

Synthesis of Poly(acrylic acid)/Sodium Humate Superabsorbent Composite for Agricultural Use

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ABSTRACT: A novel poly (acrylic acid)/sodium humate superabsorbent composite was synthesized by graft copolymerization reaction of acrylic acid (AA) on sodium humate micropowder using *N,N'*-methylenebisacrylamide (MBA) as a crosslinker and potassium peroxydisulfate (KPS) as an initiator in aqueous solution. The effects on water absorbency of factors such as reaction temperature, initial monomer concentration, and degree of neutralization of AA, amount of crosslinker, initiator, and sodium humate were investigated. The superabsorbent composite was characterized by scanning electron microscopy, and the graft copolymerization reaction of AA on sodium humate micropowder was characterized by IR spectroscopy. Results obtained from

this study show that the water absorbency of the superabsorbent composite synthesized under optimal conditions for synthesis with a sodium humate content of 5.3% exhibited absorption of 684 g H₂O/g sample in distilled water. Water-retention in soil is enhanced by the use of the superabsorbent composite. The effect of superabsorbent composite on the growth of corn is reported. The superabsorbent composite may be of use as water management materials for agriculture purposes in desert and drought-prone areas. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5137–5143, 2006

Key words: acrylic acid; sodium humate; superabsorbent composite; water absorbency; water retention

INTRODUCTION

Superabsorbents polymers (SAPs) 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, SAPs have great advantages over traditional water-absorbing materials such as cotton, pulp, and sponge.^{1–3} Because of their excellent characteristics, SAPs are widely used in many fields, such as agriculture,^{4,5} sanitary goods,⁶ sealing composites,⁷ and medicine for drug-delivery systems.^{8,9} Tests of SAPs for agriculture and horticulture applications have shown encouraging results because they have been observed to help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in the soil, and increase plant growth rates.¹⁰ But the quality and price of these products still leave a lot to be desired.¹¹ The synthesis of superabsorbent composites, because of their relatively low production cost and high water absorb-

ency, has been investigated by various workers. Wu et al.^{12,13} prepared starch-g-polyacrylamide/clay and poly (acrylic acid)/mica superabsorbent composites by graft copolymerization reaction of AA and clay mineral powder. An et al.¹⁴ prepared poly (AA)/attapulgit superabsorbent composite by graft copolymerization reaction of AA and attapulgit mineral powder.

The authors paid much attention to the nutrition requirement of the plant growth in the soil using SAPs as water retention agent in agriculture. In this direction we have done some work on the synthesis of superabsorbent composites that have been tried for the growth of plants and reported the results in the literature.^{15,16}

Humic acid contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units, and COOH groups variously placed on aromatic rings.¹⁵ It is a nutrient source for plants essentially helps move micronutrients from soil to plants, and improve water retention in the soil.^{17,18} Its benefits for plant growing have been proven both experimentally and in the field.¹⁸ To reduce costs, improve the comprehensive water-absorbing properties, and enhance nutritive functions of the superabsorbent materials for agriculture using, the grafting of AA polymer onto sodium humate (SH) and fabricating a composite that consists of polymer and SH was considered a priority. In the present investiga-

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TABLE I
Typical Recipe for Superabsorbent Composite
and Preparation Conditions^a

MBA/AA (mol/mol)	KPS/AA (mol/mol)	NaOH/AA (mol/mol)	SH/AA (wt %)
0.0005	0.008	0.6	5.3

^a Reaction temperature: 90°C; Neutralization degree: 60% (mol/mol); Initial concentration of AA: 35 (wt %).

tion the authors report the synthesis of superabsorbent composites by graft copolymerization reaction of AA on SH. The composites were characterized by IR spectroscopy and scanning electron microscopy. The effects on water absorbency of such factors as reaction temperature, initial monomer concentration, degree of neutralization of AA, amount of crosslinker, initiator, and SH were investigated. The effect of superabsorbent composites on the water retention capacity of soil was also investigated.

