Preparation and Properties of a Degradable Interpenetrating Polymer Networks Based on Starch with Water Retention, Amelioration of Soil, and Slow Release of Nitrogen and Phosphorus Fertilizer

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ABSTRACT: In this study, we aimed to develop a degradable nitrogen and phosphorus (NP) fertilizer with properties of slow release, water retention, and remediation of saline soil; the nitrogen and phosphorus was coated with starch/poly(acrylic acid-co-acrylamide) [poly(AA-co-AM)] superabsorbent (SAAmF) by reverse suspension radical copolymerization. The variable influences on the water absorbency were investigated and optimized. The results of the structure and morphology characterization of SAAmF show that poly(AA-co-AM) was grafted partly from the chain of starch, and the different contents of starch brought about a difference in the size of the three-dimensional net hole of the coating polymer. The property of water retention, the behaviors of slow release of nutrient, and the degradation of the SAAmF were evaluated, respectively, and the results revealed that the water transpiration ratio of soil with SAAmF was lower by approximately 8 percentage points than that of the blank test, about 60% nutrient was released from SAAmF by the 30th day, and 32 wt % of SAAmF with a content of starch of 20% was degraded after 55 days. Moreover, a considerable decrease in the conductivity was observed, which revealed a sharp reduction in the concentration of residual ions for the soil mixed with SAAmF. It may be inferred from these that the product seems to be a promising vehicle for the management of soils, including saline soils. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

In the past 40 years, agrichemicals such as nitrogen and phosphorus fertilizer have largely been used to ensure the increase in foodstuffs;[1] some serious environmental damages have been caused by the use of fertilizers, such as water entrofication and the destruction of near-shore marine ecosystems.[2]

Compared with common fertilizers in use, slow-release fertilizers (SRFs) have the advantages of decreasing a fertilizer's loss rate, supplying nutrient sustainably, lowering the application frequency, and minimizing potential negative effects induced by an overdose of common fertilizers. According to Shaviv and Mikkelsen,[3] SRFs are classified into following four types: (1) low-soluble inorganic materials, such as metal ammonium phosphates; (2) low-soluble and chemically or biologically degradable materials, such as urea–formaldehyde; (3) relatively soluble materials that decompose gradually in soil; and (4) water-soluble fertilizers controlled by physical barriers (e.g., coating and matrix formation).[4–6] Coated fertilizers are prepared by the coating of conventional fertilizers with various materials; this ensures the controlled release of nutrients to the

soil by diffusion through the pores or the coatings' erosion and degradation.[4–6] Recently, superabsorbents (polymers with a crosslinked three-dimensional network structure and an appropriate crosslinking degree) have been used as soil additives in agricultural and horticultural industries for the improvement of soil's physical properties, such as the water-holding capacity, nutrient retention of sandy soils, permeability, density, and structure of soil.[7–9] Superabsorbents improve the soil's aeration, prevent soil from hardening, cracking, and crusting. Wu et al.[10] prepared a double-coated nitrogen, phosphate, and potash compound fertilizer; its inner and outer coatings were chitosan and poly(acrylic acid)/diatomite-containing urea, respectively. These products have the properties of having good a slow release and water-retention capacity.

However, superabsorbents cannot be widely applied to the agricultural and horticultural industries because of their poor degradability and the generation of new pollution. Therefore, environmentally friendly, degradable superabsorbent materials are needed. Starch is a common polysaccharide that is used in many biomedical fields. Typically, it is considered to be

degradable and gelable in the presence of formaldehyde or borax.[11-13] Starch-based superabsorbents could be prepared by graft polymerization with acrylic acid (AA) or/and acrylamide (AM) with the chain of starch or interpenetration and *in situ* simultaneous crosslinking.

In this article, we report a novel and degradable coated slow-release compound, in which the nutrient was entrapped in a crosslinked starch matrix granule (SF), and the starch/poly(acrylic acid-*co*-acrylamide) [poly(AA-*co*-AM)] interpenetrating polymer networks (IPNs) were used as an outer coating [starch/poly(acrylic acid-*co*-acrylamide) superabsorbent (SAAmF)]. The optimized coating conditions, moisture preservation, behaviors of nutrient release, electrical conductivity reduction of saline–sodic soils, and the coating polymer's degradation were studied.

EXPERIMENTAL

Materials
AA was distilled at reduced pressure (boiling point = 293–294 K at 0.5 mmHg). Ammonium persulfate (APS) and N,N′-methylene bisacrylamide (MBA) were recrystallized with water and 95% ethanol, respectively. AM, corn starch, and diammonium phosphate were used without further purification. Test soil was collected from garden topsoil (0–20 cm). The concentration of organic matter in the soil was 22.2 g/kg, the concentration of alkaline hydrolyzed N was 61 mg/kg, the concentration of available P (P_2O_5) was 35 mg/kg, the available concentration of K (K_2O) was 112 mg/kg, the pH was 8.21, the volume weight was 1.33 g/cm^3, and the porosity degree was 51.8%.

Preparation of SFs
First, 2 g of starch was added to a beaker, and then, 1.5 mL of water saturated with borax was added and kept stirring at 80°C until a stiff paste was formed. Subsequently, diammonium phosphate (mass ratio of fertilizer to starch = 5 : 1) was added at 40°C. Finally, the paste was extruded, incised into SFs, and dried at 70°C.

