



Multifunctional slow-release urea fertilizer from ethylcellulose and superabsorbent coated formulations

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ABSTRACT

The aim of this study was to prepare a double-coated, slow-release, and water-retention urea fertilizer (DSWU) to reduce environment pollution derived from excessive nitrogen fertilizer use. Ethylcellulose (EC) and crosslinked poly(acrylic acid-co-acrylamide) (P(AA-co-AM)) were used as inner and outer coating materials, respectively. The structural and chemical characteristics of the product, as well as its efficiency in slowing the nitrogen release and water evaporation in soil were examined. The nitrogen content of the product was 21.1% and its water absorbency was 70 times its own weight in tap water. Additionally, the biodegradation of EC coating in soil was assessed by differential scanning calorimetry (DSC) measurements. The results showed that the glass transition temperature (T_g) of EC coating decreased with the time prolonged, which indicated the biodegradability of EC coating in soil. These studies showed that the product with good slow-release and water-retention properties, being environmentally friendly, would find good application in agriculture and horticulture.

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1. Introduction

Fertilizer and water are important factors that limit the production of agriculture, so it is very important to improve the utilization of water resources and fertilizer nutrients. Nitrogen, the most widely applied plant nutrient, has commonly been considered to be the yield limiting one. However, the degree of utilization of nitrogen fertilizers is in the range of 30–50% [1]. Among the nitrogen fertilizers, the most widely used one is urea because of its high nitrogen content (46%) and comparatively low cost of production. As a neutral organic molecule, urea cannot be absorbed easily by the charged soil particles before hydrolyzing, resulting in a great quantity of urea running off and serious environmental hazards as only a fraction is really absorbed by plants.

One possible way to improve nutrients use efficiency while reducing the environmental hazards is by using slow-release fertilizers. Compared to the conventional type, slow-release fertilizers have many advantages, such as decreasing fertilizer loss rate, supplying nutrients sustainably, lowering application frequency and minimizing potential negative effects associated with overdosage [2,3]. Shaviv and Mikkelsen [4] proposed that slow-release fertilizers can be generally classified into 4 types: (i) inorganic materials of low solubility, such as metal ammonium phosphates; (ii) chemically or biologically degradable low solubility materials, such as

urea-formaldehyde; (iii) relatively soluble materials that gradually decompose in soil; and (iv) water soluble fertilizers controlled by physical barrier, such as coated fertilizers. Coated fertilizers, physically prepared by coating fertilizer granules with various materials, are the major categories of the slow-release fertilizers [5]. Many materials have been reported to be used as coatings, such as polysulfone [6], polyvinyl chloride [7], polystyrene [8]. However, after the release of fertilizers, remaining coating materials in the soil are very difficult to degrade and can accumulate over time to become a new type of pollution. Therefore, the environmentally safe and biodegradable coating materials are expected to be used.

Ethylcellulose (EC) is an inert, non-ionic water-insoluble polymer widely used to prepare slow-release formulations of drugs and herbicides due to its controlled release property [9,10]. In addition, as a biodegradable polymer, EC can be used in fertilizer coating, which may avoid large amounts of coating materials left in soil when the nutrients are released. However, little information has been given about this. Regarding the degradation, there are many communications concerning the degradation of cellulose and cellulose derivatives by different ways [11,12]. In this experiment, the decrease of glass transition temperature (T_g) by the measurement of differential scanning calorimetry (DSC) was used to imply the biodegradability of EC coating in soil.

Superabsorbents are the three-dimensionally crosslinked hydrophilic polymers that can absorb and retain large volumes of water up to thousands of times their own weight, and the absorbed water is hardly removable even under pressure. Because of their excellent characteristics, superabsorbent polymers have

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been used extensively in agriculture and horticulture [13]. Many investigations have shown that they can help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in soil, and increase plant growth rate [14].

We have intensively studied slow-release fertilizers combined with superabsorbents to obtain both slow-release and water-retention properties. In general, combining fertilizers with superabsorbents is done by two methods. In the first method, fertilizers are blended with superabsorbents. In the second approach, fertilizers are added to the reaction mixture and polymerized in situ whereby the fertilizers are entrapped in the superabsorbents. These two methods always lead to a “burst effect” and higher release rate [15,16]. To overcome this, a new combining method is needed. In addition, previous paper [6] reported that the release rate is strongly related to the physical properties of the coatings such as the porosity and the hydrophobic/hydrophilic character. The study showed that the multicoated granules' release rate was lower because of the more compact structure of the coating and the lower porosity in comparison with that for the single coating. They also pointed out that the release rate of NH_4^+ was 3 times faster in the case of hydrophilic coating. Thus, coating materials with low porosity and hydrophobic are required.

To satisfy these requirements, we developed a double-coated urea fertilizer. The choice of the coatings is largely dictated by the problems to be addressed above. Superabsorbents were used as the outer coating instead of blending or polymerizing with fertilizers and EC was used as the inner coating. The research orientation has been ongoing to prepare a multifunctional fertilizer that can be used in agro-industries.

