewatered in excess ethanol for 48 h, and dried ( $50^\circ\text{C}$ , 12 h). The soluble content (sol) was calculated as the weight loss of the initial crude product.

### Morphologies of the hydrogels

Scanning electron microscopy (SEM) of the superabsorbent composite was performed to visualize the superabsorbent composite's pores. The morphology of the dried samples was examined with a Philips (Netherlands) XL30 scanning electron microscope operated at 25 kV after the coating of the samples with a gold film.

### Fourier transform infrared (FTIR) analysis

FTIR spectra of the samples in the form of KBr pellets were recorded with an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada).



**Figure 1** FTIR spectra of (a) kaolin, (b) Na-Alg, and (c) a crosslinked Na-Alg/kaolin composite hydrogel.

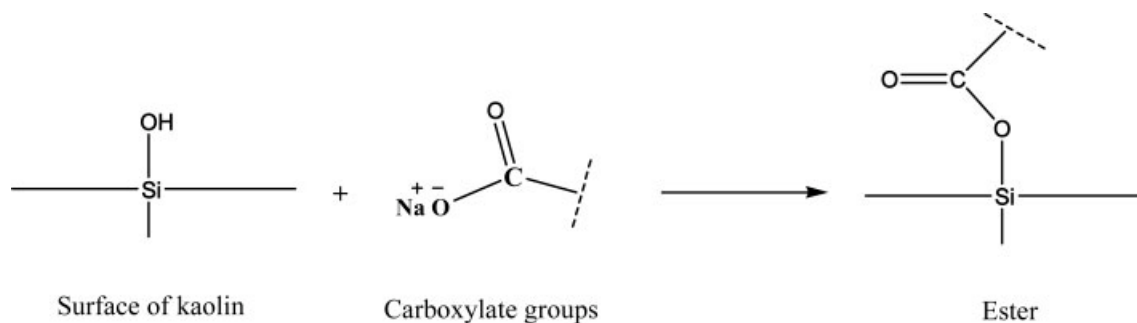
## RESULTS AND DISCUSSION

### Synthesis and characterization

The superabsorbent composite was prepared by the graft copolymerization of AA onto Na-Alg in the presence of a crosslinking agent (MBA), powdery kaolin, and APS as an initiator. The persulfate decomposes on heating and produces sulfate anion radicals that abstract hydrogen atoms from the hydroxyl groups of the alginate backbones. This redox system results in active centers capable of radically initiating the polymerization of AA, leading to a graft copolymer. Because a crosslinking agent (MBA) is present in the system, the copolymer contains a crosslinked structure. Infrared spectroscopy was carried out to confirm the chemical structure of the superabsorbent composite. The FTIR spectra of the initial substrate and the graft copolymer are shown in Figure 1. Figure 1(a) presents the spectrum of kaolin. Hydroxyl groups in the layered silicate structure produced absorption bands at  $3624\text{--}3672\text{ cm}^{-1}$ . Figure 1(b) shows the characteristic absorption bands of Na-Alg around  $1643\text{ cm}^{-1}$ , which are attributed to carboxylate stretching modes. The broad band at  $3200\text{--}3500\text{ cm}^{-1}$  is due to the stretching absorption of the hydroxyl groups of the polysaccharide. Two new absorption peaks appear at  $1576$  and  $1719\text{ cm}^{-1}$  in the spectrum of the composite hydrogel [Fig. 1(c)]. The characteristic band at  $1576\text{ cm}^{-1}$  is attributed to C=O asymmetric stretching in the carboxylate anion. This is confirmed by another peak at  $1408\text{ cm}^{-1}$ , which is related to the symmetric stretching mode of the carboxylate groups. The absorption band at  $1719\text{ cm}^{-1}$  can be correlated to the ester groups that formed during the graft polymerization. The carboxylate groups of the grafted poly(acrylic acid) can react with the hydroxyl groups on the kaolin surface, and this results in ester formation. The reaction is shown in Scheme 2.

