

Studies on Poly(acrylic acid)/Attapulgite Superabsorbent Composite. I. Synthesis and Characterization

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ABSTRACT: A novel poly(acrylic acid)/attapulgite superabsorbent composite was synthesized by graft copolymerization reaction of acrylic acid (AA) on attapulgite micropowder using *N,N'*-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator in aqueous solution. The effects on water absorbency of such factors as reaction temperature, initial monomer concentration, degree of neutralization of AA, amount of crosslinker, initiator, and attapulgite were investigated. These cross-linked superabsorbent composites were characterized by thermogravimetric analysis and scanning electron microscopy. The graft copolymerization reaction of AA on attapulgite micropowder was characterized by FTIR. The water

absorbencies for these superabsorbent composites in water and saline solutions were investigated and water-retention tests were carried out. Results obtained from this study show that the water absorbency of the superabsorbent composite synthesized under optimal synthesis conditions with an attapulgite content of 10% exhibited an absorption of 1017 g H₂O/g sample and 77 g H₂O/g sample in distilled water and in 0.9 wt % NaCl solution, respectively. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1596–1603, 2004

Key words: acrylic acid; superabsorbent; crosslinking; water absorbency; water retention

INTRODUCTION

Superabsorbents can absorb a large amount of water during a short period of time and the absorbed water can be removed only with difficulty, even under some pressure. Therefore, superabsorbents have great advantages over traditional water-absorbing materials such as cotton, pulp, and sponge, and have found a variety of valuable applications.^{1–3} Because of their excellent characteristics, these superabsorbents are widely used in many fields such as agriculture and horticulture,^{4,5} sanitary goods,⁶ sealing composites,⁷ and medicine for drug-delivery systems,⁸ for example.

The synthesis of new superabsorbents and the development of their applications are still interesting research areas. Recently, the preparation of organic-inorganic superabsorbent composites has attracted great attention because of their relatively low production cost, high water absorbency, and their considerable range of applications in agriculture and horticulture. Zhu et al.⁹ reported the synthesis of poly(acrylic acid)/kaolinite superabsorbent composite by means of inverse suspension polymerization. Wu et al.^{10,11} prepared starch-g-polyacrylamide/clay and poly(acrylic acid)/mica superabsorbent composites by graft copolymerization reaction of organic monomer and inor-

ganic clay mineral powder. Attapulgite is a layered aluminum silicate with reactive –OH groups on the surface. To reduce costs and improve the comprehensive water-absorbing properties of the superabsorbent materials, the grafting of acrylic acid polymer onto attapulgite and fabricating a composite that consists of polymer and attapulgite micropowder was considered a priority. In this article, we report the synthesis of superabsorbent composites by graft copolymerization reaction of acrylic acid on attapulgite micropowder using *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator in an aqueous solution. The effects on water absorbency of such factors as reaction temperature, initial monomer concentration, degree of neutralization of acrylic acid, amount of crosslinker, initiator, and attapulgite were investigated.

EXPERIMENTAL

Materials

Acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. *N,N'*-Methylenebisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corp., Shanghai, China) was used as purchased. Attapulgite micropowder (Xuyi Colloidal Co., Jiangsu, China) was milled

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through a 320-mesh screen, followed by a treatment with 37% hydrochloric acid for 48 h and washed with distilled water until pH 7 was reached, after which it was dried at 105°C for 8 h before use. All solutions were prepared with distilled water.

Preparation of superabsorbent composites

A series of samples with different amounts of attapulgite, crosslinker, initiator, and acrylic acid with different degrees of neutralization were prepared by the following procedure. Typically, AA (7.2 g) was dissolved in 20 mL of distilled water and then neutralized at 5°C with 12 mL of sodium hydroxide solution (5M) in a four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. Attapulgite powder (0.8 g) was dispersed in the above partially neutralized monomer solution. Under nitrogen atmosphere, the crosslinker MBA (16.0 mg) was added to the AA-attapulgite mixture solution and the mixed solution was stirred on a water bath at room temperature for 30 min. The water bath was then heated slowly to 70°C with vigorous stirring after the radical initiator APS (80.2 mg) was charged to the mixed solution. After 3 h of the reaction, the resulting product was washed several times with distilled water and then dried in a vacuum oven at 60°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 uncrosslinked poly(acrylic acid)

The preparation procedure of uncrosslinked poly(acrylic acid) [PAA] was similar to that of preparation of superabsorbent composite except without attapulgite and MBA.

