

Utilization of Wheat Straw for the Preparation of Coated Controlled-Release Fertilizer with the Function of Water Retention

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ABSTRACT: With the aim of improving fertilizer use efficiency and minimizing the negative impact on the environment, a new coated controlled-release fertilizer with the function of water retention was prepared. A novel low water solubility macromolecular fertilizer, poly(dimethylourea phosphate) (PDUP), was “designed” and formulated from *N,N'*-dimethylourea (DMU) and potassium dihydrogen phosphate. Simultaneously, an eco-friendly superabsorbent composite based on wheat straw (WS), acrylic acid (AA), 2-acryloylamino-2-methyl-1-propanesulfonic acid (AMPS), and *N*-hydroxymethyl acrylamide (NHMAAm) was synthesized and used as the coating to control the release of nutrient. The nitrogen release profile and water retention capacity of the product were also investigated. The degradation of the coating material in soil solution was studied. Meanwhile, the impact of the content of *N*-hydroxymethyl acrylamide on the degradation extent was examined. The experimental data showed that the product with good water retention and controlled-release capacities, being economical and eco-friendly, could be promising for applications in agriculture and horticulture.

KEYWORDS: *controlled release, wheat straw, water retention, degradation*

INTRODUCTION

Agriculture must feed, clothe, and provide energy to a rapidly increasing world population while optimizing nutrient use from agronomic, economic, and environmental perspectives.¹ Fertilizer is the vital input material for the sustainable development of agriculture. The high solubility of chemical fertilizers gives rise to several agronomic and environmental problems.² Controlled-release fertilizers (CRFs) represent an attempt to overcome these disadvantages.³ Water is another main factor limiting agricultural production; however, much farmland in the world is short of water in the dry season, in arid regions, and in desert regions. At the same time, most of the rainwater is lost in the rainy season, and the water resources cannot be used efficiently. So, one method for effective utilization of the water resources involves the use of a superabsorbent, which has the ability to absorb and retain large amounts of aqueous fluids.⁴ Furthermore, superabsorbent hydrogels could be used as a carrier for CRFs.⁵

A key issue in the development of superabsorbents hydrogels as a carrier for slow release, however, is developing and designing suitable cost-effective biodegradable materials. Degradability can be introduced into the networks via monomer or cross-linker.⁶ In this study, *N*-hydroxymethyl acrylamide was introduced into the polymer net, which could cross-link polysaccharide materials and poly(acrylic acid) forming ether groups.^{7,8} The superabsorbent network degrades more easily than that cross-linked by *N,N'*-methylene bisacrylamide in common use.⁹ Moreover, the adoption of wheat straw is expected to reduce production cost and improve biodegradation property of superabsorbents.

Wheat straw is a renewable agriculture byproduct and offers advantages such as being cheap, abundantly available, and biodegradable.¹⁰ The main components of wheat straw are cellulose, hemicellulose, and lignin. There are various functional

groups such as hydroxyl, carboxyl, phosphate, ether, and amino groups on these components.¹¹ The existence of these functional groups makes a good reason for wheat straw to be employed in the preparation of superabsorbent composites.^{12–14} Furthermore, when used as a coating, the recycling of crop residues could provide abundant nutrient elements¹⁵ and organic matter for improving soil fertility.¹⁶

In this study, we report the development of an eco-friendly coated CRF on the basis of a novel macromolecular fertilizer, poly(dimethylourea phosphate) (PDUP), and an economic and degradable poly(acrylic acid-2-acryloylamino-2-methyl-1-propanesulfonic acid-*N*-hydroxymethyl acrylamide)/wheat straw [P(AA-AMPS-NHMAAm)/WS] superabsorbent composite. The product was expected to improve fertilizer use efficiency and utilization of the water resources effectively and be beneficial to the ecosystem. Therefore, the main objective was to access the feasibility of using the P(AA-AMPS-NHMAAm)/WS superabsorbent composite as the coating material for the CRF system.

MATERIALS AND METHODS

Materials. Wheat straw (WS, available from commercial sources) was chopped and dried at 105 °C in an oven for 8 h and then sieved to retain the 0.16–0.30 mm (50–90 mesh) fraction. *N*-Hydroxymethyl acrylamide (NHMAAm, Tianjin chemical Reagent Co., China) was purified by recrystallization in chloroform. Acrylic acid (AA, chemically pure, Beijing Oriental Chemical Factory, Beijing, China) and 2-acryloylamino-2-methyl-1-propanesulfonic acid (AMPS, Shandong Linyi Viscochem Co., China) were used as received. Other agents were all of analytical grade and used directly as received.

Received: January 10, 2012

Revised: June 23, 2012

Accepted: June 25, 2012

Published: June 25, 2012

Preparation and Characterization of PDUP. *N,N'*-Dimethylolurea (DMU) was formulated from urea and 37% formaldehyde aqueous solution (the urea/formaldehyde molar ratio was fixed at 1:2) according to the literature.¹⁷ Subsequently, a flask was charged with 14.40 g of DMU, 13.33 g of potassium dihydrogen phosphate, and 30.0 mL of water. The contents of the flask were stirred, and the pH was adjusted to 3 using dilute hydrochloric acid. The reaction mixture was then placed in a muffle furnace at 120 °C for 3 h. Thus, a novel macromolecular fertilizer, PDUP, was obtained. It was milled and screened at 110 mesh for further study. Fourier transform infrared (FTIR) spectra of the DMU and PDUP were recorded in a Nicolet NEXUS 670 FTIR Spectrometer, with the scan range of 4500–500 cm^{-1} using KBr pellets.