Preparation of the NP Fertilizer Coated with Starch/Poly(AA-*co*-AM) (SAAmF)
Five grams of SFs obtained previously was immersed into a starch paste for 15 min; this contained 5 mL of AA partially neutralized with ammonia and certain amounts of AM (the mass ratios of starch to AA and AM was 15 wt %) and MBA, and APS (shown later in Table II). Then, the mixture was transferred into a flask equipped with a mechanical stirrer, a condenser, and a thermometer. Cyclohexane (200 mL) and 0.5 mL of sorbitan monooleate (Span 80) and poly(ethylene glycol) sorbitan monostearate (Tween 60) were added to the flask, respectively, which was kept stirring for 2 h at 70°C. Cyclohexane was removed from the mixtures by filtration. Then, the final product (SAAmF) was obtained.

Fourier Transform Infrared (FTIR) Spectroscopy
Starch and the coating polymer were pressed into a pellet with KBr and characterized by a Nicolet Nexus 670 FTIR spectrometer (Nicolet Instrument Co., USA).

Scanning Electron Microscopy (SEM) Measurement
Two SAAmF samples with different contents of starch were swollen completely in tap water at room temperature, and the coating polymer was peeled off carefully and freeze-dried with a Free-Zone 2.0 freeze dry system (LABCONCO, USA) for 15 h after the samples were frozen by liquid nitrogen to prevent the collapse of the porous structure. Then, the surface morphology of the xerogel was determined by a scanning electron microscope (SEM), JSM-5600LV SEM (JEOL Ltd., Japan).

Analysis of the Contents of Nitrogen and Phosphorus in SAAmF
The content of nitrogen in SAAmF was determined by an elemental analysis instrument, model 1106 (Germany Elemental Vario EL Corp., Germany) and was determined to be 8.28%. The content of phosphorus was determined by a spectrophotometer, model 722 (Third Analysis Instrument Corp. of Shanghai, China).[11] One gram of SAAmF was added to a beaker and nitrified with 20.0 mL of concentrated nitric acid overnight. The solution was boiled until its volume was 10.0 mL, and then, its volume was adjusted to 250 mL in a 250-mL volumetric flask. Finally, 2.50 mL of supernatant was taken out and tested with the spectrophotometer. The results show that the content of phosphorus in SAAmF was 9.03%.

Water Absorbency (WA) Measurements
The SAAmF weighed previously was immersed in tap water where the mass proportion of the sample to water was about 1 : 1000. Swelling continued until a constant weight was reached. WA was calculated by the following equation:

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

WA is expressed in grams of water retained in the swollen SAAmF granules per gram of dried SAAmF and M and M_0 denote the weights of the swollen and dry samples, respectively.

Release Behavior of SAAmF in Soil
The following experiment was carried out to study SAAmF's release behavior of nitrogen and phosphorus (P_2O_5) in soil. One gram of SAAmF was mixed with 200 g of dry soil (<30 mesh) and kept in a 250-mL glass beaker; then, 120 mL of distilled water was added to SAAmF, and this mixture was incubated for different periods of time at room temperature. Proper amounts of diammonium phosphate and urea were also mixed with the same amount of soil and incubated for the same period at room temperature. In the control tests, the total quantity of nutrition was kept same in 1 g of SAAmF. The soil in the beaker was maintained at a 30% water-holding capacity. The remaining granules in the soil were picked out and washed with distilled water and then dried overnight at room temperature after different incubation periods (1, 2, 3, 5, 8, 10, 15, 20, 25, and 30 days). The contents of nitrogen and phosphorus (P_2O_5) contained in the granules were determined by elemental analysis and a spectrophotometer mentioned previously, respectively. The accumulated release percentage (RP) was calculated with the following expression:[14]

$$RP(\%) = 250 \times C_i/1 \times C \times 100\% \qquad (2)$$

where C_i is the concentration of nitrogen or phosphorus in the remaining granules at different times (g/mL) and C is the content of nitrogen or phosphorus in the primary sample.

Table I. Experimental Control Factors (F1, F2, F3, F4, and F5) and Their Levels

Control factor	Level 1	Level 2	Level 3	Level 4
n_{AM}/n_{AA} (F1)	0.2	0.3	0.4	0.5
n_{APS}/n_{AA+AM} (%; F2)	0.13	0.16	0.19	0.22
n_{MBA}/n_{AA+AM} (%; F3)	0.047	0.07	0.093	0.117
ND (%; F4)	60	65	70	75
Temperature (°C; F5)	55	60	65	70

Water Retention Measurement

Two grams of SAAmF was mixed with 180 g of dry soil (<30 mesh) in a glass beaker; then, it was covered with another 20 g of dry soil, and 200 mL of tap water was slowly added to the beaker. The beaker and its contents were weighed (W_1). A control experiment without SAAmF was also carried out. The beakers were placed in the laboratory at room temperature (in summer, the daily maximum temperature was 37°C, and the temperature difference between day and night was up to 15°C) and weighed every 3 days (W_i). Observation was done after a period of 21 days. The water evaporation ratio [W (%)] in soil was calculated with the following expression:

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

Degradation of Starch/Poly(AA-co-AM) Superabsorbent in Soil

The degradation of the superabsorbent was monitored by the dry weight loss. starch/poly(AA-co-AM) superabsorbents with different contents of starch, which were the same as those used in the previous experiment, were prepared in a tube. They were cut into disks and then dried. After weighing, the dried disks (ca. 4 mm in diameter and 3 mm in thickness) were swollen completely in tap water and buried 30 cm beneath the surface of the garden soil at ambient temperature (in summer, the daily maximum temperature was 37°C, and the day and night temperature difference was up to 15°C). The soil aeration was kept. After 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, and 55 days, respectively, the disks were taken out, washed carefully with distilled water, and vacuum-dried to a constant weight. The percentage degradation (PD) of the superabsorbents was calculated from the following equation:

$$PD\,\% = (W_0 - W_i)/W_0 \times 100 \qquad (4)$$

where W_0 and W_i are the weights of the superabsorbent disks before and after degradation, respectively.

