

# Synthesis and Characterization of Functionalized Acrylic-Acrylamide-Based Superabsorbent Gels

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**ABSTRACT:** We have synthesized series of superabsorbent polymers (SAPs) by solution free radical polymerization of acrylic acid (AA), acrylamide (AM) with different functional monomers (FM). Three functional monomers including zwitterionic monomer [3-(methacryloylamino) propyl] dimethyl (3-sulfopropyl) ammonium (MPDSA), cationic monomer (3-acrylamidopropyl) trimethylammonium chloride (APTAC) and anionic monomer 2-acrylamidoglycolic acid monohydrate (AGAM) were selected to provide different charged groups on the superabsorbents. The effect of reaction parameters, such as degree of neutralization, content of initiator and crosslinker on the swelling capacity were assessed. The water

absorbency of the superabsorbent were characterized in the distilled water, 0.9 wt % NaCl solution and the mixed solution containing 60 mg L<sup>-1</sup> CaCl<sub>2</sub> and 30 mg L<sup>-1</sup> MgCl<sub>2</sub>, respectively. In addition, the swelling rate and water retention capacity in the soil were also investigated. Finally, the mechanism of different absorbency induced by the variety kinds of functional monomers was studied by XPS and FTIR, and tentative interpretation was presented as well. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2828–2836, 2009

**Key words:** superabsorbent; absorbency; functionalization; salt-resistant; swelling

## INTRODUCTION

Superabsorbents are slightly crosslinked hydrophilic polymers with three-dimensional structures that can absorb and retain large amount of water or other biological fluids.<sup>1–3</sup> Because of their excellence in water absorbency compared with traditional water absorbing materials, superabsorbents have been widely used in many fields, such as medical treatment, sanitation, water treatment, horticulture, agriculture, and forestry.<sup>4–6</sup> Since the first superabsorbent hydrogel was reported by the U.S. Department of Agriculture in 1961,<sup>7</sup> tremendous effort has

been made to improve their swelling capability, gel strength, and absorption rate.<sup>8,9</sup> In recent years, great interests have shown in the use of superabsorbents as water management materials.<sup>10</sup> By using this product, encouraging results have been demonstrated by reducing irrigation water consumption and the death rate of plants. Meanwhile, they can also improve soil cluster structures, the fertilizer retention of the soil and plant growth rate.<sup>11</sup> Adoption of this technology will save the resources, and leading to a better and sustainable environment.

Superabsorbent polymers based on AA have been extensively studied because AA is cheap and easily be polymerized into a three-dimensional matrix with small amount of crosslinker.<sup>12</sup> Even the AA-based superabsorbents exhibited high water absorbency in the deionized water, it demonstrated poor tolerance to salts, especially towards the aqueous multivalent cationic solution.<sup>13</sup> There are several methods have been utilized to improve the salt-resistance of AA-based superabsorbent gels, among them, introducing nonionic monomer, hydrophilic monomer, or adding inorganic clay are widely accepted.<sup>14–18</sup>

To further improve the salt-resistance of the superabsorbent gels, there are several articles have been reported to introduce functional monomer to the AA-based composites. Such as, adding anionic

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monomer 2-acrylamido-2-methyl propanesulfonic acid, zwitterionic monomer 3-methacrylamido propyl trimethylammonium, 2-acrylamido-2-methylpropane sulfonate, and cationic monomer [(3-acryloylamino) propyl] trimethylammonium chloride, etc.<sup>19–23</sup> However, there are quite few studies focusing on introducing different charged functional monomer to the AA–AM-based matrix by solution free radical polymerization.

In this article, three charged functional monomers were introduced into the AA–AM co-monomers based systems by solution free radical polymerization. We predict that MPDSA and APTAC with good hydrophilicity and relative low charge density per unit volume could change the interaction among the polymer matrix and improve their water absorbency, especially in the divalent ions solutions. Although acrylic acid has been studied to chelate calcium or magnesium ions, there is no investigation on the absorbency in the divalent ions solutions after adding different types of functional monomers. The synergistic effect between the functional monomers and acrylic acid may improve the performance of the absorbency. The high chelating of carboxyl group in AGAM could remove the cations in the salt solution to improve the anti-salt performance of the SAPs. Meanwhile, AA should maintain its original repulsive force within the matrix, and AM retains inherent good anti-salt resistance. To verify this hypothesis, the effect of different functional monomers on the swelling capacity, swelling rate, and water retention capacity of the SAPs were characterized under various conditions, including distilled water, 0.9 wt % NaCl solution and the mixed solution comprised of 60 mg L<sup>-1</sup> CaCl<sub>2</sub> and 30 mg L<sup>-1</sup> MgCl<sub>2</sub>, respectively. Particularly, this new testing solution made of divalent ions such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, which attempt to resemble the water absorbency in the soil condition was proposed for the first time.

