Synthesis, Characterization and Swelling Behavior of Chitosan-Sucrose as a Novel Full-Polysaccharide Superabsorbent Hydrogel

Ali Pourjavadi, Vagrik Aghajani, Hossein Ghasemzadeh

Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran, Iran

ABSTRACT: A novel full-polysaccharide hydrogel was prepared by crosslinking of chitosan with periodate-oxidized sucrose. A tetraaldehyde molecule is synthesized via periodate oxidation of sucrose and then applied as a crosslinking agent to form a new hydrogel network. A mechanism for the superabsorbent hydrogel formation via reductive N-alkylation was also suggested. The structure of the hydrogel was confirmed by FTIR spectroscopy, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). It is shown that crosslinking of chitosan can improve its thermal stability. The effects of crosslinker concentration, pH, and inorganic salt on the swelling behavior of the hydrogel were studied. The results indicate that the hydrogel has good pH sensitivity and pH reversible response. The smart hydrogels may have potential applications in the controlled delivery of bioactive agents and for wound-dressing application © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2648–2655, 2008

Key words: chitosan; sucrose; hydrogel; superabsorbent; periodate oxidation

INTRODUCTION

Hydrogels are three-dimensional polymer networks, which swell significantly in water and saline solutions. A variety of synthetic or natural hydrogels have been widely used as controlled release systems for drug delivery.[1–4] The pH-sensitive hydrogels have potential applications in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for low molecular weight and protein drug delivery.[5,6] Among them, chitosan hydrogels are one of the most commonly used. Chitosan is currently receiving enormous interest in medical and pharmaceutical applications, because it is a safe and friendly substance for the human organism and because it has beneficial intrinsic properties.[7–10] Chitosan is a biodegradable copolymer composed of D-glucosamine and N-acetyl-D-glucosamine. It is the deacetylated derivative of chitin, which is found in nature, present in insect exoskeletons, outer shells of crabs, shrimps, lobsters, and fungal cell walls. To obtain a full chitosan hydrogel network, crosslinking process is needed. It is desirable to use a crosslinking agent that is not only suitable for being applied in crosslinking of chitosan, but that is also of low toxicity and capable of forming stable and biocompatible crosslinked products. The most common crosslinking agents for crosslinking chitosan are glutaraldehyde,[11,12] formaldehyde,[13,14] epichlorohydrin,[15,16] and ethylene glycol diglycidyl ether,[17,18] regarded as quite toxic chemicals. To eliminate the toxicity problems, other biological crosslinkers may be used. A natural occurring agent, genipin, was used for crosslinking of a chitosan hydrogel network.[19–23] Chitosan was crosslinked by reductive alkylation with polyaldehyde prepared from periodate oxidation of some biological macromolecules such as starch, cellulose, and β-cyclodextrin.[24–26] This work focused on the design of a new hydrogel system based on chitosan using a tetraaldehyde molecule, generated from periodate oxidation of sucrose, which was used as a new crosslinker agent. The structure of the hydrodel was confirmed by solubility test, scanning electron microscopy (SEM), FTIR spectroscopy, and thermogravimetric analysis (TGA). The swelling behavior of the hydrogels in aqueous media at different pHs and in salt solutions has been examined.

EXPERIMENTAL

Materials

Low viscosity chitosan ($M_r \sim 150,000$) with degree of deacetylation 81% (determined by FTIR spectroscopy[27]) and sodium meta periodate was obtained from Fluka. Sucrose was obtained from Merck. Both were used without further purification. Mixed bed

ion exchange resin purchased from Merck (Order No. 104836). All the other reagents used were of analytical grade.

Preparation of oxidized sucrose

Sucrose (0.05 g) and 0.15 g sodium meta periodate were mixed and dissolved in 10 mL of distilled water in a light-protected glass vessel. Reaction was proceeded 2 h at room temperature with occasional shaking. Then the reaction mixture was diluted in a 500 mL volumetric flask and passed through a column (50-cm length, 2-cm diameter) packed with a mixed bed of ion-exchange resin. This process allows the separation of ions and polar molecules based on the charge properties of the molecules and removes the excess unreacted periodate and iodate ions that are formed in the reaction. This solution was stored in the dark at 4°C.

