Preparation of Poly(acrylic acid-*co*-acrylamide)/Kaolin and Release Kinetics of Urea from It

Rui Liang,[1,2] Mingzhu Liu[1]

[1]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou
730000, People's Republic of China
[2]College of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007,
People's Republic of China

ABSTRACT: A series of poly(acrylic acid-*co*-acrylamide)/kaolin [poly(AA-*co*-Am)/kaolin] composites were prepared by aqueous solution copolymerization of partially neutralized acrylic acid and acrylamide in the presence of kaolin nanopowder, which was synthesized to act as a release carrier of urea fertilizer. The superabsorbent composite was swollen in aqueous solution of urea to load urea, and the effect of urea concentration on the swelling was investigated. Furthermore, the effects of the contents of crosslinker, kaolin, and acrylamide, the neutralization degree of acrylic acid, and temperature, pH, and ionic strength of release medium on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin were studied systematically. It was found that urea loading percentage could be adjusted by urea concentration of swelling medium, and urea diffusion coefficient could be regulated through the contents of crosslinker, kaolin, and acrylamide, and the neutralization degree of acrylic acid. Additionally, temperature and ionic strength of release medium may also affect the urea release process. The conclusions obtained could provide theoretical basis for urea diffusion behavior in superabsorbent used in agriculture. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3007–3017, 2007

Key words: poly(AA-*co*-Am)/kaolin; urea; water absorbency; diffusion coefficient; mesh size

INTRODUCTION

Superabsorbents are three-dimensionally crosslinked hydrophilic polymers capable of swelling and retaining huge volumes of water in the swollen state. Recently, research on the use of superabsorbents as water management materials for agricultural and horticultural applications,[1] and as slow release carriers of agrochemicals and nutrients has attracted great attention.[2] The optimized combination of superabsorbents and fertilizers may improve nutrition of plants, and mitigate at the same time the environmental impact from water-soluble fertilizers, reduce evaporation losses, lower frequency of irrigation.[3,4]

However, its applications in this field have met some problems because most of these superabsorbents are based on pure poly(sodium acrylate), and then they are too expensive and not suitable for saline-containing water and soils.[5] Recently, there have been many reports on introducing inorganic clays into pure polymeric superabsorbents to improve swelling property, hydrogel strengths, and reduce production costs.[6]

Nitrogen is the most vital nutrient for crops. Among the nitrogen fertilizers, the most widely used one is urea because of its high nitrogen content and comparatively low cost of production. However, due to surface runoff, leaching, and vaporization, the utilization efficiency or plant uptake of urea is generally below 50%.[7] Moreover, urea is a nonelectrolyte, and then it will not decrease the water absorbency of superabsorbent strongly; but other nitrogen fertilizer, such as potassium nitrate, will affect the water absorbency strongly, which will make superabsorbent lose its water retention function in soil. So, the urea slow release from superabsorbent will be of most significance.

Loading of a hydrogel is done typically by two methods.[8] In the first method, the compound to be loaded is added to the reaction mixture and polymerized *in situ* whereby the compound is entrapped within the gel matrix. In the second approach, the dry gel is allowed to swell in the compound solution and after the equilibrium swelling, the gel is dried and the device is obtained. There are some disadvantages to the first technique. For example, the entrapped compound may influence the polymerization process and the polymer network structure[9]; moreover, polymerization could have an adverse

effect on the property of the entrapped compound. Urea, the entrapped compound in the present study, may change into biuret under the effect of polymerization heat, which is harmful to crops. Therefore, in the present study, the second method was adopted to entrap urea.

On the basis of the above background and our pervious studies on superabsorbent polymers[10,11] and slow-release fertilizers,[12,13] poly(acrylic acid-*co*-acrylamide)/kaolin [poly(AA-*co*-Am)/kaolin] superabsorbent composites were prepared by aqueous solution copolymerization of partially neutralized acrylic acid and acrylamide in the presence of kaolin nanopowder. Additionally, the effects of the contents of crosslinker, kaolin, and acrylamide, the neutralization degree of acrylic acid, and temperature, pH, and ionic strength of release medium on water absorbency and diffusion coefficient of urea release from it were studied systematically.

EXPERIMENTAL

Materials

Acrylic acid (AA, Beijing Eastern Chemical Works, China) and urea granules fertilizer were of industrial grade. Kaolin powders were provided by Fujian Tongan Kaolin Factory, China. Ammonium persulfate (APS) 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 poly(AA-*co*-Am)/kaolin

A series of samples with different amounts of kaolin, crosslinker, Am, and neutralization degree of AA were prepared by the following procedure. Typically, AA (5.76 g) and Am (1.15 g) were dissolved in 15 mL distilled water and then neutralized with ammonia (neutralization degree, 60%) in a four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. Kaolin powder (0.58 g) was dispersed in the above partially neutralized monomer solution. Under nitrogen atmosphere, the crosslinker N,N'-methylenebisacrylamide (57.6 mg) was added to the AA/Am/kaolin mixture solution and the mixed solution was stirred on a water bath at room temperature for 30 min. The water bath was then heated slowly to 70°C with vigorous stirring after the radical initiator APS (80.2 mg) was introduced to the mixed solution. After 3 h, the resulting product was dried at 100°C to a constant weight. Finally, the dried product was milled and screened. All samples used had a particle size in the range of 50–60 mesh.