### Effect of the MBA concentration on the swelling

Figure 2 exhibits the swelling and gel content values of the composite hydrogel versus the crosslinker



Scheme 2

(MBA) concentration. According to Figure 2, a reverse relationship between the swelling capacity and the concentration of crosslinker was concluded:<sup>27</sup>

$$\text{Swelling capacity} = K[\text{MBA}]^{-n} \quad (3)$$

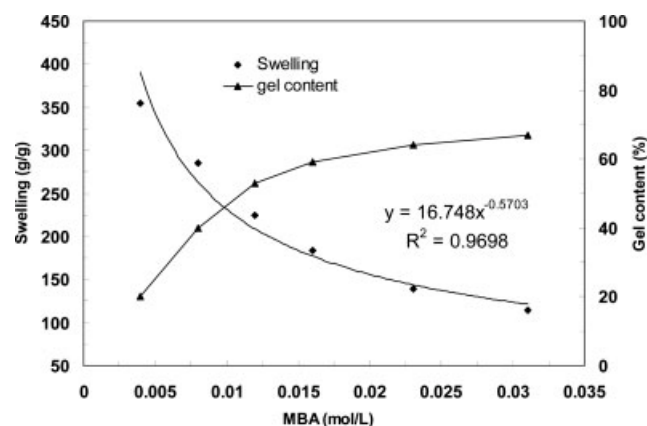
where  $K$  and  $n$  are constant values. A well-known power-law relationship<sup>28,29</sup> of the swelling versus the MBA concentration, with  $K = 16.7$  and  $n = 0.57$ , can be obtained from the curve fitted with eq. (3). This well-known behavior has been reported by others.<sup>30,31</sup> A higher crosslinker concentration increases the extent of crosslinking of the polymeric chains and decreases the free spaces between them; consequently, the swelling capacity and the gel content are reduced. According to Figure 2, a 0.01M concentration of MBA provides the best values of the swelling and gel content. At a lower amount, the gel content is diminished appreciably because of the formation of very loosely crosslinked networks, resulting in highly swollen hydrogels with very low gel strength.

Figure 3 illustrates cross-sectional views of SEM of dry composite hydrogels obtained under various conditions. These images show the porous structure in the hydrogel. Figure 3(a,b) shows the influence of the crosslinking agent on the porosity. The porosity of the composite particles in optimized sample 3a (MBA = 0.008 mol/L) was greater than that in sample 3b (MBA = 0.031 mol/L). Therefore, increasing the concentration of the crosslinking agent decreases the porosity of the hydrogel. This is because a higher crosslinking agent concentration produces more crosslink points in the polymeric network and increases the crosslink density, resulting in a lower porosity. These observed morphologies are confirmed by the fact that the equilibrium water absorption in sample 3a (285 g/g) was higher than that in sample 3b (114 g/g).

