

# Synthesis and Characterization of Superabsorbent Hydrogels Composites Based on Polysuccinimide

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**ABSTRACT:** A kind of novel superabsorbent hydrogel with high swelling ratio property that could be used for the development of water absorbing resin, soil water retention agent, and chemical sand-fixing material was synthesized in this study. The hydrogels were prepared by the crosslinking reaction of polysuccinimide (PSI). The relationships between swelling ratio and volume of solvent as well as the concentration of crosslinking agent were investigated in detail. Several composites, such as starch, carrageenan, and polyacrylamide, were added into hydrogels to enhance the swelling ratio. It was found that the swelling ratio was significantly increased, which the maximum water absorbency was enhanced 2.46 times when the composite polyacrylamide (PAM) was added compared to the control. The effects of ionic strength and sensitivity of pH on hydrogels

were also studied. The modified hydrogels products with swelling ratio less sensitivity to the salinity as well as relative high swelling ration in salinity system were also obtained by adding PAM. Through the Fourier transform infrared spectroscopy (FTIR) characterizations, the crosslinking reaction mechanism and the structure of composite were proposed. In addition, the transmission electron microscopy (TEM) examinations showed that some composite materials elevated the physical crosslinked and connected channels density substantially. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 550–557, 2006

**Key words:** superabsorbent hydrogels; polysuccinimide; composites; water absorbing resin

## INTRODUCTION

Superabsorbent hydrogels are crosslinked hydrophilic polymers, which could absorb, swell, and retain aqueous solutions up to hundreds of times of their own weight. These materials, first originated in the United States as water retention agents in agriculture, were developed in Japan in the mid 1970s in applications of personal care and hygienic products (disposable diapers, sanitary napkins, surgical pads, etc.).<sup>1</sup> These materials are formed from water-soluble polymers by crosslinking reaction either using radiation or a crosslinking agent.<sup>2</sup> Because of their excellent characteristics, these superabsorbents have raised considerable interests, which have been widely used in areas

such as drug delivery, immobilization of enzymes, dewatering of protein solutions, solute separation, baby diapers, soil for agriculture and horticulture, water-blocking tapes, absorbent pads, and numerous other applications.<sup>3–5</sup>

The desired features of superabsorbents are (a) high swelling capacity, (b) high swelling rate, and (c) excellent gel strength. Conventional hydrogels, such as synthesized by starch or acrylic acid, have some drawbacks including either very low swelling capacity and swelling rate in salinity solution or need several hours to reach to the maximum absorption capacity.<sup>6</sup> Majority of the reported superabsorbents comprise only the first feature mentioned, i.e., high absorbency,<sup>7</sup> whereas they must also comprise high rate of swelling especially in certain applications, e.g., in the absorbents incorporated in the baby napkins. A kind of superabsorbent polymer named superporous hydrogel has been developed in recent years by Park for controlled delivery of drugs.<sup>8–10</sup> Other researchers have recently extended the hydrogels applications for designing other drug delivery systems.<sup>11,12</sup> So, creation of porosity in hydrogels is very important in many applications.

Some of these superabsorbent hydrogels have been commercialized for a long time, but there would appear to be considerable scopes for gaining more insight knowledge. So far, although sufficient data on

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relationships between these swelling characteristics and molecular structure<sup>13</sup> are available in the literature, relatively little in-depth examinations of the influence of salinity medium on swelling properties are available. Specifically, few experiments have been carried out to evaluate and improve swelling ratio in high ionic strength solution. So this study was to focus on these issues. In this study, highly porous superabsorbent hydrogels were synthesized from PSI through solution polymerization at 40°C under normal atmospheric conditions. The experiment reported here was an exploratory investigation of the influence of solvent volume and crosslinking agent concentration on the capacity for absorbing water of polyaspartic acid (PASP) hydrogels. For the higher swelling ratio and hydrogels strength, some researches were carried out by adding different composites into PASP hydrogels. We found that some composite-modified hydrogels' swelling ratio still relative high compared to the control in salt solution and hydrogels strength were considerable increased as well. The modified hydrogels, which possessed of optimum swelling ratio value, was chose to investigate the influence of ionic strength and pH value on swelling ratio. Infrared (IR) spectrum and transmission electron microscopy were used to explain the mechanisms in detail.

## EXPERIMENTAL

### Materials

L-Aspartic acid was obtained from Changmao Biochemical Engineering Limited Company, China. *N,N*-Dimethylformamide (DMF) as solvent was obtained from Beijing LiYi Fined Chemical Limited Company and 1,6-hexamethylene diamine used for crosslinking agent was purchased from Shanghai Reagent Factory. The concentration of sodium hydroxide solution was adjusted to 27% (wt %).

