Fabrication and Properties of Superabsorbent Complex Gel Beads Composed of Hydrolyzed Polyacrylamide and Chitosan

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ABSTRACT: A novel method for preparing complex beads composed of hydrolyzed polyacrylamide (HPAM) and chitosan, based on the electrostatic attraction between $-COO^-$ of HPAM and Al^{3+} and between $-COO^-$ and $-NH_3^+$ of chitosan, was established. In the two-stage crosslinking process, first Al^{3+} was used as a crosslinking agent for the crosslinking of HPAM molecules, which were used as the skeleton structure of the gel beads. In the second stage, chitosan diffused into the skeleton structure. The gel beads were characterized with scanning electron microscopy, inductively coupled plasma mass spectrometry, Fourier transform infrared spectroscopy, and thermogravimetric analysis. There was a chitosan component in the gel beads, and these gel beads had porous and rough surfaces. The swelling properties of the HPAM–chitosan gel beads were measured in water, in acidic, neutral, and alkaline buffers, and in different saline solutions. The swelling ratio was as high as 3675 g/g in water and 170 g/g in a 0.15 mol/L NaCl solution. The beads showed pH sensitivity in buffers of different pH values and salt sensitivity in different saline solutions. The order of the equilibrium absorbency of the gel beads in different saline solutions was $Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Al^{3+}$. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3338–3345, 2010

Key words: crosslinking; hydrogels; polyelectrolytes; swelling

INTRODUCTION

Hydrolyzed polyacrylamide (HPAM) and its derivatives are used in many fields, such as wastewater treatment (as flocculants), oil recovery, soil conditioning, agriculture, and biomedicine.[1,2] HPAM hydrogels are also some of the most important hydrogels, and they can be used in cell and organelle immobilization, biomolecule separation, ion transportation, and protein identification.[3–6] In the process of gelation, *N*,*N*′-methylene bisacrylamide, divinyl benzene, and dialdehyde compounds are always used as crosslinking agents.[4,7] Chitosan is a natural polycationic polymer consisting of D-glucosamine and *N*-acetyl-D-glucosamine, and it is soluble in numerous diluted mineral and organic acids, except for sulfuric acid because of the protonation of its amine groups.[8] Chitosan has received much attention in the fields of pharmacology and biomedicine because of its good biocompatibility and low toxicity.[9] Many studies have been undertaken to prepare chitosan gel beads. In the process of gelation, glutaraldehyde, sodium tripolyphosphate, xanthan, and alginates are always used as crosslinking agents.[8,10–12]

In general, when polyelectrolytes with opposite charges are mixed, electrostatic interactions will be established between them and give rise to polymeric complexes; when macroscopic phase separation occurs, one phase rich in the two polymers and another rich in the pure solvent are obtained.[13,14] As a result, it is difficult to form gels composed of HPAM and chitosan by uniform mixing without another crosslinking agent. Graft polymerization is used most often for preparing HPAM–chitosan gels, and *N*,*N*′-methylene bisacrylamide, epichlorohydrin, or ethylene glycol diglycidyl ether is used in the process.[15–17]

The interaction between $-COO^-$ of HPAM and $-NH_3^+$ of chitosan has been investigated by other researchers. The results of this study indicate that there is a strong interaction between $-COO^-$ of HPAM and $-NH_3^+$ of chitosan.[13] Moreover, noncovalent crosslinked chitosan gel mixtures can be

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prepared from polyelectrolyte complexes of chitosan and polymers such as alginate, pectin, and dextran sulfate.[18–20] Polyelectrolyte complexes are highly hydrophilic materials and form highly swollen systems in water.[21]

In our investigation, a new method for preparing complex gel beads composed of HPAM and chitosan was found. The complex gel beads were synthesized by a two-stage crosslinking process. First, Al^{3+} ions were used as a crosslinking agent for preparing the HPAM–Al gel beads, which were used as a skeleton structure in the following process. In the second stage, chitosan molecules diffused into the HPAM–Al gel beads and combined with HPAM molecules. Scanning electron microscopy (SEM), inductively coupled plasma mass spectrometry (ICP–MS), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA) were used to characterize the gel beads. The result showed that there was a chitosan component in the complex gel beads. An investigation of the swelling behavior of the gel beads showed that these gel beads were salt- and pH-sensitive and superabsorbent.