EXPERIMENTAL

Materials

Acrylic acid (AA, chemically pure; Beijing Yili Chemical Factory, Beijing, China) was distilled under reduced pressure before use. Potassium Peroxydisulfate (KPS, analytical grade; Beijing Chemical Factory, Beijing, China) was recrystallized from water. *N,N'*-Methylenebisacrylamide (MBA, chemically pure; Shanghai Chemical Reagent Corp., Shanghai, China) was used as purchased. Sodium humate (SH, chemically pure; Beijing Yili Chemical Factory, Beijing, China) was milled through a 200-mesh screen before use. All solutions were prepared with distilled water.

Preparation of superabsorbent composites

The reactions were conducted in a flask equipped with a mechanical stirrer, condenser, and nitrogen line. Weighed quantity of AA was dissolved in distilled water and then neutralized with sodium hydroxide solution (30 wt %). SH powder was dispersed in this partially neutralized monomer solution. The crosslinker MBA was added to the AA-SH mixture, and the reaction medium was deaerated with nitrogen while stirring for 10 min. The water bath was then heated slowly with vigorous stirring after the radical initiator KPS was charged to the reaction mixture. After 5 h of reaction, the resulting product was washed several times with distilled water and then dried in a vacuum oven at 50°C to a constant weight. The superabsorbent composite was prepared after the dried product was milled and

screened. All samples used had a particle size in the range of 40–60 mesh. Typical recipe of superabsorbent composite and the preparation conditions were given in Table I.

Preparation of poly(acrylic acid)

The preparation procedure of poly (AA) [PAA] was similar to that of preparation of superabsorbent composite except without SH.

Water-absorbency measurement

A weighted quantity of 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 (g H₂O/g sample) of the superabsorbent composite was determined by weighing the swelled samples, and the Q (g H₂O/g sample) of the samples was calculated using the following equation:^{15,16}

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

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

IR spectra

The IR spectra of the samples were recorded on a Bio-Red WIN FTIR using KBr pellets. They show peaks corresponding to the functional groups attached to the monomer units. The infrared spectrum of superabsorbent composite (PAA/SH) is shown in Figure 1(a). This can be compared to the spectra of

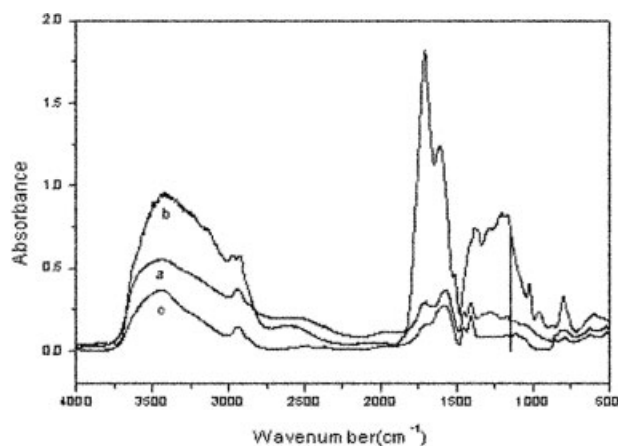


Figure 1 Infrared spectra of (a) PAA/SH, (b) SH, and (c) PAA.