2. Materials and methods

2.1. Materials

Acrylic acid (AA, chemical grade, Beijing Eastern Chemical Works, Beijing, China) and N-vinyl-pyrrolidone (NVP, 98%, ACROS) were distilled at reduced pressure before use. Acrylamide (AM, analytical grade, Shanghai Chemical Factory, Shanghai, China) and ethylcellulose (EC, viscosity 40–100 mPa·s, Shanghai Chemical Factory, Shanghai, China) were used as purchased. N,N'-azobisisobutyronitrile (AIBN) and N,N'-methylene bisacrylamide (NNMBA) were recrystallized from 95% ethanol prior to use. All other chemicals were analytical grade and used as received.

2.2. Preparation of poly(N-vinyl-pyrrolidone) hydrogels containing urea (PCU)

5 g of urea and 2.4 g of NVP were first dissolved in 4 mL of distilled water, and then 0.1% (w/w) AIBN and 6% (w/w) NNMBA were added based on the weight of the monomer, and continuously stirred to form homogeneous mixture. The mixture solution was then moved to a tube and degassed 20 min by nitrogen purging. The polymerization was carried out at 65 °C for 3 h. The resulting samples were vacuum-dried, milled, screened and stored for future use.

2.3. Preparation of DSWU

4 g of dried PCU power (below 90 mesh) and 40 g of urea were placed into a glass beaker and stirred well with 100 mL of 2% (w/w) sodium alginate (SA) solution. The mixed solution was then added dropwise into 5% (w/w) CaCl_2 aqueous solution and stirred constantly. The drops immediately turned into granules (about 4 mm in diameter) because the SA in the drop was crosslinked by Ca^{2+} at once. The granules were filtered and dried in oven at 70 °C.

A sample of dried granules (5 g) obtained as mentioned before, was added into 6% (w/v) EC ethanol solution. Then the granules coated with a thin layer of EC were removed and dried at 70 °C. Multiple EC coatings were prepared by immersion of the previously coated granules into the EC solution repeatedly. Thus, EC-coated urea granules with different coating thickness were obtained.

The EC-coated urea granules (5 g) were added into a flask equipped with a mechanical stirrer and a condenser. A certain amount of cyclohexane, sorbite anhydride monostearic acid ester (Span-80) and polyethylene glycol octyl phenyl ester (OP) were added into the flask. The temperature was raised to 65 °C under N_2 atmosphere while the contents were constantly stirred. As this process continued, a certain amount of mixed solution of AM, partially neutralized AA (by 8 mol/L NaOH), NNMBA, and ammonium persulfate (APS) were added into the flask. Two hours later, the mixture was filtered to remove the cyclohexane and dried in an 70 °C oven to obtain the final products.

2.4. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out with Nicolet NEXUS 670 FTIR spectrometer. The samples were dried completely and ground to fine power, then pushed down to piece blending with KBr.

2.5. Determination of the nitrogen content

The nitrogen contents of DSWU were determined by an elemental analysis instrument (Germany Elemental Vario EL Corp., model 1106).

2.6. Measurement of water absorbency of DSWU

1 g of DSWU was immersed into a certain amount of tap water and allowed to soak at room temperature for 90 min. The swollen DSWU was filtered through an 80-mesh sieve to remove non-absorbed water and weighted. The water absorbency (WA) was calculated using Eq. (1):

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

where M and M_0 refer to the weight of the swollen and dried DSWU, respectively.

2.7. Slow-release behavior of DSWU in soil

To study the slow-release behavior of DSWU in soil, the following experiment was carried out: 1 g of DSWU was well mixed with 200 g of dry soil (below 26 mesh) and kept in a 200 mL glass beaker properly covered and incubated for different periods at room temperature. Throughout the experiment, the soil sample was maintained at 30 wt% water-holding capacity by weighting and adding tap water if necessary, periodically. After 1, 2, 5, 10, 15, 20, 25 and 30 days, the remaining granules in the beaker were picked out, washed with distilled water, and then dried at 70 °C to a constant weight to be estimated for the content of nitrogen.

2.8. Measurement of the largest water-holding ratio of soil with DSWU

The sandy soil used in this study was representative of the area of Lanzhou, which lies in the northwest of China and is a dry and semidesert region. 2 g of DSWU was well mixed with 200 g of dry soil (below 26 mesh) and placed in a 4.5 cm diameter of PVC tube. The bottom of the tube was sealed with nylon fabric (with the aperture of 0.076 mm) and weighed (marked W_1). The soil sample was

Table 1
Characteristics of DSWU.