The content of nitrogen was determined by an elemental analysis instrument (Germany Elemental Vario EL Corp., model 1106). The contents of phosphorus and potassium were determined by an inductively coupled plasma (ICP) instrument (American TJA Corp., model IRISER/S); prior to measurement, the samples were digested in strong sulfuric acid in the presence of a catalyst.

Synthesis and Characterization of P(AA-AMPS-NHMAAm)/WS. A range of the superabsorbent composite polymers with different monomer compositions were prepared by the following procedure: 2.40 g of AA was put in a flask and then neutralized with 4.5 mL of sodium hydroxide aqueous solution (6 M) in an ice bath. After that, 0.600 g of AMPS, 0.021 g of NHMAAm, 0.008 g of ammonium persulfate (APS), 0.526 g of WS, and 5.0 mL of distilled water were added successively to the partially neutralized AA solution under vigorous stirring. Then, the flask with reaction solution was sealed and ultrasonically treated at 20 °C for 30 min. Finally, the flask equipped with a stirrer, thermometer, and nitrogen inlet tube was put in a water bath, heated slowly to 60 °C, and maintained at this temperature for 3 h under nitrogen atmosphere. The resultant polymer was sheared, placed on a dish, and dried at 60 °C to a constant weight. The dried product was milled and screened.

The samples of WS, poly(acrylic acid-2-acryloylamino-2-methyl-1-propanesulfonic acid-*N*-hydroxymethyl acrylamide) [P(AA-AMPS-NHMAAm)], and P(AA-AMPS-NHMAAm)/WS were analyzed using a FTIR spectroscopy (Nicolet NEXUS 670 FTIR Spectrometer, United States) in the region of 4000–500 cm^{-1} . Prior to the measurement, the samples were dried under vacuum until reaching to constant weight. The dried samples were pressed into the powder, mixed with KBr powder, and then compressed to make a pellet for FTIR characterization.

The crystal structures of WS, P(AA-AMPS-NHMAAm), and P(AA-AMPS-NHMAAm)/WS were measured with a X-ray diffractometer (XRD) (D/Max-2400, Rigaku). The XRD patterns were taken from 10° to 60° with a continuous scan mode to collect 2θ data using Cu $K\alpha$ radiation.

Preparation of Coated CRF Granules. The coated CRF granules were prepared on the basis of small urea particles as seeds and carboxymethyl cellulose as matrix. The process involves three steps. First, an amount of PDUP and carboxymethyl cellulose powder (below 110 mesh) was mixed well. Then, the mixture was fed into a rotating disk with urea granules (1.0–1.3 mm in diameter) in batches. The fertilizer core was obtained under water atomization and dried in an oven at 40 °C. Subsequently, the core with a desired range of sizes was fed to be treated with coating. P(AA-AMPS-NHMAAm)/WS powder (below 110 mesh) as the outer coating was adhered to the surface of the granules under rotation and formed a compact coating. Finally, the coated granules were dried and screened to obtain the final product.

Measurement of Water Absorbency of P(AA-AMPS-NHMAAm)/WS. The procedures of determination of water absorbency are as follows: 0.2 g of superabsorbents powder (40–90 mesh) was immersed into a certain amount of tap water and allowed to swell at room temperature for 60 min. The swollen superabsorbents were filtered through an 80-mesh sieve to remove nonabsorbed water and weighed. The water absorbency (WA) was calculated using the eq 1:

$$WA = \frac{M - M_0}{M_0} \quad (1)$$

where M and M_0 denote the weight of the swollen and dried superabsorbents, respectively.

Slow-Release Behavior of Coated CRF in Soil. To study the slow-release behavior of the coated CRF in soil, the following experiments were performed: 1 g of coated CRF granules was embedded into a nonwoven bag. The bag was buried into a container with 200 g of dry soil (below 18 mesh), 5 cm below the surface of soil. The proper amounts of untreated urea and the core were also carried out as the control test. Throughout the experiment, the water-holding ratio (WH) of the soil was maintained at 20% by weighing and adding tap water if necessary periodically. The bags with coated CRF granules were picked out after each incubated period (days 1, 3, 5, 10, 15, 20, 25, and 30) and then dried at room temperature. Then, the fertilizer granules were removed from the bags to be estimated for the contents of nitrogen. The sierozem soil used in this study is a representative of Lanzhou, which lies in the northwest of China and is a semiarid region.¹⁸

Measurements of Largest WH and Water Retention of Soil.

To study the effect of coated CRF on the water-holding capacity of soil, the largest WH and water-retention capacity of soil samples were measured. The soil samples used were sample A, 150 g of dry soil (below 18 mesh) only; sample B, 150 g of dry soil mixed with 1 g of coated CRF; and sample C, 150 g of dry soil mixed with 2 g of coated CRF.