## EXPERIMENTAL

### Reagents

AA was purchased from Beijing Oriental Chemical (Beijing, China) and distilled under reduced pressure before use. AM was obtained from GuangDong Xilong Chemical Industry (GuangDong, China) and recrystallized from acetone. Ammonium persulfate (APS) was from Tianjin Bodi Chemical Industry. (TianJin, China) and recrystallized from water. Cationic monomer (3-acrylamidopropyl) trimethylammonium chloride, zwitterionic monomer [3-(methacryloylamino) propyl] dimethyl (3-sulfopropyl) ammonium, anionic monomer 2-acrylamidoglycolic acid monohydrate, and crosslinker *N,N'*-methylenebisacrylamide (MBA) were all from Aldrich (St. Louis, MO) and used without fur-

ther treatment. All salts, ammonium, ethanol, and acetone were supplied from Beijing Reagent (Beijing, China).

### Aqueous solution free-radical polymerization

Series of superabsorbents with different amounts of AA, AM, and FM were polymerized according to the following procedure. First, AA was partially neutralized by 1M ammonium solution, then AM, FM, MBA, and distilled water were added to the above partially neutralized AA solution consecutively. The mixed solution of monomers and the crosslinker was poured into a 250 mL four-necked, round-bottom flask equipped with a mechanical stirrer, condenser, thermometer, and nitrogen gas inlet, respectively. Stirred under nitrogen atmosphere, the temperature was allowed to increase to 40°C in water bath, and the APS solution was dropwised into the reactor. Then the final polymerization was carried out at 75–80°C under nitrogen atmosphere for 30 min. After polymerization, the resulting polymer was washed with ethanol and acetone to remove the residue, cut into small pieces, and dried in vacuum oven at 80°C to reach a constant weight. Finally, the products were milled and ready for the test.

### Measurement of water absorbency

The water absorbency of the superabsorbent composite,  $Q$ , was calculated by the following eq. (1) to evaluate the water absorbency capability of the superabsorbent.<sup>23</sup>

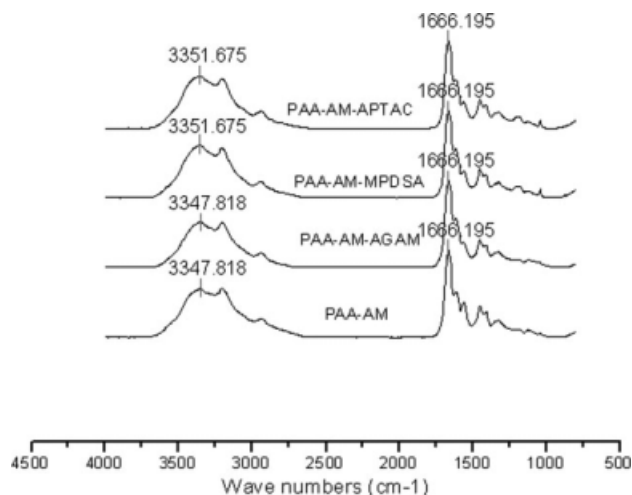
$$Q = \frac{M_2 - M_1}{M_1} \quad (1)$$

where  $M_1$  and  $M_2$  are the weights of the drying sample and the soaking gel, respectively. The  $Q$  value was defined as grams of water per gram of superabsorbent polymers.

A tea-bag made of 100-mesh nylon screen<sup>23</sup> containing 0.30 g sample was immersed entirely in 1 L volume following liquids separately: distilled water, 0.9% NaCl solution, and mixed solution composed of 60 mg L<sup>-1</sup> CaCl<sub>2</sub> and 30 mg L<sup>-1</sup> MgCl<sub>2</sub> at 25°C about 24 h to reach the swelling equilibrium. Then, hung the tea-bag up and kept for 15–30 min to drain out the excess liquid and weighed it.

### The swelling rate of the superabsorbents

Swelling rate of the superabsorbents was measured according to the above explanatory method. The weight of the water-absorbed samples was measured at certain timed intervals, and the  $Q$  was calculated using the eq. (1).<sup>23</sup>



**Figure 1** FTIR spectra of (a) PAA-AM-AGAM, (b) PAA-AM, (c) PAA-AM-APTAC, and (d) PAA-AM-MPDSA.

### Measurement of water evaporation rate of soil with SAPs

In this experiment, the sandy soil had been air-dried before use. Two grams of different series of SAPs were well mixed with 200 g dried sandy soil (sift through 0.2 mm mesh) and kept in 250 mL beakers. Then 200 mL of 60 mg L<sup>-1</sup> CaCl<sub>2</sub> and 30 mg L<sup>-1</sup> MgCl<sub>2</sub> solution was slowly added into the beaker and weighed ( $m_0$ ). A blank experiment, without SAPs, was also carried out as background. The beakers were placed in oven at 40°C and weighed every 2 h ( $m_i$ ). The whole process was finished after 40 h. Then water evaporation ratio (Er) was calculated by the following eq. (2):

$$Er = \frac{m_0 - m_i}{200} \times 100\% \quad (2)$$

Where  $m_i$  and  $m_0$  are the weights of dried and the swollen sandy soil, respectively.

### FTIR analysis

The series of superabsorbent polymers were analyzed using Fourier-transform infrared (FTIR) spectrophotometer (Nicolet Corporation, Madison, WI, Magna-IR 750). The dried sample was grounded with dried KBr powder, and dried again before subjected to FTIR spectrophotometer for measurement.

