

Hydroxyethyl Chitosan-*g*-Poly(acrylic acid-*co*-sodium acrylate) Superabsorbent Polymers

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ABSTRACT: A novel hydroxyethyl chitosan-*g*-poly (acrylic acid-*co*-Sodium Acrylate) (HECTS-*g*-(PAA-*co*-PSA)) superabsorbent polymer was prepared through graft copolymerization of acrylic acid and sodium acrylate onto the chain of hydroxyethyl chitosan. The structure of the polymer was characterized by FTIR. By studying the water absorption of the polymer synthesized under different conditions, the optimal conditions for synthesizing the polymer with the highest swelling ratio was defined. This superabsorbent polymer was further treated by the solvent precipitation method and by the freeze-drying method. We found that the water absorption rate of the treated

polymer was greatly increased and the microstructure of the treated polymer was changed from small pores to loose macro pores. The swelling processes of the polymers before and after modification fit first-order dynamic processes. The amount of the residual acrylic acid was greatly decreased after treatments. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2233–2240, 2010

Key words: hydroxyethyl chitosan; superabsorbent polymer; acrylic acid; water absorption; solvent precipitation; freeze-drying

INTRODUCTION

The superabsorbent polymers are one class of polymer with a network structure and proper degree of crosslinking.¹ They can absorb a large amount of water that is much heavier than their masses. The amount of the absorbed water could range from hundreds of times to thousands of times than its mass. These polymers have been extensively used as absorbents in personal care products, such as infant diapers, feminine hygiene products, and incontinence products. They have also received considerable attention for a variety of more specialized applications including matrices for enzyme immobilization, bioabsorbents in preparative chromatography, materials for agricultural mulches and matrices for controlled release devices.^{2,3}

Natural polymers such as cellulose or starch have been converted into superabsorbent polymers through graft polymerization with vinyl monomer on their chains and proper crosslinking.^{4–7} Chitosan is another important natural polymer with abundant

hydroxyl groups and amino groups. The vinyl monomer can also be graft polymerized on its chain.^{8–10} If the graft polymers are properly cross-linked, superabsorbent polymers with network structure can also be prepared. However, as the water solubility of chitosan is very low and it must be solved in the acidic solvent before the polymerization, the polymer processes involved as complicated and the pH value of the products was also influenced. Hydroxyethyl chitosan, an important non-ionic derivate of chitosan,¹¹ could soluble directly in water. Preparation of a superabsorbent polymer from hydroxyethyl chitosan could simplify the preparation process. But this preparation route has not yet been reported. Here we describe, a novel superabsorbent polymer prepared through graft copolymerization of acrylic acid and sodium acrylate onto the chain of hydroxyethyl chitosan via a simple synthetic route.

For superabsorbent polymers used as medical and sanitation materials, they must have high absorption rate and low residual toxic chemicals. Usually, the porous superabsorbent polymers are prepared by adding chemical reagents to produce bubbles in the polymer.^{12–14} Although the water absorption rate was high in those superabsorbent polymers, toxic chemicals are introduced during this process. In our study, the superabsorbent polymer was modified through two physical methods, the solvent precipitation method and the freeze-drying method, and the

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porous superabsorbent polymers were prepared. The processes of these methods were simple and the results were dramatic. The absorption rate of the polymer was increased greatly, and the amount of residual monomer was decreased markedly. These modification methods are not reported before. They are likely useful in the preparation of high quality superabsorbent polymers.

EXPERIMENTAL

Materials

Chitosan (CTS) was supplied by Zhejiang Yuhuan Biochemical Co. (China). Its deacetylation degree was 76%, determined by the modified alkalimetry method.¹⁵ Its average molecular weight was 1.05×10^6 , determined by the viscosity method.¹⁶ Hydroxyethyl chitosan was synthesized by ourselves according to the method reported by Fang et al.¹⁷ The substitution degree of the hydroxyethyl was 0.78, as estimated by elemental analysis.