EXPERIMENTAL

Experimental materials

HPAM was prepared by inverse emulsion polymerization. Sorbitan monooleate (0.7 g) and 0.1 g of nonylphenol polyoxyethylene ether were dissolved in 15 mL of cyclohexane. A 30% (w/w) acrylamide aqueous solution (10 g) was dropped into the cyclohexane solution with high-speed stirring. The polymerization was initiated by 0.045 mmol of potassium persulfate at 60°C in a nitrogen atmosphere. After 4 h, 10 g of 10% (w/w) sodium hydroxide was added to the emulsion, and the hydrolysis of polyacrylamide proceeded at 80°C for 24 h. Then, the emulsion was precipitated with ethanol and washed with ethanol six times and with a mixture of water and ethanol three times to remove the emulsifier, alkali, and monomer. HPAM was dried *in vacuo* at 50°C for 48 h. The weight-average molecular weight (M_w) of HPAM was 4.3×10^6 g/mol; it was calculated with the experimentally determined intrinsic viscosity ([η]) and the Mark–Houwink equation:[22]

$$[\eta](\mathrm{mL/g}) = 8.2 \times 10^{-3} M_w^{0.85}$$

[η] of HPAM in 0.5 mol/L NaCl was 3573 mL/g, which was determined by capillary viscometry. The hydrolysis degree of HPAM was 46%, which was determined by elemental analysis.

Chitosan was purchased from Jinan Haidebei Marine Bioengineering Co. (Jinan, China), refined twice by dissolution in a 0.1 mol/L HCl solution, filtered, precipitated with ethanol, and finally dried *in vacuo* at 50°C for 48 h. M_w of chitosan was 9.1×10^5 g/mol, and it was calculated with the experimentally determined [η] value and the Mark–Houwink equation:[23]

$$[\eta](\mathrm{mL/g}) = 0.104 \times 10^{-3} M_w^{1.12}$$

[η] of chitosan in 0.1 mol/L CH_3COONa and 0.2 mol/L CH_3COOH was 495 mL/g, which was determined by capillary viscometry. The deacetylation degree of chitosan was 71%, which was determined by elemental analysis.

Other materials were analytical-reagent-grade and were used as received.

Preparation of the HPAM–Al gel beads

Eight grams of an aqueous 1% (w/w) HPAM solution was extruded dropwise through a syringe fitted with a 25-gauge needle into 30 mL of a 0.2 mol/L $AlCl_3$ solution at room temperature under gentle stirring at 100 rpm, and then the gel beads were cured for 2 h. These were labeled HPAM–Al gel beads.

Preparation of the HPAM–chitosan gel beads

Chitosan was dissolved in a 0.1 mol/L HCl solution to obtain a concentration of 0.6% (w/w). The aforementioned HPAM–Al gel beads were washed with distilled water three times and immersed in a 20-mL chitosan solution for 24 h. These were labeled HPAM–chitosan gel beads. HPAM–chitosan gel beads were washed with distilled water three times and dried under reduced pressure at 50°C for 48 h.

SEM observation

The morphologies of the surfaces of the dried gel beads were observed with a scanning electron microscope (JSM-7600F, JEOL, Tokyo, Japan). The surfaces of the dried gel beads were coated with a thin layer of gold before the SEM examinations.

ICP–MS analysis

The Al content in the HPAM–Al and HPAM–chitosan gel beads was obtained by ICP–MS analysis, which was carried out on an Agilent 7500A ICP–MS system (Tokyo, Japan). The gel beads were dissolved in a 1 mol/L NaOH solution after stirring for 24 h. After that, the desired amount of 10% (w/w) HNO_3 was added to the alkaline solution so that the HNO_3 concentration of the solution was about 5% (w/w). Each kind of gel bead was tested three times.

FTIR spectroscopy analysis

FTIR spectroscopy was carried out on a Bruker Tensor 27 spectrometer (Frankfurt, Germany) with the samples prepared as KBr pellets. The samples were porphyrized first. Then, dried, spectroscopic-grade potassium bromide (200 mg) was porphyrized and mixed with the porphyrized gel beads (2 mg). The spectra were acquired in the frequency range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with a total of 16 scans.

