Granular Urea-Formaldehyde Slow-Release Fertilizer with Superabsorbent and Moisture Preservation

Mingyu Guo,[1] Mingzhu Liu,[1] Rui Liang,[1] Aizhen Niu[2]

[1]*Department of Chemistry, Lanzhou University, Lanzhou, 730000, People's Republic of China*
[2]*IFF-640, Forschungszentrum Juelish, 52425 Juelich, Germany*

ABSTRACT: To improve the utilization of fertilizer and water resource at the same time, a new type of slow-release fertilizer with superabsorbent and moisture preservation was developed, with the combination of slow-release technique and superabsorbent polymers. The coatings were formed by the inverse phase polymerization technique. The element analysis results showed that the product contained 22.58% nitrogen element, and the water absorbency of the product was 94 times its own weight if it was allowed to swell in tap water at room temperature for 2 h. The results of the slow-release behavior of N and the water absorbency and retention properties in soil showed that the product not only had good slow-release property but also had excellent water absorbency and water retention capacity, which was a significant advantage over the normal slow-release or controlled-release fertilizers. The effects of the amount of initiator, crosslinker, reaction time, and the degree of neutralization of acrylic acid on water absorbency were investigated and optimized. At the same, a rather new and simple method was used to make homogeneous urea-formaldehyde granules. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3230–3235, 2006

Key words: slow-release fertilizer; superabsorbent polymers; urea formaldehyde; moisture preservation

INTRODUCTION

Fertilizers are one of the most important products of the agrochemical industry. They are added to the soil to release nutrients necessary for plant growth.[1] However, the potential hazards of fertilizers to the environment have resulted in stringent limitations on their use. About half of the applied fertilizers, depending on their method of application and soil condition, is lost to the environment, which not only results in large economic and resource losses but also in very serious environmental pollution.[2–4] One method to effectively solve this problem is to use slow-release fertilizers, which have demonstrated many advantages over the conventional type, such as decreased rate of removal of the fertilizer from the soil by rain or irrigation water, sustained supply of nutrition for a prolonged period, increased efficiency of the fertilizer, lower frequency of application in accordance with normal crop requirement, minimized potential negative effects associated with overdosage, and reduced toxicity.

Moreover, tests of superabsorbent polymers for agricultural applications have shown encouraging results because they have been observed to help improve utilization of water, reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in the soil, and increase plant growth rates.[5–8]

Thus on the basis of the aforementioned background and our previous studies on superabsorbent polymers and slow-release fertilizers,[9–12] the objective of the present article is to provide a rather new approach for preparing a granular urea-formaldehyde (UF) slow-release fertilizer, with superabsorbent and moisture preservation (USFSMP) at the same time based on the use of urea fertilizer and superabsorbent polymers. The product we prepared not only has slow-release property but also could absorb a large amount of water and preserve the soil moisture. This is the significant advantage over the conventional slow-release or controlled-release fertilizers and superabsorbent polymers.

EXPERIMENTAL

Materials

Acrylic acid (AA, Beijing Eastern Chemical Works, China), urea granules fertilizer and sodium alginate (SA) were of industrial grade and purchased from Tianjing No. 1 Chemical Reagent Plant, China. Am-

monium persulfate was purchased from Beijing Eastern Chemical Works, China and recrystallized from water. The others were all of analytical grade and purchased from Xi'an Chemical Reagent Plant, China.

Preparation of USFSMP

UF was made from urea and 37% formaldehyde aqueous solution as described previously.[13] A sample of 10 g dried UF powder (below 60-mesh) was placed into a 100-mL glass beaker and stirred well with 50 mL 2% SA solution (by weight). The mixed solution was then added dropwise into (through a burette) 1% $CaCl_2$ aqueous solution (by weight) and was stirred constantly; the drops immediately turned to white granules (about 3 mm in diameter) because the SA in the drop was crosslinked by Ca^{2+} at once. The granules were filtrated and dried in an oven at 80°C. The diameter of the granules could be controlled by the aperture size of the burette, and this is a rather new and simple approach for making homogenous UF granules.