The soil sample was placed in a 4.5 cm diameter PVC tube. The bottom of the tube was sealed with nonwoven fabric and weighed (marked W_1). The soil sample was drenched slowly by tap water from the top of the tube until water seeped out from the bottom. When no water seeped at the bottom, the tube was weighed again (marked W_2). The largest WH (WH %) of soil was calculated from the eq 2:

$$WH \% = \frac{(W_2 - W_1) \times 100}{150} \quad (2)$$

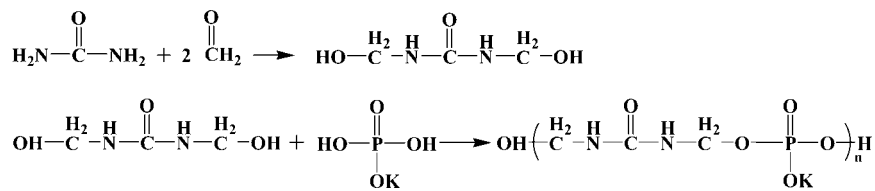
The soil sample was kept in a glass beaker. The beaker was weighed and was marked as W_0 . Then proper amount of tap water was added slowly into the beaker to make the soil saturated (has the largest WH determined previous step), and the beaker was weighed again (marked W_1). The beakers were placed in the laboratory at room temperature and weighed every 3 days (W_i), and the observation was obtained after a period of 30 days. The water-retention ratio (WR %) of soil was calculated with the following expression:¹⁹

$$WR \% = \left(\frac{W_i - W_0}{W_1 - W_0} \right) \times 100 \quad (3)$$

Degradation of P(AA-AMPS-NHMAAm)/WS Coating. The degradation studies of P(AA-AMPS-NHMAAm)/WS superabsorbent composite with different content of NHMAAm were performed. To simulate natural conditions, the degradation of superabsorbents was monitored in soil solution. The soil solution was obtained by a centrifugation method.²⁰ In a typical experiment, 100 g of soil was extracted with 500 mL of distilled water over 24 h at the ambient temperature, and the pH of the extracts was measured. Then, the sample was centrifuged at 10630g for 3 min. The degradation of superabsorbents in soil solution was performed by incubating preweighed dried slice (6.5–7.5 mm in diameter and 0.8–1.0 mm in thickness) of superabsorbents in 50 mL of soil solution at the ambient temperature. After the predetermined time period, the samples were removed from the solution by filtering through a silk sieve (300 mesh), washed repeatedly with distilled water, and dried at 40 °C to a constant weight. The extent of degradation was calculated by the following equation:

$$\text{degradation (\%)} = \frac{M_0 - M_d}{M_0} \times 100 \quad (4)$$

Scheme 1. Synthesis Mechanism of PDUP



where M_0 and M_d are the initial and final weights (before degradation and after degradation, respectively) of the dry superabsorbents.

RESULTS AND DISCUSSION

Formulation and Characterization of PDUP. Formulation of a new macromolecular fertilizer with low water solubility was done from the existing knowledge of reactions and properties of urea formaldehyde²¹ and polyphosphates.²² The fertilizer sample was synthesized via two steps: first, the DMU was prepared by reacting urea with formaldehyde under the condition of pH = 9, 25 °C, for 1 h. Subsequently, appropriate amounts of DMU and potassium dihydrogen phosphate (molar ratio was 1:1) were polycondensation under the condition of pH = 3, 120 °C, for 3 h. The reaction can be represented by the Scheme 1.

The structures of DMU and PDUP were confirmed by FTIR, as shown in the Figure 1. According to the spectrum of DMU

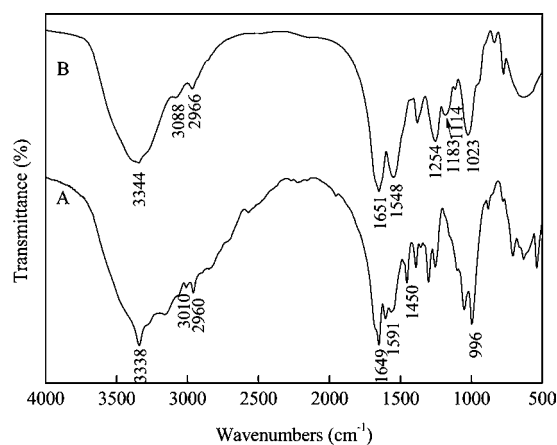


Figure 1. FTIR spectra of DMU (A) and PDUP (B).

(Figure 1A), the absorptions were observed at 3338 and 996 cm^{-1} (stretching and bending vibration of hydroxy group) and 3010, 2960, and 1450 cm^{-1} (symmetrical, asymmetrical stretching vibration, and bending vibration of methylene). This information gives direct evidence of the existence of a large number of hydroxymethyl groups. In addition, the peaks at 1649 and 1591 cm^{-1} were assigned to characteristic absorptions of amide I and amide II.²¹ It was in accordance with the standard FTIR spectrum of DMU. Comparing Figure 1B with A, it is shown that important changes did take place in the spectrum of PDUP. The bands at 1183, 1114, and 1023 cm^{-1} were ascribed as the characteristic absorptions of P–O–C. Furthermore, the characteristic absorption of hydroxy group disappeared. This information indicated that P–O–C formed via a polycondensation process. Meanwhile, the strong absorption peak appearing at 1254 cm^{-1} can be observed due to the stretching vibration of the P=O group. These results

revealed that the structure of the product of PDUP obtained in this study could be represented as shown in Scheme 1.

