Preparation and Characterization of Triple Polymer-Coated Controlled-Release Urea With Water-Retention Property and Enhanced Durability

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ABSTRACT: Triple polymer coated with controlled-release water retention fertilizer (TCWF) and enhanced mechanical property was developed by coating polyethylene (first layer), poly (acrylic acid-*co*-acrylamide) superabsorbent (second layer), and poly (butyl methacrylate) (third layer) consecutively on the granule core urea in the fluidized-bed coater. The inner layer possessed controlled-release property, the middle layer had water absorbent characteristic, and the thin outer layer aimed to protect the fragile layer of the superabsorbent. The relationship between the thickness of coating layer and the nutrient releasing properties was established. The effects of poly-merization parameters on the water absorbency of the superabsorbent were studied and optimized as well. The nutrients release behaviors of this triple-coated urea in both water and soil were investigated and compared. The results showed that TCWF not only performed as a good controlled-release fertilizer but also had excellent water retention capacity. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2103–2111, 2011

Key words: controlled-release; superabsorbent; coating; absorbency

INTRODUCTION

Fertilizer is a vital input material for the sustainable development of crop production and food security. The worldwide experiences in agricultural development have proved that rational fertilization is one of the most efficient and important methods to increase crop yields.[1] However, about half of the applied fertilizers, depending on the method of application and soil condition, is lost to the environment, which results in the contamination of water, air, etc.[2,3] However, a high concentration of fertilizer may also produce undesirable side effects on the target area that could lead to crop damage in addition to surrounding environment.[4] One method to effectively reduce losses of nutrient components is the use of controlled-release fertilizers (CRF).[5] The release of nutrient in such circumstance is expected to depend on its own solubility in solution, permeability through the membrane, water content, medium types, and the interaction among nutrients.[6]

Superabsorbent polymers (SAPs) are slightly cross-linked polymers and able to absorb more than hundreds of times weight of water than itself.[7] Compared with conventional water absorbing materials, the absorbed water is hardly removable even under pressure. Because of their excellent characteristics of water retention and absorbency, SAPs had been used in agriculture and horticulture since the first advent in 1969.[8,9] Recently, research on the use of SAPs as water managing materials for the renewal of arid and desert environment has attracted great attention, and encouraging results have been observed because they can reduce irrigation water consumption and lower the death rate of plants.[10]

The optimized combination of slow/CRFs and SAPs showed excellence in improving the nutrition of plants as well as mitigating the environmental impact from water-soluble fertilizers, reducing water evaporation losses, and lowering the frequency of

irrigation.[11] Liu and coworkers have developed series of poly (acrylic acid-co-acrylamide) (P(AA-co-AM)) based on the function of slow-release and water retention by coating a layer of superabsorbent onto urea-formaldehyde or polystyrene-coated fertilizer.[12–14] The obtained fertilizers demonstrated good slow-release of nutrient and water retention ability. However, the process of coating the superabsorbent was just to bathe the slow/CRFs in the AA-AM-based salt solution at 45°C or even higher temperature for several hours. This treatment weakened the slow release properties of the polymer barrier substantially because the fertilizers were surrounded by strong electrolytes at high temperature, which could accelerate the release of the nutrient during the coating process. Furthermore, this coating process only applicable in the laboratory flask, which was hard to scale-up; therefore, its application in industry was limited. Finally, the mechanical properties of P(AA-co-AM) coated layer were undesirable due to the fragility of outer layer of the SAPs.[15]

Based on the above background and our previous studies on CRFs and SAPs, we prepared triple-coated controlled-release and water-retention nitrogen fertilizer in this work. Its core is urea fertilizer granule, the first coating layer is polyethylene (PE), and the second coating layer is P(AA-co-AM) superabsorbent, and the third layer coating is finished by poly (butyl methacrylate) (PBMA), an excellent elastomer. By doing so, first, adding the third elastomer layer improved mechanical strength without altering the properties of previous two layers. Therefore, this process facilitated the transportation and use practice, meanwhile retained the water-retention and controlled-release merits. Second, the coating process conducted in the fluidized-bed coater instead of directly immersing fertilizer into the mixture aqueous solutions that reduced the loss of nutrients. Third, it was prepared by coating controlled-release layer, superabsorbent layer, and protective layer on granular fertilizer in the fluidized-bed coater continuously, which was easy to be scaled up in industry.

EXPERIMENTAL

Reagents

AA was distilled at reduced pressure before use, AM was recrystallized from acetone, ammonium persulfate (APS) was recrystallized from water, and all these chemicals were purchased from Beijing Chemical Reagent (Beijing, China). PBMA (Mw: 320,000), N, N′-2-methylenebisacrylamide (MBA) were supplied by Sigma-Aldrich (St. Louis, MO). Sorbite anhydride monostearic acid ester (Span-80), sodium bicarbonate (SBC), ethyl acetate, cyclohexane, and sodium hydroxide were analytical grade

from Beijing Chemical Reagent and used without further treatments. Rounded granular urea with the average diameter from 3 to 5 mm was used as the core fertilizer and purchased from Hebei Cangzhou Dahua Co., (Hebei, China). PE (PE, Mw: 90,000) was from SINOPEC Yanshan Division (Beijing, China).