A sample of 5 g dried granules obtained, as mentioned earlier, was added into a flask equipped with a mechanical stirrer, a condenser, and a drop funnel. A certain amount of tetrachloride, polyethylene glycol octyl phenyl ether (OP), and sorbite anhydride monostearic acid ester (Span-80) were added into the flask. The temperature was raised to 65°C using a water bath while the contents were constantly stirred. As this process continued, a certain amount of mixed solution of partly neutralized (by ammonia) acrylic acid, N,N'-methylenebisacrylamide (NNMBA) solution, and ammonium persulfate solution was slowly added dropwise into the flask. The mixture was filtered to remove the tetrachloride after being stirred for 2.0 h at 65°C and dried in an oven at 70°C, and then the last white homogenous granular USFSMP was obtained.

Component analysis of USFSMP

Content of nitrogen in the USFSMP and UF was determined by an element analysis instrument (Germany Elemental Vario EL Corp., model 1106). The results showed that the content of nitrogen in the USFSMP was 22.58%, and the total nitrogen in UF was 38.90%. The cold and hot water insoluble nitrogen percentages of UF were determined by the method of described in the US patent 4596,593, and the results showed that the cold and hot water insoluble nitrogen percentages were 61.25% and 30.48%, respectively. The UF with large molecular weight became insoluble both in cold and hot water, and so the other 8.27% N could not be detected in this experiment.

Water absorbency measurement

A sample of dried granular USFSMP (1.0 g) was immersed in 200 mL tap water for 2 h. The swollen granules were filtered through a silk sieve (~26-mesh) to remove the nonabsorbed liquid and weighed. Water absorbency (WA) was expressed as the absorbed liquid per gram of dried USFSMP granules.

Slow-release behavior of USFSMP in soil

A sample of 1 g granular USFSMP was well mixed with 200 g 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 40% water-holding capacity by weighing and adding distilled water if necessary, periodically. The remaining granular USFSMP in the beakers were picked out and washed well by distilled water after each incubated period (day 2, 5, 10, 15, 20, 25, 30 and 35), and then dried at 70°C to a constant weight to be estimated for the contents of N. The content of N was estimated by an element analysis instrument (Germany Elemental Vario EL Corp., model 1106).

The largest water-holding capacity of the soil with and without USFSMP

A sample of 2 g granular USFSMP was well blended with 200 g dry soil (below 26-mesh) and placed into a PVC tube of 4.5 cm diameter; the bottom of the tube was sealed by nylon fabric (with the aperture of 0.076 mm) and weighed (marked W_1). The soil samples were slowly drenched by tap water from the top of the tube until the water seeped out from the bottom. The tube was weighed (marked W_2) again when there was no water seeping out at the bottom. Control experiment, viz., with no USFSMP, was also carried out. The largest water-holding ratio (Wt %) of the soil was calculated using the following equation:

$$wt\ \% = 100(W_2 - W_1)/(W_2 - W_1 + 200) \qquad (1)$$

Water retention capacity of the soil with and without USFSMP

A sample of 2 g USFSMP granules were mixed well with 200 g dry soil (below 26-mesh) and kept in a glass beaker. Then 250 g tap water was slowly added into the beaker and weighed (marked W_1). Control experiment, viz., with no USFSMP, was also carried out. The beakers were placed in our lab at room temperature, and were weighed every 4 days (marked W_i); the observation was obtained after a period of 28 days. The water evaporation ratio (Wt %) was calculated using the following equation:
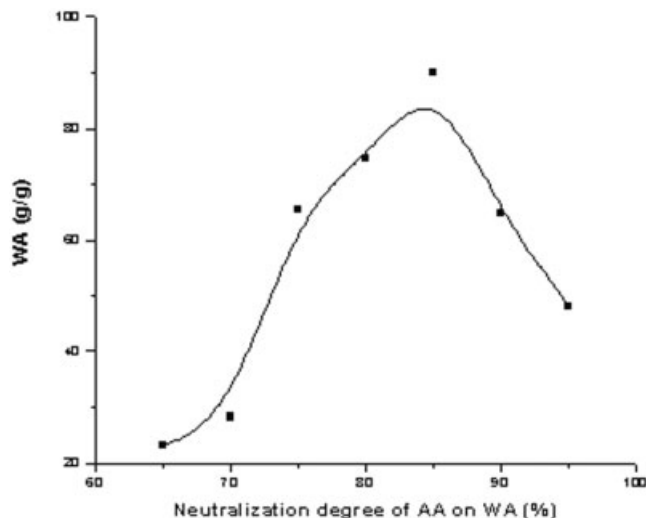
Figure 1 Effect of neutralization degree (ND) of AA on WA.

$$wt \% = 100(W_1 - W_i)/250 \qquad (2)$$

Mass ratio of the coat material to the whole USFSMP

A 0.8265-g sample of dry USFSMP was immersed in a 250-mL glass beaker, and then 50 mL distilled water was added into the beaker. The swollen USFSMP was crushed and then the UF granule inside it was removed. The swollen coat material was then washed by distilled water and dried to constant weight at 70°C, and then the weight of the coat material was obtained (0.2364 g). So, the mass ratio of the coat material to the whole USFSMP was:

$$\frac{0.2364}{0.8265} \times 100\% = 28.60\%$$

RESULTS AND DISCUSSION

Effect of neutralization degree of AA on WA

The neutralization degree (ND) of AA affected the WA of USFSMP (ND is defined as the molar percentage of carboxyls in AA neutralized by ammonia). As shown in Figure 1, WA increased first and then decreased with the increase of ND. It is easy to understand the increase of WA as ND increased from 65 to 85%; as for the decrease of WA from 85 to 95%, this could be attributed to the monomer acidity, namely, the polymerization rate of AA and the crosslinking degree depended on the pH.[10]

Effect of initiator amount on WA

The effect of initiator amount on WA was also studied and the result is presented in Figure 2. WA increased

as $W_{(initiator)}/W_{(AA)}$ rose from 0.04% to 0.08% and decreased slowly with further increase of $W_{(initiator)}/W_{(AA)}$ due to an increase in the number of radicals produced, as $W_{(initiator)}/W_{(AA)}$ increased. It is expected that with a small amount of initiator initiation reaction becomes difficult, the residual monomer in the product is more, and the crosslink density is low, and so WA becomes low. At a higher amount of initiator, the rate of polymerization becomes too fast to be controlled, the crosslink density is very high, the content of oligomers is more, and the molecular weight of the product is low, and so WA is low as well.[5,6]

Effect of crosslinker amount on WA

Figure 3 shows that there also exists a maximum in the dependence of WA of USFSMP in tap water on the amount of crosslinker. This could be attributed to the lower crosslinking density with a small amount of crosslinker, and the more soluble part of the polymer gel network. The decrease of WA after the maximum could be attributed to an overcrosslinking of the polymer gel network, which hindered the stretching of the polymer chains in the gel network and reduced the value of WA.