Characterization of poly(AA-*co*-Am)/kaolin

The poly(AA-*co*-Am)/kaolin composite superabsorbent was characterized by a Fourier-transform Infrared (FTIR) spectrophotometer (American Nicolet, model 170-SX)

Swelling studies of poly(AA-*co*-Am)/kaolin

Dried gels were left to swell in distilled water and aqueous solutions of urea with different concentrations (1, 3, 5 g/L). Swollen gels were removed from the swelling medium at regular intervals and weighed, then placed in the same bath. The measurements were continued until a constant weight was reached for each sample. This operation is repeated three times for each sample (average error 2%). Degree of swelling is then calculated from the relative weight increase compared to dry weight value.

Loading of urea

The loading of urea was carried out by immersing preweighed dry gels into the aqueous solution of urea (1 g/L) for 24 h. Thereafter, the swollen gels were dried at 40°C for 3 days.

The loading percentage was calculated by the following eq. (1),

$$\text{loading}\% = \frac{m_1 - m_0}{m_1} \times 100 \qquad (1)$$

where m_0 and m_1 are the weights of unloaded and loaded dry gels.

Release of urea from poly(AA-*co*-Am)/kaolin

The effects of crosslinker content on urea release from poly(AA-*co*-Am)/kaolin composite hydrogel was carried out as follows: 0.5 g loaded dry gels with different crosslinker contents were placed in beakers containing 200 mL distilled water (release medium) without stirring, respectively. At various intervals, 2-mL solutions were drawn from the medium to follow the urea release. Urea was determined by a spectrophotometric method using *p*-demethylaminobenzaldehyde in a hydro alcohol medium with hydrochloric acid as reagent.[14]

The effects of kaolin content, neutralization degree of AA, and Am content on urea release from poly(AA-*co*-Am)/kaolin composite hydrogel were carried out in the same method as that of the effects of crosslinker content mentioned above, except that the samples were dry gels with different kaolin contents, neutralization degree of AA, and Am contents.

The effect of temperature on the urea release from poly(AA-*co*-Am)/kaolin hydrogel were carried out

as follows: 0.5 g loaded dry gels were placed into beakers containing 200 mL distilled water. Then, the beakers were put into incubators whose temperatures were set at 5, 20, 35, 50, and 65°C, respectively.

The effects of pH on the urea release from poly (AA-*co*-Am)/kaolin hydrogel were carried out as follows: 0.5 g loaded dry gels were placed into beakers containing 200 mL solutions whose pH were adjusted to 4, 7, and 9, respectively.

The effects of ionic strength on the urea release from poly(AA-*co*-Am)/kaolin hydrogel were carried out as follows: 0.5 g loaded dry gels were placed into beakers containing 200 mL distilled water, tap water, and 0.9% NaCl solutions, respectively.

Scanning electron microscopy

Poly(AA-*co*-Am)/kaolin composites were allowed to swell in distilled water for 5 h. The swollen samples were frozen in liquid nitrogen and then lyophilized for 48 h. Lyophilized samples were then covered with a thin gold layer and observed by a scanning electron microscopy (JSM-5600LV SEM manufactured in Japan).

Diffusion coefficient

The release of an active agent from hydrogel is classically assumed to take place by diffusion.[15] Diffusion coefficient thus appears as a key parameter. A series of diffusion coefficient has been achieved according to the following process.

A kinetic equation[16] with a cubic form had been derived to describe the diffusion control release behaviors of drug for a porous matrix ($M_t/M_0 <$ 60%):

$$f_t = \frac{M_t}{M_0} = 3Kt^{1/2} - 3(Kt^{1/2})^2 + (Kt^{1/2})^3 \quad (2)$$

where f_t is the fraction of material released at time t, and K is the release rate constant.

This expression can be written in a linear form as:

$$(1 - f_t)^{\frac{1}{3}} = 1 - Kt^{\frac{1}{2}} \quad (3)$$

By plotting the left-hand side of the above expression as a function of the square root of time, a linear plot with slope K is obtained.

The release rate constant K is defined as[16]:

$$K = (\frac{1}{C_0} \times r_0)[D(2C_0 - C_s)C_s]^{\frac{1}{2}} \quad (4)$$

where C_0 is the weight of urea per unit volume of granular (it could be obtained for the urea loading percentage), C_s is the equilibrium solubility of the
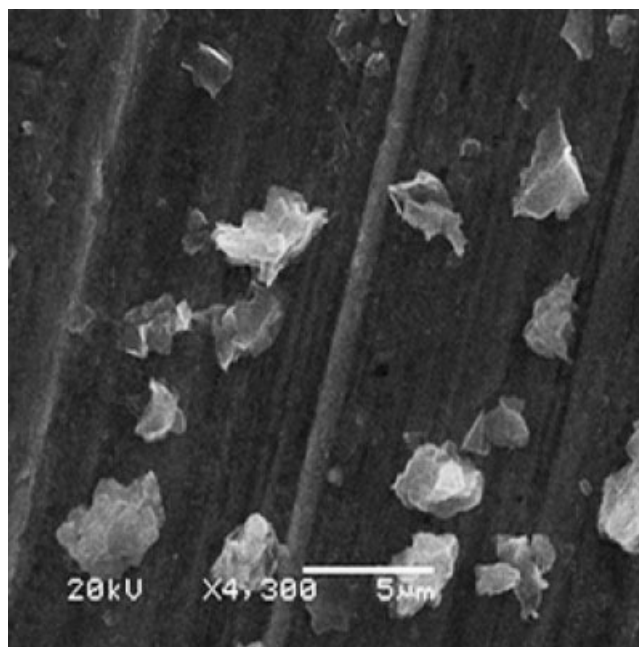
Figure 1 Scanning electron micrograph of kaolin powder.

urea in the dissolution liquid, D is the diffusion coefficient of the urea in the swollen granular (including the effect of porosity and tortuosity), and r_0 is the radius.