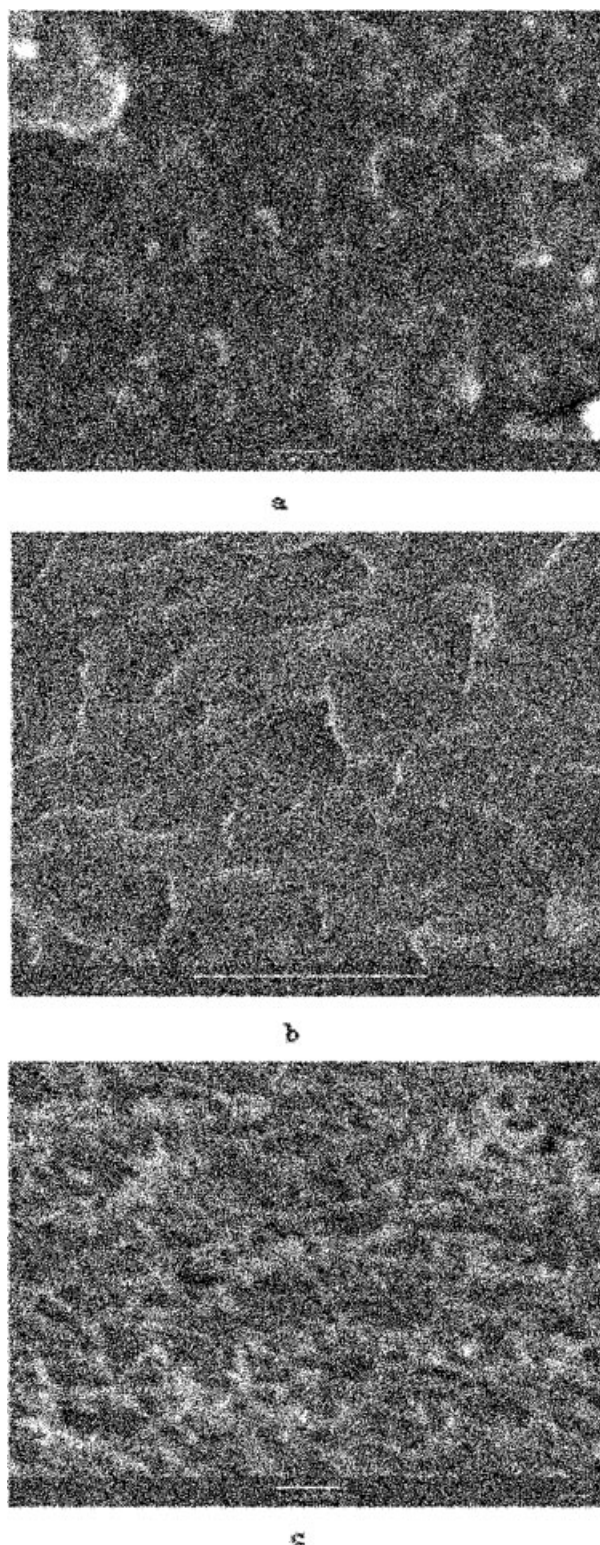


Figure 2 Micrograph of (a) SH, (b) PAA, and (c) PAA/SH.

SH and PAA shown in Figure 1(b,c), respectively. The characteristic peak observed at 1280 cm^{-1} corresponding to alkylether, which provides evidence of a graft polymerization reaction between PAA and SH.

SEM observations

The characteristics of surface morphology are very significant on water absorbency. The morphology of the samples was examined using an AMRAY-1820 SEM instrument after coating the sample with gold film. The micrographs of SH, PAA, and PAA/SH are shown in Figure 2(a–c), respectively. The SEM micrograph of SH, which has no absorbency, is shown to be nonporous [Fig. 2(a)], whereas the SEM micrographs of PAA and PAA/SH, which have good water absorbency, show the samples to be microporous. In addition, PAA/SH has a greater absorbency and shows a fine rugged network structure and has a higher specific surface area [Fig. 2(c)], whereas PAA has a broad network structure [Fig. 2(b)]. These observations are in good agreement with our water-absorbency observations.

RESULTS AND DISCUSSION

Effect of reaction temperature

Figure 3 shows that the water absorbency of the superabsorbent composite increases as the reaction temperature increases from 60 to 90°C and decreases with further increases in reaction temperature. If the temperature is too low, the three-dimensional network of the copolymers cannot form, resulting in the decrease of water absorbency.¹⁰ If the temperature is too high ($> 90^\circ\text{C}$), reaction rate will be unusually fast. A great quantity of polymerization heat generates during the process and exploding polymerization may occur,^{10,19} so the molecular weight decreases and the water absorbency also decreases.

Effect of initiator

Figure 4 shows the effect of the initiator concentration (KPS/AA, molar ratio of KPS to AA) on water

