

Preparation and Properties of a Salt-Resistant Superabsorbent Polymer

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ABSTRACT: Crosslinked sodium polyacrylate was prepared by solution polymerization with *N,N*-methylene-bis-acrylamide (bisAM) as crosslinking agent; it was subsequently surface-crosslinked by ethylene glycol diglycidyl ether (EGDE) and then was modified with inorganic salt to obtain a superabsorbent with water absorbency in 0.9 wt % NaCl aqueous solution at atmosphere and applied pressure ($P \approx 2 \times 10^3$ Pa) of 55 and 20 $\text{g}\cdot\text{g}^{-1}$, respectively. Moreover, it also had excellent hydrogel strength. The effects of reaction temperature, reaction time, neutralization degree (ND)

of acrylic acid, amount of initiator, crosslinking agent, and surface-crosslinking agent, mass ratio of inorganic salt to initial superabsorbent, molar ratio of sodium aluminate (NaAlO_2) to potassium dihydrogen phosphate (KH_2PO_4) on water absorbency (WA) in 0.9 wt % NaCl aqueous, and the hydrogel modulus were investigated and optimized. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2532–2541, 2004

Key words: superabsorbent; salt-resistant; acrylic acid; surface-crosslinked

INTRODUCTION

Superabsorbent polymer (SAP) as a special polymeric material can absorb a large amount of water and the water is hardly removed even under pressure. Because of its excellent characteristics, the superabsorbent is widely used in many applications such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, drug delivery systems, and absorbent pads.^{1–4} 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 as evinced by their notable low absorbency exhibited to electrolytic solutions such as an aqueous common salt solution. 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 these superabsorbents' salt resistance. Inorganic gel generally has excellent salt resistance, so if we prepare a hydrogel compound of polymer gel and inorganic gel, an excellent salt-resistant superabsorbent would be obtained.⁵

We have conducted a survey of the literature concerning salt-resistant superabsorbent polymers but found little information on this subject. On the basis of our previous studies,^{6–8} we prepared the salt-resistant

superabsorbent as follows. At first, we prepared crosslinked sodium polyacrylate; then, we used ethylene glycol diglycidyl ether (EGDE) to crosslink the molecular chains existing at least in the vicinity of the surfaces of the crosslinked sodium polyacrylate; last, the surface-crosslinked superabsorbent was mixed with inorganic salt powders. The superabsorbent we obtained has excellent salt-resistance, hydrogel strength, and absorption rate. Moreover, it also has high water absorbency under pressure as to aqueous salt solution. The superabsorbent can be used in hygiene products such as feminine hygiene products, disposable diapers, and so on.

EXPERIMENTAL

Sample preparation

Acrylic acid (AA, Beijing Dongfang Chemical Factory, Beijing, China) was distilled at reduced pressure (boiling point = 20–21°C at 0.5 mmHg). Sodium hydroxide (NaOH, Tianjin Chemical Regent Co., Tianjin, China), *N,N*-methylene-bis-acrylamide (bisAM, Fluka, Germany), ethylene glycol diglycidyl ether (EGDE, Fluka, Germany), hydrogen peroxide (H_2O_2 , Jiangsu Sanmu Chemical Factory, Jiangsu, China), L-ascorbic acid (Vc, Xi'an Chemical Regent Co., Xi'an, China), sodium aluminate (NaAlO_2 , Shanghai Chemical Regent Co., Shanghai, China), and potassium dihydrogen phosphate (KH_2PO_4 , Chengdu Chemical Regent Co., Chengdu, China) were of analytical grade. Ten milliliters of AA was added in a beaker and then 13.6 mL aqueous NaOH solution (25% in mass) was carefully added to partially neutralize AA. BisAM (35 mg) was added and the mixture was stirred at ambient temperature for 30 min.

