Preparation and Slow-Release Property of a Poly(acrylic acid)/Attapulgite/Sodium Humate Superabsorbent Composite

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ABSTRACT: A novel poly(acrylic acid)/attapulgite (APT)/ sodium humate (SH) superabsorbent composite was synthesized through the graft copolymerization reaction of acrylic acid on APT micropowder and SH with N,N'-methylene bisacrylamide as a crosslinker and ammonium persulfate as an initiator in an aqueous solution. Various effects on the water absorbency, including the amounts of the crosslinker, initiator, APT, and SH, were investigated. The superabsorbent composite was characterized with Fourier transform infrared spectroscopy and scanning electron microscopy. The superabsorbent composite synthesized under optimal synthesis conditions with an APT concentration of 20% and an SH concentration of 20% exhibited absorption of 583 g of H_2O/g of sample and 63 g of H_2O/g of sample in distilled water and in a 0.9 wt % NaCl solution, respectively. The slow-release property of SH from the superabsorbent composite into water was measured, and a test of the water retention of the superabsorbent composite in soil was also carried out experimentally with and without the superabsorbent composite. The results showed that the superabsorbent composite had not only good water retention but also an additional slow-release property of SH. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 37–45, 2007

Key words: composites; crosslinking; swelling

INTRODUCTION

Superabsorbents are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining possibly huge volumes of water in the swollen state. This valuable characteristic has led to many applications for these important materials, including applications in agricultural soil, in which they help to speed the absorption and retention of water, leading to a reduction in water consumption, preventing plant death, and improving fertilizer retention in the soil.[1–5] Superabsorbents are also used extensively in sanitary goods,[6] sealing composites,[7] drug delivery systems,[8] and so on.

According to the type of application and the conditions of usage, the network structure of these beneficial materials can be tailored to match the desired properties. Superabsorbent polymers used as absorbents for agricultural purposes are commonly based on acrylic monomers such as acrylamide, acrylic acid (AA), and the salt of the acid. In such applications, water absorbency and water retention are essential. To reduce costs and improve the comprehensive water-absorbing properties of superabsorbent materials based on acrylic monomers, grafting acrylic monomers onto clay and fabricating a composite consisting of a polymer and clay can be a priority.[9,10] In our previous studies,[11–14] several kinds of superabsorbent composites based on APT were prepared, and these superabsorbent composites showed high water absorbency and water retention, good salt-resistance, and low production costs in comparison with pure organic superabsorbent polymers under the same preparation conditions.

Recently, studies on superabsorbents with the slow-release property of fertilizers have attracted much attention.[15,16] In comparison with normal superabsorbents, these superabsorbents with slow-release fertilizers have great advantages due to not only their water-absorbing ability but also their slow-release properties. In addition, these superabsorbents with the slow-release property of fertilizers can be used as functional water-management materials and may prove especially practical in agricultural and horticultural applications.

Sodium humate (SH), a low-cost raw material and good fertilizer, is composed of multifunctional ali-

phatic and aromatic components and so contains large numbers of functional hydrophilic groups (e.g., carboxylates and phenolic hydroxyls).[17] Also, SH can regulate plant growth, accelerate root development, improve soil cluster structures, and improve the absorption of nutrient elements. Therefore, chemical blending through the graft copolymerization reaction of AA, APT, and SH and fabricating a superabsorbent composite can not only significantly reduce the production cost but also endow the superabsorbent composite with an additional slow-release property of fertilizers as a multifunctional water-management material. In this article, we report the synthesis of a novel superabsorbent composite based on AA, inorganic clay mineral/APT, and SH through a solution polymerization. The slow release of SH from the superabsorbent composite into water was measured. A test of the water retention of the superabsorbent composite in soil was also carried out experimentally with and without the superabsorbent composite.

EXPERIMENTAL

Materials

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*-Methylene bisacrylamide (MBA; chemically pure; Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. SH (Shuanglong Co., Ltd., Miquan, China) was milled through a 320-mesh screen. All solutions were prepared with distilled water. APT micropowder (Linze Colloidal Co., Gansu, China) was milled through a 320-mesh screen, treated with 37% hydrochloric acid for 48 h, washed with distilled water until pH 7 was reached, and then dried at 105°C for 8 h before use. All solutions were prepared with distilled water.