Preparation of TCWF

Process of preparing inner PE-coated CRF was described as following: First, 5 kg commercial granular urea (core) was placed in our customized fluidized-bed coater and preheated to 70°C for 15 min before coating get started. Then, coating solution was made by dissolution of PE in cyclohexane in a tank, mixed well with a mechanical stirrer, and the concentration of polymer solution was set at 5%. This mixture was added in chamber and sprayed onto the solid surface of the urea through high-pressure nozzle with pressure set at 0.3 MPa. The step was repeated several times to ensure that the urea particles were covered evenly by the PE layer. Finally, blow dried by continuous air blast about 30 min, and the PE-coated controlled-release urea was obtained.

Encapsulation of the second layer with water retention property was performed as following: AA was copolymerized with AM by inversion suspension polymerization, and the obtained P(AA-co-AM) suspension was used as superabsorbent materials in this layer. A certain amount of cyclohexane and span-80 were added into a four-necked flask equipped with a mechanical stirrer and a drop funnel. As the temperature of the mixture was increased to 45°C, a certain amount of mixed solution composed of AA that partially neutralized by NaOH, AM, MBA, and APS were slowly added into the flask with nitrogen atmosphere. SBC solution was added dropwise into the reactor simultaneously. After 3 h reaction at 45°C, the superabsorbent suspension was obtained. To reduce the viscosity of the coating solution, the SAPs suspension was directly sprayed onto preheated previous PE-coated urea through high-pressure nozzle in the fluidized-bed without separating the surfactants. The rest of the condition was identical to PE coating. Thus, urea with both controlled-release and water-retention was acquired.

Finally, outer layer coating solution were prepared in a round-bottomed flask equipped with a mechanical stirrer; 20 g PBMA was dissolved in 400 mL ethyl acetate, and the solution was sprayed onto 2 kg former PE/P(AA-co-AM)-coated fertilizer. The detailed process was similar to the coating of PE layer, and the triple polymer coated functional fertilizer was obtained.

The FTIR spectra of the coating materials

Each step after the polymers were coated on the granular urea surface, the polymer coated layer was peeled off from the samples were characterized by FTIR spectrometer (Nicolet Magna-IR 860 spectrometer). Spectra were recorded at 4 cm^{-1} resolution, and 4096 scans were collected per trace.

Measurement of water absorbency

One gram of TCWF was immersed into 500 mL tap water for 90 min at room temperature. The swollen TCWF was filtrated through the 200-mesh sieve to remove nonabsorbed water and weighed (M). Water absorbency (W) of per gram dried TCWF was calculated using the following equation[12]:

$$W = \frac{M}{M_0} - 1 \qquad (1)$$

M and M_0 referred to the weight of the water soaked and dry TCWF, respectively.

Nutrient release property in water

To study the release behaviors of nitrogen nutrient in water, 2 g of coated fertilizer within a nylon bag were placed in conical bottle containing 200 mL distilled water and incubated at 25°C. Every day, 2 mL solution was sampled out for urea measurement and additional 2 mL distilled water was injected into the same bottle to maintain a constant volume. The urea content in water was measured by UV-visible spectrophotometry.[5] The above tests were carried out in triplicate.

Nutrient release property in soil

To study the release behaviors of nutrients in soil, 1 g samples were well blended with 200 g dried sandy soil and 120 mL tap water in beaker.[12] The top container was wrapped and kept sealed with plastic film and put into incubators at 25°C. Throughout the experiments, the soil sample was maintained at 30% water holding capacity by weighing continuously and adding tap water if necessary. For every 2 days, the remaining granular fertilizers were taken out and washed with distilled water, dried at 80°C overnight and weighed.[12] The above experiments were performed in triplicate, and the mean value was taken as the results.

The maximum water-holding ratio of the soil with TCWF

Two grams TCWF were well mixed with 200 g dry sandy soil and placed in a 4.5 cm diameter PVC tube.[11] The bottom of the tube was sealed by nylon fabric (100 meshes) and weighed as W_1. The soil samples were slowly drenched by tap water from the top of the tube until water seeped out from the bottom. When there was no more seeping water observed at the tube bottom, the tube was weighed again as W_2. Soil without TCWF was also carried out as control experiment. The maximum water-holding ratio (W%) of the soil was calculated according to the following equation[11]:

$$W\% = \frac{(W_2 - W_1) \times 100}{W_2 - W_1 + 200} \qquad (2)$$

Measurement of the water retention of TCWF in soil

Two grams TCWF were well mixed with 200 g dry sandy soil (below 40 mesh) and placed in cup A, and the parallel test without TCWF was carried out in cup B for blank, 50 mL tap water was added into both cups, and the beakers were weighed as W_0. The beakers were kept at 25°C and the weight of water was recorded for every 2 days (W_i) to evaluate the water retention of TCWF. Water evaporation ratio of soil (Wr%) was calculated by the following formula[13]:

$$W_r\% = \frac{(W_0 - W_i) \times 100}{200} \qquad (3)$$

Scanning electron microscopy study of TCWF

The coating morphology of TCWF was examined by scanning electron microscopy (SEM). Before measurement, the samples were immersed into the liquid nitrogen for 30 min and cut into halves. The samples were coated with a thin layer of gold and observed under HITACHI S-480 SEM (Japan).