TGA

Thermal characteristics of the samples were determined by TGA. TGA was performed with a Mettler–Toledo SDTA-851 TGA system (Zurich, Switzerland). The analysis was performed with approximately 4-mg dried samples in a dynamic nitrogen atmosphere (flow rate = 100 mL/min) at a heating rate of 10°C/min.

Swelling property measurements

The water absorption capacity of the HPAM–chitosan gel beads was determined via the swelling of the gel beads in pH 2.2, 7.4, and 9.2 buffers (Clark-Lubs buffers; the pH 2.2 buffer contained 0.0925 mol/L KCl and 0.00752 mol/L HCl, the pH 7.4 buffer contained 0.05 mol/L KH_2PO_4 and 0.0393 mol/L NaOH, and the pH 9.2 buffer contained 0.0267 mol/L NaOH, 0.05 mol/L KCl and 0.05 mol/L H_3BO_3) and a variety of saline solutions at 37°C. About 3 mg of accurately weighed gel beads (weight W_o) was placed in 60 mL of the medium for the required period of time. The wet weight of the swollen beads (W_s) was determined as follows: the beads were blotted with filter paper to remove water adsorbed on the surface and then were weighed immediately on an electronic balance. The swelling ratio of the gel beads in the medium was calculated with the following formula:

$$\text{Swelling ratio (g/g)} = (W_s - W_o)/W_o$$

Each swelling experiment was repeated three times, and the average value was taken as the water absorption rate value.

RESULTS AND DISCUSSION

Morphological characteristics of the gel beads and HPAM–chitosan hydrogels

The physical appearance of the gel beads and HPAM–chitosan hydrogels is shown in Figure 1. The HPAM–Al gel beads were uniform and spherical.

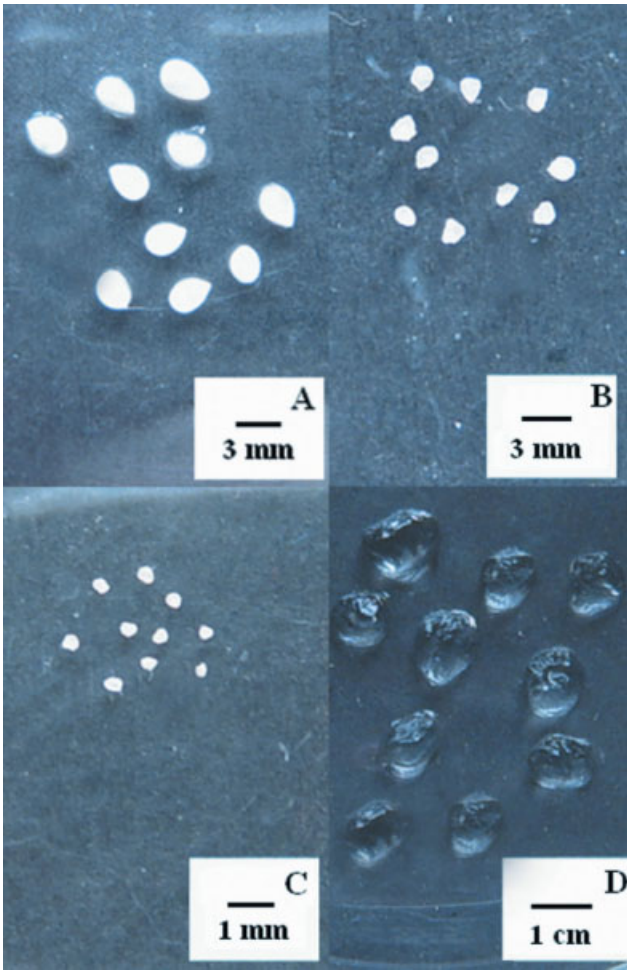

Figure 1 Optical photographs of (A) HPAM–Al gel beads, (B) wet HPAM–chitosan gel beads, (C) dry HPAM–chitosan gel beads, and (D) the HPAM–chitosan hydrogels. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Different batches of gel beads under the same conditions had the same physical appearance and a uniform size. The diameter of the HPAM–Al gel beads was about 3 mm. However, the HPAM–chitosan gel beads shrank, and their diameter was about 1 mm. Moreover, their physical appearance became irregular in comparison with the HPAM–Al gel beads. The wet HPAM–chitosan gel beads were easily dried. After being placed in air for 30 min, these gel beads shrank and became hard, and their diameter was about 0.5 mm. However, the HPAM–Al gel beads could not hold their globular shape and became flat after being dried. After being immersed in water for 3 h, the HPAM–chitosan hydrogels could hold their granular shape and showed good elastic performance. The HPAM–chitosan gel beads were not covalently crosslinked, but they were stabilized by polyelectrolyte complexation between HPAM and chitosan and between HPAM and Al^{3+}. As a result, the absence of stale, covalently bonded