### Preparation of PSI and PASP

#### Preparation of PSI

PSI with molecular weight of  $1.76 \times 10^5$  synthesized by thermal polycondensation of maleic acid was synthesized by following method: 2 kg of L-aspartic acid powder and 1.474 kg of 85% phosphoric acid were fed to a kneader (Jiangsu Rugao Tengfei Machinery Co., Ltd., China) with capacity of 5 L, and the reaction was carried out 4.5 h at 200°C under a vacuum of 0.09 MPa. The product was washed several times with methanol and water until it was neutral and then dried at 85°C under a vacuum of 0.095 MPa. Finally, the yellowish powder of PSI product was obtained.

#### Preparation of PASP

The PASP hydrogels were synthesized in two steps: in the first step, the polymer PSI was crosslinked (as

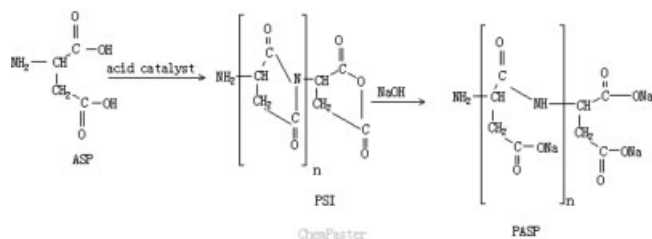


Figure 1 Preparation of PSI and PASP.

shown in Fig. 1) in the presence of the crosslinking agent and then the crosslinked PSI was hydrolyzed in the alkaline system. The detailed process was as follows: 1.000 g solidity PSI and 28 mL solvent (*N,N*-Dimethylformamide) were placed in a 250 mL beaker at room temperature (25°C) for 2 days standing time until all solidity completely dissolved. Then, 8 mL deionized water was added into the beaker and it was placed in a receptacle that was preset at the desired temperature (40°C) with constant magnetic stirring (400 rpm) for 0.5 h. Then, certain amount of crosslinking agent was added into the beaker. The first part of the reaction was carried out for 1 h, and then about 150-mL ethanol solution was added. After decanting the supernatant ethanol, the product was spread out in a tray and dried in an air-circulating oven at 60°C to a constant weight.

The dried product was powdered with a hammer-type grinder into powder. About 25 mL of 50% ethanol solution (v/v) was added to the beaker after the powder was put in. Similarly, the beaker was placed into the same receptacle that was preset at the desired temperature (40°C) and constant magnetic stirring was used (400 rpm). Some drops of sodium hydroxide solution (27%, wt %) were added to the mixture at every 30 min to adjust pH between 8 and 9 for hydrolyzation. Slowly, transparent gels appeared and the amount of crosslinked solid PSI decreased in the reactor at the same time. Finally, the solid completely dissolved and the amount of gels became the maximum; the beaker was then taken out from the receptacle and about 100 mL of ethanol was added into the beaker. The precipitate was spread out in the tray and dried in the air-circulating oven at 60°C to a constant weight. Finally, the product was stored in an airtight bag after grinding to powder.

### Preparation of composite-modified superabsorbent hydrogel

We took two different methods to synthesize composite-modified superabsorbent hydrogels for enhancing the product's swelling ratio in salt solution and various pH solutions. The detail process was described as follows:

S1: 1.000 g PSI and 32 mL DMF were added into a 250-mL open beaker for 2 days standing time until all solidity completely dissolved at room temperature. Then, 8 mL deionized water was added into the beaker. Then, the beaker was placed in a receptacle that was preset at desired temperature (40°C) and constant magnetic stirring was used (400 rpm) for 0.5 h. After that, certain amount of crosslinking agent (0.0333 mol/L) and some amount of composites (the weight range from 0.2 to 1.0 g) were added to the reactor together. The reaction was stopped 1 h later, the following process were the same before (2.2).

S2: the difference between S2 and S1 was that in S2 serial composites were added before crosslinked PSI began to be hydrolyzed.

### Swelling ratio studies

The dry superabsorbent hydrogels sample (0.200 g) was placed in a fabric bag and the bag was allowed to hydrate in excess deionized water or buffer solutions at 25°C. The weight of the hydrating sample was measured at time intervals after the residual water was removed carefully and hanging up for 15 min. The swelling ratio ( $Q$ ) was defined as:

$$Q = (W_s - W_d) / W_d$$

where  $W_s$  is the weight of the swollen superabsorbent hydrogels, and  $W_d$  is the weight of the dried superabsorbent hydrogels.

### Ionic strength-sensitivity of hydrogels

The effect of ionic strength on swelling ratio was investigated in various saline solutions. Certain amount of salt was added to maintain the solution concentration of 0.01 mol/L at 25°C. The equilibrium swelling ratio was obtained when the constant weight reached.