Calculation of diffusion coefficient D from the release rate K is possible:

$$D = \frac{(KC_0r_0)^2}{(2C_0 - C_s) \times C_s} \quad (5)$$

RESULTS AND DISCUSSION

The properties of kaolin powder

The cation exchange capacity (CEC) of kaolin powder used in this study is 4.8 mmol/100 g, and its BET specific surface area determined by nitrogen adsorption method is 28 m^2/g. The scanning electron micrograph (SEM) of kaolin powder is presented in Figure 1. SEM shows that the average diameter of kaolin powder is about 2 μm. Kaolin is phylosilicate, and the ratio of diameter to thickness is about 20:1–50:1.[17] Therefore, it could be speculated that the thickness of kaolin layer is about 40–100 nm. According to the definition of nanophase materials, i.e., any materials of dimensions between 1 and 100 nm, the kaolin used could be called nanopowder.

FTIR analysis of poly(AA-*co*-Am)/kaolin

The infrared spectra of kaolin powder, poly(AA-*co*-AM), and poly(AA-*co*-Am)/kaolin are shown in Fig-
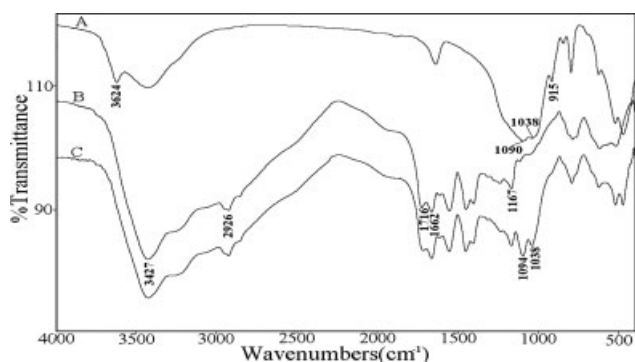
Figure 2 The FTIR spectra of kaolin (A), poly(AA-*co*-AM) (B), poly(AA-*co*-Am)/kaolin (C: kaolin content, 10%; D: kaolin content, 30%).

ure 2(A), Figure 2(B), and Figure 2(C,D) (C, kaolin content 10%; D, kaolin content 30%), respectively. The observed peaks are at 3427 cm^{-1}, corresponding to N—H stretching of acrylamide unit, 2926 cm^{-1}, corresponding to the C—H stretching of acrylate unit, 1716 cm^{-1}, corresponding to the stretching of C=O in acrylate unit, 1662 cm^{-1}, corresponding to the carbonyl moiety of the acrylamide unit, 1167 cm^{-1}, corresponding to the —CO—O$^-$ stretching of acrylate unit, 1038 cm^{-1} (1094 cm^{-1}), corresponding to the Si—O stretching of kaolin.

The infrared analysis results of poly(AA-*co*-Am)/kaolin in Figure 2(C) shows that all the characteristic groups, i.e., —COOH (or —COONa), —CONH$_2$, —CH, and Si—O, exist in the product. In addition, by comparing Figure 2(A) and Figure 2(C), the absorption peaks at 3624 and 915 cm^{-1}, contributed to —OH group on kaolin powder [see Fig. 2(A)], disappeared after the reaction [see Fig. 2(C)]. Therefore, it was suggested that graft copolymerization between —OH groups on kaolin and monomers took place during the polymerization reaction. Similar results had been reported by others.[18]

However, the absorption peaks (3620 and 916 cm^{-1}) corresponding to —OH group on kaolin powder appeared again in Figure 2(D). This was because when the kaolin content was high, part of them did not take part in the polymerization reaction and acted as a physical filler in the polymer.

The swelling of poly(AA-*co*-Am)/kaolin in urea solutions

The urea loading percentage is determined by the swelling degree of poly(AA-*co*-Am)/kaolin composite in aqueous solution of urea. Therefore, it is important to investigate the effect of urea concentration on swelling degree of poly(AA-*co*-Am)/kaolin.

Poly(AA-*co*-Am)/kaolin composite was swollen in aqueous solutions of urea with the concentrations of 0, 1, 3, and 5 g/L. The equilibrium swelling degrees

(Q_{eq}) and urea loading percentage are presented in Table I. Table I showed that Q_{eq} of poly(AA-*co*-Am)/kaolin in aqueous solutions of urea with different concentrations were also equal, but urea loading percentage could be affected strongly by urea concentration. Moreover, no important differences in swelling rate were observed (swelling rate results are not shown). That is to say, urea concentration has no obvious influences on the swelling process of poly(AA-*co*-Am)/kaolin composite.

Similar phenomenon and results had been reported by others.[19] The reason may be that urea is a neutral molecule, which could not affect the electrostatic repulsion force of —COO$^-$ on polymer chain. Moreover, urea molecule has hydrophilic sites, such as —NH$_2$. The addition of urea in water would not change the polymer–solvent interaction. Therefore, aqueous solutions of urea with different concentrations can hardly change the swelling process of poly(AA-*co*-Am)/kaolin composite.

