

Preparation of Superabsorbent Based on the Graft Copolymerization of Acrylic Acid and Acrylamide onto Konjac Glucomannan and Its Application in the Water Retention in Soils

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ABSTRACT: A new konjac glucomannan (KGM)-based superabsorbent polymer, KGM-g-poly(acrylic acid-co-acrylamide), was prepared by the free radical grafting solution polymerization of acrylic acid (AA) and acrylamide (AM) monomers onto KGM in the presence of *N,N'*-methylenebisacrylamide as a crosslinker with potassium persulfate as an initiator. The effects of reaction parameters, including the amount of crosslinking agent and initiator, the weight ratio of both (AA + AM) to KGM and AM to (AA + AM), neutralization degree of AA, bath temperature, and reaction time, on the water absorbency of the superabsorbent were investigated. The Fourier transform infrared spec-

troscopy was used to characterize the structures of the copolymer. The maximum water absorbency of the optimized product was 650 g/g for distilled water and 70 g/g for a 0.9 wt % aqueous NaCl solution. Furthermore, the water retention of the copolymer in soils was studied. The effect of the copolymers on the aggregate distribution of soils was also evaluated. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2748–2754, 2012

Key words: konjac glucomannan; graft copolymer; superabsorbent; functionalization of polymers; polysaccharides; water retaining agent in soils

INTRODUCTION

Superabsorbents are new types of functional polymer materials developed a few years ago, which have the ability to absorb considerable amount of water (tens to thousands of times their own weight) in a relatively short time and have good water-retention capacity. Superabsorbents have been widely applied in the field of industry, agriculture, medicine, etc. Moreover, as a kind of high-tech drought-resistant products, superabsorbents play an essential role in arid and semiarid area where they are used as additive in soil and water conservation and water-saving agriculture.

In general, superabsorbents can be divided into two categories: i.e., superabsorbents based on chemical synthetic polymers such as polyacrylic acid resin¹ and those based on natural polymers such as starch,² cellulose,³ chiton,⁴ and so on. However, on the one hand, for traditional superabsorbents based on polyacrylic acid, they are of high cost and sensitive to electrolyte, as well as difficult to degrade. On the other hand, for those based on starch, they do not have good performance in both water-retaining capacity and rate of water absorption. As a result, researching and developing novel superabsorbents with good water retention, good degradability and low cost are very important and attract much interest of many researchers.

As it is well known, konjac glucomannan (KGM), a more abundant neutral polysaccharide, is the main component of the tuber of *Amorphophallus konjac* C. Koch. It consists of β -1,4-linked D-mannose and D-glucose in an approximate ratio of 2 : 3. Because the hydrosol of KGM has a high viscosity and a variety of features, such as thickening, gelling, and filming properties, KGM has broad applications in medicine, textiles, petroleum, chemical, food, and other fields. The study of KGM and its modified products has become a hot spot and is of much interest for a large number of researchers, including our group.^{5–8}

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As far as the Konjac-based raw materials are concerned, its water absorption is far superior to starch-based polysaccharides. Thus a kind of new 'green' superabsorbents would be obtained by grafting water-soluble monomer onto KGM. Li et al.⁹ reported the preparation of graft polymers of KGM with acrylic acid (AA) via frontal polymerization. But they used only one monomer, AA, as grafting monomer and had not investigated its application as the superabsorbents. However, the superabsorbent containing polyacrylic acid showed poor resistance against salt. In our early work,¹⁰ we carried out the graft copolymerization of acrylamide (AM) onto KGM via inverse emulsion polymerization and focused on the synthesis conditions for obtaining a new thickener in text printing. Till now, there appeared no report on the graft copolymerization of KGM with both AA and AM to get superabsorbents. In this article, we attempt to use both AA as ionic comonomer and AM as nonionic comonomer, to get a good superabsorbent with also good salt resistance. In addition, to reduce the cost of the preparation, we select potassium persulfate as a cheap initiator instead of the traditional expensive initiator such as ammonium cerous nitrate in the graft polymerization. Furthermore, we deal with the investigation on both the water retention of the copolymers in soils and the influence of the copolymers on the aggregate distribution of soils.

EXPERIMENTAL

Materials

KGM, supplied by Hubei Hongye Konjac Co. (Enshi, China), was purified with ethanol and then dried under reduced pressure until it reached a constant weight. AA, chemically pure, was refined by distillation under reduced pressure. AM, *N,N'*-methylenebisacrylamide (MBAM), potassium persulfate, etc., are chemically pure and used directly without any treatment.