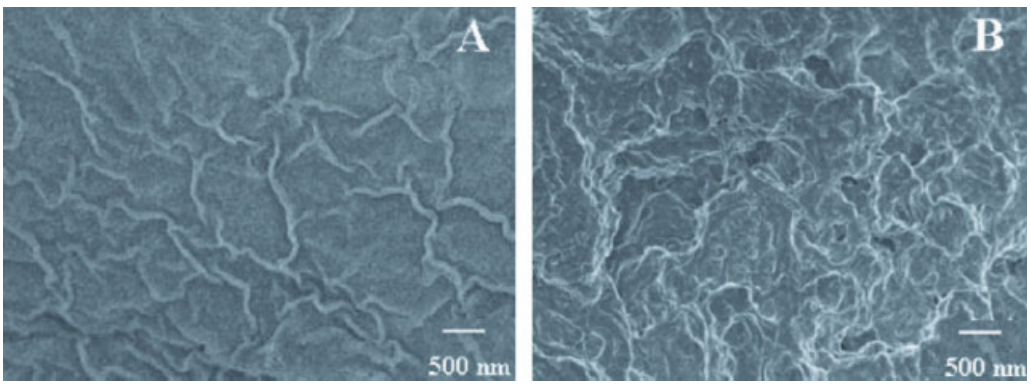

Figure 2 SEM images of (A) dried HPAM–Al gel beads and (B) dried HPAM–chitosan gel beads (magnification = 1500×). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crosslinking bridges might be a key factor explaining the high water retention of the HPAM–chitosan gel beads.

SEM analysis of the dry gel beads

The morphology of the surfaces of the dried HPAM–Al gel beads and HPAM–chitosan gel beads was observed with SEM, as shown in Figure 2. The HPAM–Al gel beads showed a corrugated surface. The HPAM–chitosan gel beads showed a more uneven surface. Moreover, unlike the HPAM–Al gel beads, there were many micropores on the surface of the HPAM–chitosan gel beads. This porous surface structure might be convenient for the penetration of water or metal ions into the network and thus enhance their swelling and absorption ability. This might be the reason for the formation of the porous surface: Al ions dissociated from the complex of Al^{3+} and $-COO^{-}$ because of its ionization equilibrium in an acidic environment, and this induced the destruction of the crosslinking structure.

Modes of formation of the gel beads

It has been reported that there generally are two methods of synthesizing similar complex gels, which are known as snake-cage resins. First, the monomers are allowed to absorb and stay in the cage resin, and then the monomers are polymerized into a linear snake resin with an appropriate method. Second, the snake resin is mixed with the monomers, and then these monomers are crosslinked with one another into a cage resin.[24] However, this study used a different method. A schematic representation of the formation of the gel beads is suggested in Figure 3. When the HPAM solution is dropped into the Al^{3+} solution, the HPAM molecules are crosslinked by