The dependence of urea loading percentage on urea concentration could be interpreted as follows: when poly(AA-*co*-Am)/kaolin swelled in aqueous solutions of urea with higher concentration, more urea molecules entered into the polymer network. After drying, these urea molecules were left in the three-dimensional network, then the urea load percentage was high and vice versa.

So, the urea loading percentage could be adjusted by changing the urea concentration of swelling medium. The higher the urea concentration in swelling medium, the higher the urea loading percentage.

The effects of crosslinker content on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin

The effects of crosslinker content on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin are shown in Figure 3. It could be seen from Figure 3 that the water absorbency decreases with the increase of crosslinker content from 0.1% to 2%. Clearly, higher crosslinker content resulted in the generation of more crosslink points, which, in turn caused the formation of additional network and decreased the available free vol-

TABLE I
The Effects of Urea Concentrations on Q_{eq} and Urea Loading Percentage of Poly(acrylic acid-*co*-acrylamide)/Kaolin

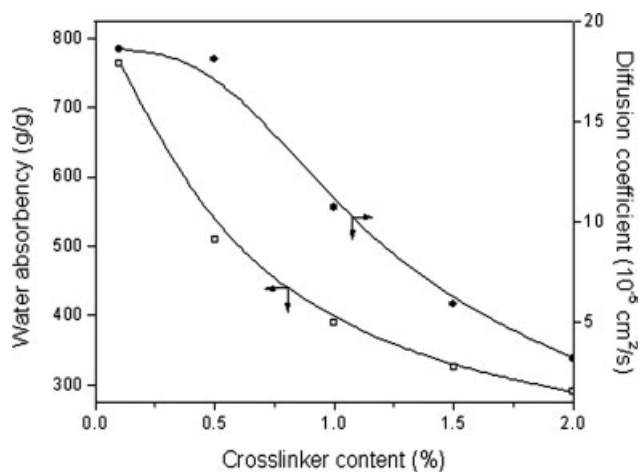| Urea concentration (g/L)	Q_{eq} (g/g)	Urea loading percentage (%)
0	390	0
1	385	27.8
3	389	53.5
5	394	65.1

Figure 3 Effects of crosslinker content on water absorbency and diffusion coefficient of urea release from poly (AA-*co*-Am)/kaolin. Other conditions: kaolin content, 10%; neutralization degree, 60%; Am content, 20%; temperature of release medium, 20°C; in distilled water.

ume in the polymer composite. When the crosslinker content was lower than 0.1%, the strength of the hydrogel is too weak to be used.

It also could be seen from Figure 3 that diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin composite decreased when the crosslinker content increased from 0.5% to 2%; however, there were no obviously difference in diffusion coefficient when crosslinker content changed from 0.1% to 0.5%.

It has been well established that the release of a solute from a polymer matrix is governed by the free volume in the system.[20] Therefore, the release of solute from the hydrogel matrixes would be affected by the degree of crosslinking density. The influence of crosslinker content on urea diffusion coefficient may be interpreted in terms of polymer chain mobility and average mesh size. On a molecular level, solute diffusion through hydrogel depends on the relative size of a solute and the mesh size of polymer network. So, any factors that could reduce polymer chain mobility and mesh size would increase the barriers to urea release. As crosslinker content increases, the average molecular weight between crosslink points decreases. This would decrease the polymer chain mobility and mesh size simultaneously, and hence increase the barriers to urea release. Therefore, diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin hydrogel decreased as crosslinker content increased from 0.5% to 2%.

However, when crosslinker content is very low, urea release is irrelevant to the crosslinker content. This may be attributed to the fact that when the crosslinker density is very little, the mesh size is very big. Then, when the mesh size of the polymer

is far bigger than urea size, the continuous increase in the mesh size would not help the urea release from the hydrogel. That is to say, there exists a critical value for crosslinker content, when the crosslinker content is lower than the critical value, urea release would be irrelevant to crosslinker content.

From Figure 3, it could be seen that diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin hydrogel decreased from 18.1×10^{-5} cm^2/s to 3.2×10^{-5} cm^2/s (the values are in general agreement with the diffusion coefficients of urea in hydrogel, i.e. about 10^{-5} cm^2/s, as reported in the literature[21]), when crosslinker contents increased from 0.5% to 2%. So, it could be concluded that the urea release process from poly(AA-*co*-Am)/kaolin composite hydrogel could be modified through crosslinker content. These results are in agreement with the reports of the literature.[22]

The effects of kaolin content on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin

The effects of kaolin content on water absorbency and diffusion coefficient of urea release from poly-(AA-*co*-Am)/kaolin composite hydrogel are shown in Figure 4. It could be seen from Figure 4 that both water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin composite hydrogel decreased as the kaolin content increased from 0% to 40%.