### XPS analysis

After swelling in the mixture solution of 60 mg L<sup>-1</sup> CaCl<sub>2</sub> and 30 mg L<sup>-1</sup> MgCl<sub>2</sub> for certain time, the superabsorbent polymers were dried to a constant weight, and analyzed by X-ray photoelectron spectroscopy (XPS; AXIS Ultra, Kratos, Manchester, England).

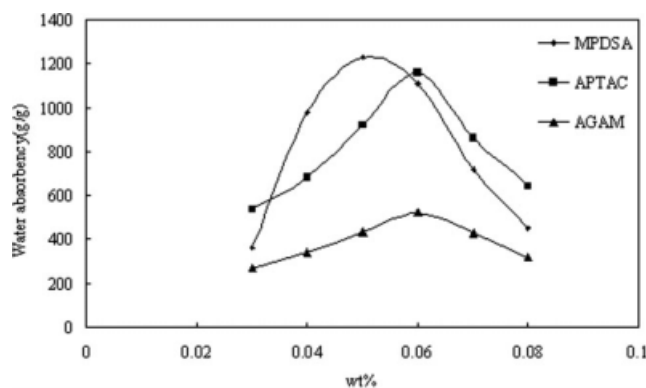
## RESULTS AND DISCUSSION

### FTIR characterization of the SAPs

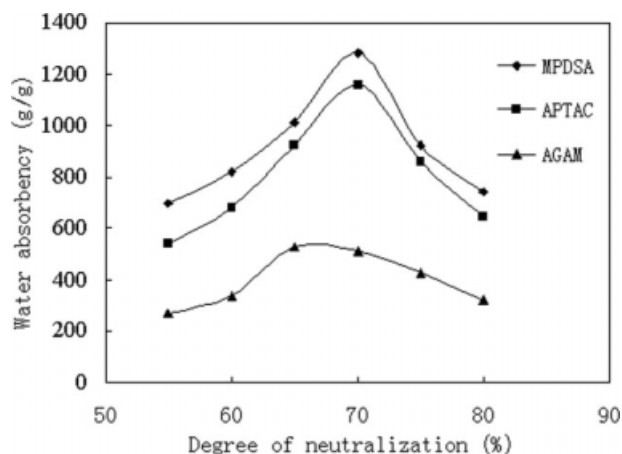
FTIR were used to characterize series of AA-AM-FM-based SAPs, which contain 1% FM such as MPDSA, APTAC, and AGAM, and spectra were shown in Figure 1. It can be seen that the characteristic absorption bands appeared in all of the SAPs at 1712 cm<sup>-1</sup>, 1580 cm<sup>-1</sup>, and 1409 cm<sup>-1</sup>, which are ascribed to -COOH stretching, -COO<sup>-</sup> asymmetric stretching, and -COO<sup>-</sup> symmetric stretching, respectively,<sup>23</sup> indicating that AA was attached on the polymer matrix, and partial AA was neutralized into NaAA. The absorbance at 3190 cm<sup>-1</sup> and a sharp absorbance at 1677 cm<sup>-1</sup>, attribute to -CONH<sub>2</sub> group, suggesting that AM was fixed in the matrix of the polymer.<sup>23</sup> It was also found that there were no obvious differences for the IR spectrum among three different functional terpolymers, since characteristic peak of 1% of functional monomer was masked by the bulk AA and AM absorption.

### Effect of crosslinker on the water absorbency

It is well known that content of crosslinker in the composite affect the water absorption performance of hydrogels. The effect of crosslinker content on the water absorbency of AA-AM-FM hydrogels in the distilled water was shown in Figure 2 (unless stated separately, all of the points in the following figures have been measured five times, and the standard deviations are less than 5%), which AA, AM, and FM were terpolymerized at the ratio of 30 : 69 : 1. It can be found that as the crosslinker content in the composite increased in range of 0.02–0.05%, water absorbency of the all of the functionalized SAPs improved with increasing crosslinker content. However, the swelling capacities of the gels were



**Figure 2** Optimization of crosslinker content on the water absorbency in distilled water. Reaction condition: reaction temperature, 75°C; weight ratio of initiator to the monomers is 0.4 wt %, concentration of monomers in the feed is 17%.



**Figure 3** Optimization of neutralization degree on the water absorbency in distilled water. Reaction condition is the same as in Figure 2.

dropped rapidly with further increase in the content of crosslinker. The above results can be explained as following: low crosslinker content results in low crosslinking density, with smaller amount of crosslinker which will make the solubility of the polymer to increase. However, after content of crosslinker reach peak point, further increase of the crosslinker content shrank the polymeric network and the water absorbency was reduced consequently. From Figure 2, it also can be observed that the swelling capacity of the zwitterionic MPDSA and cationic APTAC-based SAPs were much higher than that of anionic AGAM-based gels, the reason will be addressed later in detail.