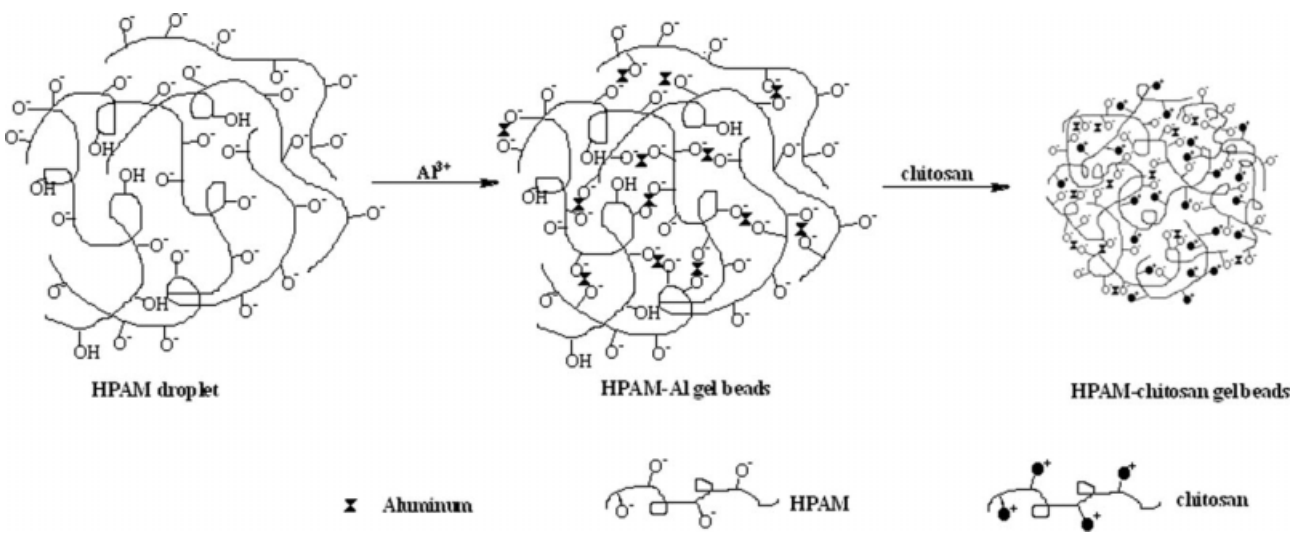

Figure 3 Schematic representation of the formation of the gel beads.

Al^{3+} ions because of the strong interaction between $-COO^-$ (HPAM) and Al^{3+}, and as a result, the skeleton structure of the HPAM–chitosan gel beads forms. When the HPAM–Al gel beads are immersed into a chitosan solution for a long time, chitosan molecules can diffuse within the HPAM–Al gel beads and can be fixed on the formed skeleton structure because of the interaction between $-COO^-$ (HPAM) and $-NH_3^+$ (chitosan), which induces the shrinkage of the HPAM–Al gel beads. In our experiment, the wet HPAM–Al beads had a soft interior and a thin crust. However, the wet HPAM–chitosan beads were elastic, solid beads. The dry HPAM–chitosan beads were also stiff, solid beads. There were no differences between their interiors and crust on a visual inspection. Moreover, SEM analysis indicated that there were many micropores on the surface of the HPAM–chitosan gel beads, and these could be the diffusion passages for chitosan. These phenomena indicate that the diffusion of chitosan into HPAM–Al gel beads might be possible.

ICP–MS analysis of the dry gel beads

The weight percentages of Al in each kind of gel bead from ICP–MS are shown in Table I. According to the results, the average weight percentage of Al in the HPAM–Al gel beads was 2.53%, and that in the HPAM–chitosan gel beads was 0.30%. The decrease in the content of Al might be mainly attributable to the appearance of the chitosan component or the partial dissociation of Al^{3+} from the gel beads.

Fourier transform infrared (FTIR) spectroscopy of the dry gel beads

Figure 4(a–d) shows FTIR spectra of HPAM, HPAM–chitosan gel beads, chitosan, and HPAM–Al gel beads, respectively. The characteristic peaks around 1630 cm^{-1} are assigned to the absorption band of the carbonyl groups of HPAM or chitosan. The observed changes in the absorption bands of the carboxyl groups can be attributed to the large number of chemical groups from both polymers contributing to the spectral region of the carbonyl. The carboxyl group absorption peaks of HPAM, HPAM–chitosan, and HPAM–Al gel beads can be observed at 1626, 1641, and 1645 cm^{-1}, respectively. Moreover, carbonyl groups of carboxylic acids usually absorb at a high wave number (1800–1650 cm^{-1}) if they are present in an acidic form. The shoulder appearing in the spectrum of the HPAM–chitosan gel beads at 1730 cm^{-1} within this spectral region is consistent with the preparation of HPAM–chitosan (acidic conditions). The presence of the chitosan component in the HPAM–chitosan gel beads is indicated by the peak at 1105 cm^{-1}, which is classically assigned to polysaccharide molecule backbone vibrations. The broad peak around 3400 cm^{-1} of the HPAM–Al gel beads can be related to the water remaining in the structure, which should be very difficult to remove completely. The peaks at 3050, 2400, and 847 cm^{-1} for the HPAM–Al gel beads are absent in the HPAM and chitosan spectra and should be assigned to the absorption of Al compounds or the absorption of the water remaining in the structure due to the process used for the preparation of the HPAM–Al gel beads. Moreover, the spectrum of the HPAM–chitosan gel beads presents at 847 cm^{-1}, and this means that the HPAM–chitosan gel beads still have a considerable number of Al^{3+} ions; this is consistent with the results from the ICP–MS analysis.