The elemental analysis and ICP results showed that the contents of nitrogen, phosphorus, and potassium of PDUP were 15.2, 15.4 (shown by P_2O_5), and 13.9% (shown by K_2O), respectively. The result further confirms the formation of PDUP containing N, P, and K.

Spectrum and XRD Characterization of the P(AA-AMPS-NHMAAm)/WS. FTIR spectra of WS, P(AA-AMPS-NHMAAm), and P(AA-AMPS-NHMAAm)/WS are shown in Figure 2. According to the spectrum of WS (Figure 2A), the

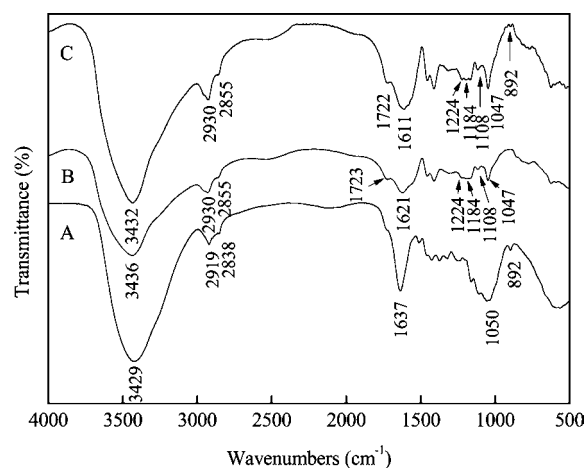


Figure 2. FTIR spectra of WS (A), P(AA-AMPS-NHMAAm) (B), and P(AA-AMPS-NHMAAm)/WS (C).

absorptions were observed at 3429 (hydroxyl stretching vibration), 1050, and 892 cm^{-1} (β -1,4-glycosidic bond) and 2912 and 2838 cm^{-1} (methylene), which were characteristic absorptions in cellulose structure.¹³ In the spectrum of P(AA-AMPS-NHMAAm) (Figure 2B), the intense band at 3436 cm^{-1} should be attributed to the stretching of N–H and O–H bonds. The bands at 1723 and 1621 cm^{-1} were ascribed to the stretching of C=O bonds in AA, AMPS, and NHMAAm. The adsorption bands at 1224, 1184, and 1047 cm^{-1} showed the appearance of the SO_3^- group in AMPS. The characteristic peak at 1108 cm^{-1} arose from the ether group –O– of P(AA-AMPS-NHMAAm) providing evidence of a cross-linking reaction between two N-hydroxymethyl groups. Comparing the FTIR spectrum of P(AA-AMPS-NHMAAm)/WS (Figure 2C) with P(AA-AMPS-NHMAAm), additional peaks of WS have been observed. In addition, the absorption at 1108 cm^{-1} became stronger; it indicated that the ether group –O– formed between N-hydroxymethyl and hydroxyl of cellulose and the graft copolymerization of vinyl and cellulose. On the basis of the analysis of FTIR, the conclusion can be drawn that a cross-linked copolymer of AA, AMPS, NHMAAm, and WS was formed.

Figure 3 showed the XRD patterns of the WS (A), P(AA-AMPS-NHMAAm) (B), and P(AA-AMPS-NHMAAm)/WS (C).

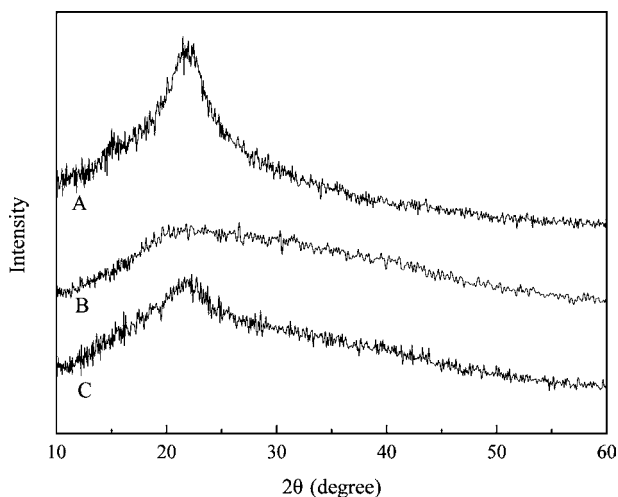


Figure 3. X-ray diffraction patterns of WS (A), P(AA-AMPS-NHMAAm) (B), and P(AA-AMPS-NHMAAm)/WS (C).