There are three kinds of way for kaolin particle in the poly(AA-*co*-Am)/kaolin[23]: the first way, kaolin particle serves as a crosslinking point chemically bonded with the polymer, in this way, both the water absorbency and network structure would be
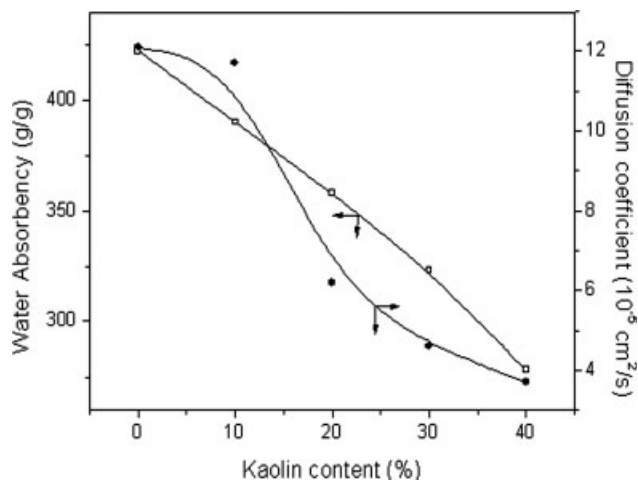

Figure 4 Effects of kaolin content on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin. Crosslinker content, 1%; and other conditions were the same as those of Figure 3.

changed; the second way, kaolin particle acts as terminal point chemically bonded with the polymer; the third way, kaolin particle serves as a filler physically filled in the network of polymer.

The reasons for the decreasing of water absorbency with the increasing of kaolin content could be interpreted as follows: firstly, the introduction of kaolin particles into the polymer increased the crosslinking density of poly(AA-co-Am)/kaolin composite, which resulted in a decrease in water absorbency; secondly, the physically filling of kaolin particle in the polymer decreases the amount of hydrophilic groups, and consequently resulted in the reduction of water absorbency.

The fact that the diffusion coefficient of urea release from poly(AA-co-Am)/kaolin composite hydrogel decreased as the increasing of kaolin content could be ascribed to the following two reasons. Firstly, kaolin particle serves as a crosslinking point. Then, with the increasing of kaolin content, the crosslinking density would increase, and the mesh size of poly(AA-co-Am)/kaolin hydrogel would decrease, which enhance the barriers of urea diffusion, so the release of urea slows down. Secondly, when the kaolin content was high, the kaolin particles were difficult to disperse and prone to aggregation, and resulted in phase separation. The kaolin aggregation acts as a nonreactive filler in the network of poly(AA-co-Am)/kaolin composite, which would block the pores and channels in the polymer matrix. This also contributed to the decrease of urea diffusion from the hydrogel.

Figure 5 shows the scanning electron microscope pictures of lyophilized poly(AA-co-Am)/kaolin composite hydrogels, A: kaolin content, 10% and B: kaolin content, 30%. It could be seen from Figure 5(A) that there were no kaolin aggregations in SEM, i.e., the poly (AA-co-Am)/kaolin composite hydrogel was homogeneous. However, there were obvious phase separation phenomena in Figure 5(B). The diameter of kaolin particle in Figure 1 was about 2 μm, but that in Figure 5(B) was far bigger than this value due to aggregation. The pores and channels in the polymer matrix were blocked by the aggregations of kaolin particles.

From Figure 4, it could be seen that urea diffusion coefficients decreased from 12.1×10^{-5} cm^2/s to 3.7×10^{-5} cm^2/s when kaolin contents increased from 0% to 40%. So, it could be concluded that the urea diffusion process from poly(AA-co-Am)/kaolin composite hydrogel could be modulated through kaolin content.

The effects of neutralization degree of AA on water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin hydrogel

The effects of neutralization degree of AA on water absorbency and diffusion coefficient of urea release
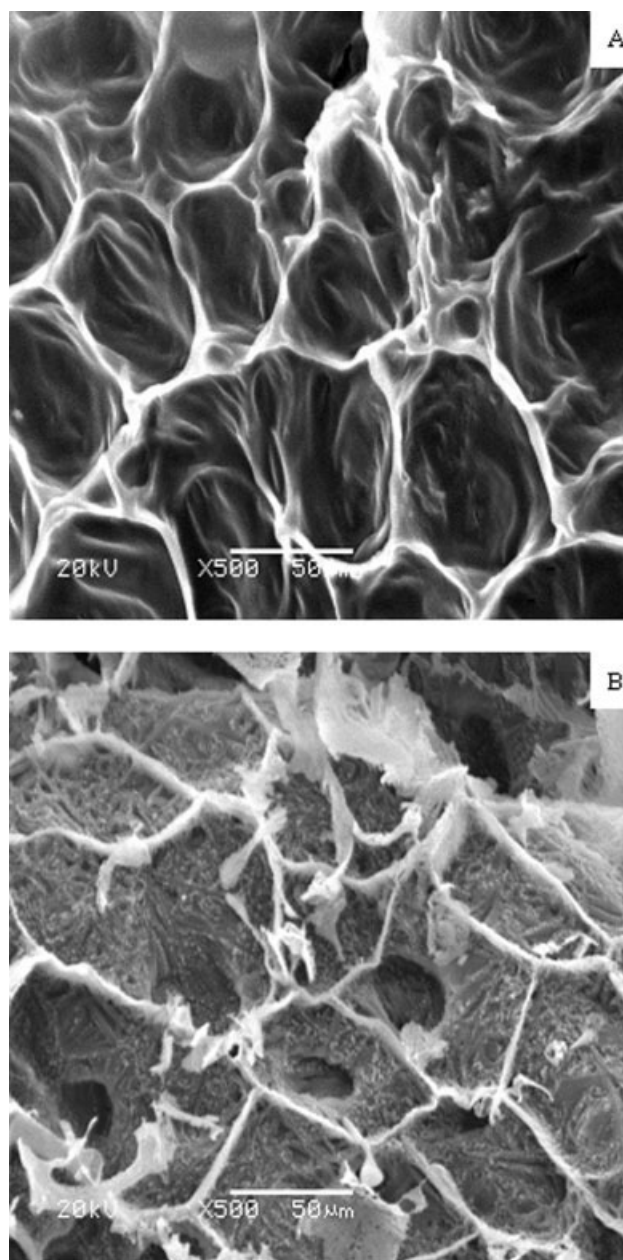