Acrylic acid (AA, A.R.) was purchased from Tianjin Chemical Reagent Institute (China) and purified through distillation under reduced pressure before polymerization. Potassium persulfate (KPS, A.R.) was used as the initiator. *N,N'*-methylene diacrylamide (MBAM A.R.) was used as the crosslinking agent. The aqueous solution of 3-(*N*-morpholino)propane-sulfonic acid (MOPS, ultra pure, Amersco, USA) was used as the mobile phase of chromatography. Normal saline of 0.9% (Beijing Double-Crane Pharmaceutical Co., China) was used as the leaching liquid of the superabsorbent polymer. Ethanol, acetic acid, and sodium hydroxide were of analytical grade and used as supplied.

Preparation of HECTS-*g*-(PAA-*co*-PSA) superabsorbent polymer

Hydroxyethyl chitosan (1.8 g) was dissolved in 100 mL deionized water in a triple-necked flask, which was equipped with a stirring apparatus and a reflux condenser. Then the solution was stirred for 30 min and heated with a water bath with the certain temperature (50–75°C) under nitrogen. Then, KPS dissolved in deionized water was slowly added into the flask to initiate the graft polymerization process. The desired quantities of MBAM and acrylic acid made neutral to extent degree by NaOH were added after 30 min. The total volume of water in the system was controlled and the stirring rate was fixed. The reaction was stopped by cooling after the desired reaction time (4–7 h). The product was precipitated by pouring ethanol into the reaction mixture. The precipitate was filtered and thoroughly washed with an ethanol/water mixture (4 : 1, v/v)

several times. Then it was soaked with the ethanol/water mixture (4 : 1, v/v) for 24 h, filtered and dried under vacuum at 70°C.

Treatment of the superabsorbent polymer by the precipitation method

The polymer used for treatment was synthesized by the following reaction conditions: crosslinker content = 0.223%, initiator content = 2.67%, $m_{(AA+SA)}/m_{HECTS}$ = 10.33, Neutralization degree = 35%; reaction time = 5 h, reaction temperature = 60°C.

The polymer (1.0 g) of 80 meshes was added into 100 mL distilled water. It was allowed to swell on the agitator in a water bath at the constant temperature of 30°C for 72 h. The polymer was recovered by precipitation with ethanol. The precipitate was filtered and dried under vacuum at 70°C.

Treatment of the superabsorbent polymer by the freeze-drying method

The polymer (0.20 g) of 80 meshes, which was synthesized at the same conditions as the above section, was added into 15 mL distilled water and allowed to swell on the agitator in a water bath at the constant temperature of 25°C for 48 h. Then it was frozen in the refrigerator of –70°C for 12 h. The frozen sample was freeze-dried on a lyophilizer (FD-1E, Beijing DETIANYOU Technology Development Co., China) under the temperature of –56°C and pressure of 5 Pa.

Structure characterization of the superabsorbent polymer

FTIR spectrum was obtained on a NEXUS-470 series FTIR spectrometer (Nicolet Co., USA). KBr pellets of the samples were used.

The surface structure of the superabsorbent polymer before and after the processing was viewed with a scanning electron microscope (CSM950 series, OPTON Co., Germany). The samples were coated with Au before SEM observation. The effective size of the pore was calculated as the mean diameter of the pores in the sample. At least 30 pores were assessed from different areas of the sample. The values were expressed as the mean \pm standard error.

Test of water absorption capability

The superabsorbent polymer (0.100 g) was weighed and put into a sieve pouch. The pouch was then immersed into distilled water for swelling. The pouch was taken out of the water at different time intervals, had the excess water removed, and weighed. Then the weight of the swollen polymer was calculated by subtracting the weight of the wet

pouch from the total weight. The swelling ratio (Q , g/g) is defined as:

$$Q = (m_2 - m_1)/m_1 \quad (1)$$

Where m_1 is the weight of the dried superabsorbent polymer and m_2 is the weight of the swollen superabsorbent polymer.

To compare the water absorption properties of the products prepared under different conditions, the polymers were swollen in distilled water or normal saline (NaCl 0.9%) for 12 h and the swelling ratio Q_{dw} and Q_{saline} was calculated, respectively.