### pH-sensitivity hydrogels

The dried hydrogels samples were immersed in desired buffers of various pH (2–13) at 25°C. The swelling measurements were carried out at time intervals until a constant weight was reached for each sample.

### TEM analysis

The micrographs of hydrogels were studied using transmission electron microscopy (TEM) to characterize the physical crosslinked density and connected channels. The samples were vacuum dried then coated with gold–palladium and examined in the TEM (HITACHI H800).

**TABLE I**  
Influence of Concentration of Crosslinking Agent on the Swelling Ratio

Concentration of crosslinking agent (mol/L)	Molar ratio of crosslinking agent/monomer	Equilibrium swelling ratio (g/g)
0.0293	144.6	282
0.0313	154.1	341
0.0333	163.7	414
0.0352	177.3	277
0.0372	182.9	184
0.0391	192.5	138

The volume of solvent was chosen at 28 mL/g PSI.

### FTIR analysis

The chemical structures of hydrogels were investigated by using Fourier transform infrared spectroscopy (FTIR). The samples were vacuum-dried and dispersed in KBr. The spectra of the samples were taken at 4000–500  $\text{cm}^{-1}$  wavelength with FTIR-60SXB.

## RESULTS AND DISCUSSION

### Influence of crosslinking agent on the water absorbency of superabsorbent hydrogels

The concentration of crosslinking agent is an important factor affecting absorption properties of the superabsorbent hydrogels. The role of crosslinking agent is to connect single monomer molecule, so the higher concentration of crosslinking agent, the higher crosslinking density with the decrease of space between the compound chains. The effect of crosslinking agent on product was studied by changing the concentration of crosslinking agent between 0.0293 and 0.0391 mol/L while the volume of solvent was chosen at 28 mL/g PSI.

From Table I, the swelling ratio of hydrogels increases with increasing of concentration of crosslinking agent from 0.0293 to 0.0333 mol/L and decreased again with further increasing of crosslinking agent concentration. The hydrogels synthesized under the concentration of crosslinking agent of 0.0333 mol/L has the optimum swelling properties. The swelling process is caused by repulsion of hydrophilic groups inside the network and osmotic pressure difference between inside of hydrogels and the external solution. The swelling ratio also decreases with increase in the crosslinking agent concentration because the network space became diminishes, and leads to less water to enter into hydrogels. At the same time, the gel strength decreases with decrease in concentration of crosslinker agent. This phenomenon explains that the lower concentration of crosslinking agent, the bigger network space in hydrogels and the hydrogels network strength declines, so it is easier to be broken

**TABLE II**  
**Influence of Volume of Solvent on the Swelling Ratio**

Volume of solvent (mL)	Equilibrium swelling ratio (g/g)
20	186
24	235
28	414
32	323
36	288
40	253

The concentration of crosslinking agent was 0.0333 mol/L.

under outside osmosis pressure. So the initial improvement in the swelling ratio could attribute to the increase in the crosslinking agent concentration: smaller network leads to bigger inside osmosis, so the osmosis difference between outside and inside hydrogels is bigger. However, after the concentration of crosslinking agent exceeds 0.0333 mol/L, the porous size dominates the swelling process, so the network space becomes too small and to hold more water, leading to the decreasing swelling ratio.

#### Influence of solvent on the water absorbency of superabsorbent hydrogels

To study the effect of the volume of solvent (DMF) on the swelling ratio, we designed the following experiments: 1.000 g PSI was added into a 250-mL open beaker, and the volume of solvent ranged from 20 to 40 mL while the concentration of crosslinking agent was 0.0333 mol/L. The results are shown in Table II.

Polymer molecules spread around in the solvent after PSI solids dissolve. When the crosslinking agent is presented in the reaction system, it plays the role of associating monomer molecules. Consequently, when

the volume of solvent is optimized, the molecules could spread fully, the appropriate network space could obtain and the most amount of water could enter the resin. On the other hand, if the amount of solvent was in excessive or inadequate, the network space between monomers either too big or too small that the hydrogels could not retain water to its utmost capacity. As is shown in Table II, the swelling ratio changes with the volume of solvent and the maximum water absorbency of the hydrogels product is found to be 414 g/g when the solvent volume is 28 mL/g PSI. For solvent volume increased from 20 to 28 mL/g PSI, the swelling ratio increased from 186 to 414 g/g. Then, the swelling ratio value decreased to 253 g/g with the volume of solvent further increased to 40 mL/g PSI.