(C). From the pattern of WS, the diffraction peaks at $2\theta = 15, 21^\circ$ were observed. That accords with the data from the literature and indicates that the WS has a crystalline structure.^{23,24} For the P(AA-AMPS-NHMAAm)/WS superabsorbent composite, it is found that the peak at 15° disappeared, and the peak at 21° became broadened. This suggests that the graft polymerization of WS with monomers weakens the ordered structures in WS.

Effect of Chemical Composition on WA of the P(AA-AMPS-NHMAAm)/WS. The influence of chemical compositions of the superabsorbents on the WA was investigated by varying the amount of AA, AMPS, NHMAAm, and WS in the feed mixture. The hydrophilic group plays an extremely important part in WA of various superabsorbents. The effect of weight ratio of AMPS to AA (ranging from 1:5 to 1:1) on the WA was investigated. As shown in Table 1 (reaction

Table 1. Effect of the Weight Ratio of AMPS to AA on WA of the P(AA-AMPS-NHMAAm)/WS

weight of AMPS (g)	weight of AA (g)	weight ratio of AMPS to AA	WA (g/g)
0.5	2.5	1:5	117
0.6	2.4	1:4	153
0.75	2.25	1:3	140
1	2	1:2	120
1.5	1.5	1:1	116

conditions: neutralization degree of AA, 60 mol %; WS, 10%; NHMAAm, 1.0%; APS, 0.4%; reaction time, 3 h; and reaction temperature, 60°C), the maximum WA was reached when the superabsorbent composite was synthesized with a weight ratio of AMPS to AA 1:4. It could be due to the fact that there are two kinds of hydrophilic groups on AMPS, an acrylamide group and a sulfonate group. The sulfonate group is more hydrophilic than the carboxyl group of AA,²⁵ which caused a stronger affinity for more absorption of water. In addition, the collaborative effect of different hydrophilic groups in the polymer chains will also lead to the higher WA.²⁶ So, the WA increased when the AMPS content is less than 25%. However, a

further increase in AMPS content causes ion shielding and diminishes the degree to which the negative charged groups repel each other.²⁷

The WA as a function of content of NHMAAm was investigated, as shown in Figure 4 (reaction conditions: weight

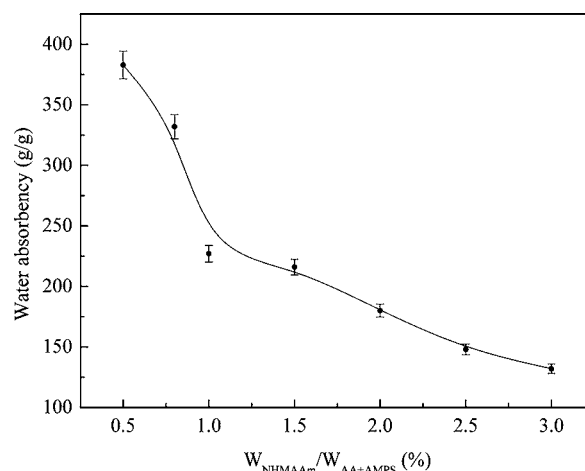


Figure 4. Effect of the NHMAAm content on the WA of the P(AA-AMPS-NHMAAm)/WS ($n = 3$).

ratio of AMPS to AA, 1:4; neutralization degree of AA, 80 mol %; WS, 10%; APS, 0.40%; reaction time, 3 h; and reaction temperature, 60°C). It can be seen that the WA significantly decreased with the increase of the amount of NHMAAm from 0.50 to 3.00%. According to Flory's network theory,²⁸ cross-linking density is an important swelling control element. The amount of cross-linker determined the cross-linking density. In the present study, NHMAAm is a bifunctional molecule with an ethylene group and a hydroxymethyl group. Hydroxymethyl is a highly reactive group with a tendency to condense with another similar molecule with loss of water.⁷ In addition, hydroxymethyl groups could react with the free hydroxyl groups of cellulose.⁸ Apparently, a higher NHMAAm content resulted in the generation of more cross-linking points, which caused the formation of an additional network and decreased the available free volume within the superabsorbent polymer network. This would make it more difficult for the network to be swollen by water, which was responsible for the decrease of WA. When the content of NHMAAm was lower than 1.0%, the swollen superabsorbents became a thin paste, and when the content of NHMAAm was lower than 0.50%, the WA of superabsorbent composite was very low, because the lower cross-linking density with a smaller amount of cross-linking points would cause the increase of the soluble material. A similar observation was reported by Chen et al.²⁹ and Li et al.³⁰ and was in conformity with Flory's network theory.