RESULTS AND DISCUSSION
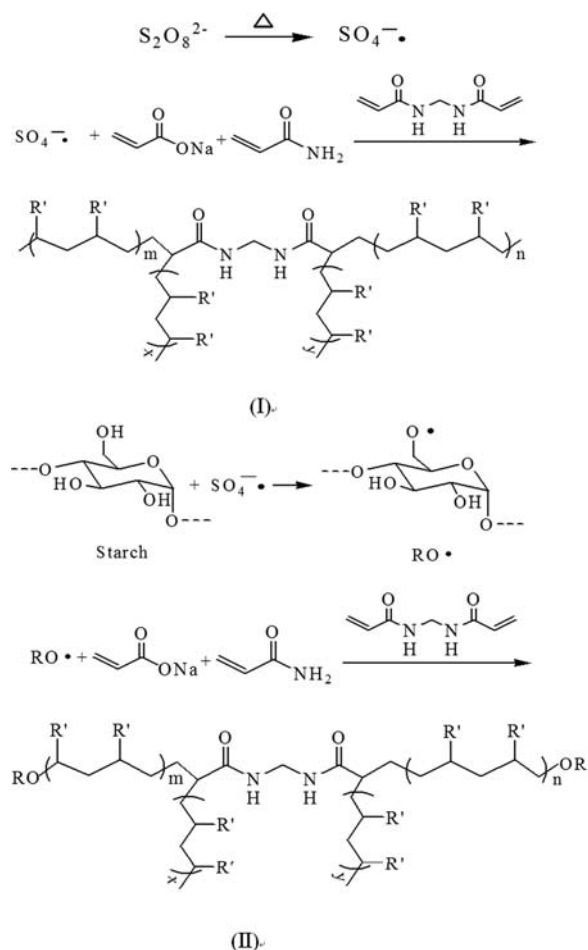
Optimization of the Copolymerization Conditions

The Taguchi method, which is a powerful experimental design tool developed by Taguchi, was used to optimize the variable influences on WA of the SAAmF. The parameter design is the key step in the Taguchi method in achieving high quality without an increase in cost. This design of the Taguchi method generally includes the following steps: (1) identification of the objective of the experiment, the quality characteristics (performance measure), and its measurement systems as well as the factors that may influence the quality characteristics and their levels; (2) selection of the appropriate orthogonal array and assignment of the factors at their levels to the orthogonal array; (3) conduction of the test described by the trials in the orthogonal array; (4) analysis of the experimental data with the analysis of variance to see which factors are statistically significant and the determination of the optimum levels of the factors; and (5) verification of the optimal design parameters through a confirmation experiment.[15] The same process was adopted in this article.

There existed a maximum WA that was dependent on the content of AM (defined as the monomer unit molar ratio of AM to AA, n_{AM}/n_{AA}), initiator APS (defined as the molar ratio of APS to the comonomers unit of AA and AM, n_{APS}/n_{AA+AM}), crosslinker MBA (defined as the molar ratio of MBA to the monomers of AA and AM, n_{MBA}/n_{AA+AM}), neutralization degree (which was defined as the molar percentage of COO^- groups in AA neutralized by ammonia), and temperature of reaction.[16] These parameters were varied at four levels, as shown in Table I, which were chosen on the basis of the preliminary experiments. The amount of starch (determined as the mass percentage of starch in the mass of comonomers AA and AM, w_{starch}/w_{AA+AM}) was chosen to be 15 wt %.

An orthogonal array with four levels and five factors is shown in Table II. Each row in the array represents a trial condition with the factor levels, which are indicated by the numbers in the row. The columns correspond to the factors specified in this study, and each column contains level 1, 2, 3, and 4 conditions. According to Table II, 16 groups of tests were carried out, WA was measured, respectively, and the results are shown in Table II as well. The optimized circumstances and the contribution of each factor were obtained by analysis. It should be emphasized that the interaction between the factors was neglected. The optimized conditions for the highest WA, 81 g/g, were a temperature of 60°C, a content of APS of 0.19%, a content of MBA of

Table II. Experimental Layout of an L16 Orthogonal Array According to Taguchi's Suggestion and the Experimental Results for WA

									Trial number							
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
F1	1	1	1	1	2	2	2	2	3	3	3	3	4	4	4	4
F2	1	2	3	4	1	2	3	4	1	3	4	5	1	2	3	4
F3	1	2	3	4	2	1	4	3	3	4	1	2	4	3	2	1
F4	1	2	3	4	3	4	1	2	4	3	2	1	2	1	4	3
F5	1	2	3	4	4	3	2	1	2	1	4	3	3	4	1	2
WA	36	40	57	51	67	51	81	64	50	31	52	47	75	67	48	37

Scheme 1. Schematic diagrams of the copolymerization of AA and AM (I) and the graft copolymerization of AA and AM from starch, in which R' = CO$_2$H or CONH$_2$.

0.117%, a content of AM of 0.3 (g/g), and a neutralization degree of 60%, respectively. It was found that the effect of the four factors on WA was similar to that reported in a previous article[16] and so is not further explained here.

FTIR Analysis of the SAAmF

The superabsorbent consisted of the rigid framework of starch together with the flexible copolymer chains of poly(AA-co-AM) and possessed the characteristic of absorbing a large amount of water, which was hardly removed, even under pressure. The initiator APS was used to initiate the copolymerization of AA and AM. Graft copolymerization was triggered from the chain of starch simultaneously, and the starch-g-poly(AA-co-AM) graft copolymer was generated. The mechanisms of the random and graft copolymerization reactions are shown in Scheme 1. For the reason that SAAmF may have been an IPN composed of crosslinked starch, poly(AA-co-AM), and starch-graft-poly(AA-co-AM), this endowed the coating polymer with a high strength and partial degradability.