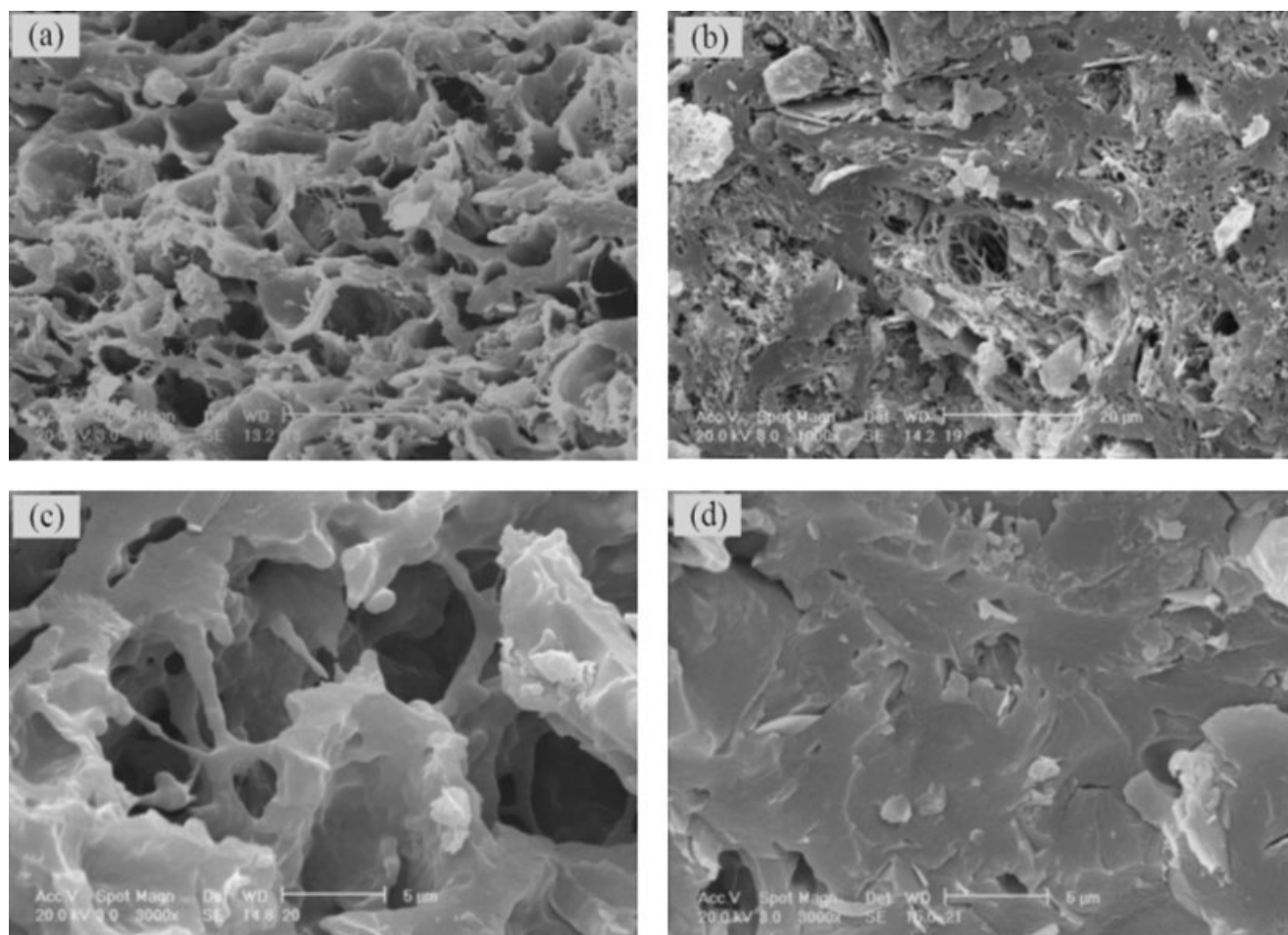
### Effect of the monomer concentration on the swelling

The influence of the total monomer concentration was studied in this series of experiments through the vari-

ation of the sodium acrylate concentration from 0.42 to 1.12 mol/L (Fig. 4). The chosen alginate/kaolin weight ratio was 1. As shown in Figure 4, both the gel content and swelling capacity increased initially with increasing monomer concentration. The initial increase in the water absorbency and gel content can be explained by the fact that an increase in the monomer concentration led to more grafting of sodium acrylate onto alginate. This led to better formation of the polymer network; consequently, the water absorbency and gel content increased. The swelling decrease after the maximum can be attributed to (1) an increase in the viscosity of the medium, which hindered the movement of free radicals and monomer molecules, and (2) an enhanced chance of chain transfer to monomer molecules. These factors prevented efficient network formation and in turn caused a decrease in the water absorbency. Such behaviors have been reported by us and other investigators.<sup>32,33</sup> The slight loss of gel content resulting from the higher monomer concentration can be attributed to the rapidly gelled system, which prevented the monomer and polysaccharide from fully participating in the crosslinking polymerization.



**Figure 2** Effect of the crosslinker concentration on the water absorbency and gel content of the superabsorbent composite.