#### Influence of composites on the water absorbency of superabsorbent

It could be seen that in S1 serial, the composite carrageenan enhanced the swelling ratio remarkably (Table III). The maximal value is found up to be 280 g/g, which is more than two times than the product without carrageenan. In serial S2, the composite starch also enhances the swelling ratio from 372 to 547 g/g. Especially, the composite polyacrylamide almost enhances the swelling ratio almost 2.5 times from 345 to 848 g/g. Other composites don't boost the value evidently that the detail reasons need further research.

#### Influence of ionic strength and salt solution on water absorbency of composite superabsorbent

Effect of ionic strength

It could be observed that the hydrogels modified by polyacrylamide has the optimum swelling ratio (848

**TABLE III**  
**Equilibrium Swelling Ratio (g/g) of Composite-Modified Hydrogels**

	Composite weight (g)					
	Control	0.2	0.4	0.6	0.8	1.0
S1 series (composite category)						
Starch	320	215	124	200	154	202
Ethyl cellulose	201	334	154	152	114	181
Carrageenan	128	272	130	200	280	264
Polyacrylamide	466	320	540	250	262	393
$\beta$ -cyclodextrin	334	271	300	275	230	340
Carboxymethyl cellulose	365	338	390	354	155	287
S2 series (composite category)						
Starch	372	547	196	261	262	132
Ethyl cellulose	299	376	266	331	318	180
Carrageenan	400	241	123	129	118	105
Polyacrylamide	345	608	685	848	430	475
$\beta$ -cyclodextrin	263	123	230	79	256	258
Carboxymethyl cellulose	370	407	340	372	375	210

The concentration of crosslinking agent was 0.0333 mol/L and the volume of solvent was 32 mL/g PSI.



**TABLE IV**  
Swelling Ratio of the Synthesized Polyacrylamide Modified Hydrogels in Saline Solution (0.01 mol/L)

Solution medium	Equilibrium swelling ratio (g/g)
NaCl	575 (35)
KCl	434 (33)
NH <sub>4</sub> Cl	204 (38)
CaCl <sub>2</sub>	102 (2)
(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	506 (18)
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	527 (39)
MgSO <sub>4</sub>	86 (9)
Cu(NO <sub>3</sub> ) <sub>2</sub>	14 (15)
KH <sub>2</sub> PO <sub>4</sub>	763 (77)
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	26 (2)
H <sub>2</sub> NCONH <sub>2</sub>	794 (222)
NH <sub>3</sub> · H <sub>2</sub> O	799 (56)

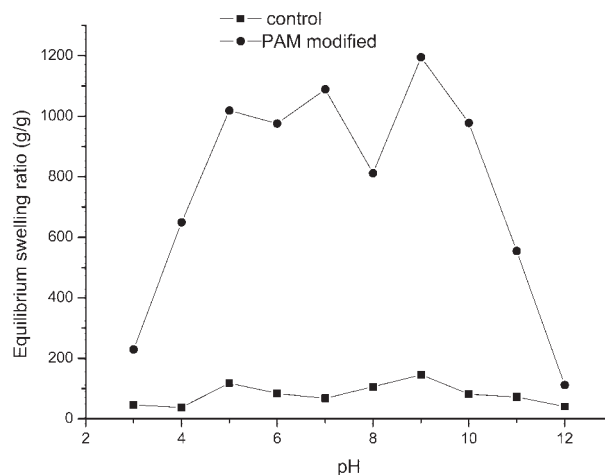
The data inside parentheses represent the swelling ratio of the unmodified hydrogels in each different saline solution.

g/g, Table III), hence in this series of experiments, the composite gels modified by polyacrylamide was chosen to determine the effect of ionic strength on the gel's swelling ratio in 0.01 mol/L saline solution. The swelling ratio data measured in these solutions are given in Table IV. It could be found that the swelling ratio in univalent cation solution is generally higher than in bivalent cation solution and there is almost no any influence in organic solution. The effect of ionic strength on swelling gel could be explained that the charge screening effect of cation leads to the reduction of osmotic pressure, so that the driving force between the gel and the aqueous phase decreases consequently; the increasing of electrostatic attraction between anionic sites of crosslinked chains and multivalent cations (Mg<sup>2+</sup>, Cu<sup>2+</sup>, and Ca<sup>2+</sup>) also leads to decrease in swelling ratio. Owing to composite-modified hydrogels excellent antiion interferential ability, the swelling ratio in the saline solution remarkably exceeds that of the control, except for copper nitrate. The reasons in detail needed further investigation.

The data in the bracket is the swelling ratio of the unmodified hydrogels in each different saline solution.