RESULTS AND DISCUSSION

Characterization of TCWF

Fluidized-bed coating of granular particles was a process which offered the advantages over the conventional coatings such as dipping process and electrostatic coating. The fluidized-bed was maintained at constant temperature, particles were well mixed, and the diluted solution was sprayed onto the granular fertilizer. As the solvent evaporated into the air, a thin even layer of solid was deposited on the surface of the particles without generating agglomeration.[16] In this work, the viscosity of the coating solution must be low, thus the diluted polymer solution and SAPs suspension was selected to prevent the nozzle from blocking.
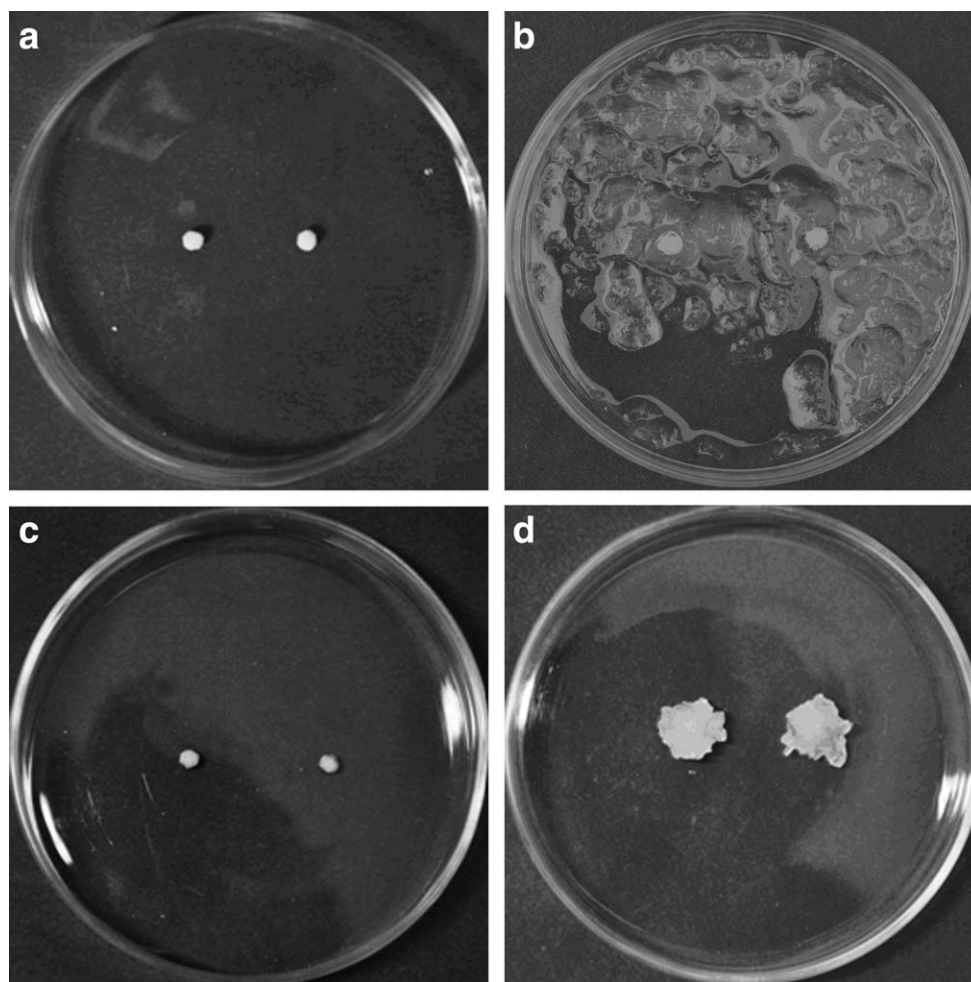
Figure 1 Photographs of PE/P(AA-*co*-AM) coated fertilizer (a) before and (b) after immersed in water; PE/P(AA-*co*-AM)/PBMA (c) before and (d) after immersed in water.

Structure of TCWF

Core part was 90 wt % granular urea, the inner coating layer was 5 wt % PE, the middle coating layer was 5 wt % P(AA-*co*-AM) superabsorbent, and the outmost coating layer was a thin film of PBMA. PE was selected as controlled-release membrane because of its excellent flexibility and hydrophobicity. This layer served as a barrier for mass transfer, thereby reduced the rate of water diffusion into the granules and the migration of the ingredients outside the granules. The P(AA-*co*-AM) superabsorbent was encapsulated onto the PE-coated granule as the second layer to provide high water absorbency and water retention capability. The third coating layer was PBMA, one kind of excellent elastomer, which was used as rate-limiting barrier for controlled-release drug, aimed to protect the brittle P(AA-*co*-AM) surface from abrasion and mechanical stress occurred during the packing, blending, and distribution procedure.[17]

Figure 1(a,b) shows the photographs of the PE/P(AA-*co*-AM)-coated fertilizer before and after immersion into water. The surface of the PE/P(AA-

co-AM)-coated fertilizer looked smooth and even. Once immersed into the tap water, the samples exhibited excellent water absorbency and swelled up to 102 g/g quickly. However, after 1 to 2 h of inflation in water, the superabsorbent layer started to dismantle from the PE-coated granular fertilizers, and two layers completely broke off with each other and superabsorbent was messy around within 24 h. The results indicated that shortly after the superabsorbent absorbed water, the strength of hydrogel was too weak to wrap the PE-coated granules. The reason was probably attributed to the case that superabsorbent suspension was directly sprayed onto the solid surface of the urea through high-pressure nozzle without purification of the surfactants and residues from the suspensions, which greatly reduced the original weak strength of the formed hydrogels.