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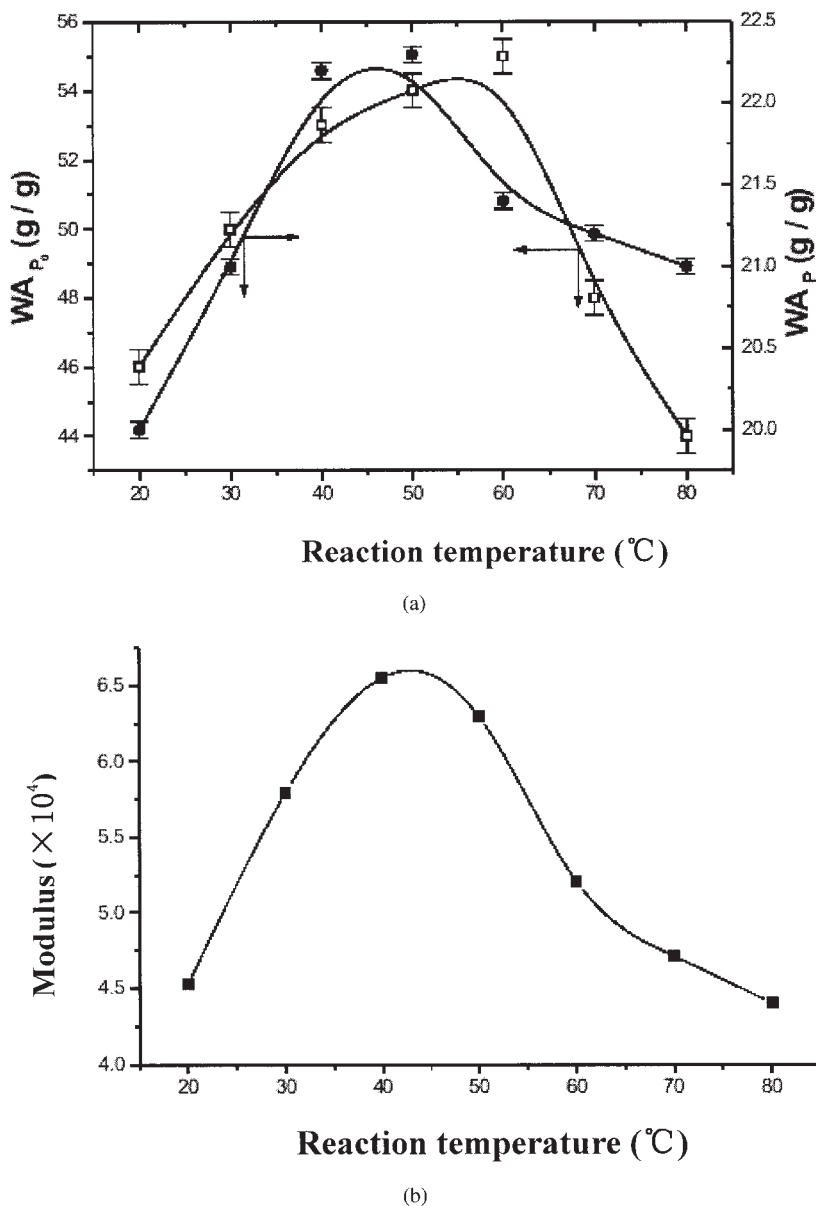
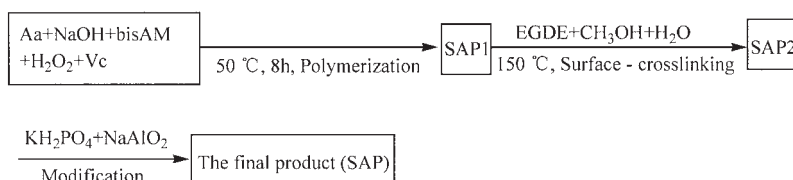


Figure 1 (a) Curves of WA_{P_0} and WA_P versus reaction temperature. (b) Curve of hydrogel modulus versus reaction temperature.

Then, 0.5 mL H_2O_2 (0.1% in mass) and 0.2 mL Vc (0.1% in mass) were introduced into the reactor. The polymerization was carried out at 50°C under nitrogen for 8 h. The resulting polymer was dried at 150°C to a constant weight. After the polymer mentioned above was reswollen in excess water to remove the soluble materials, we acquired the gel. Then, the gel was redried, reweighed, ground, and milled through 26- to 90-mesh screen (SAP1). The sample was mixed with a solution com-

pound of 1.2 wt % EGDE, 78.8 wt % methanol, and 20 wt % H_2O at a ratio of 7 g of the solution to 100 g of SAP1 particles. Then, the mixture above was heated for about 30 min at 150°C. The dried product was ground and milled again (SAP2). With the addition of 10 parts KH_2PO_4 and 4 parts $NaAlO_2$ by weight to 100 parts dried product mentioned above (SAP2), we obtained the final product (SAP). The scheme of the polymerization, the surface-crosslinking, and the modification was