#### Effect of pH sensitivity

A number of factors influencing the swelling ratio of ionic hydrogels include the property of gels and swelling medium. The results of pH-dependent equilibrium swelling ratio performed in the buffer solutions between 2 and 10 are shown in Figure 2. The products were the same as in the part of 3.4.1. The swelling ratio is relatively higher when the solution pH value being around at 7 and the maximum appeared when the pH at 9. When we measured the solutions' pH after experiment, which lasted for 24 h, it was surprising to



**Figure 2** Swelling ratio in different pH solution range from 3 to 12 under the preparation condition of the weight of polyacrylamide/polysuccinimide was 3/5, the concentration of crosslinking agent was 0.0333 mol/L, and the volume of solvent was 32 mL/g PSI.

find that while the initial solutions' pH ranged 4 from 10, the final solutions' pH closed to 7. This result indicates that the hydrogels could regulate solution pH and have excellent buffer action, so it greatly suits to practical applications (Table V). We also notice a phenomenon that there is three maximum when the solution pH ranged from 3 to 12. It could be explained as follows: the polyacrylamide used in this study is cation polymer while the PASP hydrogels synthesized by PSI is amphoteric hydrogels. When the amphoteric polyacrylamide-modified hydrogels swell in acidic or alkaline solution, the hydrogels could neutralize some H<sup>+</sup> or OH<sup>-</sup> to reduce the ionic effect. During the swelling process, the charge groups on the hydrogels are first ionized. Then, the surface swells due to the electrostatic repulsion between adjacent ionized groups. The dissociation of hydrogel networks may be enhanced as ionic strength increases up to a fixed

**TABLE V**  
Change of Solution pH Before and After Experiment

Initial solution pH	Terminal solution pH
3	3.82
4	5.93
5	6.18
6	6.39
7	6.51
8	6.49
9	6.6
10	6.7
11	10.27
12	11.78

The weight of polyacrylamide / polysuccinimide was 3/5, the concentration of cross-linking agent was 0.0333 mol/L, and the volume of solvent was 32 mL/g PSI.

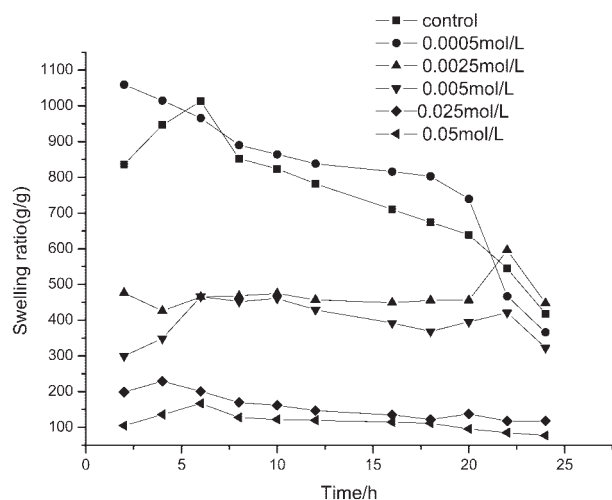
value; however, with ionic strength continuously increasing, the anionic groups on the hydrogels are screened by outside ions. So the swelling ratio decreases with the further increasing ionic strength. Thus, the polyacrylamide-modified hydrogels showed maximal swelling ratio in the solution when the pH value at 5, 7, and 9 while the control presented only two maximum (Fig. 2). Therefore, using polyacrylamide as a composite material could add new useful functions and leads to superabsorbent hydrogels with high swelling ratio and stability in strong ionic strength solution.

#### Effect of salt solution

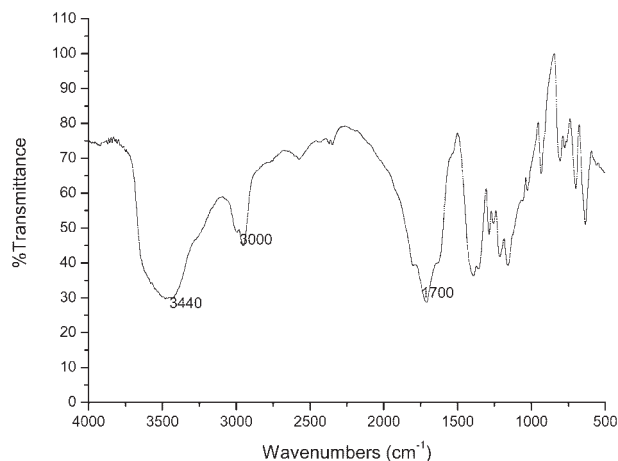
To investigate the effect of saline solution on hydrogels swelling ratio, the equilibrium swelling ratio was measured in 0.0005, 0.0025, 0.005, 0.025, and 0.05 mol/L NaCl solution of the hydrogels, which the same as in the part of 3.4.1. It could be seen that when the salt solution concentration exceeds 0.005 mol/L, the swelling ratio decreases dramatically comparing with the control (Fig. 3). This undesired swelling ratio decrease is attributing to the charge screening effect of the cations, resulted in the reduction of osmotic pressure difference between inside and outside of hydrogels as mentioned earlier.

