

Preparation of Poly(AA-AM) Water Superabsorbent by Inverse Microemulsion Polymerization

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ABSTRACT: A copolymer superabsorbent was prepared by inverse microemulsion polymerization, using cyclohexane as the continuous phase, water as the dispersed phase, *N,N*-methylene bisacrylamide as the crosslinking agent, ammonium persulfate (APS) as the initiator and OP-10 and SDS as complex surfactants. The synthetic variables (amount of crosslinking agent and initiator, water/oil ratio, monomer/surfactant ratio, and AA/AM ratio), and their effects on the absorbencies of the synthesized superabsorbents were studied. The relationships between the water absorbency and absorption time as well as the water retention capacity of the water superabsorbent were studied. The experimental results of superabsorbent polymers

(SAPs) showed the maximum water absorbency of 1432 g/g, and the water absorbency of 722 g/g within 15 min. The water retention in the soil was greatly enhanced using the above superabsorbents. SEM indicated an irregular, undulant, and microporous surface of the superabsorbent, which was convenient for the penetration of water into the polymeric network. SAPs can be considered for water-managing materials for agriculture and horticulture purposes in desert and drought-prone areas. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3859–3864, 2008

Key words: superabsorbent; inverse microemulsion; polymerization; surfactant

INTRODUCTION

Superabsorbent polymers (SAPs) are lightly cross-linked networks of flexible polymer chains and can absorb a large amount of water compared with general water-absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, SAPs have raised considerable interests and researches, and have been used in many fields such as agriculture and horticulture, sanitary products, oil drilling, and medicine for drug-delivery systems, etc.^{1–6}

The traditional method of SAPs synthesis reported is solution,^{7–9} inverse suspension,^{10,11} and inverse emulsion polymerization.¹² The extreme solution viscosity generated by solution polymerization leads to problems such as the difficulties in stirring and heat transfer, and the resin is obtained as a lump that has to be cut, dried, and pulverized before use. Although these problems may be overcome by inverse-suspension or -emulsion polymerization, the polymerization is unstable and coagulation and flocculation might occur during the inverse-suspension or -emulsion polymerization due to large particle size.

An important advantage of the inverse microemulsion polymerization of SAPs is the easier heat dissipation and lower viscosity. Moreover, the inverse microemulsion polymerization may occur at a higher rate to yield a high molecular weight polymer and keep stable due to smaller particle size. However, there is no report about the preparation of SAPs by inverse microemulsion polymerization. In this article, poly (AA-AM) superabsorbents were prepared by inverse-microemulsion polymerization technique using OP-10 and SDS as complex surfactants. The synthetic variables (amount of crosslinking agent and initiator, water/oil ratio, monomer/surfactant ratio, and AA/AM ratio) and their effects on the absorbencies of the synthesized superabsorbents were investigated. The results showed that no coagulation and flocculation occurred during the inverse microemulsion polymerization, with maximum water absorbency of 1432 g/g, and water absorbency of 722 g/g within 15 min as well as only a water loss of 30% of the water-swollen soil after 4 days water-retention test.

EXPERIMENTAL

Materials

Acrylic acid(AA), analytical grade, purified by distillation under vacuum; acrylamide (AM), chemical grade, purified by recrystallization; *N*-methylene-bisacrylamide (MBA), chemical grade, purified by

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recrystallization; sodium lauryl sulfate(SDS), Nonyl phenol polyoxyethylene ether (OP-10), chemical grade, ammonium persulfate (APS), analytical grade, used without further purification.

Preparation of superabsorbents by inverse microemulsion polymerization

A series of the superabsorbents with different amounts of crosslinker, initiator, acrylamide, and acrylic acid were prepared by the following procedure: Typically, acrylic acid (4 g) was dissolved in 11 mL distilled water, and then neutralized with 5 mL of sodium hydroxide solution in a four-necked flask fitted with a mechanical stirrer, thermometer, dropping funnel and a reflux condenser. Acrylamide (2 g) was added to the above partial neutralized monomer solution, and then the crosslinker MBA (6 mg) was added to the AA-AM mixture solution and the mixed solution was stirred at room temperature for 30 min and added dropwise to the inverse microemulsions formed by 100 g cyclohexane, 6.5 g SDS and 3.5 g OP-10. The water bath was heated slowly to 70°C with mild stirring after radical initiator APS (55 mg) was introduced to the above inverse microemulsions. After 3 h of the reaction, the resulting product was washed several times with distilled water, dried at 70°C to a constant weight, then milled and screened.