Determination of the residual acrylic acid

The amount of the residual acrylic acid could be detected by HPLC and have been reported by many literatures.^{18,19} The amount of the residual acrylic acid before and after the treatments were detected through the method of HPLC. The Agilent 1100 series HPLC (Agilent Technologies, USA) equipped with a wavelength adjustable UV detector and the chemical workstation software was used. The column was the DiamonsilTM (Diamond)-C18 (5 μ , 250 mm \times 4.6 mm). MOPS aqueous solution of 0.02M (pH = 5.70) was used as the mobile phase and the flow rate was 0.8 mL/min. The detection wavelength was 210 nm and the injection volume was 20 μ L.

Dried superabsorbent polymer (0.100 g) was accurately weighed and added to 10 mL 0.9% normal saline. The mixture was agitated on an oscillator at the room temperature for 2 h. Then it was filtered with a filter paper. The filtrate liquid was collected and used for HPLC analysis.

According to the opinion of Jamshidi et al.,¹⁸ The acrylic salt is converted to acrylic acid during sampling process for HPLC analysis. So the tested amount of the residual monomer from the extraction liquid of the polymer was the total amount of acrylic acid and sodium acrylate.

RESULTS AND DISCUSSION

Preparation of the HECTS-*g*-(PAA-*co*-PSA) superabsorbent polymer

According to the initiating mechanism proposed by Qiu,^{20,21} persulfate reacted with the derivate of chitosan to generate the radicals on the amino groups of chitosan. The radicals initiated the chain elongation and crosslinking reaction of vinyl monomers, leading to the formation of superabsorbent polymers.

Structure changes of hydroxyethyl chitosan and HECTS-*g*-(PAA-*co*-PSA) superabsorbent polymers

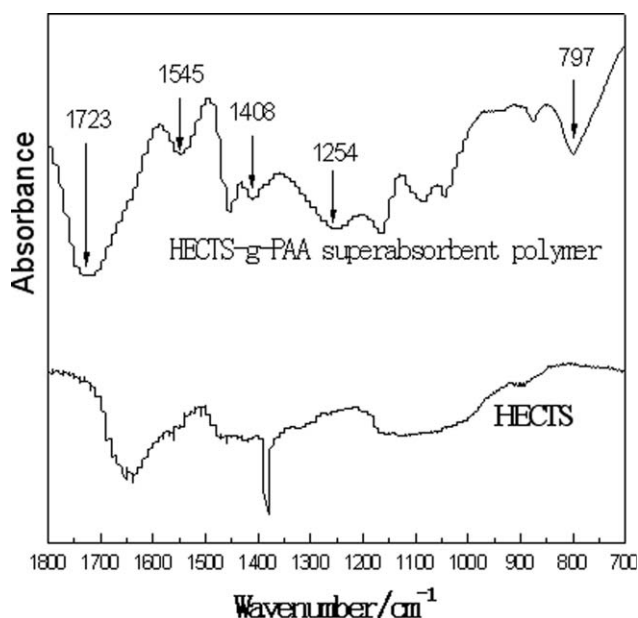


Figure 1 The FTIR spectra of hydroxyethyl chitosan and HECTS-*g*-PAA superabsorbent polymers.

were confirmed by FTIR spectroscopy (Fig. 1). The characteristic strong absorption peak at 1723 cm^{-1} from the stretching vibration of C=O was observed, and it was coincided with the extension vibration of C=O of amide I band. The absorption peak at 1564 cm^{-1} due to the bending vibration of N-H bond of amide II band was overlapped with the peak at 1545 cm^{-1} assigned to the asymmetric extension vibration of COO^- . The peak at 1408 cm^{-1} from the symmetrical stretching vibration of COO^- and the absorption peak at 1254 cm^{-1} from the extension vibration of C-O were increased greatly in the polymers. The absorption band at 889 cm^{-1} from the out-plane bending vibration of N-H of the primary amino group was decreased. When PAA-*co*-PSA branched chain was introduced, the strong absorption peak at 797 cm^{-1} from the planar rocking vibration of C-H of the long chain was observed. It is clear from the spectra that the HECTS-*g*-(PAA-*co*-PSA) superabsorbent polymer had both the characteristic peaks of PAA, PSA and the saccharide unit of hydroxyethyl chitosan, providing evidence of graft polymerization.

Effects of the synthesis conditions on the water absorption properties of the superabsorbent polymers

The structures and water absorption capacities of the superabsorbent polymers are greatly affected by their preparation conditions.^{22,23} In our study, the effects of the synthesis conditions on the water absorption properties of HECTS-*g*-(PAA-*co*-PSA)

superabsorbent polymers were systematically investigated.