To improve the durability and mechanical strength of the PE/P(AA-*co*-AM)-coated fertilizer, PBMA was used as protecting layer to wrap the above granule due to its excellent elastomer property. Figure 1(c) shows the photograph of dried PE/P(AA-*co*-AM)/
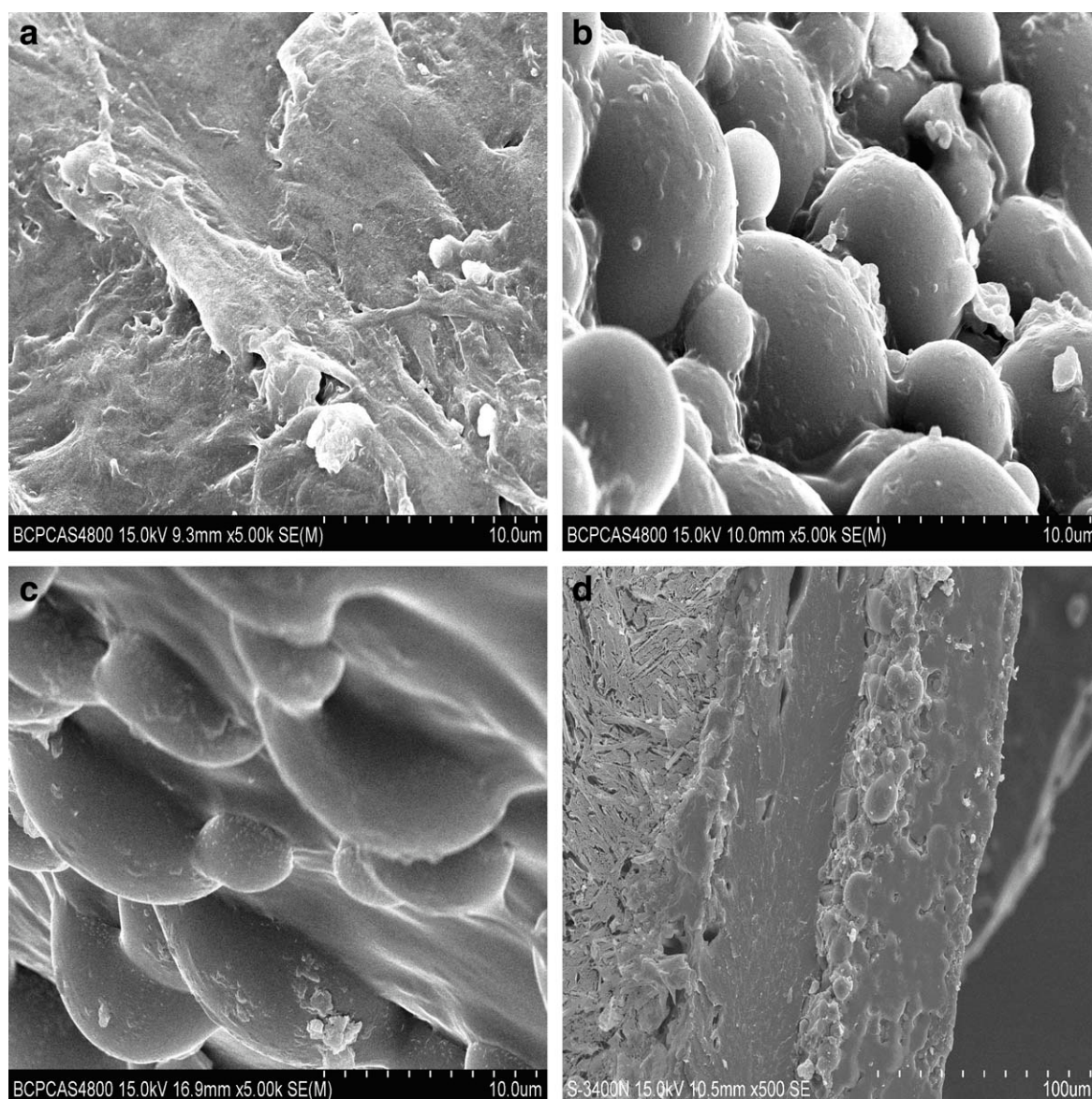
Figure 2 SEM pictures of TCWF, (a) PE layer, (b) P(AA-*co*-AM) layer, (c) PBMA layer, and (d) cross section view of the PE/P(AA-*co*-AM)/PBMA.

PBMA triple-coated TCWF whereas Figure 1(d) shows the photograph of PE/P(AA-*co*-AM)/PBMA that was soaked in water respectively. It was not only able to absorb the same amount of water as PE/P(AA-*co*-AM) double-coated granule did (120 g/g) but also remained intact [Fig. 1(d)]. This intactness was maintained in the water up to several weeks. With this protecting layer, users no longer need pay extra care to handle this fertilizer during transportation and dispension. The results suggested that the coating of PBMA on the fragile surface of the P(AA-*co*-AM) could significantly improved its durability and integrity.

FTIR analysis of each layer of TCWF

FTIR measurements were carried out to verify the successfulness in layer by layer before proceeding to

the next coating step. FTIR showed the characteristic absorption peaks of PE, P(AA-*co*-AM), and PBMA on three layers. The above results proved that triple layers, i.e., PE, P(AA-*co*-AM), and PBMA were successively attached layer by layer on the surface of the core fertilizer purposefully.