Figure 1(A) shows the infrared spectrum of starch with a characteristic absorption band at 3215–3558 cm^{-1}, which corre-

sponded to the stretching vibration of O—H (carbons 2, 3, and 6). The band was wide and gentle because of free and associated hydroxyl groups generated by hydrogen bonding. Copolymerization brought groups of carboxylic and amide groups into the polymer, which increased the intramolecular and intermolecular hydrogen bonding, so the band became sharper, and there was a positive shift from 3215 to 3247 cm^{-1}, which stemmed from a formation of intermolecular hydrogen bonding between starch and poly(AA-co-AM) and a negative shift from 3558 to about 3500 cm^{-1} due to the decrease in content of free hydroxyl groups, as shown in Figure 1(B). The band at about 3125.62 cm^{-1}, shown in Figure 1(B), was assigned to that of N—H and confirmed the introduction of NH groups after copolymerization.[17] The peak observed at 2930.25 cm^{-1} [Figure 1(A)] corresponded to the stretching vibration of saturated C—H groups, which shifted from 2930.25 to 2872.40 cm^{-1} [Figure 1(B)] due to the addition of grafting polymer chains. The characteristics for the saccharide structure of starch were absorption bands appearing at 1649.11 and 1159.07–992.53 cm^{-1}, as shown in Figure 1(A), which could be assigned to symmetric and asymmetric stretching vibrations of the C—O—C bridge, respectively. It was evident that a stronger and wider peak appearing at about 1658.70 cm^{-1}, shown in Figure 1(B), was due to the symmetric stretching vibration of the C—O—C bridge, which was overlaid with the stretching vibration of C=O (amide I). At the same time, the multiplet observed at about 1117.44 cm^{-1}, as shown in Figure 1(B), may have corresponded to the asymmetric stretching vibration of the C—O—C group of carbon 6. This fact, together with the new peak appearing at 1293.62 cm^{-1}, corresponded to its symmetric stretching vibration and implied a successful O-site grafting polymerization reaction.[18] The bending vibration absorption peak of the C—O—C group, appearing at about 541 cm^{-1} further confirmed this. The absorption bands at about 1562.63 and 1444.14 cm^{-1}, assigned to the asymmetric and symmetric stretching vibrations of the COO$^-$, respectively, signified that the starch/poly(AA-co-AM) should have been an IPN.

A further process was carried out to confirm this conclusion. A similar free-radical polymerization of AA and AM was
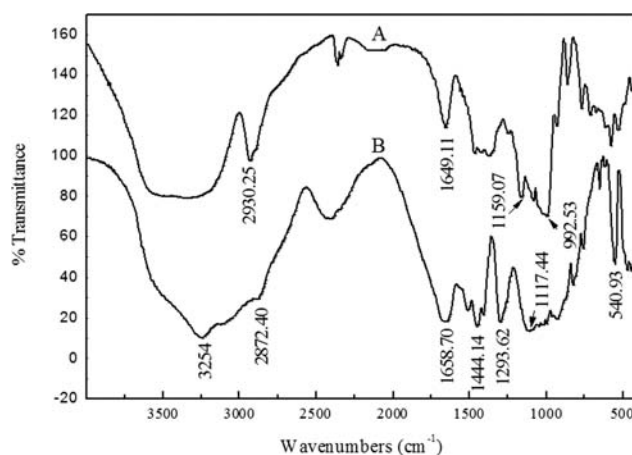

Figure 1. FTIR spectra of the (A) starch and (B) starch/poly(AA-co-AM) IPN.
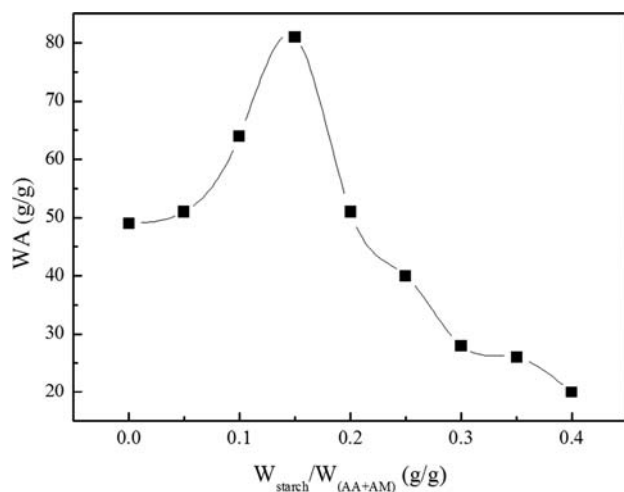
Figure 2. Mass ratio of starch to AA and AM dependence of WA of SAAmF in tap water.

performed in the presence of starch but without MBA. The product was leached with anhydrous methanol followed by precipitation into anhydrous diethyl ether. Then, it was verified by FTIR spectroscopy that the precipitate was poly(AA-co-AM) after thorough drying.

Effect of the Starch Amount on WA

Figure 2 describes the starch dependence of WA of coated slow-release SAAmF in tap water. WA increased as the amount of starch (determined as the mass percentage of starch in the monomers, w_{starch}/w_{AA+AM}) rose from 0 to 15 wt %. This may have been due to the stiff structure of starch and the hydrogen bond, which endowed the coating polymer with large amounts of effective net chain and hydrophilicity. However, WA decreased considerably with further increases in the amount of starch. This may have been due to the formation of excess hydrogen bonds and the physical entanglement among polymer chains, which would have led to a high crosslinking density, restricted the relaxation of the polymer chain, and brought about a rigid structure of the polymer matrix. The other important reason was that hydrophilic poly(AA-co-AM) was less with increasing amount of starch, which would have led to a reduced WA.