Characteristics	Value
Nitrogen content	21.1%
Diameter of dry sample	4.0–5.0 mm
Diameter of swollen sample	12–14 mm
EC coating percentage	2–2.5%
P(AA-co-AM) coating percentage	45–47%

slowly drenched 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). A control experiment without DSWU was also carried out. The largest water-holding ratio (WH%) of the soil was calculated from Eq. (2):

$$WH\% = \frac{(W_2 - W_1) \times 100}{200} \quad (2)$$

2.9. Measurement of the water-retention of DSWU in soil

2 g of DSWU was well mixed with 200 g of dry soil (below 26 mesh) and kept in a glass beaker, and then 200 g of tap water was slowly added into the beaker and weighed (marked M_1). A control experiment without DSWU was also carried out. The beaker was maintained at room temperature and weighed every 3 days (marked M_i) over a period of 24 days. The water evaporation ratio (WE%) of soil was calculated from Eq. (3):

$$WE\% = \frac{(M_1 - M_i) \times 100}{200} \quad (3)$$

2.10. Degradation of EC coating

A solution of EC (6%, w/v) in ethanol was cast on a clean glass plate as a dense film. The solvent was evaporated to dryness, and films were vacuum dried. The films thickness, measured with a micrometer, was found to be 25–45 μm . The obtained cast films (40 mm \times 20 mm) were buried 100 mm beneath the surface of the soil in a glass beaker and incubated for different periods at room temperature. Throughout the experiment, the soil sample was maintained at 30 wt% water-holding capacity by weighing and adding tap water if necessary, periodically. After 0, 30, 60 and 90 days, the films in the beaker were taken out, washed and vacuum-dried for DSC determination.

DSC measurements were performed using a Sapphire DSC (Perkin-Elmer, America) with the following parameters. Sample weight: 5–10 mg; heating rate: 10 $^{\circ}\text{C}/\text{min}$; atmosphere: nitrogen. The samples were heated up to 120 $^{\circ}\text{C}$ in order to remove their thermal history and cooled down to 25 $^{\circ}\text{C}$, and then reheated to 250 $^{\circ}\text{C}$.

2.11. Morphology of DSWU

The surface and cross-section morphologies of the granules of DSWU were examined by scanning electron microscopy (SEM). The samples were coated with gold and then observed in a JSM-5600 LV SEM (Japan).

3. Results and discussion

3.1. Structure and characteristics of DSWU

The structure of DSWU granules was the core/shell structure. Its core is urea and PCU in SA matrix, inner coating is EC, and outer coating is crosslinked P(AA-co-AM) superabsorbent polymer. The characteristics of DSWU are presented in Table 1.

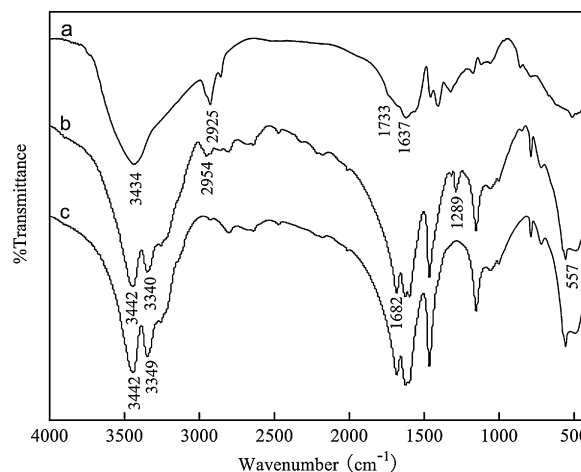


Fig. 1. FTIR spectra of P(AA-co-AM) (a), PCU (b), and urea (c).

3.2. FTIR analysis of P(AA-co-AM), PCU, and urea

Fig. 1 shows the FTIR spectra of P(AA-co-AM), PCU, and urea. Some characteristic peaks in P(AA-co-AM) spectrum (Fig. 1a) can be ascribed as: 3434 cm^{-1} for N–H stretching, 2925 cm^{-1} for C–H stretching, 1733 cm^{-1} for C=O stretching of acrylate unit, and 1637 cm^{-1} for C=O stretching of acrylamide unit [17]. Urea (Fig. 1c) has two strong N–H stretching absorption bands at 3442 and 3349 cm^{-1} , corresponding to asymmetric and symmetric vibration, respectively. It is noted that, in the spectrum of PCU (Fig. 1b), the band at 3349 cm^{-1} shifts to 3340 cm^{-1} , showing the existence of the intermolecular hydrogen bonding interactions between urea and PVP. Meanwhile, there exists the characteristic peaks of PVP (2954 cm^{-1} for C–H stretching and 1289 cm^{-1} for C–N stretching) [18] and urea (1682 cm^{-1} for C=O stretching and 557 cm^{-1} for N–CO–N), indicating the involvement of PVP and urea in PCU.

3.3. Influence of the parameters on water absorbency

One of the important properties of DSWU is the water absorbency due to the superabsorbent polymer as outer coating. To improve the water absorbency capacity of the products, various reaction parameters such as monomer ratio, crosslinker content, initiator content, and neutralization degree of AA were optimized. The details are given below.

