

Preparation of Starch-Graft-Poly(Acrylamide)/Attapulgite Superabsorbent Composite

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Received 14 June 2004; accepted 28 January 2005

DOI 10.1002/app.22302

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel starch-graft-poly(acrylamide)/attapulgite superabsorbent composite was synthesized by graft copolymerization reaction of starch, acrylamide (AM), and attapulgite micropowder using *N,N*-methylene-bisacrylamide (MBA) as a crosslinker and ammonium persulphate (APS) as an initiator in aqueous solution, followed by hydrolysis with sodium hydroxide. The effects on water absorbency, such as amount of crosslinker, initiator, attapulgite, weight ratio of acrylamide to starch in the feed, gelatinization conditions of starch and molar ratio of NaOH to acrylamide, and so forth, were investigated. These superabsorbent composites were characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The water ab-

sorbencies for these superabsorbent composites in water and saline solution were investigated, and water retention tests were carried out. Results obtained from this study showed that the water absorbency of superabsorbent composite synthesized under optimal synthesis conditions with an attapulgite content of 10% exhibit absorption of 1317 g H₂O/g sample and 68 g H₂O/g sample in distilled water and in 0.9 wt % NaCl solution, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1351–1357, 2005

Key words: acrylamide; attapulgite; starch; superabsorbent composite; water absorbency

INTRODUCTION

Superabsorbents are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining possibly huge volumes of water in the swollen state. Since the first superabsorbent polymer was reported by the U.S. Department of Agriculture,¹ superabsorbents have received significant attention, especially in the last 30 years, because of their considerable applications in many areas, such as sanitary goods,^{2,3} agriculture and horticulture,^{4–6} medicine for drug delivery systems,^{7–9} and so on.

Recently, the preparation of organic-inorganic superabsorbent composites has attracted great attention because of their relative low production cost, high water absorbency, and considerable applications in agriculture and horticulture.^{10,11} In our previous study, the preparation and the swelling behaviors of poly (acrylic acid)/attapulgite superabsorbent composite has been reported.^{12,13} In a continuation of our research in the field of organic-inorganic superabsorbent composites, we have directed our attention to-

wards the preparation of starch-based superabsorbent composites. Starch is a renewable and biodegradable natural polymer, containing a large number of hydrophilic groups –OH in their structure. The hydrophilicity of these groups makes starch the better raw material for superabsorbency. In addition, starch and attapulgite (a clay mineral) are low cost raw materials. So, the chemical blending by means of graft copolymerization reaction of acrylamide, starch, and attapulgite and fabricating a superabsorbent composite can significantly reduce the production cost and improve the comprehensive water-absorbing properties of the superabsorbent materials.

In this article, we report the synthesis of superabsorbent composites by graft copolymerization reaction of starch, acrylamide, and attapulgite using *N,N*-methylene-bisacrylamide as a crosslinker and ammonium persulphate as an initiator in an aqueous solution, followed by hydrolysis with sodium hydroxide. The factors of effect on water absorbency, such as amount of crosslinker, initiator, attapulgite, weight ratio of acrylamide to starch in the feed, gelatinization conditions of starch and molar ratio of NaOH to acrylamide, and so forth, were investigated.

EXPERIMENTAL

Materials

Corn starch was from Hua'ou Starch Co., Ltd, Inner Mongoulia, China. Acrylamide (AM, chemically pure,

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Contract grant sponsor: Western Action Project of CAS; Contract grant number: KGCXZ-SW-502.

Contract grant sponsor: the "863" major project of the Ministry of Science and Technology, P. R. China; contract grant number: 2002AA6Z0310071.

Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. MBA (chemically pure, Shanghai Chemical Reagent Corp., Shanghai, China) was used as purchased. Attapulgitic micropowder, (Xuyi Colloidal Co., Ltd, Jiangsu, China), milled through a 320-mesh screen, followed by a treatment with 37% hydrochloric acid for 48h and washed with distilled water until pH 7 was reached, was then dried at 105°C for 8h prior to use. All solutions were prepared with distilled water.