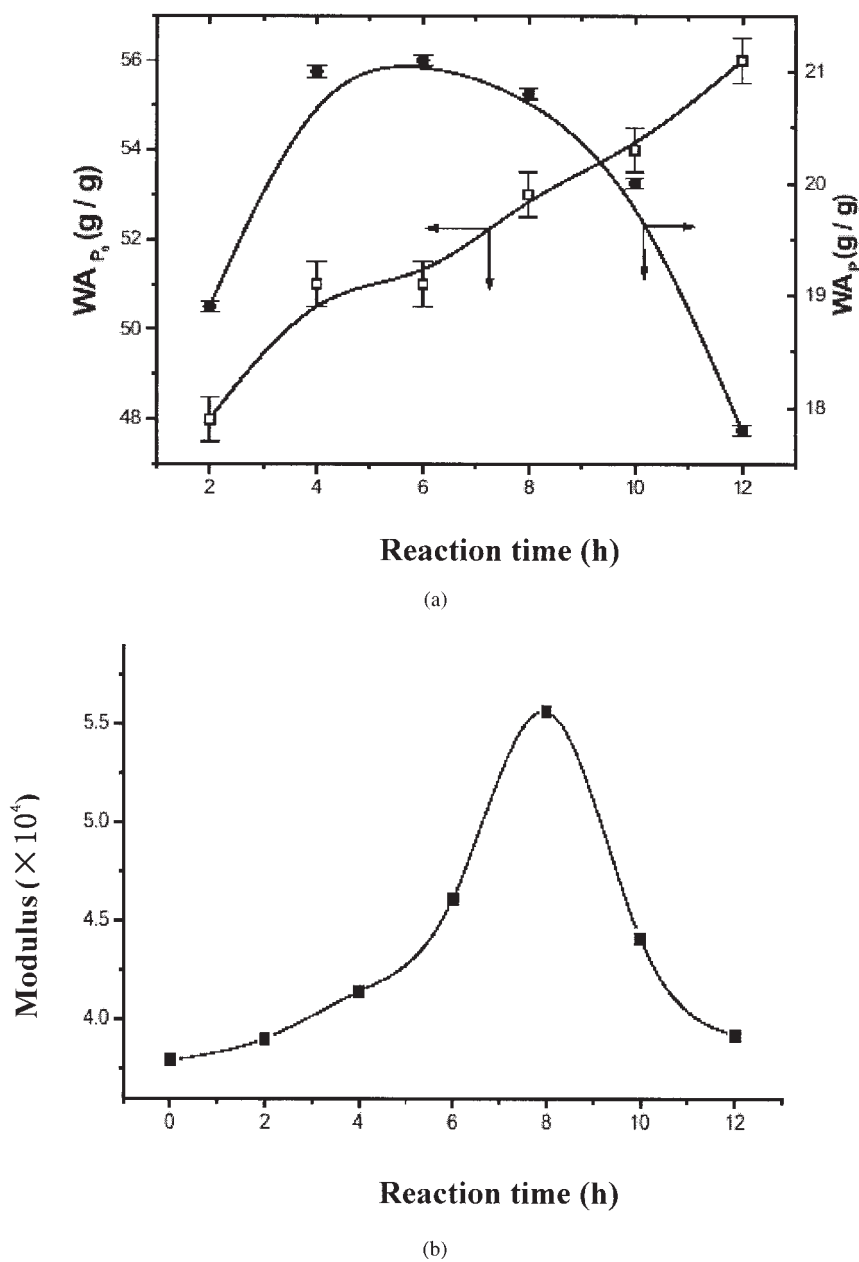


Figure 2 (a) Curves of WA_{P_0} and WA_P versus reaction time. (b) Curve of hydrogel modulus versus reaction time.

Determination of water absorbency in physiological saline solution at atmosphere pressure (WA_{P_0})

The accurately weighted SAP (about 0.2 g) was immersed into a certain amount of physiological saline solution (0.9 wt % NaCl) and allowed to soak at ambient temperature for 30 min. The swollen polymer was filtrated through an 80-mesh sieve to remove nonabsorbed water and weighted to find the amount of the solution absorbed thereby. The water absorbency was calculated by using the equation

$$WA_{P_0} = \frac{M}{M_0} - 1 \quad (1)$$

where M and M_0 denote the weight of the water swollen hydrogel and the weight of the SAP, respectively.

Determination of water absorbency in physiological saline solution at applied pressure (WA_P)

The accurately weighted SAP (about 0.9 g) was uniformly placed at the surface of 200-mesh nylon fabric sealing the bottom of a plastic hollow cylinder 2.8 cm in inner radius and 6.0 cm in height. A cylinder 123 g in weight and 2.8 cm in radius was put into the plastic hollow cylinder ($P \approx 2 \times 10^3$ Pa), weighted, and put

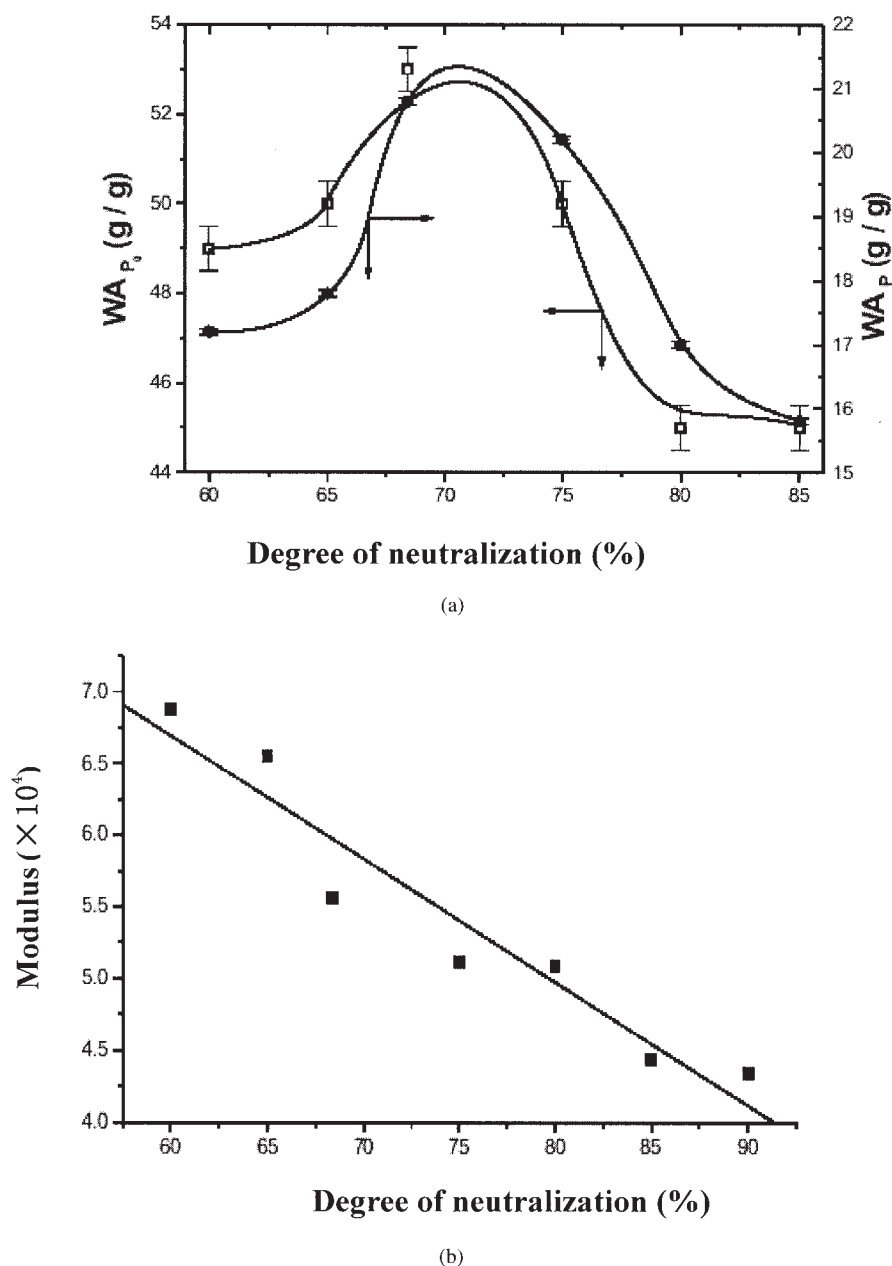


Figure 3 (a) Curves of WA_{p_0} and WA_p versus neutralization degree of acrylic acid. (b) Curve of hydrogel modulus versus neutralization degree of acrylic acid.