Preparation of uncrosslinked PAA-grafted attapulgite

AA (4.2 g) was dissolved in 15 mL of distilled water in a 250-mL four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. Under nitrogen atmosphere, attapulgite micropowder (1.0 g) was added to the AA solution and the mixture was stirred at room temperature for 30 min. APS (40 mg) was added to the mixture, which was heated at 70°C with stirring in a nitrogen atmosphere for 4 h. Then the reaction mixture was poured into a large volume of distilled water and the precipitate was filtered, dried in a vacuum oven at 40°C, and weighed. Non-graft polymer was extracted from the precipitate with ethanol for 10 h.

Water-absorbency measurement

A weighted quantity of the superabsorbent composite was immersed in distilled water 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 ($Q_{\text{H}_2\text{O}}$) of the superabsorbent composite was determined by weighing the swelled samples, and the $Q_{\text{H}_2\text{O}}$ of the samples was calculated using the following equation:

$$Q_{\text{H}_2\text{O}} = (m_2 - m_1)/m_1 \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the water-swollen sample, respectively. $Q_{\text{H}_2\text{O}}$ was calculated as grams of water per gram of sample.

Characterization

1. The IR spectra of the superabsorbent composite 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.
2. 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.
3. The morphology of the dried polymer was examined using a JSM-5600LV SEM instrument after (JEOL, Ltd.) coating the sample with gold film.

RESULTS AND DISCUSSION

Effect of initial monomer concentration

The effect of initial AA concentration (C_A , wt %) on water absorbency is shown in Figure 1. The water absorbency in distilled water decreased from 1288 to 361 g/g with the increase of C_A from 14.0 to 31.5 wt %. It was difficult to obtain a composite gel in the preparation when C_A was less than 14.0 wt % and water absorbency was hard to measure exactly because of the excessive water-soluble material. It was reported by Baker et al.¹² that the effective crosslinking density is probably less than the nominal crosslinking density at a low total monomer concentration in the preparation of cationic acrylamide-based hydrogel. The result for PAA/attapulgite superabsorbent composite conformed to the resulting cationic acrylamide-based hy-

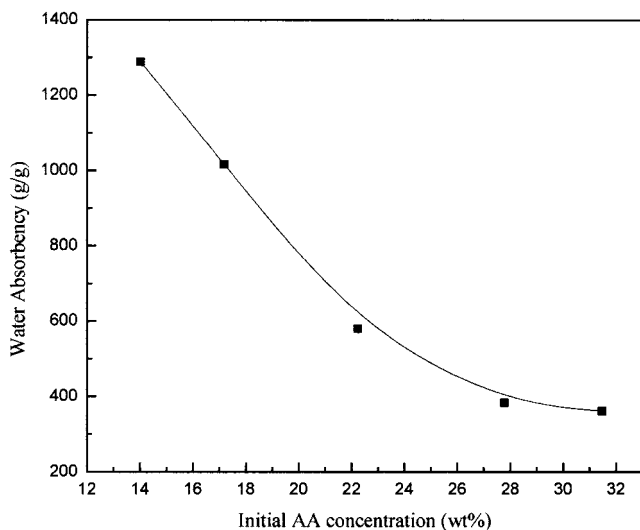


Figure 1 Effect of initial AA concentration on water absorbency of superabsorbent composite in distilled water: reaction temperature, 70°C; 60% neutralization degree; weight ratio of crosslinker, initiator, and attapulgit in the feed is 0.2, 1.0, and 10%, respectively.

drogel and similar observations were reported by others.^{13,14}

Effect of reaction temperature

Figure 2 shows that the water absorbency of the superabsorbent composite increases as the reaction temperature increases from 40 to 70°C and decreases with further increases in reaction temperature. When the