Reaction time dependence of WA

Figure 4 shows that WA increased as the reaction time increased up to 2 h. Because the monomer conversion increased as reaction time increased, the content of the soluble part in USFSMP decreased. WA approached a constant value after about 2 h, indicating that the reaction was completed by this time.
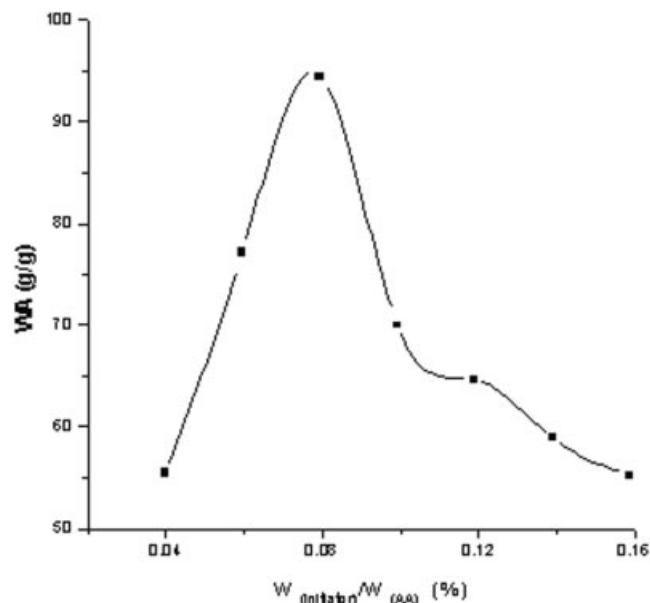

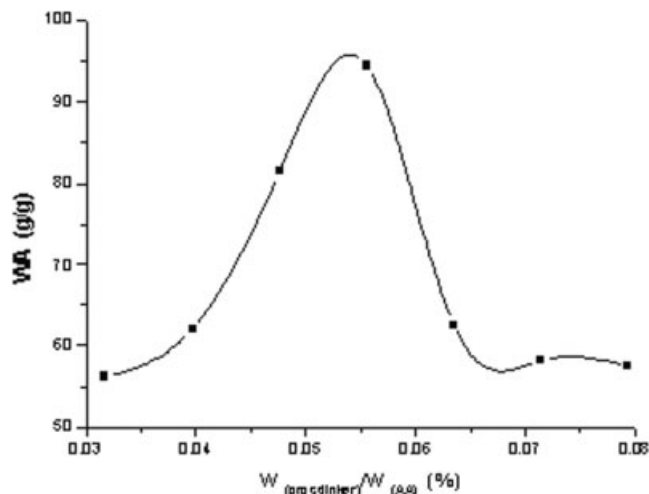**Figure 2** Effect of initiator amount on WA.

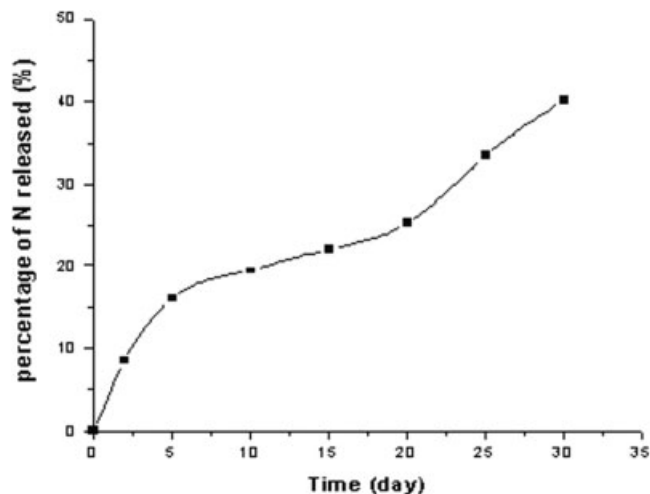**Figure 3** Effect of cross-linker amount on WA.

Figure 5 Slow-release behavior of USFSMP in the soil.