Water absorbency using filtration method

Approximately 20–30 mg of dried superabsorbents with an average particle size of 215 μm was dispersed in 60 mL of deionized water for 30 min. Then, excess water was allowed to drain through 300 mesh wire gauze. The weight of the superabsorbent containing absorbed water was measured after draining for 1 h, and the water absorbency was calculated according to the following equation:

$$\text{Absorbency (g/g)} = (W_2 - W_1)/W_1 \quad (1)$$

where W_1 and W_2 are the weight of the dry and swollen superabsorbent, respectively.

Determination of water retention

The percentage water retention (WR) was determined by weighing the mass of water-swollen soil before (m_1) and after (m_2) at 35°C for 24 h. The WR of the sample was calculated according to

$$\text{WR(\%)} = \frac{m_2}{m_1} \times 100\%$$

Characterization of the water superabsorbent

The micrographs of superabsorbents were taken using SEM (JSM-5600LV, JEOL). Before SEM obser-

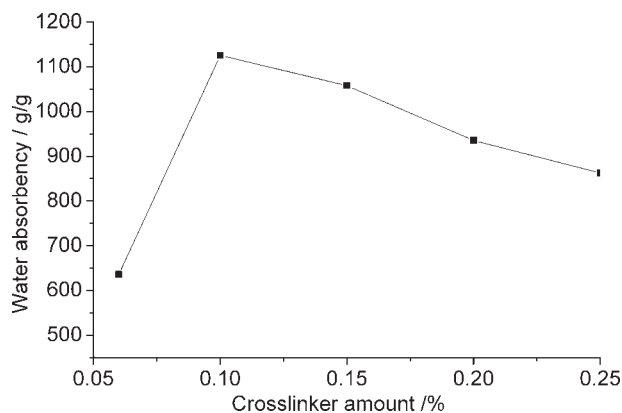


Figure 1 Effects of crosslinker content on the water absorbency of the superabsorbents; Cyclohexane : SDS : OP-10 : H₂O : AA : AM : APS = 100 : 6.5 : 3.5 : 11 : 4 : 2 : 0.1.

vation, all samples were fixed on aluminum stubs and coated with gold.

RESULTS AND DISCUSSIONS

Effects of crosslinker amount on the water absorbency

The relationship between the absorbency and network structure parameters was investigated by Flory's network theory and given as the following equation¹³:

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

where Q is the degree of swelling, i/v_u is the concentration of fixed charge referred to the unswollen networks, S^* is the ionic strength of solution, χ is the polymer-solvent thermodynamic interaction parameter, V_1 is the molar volume of water, and v_e/V_0 is the crosslinking density.

As indicated in eq. (2), 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 (based on monomer weight) on the water absorbency is shown in Figure 1. When the crosslinker content is below 0.1%, the water absorbencies decrease with decrease in crosslinker content because of an increase of soluble material. However, the water absorbencies decrease with the increase of crosslinker content from 0.1% to 0.3%. Higher crosslinker content will result in more crosslink points and denser networks, which decrease the space left for water to enter and prevent the network from expanding to its fullest extent. These results are in conformity with Flory's network theory¹³ and

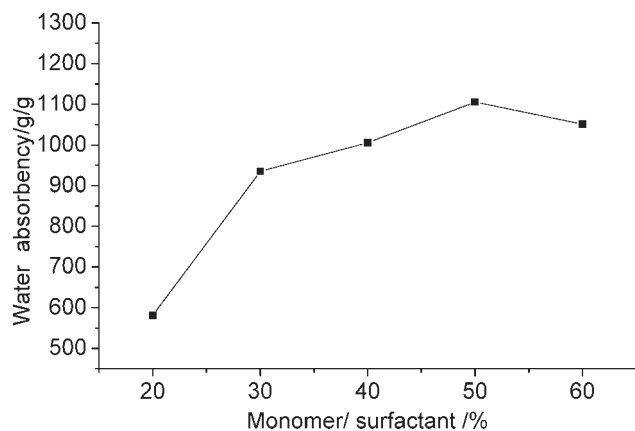


Figure 2 Effect of monomer/surfactant ratio on the water absorbency of the superabsorbent; Cyclohexane : SDS : OP-10 : H₂O : APS : MBA = 100 : 6.5 : 3.5 : 11 : 0.1 : 0.015.

similar observations were previously reported by others.^{14,15}

Effect of monomer/surfactant ratio on water absorbency of the superabsorbent

Figure 2 plots the experimental data of the water absorbency as a function of the monomer/surfactant ratio. As shown in Figure 2, with an increase of monomer/surfactant ratio, the water absorbencies increase initially and reach a maximum when the monomer/surfactant ratio is 50%. Beyond that, the water absorbencies decrease with a further increase of the monomer/surfactant ratio.