#### Effect of degree of neutralization on the swelling capacity

The degree of neutralization of acrylic acid in the composite had significant effect on the water absorbency. It can be seen from Figure 3, under all of three cases, there exist maximum points of the swelling capacity of degree of neutralization, at which the composition of AA : AM : FM is set at 30 : 69 : 1. The water absorbency increase gradually as degree of neutralization increase from 55 to 70%, and then decreased rapidly with the degree of neutralization further increased. The results is likely attributes to the reacting activity of acrylic acid is higher than that of acrylate, therefore, the lower neutralization and the faster polymerization rate will be achieved. After adding more alkali, polymerization rate slow down, the charge density of the polymeric network would increase with the high degree of neutralization, which expand the hydrogel network. After optimized point of 70% neutralization, the strong "repulsive force" between the acrylate monomer will result in polymerization rate would decrease, which

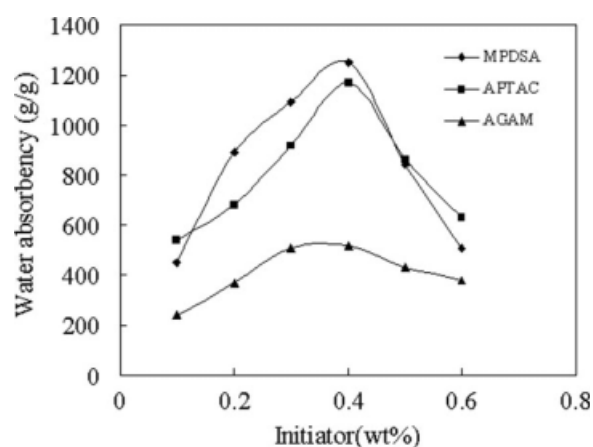
will weaken the water absorbency of the gels dramatically. In addition, the water absorbency of the MPDSA and APTAC-based SAPs were much higher than that of AGAM-based gels.

#### Effect of initiator content on the water absorbency

In the process of cross-linking and polymerization, the initiator has an impact on crosslinking degree and molecular weight between crosslinking points. The effect of initiator content on water absorbency of the different charged SAPs is shown in Figure 4. It was found that in all of the cases, the water absorbency increased with increasing initiator content up to optimum results around 0.3 wt % and then decreased with increasing initiator content. The results indicated as the initiator content is at low level, the polymerization process is slower and the polymer network is less extensive, and the water absorbency is lower. However, as the content of the initiator is beyond the optimum range, high number of produced free radicals may cause a chain transfer to polymers and led to decreasing of the water absorbency of the SAPs.

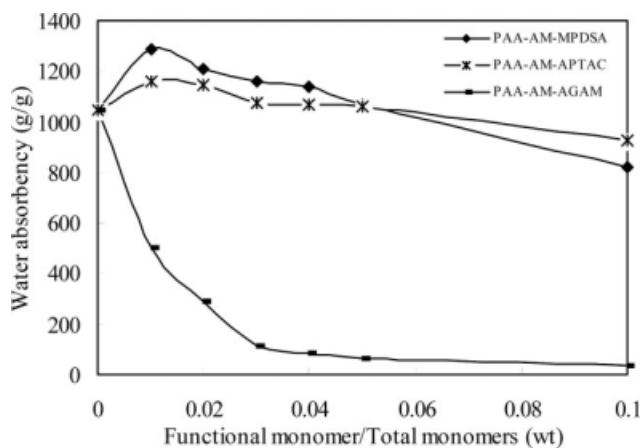
#### Effect of FM on the swelling capacity of SAPs in distilled water

To examine the effect of FM on the water absorbency of the SAPs, three types of functional monomers, i.e., zwitterionic MPDSA, cationic APTAC, and anionic AGAM were polymerized with AA and AM, respectively, and measurement of  $Q$  was carried out in distilled water correspondingly and showed in Figure 5. The most remarkable influence was adding 1% of zwitterionic MPDSA, which could increase the  $Q$  up to 20% compared with Poly (AA-co-AM). For the cationic APTAC modified composite, its water absorbency changing pattern is



**Figure 4** Optimization of initiator content on water absorbency in distilled water. Reaction condition is the same as in Figure 2.





**Figure 5** Effect of content of functional monomer on water absorbency in distilled water. Reaction condition is the same as in Figure 2.

essentially same to that of the zwitterionic gel despite of its maximum absorbency is at  $1165 \text{ g g}^{-1}$  and slightly lower than that of the MPDSA. These above results can be explained that both APTAC and MPDSA are hydrophilic monomers with stronger affinity toward water than that of AA. However, as the amount of functional monomer further increased in the hydrogel, the fixed charge per unit volume of MPDSA and APTAC-based polymer gradually decreased, the swelling capacity slightly reduced consequently. The reason MPDSA have the highest water absorbency among three SAPs maybe due to MPDSA is inner salt and hard to be dissociated into "free ions" and have relative low charge density in the network of the matrix.

