Poly(sodium acrylate-*co*-acrylamide-*co*-2-hydroxyethyl acrylate)의 제조와 고흡수 특성

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Preparation and Super-Water-Absorbency of Poly(sodium acrylate-*co*-acrylamide-*co*-2-hydroxyethyl acrylate)

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Abstract : Super water−absorbent resins were prepared by inverse suspension copolymerization of sodium acrylate, acrylamide and 2-hydroxyethyl acrylate using *N, N′*−methylene−bis−acrylamide as cross−linker. For the suspension copolymerization, monohexadecyl phosphate was employed as the dispersing agent, cyclohexane as the dispersing medium and potassium persulfate as the initiator. The dependence of water−absorption capacity on the amount of crosslinking agent, oil/water ratio, degree of neutralization and the composition of the copolymer were systematically investigated. Furthermore, the swelling kinetics of the super water−absorbent copolymer was carried out. The absorption of the resins is more than 1800 g/g for deionized water and 100 g/g for 0.9% NaCl solution, respectively. The copolymers showed an increased salt resistance and enhanced water retention of soil.

Keywords : sodium acrylate, acrylamide, 2−hydroxyethyl acrylate, inverse suspension polymerization, salt−resistance, super water−absorbent resin.

Introduction

Super water−absorbent resin, as a new kind of functional polymer materials, has been quickly developed in recent years. It can absorb water to several hundred times or even several thousand times its own mass, at the same time the absorbent water wasn't easily pressed out by mechanical pressure. These functional resins are widely used as hygienic article materials, industrial dehydrator, antistaling agent, antifogging agent, biomedical materials, lyogel materials soil modified agent in agriculture, forestry, horticulture, and so on.[1,2] In such applications, water absorbency and water retention are essential.

Super water−absorbent resins are usually prepared by bulk polymerization or aqueous solution polymerization.[3] However, the heat elimination in these polymerizations isn't very easy, and the viscosity of the reaction media was too high to react in the common reactors. There are also some particular difficulties in the post treatment. In the preparation of polymers, suspension polymerization is a widely used method in which a monomer suspension is maintained by vigorous stirring during the reaction. Suspension polymerization has many attractive features because polymers thereby obtained are in the form of beads. In comparison with polymers obtained in emulsion or solution polymerization, they are purer and directly usable in some applications after a washing and drying process. The bead size can be controlled with variations in the stabilizer agent, the agitation, and the monomer/stabilizer ratio. Polyacrylate superabsorbents, which were more widely used in recent years, generally exhibit a very high absorbency in deionized water; they, however, have the problem of poor resistance to salts. We previously reported the synthesis of super water−absorbent poly(sodium acrylate) resins by inverse suspension polymerization, using monooctadecyl phosphate

as dispersing agent.[4] It was found that such resins based merely on sodium acrylate showed lower water absorbency, especially for electrolyte−resistance. But the circumstances in which the superabsorbents are used always contain salts, such as disposable pads, sheets, and towels for surgery, adult incontinence, and feminine hygiene products. So, it is important to improve salt resistance of these superabsorbents.[5]

In this paper, we prepared a series of copolymers based on three monomers of acrylamide, sodium acrylate and 2−hydroxyethyl acrylate by inverse suspension polymerization. These novel copolymers contain a nonionic hydrophilic monomer containing hydroxyl group and amide group. Such novel polymer architecture allowed polymer chains to have different hydrophilic groups and the synergistic interreactions between the hydrophilic groups, improving the water−absorbent capacity of super water−absorbent copolymers, especially for the electrolyte. The swelling behavior and water retention of the above superabsorbent copolymers were also studied in the laboratory and in soil.

Experimental

Materials. Acrylic acid was distilled at reduced pressure to remove the inhibitor before use. Monohexadecyl phosphate was prepared as reported previously.[6,7] All other agents were used without further purification.

Synthesis Procedure. A series of the copolymer superabsorbents were prepared by the following procedure: the inverse suspension polymerizations were carried out in a florence flask reactor equipped with a reflux condenser, a dropping funnel, a thermometer and a nitrogen inlet tube, on a magnetic stirrer. 125 mL cyclohexane and monohexadecyl phosphate were added into the reactor. Reaction medium was deoxygenated with nitrogen until the entire process was completed. Then the mixture was stirred at 70 ℃, in order to make monohexadecyl phosphate dissolved in cyclohexane(continuous phase).