Hydrogel synthesis

Different amounts of oxidized sucrose solution were mixed at room temperature with a fixed amount of chitosan aqueous solution (1 wt % chitosan in 1 wt % aqueous acetic acid solution) to prepare samples with desired crosslinker concentrations. Then the mixtures were stirred for 30 min on a magnetic stirrer and poured into plastic petri plates (125 cm²). They were subsequently allowed to dry in the air for several days at room temperature. The dried samples were removed from the plates, cut to small pieces, and washed with distilled water. Then, they were soaked in aqueous sodium borohydride solution (10 g/L) for 3 h to reduce the unreacted aldehyde groups and imine bonds. Any uncrosslinked or slightly crosslinked portions were extracted with 500 mL of 1% acetic acid solution on a shaker, three times and for 3 h. The remaining parts were washed with distilled water several times and dewatered in excess ethanol for 24 h and dried (50°C, 12 h). The finally obtained hydrogel was weighed to calculate the yield (Table I.). After grinding and meshing (40–60), the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

Sol content determination

The crude products were weighed before extraction, and the gel content is calculated as the weight ratio of remaining portions (after extraction) to crude product.

Fourier transform infrared spectroscopy analysis

The Fourier transform infrared spectra (FTIR) of samples in the form of KBr pellets were recorded

TABLE I
Chitosan-Crosslinker Ratios and the Yields of Hydrogel Synthesis

Volume of chitosan (mL)	Volume of crosslinker (mL)	Crosslinker concentration (ppm)	Yiled (%)
100	1	100	19
100	2	200	40
100	4	400	57
100	6	600	79
100	8	800	88
100	10	1000	96

using an ABB Bomem, MB-100 FTIR spectrophotometer.

Scanning electron microscopy analysis

The surface of the sample particles was coated with an ultra thin layer of gold under vacuum, and their surface morphology was analyzed by scanning electron microscopy, SEM (Philips, XL30) operated at 25 kV.

Swelling measurements

Dry hydrogel samples (0.2500 g) were put into a weighed empty tea bag and immersed in 500-mL distilled water (or other swelling mediums) and allowed to soak for 3 h at room temperature. The equilibrated swollen gel was allowed to drain by removing the water from the tea bag and hanging it until no drop drained (20 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation:

$$\text{Absorbency} = (W_s - W_d)/W_s \qquad (1)$$

where W_s and W_d are the weights of the swollen gel and the dry sample, respectively. Thus, absorbency was calculated as grams of water per gram of the hydrogel (g/g). Swelling of the hydrogel was also measured in different salt solutions and in buffer solutions with desired pH (with the same ionic strength) by the same method. Deswelling water ratio of the hydrogels was evaluated from the following equation:

$$\text{Deswelling water ratio } (\%) = W_t/W_{t_0} \times 100 \qquad (2)$$

where W_{t_0} and W_t are the initial weight of the fully swollen sample and the weight of sample at the deswelling time, t, respectively.

The accuracy of the measurements was ±3%. The standard deviation (s) for a sample of data that is of limited size is given in the following equation:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(X_i - \overline{X})^2}{N-1}} \qquad (3)$$

where $(X_i - \overline{X})$ is deviation from average of ith measurement and N is the number of replicates of each measurement (here $N = 3$).

Swelling kinetics

The hydrogel samples (0.2500 g) with certain particle size (40–60 mesh) were put into weighed tea bags and immersed in 500-mL distilled water or buffer solutions with desired pH (with the same ionic strength). At consecutive time intervals, the water

absorbency of the samples was determined according to eq. (1).