The effect of the amount of WS on the WA was studied, as shown in Figure 5 (reaction conditions: neutralization degree of AA, 80 mol %; weight ratio of AMPS to AA, 1:4; NHMAAm, 1.0%; APS, 0.4%; reaction time, 3 h; and reaction temperature, 70°C). As the weight ratio increased from 0 to 20%, the WA increased gently from 204 to 220 g/g. As the content increased from 20 to 30%, the WA decreased sharply. It was expected that the action of WS in polymer network could be interpreted as the following two aspects. On the one hand, the hydroxyl groups in the cellulose may react with initiator and liberate free radicals on which the graft polymerization would take place

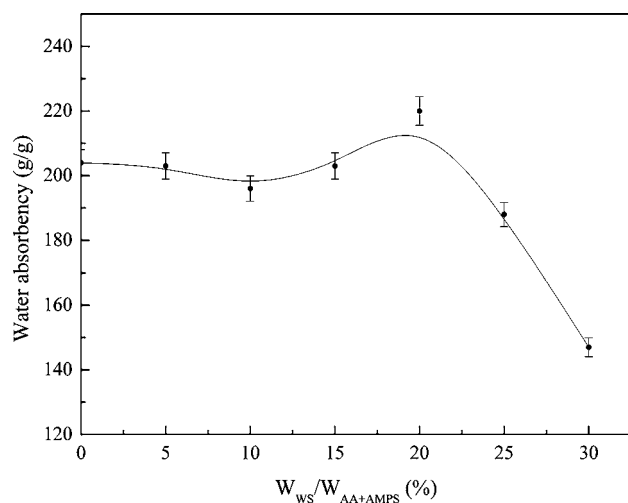


Figure 5. Effect of the WS content on the WA of the P(AA-AMPS-NHMAAm)/WS ($n = 3$).

with AA, AMPS, and NHMAAm, and the hydroxyl groups may react with the hydroxymethyl of NHMAAm to form an ether bond. These actions would result in improvement of the superabsorbent polymer network and resulted in the increase of WA. On the other hand, some of the WS would be physically filled in the polymer network. When the content of WS was more than 20%, the WS in network acted as additional network points. The cross-linking points of superabsorbent polymers increased with the increase of the content of WS, which resulted in a decrease in WA. In summary, the optimal chemical composition of P(AA-AMPS-NHMAAm)/WS was that the weight ratio of AMPS to AA was 1:4, the content of NHMAAm was 1.0%, and the content of WS was 20%.

Composition and Characteristics of Coated CRF. The coated CRF was a tan, round granule with an average diameter of 2.4 ± 0.2 mm. The content of the coating was $32.4 \pm 1.5\%$. Elemental analysis and ICP results showed that the contents of nitrogen, phosphorus, and potassium were 18.1, 4.5 (shown by P_2O_5), and 4.1% (shown by K_2O), respectively.

The photographs of the dry sample and the one swollen in tap water were presented in Figure 6. From Figure 6B, it can be seen that the coated CRF granules are capable of taking up water. It could be attributed to the coating consisting of P(AA-AMPS-NHMAAm)/WS superabsorbent composite. When the coated CRF was dipped into water, the coating of superabsorbent composite could absorb water to form a swollen hydrogel and release nutrients from it.

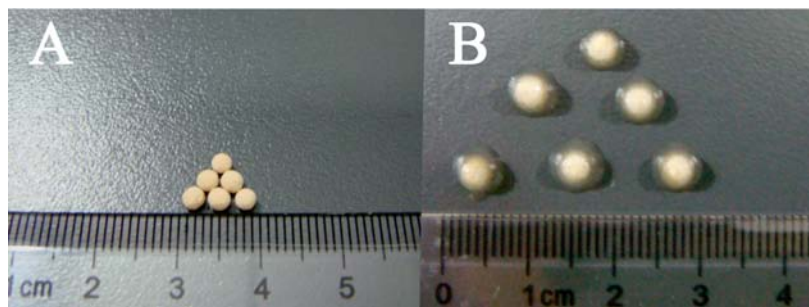


Figure 6. Photographs of dry (A) and swollen (B) coated CRF granules.

Slow-Release Behavior of Coated CRF in Soil. The most important character of the coated CRF was the slow-release property. Plots of the released percentage of nitrogen against time (days) are presented in Figure 7 for untreated urea, the

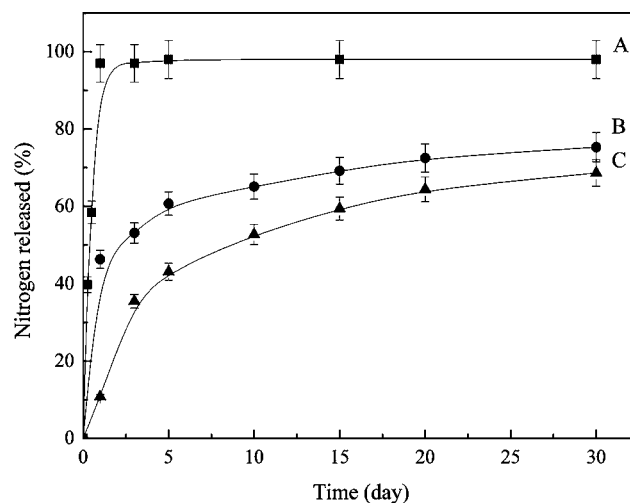


Figure 7. Nitrogen release behaviors of untreated urea (A), the core (B), and coated CRF (C) ($n = 3$).