At the same time, a flask was charged with various amount of acrylic acid(AA). Cooling in the ice−bath, sodium hydroxide solution was slowly added into the flask, to neutralize the mixture to a certain degree. Then the flask was charged with acrylamide(AM), 2−hydroxyethyl acrylate (HA), and *N, N′*−methylene−bis−acrylamide, potassium persulfate($K_2S_2O_8$). The mixture was stirred until the added agents were mixed completely. After flushed slowly with nitrogen for 5 min, the mixture was charged into a funnel, added into the reactor during half an hour at a constant rate in order to polymerize. After addition, the

reaction was allowed to proceed for 1 h at reaction temperature. The suspension solution was cooled to room temperature under stirring, put still until stratification was completed, and then poured cyclohexane out for a recycle use. The copolymers particle can be obtained by drying the product in the bottom under the infrared light.

Average Particle Size Measurement. The average particle size of superabsorbent resin, determined on a SA−CP3 centrifugal particle size analyzer, is about 80 μm, and the particle size is uniform.

Water Absorbency Measurement: A weighed quantity of the superabsorbent(0.5 g) was immersed in the excess of deionized water or 0.9 wt% NaCl(aq) in a flask for 30 min under stirring at room temperature; a 120−mesh nylon screen removed the residual water. The particles were weighed and the water absorbency was calculated by the following equation:

$$\text{Absorbency } Q(\text{g/g}) = \frac{M_0 - M}{M_c}$$

Absorbency is expressed in grams of water or saline solution retained in the resins by a gram dried particles, and M_0, M and M_c denote, respectively, the weight of the water added into the flask, the weight of the residual water and the weight of the dried particles.

Water Absorbency Rate Measurement : The resins(0.5 g, each) were immersed in 1500 mL deionized water in several 2 L beakers for different time under stirring. The swollen resins were filtered through a 120−mesh nylon screen. Then the relationship between water absorbency and absorbent time can be attained after some calculation.

Effect of the Resins to the Water Retention of Soil. Two weighed samples of dry soil were charged into two culture dishes. One of them was well mixed with the super water−absorbent resins, at a 0.2%(w/w) resins/soil ratio. Then enough water was added to make the two samples with the same humidity. Humidity was expressed as the water content per gram of dry soil. Two samples were placed into an insulation and with a temperature set on 30±0.5 ℃, weighed them for every few minutes. The water−holding rate (*R*%) was calculated by the following equation:

$$R\% = \frac{\text{wt of the surplus water}}{\text{wt of the adding water}} \times 100$$

Results and Discussion

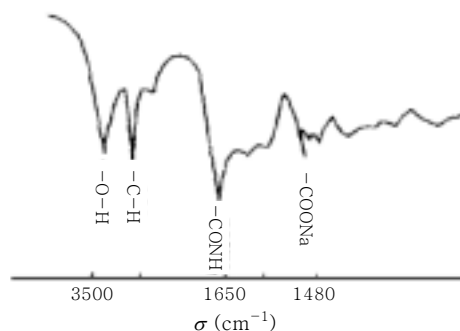**The Structure of Superabsorbent Resin.** Figure 1 showed the

Figure 1. IR spectrum of super water absorption copolymer.

Figure 2. Absorption power in water and in salt water vs. composition of monomers.

Figure 3. Influence of HA amount on the absorption power $[n_{AA}/n_{(AA+AM)}=0.4]$.

Table 1. Absorption Power of Resins in Different Aqueous Solution

	Absorption power (g/g)				
	Sample deionized water	Running water	0.5% NaOH solution	0.9% NaCl solution	0.36% HCl solution
PNaAA	920	384	75	62	11
P(NaAA–AM)	1650	487	123	103	10
P(NaAA–AM–HA)	1850	520	133	115	12

IR spectrum of superabsorbent resin poly(NaAA–AM–HA). Clearly, there were absorption bands at 3500 cm^{-1} (–OH stretching), 2900 cm^{-1} (–CH antisymmetric stretching), and two characteristic peaks at 1400 and 1565 cm^{-1} (–COONa). The characteristic peak at 1650 cm^{-1} was attributed to amide group (–CONH$_2$), which was not changed into the group of sodium carboxylate (–COONa) by alkaline hydrolysis.

Effect of Monomer Composition on Water-Absorption Power. It was found that the water absorption power of resins obtained by monomer copolymerization could be significantly enhanced (water containing deionized water, running water, 0.9%NaCl solution and other electrolyte solutions, the same below). As shown in Figure 2, absorption power of poly(NaAA–AM) was much higher than that of homopolymers. This enhanced water absorption ability was due to synergistic reaction of two kinds of hydrophilic groups in the chain. The absorbency of poly(NaAA–AM) reached the maximum when $n_{AA}/n_{(AA+AM)}=0.4$. In comparison, the absorbency of poly(NaAA–AM–HA), by introducing 2-hydroxyethyl acrylate (HA) into poly(NaAA–AM) (where $n_{AA}/n_{(AA+AM)}=0.4$), increased with the HA amount until a maximum was reached at $n_{HA}/n_{(AA+AM+HA)}=0.05$ (Figure 3).