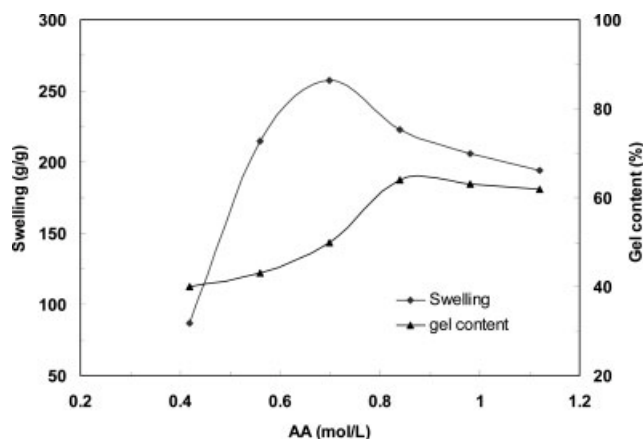


**Figure 3** Series of cross-sectional SEM images of the dry composite hydrogel under various synthetic conditions.

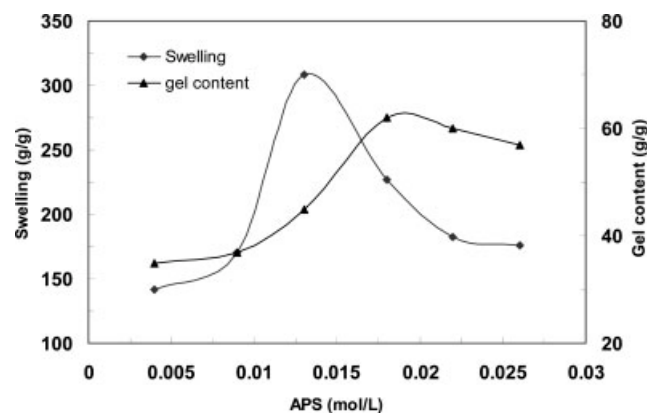
**Effect of the APS concentration on the swelling**

Figure 5 shows the effect of the initiator concentration on the water absorbency and gel content of the superabsorbent composite. The water absorbency increases

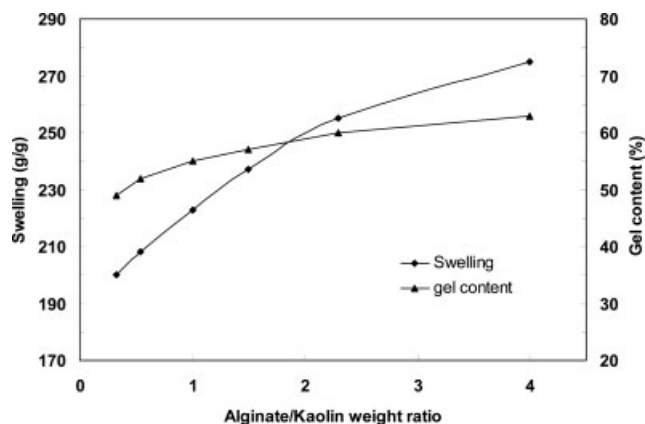
as the APS concentration rises from 0.004 to 0.013 mol/L, and then it decreases with a further increase in the concentration of APS. The maximum swelling (308 g/g) was obtained at an initiator concentration of 0.013 mol/L. An initial increase in the water absorbency and gel content can be attributed to an increase



**Figure 4** Effect of the monomer concentration on the water absorbency and gel content of the superabsorbent composite.



**Figure 5** Effect of the initiator concentration on the water absorbency and gel content of the superabsorbent composite.



**Figure 6** Effect of the Na-Alg/kaolin weight ratio on the water absorbency and gel content of the superabsorbent composite.

in the number of active free radicals on the alginate backbone, which in turn result in more extensive graft polymerization. At a low concentration of APS, a network cannot be formed efficiently with just a few radicals in free-radical polymerization reactions, and this results in a decrease in the water absorbency and gel content. The subsequent decrease in the water absorbency and gel content with further increases in the initiator concentration can be explained on the basis of (1) the predominance of homopolymerization over grafting, (2) an increase in the importance of the terminating step reaction by bimolecular collisions, which in turn increase the crosslink density,<sup>34</sup> and (3) a reduction of the molecular weight of the synthetic part of the polymer network.<sup>35</sup> On the other hand, free-radical degradation of alginate can also take place at high APS levels.