3.3.1. Effect of the monomer ratio on water absorbency

The hydrophilic groups play an extremely important part in water absorbency. In the P(AA-co-AM) polymeric system, the ratio of different hydrophilic groups can be adjusted by changing the proportion of AM to AA. The effect of the monomer ratio on water absorbency of DSWU is shown in Fig. 2a (reaction condition: neutralization degree of AA, 85%; crosslinker, 0.05%; initiator, 0.1%; reaction time, 2 h; reaction temperature, 65 $^{\circ}\text{C}$). There exists a maximum when the ratio is 0.3. The water absorbency increases when the ratio is below 0.3, and decreases with higher content of AM. The reason for the change can be explained as follows: AM is a non-ionic monomer and the ions in solution have little influence on it, so it could improve the salt-resistance ability of DSWU. Therefore, with higher amount of AM, water absorbency increases. On the other hand, $-\text{COO}^-$ has better hydrophilic ability than $-\text{CONH}_2$, so water absorbency decreases with further increase of the content of AM [19].

3.3.2. Effect of the crosslinker content on water absorbency

As we know, crosslinker is essential for the formation of three-dimensional network structures in the polymerization process. The greater the amount of crosslinker is, the higher crosslinking density of the hydrogel. As we can see from Fig. 2b (reaction condition: neutralization degree of AA, 85%; monomer ratio, 0.3; initiator, 0.075%; reaction time, 2 h; reaction temperature, 65 °C), when the crosslinker content is lower than 0.05 wt%, water absorbency increases with the increase of the crosslinker content. This could be attributed to the increase of the crosslinking density and the hydrophilicity of the network. When the crosslinker content is larger than 0.05 wt%, a further increase of the crosslinker content results in the generation of more crosslinking points, which consequently causes the formation of an additional network and decreases the space for holding water. These results are in accordance with Flory's network theory [20].

3.3.3. Effect of the initiator content on water absorbency

The effect of the initiator content on water absorbency is shown in Fig. 2c (reaction condition: neutralization degree of AA, 85%; crosslinker, 0.05%; monomer ratio, 0.3; reaction time, 2 h; reaction temperature, 65 °C). It can be seen that, the water absorbency increases as the initiator content rises from 0.025 to 0.075 wt% and decreases when the initiator content is greater than 0.075 wt%. When the initiator is lower than 0.075 wt%, the polymerization reaction rate is slow, the polymer network could not be formed efficiently, and the water absorbency is low. According to Allcock and Lampe [21], the average kinetic chain length is in inverse proportion to the square root of the initiator concentration in free-radical

polymerization. So with increasing the initiator concentration the molecular weight of the polymer backbone decreases, and then more chain ends are generated, which do not contribute to the water absorbency. Thus, further increasing the initiator is responsible for the decrease of water absorbency. Furthermore, higher initiator content, such as more than 0.075 wt%, means a faster reaction rate and higher crosslinking density, which causes the decrease of the water absorbency.

3.3.4. Effect of neutralization degree of AA on water absorbency

Fig. 2d shows the effect of neutralization degree of AA on water absorbency of DSWU (reaction condition: monomer ratio, 0.3; crosslinker, 0.05%; initiator, 0.1%; reaction time, 2 h; reaction temperature, 65 °C). Neutralization degree is defined as the molar percentage of carboxyl in AA neutralized by sodium hydroxide. Water absorbency increases as neutralization degree changes from 60% to 85%, and decreases with larger neutralization degree of AA. The neutralization degree of AA not only affects the polymerization rate, but also determines the number of charges in the three-dimensional network of P(AA-co-AM). Within a certain range of degree of neutralization, the carboxyl acid group of AA turns into carboxylate group. The negatively charged carboxylate groups attached to the polymer chains set up an electrostatic repulsion that tends to expand the network. This results in the increase of water absorbency with the increase of neutralization degree. However, when the neutralization degree of AA is larger than 85%, the screening effect of the sodium ions on the polyanion chain will reduce the electrostatic repulsion of the network, which results in the decrease of water absorbency of the P(AA-co-AM) polymer.