Figure 5 Scanning electron microscopy pictures of lyophilized poly(AA-co-Am)/kaolin hydrogels. A: kaolin content, 10%; B: kaolin content, 30%.

from poly(AA-co-Am)/kaolin hydrogel are shown in Figure 6. The neutralization degree of AA is defined as the molar percentage of carboxyls in AA neutralized by ammonia. Both the water absorbency and urea diffusion coefficient increased as neutralization degree rose from 30% to 50%, and decreased with further increase in the neutralization degree of acrylic acid.

For the changes of water absorbency, the reason is easy to be understood. When acrylic acid was neutralized by ammonia, the negatively charged carboxyl groups attached to the polymer chains set up an electrostatic repulsion, which tended to expand
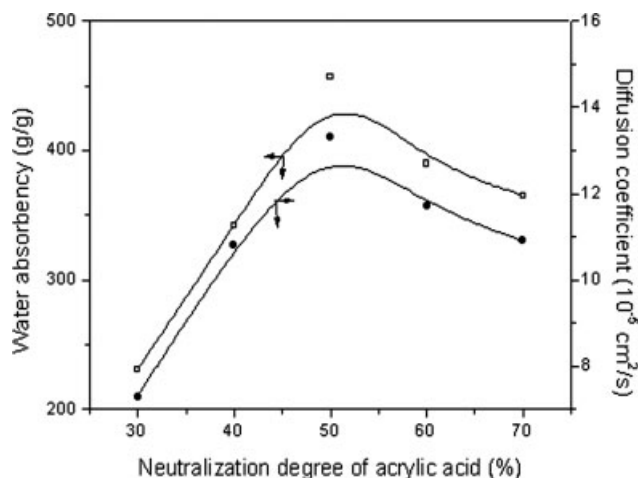
Figure 6 Effects of neutralization degree of AA on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin. Kaolin content, 10%; and other conditions were the same as those of Figure 4.

the network. In a certain range of neutralization degree, the electrostatic repulsion increased with the increase of neutralization degree, resulting in the increase of water absorbency. When the neutralization degree is more than the optimum value, the decrease of water absorbency could be ascribed to an increase in chain stiffness and to counterion condensation on the polyion (screening effect).[24]

The change tendency of urea diffusion coefficient is similar to that of water absorbency. When neutralization degree changed from 30% to 50%, the electrostatic repulsion of $-COO^-$ groups enlarged the mesh size of polymer network, which consequently reduced the barriers of urea diffusion. So, urea diffusion coefficient increased. However, when neutralization degree was above 50%, the mesh size decreased due to the screening effect,[24] and the polymer chain became stiff at the same time, which increased the barriers of urea diffusion. Therefore, urea diffusion coefficient decreased.

From the above discussions, it could be concluded that the urea diffusion process from poly(AA-*co*-Am)/kaolin composite hydrogel could be regulated through the neutralization degree of AA.

The effects of Am content on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin

The effects of Am content on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin hydrogel are shown in Figure 7. Both the water absorbency and urea diffusion coefficient increased as Am content rose from 10% to 20%, and decreased with further increase in the Am content.

The reasons for the changes of water absorbency could be explained as follows: there exists a synergistic effect among the groups of $-COOH$, $-COO^-$, $-CONH_2$, $-OH$ (on kaolin), and when they cooperate in a suitable ratio, the poly(AA-*co*-Am)/kaolin composite will exhibit the largest water absorbency. When the Am content is above the optimum values, the water absorbency will decrease due to the lower water absorbent function of $-CONH_2$.

The change trend of urea diffusion coefficient is similar to that of water absorbency. When the ratio of $-COOH$, $-COO^-$, $-CONH_2$, $-OH$ (on kaolin) groups is the optimum value, the composite has the highest water absorbency, and the mesh size of polymer network is the largest at this time. With the further increase of acrylamide content, the mesh size would decrease due to reduction of the repulsion action of $-COO^-$. Then, the barriers to urea diffusion enhanced, as a result, urea diffusion coefficient decreased.

According to the above results and discussions, it could be concluded that the urea diffusion process from poly(AA-*co*-Am)/kaolin composite hydrogel could be adjusted through acrylamide content.

The effects of temperature on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin

The influences of temperature on water absorbency and diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin composite hydrogel was undertaken at the temperatures of 5, 20, 35, 50, and 65°C, and the results are shown in Figure 8.