Preparation of the Poly(acrylic acid) (PAA)/APT/SH superabsorbent composites

A series of samples with different amounts of APT, SH, crosslinker, initiator, and AA with different degrees of neutralization were prepared with the following procedure. Typically, AA (7.2 g) was dissolved in 30 mL of distilled water and then neutralized with 12 mL of a sodium hydroxide solution (5*M*) in a four-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen line. APT (2.45 g) and SH (2.45 g) were added to the aforementioned partially

neutralized monomer solution. Under a nitrogen atmosphere, the crosslinker MBA (18.4 mg) was added to the mixture solution, and the mixed solution was stirred at room temperature for 30 min. The water bath was heated slowly to 70°C with effective stirring after radical initiator APS (122.3 mg) and 18 mL of distilled water were introduced to the mixed solution. After 3 h of the reaction, the resulting product was washed several times with distilled water, dried at 70°C to a constant weight, and then milled and screened. All samples had a particle size in the range of 40–80 mesh.

Preparation of the crosslinked PAA superabsorbent polymer

The synthesis conditions for the preparation of the crosslinked PAA superabsorbent polymer were similar to those for the preparation of the superabsorbent composite, except that was no attapulgite (APT) or SH in the reaction process.

Water-absorbency measurements

A weighed quantity of the superabsorbent composite was immersed in distilled water at room temperature to reach the swelling equilibrium. The swollen samples were then separated from unabsorbed water via screening, and the gel was allowed to drain on the sieve for 10 min. The water absorbency of the superabsorbent composite was determined via the weighing of the swollen samples, and it was calculated for the samples with the following equation:
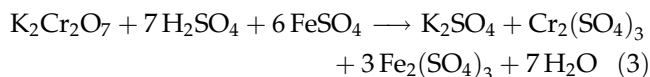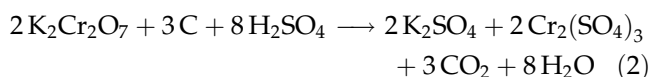
$$Q_{H_2O} = (m_2 - m_1)/m_1 \qquad (1)$$

where Q_{H_2O} is the water absorbency and m_1 and m_2 are the weights of the dry sample and water-swollen sample, respectively. Q_{H_2O} was calculated as grams of water per gram of the sample. The Q_{H_2O} data were obtained from three measurements of the samples and were expressed as the average values.

SH release experiment

The dry sample (0.20 g) was immersed in 300 mL of distilled water in a beaker at 25°C. The solution (5.00 mL) was transferred from the beaker to a 10-mL test tube at each fixed time interval. The test solution was oxidated at 100°C by the addition of 5.0 mL of a $K_2Cr_2O_7$ solution [$C(1/6K_2Cr_2O_7) = 0.8M$] and 15 mL of concentrated H_2SO_4 [eq. (2)]. The residual $K_2Cr_2O_7$ solution was titrated with a $(NH_4)_2Fe(SO_4)_2$ solution [0.1*M*; eq. (3)]. The release of SH was expressed as

the carbon content [C (mg/5 mL)] in the solution [eq. (4)]:

$$2\,K_2Cr_2O_7 + 3\,C + 8\,H_2SO_4 \longrightarrow 2\,K_2SO_4 + 2\,Cr_2(SO_4)_3 \\ + 3\,CO_2 + 8\,H_2O \quad (2)$$

$$K_2Cr_2O_7 + 7\,H_2SO_4 + 6\,FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 \\ + 3\,Fe_2(SO_4)_3 + 7\,H_2O \quad (3)$$

$$C(mg/5\,mL) = 3C_{Fe2+}(V_0 - V_1) \quad (4)$$

where C_{Fe2+} is the Fe^{2+} concentration of the $(NH_4)_2Fe(SO_4)_2$ solution (M), V_0 is the volume of the $(NH_4)_2Fe(SO_4)_2$ solution used to titrate $K_2Cr_2O_7$ in a blank solution (mL), and V_1 is the volume of the $(NH_4)_2Fe(SO_4)_2$ solution used to titrate the residual $K_2Cr_2O_7$ in a test solution.

Water retention of the superabsorbent composite in soil

An equal amount of soil (300 g) was placed in a cup, and various weight percentages of the superabsorbent composite (weight ratio of the superabsorbent composite to the soil) were thoroughly mixed with the soil in the cup. Then, 60 mL of lap water was added to the cup at room temperature, and the weight of the cup was measured at various times.

Characterization

The IR spectra of the superabsorbent composite were recorded with Fourier transform infrared (Nexus, Thermo Nicolet, Madison, WI) with KBr pellets, and the spectra were recorded from 500 to 4000 cm^{-1}. Thermal stability studies of the dry samples were performed on a PerkinElmer TGA-7 thermogravimetric analyzer (Shelton, CT) in a temperature range of 25–800°C at a heating rate of 10°C/min with a dry nitrogen purge at a flow rate of 50 mL/min. The morphology of the dried samples was examined with a JSM-5600LV scanning electron microscopy (SEM) instrument (JEOL, Ltd., Tokyo, Japan) after the coating of the sample with gold film.