Synthesis of superabsorbents

Three grams of KGM and 200 mL of distilled water were put into a three-necked flask and stirred 1 h at 40°C under an atmosphere of N₂. A predetermined amount of K₂S₂O₈ solution was added into the vessel to allow the KGM to be preoxidized for a short time, and then, MBAM as the crosslinker, and AA (neutralized to a certain degree with NaOH) as the monomer, and AM as the comonomer, were added. The reactants were allowed to react for a certain time at a certain temperature under N₂. The crude products were precipitated with ethanol, filtered, and dried to a constant weight at 60°C in a vacuum.

FTIR test

The FTIR spectra of the samples were obtained with a Fourier transform infrared spectrometer of Avater

370 of Thermo Nicolet (Madison, WI) using KBr disc method. The sample of the graft copolymer was purified at first by extraction with a mixture of glycol and glacial acetic acid (volume ratio = 6 : 4) in a Soxhlet extractor for 30 h to remove the homopolymers if present. The extracted product was washed with alcohol, and dried *in vacuo* for 24 h, and then used as a sample for FTIR. It was found that the spectrum obtained was the same as without the above treatment.

Water absorbency of superabsorbents

The water absorbency of the products was measured by a tea bag method¹¹ described as follows: The dried products were put into a tea bag (100 mesh) made of nonwoven fabric. Then they were soaked in excess distilled water for 12 h. After that the water unabsorbed into gels was removed by putting the tea bag in air for a short time. Then water on the surface of the gels and the tea bag was immediately wiped with filter paper, and the weight (m_2) of the tea bag containing the gels was measured. The water absorption of the copolymers was calculated using following equation:

$$Q = \frac{m_2 - m_1 - m_0}{m_0}$$

where m_2 , m_1 , and m_0 were the weight of the wet tea bag containing the gels, the tea bag, and the dried products, respectively. The saline absorbency of the superabsorbents was determined according to the above methods except that 0.9% NaCl solution was used to replace distilled water, which was denoted as $Q_{0.9\% \text{ NaCl}}$.

Water retentivity of the superabsorbents in soils

The soil sample was air-dried loess, collected from Enshi, China, and its water content was 7.0%. Different amounts of superabsorbents (0_{wtr}, 0.1_{wtr} %, and 0.3_{wtr} % of superabsorbent based on soils) were mixed with the soils separately and put into different plastic basins. Then an equal amount of distilled water was added according to the water content in the field. The loss weight of evaporated water was measured under natural conditions until the evaporating weight was less than 1.0 g/day.

Determination of soil aggregates

After different amounts of superabsorbents were added to the air-dried soil separately, the content of soil aggregates was determined by Yoder's wet-sieving method.¹² A set of sieves with apertures of 5.0, 2.0, 1.0, 0.5, and 0.25 mm were vibrated in water for 30 min at the speed of 30 times/min. Then different

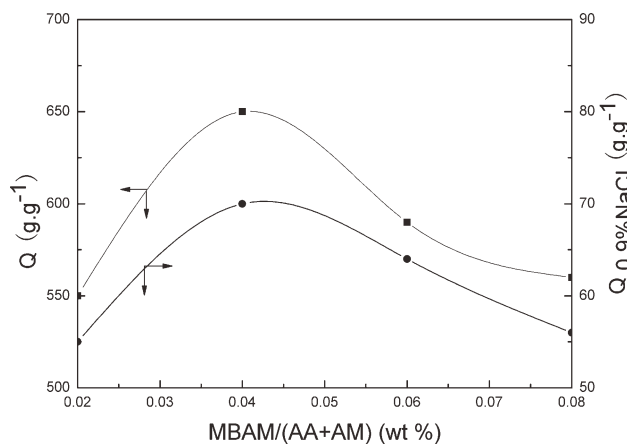


Figure 1 Effect of amount of crosslinking agent on the water absorbency of superabsorbents [0.5% $K_2S_2O_8$ /(AA + AM), 7 : 1 (AA + AM)/KGM, 30% AM/(AA + AM), 75% neutralization of AA, 60°C, 3 h].

levels of soil aggregates were collected, dried, and weighed. The content of soil aggregate was calculated according to the following equation:

$$\% \text{Soil aggregate} = \frac{m_1}{m_2} \times 100\%$$

where m_1 and m_2 are the weight of soil aggregates with different levels and that of dried soil samples, respectively. The test was repeated two times.