Slow-release behavior of USFSMP

One of the most important characteristics of the USFSMP we prepared was its slow-release property. Figure 5 represents the slow-release behavior of nitrogen in USFSMP. According to the results of Smith et al.,[14] slow-release property of urea fertilizer could be observed when incorporated with superabsorbent polymers, but a large portion of the nitrogen would released out only after 7 days; and it is well known that almost all of the urea fertilizer would quickly dissolve in the water in the soil after being added into soil during several days, especially when the soil moisture is high, and the nitrogen would be released out with that. While as shown in Figure 5, only 8.52% and 15.96% of the nitrogen in the USFSMP we prepared was released out on the second and fifth day, respectively, and only 40.2% of the nitrogen was released out
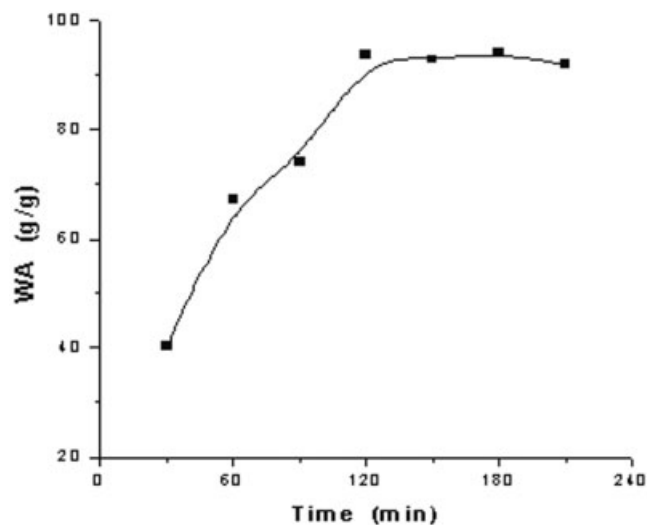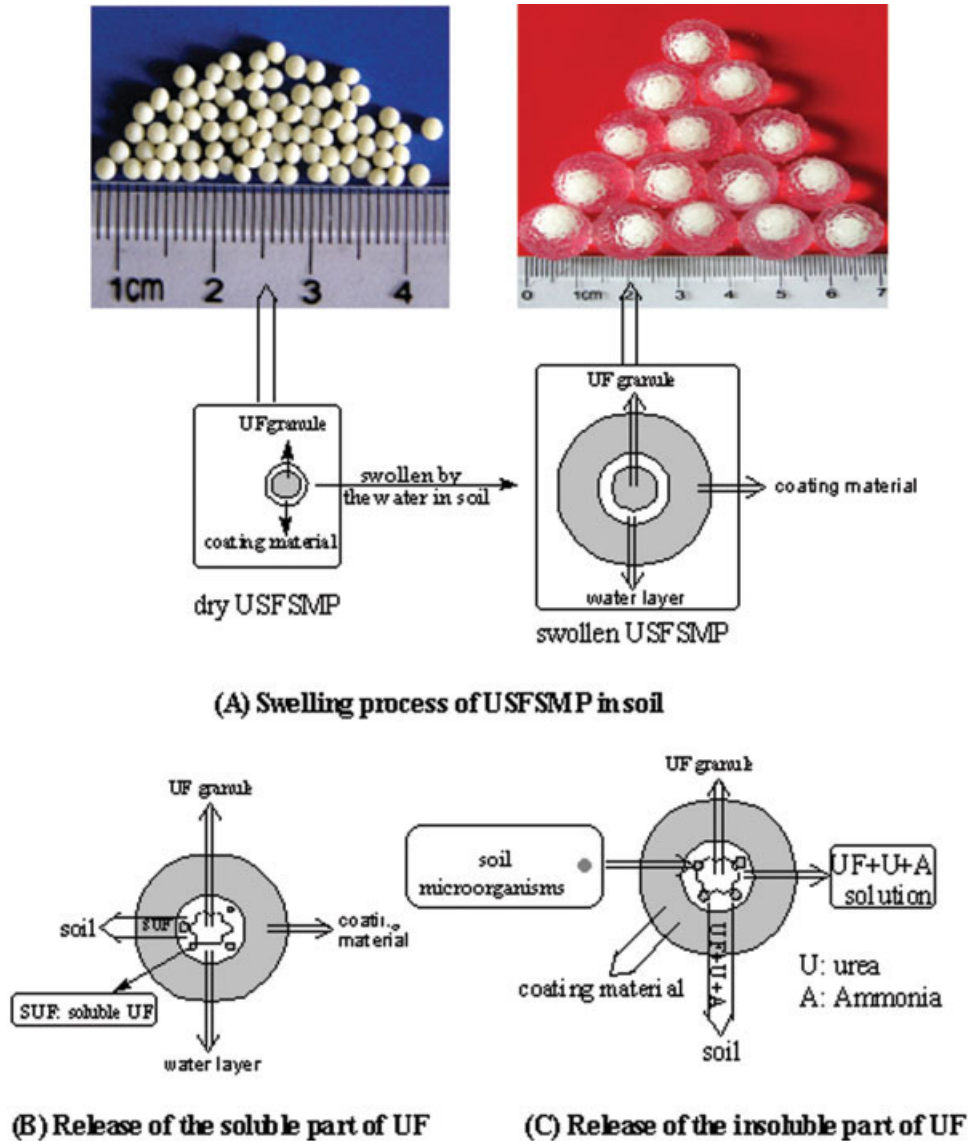
on the 30th day. This release time of nitrogen is within the recommended time,[15] and also indicated that the USFSMP we prepared had excellent slow-release property.