The strong increase in water absorbency may be attributed to the increase in particle concentration with increase in monomer/surfactant ratio. However as more monomer is added, the surface coverage ratio of surfactant decreases and the interdroplet attractive interactions lead to fusion and mass exchange. Therefore the resultant particles stick to-

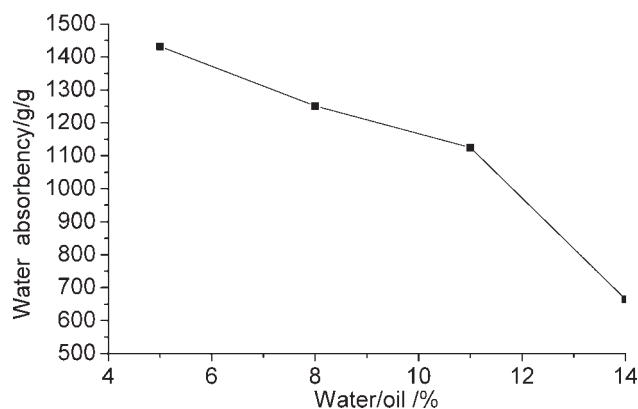


Figure 3 Effects of water/oil mass ratio on the water absorbency of the superabsorbent; Cyclohexane : SDS : OP-10 : AA : AM : APS : MBA = 100 : 6.5 : 3.5 : 4 : 2 : 0.1 : 0.006.

gether, resulting in a decrease in water absorbency, as indicated in Figure 2.

Effect of water/oil ratio on water absorbency of the superabsorbent

Effects of water/oil ratio on water absorbency of the superabsorbent are shown in Figure 3. As shown in Figure 3, the water absorbencies decrease with the increase of water/oil ratio. Small particles can be stabilized by surfactant, but as more water is added, the surface coverage ratio of surfactant decrease and the interdroplet attractive interactions lead to fusion and mass exchange. Therefore the resultant particles stick together, resulting in a decrease in water absorbency.

Effect of AA/AM ratio on water absorbency of the superabsorbent

According to Flory's network theory and eq. (2),¹³ i/v_u is the concentration of fixed charge referred to the unswollen networks and therefore the fixed charges on polymeric network of superabsorbent play an important part in the swelling of the superabsorbent. They are related to electrostatic repulsion between charges on the polymeric backbone and to osmotic pressure difference between polymeric network and external solutions. Therefore, the amount and type of hydrophilic groups on polymeric network play important roles in influencing water absorbency of the superabsorbent.

As can be seen from Figure 4, equilibrium water absorbencies increase with increasing the mass ratio of AA to AM from 40/60 to 70/30, and then decrease with further increasing the ratio to 80/20. When more AA is added, the electrostatic repulsion, ionic hydrophilic property and osmotic pressure

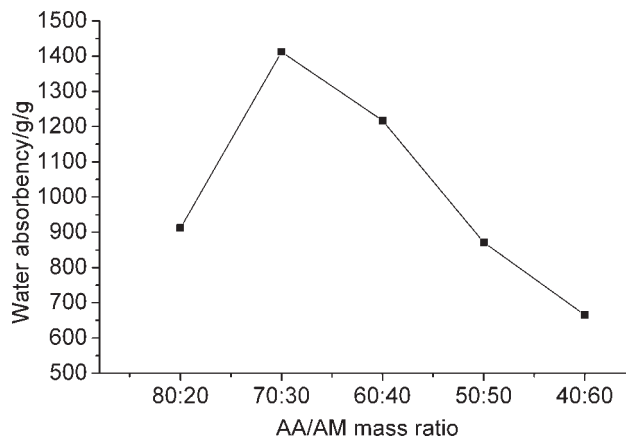


Figure 4 Effects of AA/AM mass ratio on the water absorbency of the superabsorbent; Cyclohexane : SDS : OP-10 : H₂O : monomer : APS : MBA = 100 : 6.5 : 3.5 : 5 : 6 : 0.08 : 0.006.