RESULTS AND DISCUSSION

Effect of amount of crosslinking agent on the water absorbency of superabsorbents

The crosslinking agent used in the graft copolymerization is MBAM, a monomer with two double bonds. Figure 1 shows the influence of the amount of MBAM on the water absorbency of superabsorbent, where the other conditions are fixed. As shown in Figure 1, both Q and $Q_{0.9\% \text{ NaCl}}$ increase with increasing the amount of crosslinking agent, then reach a maximum value, and afterward, decrease. As it is well known, the degree of crosslinking has significant effect on the water absorption capacity of superabsorbent. In general, the Q of superabsorbent is closely related to the network structure of the resins. A three-dimensional network structure of the graft copolymers is formed because of the presence of crosslinking agent, and then the ability to absorb water is improved. If the crosslinking agent is not added to the reaction system, the graft chains will be of linear structure instead of three-dimensional network structure, and, of course, the prepared resins are water soluble. As the amount of crosslinking agent increases, the crosslinking level of the product increases, and an effective network structure for

water absorption of the product is gradually formed, and thus the Q increases. However, when an excessive amount of crosslinking agent is used, the molecular chains between the crosslinking points become too short as the crosslinking degree is too high and the micropores of the product becomes too small, and water molecules are difficult to enter the network, so the Q decreases. This result can follow the Flory equation¹³ concerning the swelling of an ionic network:

$$q_m^{5/3} = \frac{(i/2v_u S^{*1/2})^2 + (1/2 - \chi_1)/V_1}{v_e/V_0} \quad (1)$$

where q_m is the swelling ratio, i/v_u the concentration of fixed charge referred to the unswollen network, S^* the ionic strength of added electrolyte, v_1 the interaction parameter, and v_e/V_0 the crosslink density. Hence, the higher the crosslink density, the lower the swelling ratio of the network is, or the lower the Q becomes. However, change of molecular weight distribution connected with crosslinking may also cause similar effects.

When electrolyte ions are added, the osmotic pressure is reduced because the differences of the ion concentration between the inside and outside of the network, resulting in lower $Q_{0.9\% \text{ NaCl}}$ values. It can also be inferred from Flory's equation (1): When an electrolyte is added to the aqueous system of ionic network, S^* increases and q_m will decrease.

Effect of the amount of initiator on the water absorbency of superabsorbents

The effect of the amount of initiator on the water absorption of superabsorbents is shown in Figure 2. Both Q and $Q_{0.9\% \text{ NaCl}}$ increase with the increase of the amount of initiator and exhibit a maximum at the 0.5 wt % of initiator based on the total weight of

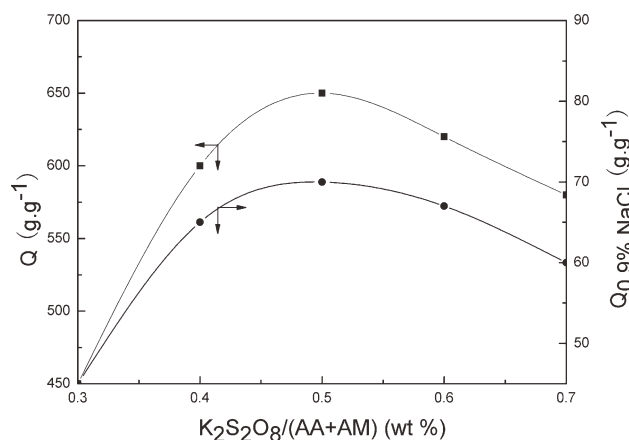


Figure 2 Effect of the amount of initiator on the water absorbency of superabsorbents [0.04% MBAM/(AA + AM), 7 : 1 (AA + AM)/KGM, 30% AM/(AA + AM), 75% neutralization of AA, 60°C, 3 h].