Whereas, adding anionic AGAM into the composite, the absorbency in the distilled water was decreased dramatically until 3% AGAM added. For example, as 1% of AGAM terpolymerized into the superabsorbent, the absorbency decreased to  $502 \text{ g g}^{-1}$ . When 2% of the AGAM was added in the composite, the absorbency dropped sharply to  $275 \text{ g g}^{-1}$ , after 3% the curve is much flatter. This was most likely due to the added AGAM is strong acid, which is easily to be dissociated into free ions and "self-crosslinking" point to be formed. Hence, the cross-linking density of the polymeric network was strengthened. This fortified inner "network" would make it difficult for the water to penetrate and led to the downward of water absorbency.

#### Effect of FM on the water absorbency of SAPs in 0.9% NaCl solutions

In many cases, SAPs was designed for feminine care products, hygiene, and baby diaper. Thus, measurement of absorbency in 0.9% NaCl solution was used as the standard method to characterize the anti-salt

properties of the SAPs. From Figure 6, it can be seen that the overall changing profile was similar to Figure 5. But compared to the distilled water,  $Q$  was much lower in the 0.9% NaCl solution. This phenomenon can be explained by the Flory's ionic elasticity gel theory as follows<sup>24</sup>:

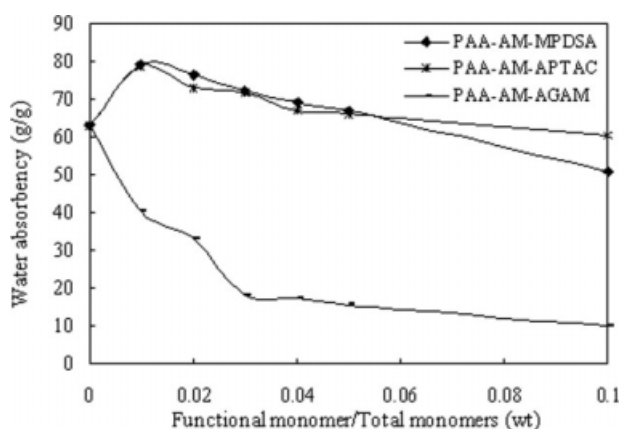
$$Q^{5/3} = \frac{\left(\frac{1}{2} \frac{i}{v_u} \frac{1}{S^{-1/2}}\right)^2 + (1/2 - x_1)/V_1}{(v_e/V_0)} \quad (3)$$

Where  $Q$  is the water absorption,  $V_e/V_0$  is the cross-linking density of polymer,  $1/2 - x_1$  is affinity between polymer and external solution,  $i/V_u$  is the fixed charge per unit volume of polymer,  $S$  is the ionic strength of external solution. It is obviously that the swelling capacity of the SAPs was affected by the ionic strength of external solution, the cross-linking density of the polymer, etc.

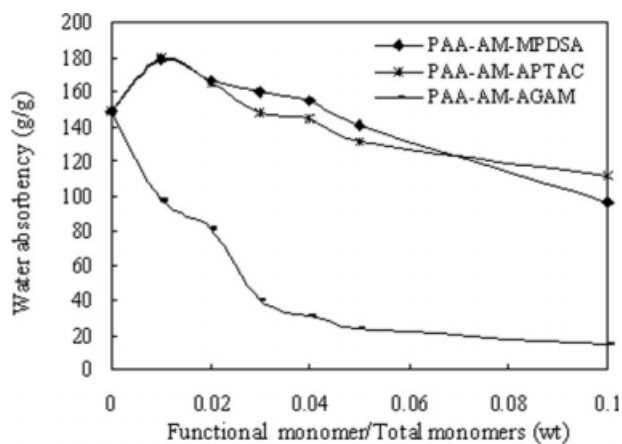
The strong ionic strength of 0.9% NaCl solution make the network of the hydrogel shrink and the water absorbency was greatly reduced compared with that in distilled water. From Figure 6, it also can be seen that adding 1% of zwitterionic MPDSA and cationic APTAC into the PAA-AM-based composite, the absorbency was improved from  $62 \text{ g g}^{-1}$  to  $78 \text{ g g}^{-1}$  in 0.9% NaCl solution. However, with the content of AGAM monomer increased in the composite,  $Q$  also decreased substantially and the level was much lower than that in the distilled water. The above results suggest that appropriate amount of zwitterionic and cationic functional monomer can improve the anti-salt properties of the SAPs.

#### Effect of FM on the water absorbency in $\text{CaCl}_2/\text{MgCl}_2$ solutions

In many cases, the SAPs was designed for the application in the field of agriculture or horticulture, thus it is more applicable to evaluate the swelling



**Figure 6** Effect of content of functional monomer on water absorbency in 0.9% NaCl solution. Reaction condition is the same as in Figure 2.



**Figure 7** Effect of weight ratio of different functional monomer to total monomers on water absorbency of superabsorbent composites in  $\text{CaCl}_2/\text{MgCl}_2$  solution. Reaction conditions: reaction temperature,  $75^\circ\text{C}$ ; weight ratio of crosslinker and initiator to the monomers is 0.05 wt % and 0.4 wt %, respectively; concentration of monomers in the feed is 17%.