RESULTS AND DISCUSSION

Effect of the crosslinker content

The crosslinking density is an extremely important swelling-control element. Relatively small changes in the crosslinking density can play a major role in modifying the properties of superabsorbent polymers. The effect of the crosslinker content on the water absorbency is shown in Figure 1. When the crosslinker concentration was lower than 0.15 wt %, the absorbency of the superabsorbent composite decreased because
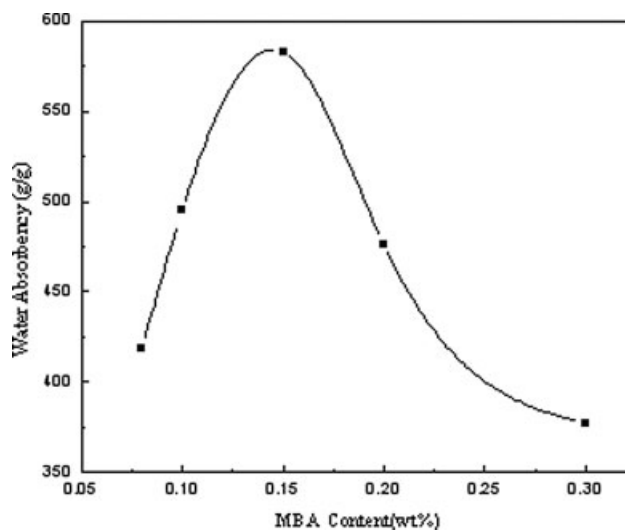

Figure 1 Effect of the crosslinker content on the water absorbency of the superabsorbent composite in distilled water [reaction temperature = 70°C; neutralization degree of AA = 60%; initiator/SH/APT weight ratio (%) in the feed = 1.0/20/20].

of an increase in soluble material. On the other hand, the water absorbency decreased with an increase in the crosslinker concentration from 0.15 to 0.30 wt %. A higher crosslinker concentration resulted in the generation of more crosslink points, which in turn caused the formation of an additional network and reduced the space left for water to enter. The results were in agreement with Flory's network theory,[18] and similar observations have been made in the preparation of acrylate-based superabsorbent systems.[19,20]

Effect of the initiator content

Figure 2 shows the effect of the initiator concentration on the water absorbency. The water absorbency increased as the APS concentration rose from 0.5 to 1.0 wt % and decreased with a further increase in the concentration of APS. The molecular weight in free-radical polymerization decreases with an increase in the initiator concentration.[21] With a reduction of the molecular weight, the relative amount of polymer chain ends increases. As mentioned in a previous study,[22] the polymer chain ends do not contribute to the water absorbency. Therefore, this was responsible for the decrease in the water absorbency with an increase in the initiator content. However, a further decrease in the APS concentration below the optimum values was accompanied by a decrease in the absorbency. This result could be attributed to a decrease in the number of radicals produced as the concentration of APS decreased. The network could not be formed efficiently with a small number of radicals in the free-radical polymerization, and this resulted in the decrease in the water absorbency.
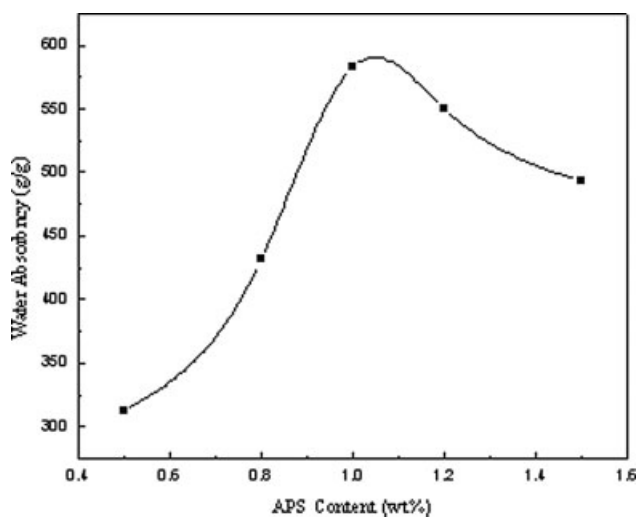
Figure 2 Effect of the initiator content on the water absorbency of the superabsorbent composite in distilled water [reaction temperature = 70°C; neutralization degree of AA = 60%; crosslinker/SH/APT weight ratio (%) in the feed = 0.15/20/20].