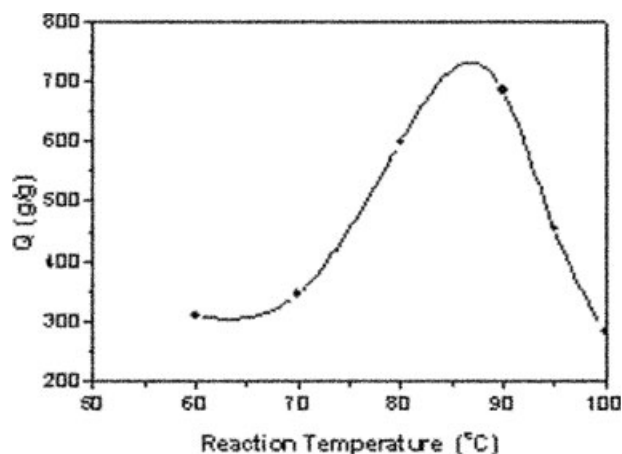


Figure 3 Effect of reaction temperature on Q of superabsorbent composite in distilled water: C_o , 35 wt %; MBA/AA (mol/mol), 0.0005; KPS/AA (mol/mol), 0.008; NaOH/AA (mol/mol), 60%; weight ratio of SH, 5.3 wt %.

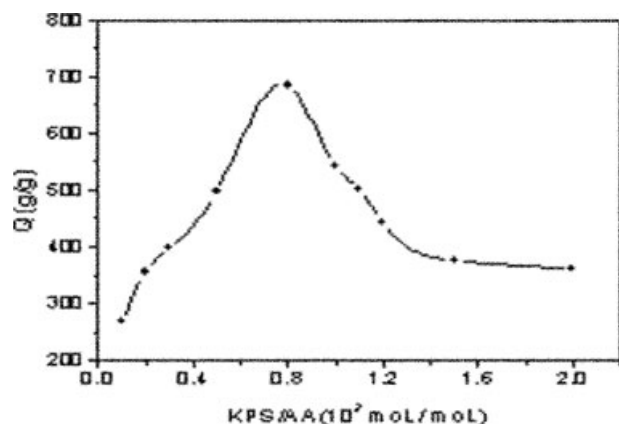


Figure 4 Effect of KPS/AA on Q of superabsorbent composite in distilled water: reaction temperature, 90°C ; C_0 , 35 wt %; MBA/AA (mol/mol), 0.0005; NaOH/AA (mol/mol), 60%; weight ratio of SH, 5.3 wt %.

absorbency. The water absorbency increases as KPS/AA increases from 0.001 to 0.008 and decreases with further increases in the content of KPS. The composite synthesized by 0.008 (KPS/AA, molar ratio of MBA to AA) has the highest water absorbency. On the basis of general kinetics,¹⁹ the rate of polymerization depends on the concentration of monomers and initiators for a bimolecular termination. The persulphate ions ($\text{S}_2\text{O}_8^{2-}$) in aqueous solution, when heated alone or in the presence of a reducing agent, decompose to sulfate radical ions ($\text{SO}_4^{\cdot-}$). These primary radicals will initiate the monomers to form free radicals, which propagate monomer molecules in succession to form a large polymeric radical and a dead polymer in the termination step. The rate of polymerization at a low concentration of persulphate ions, that is, a low quantity of free radicals so produced, is slower than that at a high concentration. At a high concentration of persulphate ions, high quantities of produced free radicals may cause a chain transfer to polymers,¹⁹ so the synthesized superabsorbent composite has a high crosslink density, which affects the water absorbency capacity. The relation between the average kinetic chain length (ν) and concentration of the initiator in free-radical polymerization is given by the following equation:^{11,14}

$$\nu = \frac{1}{2} k_p (fk_i k_t)^{1/2} [I]^{-1/2} [M] \quad (2)$$

where k_p , k_i , and k_t are the rate constants for propagation, initiation, and termination, respectively; f , the efficiency of initiation by the initiator; and $[I]$ and $[M]$, the initial concentration of the initiator and monomer, respectively. The molecular weight in free-radical polymerization will decrease with increase of the initiator concentration according to eq. (2). With

the decrease of the molecular weight, the relative amount of polymer chain ends increases. As reported in a previous study,²⁰ 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 KPS 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 KPS 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 crosslinker

The effect of crosslinker concentration (MBA/AA, molar ratio of MBA to AA) on water absorbency is shown in Figure 5. The water absorbency increases with the increase of crosslinker content from 0.01×10^{-2} to 0.05×10^{-2} (mol/mol). When the crosslinker content is $< 0.05 \times 10^{-2}$ mol/mol, 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 theory²¹ and similar observations were previously reported by others.^{10,14}