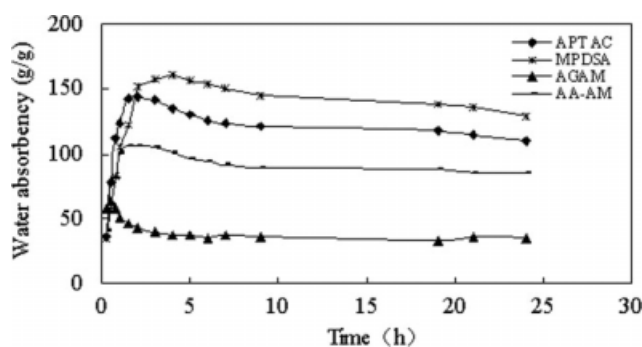
properties in the soil solution rather than in 0.9% NaCl solution. However, the composition of the soil solution was mainly comprised of divalent ions, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and the concentration of different ions varied depending on different environment and locations, which make it hard to standardize the characterization method of the absorbency in the soil. Here, the mixture of  $60 \text{ mg L}^{-1}$   $\text{CaCl}_2$  and  $30 \text{ g g}^{-1}$   $\text{MgCl}_2$  was selected as model solution to characterize the performance of different superabsorbents since the ionic strength of this mixed  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solution is similar to that of the soil solution in Beijing area.

Figure 7 is the evaluation of FM on the water absorbency in the mixture solution of  $60 \text{ mg L}^{-1}$   $\text{CaCl}_2$  and  $30 \text{ g g}^{-1}$   $\text{MgCl}_2$ , in which the AA : AM is 1 : 3. It was found that the changing pattern of absorbency of the superabsorbent in  $60 \text{ mg L}^{-1}$   $\text{CaCl}_2$  and  $30 \text{ g g}^{-1}$   $\text{MgCl}_2$  is similar to that in distilled water and the 0.9% NaCl solution. However, in all of the cases,  $Q$  is lower than that in distilled water and much higher than that in the 0.9% NaCl solution. For the PAA-AM-based copolymer gel, the  $Q$  is  $148 \text{ g g}^{-1}$  versus  $1050 \text{ g g}^{-1}$  in distilled water and  $62 \text{ g g}^{-1}$  in 0.9% NaCl solution. After adding 1% functional monomer, the  $Q$  of the SAPs reach  $179 \text{ g g}^{-1}$  in the  $60 \text{ mg L}^{-1}$   $\text{CaCl}_2$  and  $30 \text{ g g}^{-1}$   $\text{MgCl}_2$  solution versus  $1285 \text{ g g}^{-1}$  in distilled water and  $78 \text{ g g}^{-1}$  in 0.9% NaCl solution. The above results indicated that  $Q$  of the gels in distilled water is too high and it is too low in 0.9% NaCl solution,  $Q$  in the mixture solution of  $60 \text{ mg L}^{-1}$   $\text{CaCl}_2$  and  $30 \text{ g g}^{-1}$   $\text{MgCl}_2$  can reflect how much water the SAPs can absorb in the soil solution. This could be attributed to that both zwitterionic MPDSA and cationic APTAC are macromonomers with larger volume

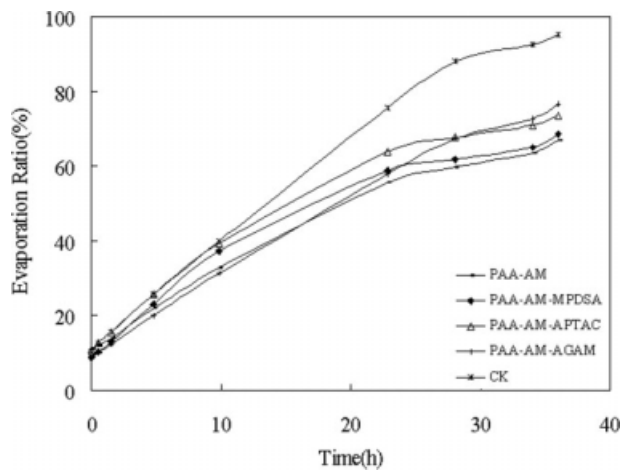
and relative lower charge density than AA, which make the polymers are not so sensitive as AA to the external divalent ions solutions. Meanwhile, adding of AGAM into the PAA-AM, the “crosslinking” point formed between the divalent ions and the active carboxyl groups of the AGAM in the polymer matrix, which greatly reduced its water absorbency in the divalent ions solutions.

#### Effect of functional monomers on the swelling rate of SAPs

Swelling rate of superabsorbent is mainly determined by swelling ability, surface area, and density of the hydrogel. The swelling rates of different kinds of functionalized superabsorbent polymers in the mixture of  $60 \text{ mg L}^{-1}$   $\text{CaCl}_2$  and  $30 \text{ mg L}^{-1}$   $\text{MgCl}_2$  have been measured and the results were shown in Figure 8. It can be seen, swelling process quickly reached saturation state in less than 2 h for the AA-AM copolymers. As time goes on, the water absorbency of the AA-AM copolymers is remained around  $105 \text{ g g}^{-1}$ . For the AA-AM-APTAC terpolymer, the water absorbency attains its maximum point at  $144 \text{ g g}^{-1}$  in 2 h. For AA-AM-MPDSA terpolymer, the water absorbency achieves its peak absorbency  $161 \text{ g g}^{-1}$  around 4 h, and the AA-AM-AGAM terpolymer is at  $63 \text{ g g}^{-1}$  in 0.5 h. It is obviously that the AA-AM-APTAC terpolymer gel has the fastest swelling rate among these superabsorbent polymers. After the peak point, saturation state of the AA-AM-APTAC, AA-AM-MPDSA, and AA-AM-based hydrogels change slightly, while the AA-AM-AGAM terpolymer was separated from absorbent water into two phases quickly and kept a lower swelling capacity later on. The interpretation could be adding of APTAC and MPDSA into the SAPs, the stronger affinity of the gels toward water