RESULTS AND DISCUSSION

Synthesis and characterization

Sucrose was oxidized by sodium periodate to generate a tetraaldehyde molecule, which is then used as a crosslinker.[28] The aldehyde groups of the crosslinker react with primary amino groups of chitosan to form imine bonds. Because the imine bonds are unstable and they can be readily hydrolyzed, a subsequent reduction by sodium borohydride is done to stabilize the conjugation. The proposed mechanism for crosslinking is illustrated in Scheme 1. In the first step, the imine formation reaction takes place between primary amine groups of chitosan and alde-
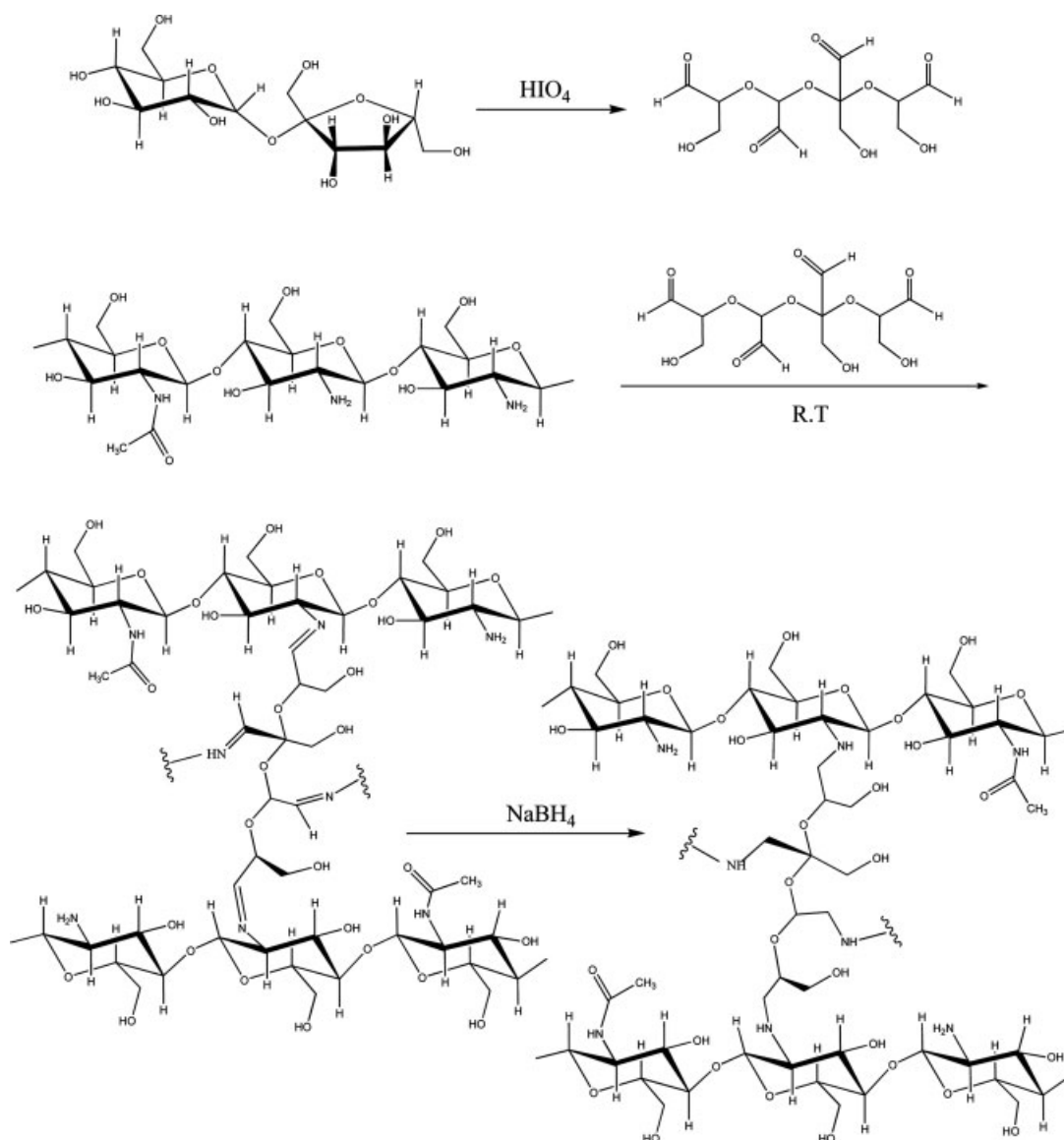
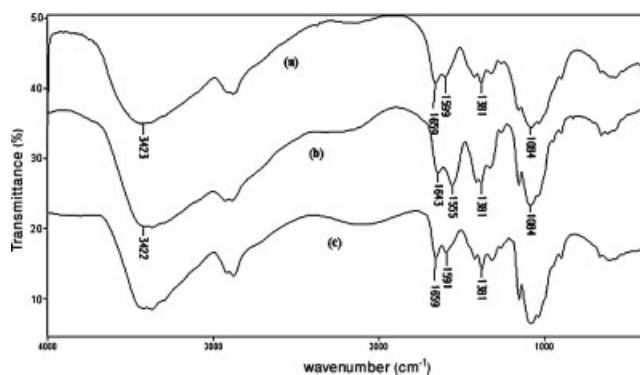**Scheme 1** Outline of the synthesis of the chitosan-sucrose superabsorbent hydrogel.