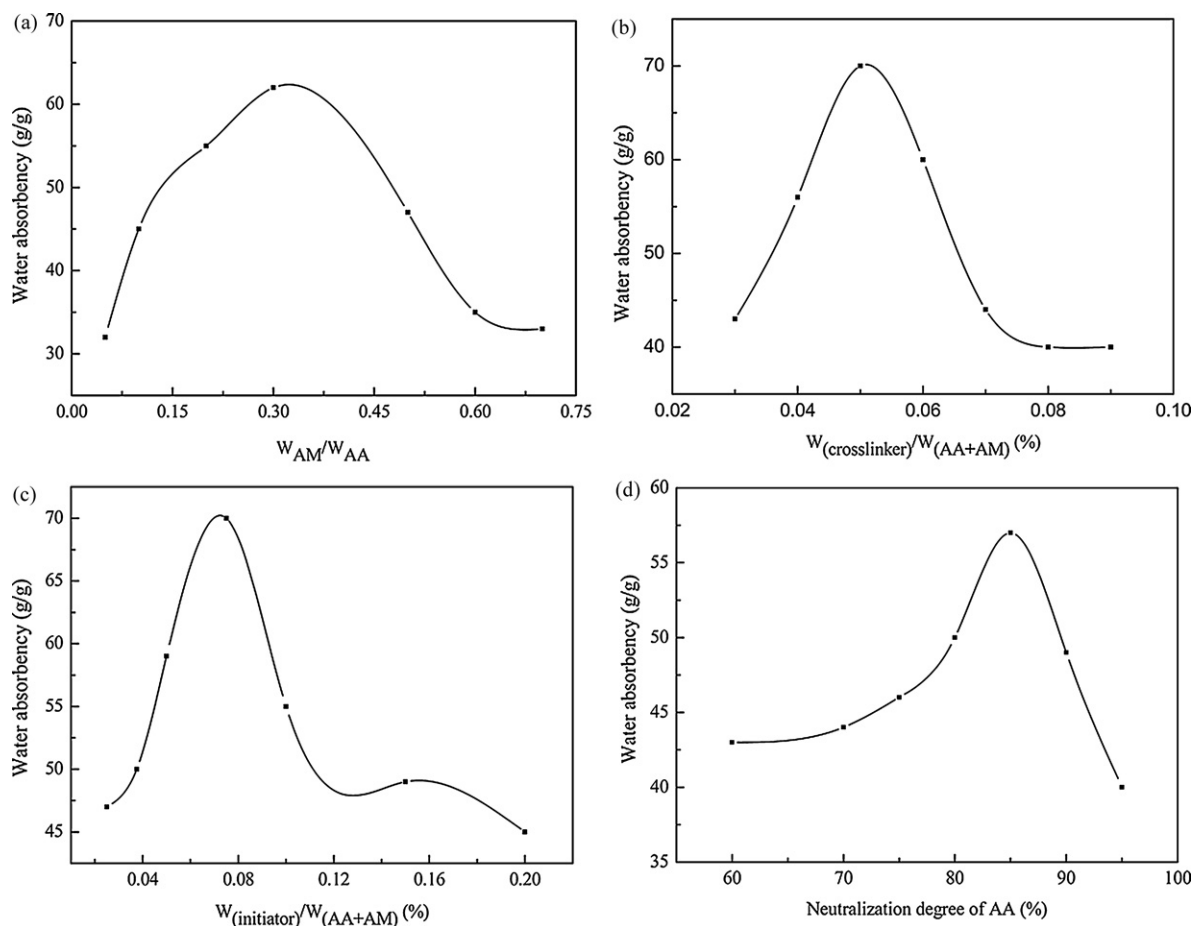


Fig. 2. Effect of the parameters on water absorbency: (a) monomer ratio, (b) crosslinker content, (c) initiator content, and (d) neutralization degree of AA.

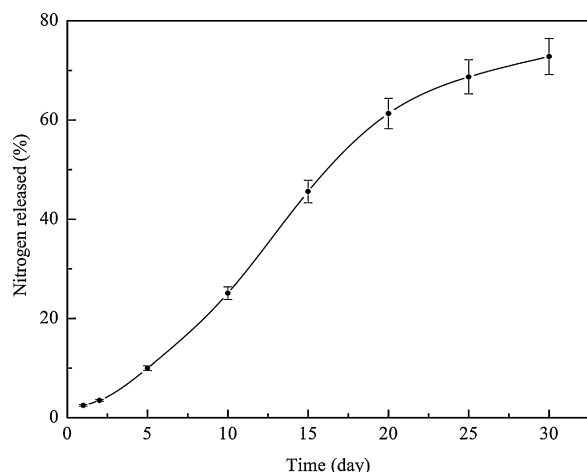


Fig. 3. Nitrogen slow-release behavior of DSUW in soil.

Meanwhile, the activity of acrylic acid is higher than that of acrylate, so the larger the neutralization degree is, the lower the polymerization rate. The low polymerization rate would result in the increase of the amount of soluble materials in the DSUW and consequently the water absorbency decreases.

3.4. Effect of ions on water absorbency

Water absorbency of the DSUW may also be influenced by the ions in the water. In this work, the effect of ions on water absorbency is investigated in tap water and distilled water. The results show that the water absorbency is larger in distilled water (134 times its weight) than in tap water (70 times its weight). This shows that the presence of ions in the swelling medium has a profound effect on the absorbency behavior of the DSUW. According to Donnan equilibrium theory, osmotic pressure is the driving force for swelling of the DSUW. In tap water, the osmotic pressure difference between the polymeric network and the external solution decreases, resulting in the decrease of the water absorbency. In addition, the penetration of counterions (such as Na^+ , Mg^{2+} and Ca^{2+} in tap water) into the polymeric network makes the screening effect of them on anionic group ($-\text{COO}^-$) more evident [22], which also decreases the water absorbency of the DSUW. Furthermore, in the case of tap water with multivalent cations, “ionic crosslinking” at surface of the DSUW causes an appreciable decrease in water absorbency. Castel et al. [23] reported that calcium ion can drastically decrease the swelling capacity for a hydrolyzed SPAN (starch and polyacrylonitrile graft copolymer), due to the complexing ability of the carboxylate groups inducing the formation of intra- and intermolecular complexes.