Morphology of SAAmF

Figure 3(A,B) shows the photographs of the dry SAAmF and the one swollen in tap water. Its core was the crosslinked starch matrix with trapped nutrients in it, and the outer coating consisted of starch-g-poly(AA-co-AM) and poly(AA-co-AM). The average thickness of the coating of the swollen SAAmF was about 2–3 mm.

The cross-sectional morphology of SAAmF with 40 and 15 wt % starch, which were swollen completely in tap water, are
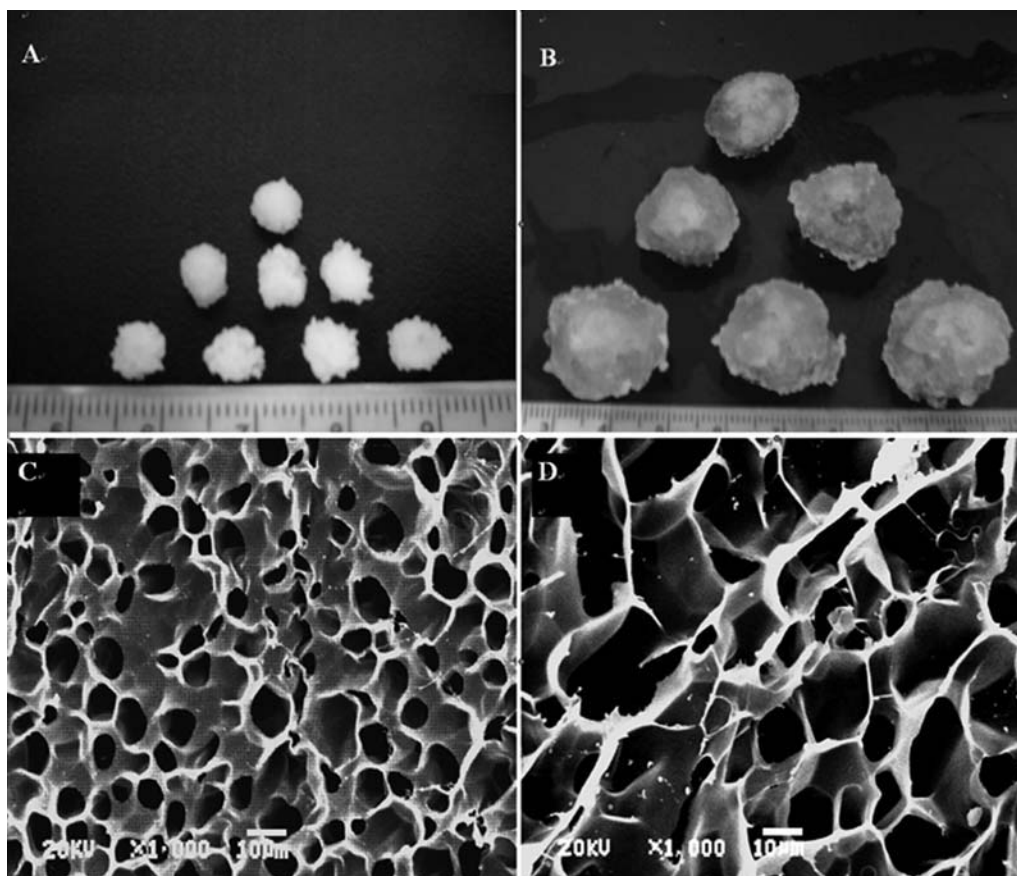

Figure 3. Photographs of (A) dry and (B) swollen SAAmF granules, (C) SEM section micrographs of SAAmF with 40 wt % starch, and (D) 15 wt % starch after equilibrium swelling in tap water.
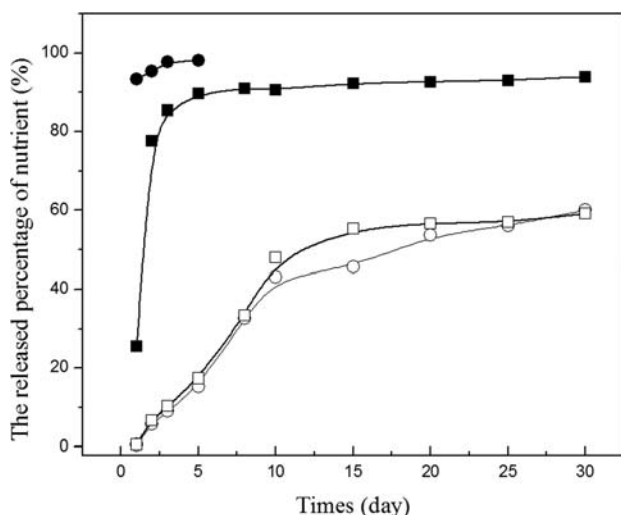
Figure 4. (○, ●) Nitrogen and (□, ■) phosphorus (P_2O_5) release behaviors from untreated fertilizer (solid) and SAAmF (hollow) in soil.

shown in Figure 3(C,D), respectively. Two peculiar features were found through comparison with the morphology of SAAmF shown in Figure 3(C,D). One was a difference in the diameter of the macropores of SAAmF. Figure 3(C) shows the smaller three-dimensional net hole due to the rather compact structure of the coating polymer with 40 wt % starch. Figure 3(D) shows the larger net hole of the coating polymer with 15 wt % starch. From these, it was easy for us to understand why the SAAmF's with different contents of starch had different swelling capacities. The other feature was the stronger wall of SAAmF with 40 wt % starch because of the stronger hydrogen bonding and rather orderly aggregates of polymer chain segments.

