

Preparation and Properties of a Slow Release NP Compound Fertilizer with Superabsorbent and Moisture Preservation

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ABSTRACT: A slow-release NP compound fertilizer with superabsorbent and moisture preservation was prepared by carboxyl methyl starch, acrylic acid, ammonia, urea, diammonium phosphate, and so on. The effects of the amount of initiator, crosslinker, and the degree of neutralization of acrylic acid on water absorbency were investigated and optimized. The product was characterized by FTIR, ICP, and element analysis, and the results showed that the product contained 22.6% nitrogen element and 7.2% phosphorus (shown by P_2O_5) element. Its water absorbency was about 85

($g \cdot g^{-1}$) times its own weight in tap water. We also investigated the water retention property of the product and the slow release behavior of N and P in the product. The results showed that the product had a good water retention capacity and slow release property. The mechanism of the release of N and P in water was also investigated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2132–2138, 2005

Key words: hydrogels; swelling; slow release fertilizer; moisture preservation; gels

INTRODUCTION

As we all know, fertilizers and water are the main factors that limit the production of agriculture, so it is very important to use the water resource and fertilizer nutrients efficiently and to keep the equilibrium of fertilizer nutrients in crops. However, about 40–70% of nitrogen and 80–90% of phosphorus of the applied normal fertilizers was lost to the environment and could not be absorbed by crops, which not only causes large economic and resource losses but also very serious environmental pollution.^{1–4} A great deal of research has shown that slow or controlled release technology could effectively check these problems, avoiding or decreasing the loss of normal fertilizers and the environmental pollution.^{5,6} At the same time, many farmlands in the world are short of water during the dry season, and most of the rainwater was lost in the rainy season because the water resource could not be used efficiently. Superabsorbent polymers, a new functional polymer material, can absorb a large amount of water and the water is hardly removed even under pressure, and so it has been widely used in agriculture.^{7–9} There are many reports about slow release fertilizers and superabsorbent polymers, but there are few reports about slow release fertilizers

with superabsorbent and moisture preservation (SRF-SMP). So on the basis of the above background and our previous studies on superabsorbent polymers,^{10–12} in this study we prepared a new type of slow release nitrogen (N) and phosphorus (P) compound fertilizer with superabsorbent and moisture preservation, which not only has slow release properties but also could absorb water and preserve the soil moisture at the same time; moreover, the slow release and water retention property in soil were also studied.

EXPERIMENTAL

Materials

Acrylic acid (AA) and carboxyl methyl starch (CMS) were all industrial grade; the others were all analytical grade. All the materials used were available from commercial sources.

Preparation of SRFSMP

The reaction was conducted in a flask equipped with a mechanical stirrer, a condenser, and a thermometer. Proper amounts of CMS, urea, and diammonium phosphate were added into the flask after being comminuted and milled through a 90-mesh screen, and then 60 mL cyclohexane was added into the flask; the crosslinker (epichlorohydrin) was added into the flask after the mixture had been stirred for 5 min. The mixture was filtered to remove the cyclohexane after

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being stirred for 1 h at 40°C and then was extruded and incised to be made into granules. The granules were then dried at 60°C.

Five grams of dry granules obtained above was added into the mixed solution of partly neutralized (by ammonia) acrylic acid, *N,N'*-methylenebisacrylamide (NNMBA) solution, and potassium persulphate solution, and then transferred into a flask equipped with a mechanical stirrer, a condenser, and a thermometer after being soaked for 30 min. A certain amount of cyclohexane and sorbite anhydride monostearic acid ester (Span-80) was added into the flask. The mixture was filtered to remove the cyclohexane after being stirred for 1 h at 70°C, and then the last granule product was obtained.

Characterization of SRFSMP by FTIR

The SRFSMP was characterized by a Fourier-transform infrared (FTIR) spectrophotometer (American Nicolet Corp., model 170-SX). The dry sample of SRFSMP was comminuted and ground with dried KBr powder. The KBr disc was dried again and subjected to the FTIR spectrophotometer.