Effects of the ratios of the reagents

The effects of the amounts of the crosslinking agent, initiator, monomer, and neutralization degree in the reaction system on the water absorption capacities of the polymers were studied. The results were listed in Table I.

When the crosslinker content was small, the water absorption capacity of the polymer was low, because the crosslinking degree was low and the polymer was partly soluble in the water. With the increase of the amount of MBAM, network structure was formed and the water absorption capacity was increased. Meanwhile, as the monomer and the radical were trapped by the increasing network, the free radicals were less likely to terminate the polymerization process and the branched polymer chain was elongated longer. Therefore, the water absorption capacity of the polymer was increased further. When the crosslinker content was around 0.178%, the water absorption capacity reached the maximum. When the amount of the crosslinking agent was increased further, the water absorption capacity was decreased because the polymer chains were heavily crosslinked and the swelling of the polymer was restricted.

Similarly, the effects of the weight content of the initiator on the water absorption capacity of the prepared polymers were studied with various initiator content. The swelling was low when a small amount of the initiator was used, because the graft polymerization was not efficient. With the increase of the amount of KPS, the reaction rate was enhanced and the number of radicals generated on the chain of chitosan was increased. The three dimensional network was formed extensively and the water absorption capacity of the polymer was increased. However, when the initiator content was too high, the number of radicals generated on the chain of hydroxyethyl chitosan was so high that the molecular weight of the branched chain was low. The formed network was not extensive enough to hold water efficiently. When initiator content was around 2.67%, the water absorption capacity of the polymer was at the highest.

The effects of the amount of the monomer were investigated with various mass ratios of AA and SA to HECTS. When $m_{(AA+SA)}/m_{HECTS}$ was less than 8.61, the water absorption capacity of the polymer was increased with the increase of the ratio. This trend could be explained by the fact that when the ratio of $m_{(AA+SA)}$ to m_{HECTS} was increased, there were more acrylic acid that could be polymerized and polymerization was more sufficient. The

TABLE I
Effects of the Ratios of Reagents on the Water Absorption Capacities of the Polymer

Crosslinker content (wt %)	Initiator content (wt %)	$m_{(AA+SA)}/m_{HECTS}$	Neutralization degree (%)	Q_{dw} (g/g)	Q_{saline} (g/g)
0.000	2.67	10.33	35	92.1	10.6
0.045	2.67	10.33	35	274.6	25.5
0.089	2.67	10.33	35	348.1	29.9
0.134	2.67	10.33	35	389.0	36.6
0.178	2.67	10.33	35	609.2	58.0
0.223	2.67	10.33	35	512.3	51.2
0.267	2.67	10.33	35	291.2	36.5
0.178	1.79	10.33	35	286.9	28.2
0.178	2.23	10.33	35	336.8	34.4
0.178	2.67	10.33	35	609.2	58.0
0.178	3.11	10.33	35	495.5	54.2
0.178	3.54	10.33	35	387.0	37.5
0.178	3.94	10.33	35	304.7	31.5
0.178	2.67	5.17	35	174.2	22.8
0.178	2.67	6.88	35	488.6	47.3
0.178	2.67	8.61	35	692.2	65.9
0.178	2.67	10.33	35	609.2	58.0
0.178	2.67	12.05	35	479.9	48.2
0.178	2.67	13.75	35	415.6	42.5
0.178	2.67	10.33	20	261.5	26.3
0.178	2.67	10.33	25	329.8	32.6
0.178	2.67	10.33	30	430.6	45.4
0.178	2.67	10.33	35	609.2	58.0
0.178	2.67	10.33	40	521.7	52.3
0.178	2.67	10.33	45	470.1	45.1

Other reaction conditions: reaction time = 5.0 h, reaction temperature = 60°C.

increased content of the carboxyl groups also increased the water absorption capacity of the polymer. However, the water absorption of the polymer was decreased with the increase of the mass ratio when the ratio was higher than 8.61. Under high ratio of $m_{(AA+SA)}$ to m_{HECTS} , the branched polymer chains were longer and the tangle effect of the branched chains were enhanced, and crosslinking degree of the network may be increased and the water absorbing capacity of the polymer were decreased. The swelling ratio reached the maximum when $m_{(AA+SA)}/m_{HECTS}$ was around 8.61.