Morphology of TCWF

The surface morphology of different polymer coated granules were studied by SEM and presented in Figure 2. After coating PE layer is shown in Figure 2(a), the surface looked smooth, some small cracks, and pores can be seen. After the P(AA-*co*-AM) was coated on the PE surface, the surface was bumpy with spikes and ditches which was the suspension beads of P(AA-*co*-AM) deposited on

the surface of PE [Fig. 2(b)]. After treating with the PBMA thin layer [Fig. 2(c)], the surface was smoother with less smaller holes left compared with the preceding P(AA-co-AM) layer, which was probably due to the PBMA's spreading out and flattening the uneven surface of P(AA-co-AM) to some extent. Figure 2(d) shows the cross-section view of triple polymer coated structure of TCWF. In our case, for the first coated layer, which was homogenous and stick solidly to the core urea, acted as a controlled-release membrane, and the thickness of the PE layer was measured about 50 μm. For the second coated layer, it was also closely contact with the first PE layer although with much rougher surface. There were some cracks and pores on this layer, the thickness of the P(AA-co-AM) superabsorbent was around 50 μm. Because the third layer was ultra thin film with super elasticity, it closely mantled with the second coated layer and barely can be seen. These layers were all stick with their neighborhood tightly and no visible gap between any adjacent layers was seen from SEM pictures.

The nutrient release properties of PE-coated CRFs

According to Shaviv et al.'s study,[18] the diffusion mechanism dominates the release from thermoplastic coated CRF. Specifically, the release behavior is controlled by the mass transfer properties of the coating polymer, properties of the fertilizer, and coating thickness. In this section, the study mainly focused on the effect of the polymer membrane thickness on the release properties, the influence of temperature was also investigated briefly.

The influence of thickness on the nutrient release properties of PE-coated urea

Figure 3(a) showed the nutrient release behaviors of PE-coated urea with different thickness of coating layer in distilled water at 25°C. It could be found that in all the cases the initial releasing rate (within 24 h) of PE-coated urea were less than 4.2%, far below 15%, the Criteria of European Committee for Standardization,[19] which indicated that the surface of the fertilizer was compactly coated by the PE. It also can be seen that as the thickness of the coating layer was 25 μm, the cumulative release rate of nutrient was 4.2% within 24 h, 38% at day 7, and 56% at day 14. As the coating layer was thicker than 50 μm, the cumulative release rate increased to 0.15% within 24 h, 13.5% at day 7, and gradually climbed up to 24% at day 14. With the thickness of the coating layer further increased, the cumulative release rate was even lower. As the coating layer was thicker than 75 μm, the cumulative release rate increased to 0.1% within 24 h, 10.1% at day 7, and gradually climbed up to 10.3% at day 14. The results
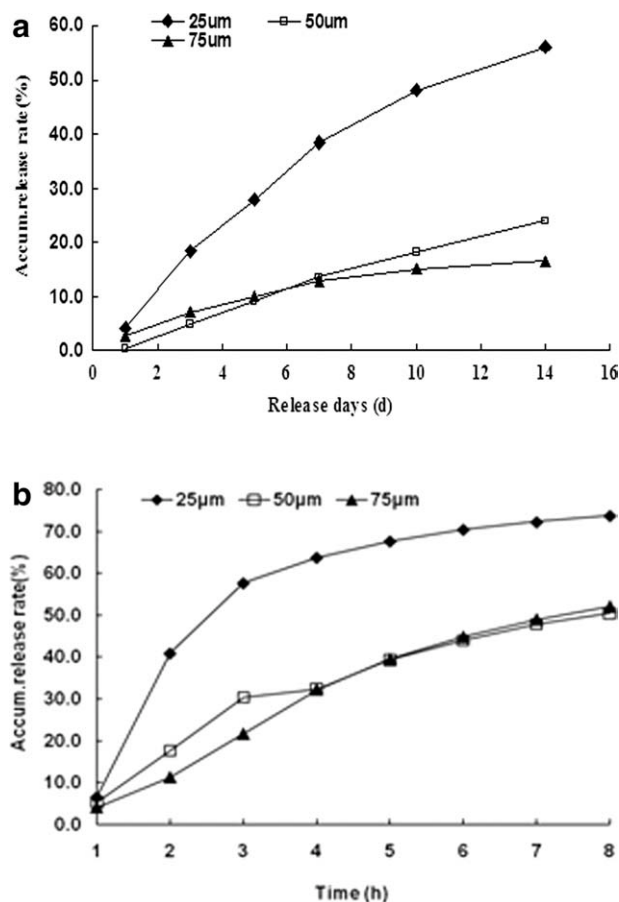

Figure 3 The nutrient release properties of PE-coated urea with different thickness in distilled water at temperature of (a) 25°C, and (b) 80°C.

could be interpreted as following: as water initially diffused into the coated granule, the internal pressure inside the polymer layer increased, more and more nutrient diffused out to the outer surroundings. Thus, the thicker the PE coating layer is, the tougher the nutrient diffuse through the PE membrane. According to Shaviv et al.'s study,[18] CRFs proposed is consisting of three stages; (i) a lag period, (ii) a period of linear release, (iii) a period of "decaying release." For example, as the thickness of the coating layer is 25 μm at 25°C, the release pattern of urea can be simulated by $Y = 3.9283x + 5.8838$, $R^2 = 0.9493$, Y is cumulative release amount, x is time, R is the curve fit correlation coefficient. It was obvious that the release pattern of urea is linear, which fit the Fickian law.