Component analysis of SRFSMP

Contents of nitrogen and phosphorus in the SRFSMP were determined by an element analysis instrument (Germany Elemental Vario EL Corp., model 1106) and inductively coupled plasmas (ICP) instrument (American TJA Corp., model IRISER/S). The results showed that the contents of nitrogen and phosphorus (shown by P₂O₅) in the SRFSMP were 22.6 and 7.2%, respectively.

Water absorbency of SRFSMP in tap water

The accurately weighted SRFSMP (about 0.5 g) was immersed into a certain amount of tap water and allowed to soak at room temperature for 60 min. The swollen SRFSMP was filtrated through a 80-mesh sieve to remove nonabsorbed water and weighed. The water absorbency was calculated using the following equation:

$$WA = M/M_0 - 1 \quad (1)$$

Here M and M_0 denote the weight of the water swollen SRFSMP and the weight of the dry SRFSMP, respectively, and WA is the water absorbency per gram of dried SRFSMP.

Time dependence of WA

To establish how long it will take for the SRFSMP to reach swelling equilibrium in different solutions, the following experiment was conducted: 0.50 g SRFSMP

was added into a plastic beaker, which had been filled with 200 mL distilled water, tap water, and 0.9% NaCl solution, respectively. The experiment conducted in the same solution was carried out in eight different plastic beakers, which were filtrated and weighed at 10, 20, 30, 40, 50, 60, 70, and 80 min after the addition of SRFSMP, respectively. WA was calculated using eq. (1).

Slow release behavior of SRFSMP

SRFSMP (0.50 g) was added into a tapered bottle, which had been filled with 200 mL distilled water, tap water, and 0.9% NaCl solution respectively. The contents of N and P in the aqueous solution was determined, respectively, at 0.5, 1, 3, 6, 10, 15, 24, and 48 h since the addition of SRFSMP, from which the release curves of N and P in different water absorbency SRFSMP were obtained.

To study the slow release behavior of SRFSMP in soil, the following experiment was carried out: 1 g SRFSMP was well mixed with 180 g dry soil (below 2 mm in diameter) and kept in a 200-mL plastic beaker properly covered and incubated for different periods at room temperature. Throughout the experiment, the soil was maintained at 40% water-holding capacity by weighing and adding distilled water if necessary, periodically. Blank and control experiments, viz., without any fertilizers and with untreated urea and diammonium phosphate (the total contents of N and P were the same as that of 1 g SRFSMP), respectively, were also carried out. The soils were extracted by 0.01M CaCl₂ solution¹³ and 0.05M NaHCO₃ solution,¹⁴ respectively, after each incubation period (1, 2, 5, 10, 15, 20, 25, and 30 days) and estimated for the contents of N and P. The contents of N and P were estimated by the Kjeldahl method of distillation¹⁵ and ICP instrument, respectively.

Largest water-holding ratio of the soil

SRFSMP (2 g) was well mixed with 200 g dry soil (below 2 mm in diameter) and kept in a PVC tube of 4.5 cm diameter; the bottom of the tube was sealed by nylon fabric (with the aperture of 0.076 mm) and weighed (marked W_1). The soil samples were slowly drenched by tap water from the top of the tube until the water seeped out from the bottom. The tube was weighed (marked W_2) again when there was no seeping water at the bottom. A control experiment, viz., with no SRFSMP, was also carried out. The largest water-holding ratio ($W\%$) of the soil was calculated using the following equation:

$$W\% = (W_2 - W_1) \times 100 / (W_2 - W_1 + 200) \quad (2)$$

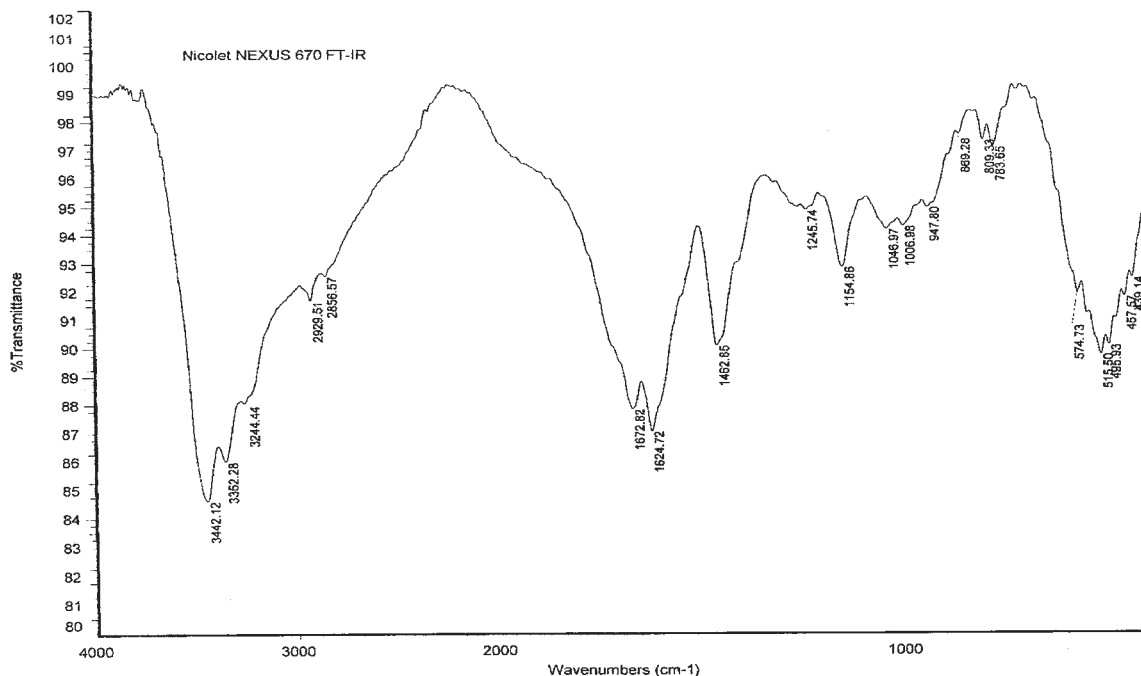


Figure 1 FTIR spectrum of SRFSMP.

Measurement of the water retention of SRFSMP in soil

SRFSMP (2 g) was well mixed with 200 g dry soil (below 2 mm in diameter) and kept in a plastic beaker and then 200 g tap water was slowly added into the beaker and weighed (marked W_1). Control experiment, viz., with no SRFSMP, was also carried out. The beakers were placed in our lab at room temperature and were weighed every 5 days (marked W_i); the observation was obtained after a period of 30 days. The water evaporation ratio ($W\%$) in soil was calculated using the following equation:

$$W\% = (W_1 - W_i) \times 100/200 \quad (3)$$

RESULTS AND DISCUSSION

FTIR analysis of SRFSMP

Figure 1 showed the infrared spectrum of SRFSMP from which we could find the characteristic peaks of polyacrylate (2,929 and 2,856 cm^{-1}) and CMS (577, 763, and 860 cm^{-1}), additionally, the characteristic peaks of urea were observed at 3,442, 3,352, 1,672, 1,624, and 1,462 cm^{-1} ,¹⁶ and the peaks at 1,154 and 947 cm^{-1} corresponded to the characteristic peaks of H_2PO_4^- .¹⁷ We could not find the characteristic peaks of polyacrylamide and those of the reaction products of CMS and phosphate, therefore, we might confirm that urea did not react with acrylic acid and CMS did not react with phosphate either. These results showed that the SRFSMP was the admixture of polyacrylate,

CMS, urea, and phosphate, and the urea and phosphate existed as themselves.