Preparation of superabsorbent composites

A series of samples with different amounts of attapulgitic, crosslinker, initiator, starch, and acrylamide was prepared by the following procedure: A weight quantity of starch and distilled water were put in a 250-mL four-necked flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. The slurry was heated to 95°C for 30 min under nitrogen atmosphere. The heating was stopped, and the initiator APS was added when the temperature reached 40°C. Fifteen minutes later, the acrylamide, MBA, and attapulgitic mixture solution was added. The water bath was heated slowly to 70°C and kept for 3h. Then, the resulting product was transferred into a sodium hydroxide solution (2mol/L) and allowed to react at 90–95°C for 2h. The hydrolyzed product was washed several times with distilled water until pH 7 was reached to remove any ungrafted molecules, monomer, and base, then washed with ethanol and dried at 70°C to a constant weight. Thus, the superabsorbent composite was prepared after the dried product was milled and screened. All samples used had a particle size in the range of 40–80 mesh.

Preparation of crosslinked starch-graft-poly(acrylamide) polymer

The procedure of preparation of crosslinked starch-graft-poly(acrylamide) polymer is similar to that of preparation of superabsorbent composites except that attapulgitic is omitted.

Water absorbency measurement

A weighted quantity of the superabsorbent composite was immersed in distilled water or saline solutions at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering over a 100-mesh screen. The water absorbency (Q_{H_2O}) of the superabsorbent composite was determined by weighing the swelled samples, and the Q_{H_2O} of the samples was calculated using the following equation:

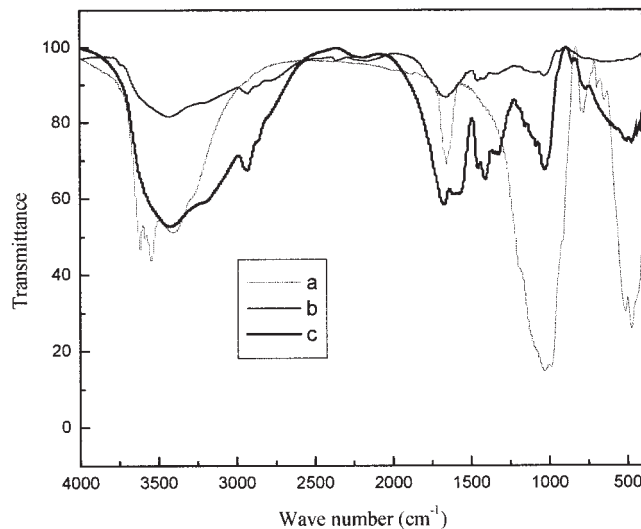


Figure 1 Infrared spectra of: (a) attapulgitic, (b) crosslinked starch-graft-poly(acrylamide) polymer, and (c) starch-graft-poly(acrylamide)/attapulgitic superabsorbent composite.

$$Q_{H_2O} = (m_2 - m_1) / m_1 \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the water-swollen sample, respectively. Q_{H_2O} was calculated as grams of water per gram of sample.

Characterization

The IR spectra of the superabsorbent composites were recorded on a Bio-Rad WIN FTIR (Bio-Rad, Hercules, CA) using KBr pellets. The IR spectrum of the superabsorbent composite shows absorption bands corresponding to the functional groups attached to the monomeric units. Thermal stability studies of dry samples were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT), with a temperature range of 25–800°C at a heating rate of 10°C/min using a dry nitrogen purge at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

IR spectra

The infrared spectra of starch-graft-poly(acrylamide)/attapulgitic superabsorbent composite (10% attapulgitic content) is shown in Figure 1(c). This can be compared to the spectrum of attapulgitic and crosslinked starch-graft-poly(acrylamide) polymer (the sample used before hydrolysis) shown in Figures 1(a) and 1(b), respectively. According to the infrared spectra of starch-graft-poly(acrylamide)/attapulgitic superabsorbent composite, the peaks observed at 3443 cm^{-1} are attributed to NH_2 groups. Absorption peaks appear at 2930 cm^{-1} , corresponding to the $-C-H$ stretching of