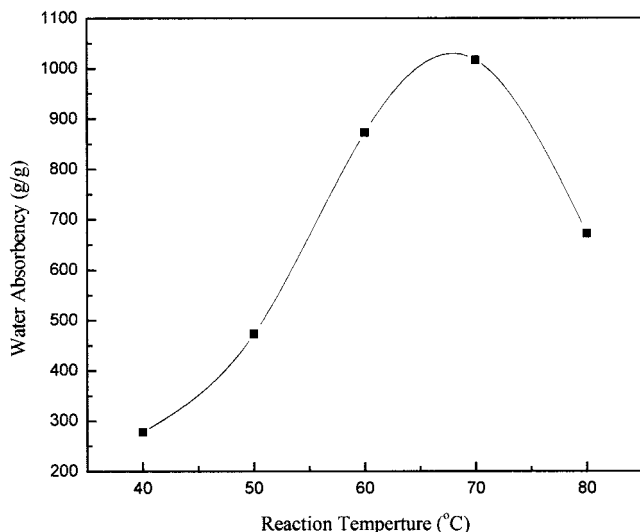


Figure 2 Effect of reaction temperature on water absorbency of superabsorbent composite in distilled water: 60% neutralization degree; C_A , 17.2 wt %; weight ratio of crosslinker, initiator, and attapulgit in the feed is 0.2, 1.0, and 10%, respectively.

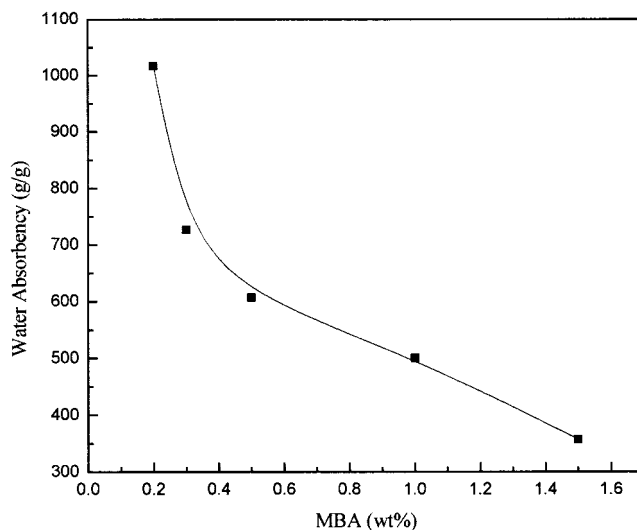


Figure 3 Effect of crosslinker content on water absorbency of superabsorbent composite in distilled water: reaction temperature, 70°C; 60% neutralization degree; C_A , 17.2 wt %; weight ratio of initiator and attapulgit in the feed is 1.0 and 10%, respectively.

reaction temperature is decreased, the rate of polymerization also decreases, which results in the enhancement of crosslinking efficiency.¹⁵ At the same crosslinker content, the water absorbency decreases with the increase of the crosslinking efficiency according to Flory's network theory.¹⁶ However, when the polymerization temperature is higher than 70°C, the water absorbency is decreased. With the increase of reaction temperature, the polymerization reaction rate increases and the molecular weight decreases, so the water absorbency is also decreased.

Effect of crosslinker content

Crosslinking density is an extremely important swelling control element. Relatively small changes in crosslinking density can play a major role in modifying the properties of superabsorbent polymers. The effect of crosslinker content on water absorbency is shown in Figure 3. It can be seen that the water absorbency decreases with the increase of crosslinker content from 0.2 to 1.5 wt %. When the crosslinker content is <0.2 wt %, the absorbency of superabsorbent composite decreases because of an increase of soluble material. On the other hand, a higher crosslinker content results in the generation of more crosslink points, which in turn causes the formation of an additional network and decreases the space left for water to enter. The results are in conformity with Flory's network theory¹⁶ and similar observations were previously reported by others.^{14,15}

Effect of initiator content

Figure 4 shows the effect of the initiator content on water absorbency. The water absorbency increases as