Nutrient Release Behavior of SAAmF in Soil
One of the most important characteristics of SAAmF was its slow-release properties. The rate of NP release as a function of time (days) was investigated for SAAmF's with different contents of starch. Figure 4 shows plots of the RP of nitrogen and phosphorus (P_2O_5) for untreated fertilizer and SAAmF with a content of 20 wt % starch in soil. More than 93% of the nitrogen and 76% of the phosphorus were released from the untreated fertilizer by the second day, as shown in the solid curves of Figure 4. Comparatively, the release rate of nutrient from SAAmF decreased sharply. About 7, 17, 45, and 60% of nitrogen were released from SAAmF by the 2nd, 5th, 15th, and 30th days, respectively. These results indicate that SAAmF had excellent slow-release properties, which agreed with the standard of SRFs of the Committee of European Normalization.[19]

It is well known that diammonium phosphate and urea dissolve quickly in water after being added to soil, and the nutrient released out with that. The SF swelled slowly because of hydrogen bonding and polymer–boron ion complex formation with the crosslinking reaction at the O—H site of starch, as revealed by FTIR.[20] This restricted the relaxation of polymer chains and brought about a decrease in the diffusion of water molecules and a subsequent reduction in the solution of phosphate. After the coating polymer slowly absorbed the water in the soil and

swelled, there was an increase in the pore size of the three-dimensional network, which benefitted the diffusion of the fertilizer solution. SF in the core of SAAmF swelled slowly because of the breakage of the interaction of hydroxyl groups and boron ions in water absorbed in hydrogel network, and the entrapped molecules dissolved slowly.[20] There existed a dynamic exchange between the free water in the hydrogel and the one in soil,[21,22] and then, the nutrient was released slowly into the soil through the grids with dynamic exchange.[14,23]

The influence of WA on the release behavior of nitrogen from SAAmF in soil is shown in Figure 5, in which the contents of starch were 15, 20, and 30 wt % and the corresponding WAs were about 81, 51, and 28 g/g, respectively. From this figure, we can see that all of the curves were similar, and the higher the WA was, the higher the release rate was. The reason was that the apertures in the three-dimensional network of the swollen hydrogel were bigger with higher WAs. As a result, the exchange of free water between the solution and the network and the nutrient released through it was easier. Furthermore, this resulted in an increase in the concentration gradient between the coating polymer and the core, which was the driving force of nutrient release from the core. Consequently, this resulted in an increase in the release rate.[24] For SAAmF with a content of starch of 30 wt %, the release rate of nitrogen was lower than that with a starch content of 20 wt % by the 15th day but was close to that after it. This may have been due to a cooperative effect of WA and the degradation of SAAmF. During the period investigated after 15 days, the sample with 30 wt % starch lost weight faster than the others, so the rate of release of nitrogen was faster and close to that with 20 wt % starch. The influence of WA on the release behavior of phosphorus from SAAmF in soil was also established, and the results were very similar to those of nitrogen.

Water Retention Behavior of SAAmF in Soil
Besides its slow-release properties, as discussed previously, another important property of SAAmF was its water retention characteristics in soil. The coating polymer could absorb water
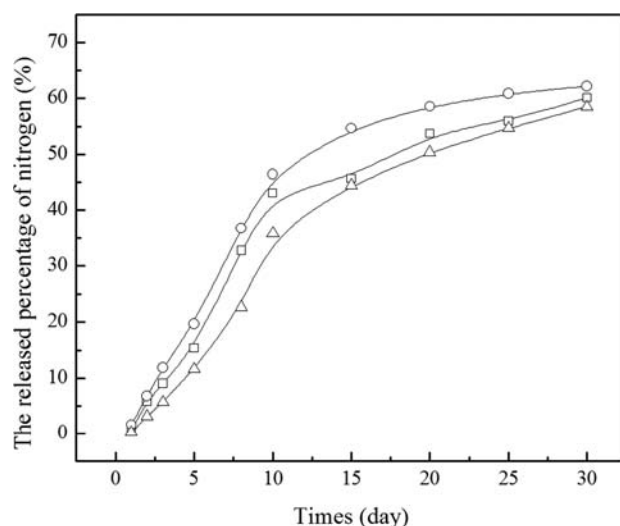

Figure 5. Nitrogen-release behaviors from SAAmF with different WAs: (○) 81, (□) 51, and (△) 28 g/g in soil.
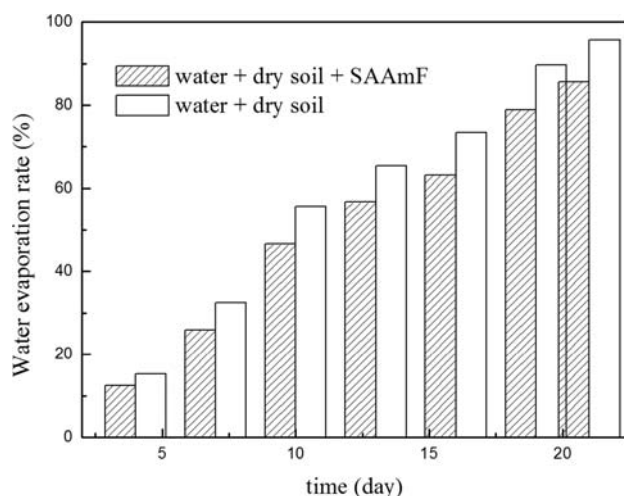
**Figure 6.** Water retention behavior of SAAmF in soil.

during rainfall and irrigation and was released slowly into the soil in dry times. This was especially important in drought-prone areas, where the availability of water was insufficient. Photographs of the swollen samples, presented in Figure 3, show that SAAmF was capable of absorbing water into the hydrogel matrix. This indicated that SAAmF could effectively store rainwater or irrigation water and could improve the utilization of water resources.