Effect of initial monomer concentration

As the initial AA concentration (C_A , wt %) increases, the absorbency of superabsorbent composite increases up to a certain level, but with higher C_A the absorbency of superabsorbent composite decreases

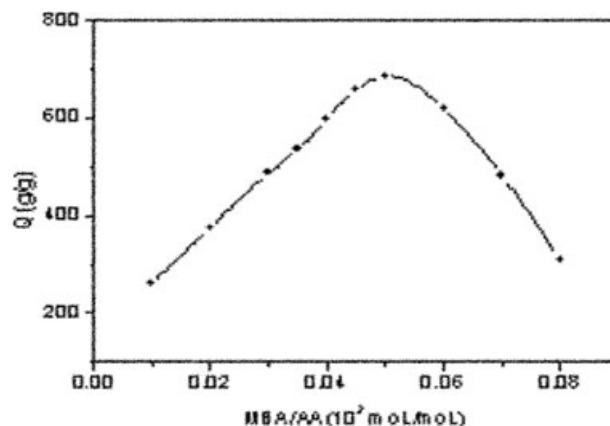


Figure 5 Effect of MBA/AA on Q of superabsorbent composite in distilled water: reaction temperature, 90°C ; C_0 , 35 wt %; KPS/AA (mol/mol), 0.008; NaOH/AA (mol/mol), 60%; weight ratio of SH, 5.3 wt %.

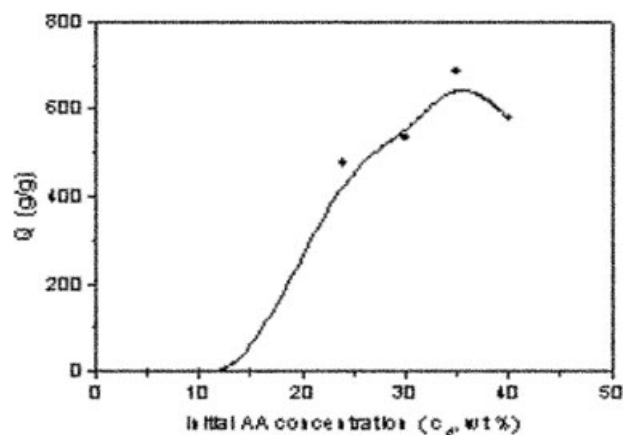


Figure 6 Effect of the concentration of AA on Q of superabsorbent composite in distilled water: reaction temperature, 90°C; MBA/AA (mol/mol), 0.0005; KPS/AA (mol/mol), 0.008; NaOH/AA (mol/mol), 60%; weight ratio of SH, 5.3 wt %.

drastically. The effect of C_A on water absorbency is shown in Figure 6. It can be seen that with the increase of C_A from 24 to 35 wt %, the water absorbency of the superabsorbent composite increases from 476 to 684 g/g, and decreases with further increase in C_A .

It was difficult to obtain a composite gel in the preparation when C_A was less than 24 wt %, for the water absorbency of composite gel was hard to measure exactly because of the excessive water-soluble material. The influence of C_A on the amount of water-soluble material (ω_{sol} , wt %) and the yield of superabsorbent composite is shown in Table II. The average kinetic chain length increases with increase of the monomer concentration according to eq. (2); then, crosslinking efficiency increases, and the ω_{sol} decreases. Furthermore, with the increase of crosslinking network density, water absorbency decreases.²⁰ The similar observations were also reported by others.^{11,14}

Effect of neutralization degree

The effect of neutralization degree (NaOH/AA, molar ratio of NaOH to AA) on the water absorb-