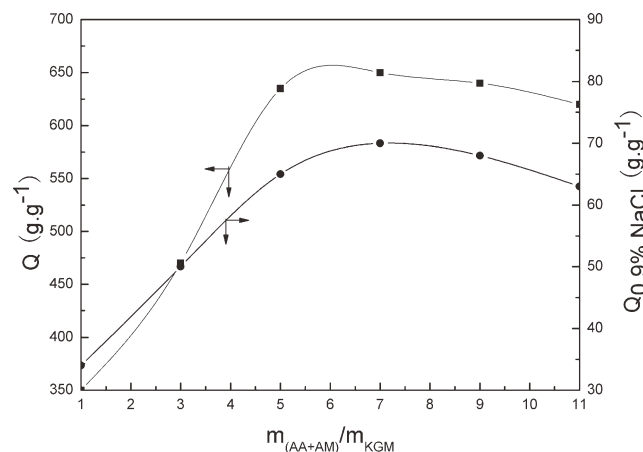


Figure 3 Effect of the amount of monomers on the water absorbency of superabsorbents [0.04% MBAM/(AA + AM), 0.5% $\text{K}_2\text{S}_2\text{O}_8$ /(AA + AM), 30% AM/(AA + AM), 75% neutralization of AA, 60°C, 3 h].

both AA and AM. When the dosage of initiator is too low, the active sites in the molecular chain of KGM is little and the graft reaction is not complete lead to low graft yield and graft efficiency, resulting in low values of water absorbency. With the increase of the amount of initiator, the active sites in the molecular chains of KGM increase and both graft yield and graft efficiency increase correspondingly, so the Q and $Q_{0.9\% \text{ NaCl}}$ increase. However, excessive amount of initiator will lead to the increase of probability of homopolymerization between monomers, resulting in the decrease of the Q and $Q_{0.9\% \text{ NaCl}}$.

Effect of the amount of monomers on the water absorbency of superabsorbents

Figure 3 indicates the effect of the amount of monomers on the water absorbency of superabsorbents. When the mass ratio of monomers (the weight percent of AM based on AM and AA is fixed at 30%) to KGM is less than 7 : 1, both Q and $Q_{0.9\% \text{ NaCl}}$ increase faster with rising the amount of monomers. However, when the mass ratio of monomers to KGM is higher than 7 : 1, the water absorbency of superabsorbents declines slightly. This phenomenon could be interpreted as follows: When the amount of monomers is too little, effective networks can not be formed due to the short graft chains, and thus the water absorbency is not high. As the amount of monomers increases the graft chains constantly grow, which lead to effective networks and a higher values of the water absorbency. When the amount of monomers rises to a certain extent, the homopolymerization competing with the graft copolymerization would probably increase, thereby reducing the length of graft chains, and then the values of the water absorbency do not increase any more, and

tend to level off or decline slightly. Therefore, the optimal mass ratio of monomers to KGM is 7 : 1.

Effect of monomer ratio on the water absorbency of superabsorbents

The influence of AM/(AA + AM) mass ratio on the water absorbency is studied. As shown in Figure 4, in the case of the total mass of monomers being fixed, with the increase of AM/AA mass ratio, the values of the water absorbency raise at first and then decrease. A maximum value occurs at 30% of AM/(AA + AM). As it is well known, AA contains $-\text{COOH}$ groups and AM contains $-\text{CONH}_2$ groups, and the order of ability to absorb water for the hydrophilic groups is as follows: $-\text{COOH} > -\text{CONH}_2 > -\text{OH}$. Of course, the more the AA used, the more the numbers of hydrophilic groups in the network contains, and the higher the water absorbency is. However, if an appropriate amount of nonionic monomer AM is added to the system, the absorbency especially the salt absorbency will improve because of the synergistic effect of the multiple groups in the system. Obviously, the water absorbency will decline in the case of excessive AM used.

Effect of temperature on the water absorbency of superabsorbents

Figure 5 shows the temperature on the water absorption. It can be seen from the figure that increasing temperature favors the improvement of the water absorbency until the temperature reaches 60°C and then the Q and $Q_{0.9\% \text{ NaCl}}$ decline. With increasing temperature, the radical formation rate increases, and the rate of chain propagation increases, and then the values of water absorbency also increase. As temperature increases above 60°C,