Figure 1 FTIR spectra of (a) chitosan, (b) chitosan-sucrose hydrogel before reduction, and (c) chitosan-sucrose hydrogel after reduction with NaBH$_4$.

hyde groups of the crosslinker. Reduction by sodium borohydride reduces imines groups to amines and stabilizes the conjugation between chitosan chains. A simple method to improve the crosslinking and formation of the chitosan-sucrose hydrogel can be based on the solubility difference between the crosslinked and the noncrosslinked polymer chains. Chitosan and sucrose are soluble in 1 wt % acetic acid aqueous solution and water, respectively. When the reaction product was washed with water and alternately with 1 wt % acetic acid solution for 24 h, an insoluble gel product remains. A crude hydrogel sample was synthesized with the same method but with no crosslinker. It was treated in the same way and was found to dissolve completely. Therefore, it is obvious that the crosslinked network is formed, and some chemical bonds must exist among the chitosan chains. The FTIR spectra of chitosan and chitosan-sucrose hydrogel before and after reduction with sodium borohydride are shown in Figure 1. The main characteristic absorption bands of chitosan appear at 1659 cm^{-1} (C=O stretching), 1590–1599 cm^{-1} (NH angular deformation), 3350–3450 cm^{-1} (OH hydroxyl group), and 1150–1040 cm^{-1}(C—O—C in glycosidic linkage), respectively [Fig. 1(a)]. Figure 1(b) clearly shows that the new peaks appeared at 1643 cm^{-1}, which can be attributed to imine C=N stretching. Figure 1(c) shows the FTIR spectra of chitosan-sucrose hydrogel after reduction with sodium borohydride. Appearance of the new peak at 1591 cm^{-1} shows that the imine groups (C=N bonds) are converted to amine groups (C—N bonds). The characteristic peaks between 1548 and 1560 cm^{-1} indicated the presence of —NH$_3$$^+$ groups in the hydrogel.

Effect of the crosslinker concentration

The water absorbency of the hydrogels with different concentrations of crosslinker is shown in Figure

2. As shown in this figure, the equilibrium swelling of the chitosan sucrose hydrogels decreased with the increasing crosslinker concentration. Also, the gel content increased with an increase in the crosslinker concentration. Higher crosslinker concentration produces more crosslinked points in polymeric chains and increases the extent of the polymer network, which results in the development of the gel content and, consequently less space for water within the matrix of the gel and less swelling when it is brought into contact with the solvent. This is a known behavior of hydrogels. Similar observations have been reported in the literature.[29,30]

SEM microphotographs of the hydrogels show the influence of crosslinker concentration on its microstructure and porosity [Fig. 3(a,b)]. The porosity of the hydrogel particles in sample 3a (containing 300 ppm of crosslinker) is greater than in sample 3b (containing 1200 ppm of crosslinker). These observations confirm that increasing the crosslinker concentration led to the more crosslinking of the hydrogel, which, in turn, led to a denser structure and smaller polymer network space. Consequently, the porosity is decreased. These observed morphologies are consistent with the fact that the equilibrium water absorption in sample 3a (100 g/g) was greater than that of sample 3b (20 g/g).

PH-dependent swelling of the hydrogel

The swelling behavior of the superabsorbent hydrogel was studied at various pH values between 2.0 and 10.0 at room temperature (Fig. 4). The swelling of the superabsorbent hydrogel decreased with increasing pH from 2 to 10. Swelling behavior is controlled mainly by amino groups (—NH$_2$) on the C-2 carbon of the chitosan. It is a weak base with an intrinsic pK_a of about 6.5, so it is protonated, which
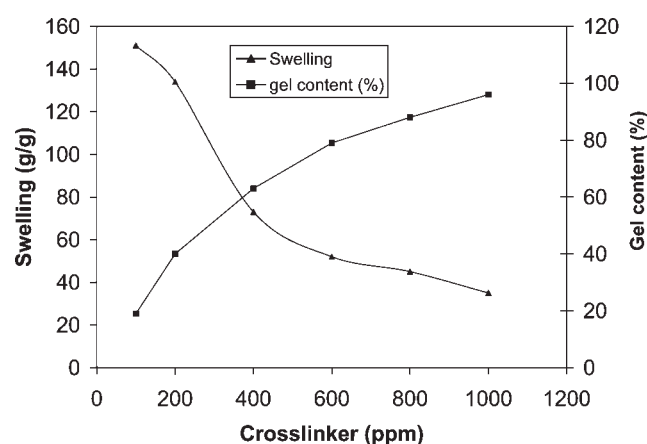