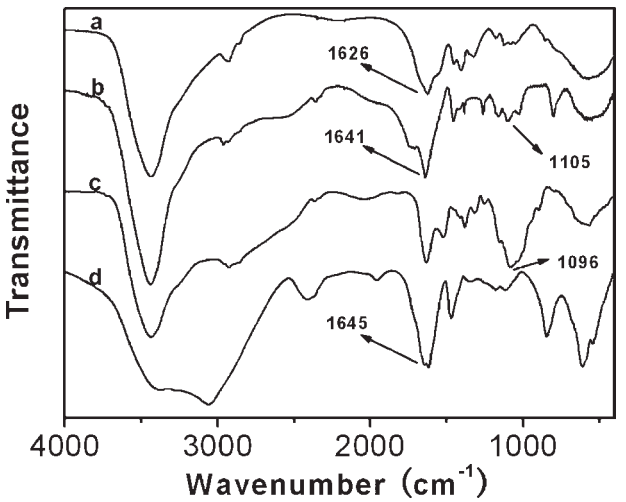

Figure 4 FTIR spectra of (a) HPAM, (b), HPAM–chitosan gel beads, (c) chitosan, and (d) HPAM–Al gel beads.

TABLE I
Weight Percentages of Al in the Gel Beads for the ICP–MS Analysis

	HPAM–Al gel beads			HPAM–chitosan gel beads		
Test number	1	2	3	1	2	3
Al	2.60	2.52	2.47	0.31	0.30	0.28

TGA of the dry gel beads

Thermal characteristics of the HPAM–Al gel beads and HPAM–chitosan gel beads were examined with TGA. Figures 5(a–d) and 6(a–d) show the TGA and differential thermogravimetric analysis (DTGA) curves of the HPAM–Al gel beads, chitosan, HPAM, and HPAM–chitosan gel beads. Although the HPAM–Al and HPAM–chitosan gel beads were dried under reduced pressure in the same way, in

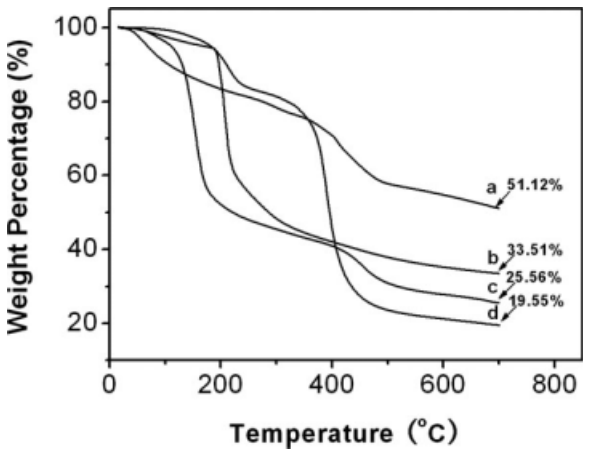

Figure 5 TGA curves of (a) HPAM–Al gel beads, (b) chitosan, (c) HPAM, and (d) HPAM–chitosan gel beads.

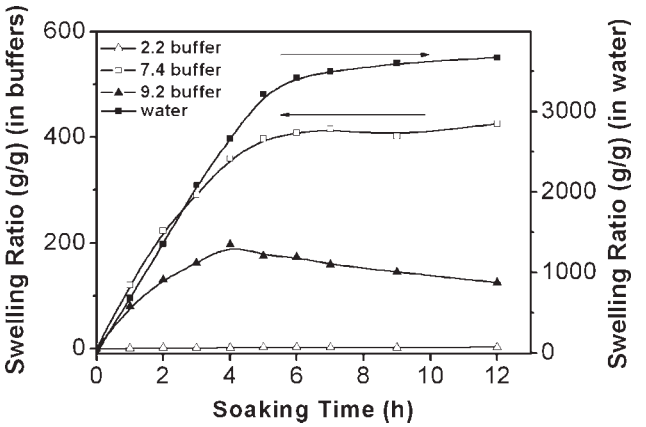

Figure 7 Swelling ratio of the HPAM–chitosan gel beads in water and buffers of different pH values at 37°C.