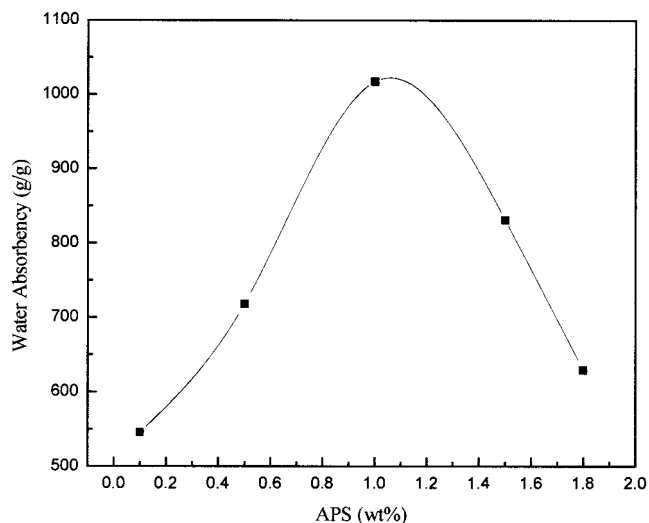


Figure 4 Effect of initiator content on water absorbency of superabsorbent composite in distilled water: reaction temperature, 70°C; 60% neutralization degree; C_{A_1} , 17.2 wt %; weight ratio of crosslinker and attapulgit in the feed is 0.2 and 10%, respectively.

APS content increases from 0.1 to 1.0 wt % and decreases with further increases in the content of APS. The relation between the average kinetic chain length (\bar{v}) and concentration of the initiator in free-radical polymerization is given by the following equation¹⁷:

$$\bar{v} = \frac{1}{2} K_p (f K_i k_t)^{-1/2} [I]^{-1/2} [M] \quad (2)$$

where k_p , k_i , and k_t are the rate constants for propagation, initiator, and termination, respectively; f is the efficiency of initiation by the initiator; and $[I]$ and $[M]$ are the initial concentration of the initiator and monomer, respectively. According to eq. (2), the molecular weight in free-radical polymerization will decrease with an increase of initiator concentration. With the decrease of the molecular weight, the relative amount of polymer chain ends increases. As reported in a previous study,¹⁸ the polymer chain ends do not contribute to the water absorbency. Therefore, the increase of initiator content is responsible for the decrease in water absorbency. However, further decreases in APS content below the optimum values are accompanied by a decrease in absorbency. This result may be attributed to a decrease in the number of radicals produced as the content of APS decreases. The network cannot form efficiently with a small number of radicals in the free-radical polymerization that results in the decrease of the water absorbency.

Effect of neutralization degree

The effect of neutralization degree on the water absorbency is shown in Figure 5. It is obvious that the water

absorbency increases from 40 to 60% and decreases with further increases in the neutralization degree of AA. This behavior may be interpreted as a cooperative absorbing effect between carboxylic acid and carboxylate group that is superior to either group. According to Flory's network theory, the swelling ability of ionic network is attributed to the rubbery elasticity, ionic osmotic, and affinity of polymer toward water. When poly(acrylic acid) is neutralized with sodium hydroxide, the negatively charged carboxyl groups attached to the polymer chains set up an electrostatic repulsion that tends to expand the network. In a certain range of neutralization degree, the electrostatic repulsion increases with the increase of neutralization degree, resulting in the increase of water absorbency. However, further increases in the neutralization degree of PAA result in the generation of more sodium ions, which reduce the electrostatic repulsion by screening the negative charges of carboxyl groups, thus resulting in the decrease of water absorbency. Under our experimental conditions, a neutralization degree of 60% of PAA possesses the highest water absorbency. Similar results were reported in previous studies.^{15,19}

Effect of attapulgit

The effect of the amount of attapulgit in the superabsorbent composite on the water absorbency is shown in Table I. When a prepared superabsorbent composite contained a small amount of attapulgit (5%), the water absorbency of the resulting product significantly improved. When the content of attapulgit in superabsorbent composite was >5%, the water