Cross-sectional SEM images of the dry composite hydrogel in Figure 3(c,d) show the influence of the initiator concentration on its porosity. The porosity of the composite particles in optimized sample 3c (APS = 0.013 mol/L) is greater than that in sample 3d (APS = 0.026 mol/L). These observations confirm that increasing the initiator concentration led to more crosslinking of the hydrogel, which in turn led to a denser structure and smaller polymer network space, resulting in decreased porosity. These observed morphologies are consistent with the fact that the equilibrium water absorption in sample 3d (307 g/g) was lower than that of sample 3c (57 g/g).

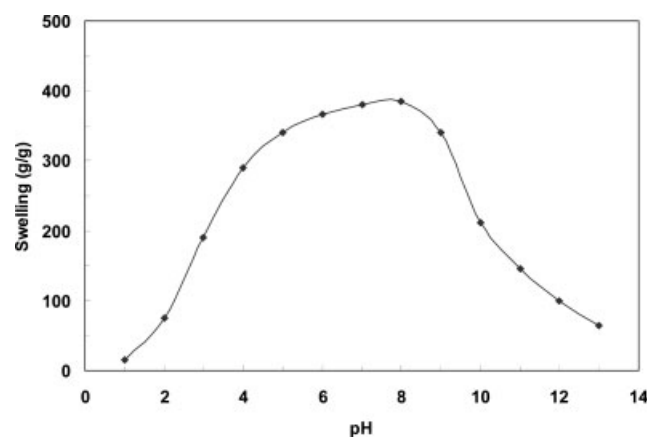
#### Effect of the kaolin amount on the swelling

To investigate the effect of the kaolin amount on the water absorbency of the composite hydrogel, the alginate/kaolin weight ratio was varied from 0.33 to 4, whereas other reaction variables were constant. Figure 6 indicates that the water absorbency and gel content of the superabsorbent composite is increased

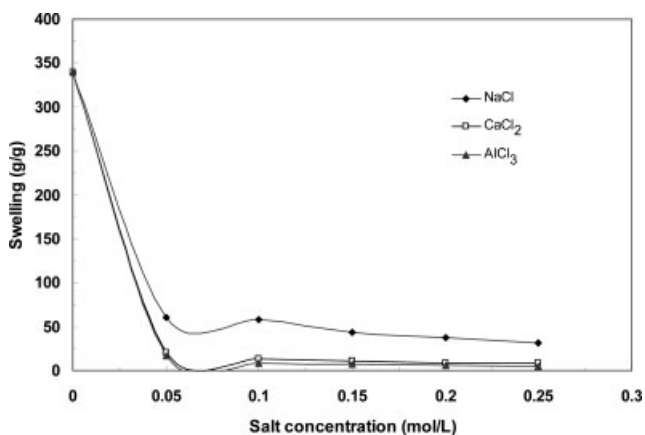
with an increase in the alginate/kaolin weight ratio. The clay in the polymerization reaction can be considered to act as a crosslinking agent. This means that the carboxylate groups of the sodium polyacrylate) chains react with kaolin, as is obviously proved by FTIR spectra (Fig. 1). Therefore, the decrease in the water absorbency may be attributed to kaolin, which acts as a crosslinker agent.<sup>17,36</sup> For the gel content variation shown in Figure 6, it can be proposed that, with the higher alginate/kaolin weight ratio, more efficient crosslinking along with network formation occurs. In other words, in comparison with alginate/kaolin, alginate tends to react with the crosslinker more effectively, so the gel content is increased.

#### Effect of the pH on the swelling

The swelling behavior of the superabsorbent composite was studied at room temperature at various pH values between 1.0 and 13.0 (Fig. 7). To prepare the pH media, standard HCl (pH 1.0) and NaOH (pH 13.0) solutions were diluted with distilled water to reach the desired acidic and basic pHs, respectively. The swelling of the hydrogel composite increased with increasing pH from 1 to 8, but it decreased in the pH range between 8 and 13. The maximum water absorbency of the hydrogel was achieved at pH 8. At this point, all the  $-\text{COOH}$  groups were converted to  $-\text{COO}^-$ , and this resulted in high anion-anion repulsion and high swelling capacity. In an acidic solution, the ionic strength of the medium was increased, and the charge of the  $-\text{COO}^-$  anions was shielded by the counterions, so efficient repulsion was prevented. At pHs greater than 8, the  $\text{Na}^+$  cations from NaOH shielded the  $-\text{COO}^-$  groups and prevented perfect anion-anion repulsion. Also, the ionic strength of the medium increased, and consequently, the swelling decreased.