core, and coated CRF in soil, respectively. It is well-known that water-soluble compound fertilizer will be quickly dissolved in the soil solution after being added into soil, and the nutrient will be quickly exhausted. More than 98% of nitrogen in untreated urea was released within 24 h, as shown in Figure 7A. As compared with the untreated urea, the release rate of nitrogen in the core shown in Figure 7B decreased sharply, and about 46.3, 53.1, and 75.3% of nitrogen was released from the core after 1, 3, and 30 days, respectively. It could be attributed to the low water solubility of PDUP in the core. Meanwhile, the PDUP was used as physical barrier to decrease the dissolution of the urea. As shown in Figure 7C, about 10.8, 35.5, and 68.6% of nitrogen released from the coated CRF by the 1, 3, and 30 days, respectively. Comparing with the release rate of nitrogen in the core, the initial release rate of the coated CRF was decreased significantly. This is mainly due to the fact that the coating material was P(AA-SMPS-NHMAAm)/WS superabsorbent composite, which could be slowly swollen by soil solution and transformed into hydrogel after the coated CRF was added into soil. The nutrients in the core of coated CRF would dissolve slowly in water absorbed in the swollen hydrogel network. There exists a dynamic exchange between the free water in the hydrogel and the water in soil.³¹ The

nutrients would be slowly diffused out of the granule through the dynamic water exchange.

CRFs are expected to be designed to provide good control over release in soil and to match plant demand to provide high use efficiency and minimize adverse effects on the environment.³² The time pattern of macronutrient uptake by seasonal crops is generally sigmoidal.³³ Therefore, synchronizing nutrient supply with plant demand using a sigmoidal pattern of supply will provide optimal nutrition for plant growth and reduce losses by the processes competing with nutrient uptake. In the present study, the nitrogen release curve of the coated CRF is still characterized by a high initial release.

Water-Holding and Water-Retention Capacity of Soil with Coated CRF. Besides its slow-release property, another of the most important characteristics of the coated CRF was the water-holding and water-retention capacity. In this regard, the test of coated CRF for the largest WH and water-retention capacity of soil was carried out.

For the soil samples, (A) 150 g of soil only, (B) 150 g of soil mixed with 1 g of coated CRF, and (C) 150 g of soil mixed with 2 g of coated CRF, the largest WHs were 33.1, 40.0, and 46.8%, respectively, as shown in Figure 8. From it, we can conclude

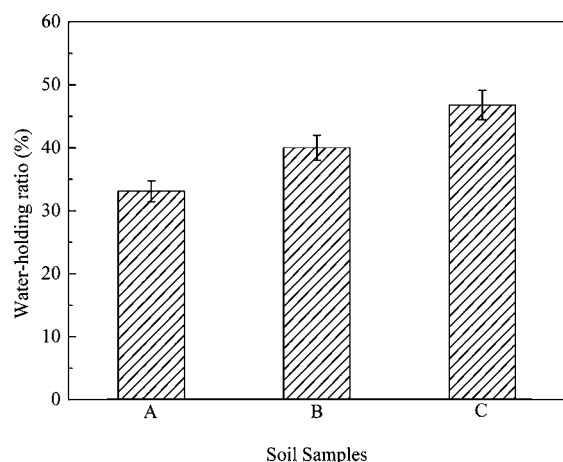


Figure 8. Largest WH of soil sample: (A) 150 g of soil only, (B) 150 g of soil mixed with 1 g of coated CRF, and (C) 150 g of soil mixed with 2 g of coated CRF ($n = 3$).

that the addition of coated CRF to soil could improve the water-holding capacity of the soil, and the water content increased with an increasing amount of the coated CRF in the soil. So, the soil with the addition of coated CRF could hold much more water during the irrigation period or raining time than the soil without it and could efficiently reduce irrigation water consumption.

Figure 9 presented the water-retention behavior of the soil samples A, B, and C. From it, we can find that the water-retention capacity of the soil samples with the coated CRF was greater than that without it, and it was increased with the increase of the content of the coated CRF. The WRs of the soil sample A were 41.0 and 6.5% on the 15th and 30th days, respectively, whereas WRs reached 50.3 and 17.9% for the soil sample B and 65.6 and 24.8% for the soil sample C, on the 15th and 30th days, respectively. The time needed for 50% of WR was about 12 days for the soil sample A, and it was about 15 and 20 days for the soil samples B and C, respectively. This property resulted from the fact that the coating material was P(AA-AMPS-NHMAAm)/WS superabsorbent composite,

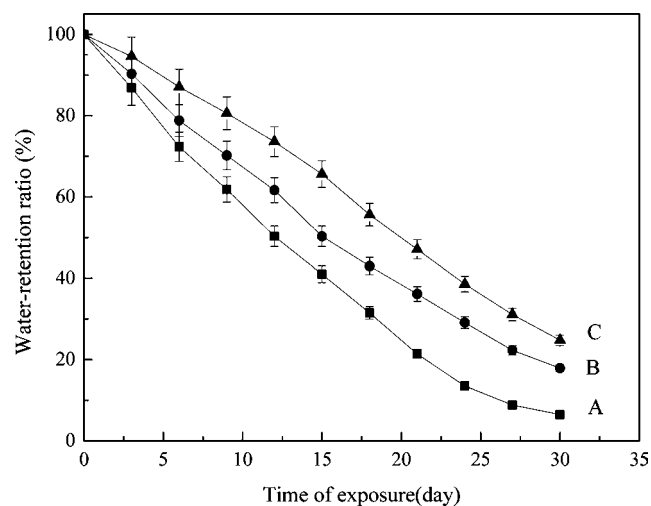


Figure 9. Water-retention behaviors of soil sample: (A) 150 g of soil only, (B) 150 g of soil mixed with 1 g of coated CRF, and (C) 150 g of soil mixed with 2 g of coated CRF ($n = 3$).

which has an excellent WA and water-retention capacity. Therefore, the soil with the addition of the coated CRF could prolong irrigation cycles, reduce irrigation frequencies, and strengthen the ability of plants to fight against drought.