Effect of the SH content

The effect of the amount of SH on the water absorbency is shown in Figure 3. The water absorbency sharply increased with an increasing amount of SH in a weight range of 5–20% in the feed. When the concentration of SH in the feed was greater than 20%, the water absorbency decreased with an increase in the amount of SH. There were two main possibilities that could account for the effects of SH in the composite.[23] On the one hand, there was a lot of Na^+ in the SH particles, and the introduction of SH into the PAA polymer increased the concentration of charges of the composite network. When PAA/SH was swelling in water, the additional Na^+ increased the osmotic pressure difference between the superabsorbent composite and the external aqueous solution, and this resulted in a increase in the water absorbency. On the other hand, SH is composed of multifunctional aliphatic and aromatic components and so contains large numbers of functional hydrophilic groups (e.g., $-COO^-$, $-OH$, and $-SO_3^{2-}$).[17] The reactive groups on SH can interact with PAA through some uncertain reaction.[23] Therefore, the structure of the network was improved, and in turn the water absorbency increased. When the SH concentration was less than 20%, nearly all SH acted as a reactant but not as a filler. This may have been responsible for the water-absorbency increase with an increase in the SH concentration in the range of 0–20%. However, a further increase in the SH concentration above the optimum value (20%) was accompanied by a decrease in the absorbency. This result could be attributed to a decrease in the number of elastic PAA chains in the unit of volume of the network.

Effect of APT

The effect of the amount of APT in the superabsorbent composite on the water absorbency is shown in Table I. The water absorbency decreased with an increase in the APT concentration. As described in our previous study,[11,12] the inorganic APT mineral particle in the network acted as an additional network point. The crosslinking density of the superabsorbent composite increased with an increase in the APT content, and this resulted in a decrease in the water absorbency. Table I also shows that the superabsorbent composite had a high water-absorbing capacity of 583 g/g in distilled water, even when the composite had a high APT concentration of 20 wt % and an SH concentration of 20 wt %. This could significantly reduce the production cost.

IR spectra

The IR spectra of APT, SH, PAA, and the PAA/APT/SH superabsorbent composite are shown in Figure 4. The absorption peaks at 3621 and 3549 cm^{-1}, attributed to the $-OH$ groups on APT [Fig. 4(a)], disappeared after the reaction [Fig. 4(d)]; this provided evidence of a graft polymerization reaction between $-OH$ groups on the APT and AA monomer.[12] The absorption peaks at 1608 cm^{-1}, attributed to the $-COO^-$ asymmetric stretching of SH [Fig. 4(b)], nearly disappeared after the reaction [Fig. 4(d)]; this suggested that some uncertain reactions between $-COO^-$ groups on the SH and AA monomer took place during the polymerization process.[23] The absorption peaks at 1452 cm^{-1}, which appeared in the IR spectra of SH and the superabsorb-
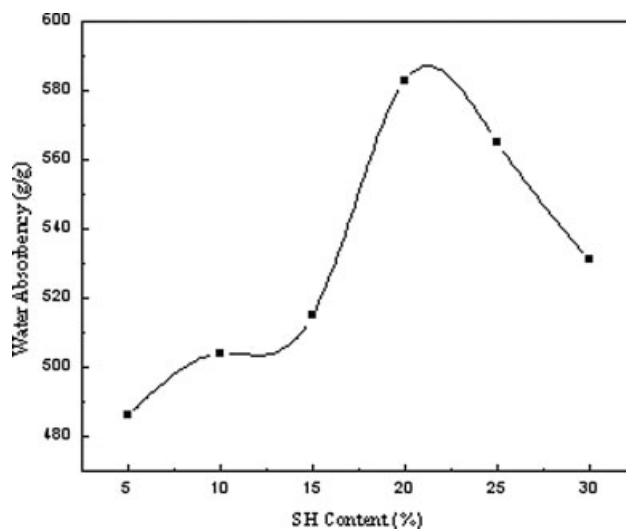

Figure 3 Effect of the SH content on the water absorbency of the superabsorbent composite in distilled water [reaction temperature = 70°C; neutralization degree of AA = 60%; initiator/crosslinker/APT weight ratio (%) in the feed = 1.0/0.15/20].

TABLE I
Effect of the Amount of APT on the Water Absorbency of the Superabsorbent Composites

| Sample | APT (wt %) | Q_{H_2O} (g/g) | |
		Distilled water	0.9 wt % NaCl
PAS$_1$	5	1817	100
PAS$_2$	10	845	82
PAS$_3$	15	676	67
PAS$_4$	20	583	63
PAS$_5$	25	404	45
PAS$_6$	30	378	36

Reaction conditions: reaction temperature = 70°C; neutralization degree = 60%; crosslinker/initiator/SH weight ratio (%) in the feed = 0.15/1.0/20.

ent composite, were attributed to the aromatic C=C stretching of SH. The bands near 1407 and 1174 cm^{-1} [Fig. 4(c,d)], which were absent in the spectra of SH and APT, were attributed to the characteristic groups of PAA. The IR analysis results showed that the reaction between both APT and SH with the AA monomer took place during the polymerization process, and the resulting product was a composite based on PAA incorporating SH and APT. The IR data of SH, APT, PAA, and the superabsorbent composite are presented Table II.