3.5. Slow-release behavior of DSUW in soil

One of the important characteristics of the DSUW we prepared is its slow-release property. Fig. 3 represents the nitrogen slow-release behavior of DSUW in soil. It is well known that almost all of the urea would quickly dissolve in water after being added into soil, and then the nitrogen is released completely during several days. According to the results of our previous study [8], more than 98.5 wt% of nitrogen in untreated urea granules was released within 12 h. As shown in Fig. 3, the nitrogen in DSUW we prepared possesses excellent slow-release property: the nitrogen in DSUW released 3.5, 10, and 72.8 wt% within 2, 5, and 30 days, respectively. The DSUW nitrogen release does not exceed 15 wt% by the second day and is not above 75 wt% on the 30th day. These results indicate that the slow-release property of DSUW conforms to the

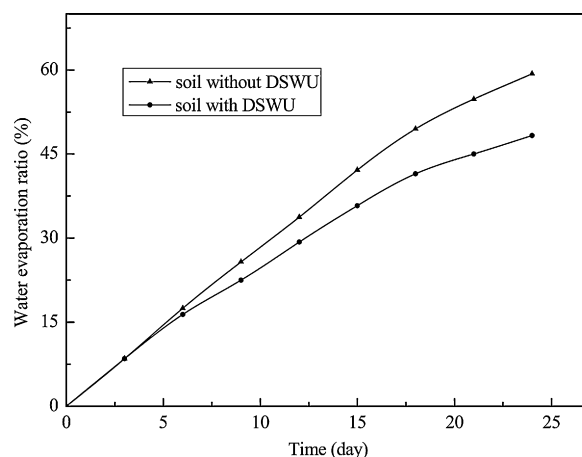


Fig. 4. Water-retention behavior of soil without and with DSUW.

standard of slow-release fertilizers of the Committee of European Normalization (CEN) [24].

The nutrient release mechanism of DSUW fertilizer can be described as the following: (1) The outer P(AA-co-AM) superabsorbent coating was swollen and then transformed into hydrogel after being added into soil. (2) When the free water in the P(AA-co-AM) outer coating was transferred to the inner layer (EC coating), it penetrated the inner coating slowly through the tiny pores and holes. (3) This part of water would continue to diffuse into the crosslinked network of SA and PCU, and then dissolve the soluble urea. (4) The dissolved urea diffused out from the EC coating and entered the P(AA-co-AM) layer, and then released into soil through the dynamic exchange of free water. So the existence of the outer coating and the inner coating regulated the release behavior of urea and minimized the burst release effect of fertilizers. Meanwhile, the use of SA and PCU made the nitrogen release slowly, because of the physical barrier of the hydrogel matrix and the intermolecular hydrogen bond between poly(N-vinyl-pyrrolidone) and urea.

3.6. Maximum water-holding ratio of soil

Water-holding capacity of soil is crucial to plants. The experiment showed that the maximum water-holding ratio of the soil with DSUW was 70.0 wt%, while that of the soil without DSUW was 45.0 wt%. It is due to the excellent water absorbency capacity of the P(AA-co-AM) superabsorbent. This shows that the DSUW we prepared has excellent water absorbency and could obviously reduce

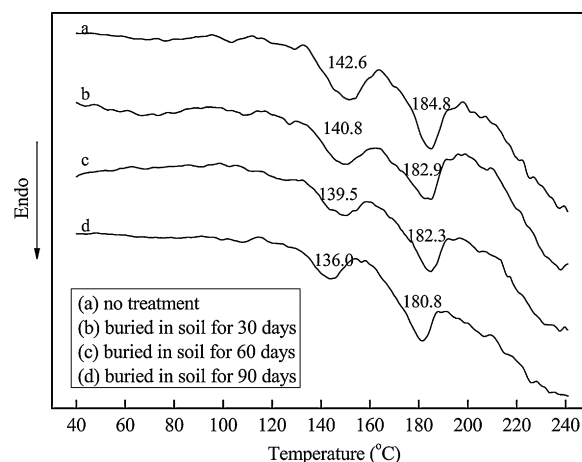


Fig. 5. Measurement of T_g of EC coating by DSC.

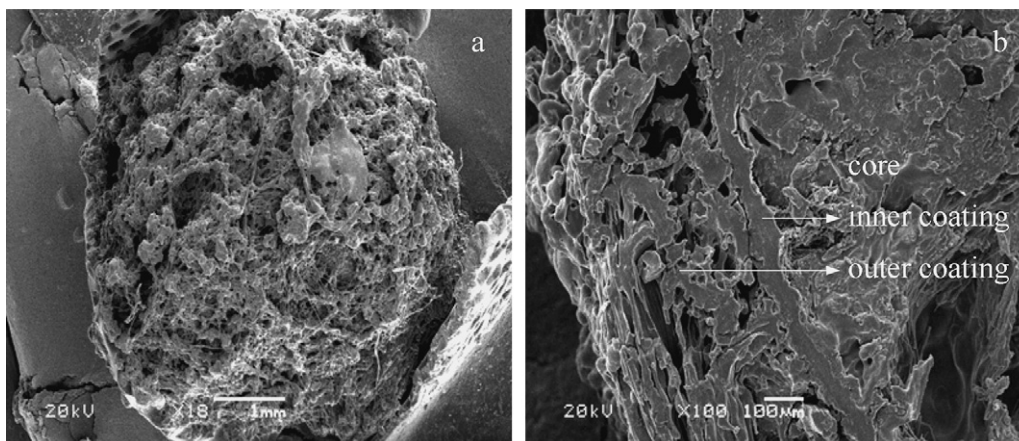


Fig. 6. SEM images of the surface (a) and cross-section (b) of DSWU.

water evaporation, improve the water-holding capacity of soil, and efficiently reduce irrigation water consumption.