Influence of temperature on the nutrient release properties of PE-coated urea

However, as the temperature of the soaking solution was 80°C as in Figure 3(b), all of the cumulative release rates were faster than at 25°C as in Figure 3(a). The release rate of the nutrient was 72.3% at 80°C in 7 h whereas 38.3% at 25°C at day 7 with the thickness of coating layer is 25 μm. As the
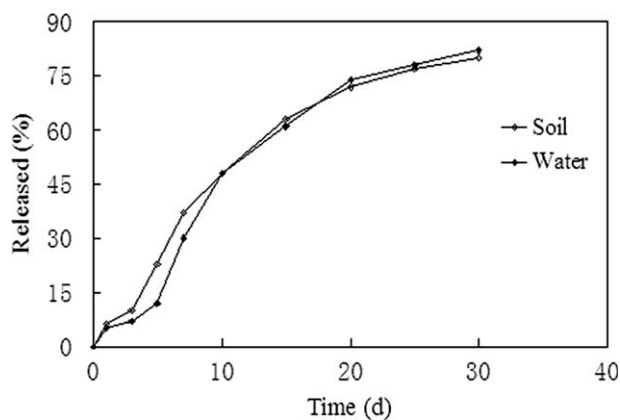
Figure 4 The nutrient release properties of PE-coated urea in (a) water and (b) soil.

thickness of the coating layer is 75 μm, the cumulative release rate was 49.1% at 80°C in 7 h versus 10.1% at 25°C in day 7. The results suggested that the temperature had a significant influence on the release of nutrient. The dependence of the dissolution rate of the encapsulated materials on the temperature was mainly originated from the increased solubility of the base fertilizer and a higher diffusion rate as the temperature increases. The results provided solid evidence that as the CRF immersed into the aqueous solution at high temperature, the nutrient release much faster. Thus, to reduce the nutrient loss during the coating process, the fluidized-bed coater should be adopted.

The release behaviors of PE-coated urea in water and soil

Figure 4 also shows the nutrient release behaviors of PE-coated urea in water and soil, respectively. It can be observed that as the time goes on, the release rates in both water and soil increase gradually, and the changing profile of curves were similar as shown in the Figure 3(a). For example, the release rate of the PE-coated urea was 48% in water compared with 48% in the soil after 10 days. The release rate of the fertilizer was 74% in water compared with 72% in the soil at day 20. The results indicated that the nutrient release behaviors of PE-coated urea in water and soil were basically the same. The results were in accordance with the article published.[20]

Optimization of water absorbency of P(AA-co-AM)-based SAPs

According to Flory's theory, the water absorbency of SAPs depends on the amount of the hydrophilic groups, crosslinking density, elasticity of the polymer networks, type of solvent, and ionic strength of the external solution, etc.[21] To improve the swelling capacity of the SAPs, optimization of various reaction parameters were conducted. The details of the influ-

ences of the polymerization parameters on water absorbency, such as the neutralization degree of AA, the concentration of crosslinker and initiator were given below. Other polymerization condition was set as following: monomer = 40 wt %; AA : NaA : AM = 30 : 20 : 50; emulsifier = 3.8%; $V_0/V_w = 0.4$.

Effect of neutralization degree of AA on the water absorbency

The effect of neutralization degree of AA on the water absorbency in tap water was shown in Figure 5(a). The water absorbency increased when neutralization degree of AA was from 55 to 65% and dropped further increased its amount. When AA was neutralized, part of the ─COOH turned into ─COO⁻. In water, the carboxyl groups set up an electrostatic repulsion which tended to expand the polymer network. Furthermore, the osmotic pressure increased with the higher of neutralization degree, which also contributed to the improvement of water absorbency.[12] In a certain range of neutralization degree, the electrostatic repulsion increased with the increase of neutralization degree. However, further increase in the neutralization degree of AA, water absorbency dropped due to the increased solubility of the superabsorbent composite. The optimum neutralization degree of AA is 65% in our research.

Effect of crosslinker concentration on the water absorbency

SAPs were slightly cross-linked copolymers, so the crosslinking agent plays an important role in the formation of "three-dimensional network" structures permanently in the polymerization process.[15] As shown in Figure 5(b), water absorbency increases with higher amount MBA concentration when the MBA concentration was lower than a critical concentration, and water absorbency dropped with increasing MBA concentration after the concentration was greater than critical concentration. The critical concentration of MBA was 0.078%. The above results can be explained as following: low crosslink agent content resulted in low crosslinking density, with smaller amount of crosslinking agent which would enable the polymer to be partly dissolved in water solution. However, after content of crosslinker reached summit point, further increase of the content crosslinking agent shrank the polymeric network and the water absorbency reduced consequently.