We assumed that the mechanism of nitrogen released from USFSMP granules is the same as presented in Scheme 1. Firstly, the superabsorbent coating materials would be swollen by the water in the soil after being added into the soil, and transformed into hydrogel, which would contribute to increase of the aperture size of the three-dimensional network of the coating materials, so that it benefits the diffusion of the fertilizer nutrition in the core of the gel network. And so there formed a layer of water between the swollen coatings and the UF granule core(as shown in Scheme 1(A)). Secondly, this part of water would continue to slowly diffuse into the crosslinked network of SA and dissolve the soluble part of UF in it, and then this part of the soluble fertilizer nutrition would slowly be released into the soil through the griddings of the swollen network with the dynamic exchange of the water in the hydrogel and the water in the soil(as shown in Scheme 1(B)). Lastly, the soil microorganisms would penetrate through the swollen coatings and assemble around the UF granule, the insoluble part of nitrogen in UF granule would be degraded into urea and ammonia by them,[16] and then slowly released into the soil with above dynamic exchange(as shown in Scheme 1(C)). The remaining fertilizer nutrient in the UF seemed to be released completely because the UF was degradable, to some extent, by soil microorganisms.[4]

The largest water-holding capacity of the soil with and without USFSMP

The experimental results of the largest water-holding ratio of the soil indicated that the largest water-hold-

Figure 4 Reaction time dependence of WA.

(A) Swelling process of USFSMP in soil

(B) Release of the soluble part of UF   (C) Release of the insoluble part of UF

Scheme 1   Slow-release mechanism of USFSMP in the soil.

ing ratio of the soil without USFSMP was 33.2%, and that of the soil with USFSMP was 44.5%(the mass ratio of USFSMP to soil was 1 : 100), 11.3% higher than the former. This showed that the USFSMP we prepared still had excellent water absorbency in soil, could obviously improve the water-holding capacity of the soil, and efficiently store the rain or irrigation water.

Water retention capacity of USFSMP in soil

Besides its slow-release property, another one of the most important characteristics of USFSMP is its water retention property. The result of the water retention experiment is showed in Figure 6, from which we could find that the water transpiration rate of soil with USFSMP obviously decreased, compared with the soil without it. The water transpiration rate of soil without
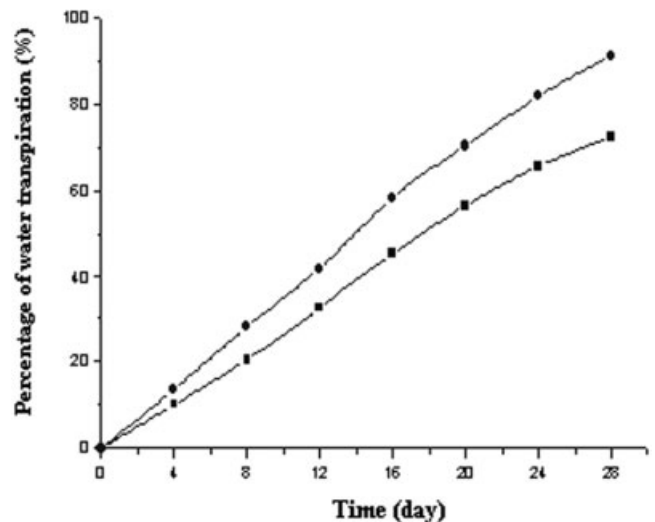