#### Spectral characterization

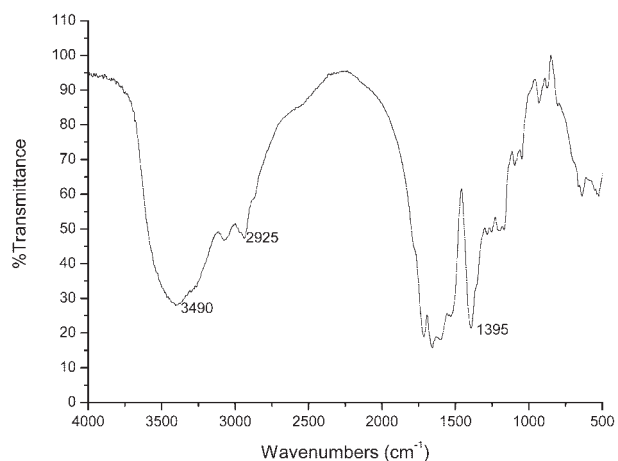
The copolymerization is confirmed by comparing the FTIR spectra of the polyaspartic acid with that of grafted product. The infrared (IR) spectra of polymer polysuccinimide'crosslinked polysuccinimide and



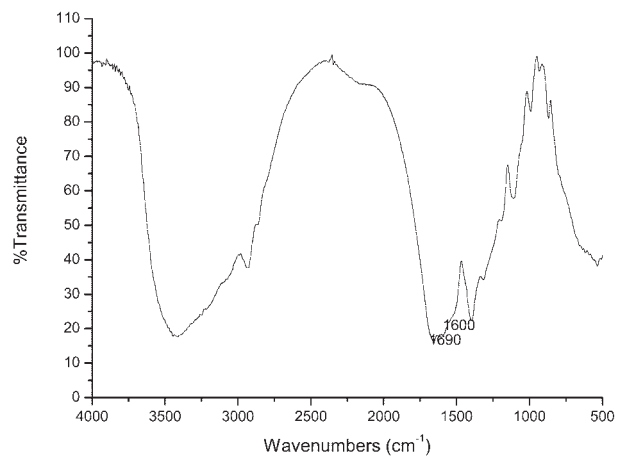
**Figure 3** The salt sensitivity for polyacrylamide-modified hydrogels synthesized in this work under the preparation condition of the weight of polyacrylamide/polysuccinimide was 3/5, the concentration of crosslinking agent was 0.0333 mol/L, and the volume of solvent was 32 mL/g PSI.



(a)



(b)



(c)

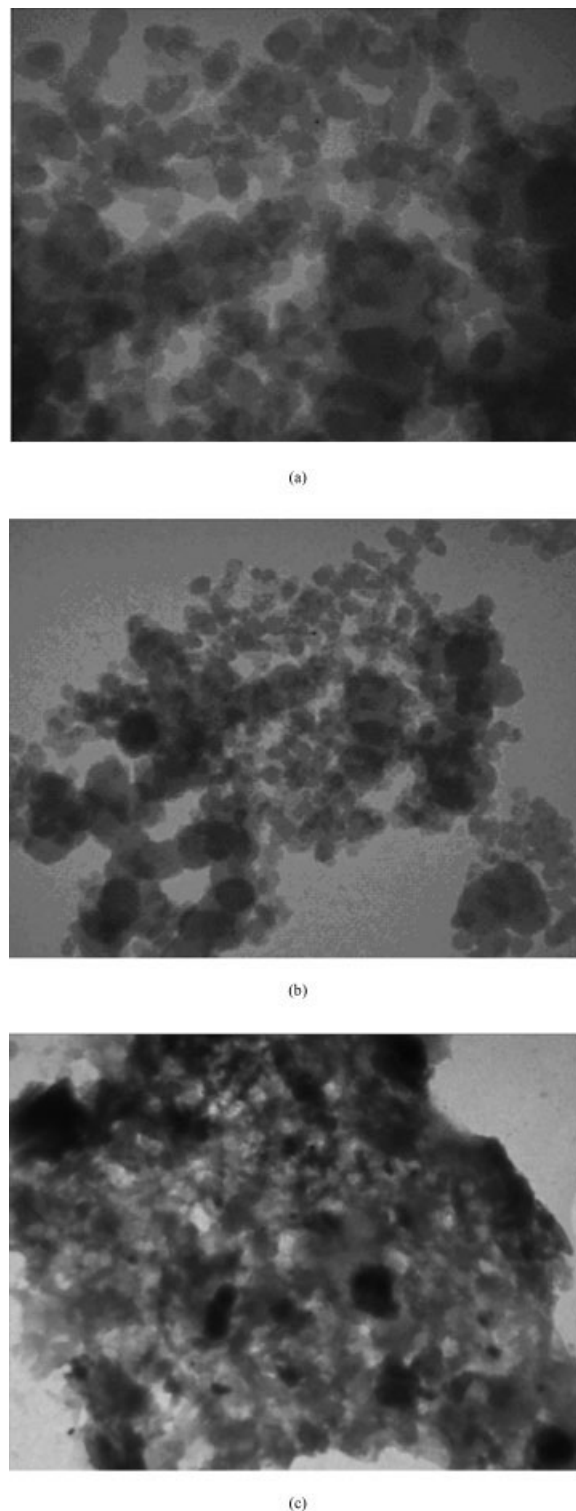
**Figure 4** The infrared spectrum of polysuccinimide (PSI) (a), the infrared spectrum of crosslinked polysuccinimide-polyaspartic acid (PASP) (b), and the infrared spectrum of polyaspartic acid modified by polyacrylamide (PASP-PAM) (c).