The effects of neutralization degree of acrylic acid on the water absorption capacity of the polymer were also studied. Table I shows that when the degree of neutralization of acrylic acid was around 35%, the water absorbency of the polymer reached a maximum value. At lower degree of neutralization, the dissociation of AA is very weak, The content of the PSA segments was low and the anion-anion repulsive forces between the polymer chains are eliminated and the water absorbency of the polymer is thus decreased. If the degree of neutralization is increased, the content of $-\text{COONa}$ groups is increased and the difference in osmotic pressure

between the inside and outside of the network is increased and the swelling ratio of the polymer is enhanced. However, at a higher neutralization degree of AA and high content of SA, reduced swelling is observed, because of various reasons. The charge-screening effects of excess Na⁺ ions shield the carboxylate anions on the chains of (PAA-*co*-PSA) and inhibit effective anion-anion repulsive forces. Furthermore, with increase of the NaOH concentration, the ionic strength of the swollen solution is increased. As a result, the osmotic pressure of the gel phases is reduced and the swelling ratio is consequently decreased.

Effect of reaction time and temperature

The effect of reaction time from 4 to 7 h on the water absorption capacity of the synthesized polymer was studied. As summarized in Table II, the water absorption capacity of the polymer was increased with the increase of reaction time at first. It reached the maximum at about 5 h and started to decrease with the further increase of reaction time. It is likely that when the reaction time was short, the three dimensional network of the polymer did not formed maturely. Therefore, the water absorption capacity was low. The complete three dimensional network of the polymer was formed with the increase of reaction time and the synthesized polymer had higher water absorbing capacity. However, when the reaction time was too long, the length of the PAA-*co*-PSA chain was increased and the chains were cross-linked more extensively. There was less flexibility to expand when water entered the polymer; therefore the water absorption capacity of the polymer was decreased.

The water absorbing capacity of the polymer was also affected by the reaction temperature. As shown in Table II, when the temperature was lower than 60°C, the swelling was increased with the increase of reaction temperature. However, the water absorption capacity was decreased when the temperature was increased further. For the radical polymerization reaction, the reaction rate was influenced greatly by the generation rate of the initiator, which was affected by the reaction temperature. When the reaction temperature was low, the generation rate of the initiator was low and the number of radicals formed was small. As a consequence, the polymerization reaction was slow and the crosslinking was not efficient. The resulting polymer was partly soluble in water and the water absorbing capacity was low. When the temperature was raised, the polymerization and crosslinking reaction was more efficient and the network with a proper degree of crosslinking was formed. As a result, the absorption capacity of the polymer was improved. However, when the

TABLE II
Effects of the Reaction Time and Temperature on the Water Absorption Capacities of the Polymer

Temperature (°C)	Time (h)	Q _{dw} (g/g)	Q _{saline} (g/g)
60	4.0	316.3	30.8
60	4.5	432.0	46.6
60	5.0	609.2	58.0
60	5.5	560.5	53.8
60	6.0	501.8	48.6
60	6.5	463.2	46.7
60	7.0	410.9	42.3
50	5.0	232.0	25.2
55	5.0	469.7	49.5
60	5.0	609.2	58.0
65	5.0	515.6	51.6
70	5.0	338.5	41.6
75	5.0	281.6	32.9

Other reaction conditions: Crosslinker content = 0.178%, initiator content = 2.67%, $m_{(AA+SA)}/m_{HECTS} = 10.33$, Neutralization degree = 35%.

temperature was higher than 60°C, the generation rate of the initiator was so high that the polymerization was very fast. A network with high degree of crosslinking was formed at the early stage of polymerization. The rigid network limited the expansion of the polymer when water was absorbed, and the absorption capacity was decreased. The maximum water absorbing capacity was obtained when the polymer was synthesized at 60°C.