Effect of the amount of initiator on WA of SRFSMP in tap water

Figure 2 showed the effect of the amount of initiator on WA of SRFSMP. Evidently, WA increased with the increase of $W_{(\text{initiator})}/W_{(\text{AA})}$ at first and then decreased. It was expected that the decomposition velocity of the initiator was slow when the amount of initiator was small, and this resulted in the slow ini-

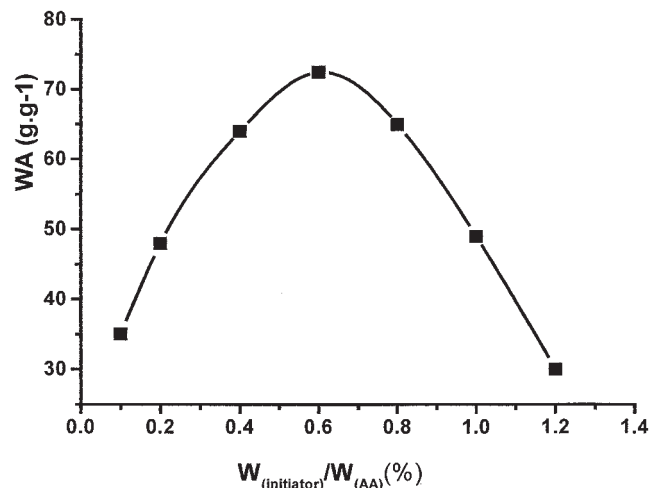


Figure 2 Amount of initiator dependence of WA of SRFSMP in tap water.

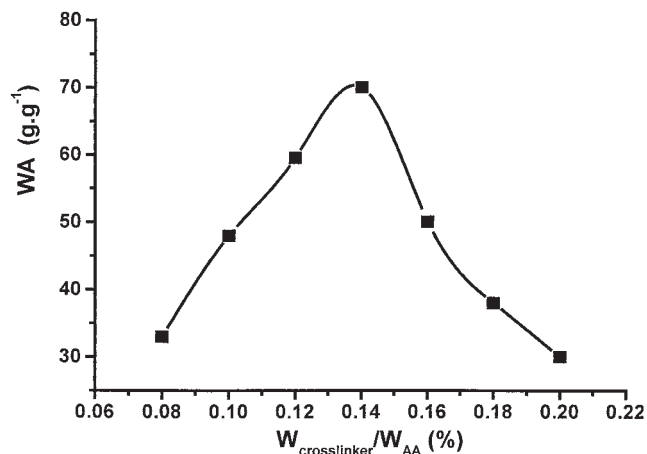


Figure 3 Amount of crosslinker dependence of WA of SRFSMP in tap water.

tiation and polymerization reaction; the residual monomers in the product increased during the same reaction time, so WA was low. But the collision between monomer free radicals would increase with the increase of the amount of initiator, and so the rate of polymerization would be increased with that. A high rate of polymerization would result the increase of the content of oligomers in SRFSMP, viz., the soluble parts in SRFSMP increased. So WA decreased with a further increase of $W_{(\text{initiator})}/W_{(\text{AA})}$.

Effect of the amount of crosslinking agent on WA of SRFSMP in tap water

Figure 3 showed that, with the increase of the amount of crosslinker, WA reached maximum at $W_{\text{crosslinker}}/W_{\text{AA}} = 1.4 \times 10^{-3}$. As we know, the greater the amount of crosslinker used, the higher crosslinking density of the hydrogel and the lower soluble part of the polymer in SRFSMP. When $W_{\text{crosslinker}}/W_{\text{AA}}$ was less than 1.4×10^{-3} , the soluble part of the polymer in SRFSMP would decrease with the increase of $W_{\text{crosslinker}}/W_{\text{AA}}$, and this led to the increase of WA of SRFSMP. When the $W_{\text{crosslinker}}/W_{\text{AA}}$ was above 1.4×10^{-3} , the crosslinking density of the hydrogel in SRFSMP would be higher with the increase of $W_{\text{crosslinker}}/W_{\text{AA}}$, the hydrogel would be more difficult to swell by water, and this would result in the decrease of WA of SRFSMP; this phenomena accorded with the theory of Flory.¹⁸

Effect of neutralization degree of acrylic acid on WA of SRFSMP in tap water

The neutralization degree (ND) dependence of WA of SRFSMP was presented in Figure 4. ND was defined as the molar percentage of carboxyls in AA neutralized by ammonia. As shown in Figure 4, WA in-