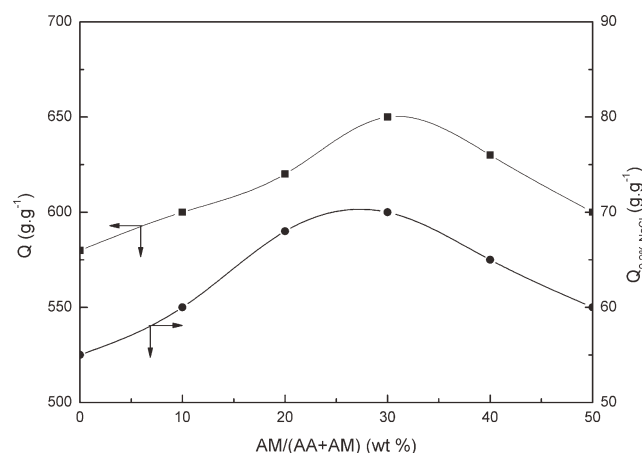


Figure 4 Effect of monomer ratio on the water absorbency of superabsorbents [0.04% MBAM/(AA + AM), 0.5% $\text{K}_2\text{S}_2\text{O}_8$ /(AA + AM), 7 : 1 (AA + AM)/KGM, 75% neutralization of AA, 60°C, 3 h].

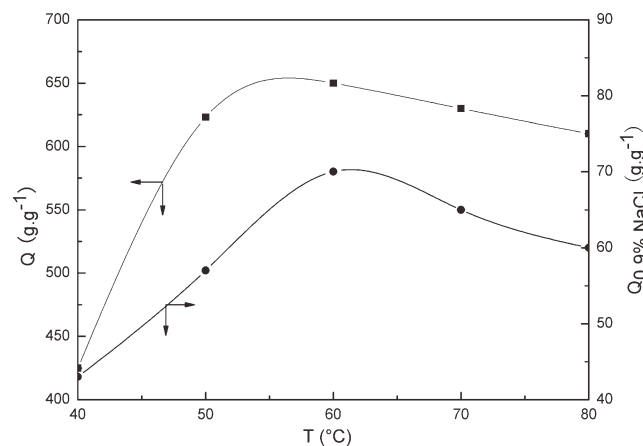


Figure 5 Effect of temperature on the water absorbency of superabsorbents [0.04% MBAM/(AA + AM), 0.5% $K_2S_2O_8$ /(AA+AM), 7 : 1 (AA + AM)/KGM, 30% AM/(AA + AM), 75% neutralization of AA, 3 h].

the reaction occurs too fast and both chain transfer and other side reactions increase, resulting in too much high degree of crosslinking for the system, and, therefore, the water absorbency decreases.

Effect of neutralization degree of AA on the water absorbency of superabsorbents

The relationship between the degree of AA and the water absorbency is shown in Figure 6. It can be seen that both Q and $Q_{0.9\% NaCl}$ exhibit a maximum as the neutralization degree of AA increases. This phenomenon is related to the special structure of the superabsorbents. On the one hand, at the low neu-

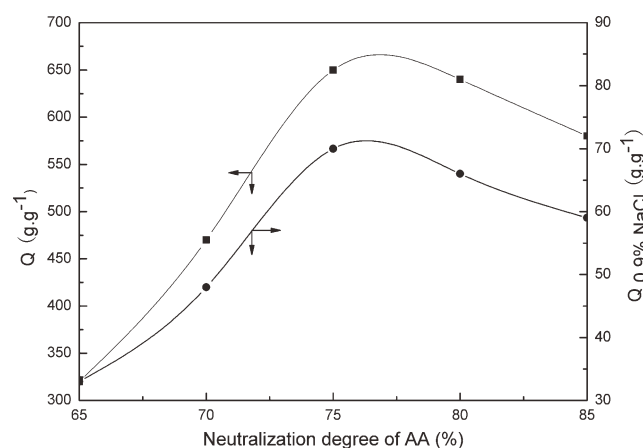


Figure 6 Effect of neutralization degree of AA on the water absorbency of superabsorbents [0.04% MBAM/(AA + AM), 0.5% $K_2S_2O_8$ /(AA + AM), 7 : 1 (AA + AM)/KGM, 30% AM/(AA + AM), 60°C, 3 h].

tralization degree, because of the low pH values for the reaction system and the high activity for AA, the polymerization is difficult to be controlled, which easily results in highly crosslinked polymers, and