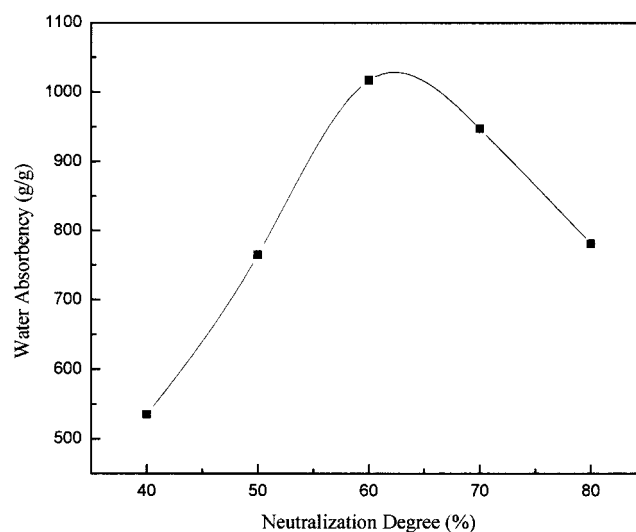


Figure 5 Effect of neutralization degree on water absorbency of superabsorbent composite in distilled water: reaction temperature, 70°C; C_{A_1} , 17.2 wt %; weight ratio of crosslinker, initiator, and attapulgit in the feed is 0.2, 1.0, and 10%, respectively.

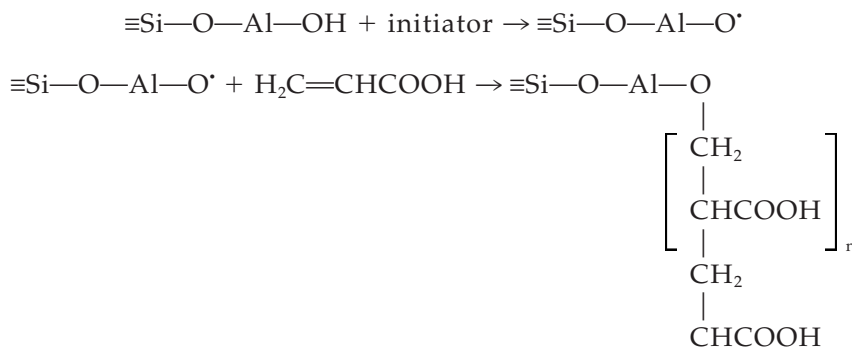
TABLE I
Effect of Amount of Attapulgite on Water Absorbency of the Superabsorbent Composites^a

Sample	Attapulgite percentage (wt %)	Q_{H_2O} (g/g)	
		Distilled water	0.9 wt % NaCl
PAA	0	712	69
PA ₁	5	1325	117
PA ₂	10	1017	77
PA ₃	20	787	74
PA ₄	35	773	71

^a Reaction conditions: reaction temperature, 70°C; 60% neutralization degree; C_A , 17.2 wt %; weight ratio of crosslinker and initiator in the feed is 0.2% and 1.0%, respectively.

absorbency decreased with the increase of the amount of attapulgite. This may be attributed to the fact that a greater amount of attapulgite results in the generation of more crosslink points, which increases the crosslinking density of the superabsorbent composite and reduces the absorbency of the composite.

The mechanism of polyacrylonitrile grafting onto mica was reported in a previous study.²⁰ It was presumed that the hydroxyl groups in attapulgite may react with APS by a similar mechanism and liberate free radicals on the attapulgite structure and that the graft polymerization will take place on these free radicals, giving PAA branches on the attapulgite backbone as given in the following set of equations:



Infrared spectra

The infrared spectrum of uncrosslinked PAA-grafted attapulgite is shown in Figure 6(a). This can be compared to the spectra of attapulgite and uncrosslinked PAA shown in Figure 6(b) and (c), respectively. The characteristic peak at 1717 cm^{-1} arises from the carbonyl group $\text{C}=\text{O}$ of PAA, which provides evidence of a graft polymerization reaction between PAA and attapulgite.