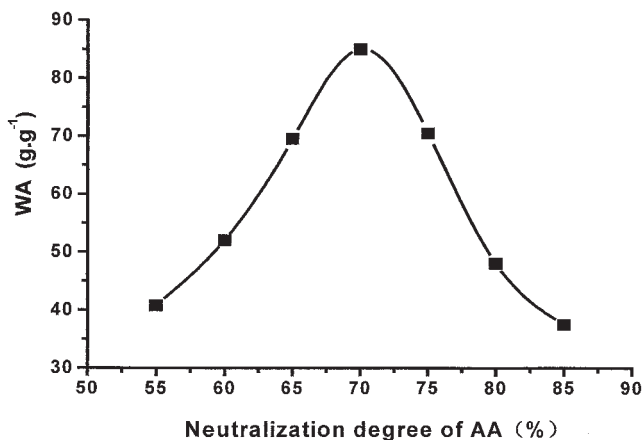


Figure 4 Neutralization degree dependence of WA of SRFSMP in tap water.

creased at first and then decreased gradually with the increase of ND and reached maximum at ND = 70%. It was expected that the activity of acrylic acid is higher than acrylate, when the ND was lower than 70%, the lower ND was faster than the rate of the polymerization, the content of the oligomers would increase, and the content of acrylate would decrease, so the soluble part increased and the electrostatic repulsion between the attached carboxylate anions decreased, so that the stretching extend of hydrogel network decreased, and this resulted in WA increasing with the increase of ND. It was expected that the activity of acrylic acid is higher than acrylate so the lower the ND was, the faster the polymerization rate was, and the high polymerization rate would result the increase of the content of oligomers (the soluble part) in SMUSMP. At the same time, the charge density of the network would increase with the increase of ND, and this would result the increase of the stretching extend of the hydrogel network, so it is easy to understand the increase of WA as the ND increased from 0 to 70%.

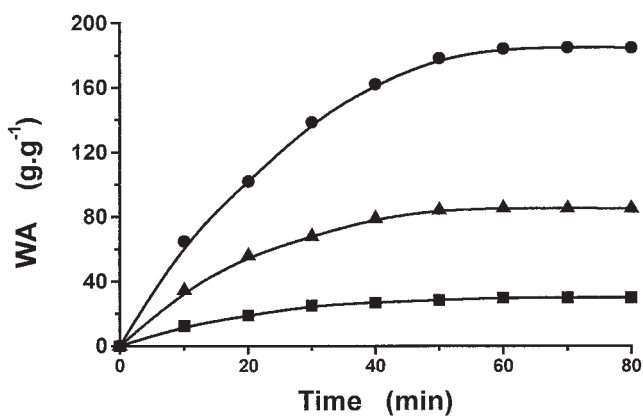


Figure 5 Time dependence of WA in different solutions.

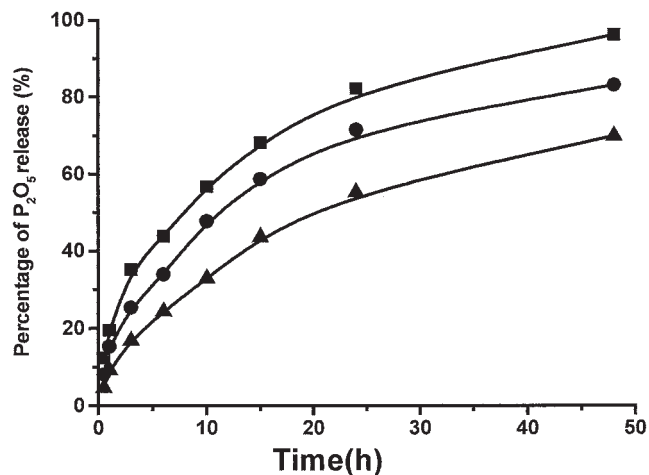


Figure 6 Release of P_2O_5 in SRFSMP with different water absorbency.