**Figure 8** Swelling rate of different functional superabsorbent composites in  $\text{CaCl}_2/\text{MgCl}_2$  solution. Reaction conditions: reaction temperature,  $75^\circ\text{C}$ ; weight ratio of functional monomer, crosslinker and initiator to the total monomers is 1 wt %, 0.05 wt %, and 0.4 wt %, respectively; concentration of monomers in the feed is 17%.

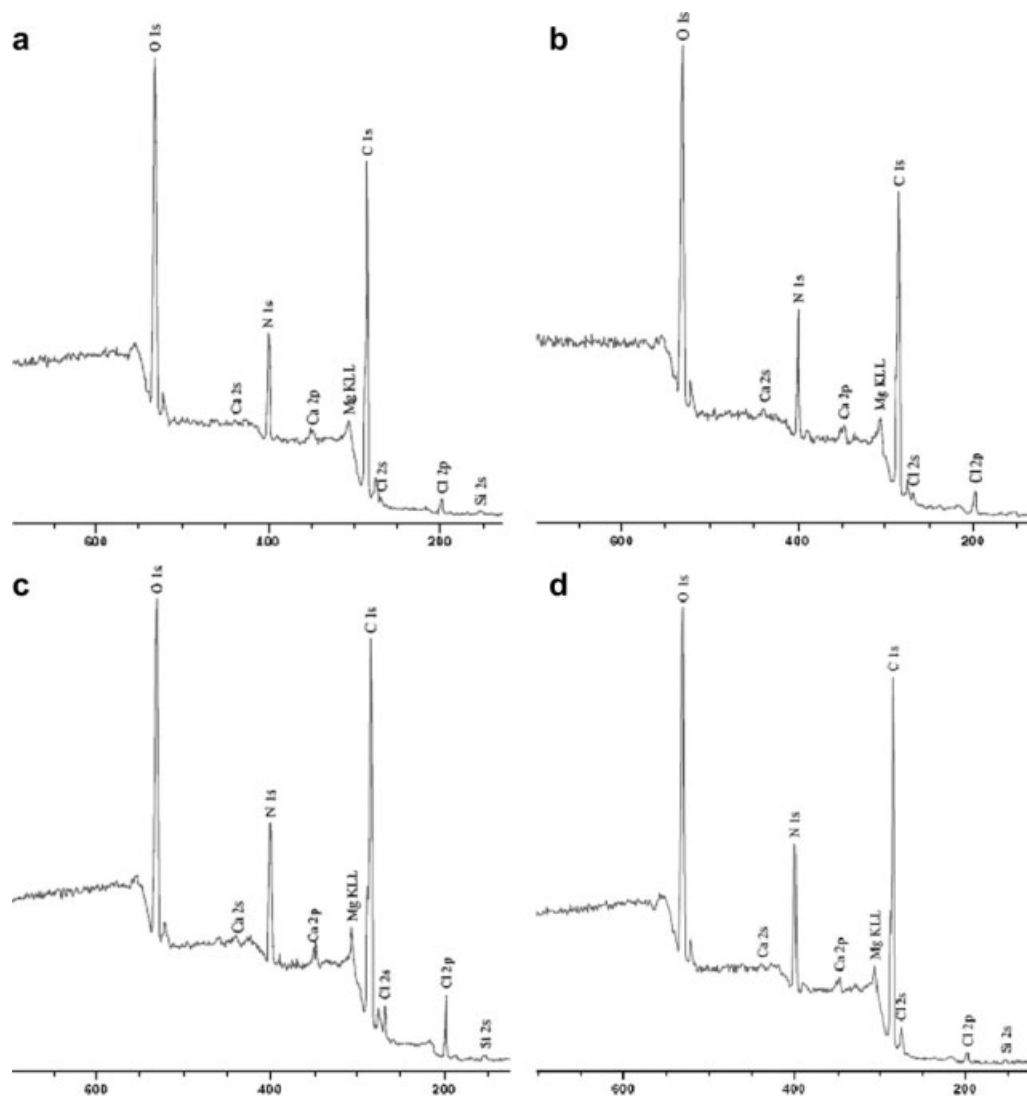


**Figure 9** Water retention of different superabsorbent composites in sandy soil. The experiment was tested at 40°C, the weight ratio of the superabsorbent to the soil is 0.5%. Reaction condition is the same as in Figure 8.