contrast to the HPAM–chitosan gel beads, there is a mass-loss peak before 100°C in the DTGA curve of the HPAM–Al gel beads. The curve of the HPAM–chitosan gel beads shows two major mass-loss steps under a nitrogen atmosphere. The first transition occurs near 213°C and is associated with the loss of the chitosan component. The second transition occurs at about 391°C and may be associated with the decomposition of carboxylic groups. In comparison with HPAM, the second transition of the HPAM–chitosan gel beads occurs at a lower temperature. The reason may be that —COONa provides better heat resistance than —$COO^{-}\cdots NH_3^{+}$—. The char formation is also shown in Figure 5. The results indicate that, in comparison with HPAM, Al or chitosan components have a great influence on char formation for each kind of gel bead.

Swelling properties of the dry gel beads

In our investigation, the HPAM–Al gel beads converted into a membraniform precipitate and were not able to form a hydrogel after being immersed in water, an acidic medium, or an alkaline medium for 48 h. However, as shown in Figure 7 and Figure 8, the swelling ratio of the HPAM–chitosan gel beads could be up to 3675 g/g in water and 170 g/g in a 0.15 mol/L NaCl solution after swelling for 9 h at 37°C. Many researchers have reported complex superabsorbent materials in which one of the components is polyacrylamide or chitosan. The swelling ratio has been around 300–1000 g/g in water for most of them.[25–28] As a result, these gel beads could provide better swelling performance.

Polyelectrolyte hydrogels are based on charged networks that contain ionized groups. Negatively or

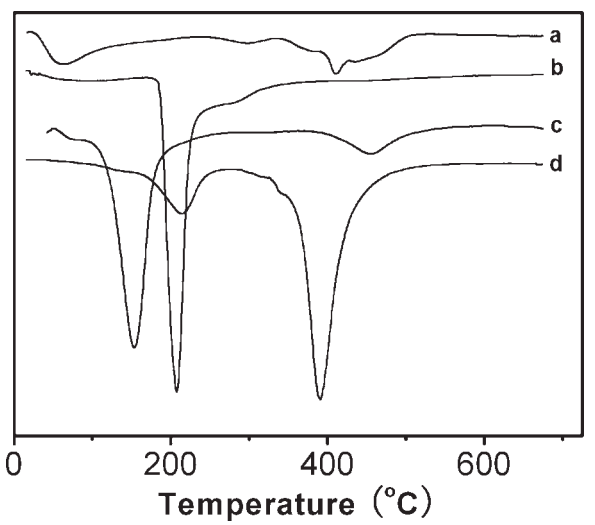

Figure 6 DTGA curves of (a) HPAM–Al gel beads, (b) chitosan, (c) HPAM, and (d) HPAM–chitosan gel beads.

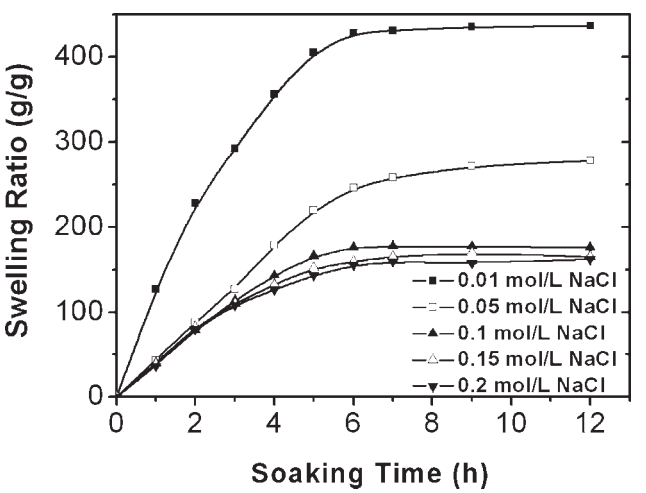

Figure 8 Swelling ratio of the HPAM–chitosan gel beads in NaCl solutions of different concentrations at 37°C.