Thermal analysis

The thermogravimetric analysis (TGA) of crosslinked PAA and PAS$_4$ is shown in Figure 5(a,b), respectively.

Both crosslinked PAA and PAS$_4$ showed a very small weight loss below 100°C, which implied a loss of moisture. The major weight loss of crosslinked PAA started at 420°C (51.4%), whereas PAS$_4$ had a major weight loss starting at 432°C (70.8%). Therefore, crosslinked PAA and PAS$_4$ had initial decomposition temperatures of 420 and 432°C, respectively. The results also indicated that the introduction of APT to the polymer network resulted in an increase in the thermal stability.

Water-retention test

It is important to know the water retention of a superabsorbent for practical applications. The water retention of the swollen superabsorbent composite was determined with a heating oven test.[11] Figure 6 shows the water-retention capacities of the swollen superabsorbent composites (25 g, 20 wt % APT, and different SH concentrations) at 60°C. The three swollen samples showed a decreasing tendency of the water retention with increasing time. All the absorbed water of the three samples was lost within approximately 6, 7, and 8.5 h at 60°C, respectively. In addition, the sample with 20 wt % SH showed better water-retention ability than the other two samples. The result also indicated that the best water retention of the superabsorbent composite could be achieved when the composite consisted of 20 wt % SH prepared with the same APT concentration. This result was in good agreement with our water-absorbency observations.
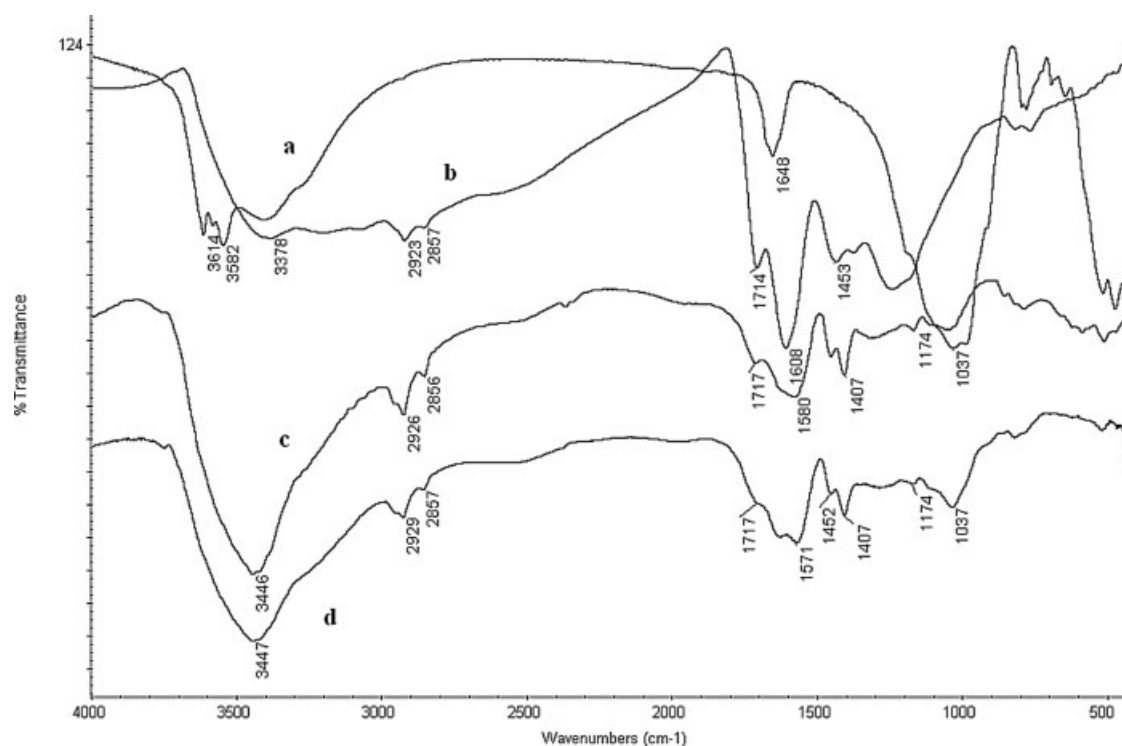

Figure 4 IR spectra of (a) APT, (b) SH, (c) PAA, and (d) PAA/APT/SH.