Studies of the water absorbing properties of the treated polymers

Effect of the treatments on the water absorption rate of the polymers

The water absorption rates of the polymers were increased greatly after further treatments by solvent precipitation and lyophilization. As the swelling rate is extremely affected by the sample particle size, the swelling kinetics tests had to be conducted by employing samples with the same particle size and the particle size used for test was from 80 to 100 mesh size.

It can be seen from Figure 2 that it took about 40 min to reach the steady state of absorption before treatments. For the polymer treated with solvent precipitation method, the water absorption rate reached steady state in 20 min. For the polymer treated with the freeze-drying method, it took about 15 min to reach the steady water absorption rate. The freeze-drying method promoted the swelling velocity of the polymer more remarkably than the solvent precipitation method.

On the assumption that the swelling of the polymer fits a first-order process,²⁴ the swelling rate at a given temperature is:

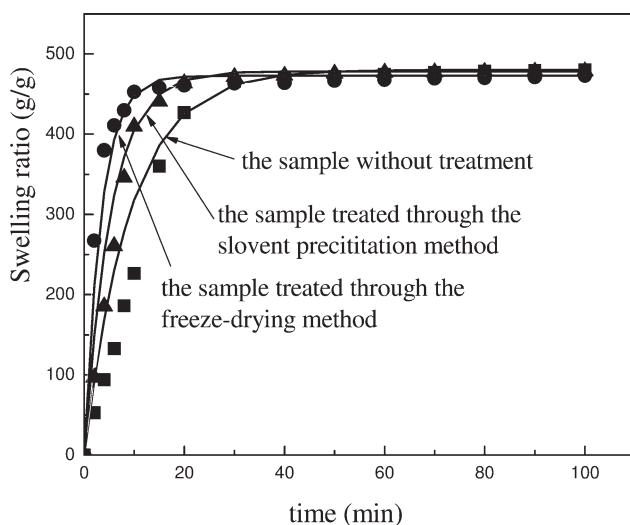


Figure 2 Water absorption rates before and after treatments.

$$dQ_t/dt = k(Q_e - Q_t) \quad (2)$$

Where t is the swelling time, Q_t is the swelling ratio at that time, Q_e is the equilibrium swelling ratio. eq. (1) is integrated to:

$$\int_{Q_0}^{Q_t} dQ_t/(Q_e - Q_t) = \int_0^t k dt \quad (3)$$

the result is:

$$\ln[(Q_e - Q_0)/(Q_e - Q_t)] = kt \quad (4)$$

then the following equation is gained:

$$Q_t = Q_e - (Q_e - Q_0)/e^{kt} \quad (5)$$

The curve between $\ln[(Q_e - Q_0)/(Q_e - Q_t)]$ and t (the diagonal part of the water absorption curve) was drawn, and the slope was the swelling rate constant (k). The k value of the sample that was not treated was 0.109; the k values were 0.188 and 0.296 for the samples treated with the solvent precipitation method and freeze-drying method, respectively. The k values also indicated that the water absorption rates of the polymer were increased dramatically after treatments. The theoretical swelling curves of the polymer were obtained by introducing the k values into eq. (5) (the solid line in Fig. 2). The results of theoretical calculation and experiment data agreed well, indicating that the assumption of a first-order process was valid.

The microstructures of the polymers before and after treatments were examined by SEM (Fig. 3). The SEM photographs showed that the microstructures

of the polymer were changed from small pores to loose macro pores in the polymers underwent treatments. The mean pore size of the polymer before treatments was $6.3 \pm 2.5 \mu\text{m}$. It was increased to $21.5 \pm 7.7 \mu\text{m}$ for the solvent precipitation treated polymer, and $18.9 \pm 5.9 \mu\text{m}$ for the freeze-drying treated polymer. At the first step of the solvent precipitation method, the polymer was extensively swollen in water. When the organic solvent that is miscible with water was added, water was replaced from the network by the organic solvent. During this displacement process, the polymer retained its expanded porous structure. In addition, the organic solvent left in the precipitated polymer was easily removed by vacuum drying, and the porous structure remained. During the freeze-drying treatment, the water in the polymer was evaporated at low temperature and the structures of macro pores were largely maintained.