3.7. Water-retention behavior of DSWU in soil

Another principal property of DSWU we prepared is its water-retention capacity. Fig. 4 shows the water-retention behavior of soil with and without DSWU. It can be found that the water transpiration ratio of soil without DSWU had reached 42.1 and 59.3 wt% on the 15th and 24th day, respectively, while that of soil with DSWU was 35.8 and 48.3 wt%, respectively. The results indicate that the addition of DSWU to soil could obviously increase the water-retention and decrease the water evaporation. Similar phenomena were also found by others [25,26]. It could be inferred that the absorbed water in the P(AA-co-AM) coating could be gradually released with the decrease of the soil moisture, and then taken by plants. At the same time, fertilizer nutrients could also be released slowly with the water. Therefore, the swollen DSWU is just like a microreservoir for plants. This is a significant advantage of DSWU over normal slow-release fertilizers.

3.8. Degradation of EC coating

The glass transition temperature (T_g) of EC is not only important in terms of the mechanical performance of the coating but also a fundamental parameter of the polymer related to its chemical structure [27]. Fig. 5 shows the change of T_g of EC coating with increasing periods of soil microorganism treatment. It can be seen that, the T_g of EC coating is 140.8 °C on the 30th day, 139.5 °C on the 60th day, and 136.0 °C on the 90th day, respectively, while that of untreated EC coating is 142.6 °C. The decrease of T_g illustrates the biodegradation of EC coating. The evidence also comes from the decrease of the softening point at about 180 °C. This may result from partial destruction of intra- and intermolecular hydrogen bonds in crystal zone of EC by the action of soil microorganism. In general, 15–30% of the fertilizer packed in a coating material is difficult to release because of the decrease in the concentration difference between the inside and outside of the coating material [28]. So the use of biodegradable EC coating material enables the remaining nutrients release completely in the later stage of release.

3.9. Morphology of DSWU

The SEM of the surface and cross-section of DSWU are shown in Fig. 6. Fig. 6a displays the rough surface of DSWU and there are many apertures on it, so water can be absorbed quickly by the fertilizer granules because of the high specific surface area. Fig. 6b shows

the three-layer structure of the DSWU. The outer layer is P(AA-co-AM) superabsorbent composite, which can not only absorb a lot of water and preserve the soil moisture but also regulate the slow-release behavior of the products. The middle layer is EC, which serves as a physical barrier for reducing the rate of water diffusion into the core and the nutrient diffusion outside the core. The core is SA granules crosslinked by Ca^{2+} containing urea and PCU. In summary, the two layers enable DSWU to have the water-retention and slow-release properties.

4. Conclusion

A double-coated, slow-release and water-retention urea (DSWU) fertilizer was prepared, which possessed a three-layer structure: the core was pure urea and poly(N-vinyl-pyrrolidone) hydrogel containing urea in a sodium alginate matrix, the inner coating was ethylcellulose, and the outer coating was crosslinked poly(acrylic acid-co-acrylamide) superabsorbent. Elemental analysis showed that the nitrogen content of the product was 21.1%. Its water absorbency was 70 times its own weight in tap water. The results of the slow-release experiment showed that the release ratio of the effective nutrient was below 75% after being incubated in soil for 30 days. The addition of DSWU into soil could significantly improve the water-holding capacity and water-retention property of soil. The results of the present work indicated that DSWU was a multifunctional slow-release fertilizer, which may find application in agriculture and horticulture, especially in drought-prone areas where the availability of water is insufficient. Further studies are required to reduce the cost of the product and improve its performance, and these studies are currently in progress in our group.

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References

- [1] A.A. Ibrahim, B.Y. Jibril, Controlled release of paraffin wax/rosin-coated fertilizers, *Ind. Eng. Chem. Res.* 44 (2005) 2288–2291.
- [2] S.M. Al-Zahrani, Utilization of polyethylene and paraffin waxes as controlled delivery systems for different fertilizers, *Ind. Eng. Chem. Res.* 39 (2000) 367–371.
- [3] M.Y. Guo, M.Z. Liu, R. Liang, A.Z. Niu, Granular urea-formaldehyde slow-release fertilizer with superabsorbent and moisture preservation, *J. Appl. Polym. Sci.* 99 (2006) 3230–3235.