on a porous glass slice, which was placed in a evaporating dish filled with physiological saline solution (0.9 wt % NaCl) and allowed to soak at ambient temperature for 60 min, then removed from the solution and left draining, and weighted again to find the amount of the solution absorbed thereby.⁹ The water absorbency was calculated by using the equation

$$WA_p = \frac{M_2 - M_1}{M_0} \quad (2)$$

where M_1 and M_2 denote the weight of the total plastic cylinder with the superabsorbent and cylinder were

placed in when the hydrogel was dry and swollen, and M_0 denoted the weight of SAP.

Determination of hydrogel strength (G)

A sample in the form of swelled hydrogel was tested for the hydrogel strength by using an apparatus composed of micrometer gauge, weight support, and sample pond.¹⁰ The swelled hydrogel was obtained by allowing a salt-resistant superabsorbent polymer to swell in physiological saline solution (0.9 wt % NaCl) for 30 min. The height of the sample under pressure was read from the gauge. The pressure applied to the

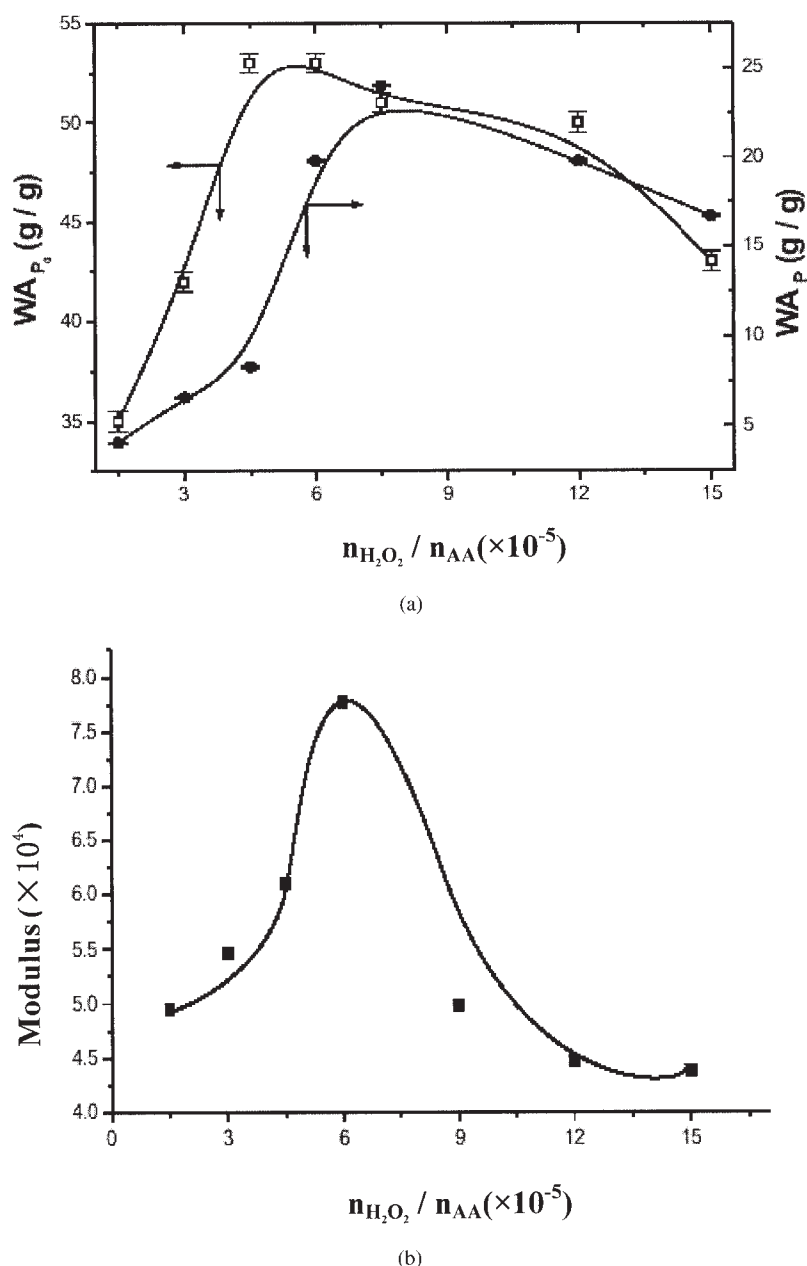


Figure 4 (a) Curves of WA_{P_0} and WA_P versus amount of initiator. (b) Curve of hydrogel modulus versus amount of initiator.

sample was calculated from the weights and the contract area of the sample pond. The hydrogel strength was the slope of the plot of the pressure applied to the sample versus the height of the sample.