Figure 6 shows that the water retention behavior of soil with SAAmF that contained 20 wt % starch was greater than that without it. The water transpiration ratios of soil without SAAmF reached 55.65 and 95.75% on the 10th and 21th days, respectively, whereas those of the soil with SAAmF were 48.65 and 89.32%, respectively. This property resulted from the coating polymer, which absorbed and stored a large quantity of water and allowed it to release slowly when the soil moisture decreased. The swollen coating was just like a reservoir for the plant–soil system. Consequently, it would prolong irrigation cycles, reduce irrigation frequencies, and strengthen the ability of plants to fight against drought. It was also noted that many granular structures formed in the soil with SAAmF; these granular structures would contribute to great improvements in aeration and permeability and prevent the soil from hardening, cracking, and crusting.[9]

Effect of SAAmF on the Electrical Conductivity of the Soil

It is also worth noting that the salinization of soil is more and more serious; in other words, there has been an increase in the salinity parameters (electrical conductivity, pH, and sodium

adsorption ratio) of soil.[25,26] A study revealed that starch showed a significant adsorption capacity for Cu^{2+} ions, which bind to this material to form chelated compounds.[27] In this investigation, the electrical conductivity (κ) of 185 mL of dilute leaching liquor of a mixture of 20 g of saline soil and 2 g of SAAmF (content of starch = 20 wt %) was measured. It was incubated for different periods at ambient temperature (in summer, the daily maximum temperature was 37°C, and the day and night temperature difference was up to 15°C) before leaching. The tested saline soil was collected from Zhangye Prefecture in China. The results are represented in Table III. From them, we can see the different tendencies of conductivity when SAAmF and commercial fertilizer were used, respectively. This fact verified that SAAmF may have contributed to the reclamation of saline–alkaline soil because a dramatical decrease in the conductivity was observed, which revealed a sharp decrease in the concentration of residual ions for the soil. This was attributed to the polymer matrix used in the core and the coating. That is, cation adsorption on the surface of the coating polymer was assumed to occur through ion exchange and chelation between positively charged ions, such as Na^+ or Ca^{2+}, and carboxylic groups or hydroxyl groups within the polymer, which are schematically presented in the following equations:
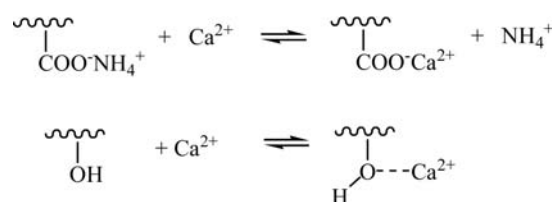
The adsorption mechanism could be given evidence by three changes in the characteristic absorption bands of starch/poly(AA-co-AM), shown in Figure 7; this was made a process of absorption in 0.02 mol/L $CaCl_2$ aqueous solution followed by drying. We know that the hydroxyl group of starch/poly(AA-co-AM) exhibited stretching vibration peaks around 3247 and 3500 cm^{-1} [Figure 1(B)]. The strong absorption bands of 3247 cm^{-1} shifted to higher wave numbers of about 3416 cm^{-1}. This may have been due to the chelation between Ca^{2+} and OH groups, which certainly weakened the hydrogen-bond interaction of hydroxyl groups. The COO^- groups on the poly(AA-co-AM) chain exhibited two peaks at approximately 1629.89 and 1444.13 cm^{-1}, which were assigned to asymmetric and symmetric stretching vibrations, respectively. In this study, the intensity of these bands increased after the ion exchange of Ca^{2+} and NH_4^+ because of an increase in the bonding strength of COO^-

Table III. Electrical Conductivity (κ; μs/cm) of the Saline Soil

	Time (days)								
	0	1	2	5	10	15	20	25	30
κ (μs/cm)[a]	0.900	0.880	0.840	0.802	0.810	0.779	0.705	0.700	0.699
κ (μs/cm)[b]	0.900	0.740	0.620	0.580	0.582	0.558	0.430	0.390	0.378

[a]After being mixed with commercial nitrogen fertilizer for different periods at ambient temperature.
[b]After being mixed with SAAmF for different periods at ambient temperature.
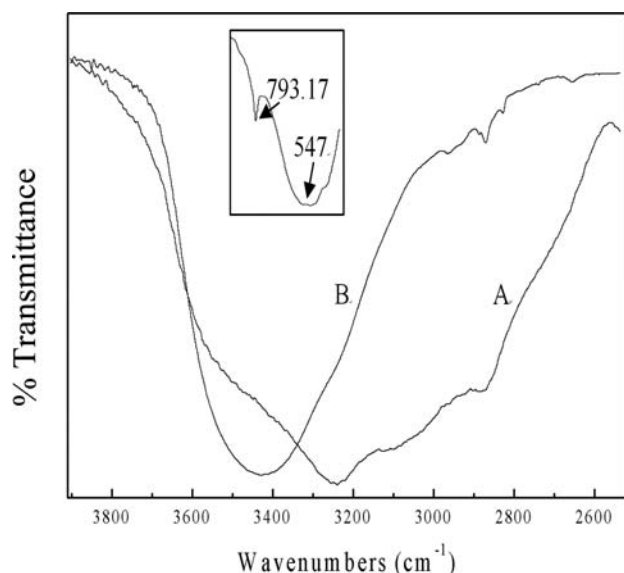
Figure 7. FTIR spectra of the starch/poly(AA-co-AM) IPN (A) before and (B) after absorption in a 0.02 mol/L CaCl₂ aqueous solution.

and Ca^{2+}. What is more, a strong absorption band appearing at 547 cm^{-1} may have been due to $O=C-Cl$, which further confirmed the chelation between COO^- and Ca^{2+}.