TABLE II
IR Spectra of SH, APT, PAA, and the Superabsorbent Composite (cm^{-1})

Group	SH	APT	PAA	PAA/APT/SH
—OH	3378	3614, 3582	3446, 1407	3447, 1407
—C—H	2923, 2857	—	2926, 2856	2929, 2857
—C=O	1714	—	1717	1717
—COO$^-$	1608	—	1580	1571
—C=C	1453	—	—	1452
—Si—O	—	1037	—	1037

Swelling rate

The swelling rates of the superabsorbent composites were determined, and the results are shown in Figure 7. The swelling rates of all three samples were high in 0–10 min; after 30 min, the swelling rates became low; and the maximum swelling capacities of all three samples were reached within approximately 90–120 min. Moreover, the sample containing 20 wt % SH showed a better initial swelling rate than the other two samples. According to a previous study,[24] the initial swelling rate is controlled by the diffusion process of water that has penetrated the inside of gels. In a relatively low SH concentration range (10–20%), the crosslinking density of the superabsorbent composite network could be improved and became looser with an increasing SH concentration; this was easy for water to penetrate. Therefore, the initial swelling rate increased with increasing SH concentration. However, further increasing the SH concentration resulted in a decrease in the number of elastic PAA chains in a unit of volume of the network. Therefore, the initial swelling rate decreased with increasing SH concentration in a high SH concentration range (20–30%).
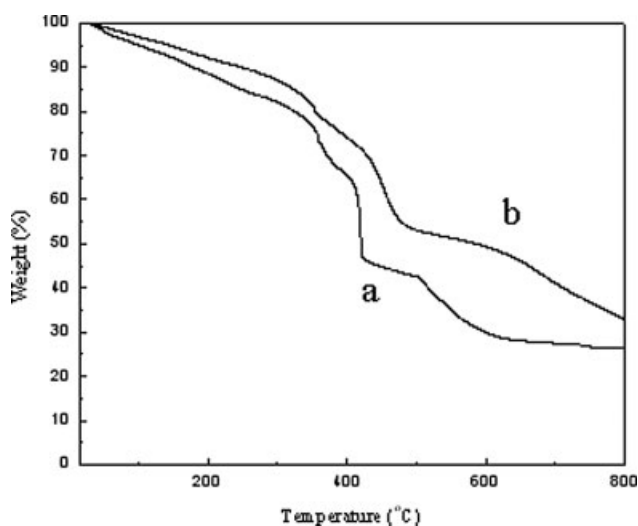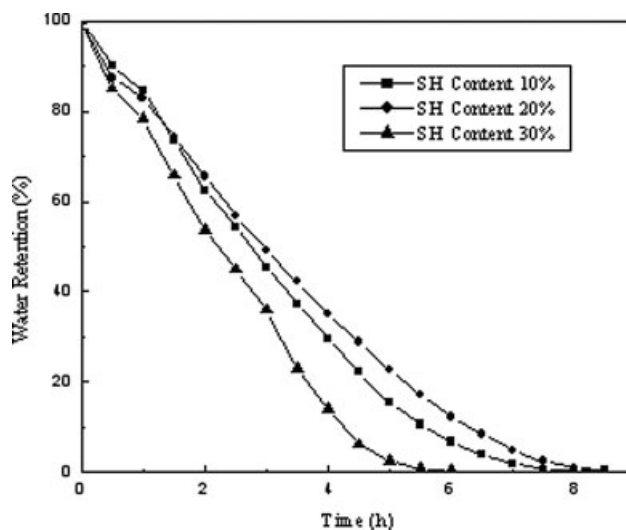

Figure 6 Water retention of the swollen samples as a function of time at 60°C.

Test for SH slow release

There is an interesting phenomenon: some SH can be slowly released from the network when the superabsorbent composite is swelling in water. Photographs of the superabsorbent composite (sample PAS$_4$) immersed in water are presented in Figure 8. The external aqueous solution became brown when the superabsorbent composite was swelling. In addition, the water solution became more and more opaque with increasing swelling time. This indicated that SH could be slowly released from the sample. To investigate the slow-release character of SH from the superabsorbent composite, we tested the measurement of the carbon content of the water solution. Figure 9
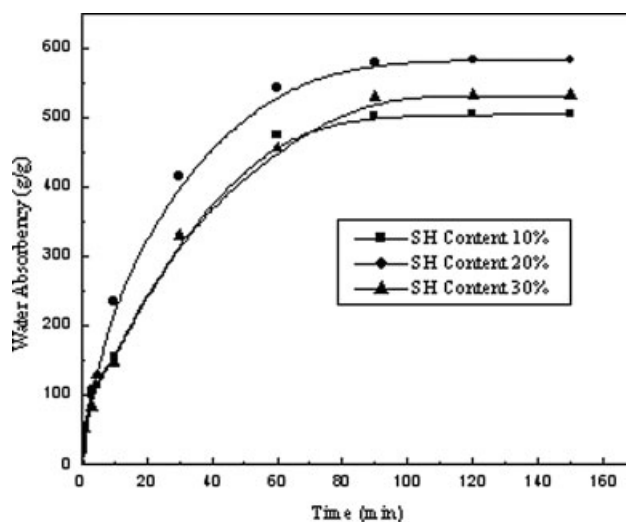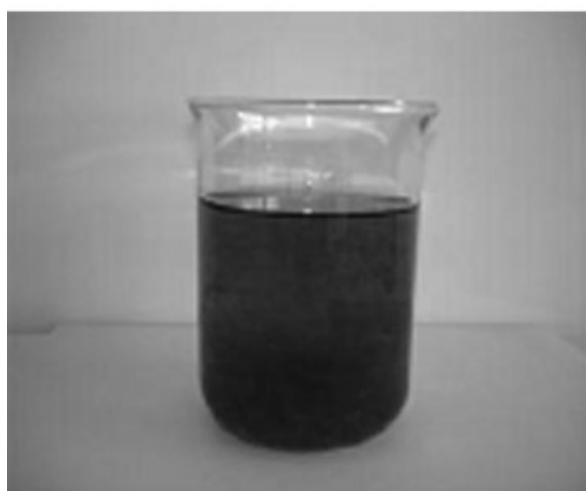