the acrylate unit and starch; 1673 cm^{-1} , corresponding to the $\text{C}=\text{O}$ stretching ($-\text{CONH}_2$); 1585 cm^{-1} , corresponding to the $\text{C}=\text{O}$ stretching ($-\text{COONa}$); 1079 cm^{-1} and 1172 cm^{-1} , corresponding to the $\text{C}-\text{O}$ stretching in starch; and 1022 cm^{-1} , corresponding to the $\equiv\text{Si}-\text{O}$ stretching of attapulgite. The infrared analysis result of the superabsorbent composite in Figure 1(c) shows that all characteristic groups, that is, $-\text{CONH}_2$, $-\text{COONa}$, $\text{C}-\text{O}$ (in starch), $-\text{CH}$, and $\equiv\text{Si}-\text{O}$, exist in the product. By comparing Figures 1(a) and 1(c), the absorption peaks at 3621 cm^{-1} and 3549 cm^{-1} , attributed to the OH groups on attapulgite [Fig. 1(a)], disappeared after the reaction [Fig. 1(c)]; it is suggested, therefore, that graft copolymerization between OH groups on attapulgite and monomers took place during the reaction.¹² Moreover, by comparing with the infrared spectra of the crosslinked starch-graft-poly(acrylamide) polymer and starch-graft-poly(acrylamide)/attapulgite superabsorbent composite, only $\text{C}=\text{O}$ stretching (1650 cm^{-1}) in $-\text{CONH}_2$ appears in the infrared spectra of crosslinked starch-graft-poly(acrylamide), whereas both $\text{C}=\text{O}$ stretching in $-\text{CONH}_2$ and $\text{C}=\text{O}$ stretching in $-\text{COONa}$ appear in the infrared spectra of starch-graft-poly(acrylamide)/attapulgite superabsorbent composite. These results also indicate that the partial amide groups have been successfully converted to $-\text{COONa}$ after the hydrolysis of the superabsorbent composite.

Thermal analysis

The thermogravimetric analyses (TGA) of crosslinked starch-g-poly(acrylamide) polymer and crosslinked starch-g-poly(acrylamide) superabsorbent composite (20% attapulgite content) are shown in Figures 2(a)

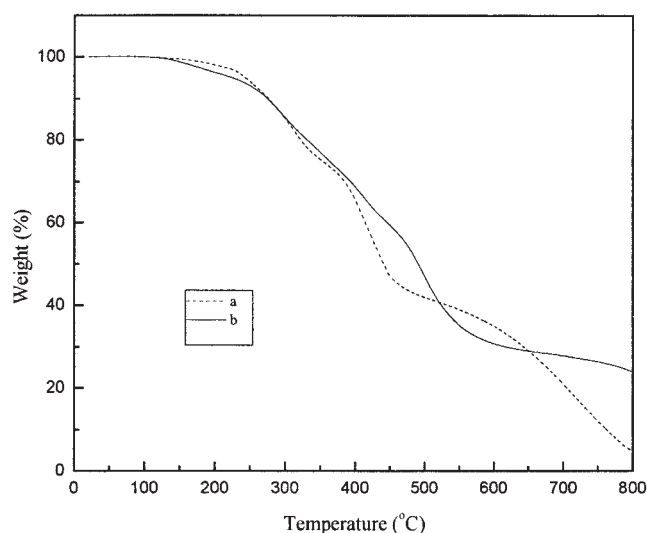


Figure 2 TGA curves of: (a) crosslinked starch-g-poly(acrylamide) polymer and (b) starch-g-poly(acrylamide)/attapulgite superabsorbent composite at a heating rate of $10^\circ\text{C}/\text{min}$.