Figure 2 Effect of the crosslinker concentration on water absorbency and gel content of the superabsorbent hydrogel.
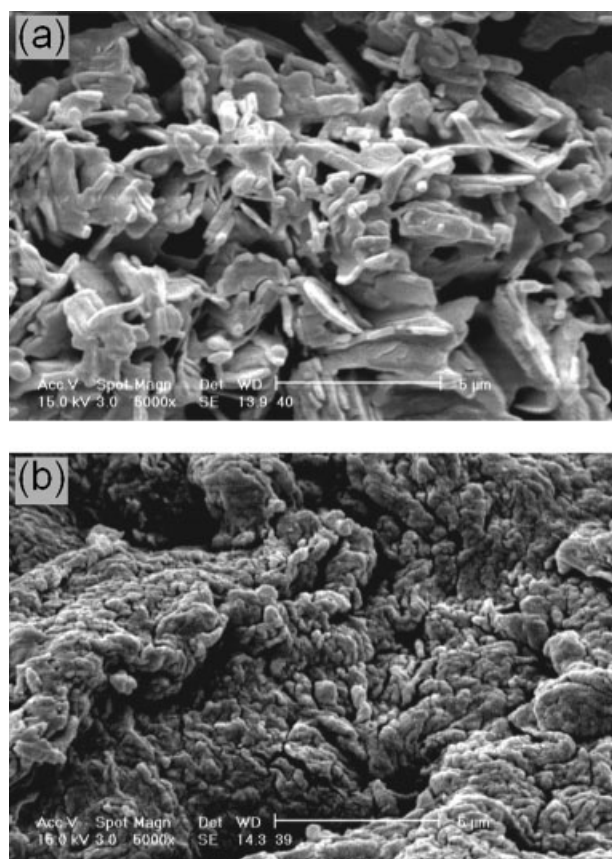
Figure 3 SEM micrographs of the superabsorbent hydrogel with different crosslinker concentrations: (a) 300 ppm and (b) 1200 ppm.

Figure 5 The pH-responsiveness (on–off switching) behavior of chitosan-sucrose superabsorbent hydrogel in 0.15M sodium phosphate buffer solution: (a) pH = 2.0 and (b) pH = 8.0.

fore, we investigated the reversible swelling–deswelling behavior of this hydrogel in buffer solutions with pH 2.0 and 8.0 (Fig. 5). At pH 2.0, the hydrogel swells up to 30 g/g due to cation–cation electrostatic repulsion, while, at pH 8.0, it shrinks within a few minutes due to deprotonation of amino groups. This sharp swelling–deswelling behavior of the hydrogels makes them suitable candidates for controlled drug-delivery systems. Such on–off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels.[31,32]

increase charge density on the polymer, which enhances the osmotic pressure inside the gel particles because of the NH_3^+—NH_3^+ electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the gel. The synthesized chitosan-sucrose hydrogel has different water absorbency in acidic and basic pH solutions. There-
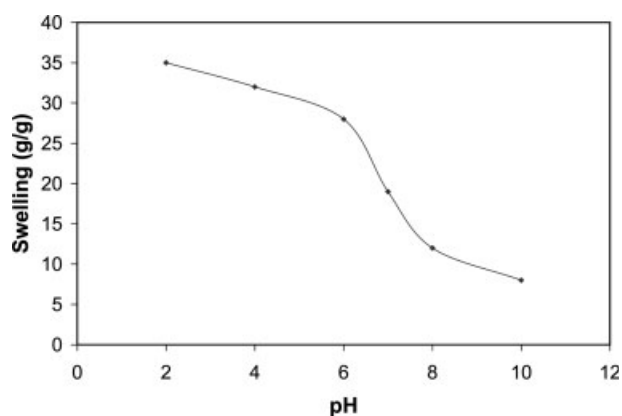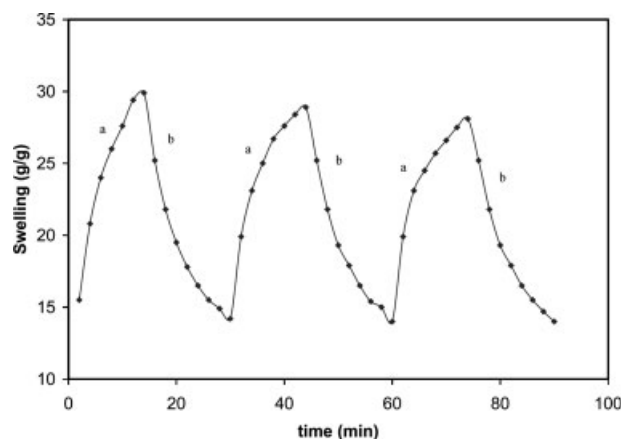
Swelling in salt solutions