Table 1 shows the water absorption power and electrolyte-resistance of poly(NaAA), poly(NaAA–AM) and poly(NaAA–AM–HA). Many nonionic hydrophilic groups existed in the chain of poly(NaAA–AM–HA), the hydrolysis degree was not large and hardly affected by ionic strength (as Na$^+$, Cl$^-$, OH$^-$). So the electrolyte-resistance of copolymeric resin with nonionic monomer was obviously improved. However, there was a critical value for nonionic monomer, especially for the monomer HA with lower hydrophilic property. The higher amount of HA, inversely led to a decrease in absorption power and electrolyte-resistance. Our results indicated that the absorbency and electrolyte resisting of poly(NaAA–AM–HA) were better than that of poly(NaAA–AM) in a certain range of monomer
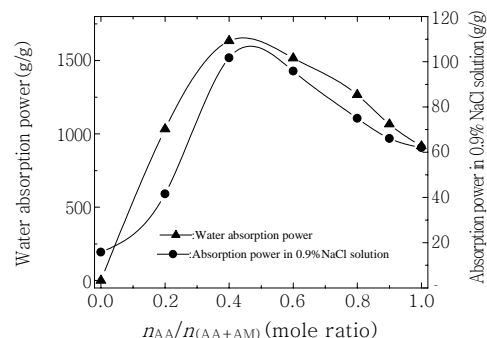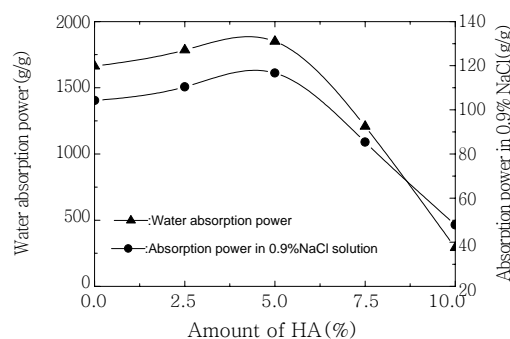
composition. It is a satisfactory method to improve salt-resistance of absorbent resin with using different hydrophilic groups.

Effect of Cross-linking Agent Amount on Water-Absorption Power. Table 2 shows that the cross-linking agent amount increased, the water absorption power increased in the concentration of less than 0.027%, but decreased when cross-linking agent amount was higher than 0.027%. This is because the cross-linking agent amount is too high, the cross-linking density increases but water contained inside the three-dimensional polymer network decreases. At lower cross-linking agent amount, the average length of the subchains between two neighboring cross-linking points is longer and can absorb much more water. But in such case, some parts of the resin are soluble and the absorption power, in essence, is not improved. So there existed an

Table 2. Effect of Amount of Crosslinking Agent on Water-Absorption Power

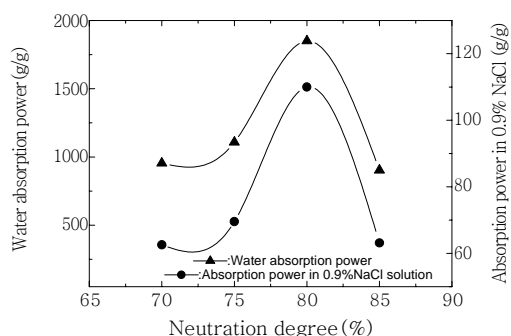| Amount of crosslinking agent	Salt-free water (g/g)	0.5% NaOH solution (g/g)	0.9%NaCl solution (g/g)
0	350	10	30
0.007	1100	80	65
0.013	1250	85	62
0.020	1350	92	73
0.027	1850	133	115
0.033	850	78	64
0.040	634	60	41

optimal value at cross-linking agent/monomer=0.027% (weight ratio) for the absorbency of resin.

Effect of Ratio Oil/Water on Water-Absorption Power. Table 3 shows the relationship between the ratio oil/water in volume and water absorption power of copolymers. As the ratio oil/water increased from 2.5:1 to 3.0:1, the particle size of copolymers became small and water absorption power was improved. But with the ratio increased continuously, the absorbency decreased. This is because at higher oil/water ratio, monomer was easily dispersed in smaller bead, the reaction heat easily diffused, and self-cross-linking degree declined. But at the same time, the bead was too small, to some extent namely lower monomer concentration, the rate of copolymerization became slow obviously, and molecular weight decreased, so water absorption power decreased accordingly.