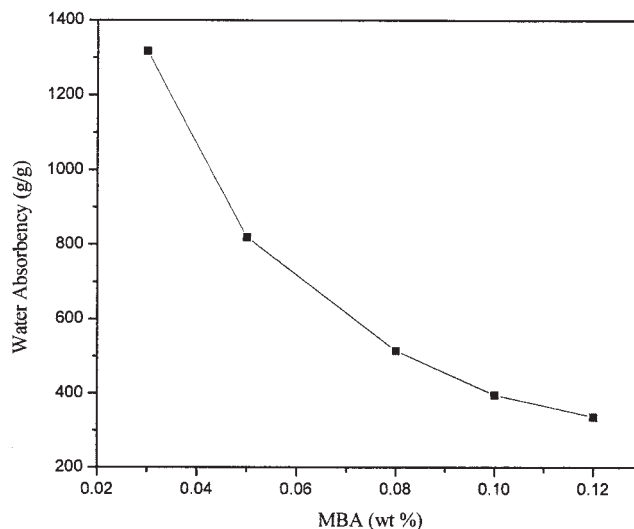


Figure 3 Effect of crosslinker content on water absorbency of superabsorbent composites in distilled water. Reaction conditions: reaction temperature, 70°C ; weight ratio of AM to starch, 3 : 1; weight ratio of initiator and attapulgite in the feed is 1.5 wt % and 10 wt %, respectively.

and 2(b), respectively. Both crosslinked starch-g-poly(acrylamide) polymer and the superabsorbent composite show a very small weight loss below 200°C , implying a loss of moisture. At around 250°C , starch-g-poly(acrylamide) polymer and superabsorbent composite have weight losses of 1.6% (240°C) and 7.2% (260°C), respectively. The major weight loss of starch-g-poly(acrylamide) polymer started at 387°C (30.0%), whereas the superabsorbent composite has a major weight loss that started at 473°C (43.9%). Therefore, starch-g-poly(acrylamide) polymer and the superabsorbent composite have a decomposition temperature of 387°C and 473°C , respectively. The results also indicated that the introduction of attapulgite to the polymer network results in an increase in thermal stability.

Effect of crosslinker content

The crosslinker content can notably affect the water-absorbing ability of a superabsorbent hydrogel. The effect of crosslinker content on water absorbency is shown in Figure 3. The water absorbency decreases with the increase of crosslinker content from 0.03 wt % to 0.12 wt %. When the crosslinker content is below 0.03 wt %, the superabsorbent composite is semi-soluble and the water absorbency can hardly be measured. The results may be due to the fact that the network of the superabsorbent composite cannot be formed efficiently because of few crosslink points when the crosslinker content is low. On the other hand, higher crosslinker content results in the generation of more crosslink points, which in turn causes the formation of an additional network and decreases

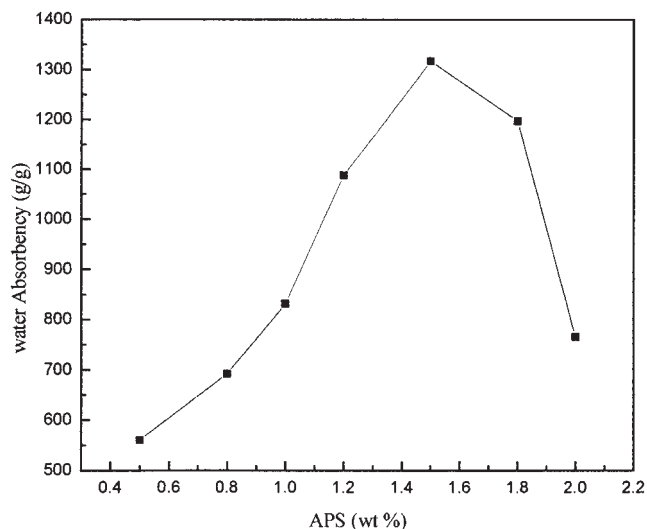


Figure 4 Effect of initiator content on water absorbency of superabsorbent composites in distilled water. Reaction conditions: reaction temperature, 70°C; weight ratio of AM to starch, 3 : 1; weight ratio of crosslinker and attapulgite in the feed is 0.03 wt % and 10 wt %, respectively.

the space left for water to enter. The results are in conformity with Flory's network theory,¹⁴ and similar observations have been reported by others.^{15,16}