It could be seen from Figure 8 that the water absorbency of the superabsorbent composite decreased slightly as the temperature increased from
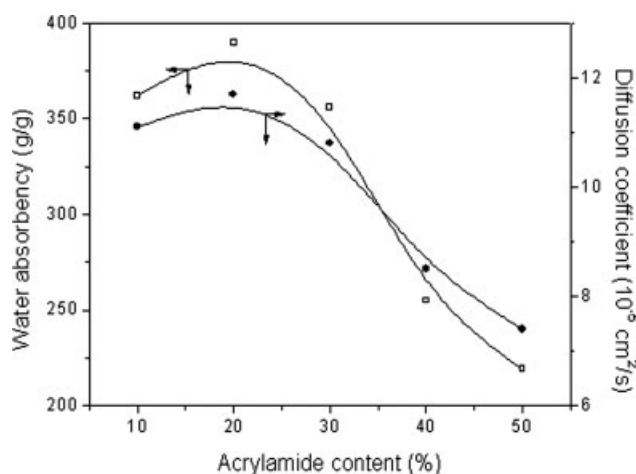

Figure 7 Effects of Am content on water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin. The neutralization degree of AA, 60%; and other conditions were the same as those of Figure 6.
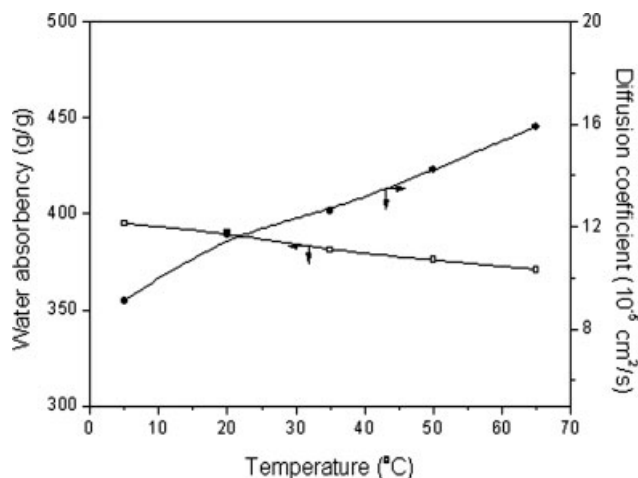
Figure 8 Effects of temperature on water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin. Am content, 20%; and the other conditions were the same as those of Figure 7.

5 to 65°C. This was because the bounded water in the composite network at the low temperature became free water or nonbinding water at the high temperature, and then it could move rapidly out of the network; this led to a decrease in the water absorbency.[25]

It could also be seen from Figure 8 that the urea diffusion coefficient increased obviously with the increasing of the temperature. The dependence of the urea diffusion coefficient on the temperature may be explained as follows: when the temperature increased, the polymer network shrunk slightly (water absorbency decreased), which would lead to the diminishing of mesh size. This was a hindering effect to the diffusion of urea. On the other hand, the increase of the temperature enhanced both the chain segmental mobility and urea molecular motion ability. This was an accelerating effect to the diffusion of urea. However, the former hindering effect was very little because the network shrinking was weak. So, urea diffusion coefficient increased significantly when the temperature increased from 5 to 65°C.

From Figure 8, it could be seen that urea diffusion coefficients increased from 9.1×10^{-5} cm^2/s to 15.9×10^{-5} cm^2/s when the temperature increased from 5 to 65°C. That is to say, the temperature of swelling had a considerable effect on the urea release rate.

The effects of pH on water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin

Partially neutralized poly(acrylic acid), which is the main component in poly(AA-co-Am)/kaolin composite, is a pH-sensitive polymer, so the influences of

pH on the water absorbency and diffusion coefficient of urea release were also investigated. To match the pH of most soils, we chose three pH values, 4, 7, and 9, as the experimental conditions. However, experimentations showed that pH had no significantly effect on water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin (results are not shown).

This was probably due to the complex of H$^+$ and urea (U). There were two equilibriums[26] after the poly(AA-co-Am)/kaolin composite was swollen.

$$U + H^+ \rightleftharpoons UH^+ \tag{6}$$

$$R—COOH \rightleftharpoons R—COO^- + H^+ \tag{7}$$

At pH = 4, H$^+$ complexes with the loaded urea molecules in the poly(AA-co-Am)/kaolin composite. At pH = 9, UH$^+$ dissociates to produce H$^+$. Moreover, partially neutralized poly(acrylic acid) also possesses buffer action after swollen.[27] As a result, the water absorbency and mesh size of poly(AA-co-Am)/kaolin composite will not be affected by pH (pH = 4–9). Therefore, the change of pH will not have influences on the urea diffusion process.

The effects of ionic strength on water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin

Because of the existence of many kinds of ions in soil, it is important to know the influences of ionic strength on the water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin composite hydrogel. Figure 9 shows the water absorbency of poly(AA-co-Am)/kaolin and diffusion coefficient of urea release from it in distilled water,
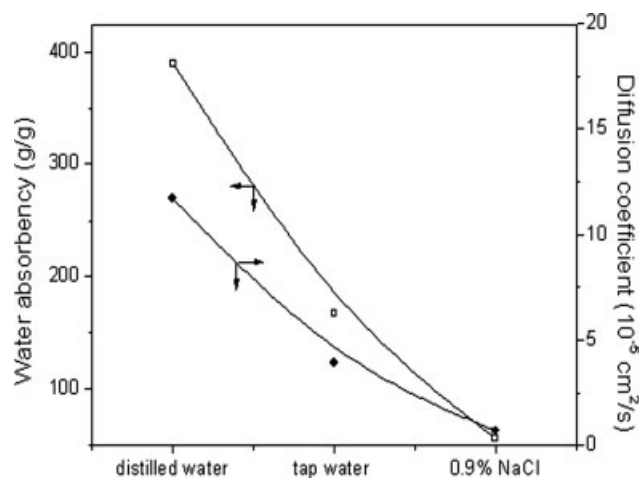

Figure 9 Effects of ionic strength on water absorbency and diffusion coefficient of urea release from poly(AA-co-Am)/kaolin. The temperature of release medium, 20°C; and other conditions were the same as those of Figure 8.

tap water, and 0.9% NaCl aqueous solution, respectively. It could be seen from Figure 9 that both the water absorbency and urea diffusion coefficient decreased as the increase of ionic strength.