Time dependence of WA

The time required to reach swelling equilibrium for SRFSMP in different solutions was studied and the results were presented in Figure 5. The results indicated that the SRFSMP immersed in the three different solutions absorbed the maximum amount of water within 60 min and also indicated that the system had reached swelling equilibrium, because WA had reached a constant at this time; in other words, it will take about 60 min for the SRFSMP we prepared to reach swelling equilibrium in different solutions. The results also indicated that the properties of the solution had no or little influence on the time required to reach swelling equilibrium for SRFSMP.

Slow release behavior of SRFSMP

The slow release behaviors of the N and P in SRFSMP with different water absorbency were shown in Fig-

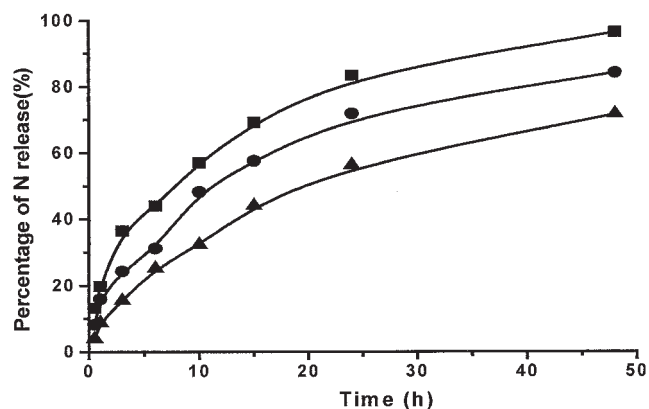


Figure 7 Release of nitrogen in SRFSMP with different water absorbency.

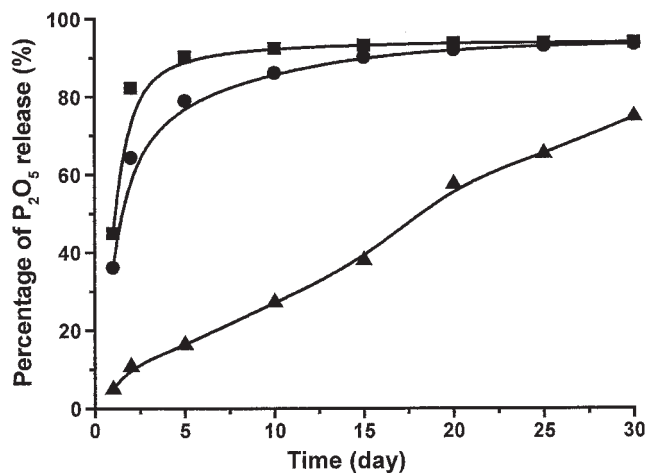


Figure 8 Release of P_2O_5 in SRFSMP in soil.

ures 6 and 7, respectively. All the curves were similar; the difference was that, the lower the WA, the lower the release rate. This was because CMS and ammonium-acrylate were all transformed into three-dimensional network polymers after the crosslinking reaction, and the small fertilizer molecules [urea and $(NH_4)_2HPO_4$] were encapsulated in the gridings of the network. The SRFSMP would be swollen by water when it was added into solutions; urea and $(NH_4)_2HPO_4$ were then dissolved in this part of water. At first, the water in solution constantly came into the network and did not come out before the emergence of the free water in the swollen network,^{19,20} which could exchange with the water in solutions through the mesh of the swollen network and formed a dynamic equilibrium. The urea and $(NH_4)_2HPO_4$ dissolved in the network would slowly diffuse into the solutions through the dynamic exchange. So the aperture size of the swollen network would determine the release rate of urea and $(NH_4)_2HPO_4$. As a result, the higher the WA of SRF-