RESULTS AND DISCUSSION

Effect of reaction temperature on WA_{P_0} , WA_P and G

Figure 1 showed that WA_{P_0} , WA_P , and G were increased as the reaction temperature increased up to 43°C, while it decreased when reaction temperature was higher than 56°C. There was an optimal reaction temperature range of 43–56°C, at which WA_{P_0} , WA_P , and G all reached their own preferable values. It was

known that polymerization velocity increased as the reaction temperature increased; that is to say, the monomer conversion increased, which would lead to the increase of insoluble parts, so that WA_{P_0} , WA_P , and G increased before the optimal range. After 56°C, any further increasing temperature would result in the crosslinking and chain termination dominant, in accompaniment with WA_{P_0} , WA_P , and G decreasing.

Effect of reaction time on WA_{P_0} , WA_P and G

Figure 2(a, b) showed that WA_{P_0} increased monotonously as reaction time increased because the monomer conversion increased as reaction time increased in

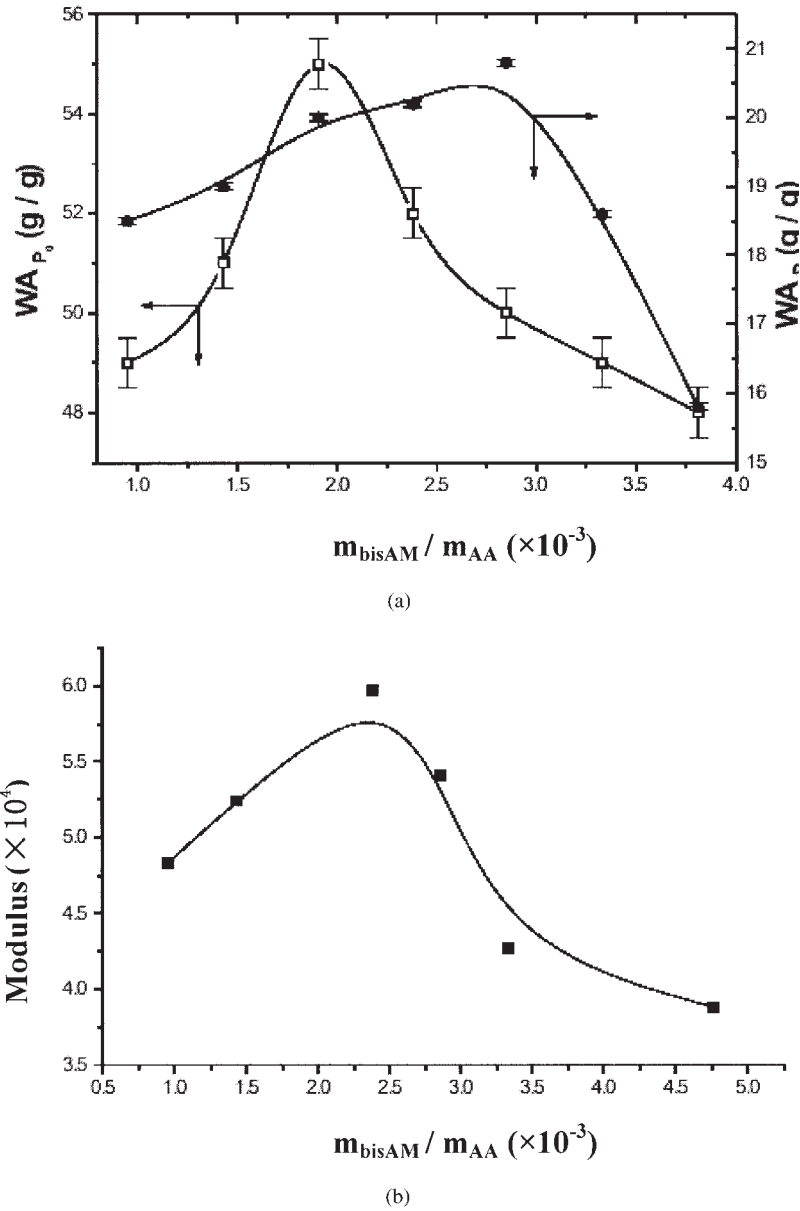


Figure 5 (a) Curves of WA_{P_0} and WA_P versus amount of crosslinking agent. (b) Curve of hydrogel modulus versus amount of crosslinking agent.

radical reaction but WA_P and G could reach maximums, respectively, as reaction time increased. It is given that G relates to the network crosslink density by the equation¹¹

$$G = ART \frac{\rho}{\bar{M}_c} (\nu_2^0)^{2/3} (\nu_2)^{1/3} \quad (3)$$

where ρ is the polymer density, \bar{M}_c is the molecular weight of the network chains, ν_2 is the volume fraction of crosslinked polymer in equilibrium swollen gel [i.e., $\nu_2 = 1/(WA_{P_0}\rho)$], ν_2^0 is the volume fraction of crosslinked polymer in zerogel, and R and T are their usual meanings. Because $\nu_2^0 \approx 1$ for the zerogel, G becomes

$$G = ART \frac{\rho^{2/3}}{\bar{M}_c} (1/WA_{P_0})^{1/3} \quad (4)$$

According to eq. (4), we concluded that G increased as WA_{P_0} increased, so that WA_P and G decreased as reaction time increased in the range of 8–12 h.