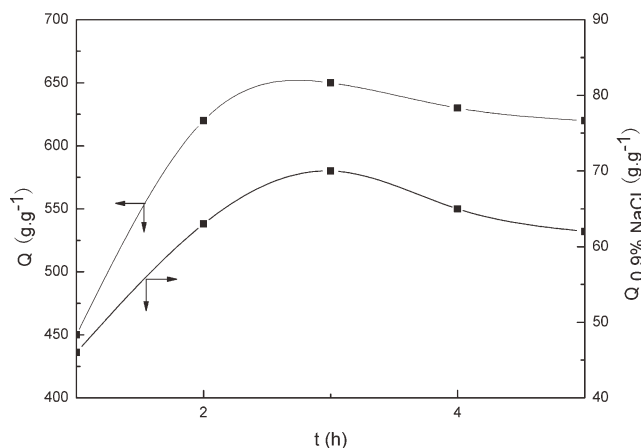


Figure 7 Effect of reaction time on the water absorbency of superabsorbents [0.04% MBAM/(AA + AM), 0.5% $K_2S_2O_8$ /(AA + AM), 7 : 1 (AA + AM)/KGM, 30% AM/(AA + AM), 75% neutralization of AA, 60°C].

thus the value of water absorbency is relatively low. On the other hand, at the high neutralization degree, the crosslinking degree decreases due to the low reaction rate; and meanwhile, the hydrophilic groups such as $-COONa$ groups increases. As the superabsorbent is in contact with water, because of the electrostatic repulsion between the neutralized carboxyl groups, the networks of superabsorbents are expanded. Because the ion concentration within the network is higher than the outside, the water will enter into the networks due to the role of osmotic pressure, which gives rise to an increased water absorbency. It can also be inferred from Flory's equation (1): the higher the i/V_{ur} , the higher the Q . However, when AA is neutralized in excess, the crosslinked structure of KGM may be damaged, and the water-soluble polymers would increase, resulting in a decreased Q .

Effect of reaction time on the water absorbency of superabsorbents

Reaction time plays a significant role on the water absorbency, as shown in Figure 7. Water absorbency exhibits a maximum at 3 h. At the beginning of the reaction, the reaction rate increases when the amount of monomers is high. Therefore, Q increases with increasing reaction time. However, with too long a reaction time, the amounts of both monomers and radicals decrease, and moreover, side reactions, such as the hydrolysis of KGM, might occur, which decrease Q .

Fourier transforms infrared (FTIR) analyses of the samples

The FTIR spectra of KGM (a) and purified KGM graft copolymer (b) are shown in Figure 8. The broad band [Fig. 8(a)] at 3400 cm^{-1} was due to the

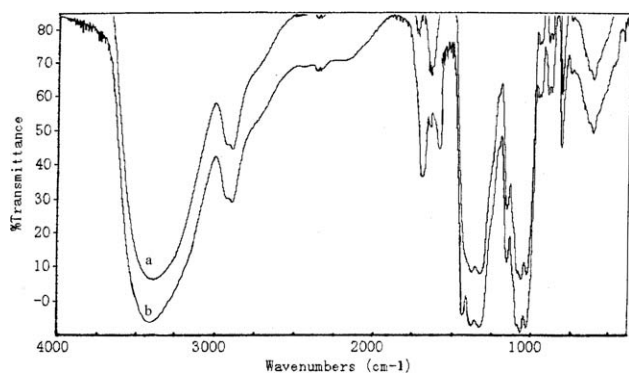


Figure 8 FTIR spectra of (a) KGM and (b) graft copolymer of KGM.

stretching mode of the O—H groups. Intense bands at 1728 and 1637 cm^{-1} were for the first overtone of O—H bending vibration and the intramolecular hydrogen bonds, respectively. The bands at 1160 and 2927 cm^{-1} were assigned to C—O stretching and C—H stretching, respectively. Two strong bands at 1091 and 1018 cm^{-1} were attributed to C—O—C stretching vibrations. Figure 8(b) shows the FTIR spectrum of KGM graft copolymer. In addition to the bands described for the KGM spectrum, the presence of an additional strong band at 1724 cm^{-1} is assigned to the C=O stretching vibration of —CONH₂. Moreover, the graft copolymer gives rise to two characteristic bands at 1569 and 1409 cm^{-1} , which belong to the symmetric and the asymmetric vibration absorption of —COO[−], respectively. These are the proofs that both AA and AM have been grafted onto KGM.