All the information suggested that along with the shift or increases in the intensity of some characteristic adsorption peaks, ion exchange and chelation occurred between the adsorbent and adsorbate.[27]

Degradation of the Starch/Poly(AA-co-AM) Superabsorbent

With the development of polymer hydrogels, researchers have focused on the incorporation of biodegradable, environmentally friendly polysaccharides, such as starch,[27–29] cellulose,[30,31] and chitosan,[32,33] into the hydrogel. Starch is an abundant, inexpensive, renewable, and fully biodegradable natural raw material. Modified starch via vinyl copolymerization constitutes the most important field for affording hydrogels with biodegradability and biocompatibility.[27]

In this study, the degradation of starch/poly(AA-co-AM) superabsorbent was monitored by the examination of the weight loss of the polymer with incubation time in soil at ambient temperature. Figure 8 shows the PD of starch/poly(AA-co-AM) superabsorbent with different contents of starch versus the incubation time and its section micrograph with 50 wt % starch after 50 days of degradation. A decrease in weight demonstrated the degradability of the superabsorbent. Kelner and Schacht[34] reported that the type of degradable link and the structure of the network play important roles in the control of the degradation behavior. Scheme 1 indicates that the connectivity of the starch/poly(AA-co-AM) hydrogel network was maintained by the glycosidic bonds of the starch molecules, amide links ($-CO-NH-$) from the crosslinker, ether links ($-O-$) of grafted poly(AA-co-AM), and alkyl linkages formed via radical copolymerization. Therefore, the degradation of the superabsorbent was caused by the breakage of glycosidic bonds, amide links, and ether bonds. Soil is a complex ecosystem, and there are different bacterial communities. The starch was invaded by bacteria, fungi, and other microorganisms under the appropriate temperature and moderate conditions when SAAmF was incubated in soil. Simultaneously, amide links and ether links were broken through hydrolysis. Finally, these actions were sufficient to degrade the polymer into carbon dioxide and water.[35]

PD increased with increasing starch content. During the period we investigated, the sample with 50 wt % starch lost weight faster than the others, but the rate of weight loss of pure poly(AA-co-AM) was the slowest. As shown in Figure 8, after 55 days, the PD values were 41.7, 36.8, 32, and 18.1% for samples with starch contents of 50, 35, 20, and 0 wt %, respectively. These results indicate that starch/poly(AA-co-AM) superabsorbent was partially degraded and could be used as a coating for fertilizers to alleviate the environmental pollution.[2,16]
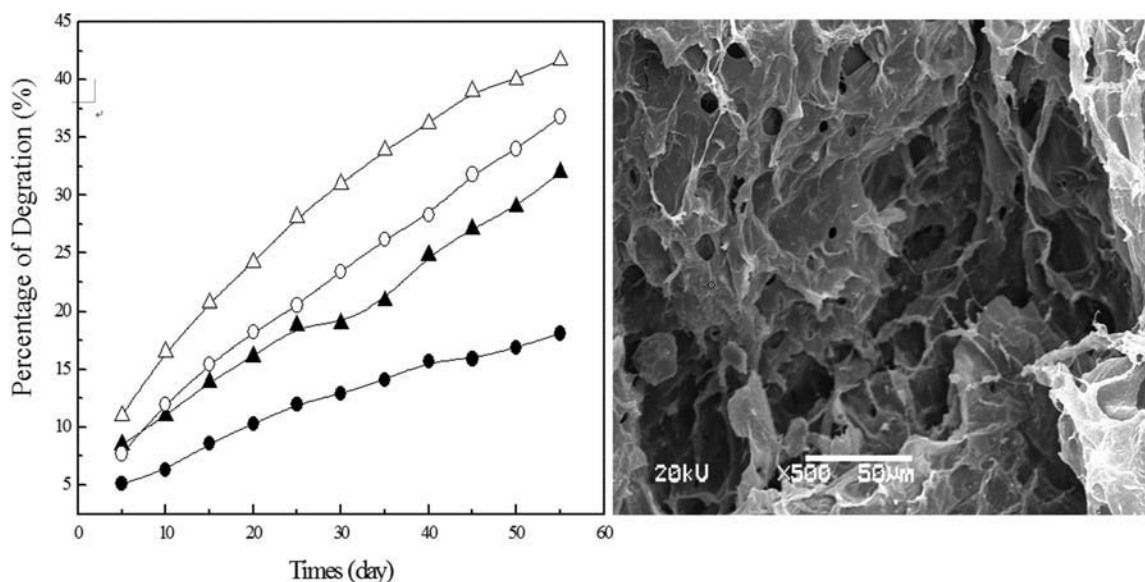

Figure 8. Degradation behavior of SAAmF with different contents of starch [(l) 0, (∼) 20, (*) 35, and (∼) 50 wt %] versus incubation time and SEM micrograph of the superabsorbent with starch 50 wt % after degradation for 50 days.

CONCLUSIONS

A slow-release and partially degradable NP fertilizer coated with starch/poly(AA-co-AM) superabsorbent proved to be an efficient and superior source of nitrogen and phosphorus and could be applied to improve the utilization efficiency of fertilizer and water, and it has potential practical applications in the remediation of saline soil.

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