It is obvious that swelling in salt solutions strongly depends on the "type" and "concentration" of the salt added to the swelling medium. In salt solutions, the osmotic pressure difference between the gel and aqueous phase increases. Consequently, the absorbency amount of hydrogel significantly decreases. In addition, with multivalent ions, "ionic crosslinking" causes an appreciable decrease in the swelling capacity. Figure 6 illustrates the relationship between concentration of salt solutions (NaCl, $CaCl_2$, and $AlCl_3$) and swelling capacity of the hydrogel. As shown in Figure 6, swelling capacity decreases for $CaCl_2$ probably due to higher ionic strength than NaCl, but it is considerably increased for $AlCl_3$ due to repulsion between —NH_2^+-groups in the polymer backbone. $AlCl_3$ dissociates in water very quickly and hydration occurs immediately with the formation of the corresponding aqua ion $Al(H_2O)_6^{3+}$. Because aluminum chloride produces an acidic solution (pH $\approx$ 3.7) when dissolved in water, the equilibrium between —NH— and —NH_2^+ shifts to the protonated form and consequently could be led to an increase in repulsion between the —NH_2^+

Figure 4 pH-dependent swelling of the superabsorbent hydrogel (in 0.15M sodium phosphate buffer solution).
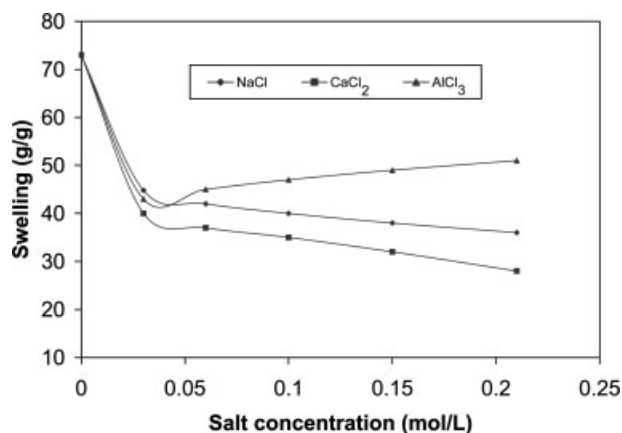
Figure 6 Swelling capacity variation of the superabsorbent hydrogel in saline solutions with various concentrations.

groups. To study the effect of cation radius on swelling behaviors, the equilibrium swelling absorbency was measured in the series of $0.15M$ chloride salt solutions of Li^+, Na^+, K^+, Rb^+, and Cs^+ (Fig. 7). As shown in this figure, swelling of the synthesized hydrogels in chloride solutions of the group (I) elements is almost equal, and no substantial effect is observed for swelling with the change in the cation radius. On the other hand, because the synthesized hydrogels in this work comprise a lot of ''cationic'' ammonium groups, the effect of anion radius on swelling behaviors is significant. As shown in Figure 7, the water absorbency in monovalent anions salt solutions of the group (VII) elements is in the order of NaF > NaCl > NaBr > NaI, respectively. This can be attributed to the charge screening effect that can shield the cations and prevent efficient electrostatic cation–cation repulsion. An additional reason is that large anions interact more strongly than large anions with polysaccharide chain, which results in decreasing the water absorbency of the hydrogel. The effect
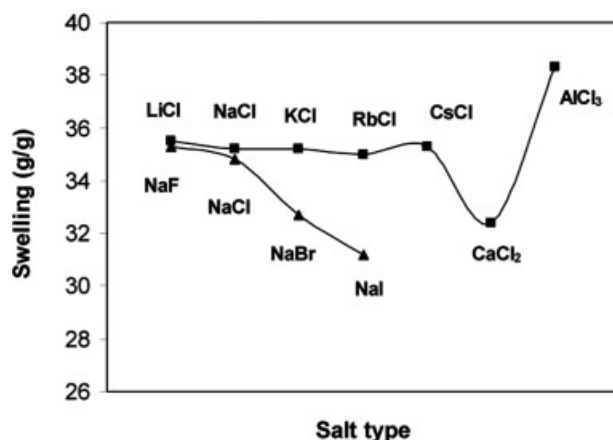