- [4] A. Shaviv, R. Mikkelsen, Controlled-release fertilizers to increase efficiency of nutrient use and minimize environmental degradation—a review, *Nutr. Cycl. Agroecosyst.* 35 (1993) 1–12.
- [5] M. Tomaszewska, A. Jarosiewicz, K. Karakulski, Physical and chemical characteristics of polymer coatings in CRF formulation, *Desalination* 146 (2002) 319–323.
- [6] A. Jarosiewicz, M. Tomaszewska, Controlled-release NPK fertilizer encapsulated by polymeric membranes, *J. Agric. Food Chem.* 51 (2003) 413–417.
- [7] M.M. Hanafi, S.M. Eltaib, M.B. Ahmad, Physical and chemical characteristics of controlled release compound fertiliser, *Eur. Polym. J.* 36 (2000) 2081–2088.
- [8] R. Liang, M.Z. Liu, Preparation and properties of a double-coated slow-release and water-retention urea fertilizer, *J. Agric. Food Chem.* 54 (2006) 1392–1398.
- [9] G.S. Rekhi, S.S. Jambhekar, Ethylcellulose—a polymer review, *Drug Dev. Ind. Pharm.* 21 (1995) 61–77.
- [10] O.D. Dailey, C.C. Dowler, B.G. Mullinix, Polymeric microcapsules of the herbicides atrazine and metribuzin: preparation and evaluation of controlled-release properties, *J. Agric. Food Chem.* 41 (1993) 1517–1522.
- [11] C.H. Choi, A.P. Mathews, Two-step acid hydrolysis process kinetics in the saccharification of low-grade biomass. 1. Experimental studies on the formation and degradation of sugars, *Bioresour. Technol.* 58 (1996) 101–106.
- [12] H.B. Klinke, B.K. Ahring, A.S. Schmidt, A.B. Thomsen, Characterization of degradation products from alkaline wet oxidation of wheat straw, *Bioresour. Technol.* 82 (2002) 15–26.
- [13] F.L. Buchholz, A.T. Graham, *Modern Superabsorbent Polymer Technology*, Wiley-VCH, New York, 1998.
- [14] D.L. Bouranis, A.G. Theodoropoulos, J.B. Drossopoulos, Designing synthetic polymers as soil conditioners, *Commun. Soil Sci. Plant Anal.* 26 (1995) 1455–1480.
- [15] L. Wu, M.Z. Liu, R. Liang, Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention, *Bioresour. Technol.* 99 (2008) 547–554.
- [16] M.Z. Liu, R. Liang, F.L. Zhan, Z. Liu, A.Z. Niu, Preparation of superabsorbent slow release nitrogen fertilizer by inverse suspension polymerization, *Polym. Int.* 56 (2007) 729–737.
- [17] J.P. Zhang, A. Li, A.Q. Wang, Synthesis and characterization of multifunctional poly(acrylic acid-co-acrylamide)/sodium humate superabsorbent composite, *React. Funct. Polym.* 66 (2006) 747–756.
- [18] O. Şanlı, E. Biçer, N. Işıklan, In vitro release study of diltiazem hydrochloride from poly(vinyl pyrrolidone)/sodium alginate blend microspheres, *J. Appl. Polym. Sci.* 107 (2008) 1973–1980.
- [19] J.H. Wu, Y.L. Wei, J.M. Lin, S.B. Lin, Study on starch-graft-acrylamide/mineral powder superabsorbent composite, *Polymer* 44 (2003) 6513–6520.
- [20] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- [21] H.R. Allcock, F.W. Lampe, *Contemporary Polymer Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1990.
- [22] J.P. Zhang, H. Chen, A.Q. Wang, Study on superabsorbent composite. III. Swelling behaviors of polyacrylamide/attapulgitite composite based on acidified attapulgitite and organo-attapulgitite, *Eur. Polym. J.* 41 (2005) 2434–2442.
- [23] D. Castel, A. Ricard, R. Audebert, Swelling of anionic and cationic starch-based superabsorbents in water and saline solution, *J. Appl. Polym. Sci.* 39 (1990) 11–29.
- [24] M.E. Trenkel, *International Fertilizer Industry Association, Stratospheric Ozone*, HMSO, London, 1997.
- [25] M.S. Johnson, The effects of gel-forming polyacrylamides on moisture storage in sandy soils, *J. Sci. Food Agric.* 35 (1984) 1196–1200.
- [26] M. Bakass, A. Mokhlisse, M. Lallemand, Absorption and desorption of liquid water by a superabsorbent polymer: effect of polymer in the drying of the soil and the quality of certain plants, *J. Appl. Polym. Sci.* 83 (2002) 234–243.
- [27] P. Sakellariou, R.C. Rowe, Interactions in cellulose derivative films for oral drug delivery, *Prog. Polym. Sci.* 20 (1995) 889–942.
- [28] J.J. Ge, R. Wu, X.H. Shi, H. Yu, M. Wang, W.J. Li, Biodegradable polyurethane materials from bark and starch. II. Coating material for controlled-release fertilizer, *J. Appl. Polym. Sci.* 86 (2002) 2948–2952.