Figure 5 TGA curves of (a) crosslinked PAA and (b) PAS$_4$.

Figure 7 Water absorbency of the superabsorbent composites as a function of time.

(a)

(b)

(c)

Figure 8 Photographs of the superabsorbent composite (PAS$_4$) swelling in water: (a) 1, (b) 10, and (c) 30 days.

shows the variation of the carbon content of water solutions as a function of the swelling time. The carbon content increased with increasing swelling time.

When the swelling time reached approximately 50 days, the carbon content did not increase obviously with further increasing swelling time, and this indicated that the release of SH from the superabsorbent composite had reached equilibrium. The slow release of SH may have been due to the fact that SH could partially dissolve in the water. When the superabsorbent composite swelled in water, the soluble part of SH dissolved into water from the superabsorbent composite network. The encapsulated part of SH in the superabsorbent composite network was released quickly, and then a relatively quick increase in the carbon content was seen in the beginning (<30 days). When this process ended, the soluble part of SH that chemically bonded to the PAA chains was also slowly released from the network of the superabsorbent composite and exhibited a slow increase in the carbon content in the following 20 days, and the release equilibrium was reached in approximately 50 days. This observation indicated that the superabsorbent composite was endowed with an additional slow-release property of fertilizers by the introduction of SH into the superabsorbent composite system.

After swelling for 60 days, the swollen sample was then separated from unabsorbed water by screening and dried at 70°C to a constant weight. The SEM image of the resulting dried sample is shown in Figure 10(b). This can be compared with the micrographs of the sample before the SH release test [Fig. 10(a)]. In the SEM image of the sample before the SH release test, the surface is smooth and nonporous. In the SEM image of the sample after the SH release test, the sample appears microporous. This result also indicated that the release of SH from the network led a change in the morphology of the superabsorbent composite.
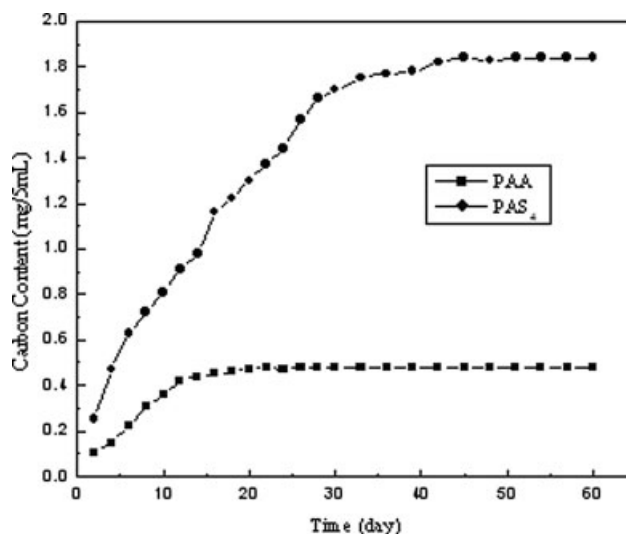

Figure 9 Variation of the carbon content in water solutions as a function of the swelling time.