Effect of initiator content

Figure 4 shows the effect of the initiator content on the water absorbency of the superabsorbent composite. It can be seen that with the increase in the content of APS, the water absorbency of the superabsorbent composite increased, and reached a maximum of 1317 g/g at an APS content of 1.5 wt %; a further increase in APS resulted in the decline of water absorbency of the superabsorbent composite. A similar observation was also found in a study on factors influencing absorbent properties of saponified starch-g-(acrylic acid-co-acrylamide), which was reported by Athawale and Lele.¹⁷ As interpreted by Athawale and Lele, at low content, APS must have been mostly utilized in producing a large number of free-radical sites on the starch backbone at which the monomers can be grafted. Therefore, the grafting yield and, in turn, the absorbency of the graft polymer increase with increase in APS content. However, above a critical content of 1.5 wt %, the excess of APS was utilized in the homopolymerization of monomers, which results in the decrease of water absorbency.

It should be noted that the presence of initiator in the polymerization system leads not only to grafting but also to the initiation of homopolymerization. The homopolymers of poly (acrylamide) are soluble in the medium of the reaction (water) and would be filtered off during filtration. However, in the presence of

crosslinker with such a high percentage as 0.03 wt %, the homopolymers cannot be extracted completely from the reaction mixture. In addition, these homopolymers would also be crosslinked and form the network. Since the residual homopolymers in the network would help in enhancing the water absorbency of the final product, no attempt was made to extract the homopolymers from the superabsorbent composite.

Effect of weight ratio of am to starch

The effect of the weight ratio of AM to starch on the water absorbency of superabsorbent composites was also investigated, and the results are shown in Table I. It can be seen from Table I that the water absorbency increases with increasing the amount of AM and decreases with further increase in the amount of monomers. The maximum water absorbency is reached when the superabsorbent composite was synthesized with a weight ratio of AM to starch of 3 : 1. When the amount of monomers increased, both grafting and the molecular weight of the grafted PAM chains increased, which result in an increase in the water absorbency.¹⁸ With further increasing of the AM amount, the water absorbency decreased. This result may be attributed to an increase in homopolymer percentages of PAM, which in turn results in an increase in soluble materials at fixed crosslinking density.¹⁹ A similar observation was also reported by Lu and coworkers.²⁰

Effect of gelatinization conditions

Table II shows the effect of gelatinization of starch on the water absorbency of superabsorbent composites. Increasing both gelatinization temperature and gelatinization time can lead to an increase in water absorbency. It has been reported by Athawale and colleagues¹⁷ that when the aqueous starch slurry is heated, the large starch granules absorb water and

TABLE I
Effect of Weight Ratio of AM to Starch in the Feed on the Water Absorbency of Superabsorbent Composites

Weight ratio of AM to starch		Water absorbency (g/g)
AM	starch	
1	1	367
2	1	789
3	1	1317
4	1	942
5	1	577

Reaction conditions: reaction temperature, 70°C; weight ratio of initiator, crosslinker, and attapulgite in the feed is 1.5 wt %, 0.03 wt %, and 10 wt %, respectively.

TABLE II
Effect of Gelatinization Temperature and Gelatinization Time on the Water Absorbency of Superabsorbent Composites

Temperature (°C)	Time (min)	Water absorbency (g/g)
75	30	784
75	60	845
95	30	1317
95	60	1370

Reaction conditions: reaction temperature, 70°C; weight ratio of AM to starch, 3 : 1; weight ratio of initiator, crosslinker, and attapulgite in the feed is 1.5 wt %, 0.03 wt %, and 10 wt %, respectively.

swell rapidly, which would facilitate grafting by making a large surface area available where the monomers can be grafted at. But the smaller starch granules swell only at higher temperature (>75°C). Therefore, when the gelatinization temperature is above 75°C, the smaller starch granules can also be swollen and enlarge the surface area of starch granules, which in turn enhances the grafting. Gelatinization time can also affect the grafting. When starch gelatinized at high temperature, the swelling of starch granules by absorption of water initiates at the outer surface of granules and then the water slowly diffuses into the core of the granules.²¹ So, the starch granules would swell completely with the longer gelatinization time, which is also helpful to grafting. In a word, the water absorbency of superabsorbent composites increases with increasing both gelatinization temperature and gelatinization time, and this may be due to the fact that the surface area of the starch granules increased, which results in a higher percentage of grafting.