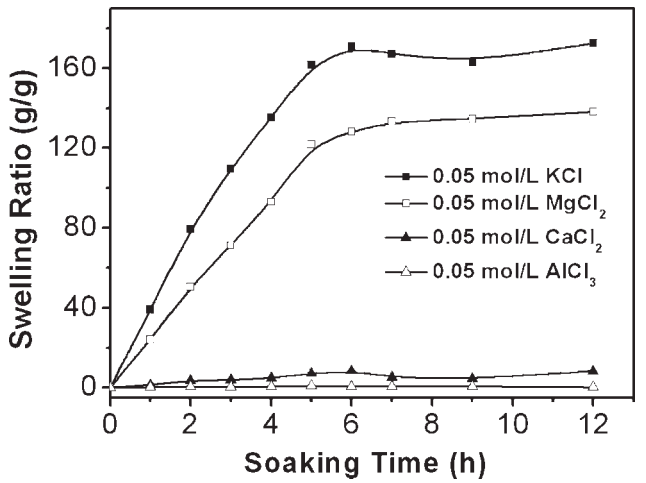

Figure 9 Swelling ratio of the HPAM–chitosan gel beads in different saline solutions at 37°C.

positively charged hydrogels usually exhibit different degrees of equilibrium swelling at different pH values depending on the ionic composition of the polymers.[29] The HPAM–chitosan gel beads contained positively and negatively charged groups; as a result, we expected the swelling capacity of these gel beads to change in solutions with different pH values. Figure 7 shows the swelling behavior of the HPAM–chitosan gel beads in buffers with different pH values. In the pH 2.2 medium, the gel beads only slightly swelled and did not dissolve. This result could be explained as follows: carboxyl groups existed as —COOH in a lower pH solution and the gel had a low tendency to dissociate because of the presence of a strong hydrogen bond between —COOH and amide groups. In the pH 9.2 buffer, the water absorption rate significantly increased in comparison with that in the pH 2.2 medium, and it depended on the swelling time. This result could be due to the dissociation of both —COOH and $—COO^{-}\cdots NH_3^{+}—$ groups, and the physical gel tended to dissolve slowly in an alkaline medium. The water absorption rate in the pH 7.4 medium and water tended to level off after swelling for 6 h. This might indicate that the crosslinking structure was stable in a neutral medium.

Generally, the swelling capacity of ionic hydrogels in salt solutions significantly decreased in comparison with the absorbency values in distilled water. To investigate the salt sensitivity of the HPAM–chitosan gel beads, the swelling capacity was measured in NaCl solutions at different concentrations and in different saline solutions at the concentration of 0.05 mol/L. The results are shown in Figures 8 and 9, respectively. Figure 8 indicates that the swelling capacity of the HPAM–chitosan gel beads decreased sharply in a saline solution in comparison with the value measured in water. However, the swelling capacity of the gel beads was not strongly dependent on the salt concentration when the concentration of NaCl was more than 0.1 mol/L.

In comparison with the equilibrium swelling data obtained with chloride salt solutions of the same concentration, the swelling capacity decreased with the charges of metal cations increasing ($K^+ > Mg^{2+}$, $Ca^{2+} > Al^{3+}$), as shown in Figure 9. The gel beads exhibited good water absorption in KCl and $MgCl_2$ solutions but poor water absorption in a $CaCl_2$ solution, and the gel beads could hardly absorb water in an $AlCl_3$ solution. This may be explained by the complexing ability arising from the coordination of the multivalent cations with carboxylate groups. This leads to an increase in the crosslinking density, which makes network shrink.[30]

CONCLUSIONS

HPAM–chitosan gel beads were prepared with the aid of Al^{3+} in an acidic solution and were characterized with SEM, ICP–MS, FTIR, and TGA. The results showed that these gel beads were porous complexes of HPAM, Al^{3+}, and chitosan. The swelling properties of these gel beads were investigated in different media. The results showed that they could form salt- and pH-sensitive superabsorbent hydrogels. They exhibited good swelling in neutral solutions and in NaCl, KCl, and $MgCl_2$ solutions and poor swelling in low pH solutions and in $CaCl_2$ and $AlCl_3$ solutions.

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