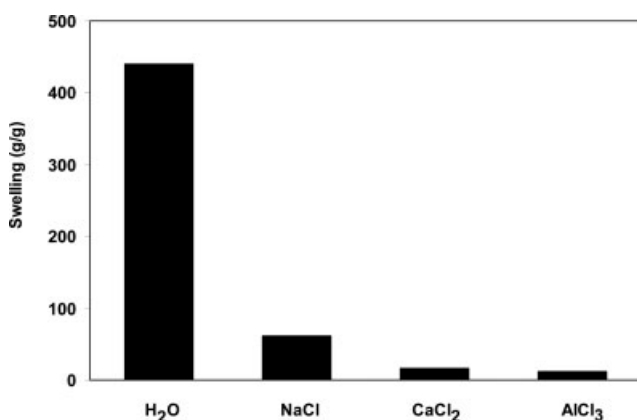
**Figure 7** pH-dependent swelling of the (Na-Alg/kaolin)-g-poly(sodium acrylate) (PAANa) superabsorbent composite.



**Figure 8** Swelling capacity variation of the composite hydrogel in saline solutions with various concentrations.

### Swelling behavior in salt solutions

The ionic strength of the environment affects the swelling capacity of superabsorbents. Figure 8 shows the effects of various salt solutions on the water absorbency of the composite hydrogel. A decrease in the swelling capacity of the hydrogel is attributed to the osmotic pressure difference between the hydrogel and the aqueous phase. Another factor that influences the swelling capacity in salt solutions is the charge screening effect or shielding effect, in which perfect anion–anion repulsion is prevented by cations.<sup>37</sup> In addition, the swelling of the superabsorbent composite depends on the type and valence of the cations. As shown in Figure 9, multivalent cations decrease the swelling capacity considerably. The superabsorbent composites contained carboxylate groups in their structures. This dramatic decrease in the water absorbency in multivalent cationic solutions could be due to the complexing ability of the carboxylate groups inducing the formation of intramolecular and



**Figure 9** Swelling capacity of the composite hydrogel, (Na-Alg/kaolin)-g-poly(sodium acrylate) (PAANa), in different chloride salt solutions (0.05M).

intermolecular complexes, which resulted in an increase in the crosslinking density of the network.<sup>38</sup> The well-known relationship between the swelling and salt solution concentration is stated in eq. (4):<sup>27</sup>

$$\text{Swelling} = k[\text{Salt}]^{-n} \quad (4)$$

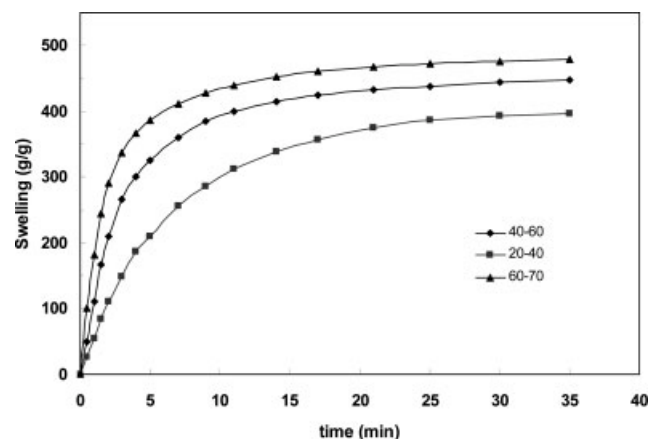
where  $k$  and  $n$  are constants for an individual superabsorbent. The  $k$  value is the swelling at a high concentration of salt ( $\sim 0.01M$ ), and the value of  $n$  is a measure of the dependence of the swelling on the salt concentration. The  $n$  value changes with the cation valence enhancement. Here, the ionic crosslinking is more effective against swelling than the charge screening effect of the cation.