Thermal stability

Thermogravimetric analysis (TGA) curves of crosslinked PAA and PA₃ are shown in Figure 7(a) and (b), respectively. Both crosslinked PAA and PA₃ show a very small weight loss below 100°C, implying a loss of moisture. At around 240°C, crosslinked PAA and PA₃ have similar significant weight losses of 10.0% (244°C) and 9.3% (237°C), respectively. The major weight loss

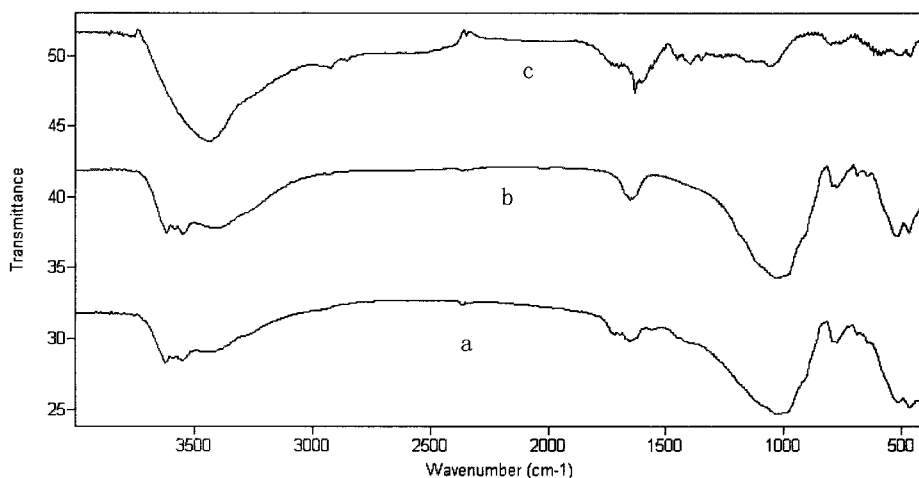


Figure 6 Infrared spectra of (a) poly(acrylic acid)-grafted attapulgite, (b) attapulgite, and (c) uncrosslinked PAA.

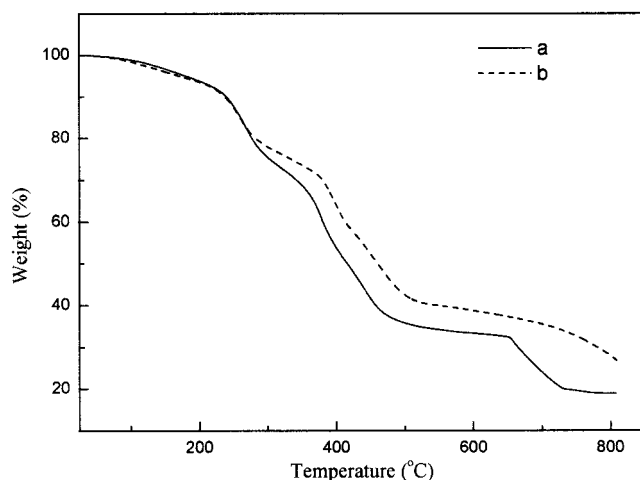


Figure 7 TGA curves of (a) crosslinked PAA and (b) PA₃ at a heating rate of 10°C/min.

of crosslinked PAA started at 360°C (21.7%), whereas PA₃ has a major weight loss starting at 382°C (29.2%). Therefore, crosslinked PAA and PA₃ have initial decomposition temperatures of 360 and 382°C, respectively. The results also indicated that introduction of attapulgite to the polymer network results in an increase in thermal stability.