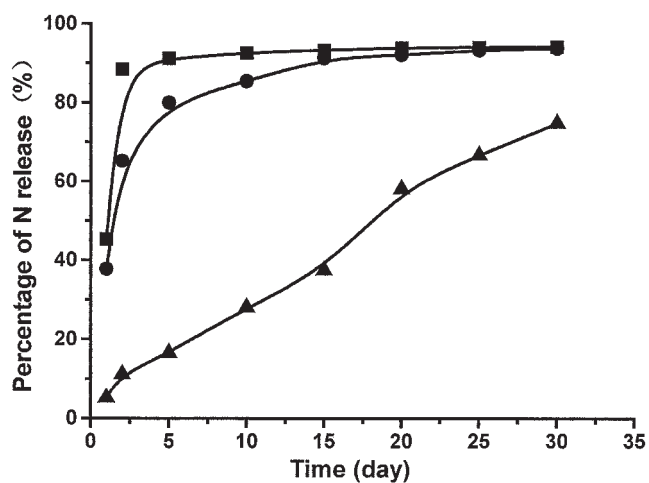


Figure 9 Release of nitrogen in SRFSMP in soil.

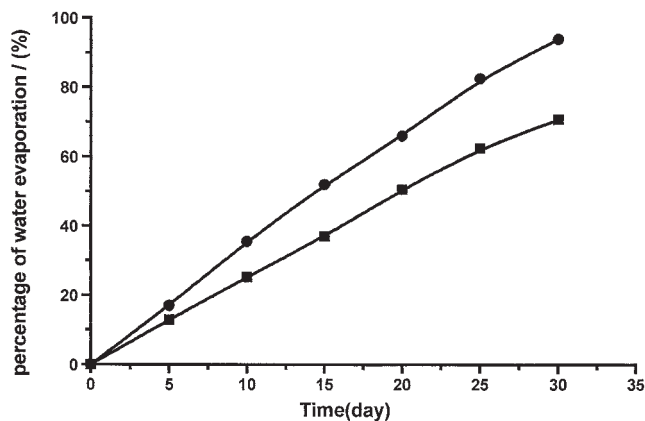
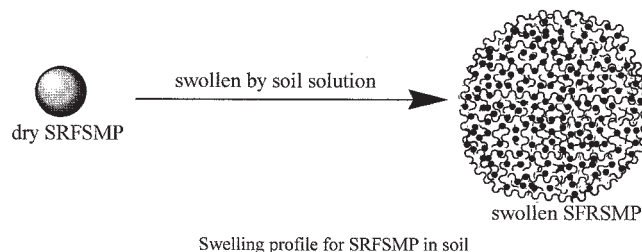


Figure 10 Water retention of SRFSMP.

SMP, the larger the aperture size, and the easier exchange of the water in and out the network, the higher the release rate.

Figures 8 and 9 show the slow release behaviors of N and P in soil. As shown in Figures 8 and 9, the N and P in normal fertilizers had released out more than 80 and 90% within 2 and 5 days, respectively, while the release rate of the fertilizers mixed with superabsorbent polymers decreased compared with normal fertilizers; this was in accordance with the results of Smith and Harrison²¹ but still was obviously higher than that of the SRFSMP we prepared. The N and P in SRFSMP only released 5.24 and 4.87% on the second day, respectively, lower than 15%, and did not rise above 75% on the 30th day. This was in accordance with the standard of slow release fertilizers of Committee of European Normalization (CEN)²² and also indicated that the SRFSMP had an excellent slow release property. As we know, urea and $(\text{NH}_4)_2\text{HPO}_4$ are easily dissolved in water, so they would quickly dissolve in the soil solution after being added into the soil, and the nutrient in them would be released out. While the superabsorbent polymers could absorb a lot of the water in soil, and translated into hydrogel, the urea fertilizer dissolved in the water in soil would be absorbed into it or on its surface. At the same time, this kind of fertilizer could be released out or desorbed with the exchange of minerals dissolved in the water in soil, and slowly came into the soil, therefore a slow release property was observed. The slow release

mechanism of SRFSMP in soil was that, the aperture of the three-dimensional network of the dry SRFSMP was constrictive, but the SRFSMP would be slowly swollen by soil solution and transformed into hydrogel after being added into soil, which would contribute to the increase of the aperture size of the three-dimensional network (as the following profile shows) so that the fertilizer in the network slowly defuses into the soil.