Effect of neutralization degree of acrylic acid on WA_{P_0} , WA_P , and G

Figure 3(a, b) showed that WA_{P_0} and WA_P increased as neutralization degree (ND) increased until it reached an optimal range of 70–72%. G decreased monotonously as ND increased. It was known that the electrostatic repulsion between attached carboxylate an-

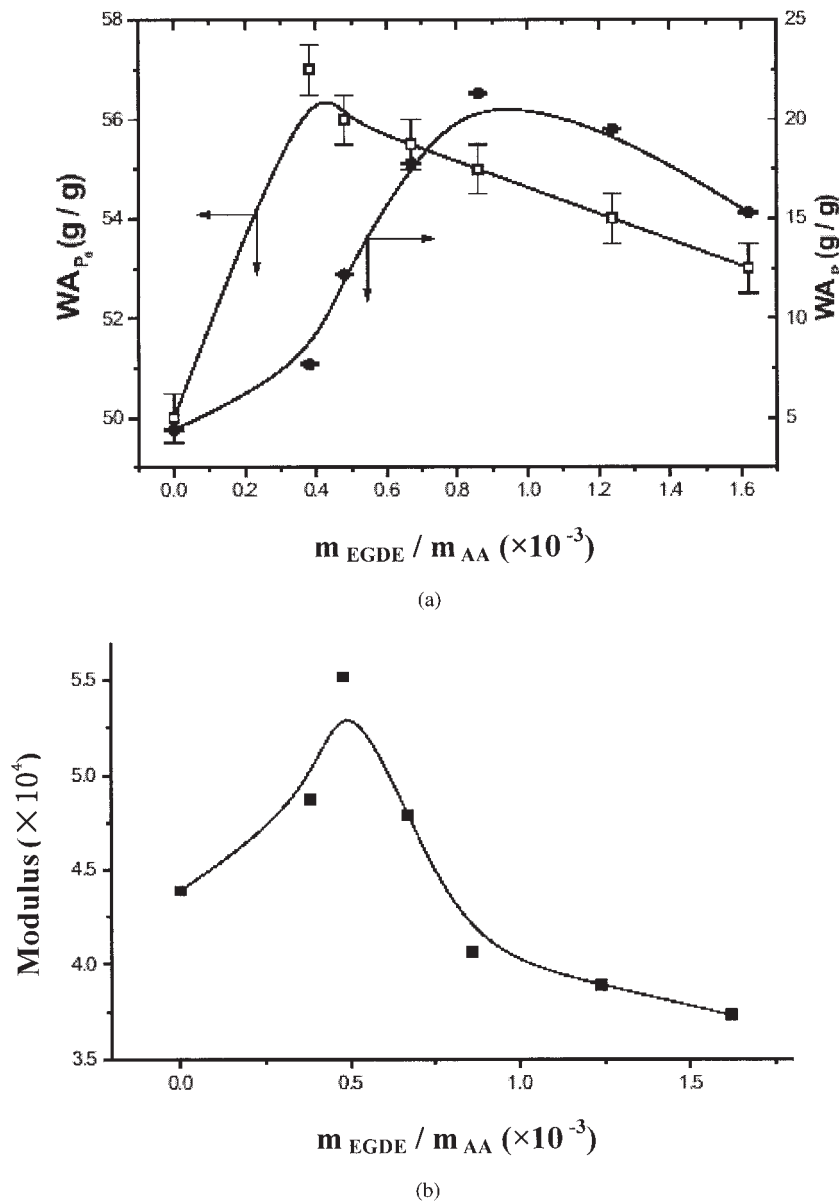


Figure 6 (a) Curves of WA_{P_0} and WA_P versus amount of surface-crosslinking agent (EGDE). (b) Curve of hydrogel modulus versus amount of surface-crosslinking agent (EGDE).

ions increased as the concentration of anions increased, so that the stretching extent of hydrogel network increased. Moreover, the increase in the osmotic pressure difference between hydrogel and external solution would lead to excellent WA_{P_0} and WA_P . A further increase in ND made part of the polymer hydrogel network become soluble, thus both WA_{P_0} and WA_P decreased in the range of 72–85%. The effect of the electrostatic interaction of charged groups on elastic free energy decreased the elastic modulus, so that G decreased monotonously as ND increased.¹¹

Effect of the amount of initiator on WA_{P_0} , WA_P , and G

Figure 4(a, b) showed that WA_{P_0} , WA_P , and G reached maximums at $n_{H_2O_2}/n_{AA} = 5.2 \times 10^{-5}$, 8.0×10^{-5} , and

6×10^{-5} . It was known that monomer conversion increased as the concentration of initiator increased, so that WA_{P_0} , WA_P , and G increased while $n_{H_2O_2}/n_{AA} < 5.2 \times 10^{-5}$, but with an increase in amount of initiator, the collision between monomer-free radicals also increased, which led to the increase of the soluble parts; thereby WA_{P_0} , WA_P , and G increased, while $n_{H_2O_2}/n_{AA} > 7.5 \times 10^{-5}$.

Effect of the amount of crosslinking agent on WA_{P_0} , WA_P , and G

Figure 5(a, b) showed that WA_{P_0} , WA_P , and G reached maximums at $m_{bisAM}/m_{AA} = 1.9 \times 10^{-3}$, 2.7×10^{-3} , and 2.4×10^{-3} , respectively. As we knew, the more the amount of bisAM, the higher crosslink-