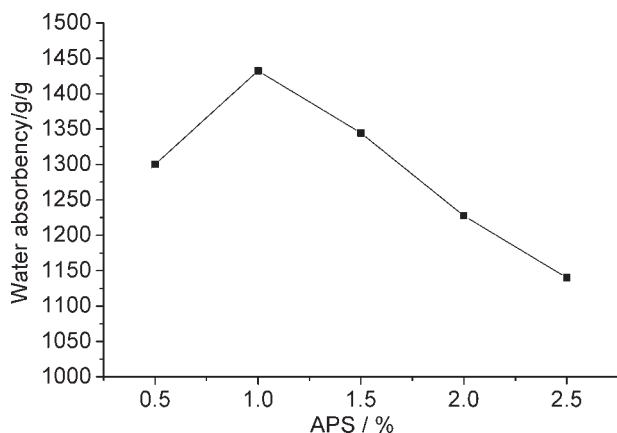


Figure 5 Effects of initiator content on the water absorbency of the superabsorbents; Cyclohexane : SDS : OP-10 : H₂O : AA : AM : MBA = 100 : 6.5 : 3.5 : 5 : 4 : 2 : 0.006.

difference increase, and the network can be expanded more easily because of the increasing electrostatic repulsion, which result in an increase of equilibrium water absorbency. However, further increasing the AA/AM mass ratio to a certain extent generate more sodium ions in the polymeric network, which reduce the electrostatic repulsion by screening the negative charges of $-\text{COO}-$ groups, and thus decrease the equilibrium water absorbency. Besides, although the replacement of ionic monomer segments by nonionic ones would be expected to reduce the stress responsible for the expansion of the polymer network by decreasing the number of ionic repulsions, introducing some acrylamide into an acrylic acid polymer can speed up absorption by lowering resistance to permeation. This is attributable to higher chain mobility or more free volume.

Effect of initiator content on the water absorbency

Figure 5 shows the effect of the initiator content on water absorbency. The water absorbencies increase as APS content increase from 0.5% to 1.0 wt % and decrease with further increases in the content of APS. With increase of the initiator concentration, the molecular weight of the macromolecules decrease, and the relative amount of polymer chain ends increase. As mentioned in previous study,^{16,17} the polymer chain ends do not contribute to the water absorbency. Therefore, the water absorbencies decrease with increase of the initiator content.

However, when the content of initiator is below the optimum value of 1%, the swelling capacities of the superabsorbent also decrease. This may due to a decrease in the number of radicals produced by initiator and small amount of radicals can not guarantee the rapid crosslinking reaction by inverse microemulsion polymerization. Therefore the network cannot be formed efficiently during inverse

microemulsion polymerization, and the water absorbencies decrease.

Water absorbency rate of the superabsorbent

Relationship between water absorbency and absorption time is shown in Figure 6. Water absorption is rapid, requiring 15 min to reach 722 g/g and 60 min to reach maximum uptake (1432 g/g). An increase in rate of absorption might be expected from the increase in surface area with decreasing particle size prepared by inverse microemulsion polymerization. Besides, the inverse microemulsions keep stable and relatively perfect polymer network might be formed, which will increase the initial water absorbency and the equilibrium water absorbency.

Soil-water retention study of the water superabsorbents

One of the most important applications of water superabsorbent is for agricultural and horticultural purposes, especially for the effective utilization of water in dry and desert regions, to transform these dry and desert regions into green fertile lands.

Figure 7 shows the water-retention capacity of water-swollen soil and untreated soil at 35°C with different superabsorbent usages. It can be seen that both water-swollen soil and untreated soil have decreasing trends of water retention with prolonging the time. However with increase amount of superabsorbent used in soil, the dewatering rate is largely decreased and for a given duration of time the water retention increases. In the 35°C water-retention test, the water loss of untreated soil reaches almost 98%, whereas water-swollen soil with 4% superabsorbent used in soil has only a water loss of 30% after the 4 day water-retention test.