The decrease of water absorbency could be attributed to the reduction in the osmotic pressure difference between the poly(AA-*co*-Am)/kaolin composite hydrogel and the external medium with the increasing of ionic strength. In addition, the screening effect of the counterion (positive ion) on the anionic group (—COO$^-$) reduced the electrostatic repulsion force.[28] The effect of the ionic strength on the swelling was determined with the following relation suggested by Hermans[29]:

$$Q_{eq}^{5/3} = A + Bi^2/I \qquad (8)$$

where Q_{eq} is water absorbency at equilibrium; i is the concentration of the charges bound to the gel; I is the ionic strength of the external solution; A and B are the empirical parameters.

The decrease in water absorbency would lead to the reduction of mesh size of polymer network, as a result, the barriers to urea diffusion was enhanced obviously. Therefore, ionic strength could influence the diffusion coefficient of urea release from poly(AA-*co*-Am)/kaolin composite hydrogel.

CONCLUSIONS

A series of poly(acrylic acid-*co*-acrylamide)/kaolin composites were prepared to act as a release carrier of urea fertilizer by aqueous solution copolymerization of partially neutralized acrylic acid and acrylamide in the presence of kaolin nanopowder. The loading of urea was carried out by swelling the superabsorbent composite in aqueous solution of urea, and urea loading percentage could be adjusted by changing the urea concentration of swelling medium. However, there were not important differences of swelling results at different urea concentration. The release of urea could be affected by many factors, such as the contents of crosslinker, kaolin, and acrylamide, the neutralization degree of acrylic acid, and temperature, pH, and ionic strength of release medium, etc. In a word, under the effect of these factors, the values of urea diffusion coefficient were proportional to those of water absorbency. Therefore, there is a contradiction between the release rate and water absorbency. To gain a slow release rate of urea, we must decrease the water absorbency.

References

1. Mohana, R. K.; Padmanabha, R. M.; Murali, M. Y. Polym Int 2003, 52, 768.
2. Shavit, U.; Reiss, M.; Shaviv, A. J Control Release 2003, 88, 71.
3. Li, A.; Zhang, J. P.; Wang, A. Q. Polym Adv Technol 2005, 16, 675.
4. Chatzoudis, G. K.; Valkanas, G. N. Commun Soil Sci Plant Anal 1995, 26, 3099.
5. Mohan, Y. M.; Murthy, P. S. K.; Raju, K. M. React Funct Polym 2005, 63, 11.
6. Wu, J.; Wei, Y.; Lin, J.; Lin, S. Polymer 2003, 44, 6513.
7. Abraham, J.; Pillai, V. N. R. J Appl Polym Sci 1996, 60, 2347.
8. Bajpai, A. K.; Giri, A. React Funct Polym 2002, 53, 125.
9. Ward, J. H.; Peppas, N. A. J Control Release 2001, 71, 183.
10. Ma, S. M.; Liu, M. Z.; Chen, Z. B. J Appl Polym Sci 2004, 93, 2532.
11. Liu, M. Z.; Guo, T. H. J Appl Polym Sci 2001, 82, 1515.
12. Zhan, F. L.; Liu, M. Z.; Guo, M. Y.; Wu, L. J Appl Polym Sci 2004, 92, 3417.
13. Guo, M. Y.; Liu, M. Z.; Liang, R.; Niu, A. Z. J Appl Polym Sci 2006, 99, 3230.
14. Watt, G. W.; Chrisp, J. D. Anal Chem 1954, 26, 452.
15. Muhr, A. H.; Blanshard, J. M. V. Polymer 1982, 23, 1012.
16. Cobby, J.; Mayersohn, M.; Walker, G. C. J Pharm Sci 1974, 63, 725.
17. Sun, X. W.; Wu, Z. H. Paper Chem 2004, 3, 52.
18. Li, A.; Wang, A. Q.; Chen, J. M. J Appl Polym Sci 2004, 92, 1596.
19. Karadag, E.; Üzüm, O. B.; Saraydin, D.; Güven, O. Int J Pharm 2005, 301, 102.
20. Wesselingh, J. A. J Control Release 1993, 24, 47.
21. Favre, E.; Girard, S. Eur Polym J 2001, 37, 1527.
22. Iza, M.; Stoianovici, G.; Viora, L.; Grossiord, J. L.; Couarraze, G. J Control Release 1998, 52, 41.
23. Lin, J. M.; Wu, J. H.; Yang, Z. F.; Pu, M. L. Macromol Rapid Commun 2001, 22, 422.
24. Ende, M.; Hariharan, D.; Pappas, N. A. React Polym 1995, 25, 127.
25. Warren, T. C.; Prins, W. Macromolecules 1972, 5, 506.
26. Braud, C.; Muller, G.; Selegny, E. Eur Polym J 1978, 14, 479.
27. Li, A.; Wang, A.; Chen, J. J Appl Polym Sci 2004, 94, 1869.
28. Lee, W. F.; Wu, R. J. J Appl Polym Sci 1996, 62, 1099.
29. Hermans, J. J. Flow Properties of Disperse System; Wiley-Interscience: New York, 1953; p 61.