The fertilizers in the hydrogel network would be dissolved by the free water in the swollen hydrogel network. Before the emergence of the free water in the swollen network,^{19,20} the fertilizer solution in the network could not release out, and so do the fertilizers. But there existed a dynamic exchange between the free water in the hydrogel and the water in soil solution, the fertilizer would slowly release into the soil through the griddings of the swollen network with this kind of dynamic exchange. With the decrease of the fertilizer concentration in the free water, the fertilizers dissolved in the nonfree water of the hydrogel would diffuse into the free water with that, and then slowly released into the soil through the above dynamic exchange.

The largest water-holding ratio of the soil

The experimental results indicated that the largest water-holding ratio of the soil without SRFSMP was 30.56% and that of the soil with SRFSMP was 42.53%, about 12% higher than the former. This showed that the SRFSMP we prepared still had an excellent water absorbency in soil and could obviously improve the water-holding capacity of the soil, efficiently storing the rain or irrigation water, thus improving the utilization efficiency of the water resource. This was one of

TABLE I
Water Transpiration Rate and Content of the Soil With and Without SRFSMP

Time (days)	Water Transpiration Rate		Water content of soil	
	Without SRFSMP (%)	With SRFSMP (%)	(%) Without SRFSMP	(%) With SRFSMP
10	35.5	25.2	32.5	37.2
20	66	50.5	17	24.6
30	94	70.8	3	14.5

the advantages over the normal slow release fertilizers.

Water retention behavior of SRFSMP in soil

Figure 10 shows the water retention behavior of SRFSMP in soil. From this we could find that the water evaporation ratio in soil with SRFSMP was obviously lower than the soil without it. The water transpiration rate of soil with SRFSMP was about 10, 15.5, and 24% lower than the soil without SRFSMP on the 10, 20, and 30th day, respectively.

Table I shows the water transpiration rate and content of the soil with and without SRFSMP. The results show that the water content of the soil with SRFSMP was obviously higher than that of the soil without SRFSMP; the water content of the soil without SRFSMP was only 3% on the 30th day, while that of the soil with SRFSMP was 14.5%, about 12% higher than the former.

These results showed that the SRFSMP we prepared had excellent water absorbency, water retention, and moisture preservation capacity besides its slow release property. These were the significant advantages over the normal controlled release fertilizer, which always only had a controlled release property. The reason was that the superabsorbent polymer in SRFSMP could absorb a large quantity of water and let the water absorbed in it slowly release out with the decrease of the soil moisture. This let the water in the soil slowly evaporate so that it could be efficiently used, and the utilization efficiency of water was greatly improved. This could prolong irrigation cycles and reduce irrigation frequencies, strengthening the ability of crops to fight a drought. At the same time, we also observed that many granular structures would form in the soil after the addition of SRFSMP. It had been reported in the literature²³ that these clay granule structures contribute to stabilization of the soil structure, improve the aeration, permeability, and tillability of the soil, reduce soil packing and cracking, minimize soil crusting to prevent soil from hardening, and offer a favorable environment for crops to grow, so there would be a good potentiality in the drought-prone and desert areas.

CONCLUSION

A new type of slow release N and P compound fertilizer with superabsorbent and moisture preservation was prepared by carboxyl methyl starch, acrylic acid, ammonia, urea, diammonium phosphate, and so on. The product was characterized by FTIR, ICP, and element analysis, and the results showed that it contained 22.6% nitrogen element and 7.2% phosphor

(showed by P_2O_5) element, and the N and P in it were in the form of urea and $(NH_4)_2HPO_4$. Its water absorbency was about $85 (g \cdot g^{-1})$ times its own weight in tap water. The water-holding capacity experiment showed that the largest water-holding ratio was about 12% higher than that without it, and the water retention experiment showed that it still had excellent moisture preservation capacity in soil. The results of the slow release experiment showed that the release ratio of the effective nutrient in it was not above 75% on the 30th day. The product could not only efficiently improve the utilization efficiency of fertilizers but also the water resource.

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