Water retention of the superabsorbent composite in soil

Some of the most important applications of superabsorbent polymers involve agriculture and horticulture, especially in arid regions and desert. In this investigation, a test of the water retention of the superabsorbent composite in soil was carried out. Figure 11 shows the variation of the weight of water in soil with and without the superabsorbent composite as a function of time. The loss of water for the untreated soil (control) and all treated soil samples increased with increasing time. In the first several days, the difference in the water loss for the control and all treated soil samples was not obvious. After 5 days of testing, the water loss for all treated soil samples was obviously lower than that of the control. Also, the water loss decreased with an increase in the superabsorbent composite content for all treated soil samples at a given time. After 30 days of testing, all the absorbed water in the control was com-
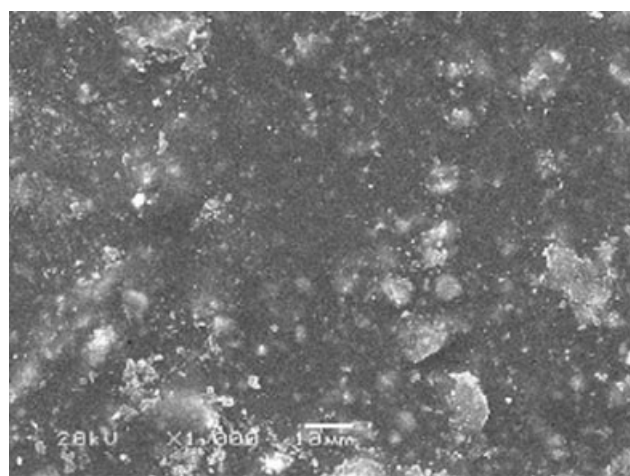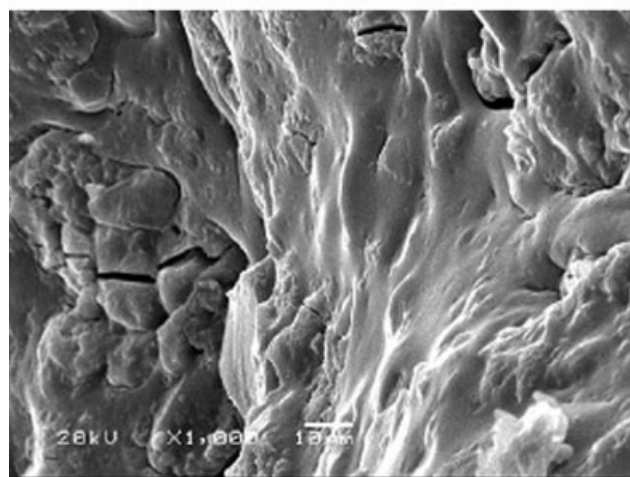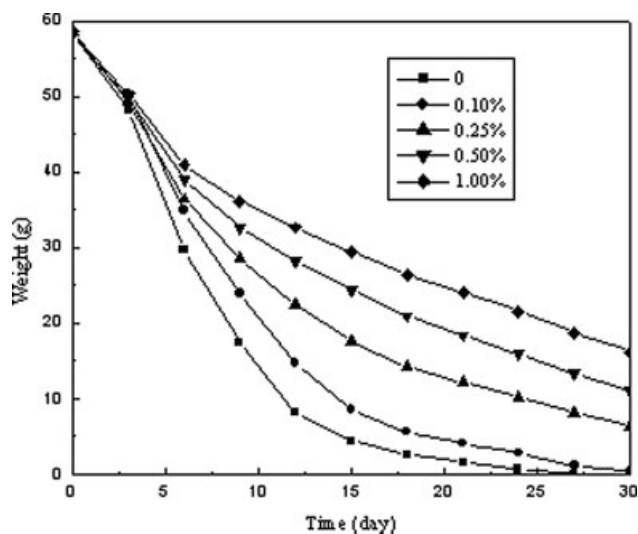

Figure 11 Variation of the weight of water in soil with and without the superabsorbent composite as a function of time.

pletely lost, whereas approximately 0.5, 10.5, 18.4, and 27.0% of the initially absorbed water was kept by the treated soils with superabsorbent composite concentrations of 0.10, 0.25, 0.50, and 1.00%, respectively. Clearly, the water retention of the soil was enhanced with the superabsorbent composite under the same conditions, especially when the superabsorbent composite concentration was higher than 0.10%.

CONCLUSIONS

Novel superabsorbent composites of crosslinked PAA/APT/SH were prepared through the graft copolymerization reaction of AA on APT micropowder and SH with MBA as a crosslinker and APS as an initiator in an aqueous solution. A PAA/APT/SH superabsorbent composite with a water absorbency of 583 g of H_2O/g was acquired with a composition of 0.15% crosslinker, 1.0% initiator, 20% APT, and 20% SH. SH was slowly released from the network when the superabsorbent composite was swelling in water. This observation indicated that the superabsorbent composite was endowed with an additional slow-release property of fertilizers by the introduction of SH into the superabsorbent composite system. A test of the superabsorbent composite for water retention in soil was also carried out with and without the superabsorbent composite. The results obtained from this investigation showed that the water retention of soil was enhanced by the superabsorbent composite, and more than 27% water was held in comparison with the control under the same conditions after 30 days of water-retention testing. This novel superabsorbent composite could be used as a functional

Figure 10 SEM micrographs of PAS$_4$ (a) before the SH release test and (b) after the SH release test.

water-management material for agriculture and horti-culture in desert and drought-prone areas.

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