SEM observations

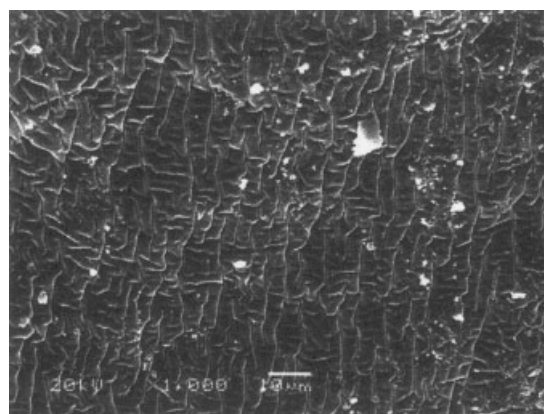
The micrographs of uncrosslinked PAA, crosslinked PAA, and PA₃ are shown in Figure 8(a), (b), and (c), respectively. The SEM micrograph of uncrosslinked PAA, which is water-soluble and has no absorbency, is shown to be nonporous [Fig. 8(a)], whereas the SEM micrographs of crosslinked PAA and PA₃, which have good water absorbency, show the samples to be microporous. In addition, PA₃ has a greater absorbency and shows a broad network structure [Fig. 8(c)], whereas crosslinked PAA has a fine network structure [Fig. 8(b)]. These observations are in good agreement with our water-absorbency observations.

Water-retention test

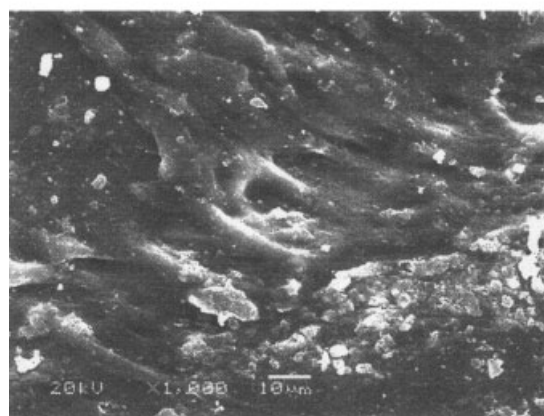
Water retention of the swollen superabsorbent composites was determined by a heating oven test at 60 or 100°C and centrifuging the samples at 4000 rpm for 30 min. Water-retention values of the swollen superabsorbent composite samples and the swollen PAA sample are presented in Table II. From Table II we can see that all swollen superabsorbent composite samples show good water-retention ability and can retain approximately 97% of the distilled water after centrifugation at 4000 rpm for 30 min.

Figure 9 shows the water-retention capacity of swollen superabsorbent composite and crosslinked PAA at

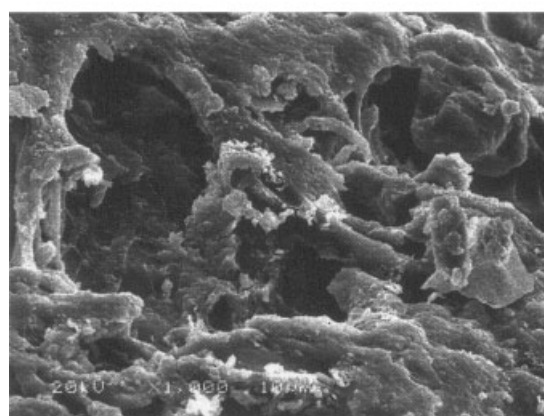
different temperatures (60 or 100°C). It can be seen that both PAA and PA₃ have a decreasing trend of water retention with prolonging the time: about 88 and 87% of distilled water for PA₃ and PAA, respectively, maintained at 60°C after 5.5 h of water-retention test. Moreover, for a given duration of time the



a



b



c

Figure 8 Scanning electron micrographs of (a) uncrosslinked PAA, (b) crosslinked PAA, and (c) PA₃.

TABLE II
Water Retention for the Swollen Samples of
Superabsorbent Composite and Crosslinked PAA

	Sample				
	PAA	PA ₁	PA ₂	PA ₃	PA ₄
Water retention (%)	95.4	98.5	96.8	98.4	97.5

water retention of the PA₃ sample is slightly better than that of PAA. In the 100°C water-retention test, the water loss of PA₃ reached almost 96.2%, whereas PAA had a water loss of 60.4% after the 5.5-h water-retention test. According to a previous study,²¹ the water in a hydrogel can be classified into bound water, half-bound water, and free water. Compared to bound water and half-bound water, the free water in a hydrogel has high mobility and can easily be lost. The number of hydrophilic groups (COOH and COONa) in a unit volume in superabsorbent composite is smaller than that in PAA, so the percentages of bound water and half-bound water content in swollen PAA are higher than those in swollen PA₃; that is, swollen PA₃ has a higher percentage of free water content than that of swollen PAA. As a result, PAA has a better water-retention ability than PA₃ under higher temperature.