Water retention of the superabsorbents in soils

Figure 9 indicates the water retention of the superabsorbents in soil. With the passage of time, the water content of all soil samples shows a downward trend due to the evaporation of moisture in soil. However, the reduced water content in soil samples, which contain different amount of superabsorbents is different. It can be seen that different amount of superabsorbents added in soil samples all have certain inhibitory effect on the evaporation of moisture in soil and this effect increased with the increase of super-

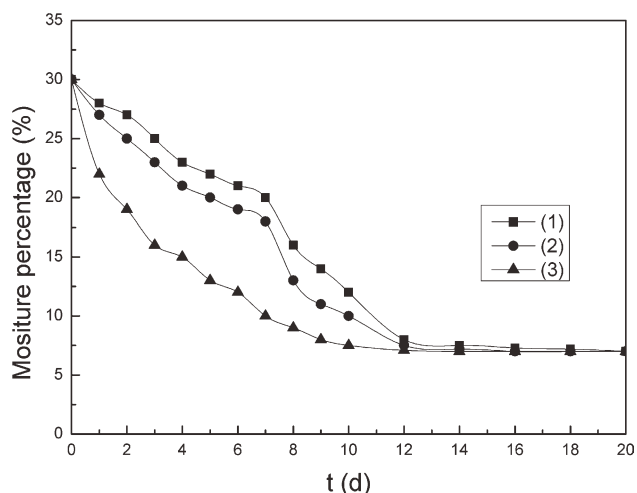


Figure 9 Water retention of the superabsorbents in soils (■, 0.3% superabsorbents added; ●, 0.1% superabsorbents added; ▲, control soil without superabsorbents).

absorbents used. Moreover, the most marked difference of water content between the soils with the superabsorbents and the soil without superabsorbents (control soils) occurred after 7 days, which indicates that superabsorbents have significantly inhibitory effect on the evaporation of water in soil at that time. However, when the water content is close to air-dried water content, the difference of inhibitory effect on the evaporation of water in soils between the different amounts of superabsorbents used decreases.

Effect of amount of superabsorbents on the soil aggregate distribution

The amount of superabsorbents added to soil has evident effect on the aggregated structure of soil, as shown in Table I. When the amount of superabsorbents added is 0, 0.1, and 0.3%, the content of soil aggregates (size of groups < 0.25 mm) are 72.4, 36.6, and 17.1%, respectively. This result indicates that the number of soil aggregates increases with the increase of amount of superabsorbents added to soil. This phenomenon can be explained as follows: The cohesive force between soil particles that are easily dispersed can be enhanced by the polymer chain structure of superabsorbents, which makes the soil

TABLE I
Effect of Amount of Superabsorbents on the Aggregate Size Distribution

ω (wt %) ^a	% Soil aggregate				
	<0.25 mm	0.25–0.5 mm	0.5–1.0 mm	1.0–2.0 mm	>5.0 mm
0	72.4	11.0	7.0	6.1	3.5
0.1	36.6	37.0	12.3	8.0	6.1
0.3	17.1	44.0	16.6	12.3	10.0

^a Weight percent of superabsorbents added based on the weight of soil.

particles bonded together and causes the changes of soil aggregates. Obviously, the increase in the number of soil aggregates can improve the permeability of soil, prevent the surface soil from forming a layer of skin and reduce the water evaporation in soils.

CONCLUSIONS

Superabsorbent polymer based on KGM could be obtained from KGM-*g*-poly (AA-*co*-AM) using the method of free radical grafting solution polymerization in the presence of MBAM as a crosslinker with potassium persulfate as an initiator. The optimum synthesized conditions are: 0.04% MBAM/(AA + AM), 0.5% K₂S₂O₈/(AA + AM), 7 : 1 (AA + AM)/KGM, 30% AM/(AA + AM), 75% neutralization of AA, a reaction temperature of 60°C and a reaction time of 3 h. At the optimum conditions, the maximum water absorbency of the optimized product was 650 g/g for distilled water and 70 g/g for a 0.9 wt % aqueous NaCl solution, respectively.

In addition, the water retention of the copolymers in soils was also investigated. The results showed that different amount of the copolymers added in soil samples all have certain inhibitory effect on the evaporation of soil moisture and these effects increased with the increase of the copolymers used. Moreover, the amount of copolymers added to soil

has evident influence on the aggregate distribution of soil, indicating that the number of soil aggregates increases with the increase of copolymers added to soil. In other words, the copolymer used can improve the permeability of soil and could be used as a good soil water retaining agent.

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