Effect of molar ratio of naoh to am

Figure 5 shows the effect of the molar ratio of NaOH to AM on the water absorbency of superabsorbent composites. The hydrolysis of the graft copolymer results in a product with a higher water absorbency. When the sample was hydrolyzed in sodium hydroxide solution, the amide groups on the graft PAM (or partial PAM homopolymer) chains can turn into carboxylate groups. It is well known that the carboxylate group has a higher hydrophilicity than the amide group. Moreover, the negatively charged carboxylate groups attached to the polymer chains set up an electrostatic repulsion, which tends to expand the network of the swollen superabsorbent composite. In a certain range of hydrolysis degree, the electrostatic repulsion increases with the increase of hydrolysis degree, resulting in the increase of water absorbency. However, further increase in the hydrolysis degree of PAM re-

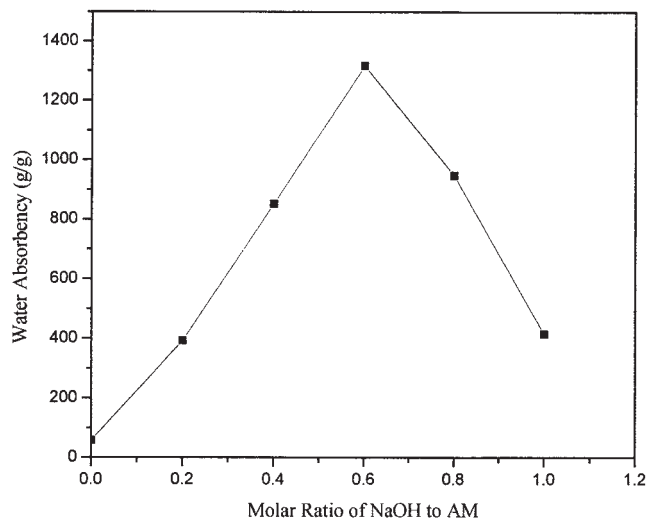


Figure 5 Effect of molar ratio of NaOH to AM on the water absorbency of superabsorbent composites. Reaction conditions: reaction temperature, 70°C; weight ratio of AM to starch, 3 : 1; weight ratio of initiator, crosslinker, and attapulgite in the feed is 1.5 wt %, 0.03 wt %, and 10 wt %, respectively.

sults in the generation of more sodium ions, which reduces the electrostatic repulsion and increases the chain stiffness by screening the negative charges of the carboxyl groups,²² thus resulting in a decrease of water absorbency.

Effect of attapulgite

Table III shows the effect of attapulgite content on the water absorbency. The water absorbency decreases with the increase of attapulgite content. As described in a previous study,^{11,12} the inorganic clay mineral particle in the network acts as an additional network point. The crosslinking density of superabsorbent composites increases with the increase of attapulgite content, which results in a decrease in water absorbency.

TABLE III
Effect of Amount of Attapulgite on Water Absorbency of the Superabsorbent Composites

Sample no.	Attapulgite percentage (wt %)	Q _{H2O} (g/g)	
		Distilled water	0.9 wt % NaCl
SPAmA ₀	0	545	54
SPAmA ₁	10	1317	68
SPAmA ₂	20	984	61
SPAmA ₃	30	791	60
SPAmA ₄	40	651	57

Reaction conditions: reaction temperature, 70°C; weight ratio of AM to starch, 3 : 1; weight ratio of initiator and crosslinker in the feed is 1.5 wt % and 0.03 wt %, respectively.