Figure 7 Swelling with the change in the cation and anion radius in different salt solutions (0.15M).
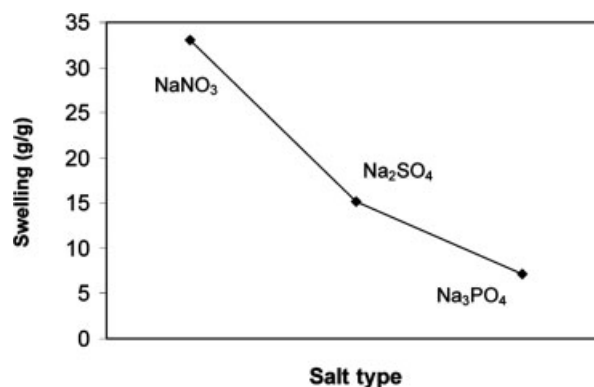

Figure 8 Swelling capacity of the hydrogel with the change in the charge of the anion (in 0.15M salt solutions).

of the charge of the anion on swelling can also be concluded from Figure 8. By increasing the charge of anion, the degree of crosslinking is increased, and the swelling is considerably decreased. In other words, with multivalent anions, ''cationic crosslinking'' causes an appreciable decrease in swelling capacity (Fig. 8).

To achieve a comparative measure of salt sensitivity of the hydrogels, a dimensionless salt sensitivity factor (f) is defined[33] as follows:

$$f = 1 - (S_s/S_w) \qquad (4)$$

where S_s and S_w refer to the swelling in desired salt solution and swelling in distilled water, respectively. The f values are given in Table II. The low values of f show clearly that the synthesized hydrogels have low salt sensitivity. Therefore, the swelling capacity of these hydrogels in salt solutions was not significantly decreased in comparison with water absorbency values, except for the salts that contain multivalent anions.

Swelling and deswelling kinetics

A preliminary study was conducted on the hydrogel-swelling kinetics. Figure 9 represents the dynamic swelling behavior of a hydrogel sample with

TABLE II
Swelling and Salt Sensitivity (f) of Chitosan-Sucrose Hydrogel in Distilled Water and Different Salt Solutions (0.15M)

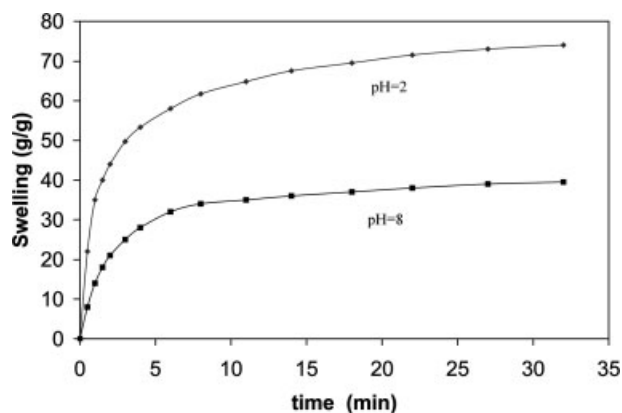| Swelling medium	Swelling ratio (g/g)	f
H_2O	73	0
NaCl	38	0.48
$CaCl_2$	32	0.56
$AlCl_3$	49	0.33
$NaNO_3$	33	0.55
Na_2SO_4	15	0.79
Na_3PO_4	7.2	0.90

Figure 9 Representative swelling kinetics of the superabsorbent hydrogel at pH = 2 and pH = 8 (particle size of the dried gel was 250–350 μm).