After the swollen superabsorbent composite thoroughly loses its absorbed water, the resulting dry sample still retains a good water-absorbing ability. It can be seen from Figure 10 that PA₃ still retains approximately 85% of its initial water absorbency (initial water absorbency of PA₃; see Table I), even after repeating the swelling-deswelling-swelling test five times (the heating oven test repeated five times at

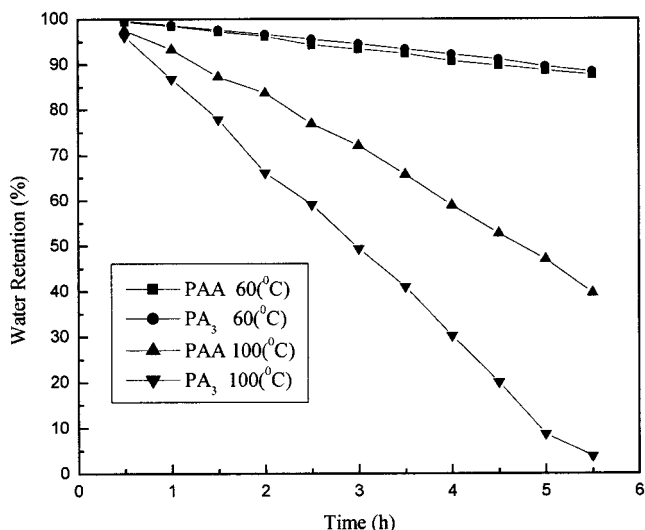


Figure 9 Water retention of swollen samples as a function of time at 60 and 100°C.

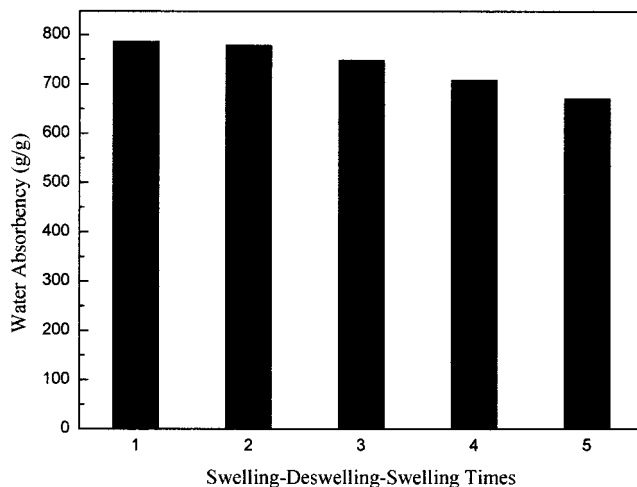


Figure 10 Water absorbency of PA₃ as a function of swelling-deswelling-swelling times.

100°C). These superabsorbent composites may prove useful in recyclable superabsorbent materials.

CONCLUSIONS

Novel superabsorbent composites of crosslinked poly(acrylic acid)/attapulgite were prepared in an aqueous solution by graft copolymerization reaction of acrylic acid on attapulgite micropowder using *N,N*-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator. These crosslinked superabsorbent composites were characterized by TGA and SEM. The graft copolymerization reaction of acrylic acid on attapulgite micropowder was characterized by IR. The effects of initial monomer concentration, reaction temperature, degree of neutralization, amount of crosslinker, initiator, and attapulgite on the water absorbency of superabsorbent composites were investigated. Under our experimental conditions, a crosslinked poly(acrylic acid)/attapulgite superabsorbent composite with a water absorbency greater than 1000 g H₂O/g was synthesized, which has a composition of 0.2 wt % of crosslinker, 1.0 wt % of initiator, 10 wt % of attapulgite, a neutralization degree of 60%, and a reaction temperature of 70°C. It was also found that crosslinked poly(acrylic acid)/attapulgite superabsorbent composite is characterized by good water retention under load. This excellent water absorbency and water retention under load may be especially useful in agricultural and horticultural applications.

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