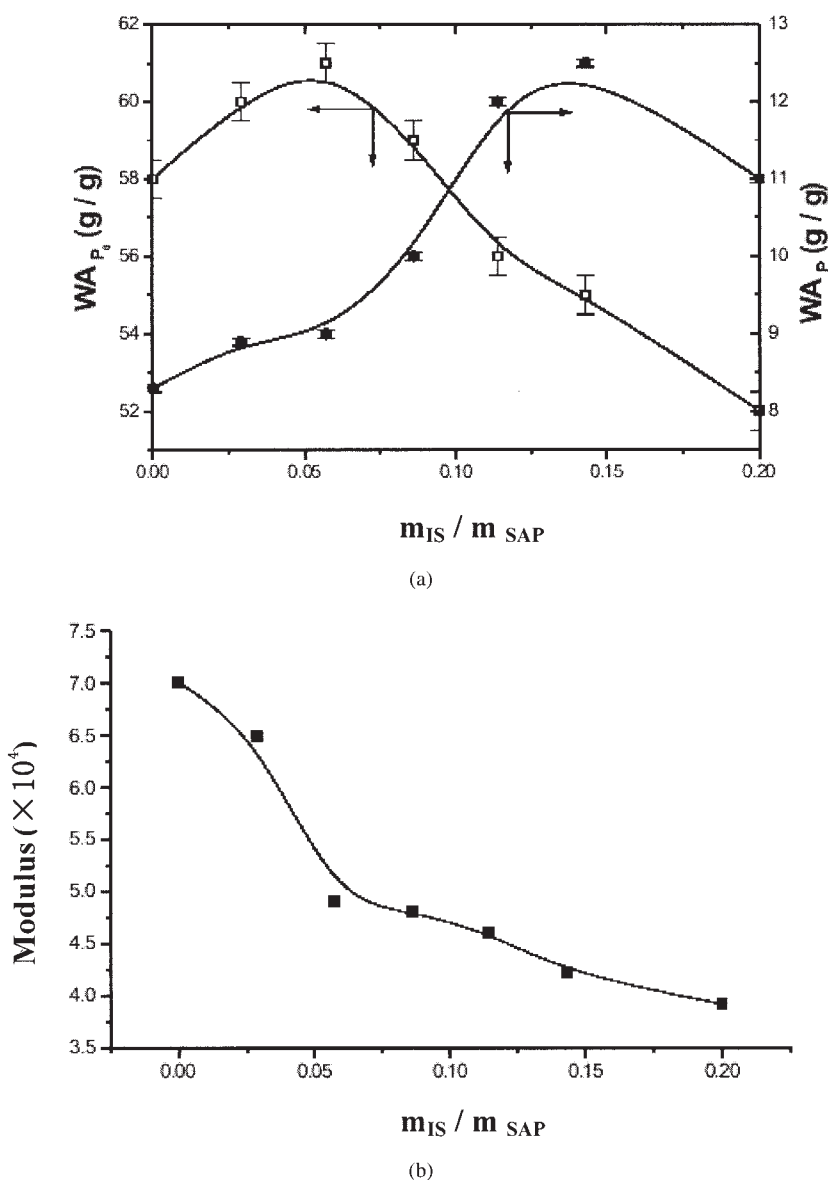


Figure 7 (a) Curves of WA_{P_0} and WA_P versus amount of inorganic salt (IS). (b) Curve of hydrogel modulus versus amount of inorganic salt (IS).

ing density of the hydrogel, and the higher the elastic chain force, the lower soluble parts of the polymer.¹² The elastic chain force of the hydrogel network was the only negative effect on water absorbency¹³; however, the decrease of the soluble part of the polymer had a positive effect on water absorbency. This was why there existed maximums in Figure 5(a). According to eq. (3), the greater the crosslinking density, the higher the hydrogel modulus, but the result did not obey the equation, and G gradually decreased, when $W_{bisAM}/W_{AA} > 2.4 \times 10^{-3}$. It was mainly due to the high crosslinking density of the polymer hydrogel network, which decreased the degree of crystallization and reduced hydrogel modulus.

Effect of the amount of surface-crosslinking agent on WA_{P_0} , WA_P , and G

The superabsorbent polymer particles (SAP1) were surface-crosslinked by EGDE to crosslink molecular chains existing at least in the vicinity of the surfaces of the superabsorbent polymer particles. The effect of the amount of surface-crosslinking agent (EGDE) on WA_{P_0} , WA_P , and G should accord with the effect of amount of crosslinking agent. The result of Figure 6(a, b) proved in accordance.

Effect of the mass ratio of inorganic salt to initial superabsorbent on WA_{P_0} , WA_P , and G

Figure 7(a) showed that WA_{P_0} and WA_P increased as the amount of inorganic salt that consisted of