With the increase of the mean pore size, the specific surface area of the polymer is increased greatly. The Na^+ ions move to the outside of the polymer more easily, and the hydrophilic $-\text{COO}^-$ groups attract more water molecules. Therefore, the water absorption rate of the polymer was enhanced greatly. Moreover, the distance between the polymer chains was increased and the contractibility of the polymer was decreased, leading to ultimate increase in the water absorption rate.

During the process of the freeze-drying treatment, the water was evaporated gradually from the inner of the polymer. The network structure was shrunked in a certain extent because the rate of water evaporation was slow. As a result, the increase of the meaning pore size was moderate. However, absorption rate of the freeze-dried sample is higher than that treated with solvent precipitation method. It was found that the sample prepared from freeze-drying treatment was crisp, so that it is probably grounded intensively produced a considerable fraction of very low sized particles and the water absorption rate was increased.

Effects of the treatments on the amount of the residual acrylic acid monomer

The standard calibration curve between the concentration of acrylic acid and the area of the chromatographic peak was generated by analyzing a series of acrylic acid aqueous solutions at 20, 10, 5, 2, 1, 0.5, 0.2, 0.1, 0.05 $\mu\text{g}/\text{mL}$ by HPLC. The relationship between them was expressed as:

$$y = 24.62057 + 152.87579 x \quad (6)$$

where y is the area of the chromatographic peak, x is the concentration ($\mu\text{g}/\text{mL}$) of the acrylic acid, and $R = 0.99981$.