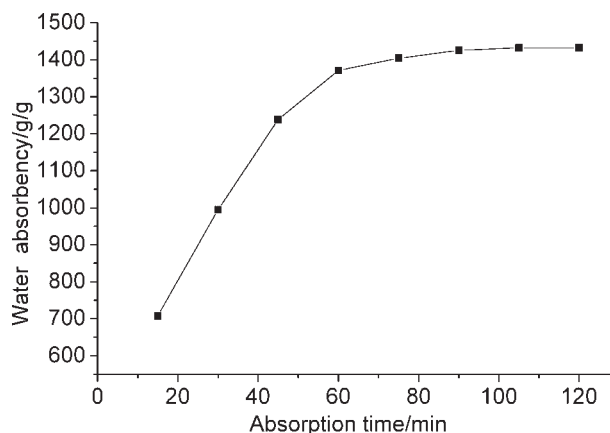


Figure 6 Relationship between water absorbency and absorption time of the superabsorbent; Cyclohexane : SDS : OP-10 : H₂O : AA : AM : APS : MBA = 100 : 6.5 : 3.5 : 5 : 4 : 2 : 0.06 : 0.006.

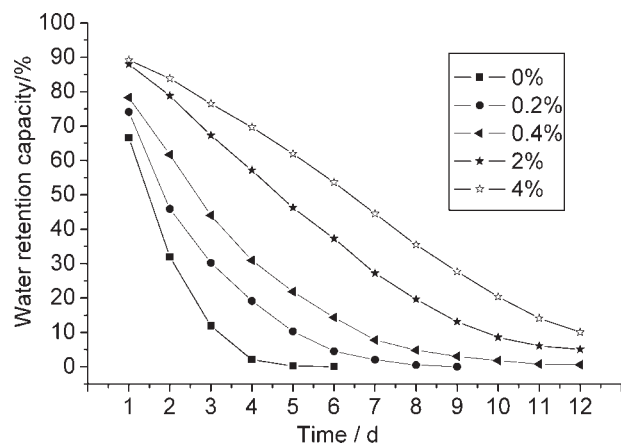


Figure 7 Soil-water retention capacity of the water superabsorbents with different usages; Cyclohexane: SDS : OP-10 : H₂O : AA : AM : APS : MBA = 100 : 6.5 : 3.5 : 5 : 4 : 2 : 0.06 : 0.006.

The water in the superabsorbent can be classified into bound water, half bound water, and free water.¹⁸ When compared with bound water and half-bound water, the free water in a superabsorbent has high mobility and can easily be lost. The number of hydrophilic groups (COOH and COONa and —CONH₂) in a unit volume in superabsorbent is high in superabsorbent, so the percentages of bound water and half-bound water content are also high in swollen-soil. As a result, swollen-soil has better water-retention ability than untreated soil under higher temperature. Therefore these superabsorbents may prove useful in agricultural and horticultural purposes.

SEM observations of the superabsorbent

The microphotographs of the particles for two series of superabsorbents with different crosslinker content

observed from SEM are shown in Figure 8. As shown in these Figures, the particles obtained from inverse microemulsion polymerization approach irregular, undulant and microporous surfaces and some aggregates occur, indicative of particle conglomeration after remove of surfactant and water by washing and drying. Although these undulant and microporous surfaces are convenient for the penetration of water into the polymeric network, the particles prepared with more crosslinker content (0.3%) shows a smaller pore size and a less porous structure compared with those with less crosslinker content (0.1%). These different shapes will affect their water absorption behavior and these observations are in good agreement with our water-absorbency observations. As indicated in Figure 1, the water absorbency of the superabsorbents prepared with 0.3% crosslinking agent was lower than those with 0.1% crosslinking agent because these pores make an increased surface area and thus increase the water absorbency.