Degradability Studies of the P(AA-AMPS-NHMAAm)/WS Coating. The degradation property of the coating material is of major interest in designing the coated CRF.³⁴ To simulate natural conditions, we examined the degradation behavior of the coating in soil solution in the absence of soil material by detecting weight loss. The method offers the advantages of handling controlling, giving representative data, and shortening experimental times. Furthermore, the cross-linking agent is known to exert a profound effect on the overall properties of a polymeric matrix. In the present study, the degradation profiles of the P(AA-AMPS-NHMAAm)/WS with NHMAAm contents 1, 2, and 3% in the soil solution (pH = 7.8) at the ambient temperature were investigated. The results obtained were depicted in Figure 10. We can see from it that the extent of degradation of P(AA-AMPS-NHMAAm)/WS superabsorbent composite was dependent on the content of NHMAAm in the composition, which was related to the swelling of the

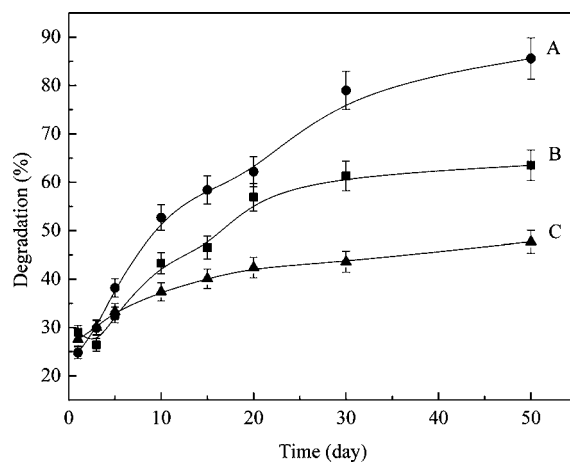


Figure 10. Degradation of P(AA-AMPS-NHMAAm)/WS superabsorbents: (A) 1% NHMAAm, (B) 2% NHMAAm, and (C) 3% NHMAAm ($n = 3$).

superabsorbent composite. The higher content of NHMAAm was associated with the lower extent of degradation, which confirmed reasonably well with their WA (WA was 227, 180, and 132 g/g, respectively). Similar results were reported in the literature.^{35,36} As the slice of P(AA-AMPS-NHMAAm)/WS was incubated in the solution, it was swelled, and the water molecules diffused into the network of the superabsorbent composite. Meanwhile, the degradation occurred, and the ether linkages between $-\text{CH}_2\text{OH}$ and $-\text{OH}$ or two $-\text{CH}_2\text{OH}$ broke homogeneously throughout the degradation process. This ongoing break of cross-links within the polymer decreased the cross-linking density of the network. So, the high WA could result in a high extent of degradation. In addition, as the Figure 10 caption describes, the extent of degradation increased with the time prolonging. After degradation in soil solution for 50 days, the extent of degradation of P(AA-AMPS-NHMAAm)/WS reached to 85.6, 63.5, and 47.7% for NHMAAm contents 1, 2, and 3%, respectively. It is remarkable that the coating material based on WS and NHMAAm imparted the product with a high extent of degradation, low production cost, and broad application in general agricultures. The new approach was shown to be promising in utilizing agrowaste and simultaneously make the technique quite environmentally friendly.

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Funding

We gratefully acknowledge the financial support of the Special Doctoral Program Fund of the Ministry of Education of China (Grant No. 20090211110004) and Gansu Province Project of Science and Technologies (Grant No. 0804WCGA130).

Notes

The authors declare no competing financial interest.

ABBREVIATIONS USED

AA, acrylic acid; AMPS, 2-acryloylamino-2-methyl-1-propane-sulfonic acid; APS, ammonium persulfate; CRF, controlled-release fertilizer; DMU, *N,N'*-dimethylolurea; FTIR, Fourier transform infrared; ICP, inductively coupled plasma; NHMAAm, *N*-hydroxymethyl acrylamide; P(AA-AMPS-NHMAAm), poly(acrylic acid-2-acryloylamino-2-methyl-1-propanesulfonic acid-*N*-hydroxymethyl acrylamide); P(AA-AMPS-NHMAAm)/WS, poly(acrylic acid-2-acryloylamino-2-methyl-1-propanesulfonic acid-*N*-hydroxymethyl acrylamide)/wheat straw; PDUP, poly(dimethylolurea phosphate); WA, water absorbency; WH, water-holding ratio; WR, water-retention ratio; WS, wheat straw; XRD, X-ray diffractometer

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