Effect of initiator concentration on the water absorbency

Figure 5(c) shows the dependence of water absorbency in tap water on initiator concentration. In this article, redox initiator was introduced which would reduce the temperature of the polymerization. There
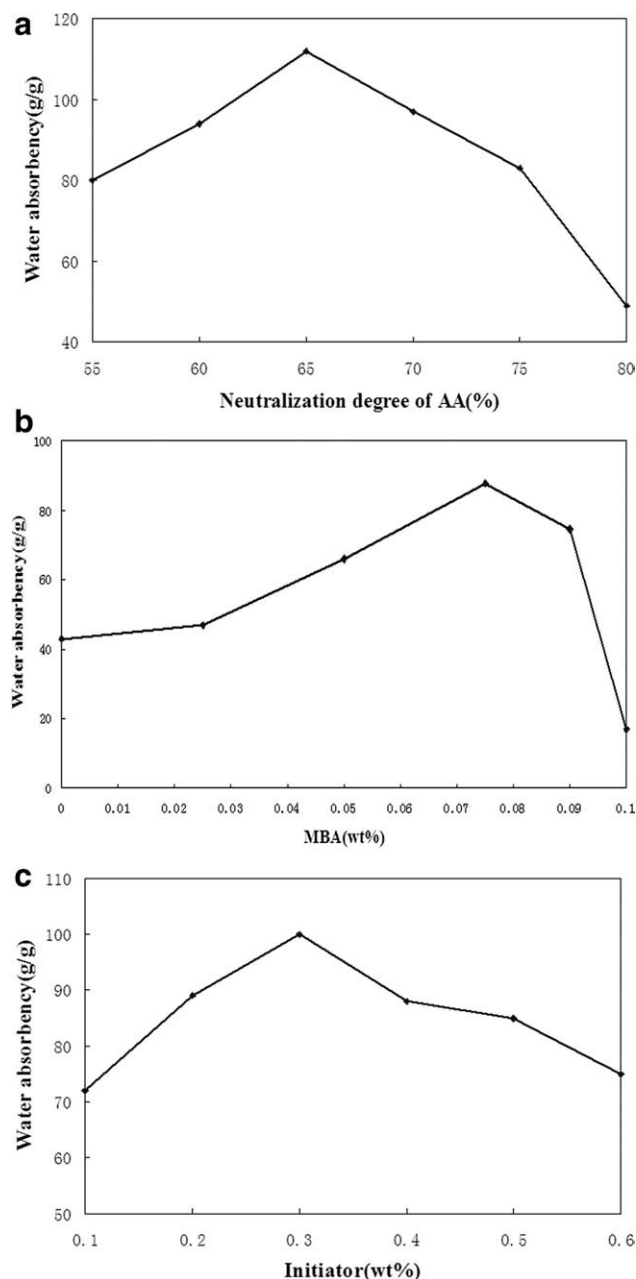
Figure 5 The effect of (a) neutralization degree of AA, (b) crosslinker concentration, and (c) initiator concentration on the water absorbency of the superabsorbent.

was a maximum water absorbency of the gels when the initiator concentration was 0.3 wt %. The water absorbency of gels increased with amount of initiator increase when the initiator concentration was below 0.3 wt % and then decreased gradually after that point. The results indicated as the initiator content was at low level, the slower the polymerization process, the less extensive the polymer network obtained, and the water absorbency was decreased consequently. However, as the initiator concentration increased, the higher the extent of chain transfer to the polymer and hence the crosslinking density,

i.e., the concentration of initiator and crosslinker have the same effect.[10]

Overall characterization of water retention and controlled release properties of TCWF

To evaluate overall performance of the PE/P(AA-*co*-AM)/PBMA triple layered fertilizer, the following experiment was conducted in this section.

Water retention behavior of TCWF in soil

Water retention capacity is one of the most important characteristics of TCWF. Figure 6 showed the water retention performance in the soil with (a) and without (b) TCWF. It can be found that the addition of TCWF to soil clearly increased the water retention. The water retention ratio of soil without TCWF remained 11.2 wt % at day 10, whereas that of the soil with TCWF was 14.2 wt %. After 20 days, the soil without TCWF had almost given off all the water, whereas the soil with TCWF still had 6 wt % water retention capacity. The trapped water in soil was primarily absorbed by TCWF and the water could be slowly released with the decrease of the soil moisture, and then assimilated by the plants.

The largest water-holding ratio of the soil with TCWF

It was reported that the use of SAPs in the agricultural field could increase the largest water-holding capacity and water retention capacity of soil.[12] Therefore, experiments to test the water-holding capacity and water retention behavior of soil with the adding of TCWF were performed. The result showed that the largest water-holding ratio of the soil with the adding of TCWF was 41.6 wt %, whereas that of the soil without TCWF was 33.2 wt %. Thus, indicating that the adding of TCWF to soil could improve the largest water holding capacity of the soil. Moreover, it was also observed that the water
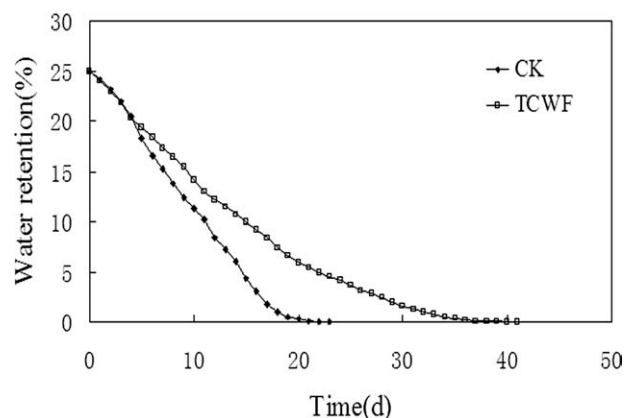

Figure 6 Water retention behaviors of soil with (a) TCWF and soil without (b) TCWF.
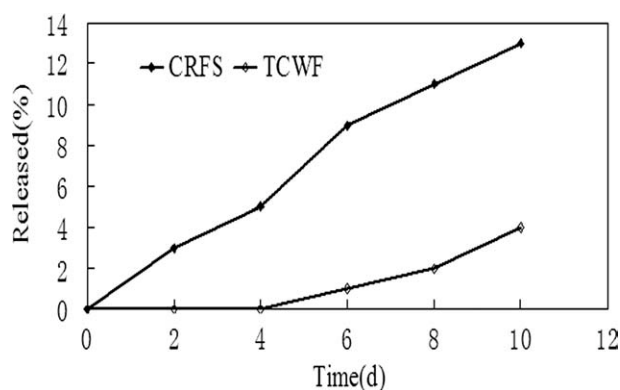
Figure 7 Influence of adding second and third layer on the nutrient release behaviors in soil with (a) P(AA-*co*-AM)/PBMA and without (b) P(AA-*co*-AM)/PBMA.

flow rate through the soil was slowed down when TCWF was added to the soil. This was a significant advantage of TCWF over regular CRFs. The results showed that the TCWF not only performed as good CRFs but also had excellent water retention capacity, which could effectively improve the use of nutrients of the fertilizer and water resource for the plant.