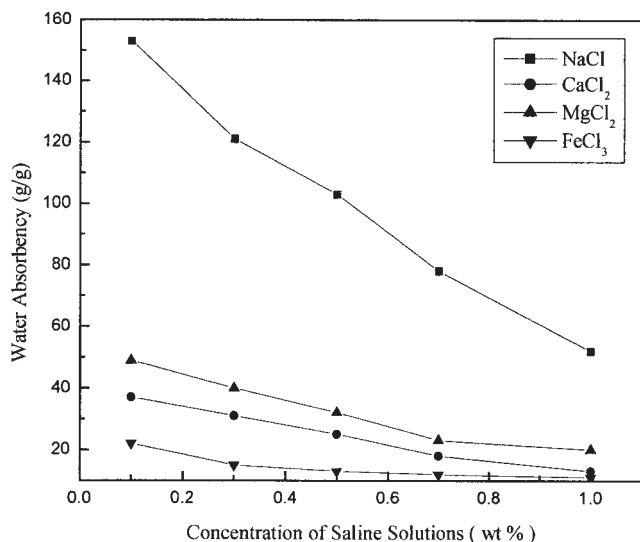


Figure 6 Water absorbency of SPAmA₁ in NaCl, CaCl₂, MgCl₂, and FeCl₃ aqueous solutions with various salt concentration.

Effect of saline solutions

Figure 6 shows the effect of salt solutions (NaCl_(aq), CaCl_{2(aq)}, MgCl_{2(aq)}, and FeCl_{3(aq)}) on water absorbency of superabsorbent composites (SPAmA₁). As shown in Figure 6, the water absorbency decreases with the increase of concentration of all four salt solutions. According to a previous study,²³ the water absorbency of superabsorbent composites decreases with increase of ionic strength of external solutions. This decrease in water absorbency with increasing ionic strength may be attributed to the decrease in the osmotic pressure difference between the superabsorbent composite and the external salt solution. It also can be seen from Figure 6 that for a given concentration of salt solution, the water absorbency in NaCl solution is far higher than that in CaCl₂, MgCl₂, and FeCl₃ solutions. This dramatic decrease of water absorbency in multivalent cationic solutions may be due to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which result in an increase in the crosslinking density of the network.²⁴

Water retention test

Water retention of the swollen superabsorbent composites was determined by centrifuging them at 4000 rpm for 10 min; the results are presented in Table IV. From Table IV we can see that all swollen superabsorbent composite samples show good water retention ability and can keep approximately 93% of the dis-

tilled water after centrifuging at 4000 rpm for 10 min. This excellent water retention under load may be especially useful in agricultural and horticultural applications.

CONCLUSIONS

A novel starch-*graft*-poly(acrylamide)/attapulgite superabsorbent composite was synthesized by graft copolymerization reaction of starch, acrylamide (AM), and attapulgite micropowder using *N,N*-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulphate (APS) as an initiator in aqueous solution, followed by hydrolysis with sodium hydroxide. These crosslinked superabsorbent composites were characterized by FTIR and TGA. The factors of effect on water absorbency, such as amount of crosslinker, initiator, attapulgite, weight ratio of acrylamide to starch in the feed, gelatinization conditions of starch and molar ratio of NaOH to acrylamide, and so forth, were investigated. Results obtained from this study show that the water absorbency of superabsorbent composites synthesized under optimal synthesis conditions with an attapulgite content of 10% exhibit absorption of 1317 g H₂O/g sample and 68 g H₂O/g sample in distilled water and in 0.9 wt % NaCl solution, respectively. As a novel superabsorbent composite material, the water absorbencies in distilled water and in 0.9% NaCl solution were both improved and the production cost was significantly reduced compared with crosslinked starch-g-poly(acrylamide) superabsorbent polymer. The effect of saline solutions on the water absorbency was discussed. The water absorbency in monovalent and multivalent cationic salt solutions decreases with an increase in the concentration of the salt solutions. The dramatic decrease of water absorbency in multivalent cationic solutions may be due to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which result in an increase in the crosslink density of the network. Water retention tests were carried out. It was found that the superabsorbent composite has good water retention ability under load. This excellent water absorbency and water retention under load may be especially useful in agricultural and horticultural applications.

TABLE IV
Water Retention for the Swollen Samples of Superabsorbent Composites

Sample	SPAmA ₁	SPAmA ₂	SPAmA ₃	SPAmA ₄
Water retention (%)	95.1	93.6	92.7	92.5

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