### Swelling kinetics

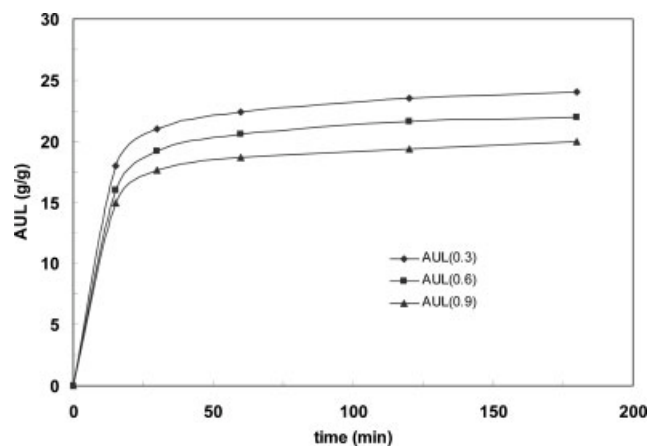
A preliminary study was conducted on the swelling kinetics of the superabsorbent composite. Figure 10 presents the dynamic swelling behavior of the superabsorbent hydrogel composite with various mesh sizes. Initially, the rate of water uptake sharply increases, and then it begins to level off. The equilibrium swelling was achieved after 30 min. A power-law behavior is obvious from Figure 10. The data may be well fitted with a Voigt-based equation:<sup>39</sup>

$$S_t = S_e(1 - e^{-t/\tau}) \quad (5)$$

where  $S_t$  (g/g) is the swelling at time  $t$ ,  $S_e$  is the equilibrium swelling (power parameter; g/g),  $t$  is the time for swelling (min), and  $\tau$  stands for the rate parameter (min). The rate parameters were found to be 2.12, 3.26, and 6.29 min for the superabsorbent composite with particle sizes of 100–250, 250–400, and 400–550  $\mu\text{m}$ , respectively.



**Figure 10** Representative swelling kinetics of superabsorbent hydrogels with particle sizes of 100–250, 250–400, and 400–550  $\mu\text{m}$ .



**Figure 11** Time dependence of the AUL values for a superabsorbent composite sample swollen in a saline solution.

## AUL

When superabsorbents are under a load, the swelling capacity is considerably reduced. Therefore, AUL is often defined and reported, especially in technical data. Because AUL values logically change with the mechanical strength of the swollen gel proportionally, AUL can be considered a measure of the gel strength of the superabsorbent composite. Therefore, many efforts have been made to achieve superabsorbents having higher AUL values or higher strengths of the swollen gel.<sup>40,41</sup> To determine the swollen gel strength, we used a superabsorbent composite sample under different loads in a saline solution. As shown in Figure 11, the minimum time needed for the highest AUL in the case of each load was estimated to be 180 min. After this time, the AUL values were almost unchanged. In addition, the curves show as expected that AUL decreases with an increasing loading. The maximum swelling was found to be 24, 22, and 20 (g/g) for the applied pressures of 0.3, 0.6, and 0.9 psi, respectively.

## CONCLUSIONS

Superabsorbent hydrogel composites, composed of Na-Alg, kaolin, and sodium acrylate, were prepared via a polymerization process under atmospheric conditions. We modified a superabsorbent hydrogel by incorporating an inorganic material to improve the swollen gel strength and to minimize the cost of the product. The radical polymerization started and proceeded without the reaction being protected from air. Thus, a highly practical preparative system was systematically investigated to produce a novel hydrogel composite having superswelling properties. Overall, the reaction conditions may be concluded as follows: an alginate/kaolin weight ratio of 2 : 1, an MBA con-

centration of 0.01 mol/L, an APS concentration of 0.017 mol/L, and a reaction temperature of 80°C. The structural and morphological characteristics of the hydrogel composite were studied with FTIR and SEM, respectively. The results indicate that the superabsorbent hydrogel has relatively good potential to hold water and saline solutions both as values of the load-free absorbency (free swelling) and as values of AUL. The composite superabsorbent hydrogel may potentially be used in agriculture, pharmaceuticals, and biosensors.

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