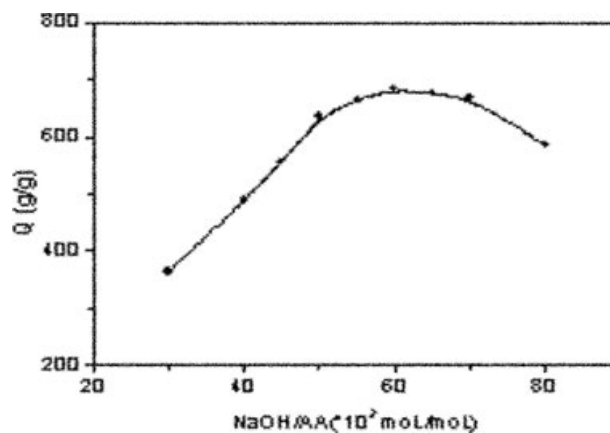


Figure 7 Effect of neutralization degree on Q of superabsorbent composite in distilled water: reaction temperature, 90°C; C_0 , 35 wt %; MBA/AA (mol/mol), 0.0005; KPS/AA (mol/mol), 0.008; weight ratio of SH, 5.3 wt %.

ency is shown in Figure 7. The water absorbency increases from 30 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,²¹ the swelling ability of ionic network is attributed to the rubbery elasticity, ionic osmotic, and affinity of polymer toward water. When poly (AA) 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, and 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.^{13,14,18}

TABLE II
Influence of C_A on the Amount of Water-Soluble Material (ω_{sol} , wt %) and the Yield of Superabsorbent Composite^a

	C_A (wt %)						
	5	10	15	24	30	35	40
ω_{sol} (wt %)	100	100	100	20.14	14.01	10.68	5.12
Yield (wt %)	0	0	0	78.86	85.99	89.32	94.88

^a Reaction conditions: reaction temperature, 90°C; MBA/AA (mol/mol), 0.0005; KPS/AA (mol/mol), 0.008; NaOH/AA (mol/mol), 60%; weight ratio of HA, 5.3 wt %.

Effect of sodium humate

Humic acids are thought to be complex aromatic macromolecules. The hypothetical structure for humic acid (or sodium humate), shown in Figure 8, contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units, —COOH and —NH₂ groups variously placed on aromatic rings.^{17,18}

The effect of the amount of sodium humate in the superabsorbent composite on the water absorbency

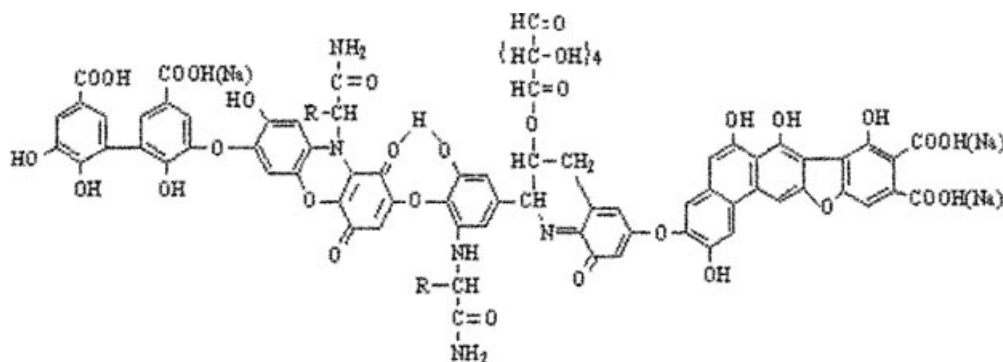


Figure 8 Model structure of humic acid (or sodium humate).

is shown in Figure 9. When a prepared composite contained a small amount of sodium humate (< 5.3%), the water absorbency of the resulting product significantly improved, which may result from the increase in the amount of phenolic hydroxyl and acylamino groups in sodium humate structure in the system. This behavior may be interpreted by postulating that the collaborative absorbent effect of $-\text{CONH}_2$, $-\text{OH}$, and $-\text{COOH}$ or $-\text{COONa}$ groups are superior to that of single $-\text{COOH}$ or $-\text{COONa}$ groups. Similar phenomena were also reported by others^{12,14} as well as by ourselves.^{15,16} However, When the content of sodium humate in superabsorbent composite was > 5.3%, the water absorbency decreased with the further increase in the amount of sodium humate. This may be attributed to the fact that sodium humate contains condensed aromatic rings structures.¹⁷ A greater amount of sodium humate results in the generation of much more density (or stiffness) of the composite and reduces the water absorbency. This behavior obeys the Flory theory,²¹ which states that increasing the density of the network would enhance the elastic forces