Influence of adding P(AA-co-AM)/PBMA on the nutrient release behaviors in soil

Figure 7 shows the release properties of the PE-coated CRFs in soil with the P(AA-*co*-AM)/PBMA (a) and without the P(AA-*co*-AM)/PBMA (b). For the PE-based CRF, the nutrient release rate was less than 3% within 2 days, and the release rate was around 12% in 10 days. For the PE/P(AA-*co*-AM)/ PBMA-based fertilizer, the release rate was much slower than that of the only PE-coated fertilizer. The nutrient did not release at the first several days, as the time was going on, the release rate increased slowly and reach 3% within 10 days. The phenomena was straightforward due to the double coated P(AA-*co*-AM)/PBMA, which added another barrier to prevent the nutrient transfer through the membrane. Behind this, the nutrient release mechanism of the PE/P(AA-*co*-AM)/PBMA-coated urea in the soil was quite different from PE-based CRFs due to the added superabsorbent layer and possible process can be described as followings: P(AA-*co*-AM)/ PBMA was slowly swollen by the soil solution and the PE layer was completely surrounded by the soil solution. After that, the soil solution gradually penetrated into the PE layer and dissolved the urea. As the internal pressure inside the PE shell increased, the nutrient gradually diffused the PE/P(AA-*co*-AM)/PBMA layer and released into the soil. Because P(AA-*co*-AM)/PBMA could not only block the soil solution from direct contact with the PE layer but also slow the release rate of nutrient ions into the soil, thus, the nutrient release of the PE was faster than

that of the PE/P(AA-*co*-AM)/PBMA. Therefore, the spongy TCWF was just like a microreservoir to retain and supply moisture and nutrition to crops, and thus could increase the utilization efficiency of water and fertilizer simultaneously. The study demonstrated that besides its controlled release property, the TCWF had excellent water retention, which the regular CRFs did not have. It could have potential application for the arid and desert areas in agriculture.

CONCLUSIONS

A triple polymer coated, controlled-release, and water retention fertilizer (TCWF) was prepared and characterized. Its core was urea fertilizer granular, the inner coating was PE, the middle coating was P(AA-*co*-AM) superabsorbent and the outer coating was PBMA. The adding of TCWF into soil could greatly improve the water holding ability and water retention property of the soil, and improve the availability of fertilizer and water resource to crops. The nutrients release behaviors of this triple-coated urea in both water and soil were showed that release behaviors in water and soil were basically the same. The results showed that the TCWF not only performed as a good CRF but also has excellent water retention capacity, which could effectively improve the utilization of nutrients of the fertilizer and water resource for the plant.

References

1. Schahram, B.; Sharyar, B.; Peter, W. Eur J Agron 2008, 28, 1.
2. Wang, F. L.; Alva, A. K. Soil Sci Soc Am J 1996, 60, 1454.
3. Alva, A. K.; Paramasivam, S.; Graham, W. D. J Environ Qual 1998, 27, 904.
4. Douglass, F.; Francis, K.; John, R. For Ecol Manage 2005, 214, 28.
5. Shaviv, A. Adv Agron 2001, 71, 1.
6. Tomaszewska, M.; Jarosiewicz, A. J Agric Food Chem 2002, 50, 4634.
7. Wallace, J. Agric Ecosyst Environ 2000, 82, 105.
8. Chan, A.; Whitney, R.; Neufeld, J. Biomacromolecules 2009, 10, 609.
9. Lu, S.; Duan, M.; Lin, S. J Appl Polym Sci 2003, 88, 1536.
10. Bakass, M.; Mokhlisse, A.; Lallemant, M. J Appl Polym Sci 2002, 83, 234.
11. Guo, M.; Liu, M.; Hu, Z.; Zhan, F.; Wu, L. J Appl Polym Sci 2005, 96, 2132.
12. Liang, R.; Liu, M. J Agric Food Chem 2006, 54, 1392.
13. Guo, M.; Liu, M.; Liang, R.; Niu, A. J Appl Polym Sci 2006, 99, 3230.
14. Liang, R.; Liu, M. Ind Eng Chem Res 2006, 45, 8610.
15. Park, K.; Chen, J.; Park, H. PCT: 9851408, A1 19981119.
16. Watano, S.; Nakamura, H.; Hamada, K.; Wakamatsu, Y.; Tanabe, Y.; Dave, R.; Pfeffer, R. Powder Technol 2004, 141, 3172.
17. Simms, R.; Cunningham, M. Macromolecules 2007, 40, 860.
18. Shaviv, A.; Smadar, R.; Zaidel, E. Environ Sci Technol 2003, 37, 2251.
19. Trenkel, M. E. Stratospheric Ozone; HMSO: London, 1997.
20. Xie, Y.; Yang, X.; Cao, Y.; Jiang, R.; Zhang, F. Plant Nutr Fert Sci 2007, 13, 491.
21. Flory, P. J. Principle of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.