Effect of Neutralization Degree of AA on Water-Absorption Power. As shown in Figure 4, the neutralization degree of AA has great influence on absorption power of poly

Table 3. Effect of Varying Ratio Oil/Water on Water-Absorption Power of Copolymer

Oil/Water	2.5 : 1	3.0 : 1	3.5 : 1	4.0 : 1
Deionizing water (g/g)	1680	1850	1840	1750
0.9% NaCl solution (g/g)	74	133	85	82

Figure 4. Water-absorption power vs. neutralization degree of AA.

(NaAA-AM-HA). The polymerization rate of AA, which has a high activity, was quicker than sodium acrylate. If the neutralization was too low, it is not easy to control copolymerization but easy to form overcrosslinking polymers, resulting in a decrease in absorption power. On increasing the neutralization, the absorption power enhanced. For one thing, the reaction speed slowed down and crosslinking degree declined. For another, the strong hydrophilic group of sodium carboxylate(-COONa) increased the osmotic pressure in polymer network. However, in the high neutralization range(>80%), part of the copolymeric resin became soluble and absorption power decreased.

Swelling Kinetics. The water is absorbed by superabsorbent resin and the swelling rate is described by the following experimental equation:

$$\frac{dQ}{dt} = K(Q_{max} - Q) \tag{1}$$

Where Q_{max} is the maximum absorbency; Q, the characteristic absorbency; and K, the swelling kinetic constant.
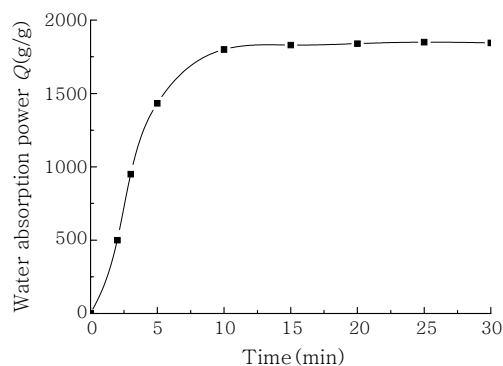
Integration from (1) gives

$$-\ln(Q_{max} - Q) = Kt + C \tag{2}$$

$$-\log(Q_{max} - Q) = Kt/2.303 + C \tag{3}$$

Where t is the characteristic swelling time; and c, the integration constant. As a consequence of $t=0$, $Q=0$, and $-\log Q_{max} = C$, therefore,

$$\log(Q_{max}/(Q_{max} - Q)) = Kt/2.303 \tag{4}$$

For an example, the swelling rate of sample($Q_{max}=$ 1850 g/g) is given in Figure 5. It is evident that the sample

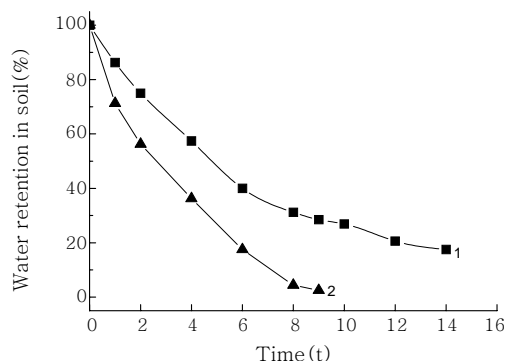**Figure 5.** Water-absorption power (Q) of copolymer vs. Time in water(Q_{max}=1850 g/g).

Figure 6. Water retention of soil copolymer resin content: 1, 0.2 %(based on soil wt.)∶2∶0%.

was characterized by an extremely high swelling rate. It could absorb up to 90% of its maximum in ten minutes. The K is determined to be 0.2302 by Eq. (4).

Water Retention in Soil. As shown in Figure 6, using the superabsorbent resin has enhanced the water retention of soil. Only adding 0.2% absorbent to soil, the soil could remain 40% moisture in a week at the high temperature of 30 ℃. And the moisture in soil without absorbent was nearly vanished. This demonstrated that there is a better water retention of soil with superabsorbent resin.

Conclusions

By introducing nonionic monomer to the copolymer, the electrolyte resistance of absorbent resin was remarkably improved. Electrolyte−resistance of poly(NaAA−AM−HA) was better than that of poly(NaAA−AM). It indicated that mixing different hydrophilic groups was an effective way to improve salt−resistance of absorbent resin. Moreover, our results showed that the optimal reaction conditions were $n_{AA}/n_{(AA+AM)}=0.4$, $n_{HA}/n_{(AA+AM+HA)}=0.05$, cross−linking agent/$W_{(AA+AM+HA)}=0.027\%$, and 80% neutralization, a 3.0∶1(v/v) oil/water ratio, thus the copolymeric resins have the best water absorption power and electrolyte−resistance. The water absorption amount of the resin is more than 1800 and 100 g/g in case of deionized water and 0.9% NaCl solution, respectively.

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