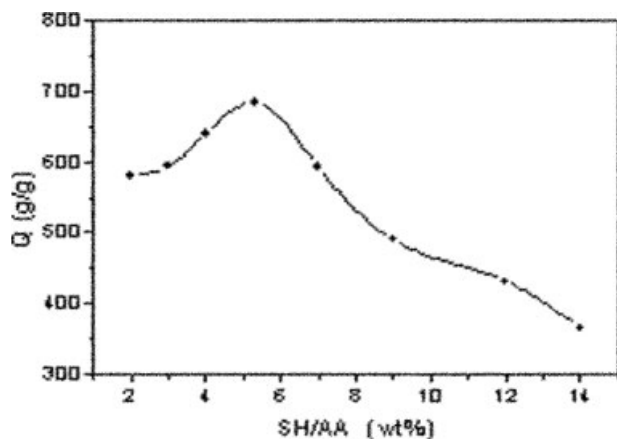


Figure 9 Effect of SH/AA on Q of superabsorbent composite in distilled water: reaction temperature, 90°C ; C_0 , 35 wt %; MBA/AA (mol/mol), 0.0005; KPS/AA (mol/mol), 0.008; NaOH/AA (mol/mol), 60%.

between the segments of the gel, which leads to the retardation of the water diffusion and consequently a decrease in the absorbency.^{21,22}

Water-retention

One of the most important applications of superabsorbent composites is for agricultural and horticultural purposes, especially for effective utilization of water in dry and desert regions and to transform them into "green and fertile lands." In this regard the preliminary testing of these superabsorbents for water retention is carried out by growing the corn seeds into plants with the samples: (A) soil only, (B) soil mixed with 1.0 wt % of PAA, and (C) soil mixed with 1.0 wt % of PAA/SH. Equal amounts of the samples (2 kg) were placed in three plastic pots, respectively. Healthy seeds were placed in each of the three pots together with 500 mL of water. The growth pattern of plants was observed and care was taken to see that no pests and other diseases affected the plants. There was little difference in the growth of the plants in three pots for up to 10 days. However, after 20 days the plant in the pot containing no superabsorbents (A) started wilting, whereas the plants in the pots containing soil with PAA (B) and soil with PAA/SH (C) were fresh. Even after 30 days of growth the plants in the soil with PAA/SH (C) were fresh, whereas the plants in the soil with PAA (B) started wilting. It can be seen that PAA/SH enhanced the water-retention of the soil, and can make the plant grow much more sturdily.

TABLE III
Water-Retention for Soil with 1.0% of PAA/SH, Soil with 1.0% of PAA, and Soil Only^a

	A (soil only)	B (soil with 1.0% PAA)	C (soil with 1.0% PAA/SH)
Water-retention (%)	0.55	17.2	21.8

^a Drying conditions: temperature, 40°C ; time, 7 days, amount of sample, 100 g.

The study of water retention of the superabsorbent composite was also carried out by using the three samples (A), (B), and (C), which were water saturated and dried at 40°C in an oven for 7 days, respectively. Table III shows the water-retention values of these samples. From Table III we can see that soil with 1.0% of PAA/SH (C) and soil with 1.0% of PAA (B) can retain 21.8% and 17.2% of the water after 7 days, respectively, but soil (A) just retains 0.55% of the water.

From the studies, it can be inferred that the presence of PAA/SH in soil can reduce water loss in the process of irrigation, and improve the life span and quality of plants.

CONCLUSIONS

Novel superabsorbent composites were synthesized in an aqueous solution by copolymerization of the AA and SH with MBA as the crosslinking agent and KPS as the initiator. The absorbency of the superabsorbent composites is at a maximum [$Q_{\max} = 684$ g H₂O/g] while having a composition of 0.05% of crosslinker (molar ratio of MBA to AA), 0.8% of initiator (molar ratio of KPS to AA), 5.3 wt % of sodium humate, a neutralization degree of 60%, a initial AA concentration of 35 wt %, and a reaction temperature of 90°C. The use of superabsorbent composite enhanced the water retention of the soil and it can also make plants grow sturdily. The results of the work indicate that PAA/SH will find application in agriculture, especially in drought and desert regions where the availability of water is insufficient.

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