polyacrylamide-modified polyaspartic acid composite are shown in the Figures 4(a)–4(c), respectively. The absorption peaks at  $\sim 3440$  and  $\sim 1700\text{cm}^{-1}$  contribute

to  $-\text{CONH}$ ,  $-\text{CO}$  groups on polysuccinimide, respectively, [Fig. 4(a)], and the band at  $\sim 3000\text{ cm}^{-1}$  may due to  $-\text{CO}$  group partly changes to  $-\text{COOH}$  group when PSI was synthesized at high temperature ( $200^\circ\text{C}$ ). The absorption peaks at  $\sim 1395$ ,  $\sim 3490$ , and  $\sim 2925\text{ cm}^{-1}$  attribute to  $-\text{COOH}$ ,  $-\text{NH}$ , and  $-\text{CH}_2$  groups, respectively, [Fig. 4(b)]. The absorption peak of  $-\text{NH}$  group becomes weaker since the characteristic absorption peak for  $-\text{NH}$  group on PSI and PASP change after copolymerization reaction, this suggests that the  $-\text{CONH}-$  group on polysuccinimide participate in the crosslinking reaction and lead to the formation of network structure and water absorbent group [Fig. 4(b)]. After reaction of polysuccinimide with composite polyacrylamide, the strong absorption peaks at  $\sim 1690$  and  $\sim 1600\text{ cm}^{-1}$  attribute to  $-\text{CONH}_2$  group on polyacrylamide [Fig. 4(c)], this suggests that the reaction take place between polysuccinimide and polyacrylamide molecules, which is highly hydrophilic group, and the type and molar percentage of hydrophilic groups  $-\text{COOH}$  and  $-\text{CONH}_2$  could affect water absorbency of composites modified superabsorbent. So the swelling ratio is about 2.5 times comparing with the control (Table III). It could be seen that the mass ratio of polyacrylamide/polysuccinimide increased from 1/5 to 3/5 caused swelling ratio to increase evidently. When the ratio exceeded 3/5, the swelling ratio decreased. This behavior may be interpreted that the collaborative absorbent effect of  $-\text{COOH}$  and  $-\text{CONH}_2$  groups is superior to that of single  $-\text{COOH}$  and  $-\text{CONH}_2$  group. On the other hand, in spite of weaker water absorbent ability, compared with other groups such as  $-\text{COONa}$  that can ionize into  $\text{Na}^+$  and  $-\text{COO}^-$  ion in water, higher absorbent ability due to their ionic hydrophilic and osmotic effect,  $-\text{COOH}$  and  $-\text{CONH}_2$  group show neutral electric charge in water, the electric repelling action between groups is smaller. Therefore, when the ratio of  $-\text{CONH}_2$  and  $-\text{COOH}$  groups in the composite hydrogels is appropriate, the repelling interaction between these ions would be reduced. So the higher water swelling ratio would approach. Consequently, the product modified by composite materials such as polyacrylamide and starch, the swelling ratio increased evidently. In our experiment, when the mass ratio of polyacrylamide/polysuccinimide polymer was 3/5, the modified product possessed the highest absorption ability.