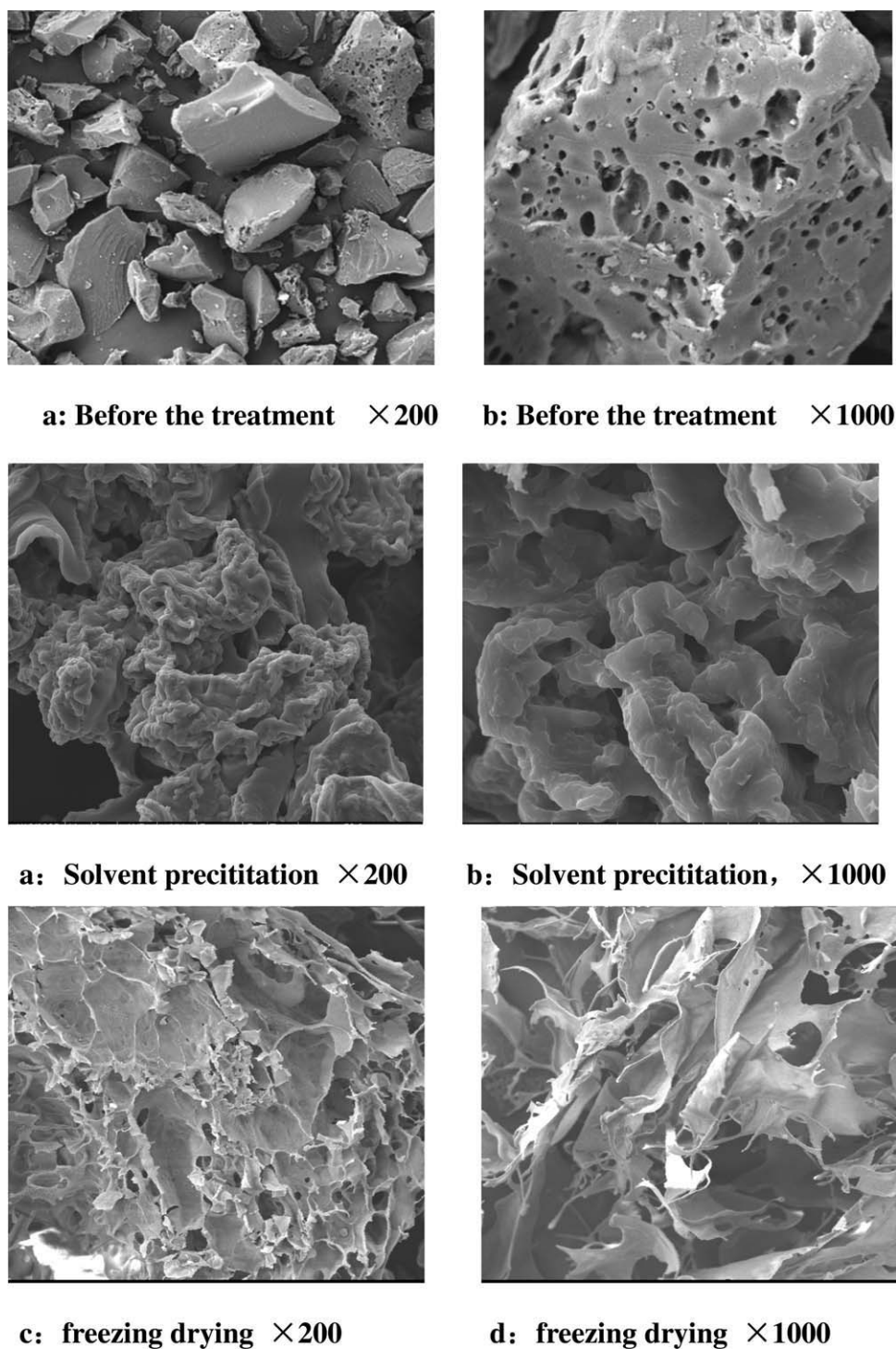


Figure 3 SEM pictures of the products modified through different methods.

Because of the special network structure of the superabsorbent polymers, acrylic acid monomers are easily trapped inside the polymer. To be used as medical materials and sanitarian materials, the amount of the residual monomer must be kept as low as possible (<300 ppm for sanitary napkins¹⁸). We used solvent precipitation and freeze-drying to remove and HPLC to detect the residue acrylic acid.

It was found that the amount of the residual acrylic acid was decreased markedly after treatments with the solvent precipitation method (the amount was decreased from 62.5 to 12.7 ppm). This dramatic decrease was because, during the process of treatment, the network of the polymer was swollen fully and the residual hydrophilic acrylic acid monomer was diffused from the network to the water.

Moreover, because a large excess of water was added to swell the polymer, even after organic solvent precipitation, few monomers were trapped in the polymer. During the process of the freeze-drying method, acrylic acid was evaporated with water together. The amount of the residual acrylic acid was also decreased greatly (decreased to 38.7 ppm). But during the process of freeze-drying, some of the acrylic acid was hard to be removed because of the strong interaction of residual acrylic acid with the amino group of the chitosan. As a result, the removal of the residual monomer was limited.

In fact, the detected amount of residual acrylic acid was the amount of the monomer that was leached into the normal saline. When the samples were contacted with the normal saline, the mesh of the sample unmodified was so small that the acrylic acid was not easy to be leached, however, the residual monomer in the modified samples was very easy to be penetrated from the network to the normal saline as the formation of the macro pores, so the detected value of the unmodified sample was on the low side. It can be considered that the amount of the residual acrylic acid was decreased greatly for all of two modification methods.

CONCLUSION

A novel HECTS-*g*-(PAA-*co*-PSA) superabsorbent polymer was prepared and the structure was characterized by FTIR. By studying the water absorption of the polymers synthesized under different conditions, we found that the optimal conditions to synthesize the polymer with the highest water absorbing capacity was as follows: $m_{(AA+SA)}/m_{HECTS}$ was around 8.61; the weight content of the initiator and the crosslinker was 2.67% and 0.178%, respectively; the neutralization degree of acrylic acid was around 35%; the reaction temperature was 60°C and the reaction time was 5.0 h. The polymer (1 g) synthesized under these conditions absorbed over 710 g distilled water, over 67 g normal saline, over 61 g artificial blood and over 58 g artificial urine. The sol content of the polymer synthesized under these conditions was lower (0.003 g/g).

The superabsorbent polymer was further treated with the solvent precipitation method and the freeze-drying method. After the treatments, the microstructure of the polymer was changed from the small pores to the loose macro pores and the pore structures were characterized by SEM images. The

water absorption rate of the polymer was increased greatly and it was found that the freeze-drying method promoted the swelling velocity of the polymer more remarkably than the solvent precipitation method. The water absorption process of the polymers with and without treatments fit a first-order dynamic process. The amount of the residual acrylic acid was decreased from 62.5 ppm for the polymer without treatment to 12.7 ppm for the polymer treated through the solvent precipitation method and 38.7 ppm for the polymer treated through the freeze-drying method, which were detected through the HPLC method.

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