Figure 6   Water retention behavior of USFSMP in the soil (●): water + dry soil; (■): water + dry soil+ USFSMP.

USFSMP had reached 42% and 91.5% on the 12th and 28th day, respectively, while that of the soil with US-FSMP was 32.5% and 72.5%, respectively. This indicated that water in the soil with USFSMP could be saved and managed in dry and desert regions, so that it could be effectively used for the growth of plants. The reason was that, the superabsorbent polymer in USFSMP could absorb and store a large amount of the water in soil, and let the water absorbed in it to be slowly released out with the decrease of the soil moisture. This let the water in the soil evaporate more slowly, and obviously improved the utilization efficiency of water, thus strengthening the ability of plants to fight a drought. So, it is expected to have a great potential for applications in the arid and desert areas.

CONCLUSIONS

Granular urea-formaldehyde slow-release fertilizer with superabsorbent and moisture preservation (USFSMP) was prepared. Its core was UF granule and the coating material was a superabsorbent polymer (poly(ammonium-acrylate)). Experimental results showed that: (1) the USFSMP contained 22.58% of nitrogen element; (2) its water absorbency was about 94 (g/g) times its own weight in tap water; (3) it could obviously improve the water holding capacity of the soil; (4) USFSMP had excellent slow-release property and moisture preservation capacity in soil, and could efficiently improve the utilization of fertilizer and water resource at the same time.

References

1. Maria, T.; Anna, J. J Agr Food Chem 2002, 50, 4634.
2. Morrison, I. K.; Foster, N. W. Soil Sci Soc Am J 1977, 41, 441.
3. Dave, A. M.; Mehta, M. H.; Aminabhavi, T. M.; Kulkarni, A. R.; Soppimath, K. S. A. Polym Plast Technol Eng 1999, 38, 675.
4. Ge, J. J.; Wu, R.; Shi, X. H.; Yu, H.; Wang, M.; Li, W. J. J Appl Polym Sci 2002, 86, 2948.
5. Liu, M. Z.; Zhan, F. L.; Lan, W.; Guo, M. Y. J Polym Mater 2004, 21, 213.
6. Chen, Z. B.; Liu, M. Z.; Ma, S. M. React Funct Polym 2005, 62, 85.
7. Shimomura, T. Mater Sci Eng 1993, 69, 485.
8. Hogari, K.; Ashiya, F. Advances in Superabsorbent Polymers; American Chemical Society: Washington, DC, 1994.
9. Liu, M. Z.; Cheng, R. S.; Wu, J. J. Chin J Polym Sci 1996, 14, 48.
10. Liu, M. Z.; Guo, T. H. J Appl Polym Sci 2001, 82, 1515.
11. Ma, S. M.; Liu, M. Z.; Chen, Z. B. J Appl Polym Sci 2004, 93, 2532.
12. Zhan, F. L.; Liu, M. Z.; Guo, M. Y.; Wu, L. J Appl Polym Sci 2004, 92, 3417.
13. Wang, Y.; Wan, T. Chin J Soil Sci 2001, 32, 73.
14. Smith, J. D.; Harrison, H. C. Commun Soil Sci Plant Anal 1991, 22, 559.
15. Trenkel, M. E., International Fertilizer Industry Association; Stratospheric Ozone; HMSO: London, 1997; p 11.
16. Jahns, T.; Kaltwasser, H. J Polym Environ 2000, 8, 11.