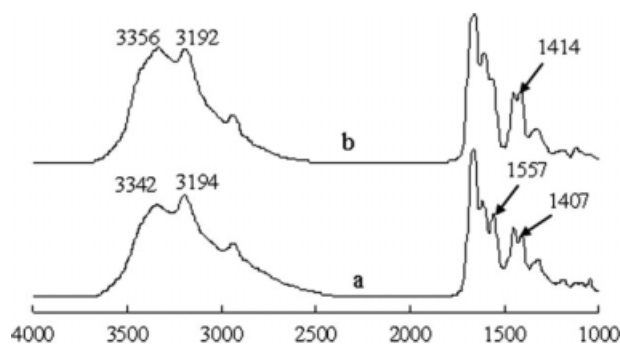
make the swelling rate increased. However, as the anionic AGAM introduced into the polymer, the formed physical crosslinking between the matrix making the swelling rate reduced.

#### Water retention behavior of the SAPs in sandy soil

Besides the water absorbency and the swelling rate, another important parameter to characterize the superabsorbent polymers was its water holding capacity in the soil, especially its effective utilization of moisture in arid and desert regions. It has been reported that superabsorbents gels used in agricultural field could increase water retention capacity of soil through reducing water losses from evaporation and infiltration. In this section, we studied the influence of different hydrogels on the water evaporation of sandy soil at 40°C, and the results are shown in Figure 9.



**Figure 10** XPS spectra of  $\text{Ca}^{2+}$ ,  $\text{MgCl}_2^{+}$ , absorbed on (a) PAA-AM, (b) PAA-AM-MPDSA, (c) PAA-AM-APTAC, and (d) PAA-AM-AGAM in the fully binding energy range. Reaction condition is the same as in Figure 8.



**Figure 11** FTIR spectra of PAA-AM-APTAC (a) dried sample, (b) sample which had been immersed in the mixture solution of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . Reaction condition is the same as in Figure 8.

It was obvious that after adding SAPs gel into the sandy soil, the water evaporation ratios were lower than that without superabsorbents in the sandy soil. The  $E_r$  of the sandy soil reached 95.3% after 36 h, however, the  $E_r$  of the soil added with the AA-AM-MPDSA, AA-AM-APTAC, and AA-AM-AGAM terpolymer were 68.5%, 73.6%, and 76.7% under the same period of time, respectively. There is no obvious difference in terms of water retention capacity of soil between the AA-AM-MPDSA and AA-AM-APTAC polymers. The above results confirmed that the SAP gels improved the water retention capacity in the soil.

#### Mechanism of the absorbency for the different SAPs

To investigate the mechanism of swelling properties behind adding different charged functional polymers, XPS was applied for chemical analysis. From Figure 10, it showed that the binding energy of the O (1s), N (1s), and C (1s) were around 530 eV, 400 eV, and 280 eV, respectively. The binding energy of Ca, Mg, and Cl were also displayed in the spectrum indicated that  $\text{CaCl}_2$  and  $\text{MgCl}_2$  were attached on the polymer matrix.<sup>9</sup> In addition, the area of binding energy for the AGAM-based terpolymer was lower than that of APTAC and MPDSA polymers. The above results proved that metal ions in the solution could be adsorbed onto the polymeric gels, and the anionic-based polymer showed inferior capability in adsorbing the metal ions.

Besides XPS analysis, the FTIR was used to investigate the three kinds of samples which had been immersed in the mixture solution of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . It was found from Figure 11 that the absorption band at  $1414\text{ cm}^{-1}$ , the symmetric stretching of  $-\text{COO}^-$  increased sharply.<sup>23</sup> The results demonstrated that part of  $-\text{COOH}$  group in the matrix

was chelated by the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the solution, and the  $-(\text{COO})_2\text{Ca}$  and  $-(\text{COO})_2\text{Mg}$  formed. The increased crosslinking points make the swelling capacity in the  $\text{CaCl}_2$  and  $\text{MgCl}_2$  solution was lower than that in the distilled water.

#### CONCLUSIONS

Three functional superabsorbent polymers containing the MPDSA, APTAC, and AGAM have been successfully synthesized by solution free radical terpolymerization with AA and AM. On the basis of the optimized reaction condition, such as degree of neutralization, content of initiator, and crosslinker, the water absorbency of three superabsorbent polymers were characterized and compared in distilled water, 0.9 % NaCl solution, and mixture solution of  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . The water absorbency was increased to 20% as appropriate amount of zwitterionic monomer and cationic monomer were attached on the gels compared to that of poly (AM-co-AA) in all testing solutions. Meanwhile, the swelling rate was also accelerated when the APTAC and MPDSA monomer was introduced into the polymeric gel, and the initial swelling rate of the gel containing APTAC was higher than that containing MPDSA. The influence after adding three functional monomers in the divalent ions solution may results from change of the interactions between the functional group with AA and AM. However, as anionic functional monomer was introduced into the hydrogels, the swelling property was decreased dramatically due to formed crosslink point. Introducing the functional monomers in the polymer gels demonstrated good water retaining in the sandy soil.

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