### Morphological studies

The transmission electron microscopies (TEM) of samples are shown in the Figure 5. The black spherical particles connected together to form the network of hydrogels and there are some differences in aggregation, porosity and connected channels. The sample in the Figure 5(a) has relative big pore size, so the swell-



**Figure 5** TEM micrographs of dried polyaspartic acid (PASP) (a) PASP modified by carrageenan, (b) and PASP modified by polyacrylamide, (c) (Scale bar = 200 nm).

ing ratio is correspondingly low. The pore size in Figure 5(b), which contains carrageenan, is smaller than that in the Figure 5(a). The increase in swelling ratio would be expected from the decreasing in parti-

cle size and increasing in surface area. It could be seen that carrageenan molecules combine with polyaspartic acid molecules together closely. The porous size in Figure 4(c) is even smaller and the connected channels denser than that in Figure 5(a) and 5(b). The silk microstructure in polyacrylamide modified hydrogels forms many small porous structures inside of network. In the aqueous environment, hydrogels swell after the water molecules diffusing into the superabsorbent hydrogels through channels, which originate from crosslinking reaction stage. An increase in swelling ratio would be expected from the increase in surface area with decreasing particle size and more precise size distribution. The shift toward to smaller particle size has higher swelling ratio provides an explanation by smaller pore has higher osmotic pressure of solution inside, thus it's easier to exceed that of the external solution pressure and absorb more water before it obtains osmotic pressure equilibrium. Therefore, the effect of ionic strength and salt solution is not very obvious on composite-modified products comparing to the control. In addition, polyacrylamide could provide many hydrophilic groups, which help to heighten swelling ratio. So the product modified by polyacrylamide substantially increases in the swelling ratio and is also responsible for the high swelling ratio in the considerable ionic strength medium and salt solution as has mentioned earlier. Moreover, we tentatively put forward that the modified hydrogels forming by graft-copolymerizing reaction between polyacrylamide and polysuccinimide by the way that polyacrylamide particle as a crosslink point chemically bond with polymer polysuccinimide. Because only in this way, the network structure and the water absorbent ability would be controlled by changing the mass of polyacrylamide added into composite.

### CONCLUSIONS

A series of hydrogels were synthesized by polymerization based on PSI. On the basis of data collected in series experiments, it could be concluded that the product's absorbent ability could be changed by adjusting the concentration of crosslinking agent and the volume of solvent. The higher crosslinking agent con-

centration leads to higher crosslinking density and decrease in the space between the copolymer chains. The maximum water absorbency was achieved under the optimum conditions that found to be the crosslinking agent concentration of 0.0333 mol/L and the solvent volume of 28 mL/g PSI. The hydrogels absorbency could be improved by controlling the amount of various components and caused several changes in the swelling properties and microstructure. The maximum swelling ratio could be enhanced more than 2.4 times when the mass ratio of polyacrylamide/poly-succinimide polymer was 3/5. In addition, the polyacrylamide-modified product had good buffer ability in solution when the pH ranged from 4 to 10 and the influence of ionic strength on swelling ratio was smaller compared to the control. By the IR and TME characterization, the polymerization reaction mechanisms and structures of the composite were studied, which indicated that the crosslinking agent and composite played a crucial role in the formation of network structure of the superabsorbent polymers. So, the hydrogels could be considered as a good candidate to design production of the fast-swelling and high swelling ratio in the salinity medium superabsorbent polymers.

### References

1. Buchholz, F. L.; Graham, T. *Modern Superabsorbent Polymer Technology*; Wiley-VCH: New York, 1998; p 1152.
2. Po, R. *J Macromol Sci Rev Macromol Chem Phys* 1994, 34, 607.
3. Hoffman, A. S. In *Polymeric Materials Encyclopedia*, Vol. 5; Salamone, J. C., Ed.; CRC: Boca Raton, Florida, 1996; p 3282.
4. Kost, J. In *Encyclopedia of Controlled Drug Delivery*, Vol. 1; Mathiowitz, E., Ed.; Wiley: New York, 1999; p 445.
5. Yao, K.-J.; Zhou, W.-J. *J Appl Polym Sci* 1994, 53, 1533.
6. Kabiri, K.; Omidian, H.; Hashemi, S. A. *Eur Polym J* 2003, 39, 1341.
7. Huglin, M. B.; Liu, Y.; Velada, J. L. *Polymer* 1997, 38, 5785.
8. Chen, J.; Park, K. *Carbohydr Polym* 1995, 28, 69.
9. Chen, J.; Park, H.; Park, K. *J Biomed Mater Res* 1999, 44, 53.
10. Chen, J.; Blevins, W. E.; Park, H.; Park, K. *J Controlled Release* 2000, 65, 73.
11. Dorkoosh, F. A.; Brusee, J.; Verhoef, J. C.; Borchard, G.; Tehrani, M. R.; Junginger, H. E. *Polymer* 2000, 41, 8213.
12. Dorkoosh, F. A.; Brusee, J.; Verhoef, J. C.; Borchard, G.; Tehrani, M. R.; Junginger, H. E. *J Controlled Release* 2001, 71, 307.
13. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. *Polymer* 1998, 39, 6697.