FTIR spectrum of the superabsorbent

The FTIR spectrum in the range 4000–400 cm⁻¹ of superabsorbent is shown in Figure 9. The absorption peaks at 3430 cm⁻¹ contribute to the OH and NH stretching frequencies, and the bands at 2860 and 2927 cm⁻¹ correspond to the symmetrical and asymmetrical of methene, respectively. Further, the spectrum also shows peaks at 1730 cm⁻¹ corresponding to the carbonyl group of acid moiety of the AA unit, and 1564 and 1402 cm⁻¹ corresponding to the COO— and 1659 cm⁻¹ corresponding to the amide moiety of the AM unit, and the peaks at 1118 cm⁻¹ corresponding to C—O—C group. This FTIR analysis indicates that all of the monomeric units- acrylamide,

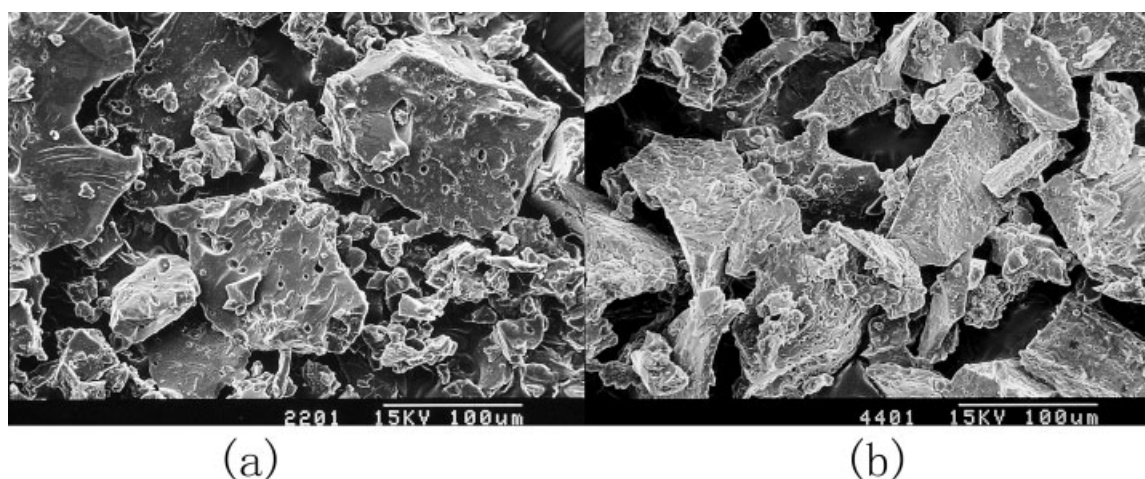


Figure 8 SEM images of the inverse microemulsion superabsorbent, (a) crosslinking agent content = 0.25%; (b) crosslinking agent content = 0.1%.

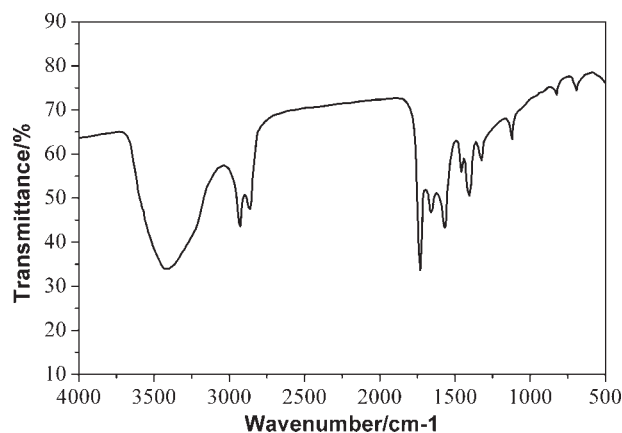


Figure 9 FTIR spectrum of the water superabsorbent.

sodium acrylate, and acrylic acid are incorporated in the copolymer backbone.

CONCLUSIONS

A high water superabsorbent poly acrylic acid-coacrylamide was prepared by inverse microemulsion polymerization, using cyclohexane as the continuous phase, water as the dispersed phase. *N, N'*-methylene bisacrylamide as the crosslinking agent and ammonium persulfate (APS) as the initiator, and OP-10 and SDS as complex surfactants. Factors affecting the water absorbency of the water superabsorbent, such as amount of crosslinking agent, water/oil ratio, monomer/surfactant ratio, AA/AM ratio and initiator were systematically studied. The relationship between the water absorbency and absorption time, and also the water retention capacity of the water superabsorbent have been studied. The results showed that water superabsorbent has the maximum water absorbency of 1432 g/g, and the water

absorbency of 722 g/g within 15 min, as well as only a water loss of 30% of the water-swollen soil after the 4 day water-retention test. SEM indicated an irregular, undulant and microporous surface of the superabsorbent, which is convenient for the penetration of water into the polymeric network. FTIR indicated the structure of the acrylic acid and acrylamide copolymer.

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