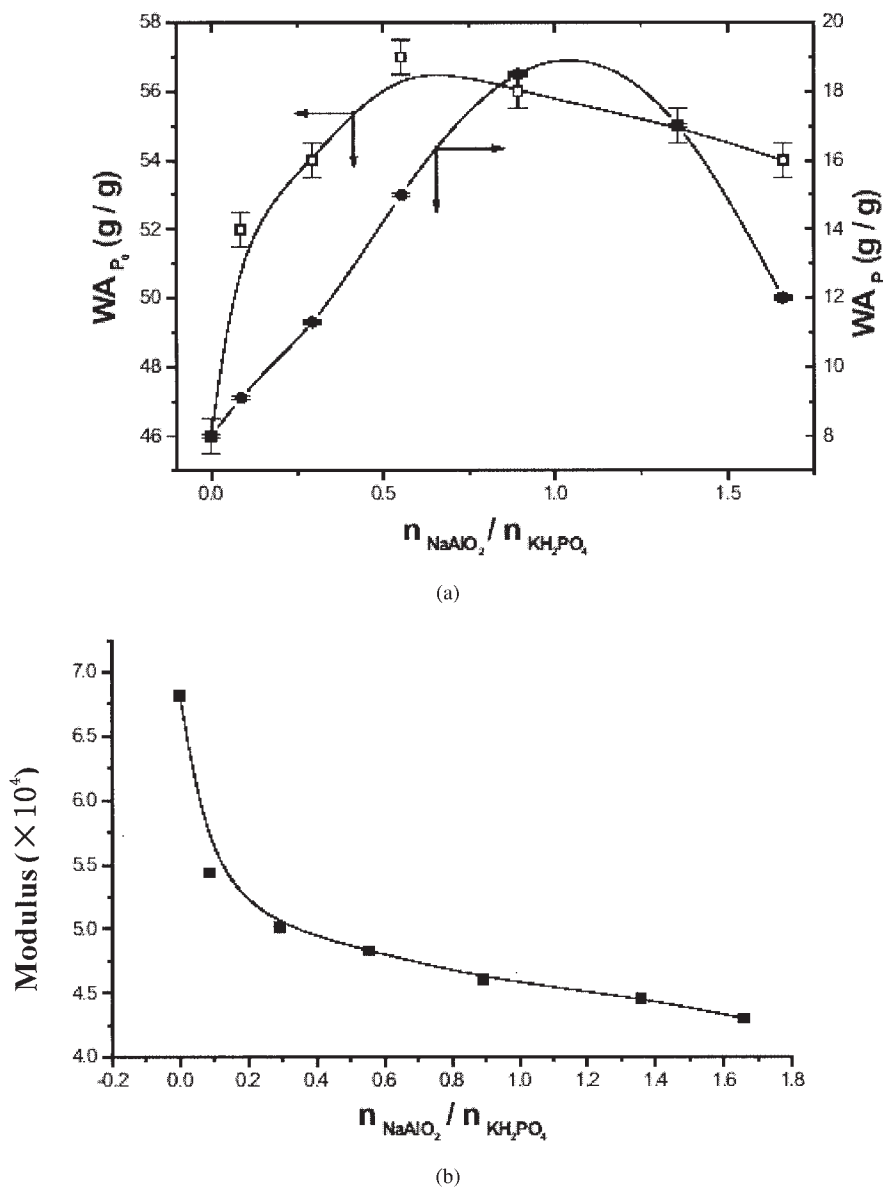


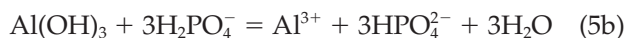
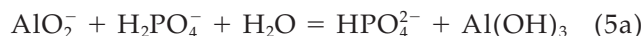
Figure 8 (a) Curves of WA_{P_0} and WA_P versus molar ratio of sodium aluminate ($NaAlO_2$) to potassium dihydrogen phosphate (KH_2PO_4). (b) Curve of hydrogel modulus versus molar ratio of sodium aluminate ($NaAlO_2$) to potassium dihydrogen phosphate (KH_2PO_4).

29 wt % $NaAlO_2$ and 71 wt % KH_2PO_4 increased, while $m_{IS}/m_{SAP} < 0.05$, but decreased gradually while $m_{IS}/m_{SAP} > 0.15$. It was known that inorganic gel had excellent salt resistance so that the salt resistance increased with increasing the amount of inorganic salt. A further increase in the amount of inorganic salt decreased the osmotic pressure difference between the gel and the external solution, and WA_{P_0} and WA_P decreased. Figure 7(b) showed that G decreased monotonously as the amount of inorganic salt increased. This explained that the elasticity modulus of the hydrogel was higher than that of the inorganic hydrogel.

Effect of the molar ratio of sodium aluminate to potassium dihydrogen on WA_{P_0} , WA_P , and G

Figure 8(a) showed that WA_{P_0} and WA_P increased as the amount of $NaAlO_2$ increased, while $n_{H_2O_2}/n_{KH_2PO_4} < 0.67$. When the salt-resistant superabsorbent swelled in physiological saline solution, AlO_2^- interacted with $H_2PO_4^-$ and produced $Al(OH)_3$ according to the following two reactions (a, b). From the reactions, we could see that the smaller the amount of $NaAlO_2$ was, the less $Al(OH)_3$ was produced, and the salt resistance of the superabsorbent decreased, while $n_{NaAlO_2}/n_{KH_2PO_4} < 0.67$. The excessive $NaAlO_2$ interacted with $H_2PO_4^-$ yielded to the ion pair, which

formed an electric double layer, and the electric double layer kept the colloidal particles relatively stable when $n_{\text{NaAlO}_2}/n_{\text{KH}_2\text{PO}_4} = 0.67$. As the molar ratio increased, more antiparticles entered the electric double layer and the stability of the colloidal particles was destroyed so that there existed an optimal range ($0.67 < n_{\text{NaAlO}_2}/n_{\text{KH}_2\text{PO}_4} < 1.1$), in which WA_{P_0} and WA_P had a higher value. Figure 8(b) showed that G decreased monotonously as the amount of NaAlO_2 increased, this mainly due to the increase of $\text{Al}(\text{OH})_3$.



CONCLUSION

Crosslinked sodium polyacrylate after being surface-crosslinked by EGDE and being modified by inorganic salt had excellent salt resistance and hydrogel modulus. The water absorbency first increased with increasing reaction temperature, neutralization degree of acrylic acid, amount of initiator, crosslinking agent, and surface-crosslinking agent, mass ratio of inorganic salt to initial superabsorbent, and molar ratio of sodium aluminate (NaAlO_2) to potassium dihydrogen phosphate (KH_2PO_4) and then decreased continu-

ously. The results indicated two opposite effects of the above-cited reaction conditions.

The hydrogel modulus had the same tendency with water absorbency when it depended on reaction temperature, reaction time, amount of initiator, crosslinking agent, and surface-crosslinking agent, but decreased monotonously with increasing neutralization degree of acrylic acid, mass ratio of inorganic salt to initial superabsorbent, and molar ratio of NaAlO_2 to KH_2PO_4 .

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