certain particles sized 40–60 mesh in water at room temperature. Initially, the rate of water uptake sharply increases and then begins to level off. The equilibrium swelling was achieved after 25 min. The data may be well fitted with a Voigt-based eq. (5).[34]

$$S_t = S_e(1 - e^{-t/\tau}) \tag{5}$$

where S_t is swelling at time t (g/g), S_e is equilibrium swelling (''power parameter,'' g/g), t is time (min) for swelling S_t, and τ stands for the'' rate parameter'' (min). To calculate the rate parameter, using eq. (5) and a little rearrangement, we can plot $\ln(1 - S_t/S_e)$ versus t. The rate parameters can be computed out of the slope of the straight line fitted (slope = $-1/\tau$) to be 1.98 and 2.51 min for the hydrogel with pH = 2 and pH = 8, respectively. It is well known that the swelling kinetics for chitosan hydrogels is significantly influenced by the pH,[35] that is, the lower the pH, the higher the rate of water uptake. The deswelling water ratios of the hydrogels were measured, using eq. (2), to quantify the degree of deswelling.
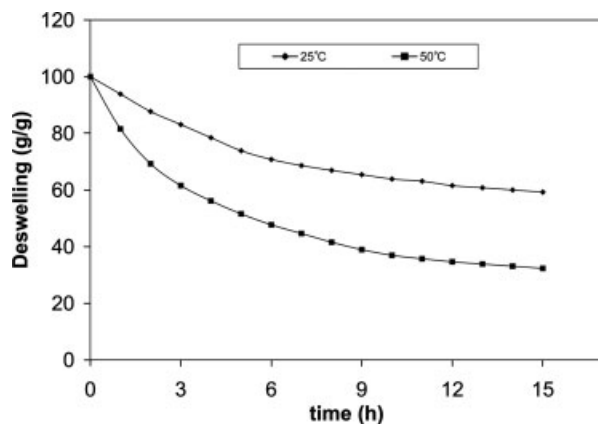

Figure 10 Time-dependent deswelling water ratio of the chitosan-sucrose hydrogels at 25 and 50°C.
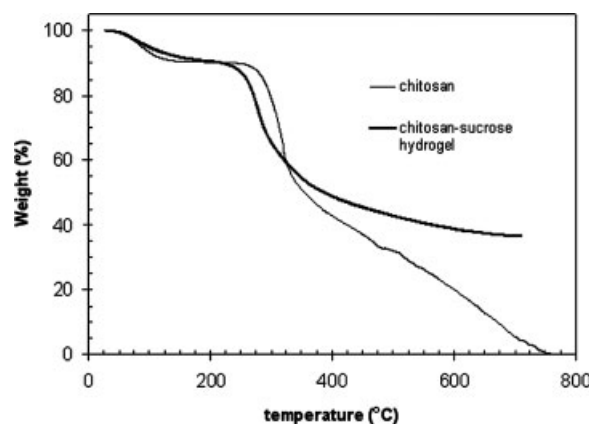
Figure 11 Thermogravimetric analysis (TGA) of chitosan and chitosan-sucrose hydrogel.

Figure 10 shows the ratio of the remaining water as a function of time dependent on the temperature. As shown in this figure, deswelling water ratio of the hydrogels indicate a weight reduction of about 40% at room temperature and about 65% from its original weight at 50°C after 15 h. As a result, the hydrogel has a good potential to hold the water at room temperature.

Thermal analysis

TGA method was used to thermally characterize the hydrogel in comparison with the intact polysaccharide (Fig. 11). A thermal analyzer (STA-625, Reometric Scientific) was used for thermogravimetric analysis (TGA) of chitosan and chitosan-sucrose hydrogel under nitrogen atmosphere. The heating rate was 20°C/min. Figure 11 shows that about 80% weight loss takes place at 600°C for chitosan, and it can degrade completely at 760°C. However, in the chitosan-sucrose hydrogel sample, a residual weight of 39% was observed at 600°C. The chitosan-sucrose hydrogel sample cannot degrade completely at 760°C, because inorganic salt exists in these remnants. Therefore, it may be concluded that crosslinking of chitosan improves its thermal stability. Similar results were reported by others which indicated that the chemical crosslinking of linear polymers may provide feasible route for the improvement of the thermal stability.[36–39]

CONCLUSIONS

A novel superabsorbent hydrogel based on chitosan was prepared using periodate oxidized sucrose as a new crosslinking agent. Swelling measurements of the synthesized hydrogel in different salt solutions showed appreciable swelling capacity, especially in AlCl₃ solution. The hydrogel has a good response to

external stimuli such as pH and ionic strength of the swelling media and good ability for pH reversible response. The hydrogel will most probably possess higher biodegradability due to natural part and lower toxicity, because no toxic material is used in the synthesis process. This practical approach may be preferred as a relative "green process." The smart hydrogels may have potential applications in the controlled delivery of bioactive agents and for wound-dressing application in the form of sheets or film.

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