Superabsorbency, pH-Sensitivity and Swelling Kinetics of Partially Hydrolyzed Chitosan-g-poly(Acrylamide) Hydrogels

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Acrylamide (AAm) monomer was directly grafted onto chitosan using ammonium persulfate (APS) as an initiator and methylenebisacrylamide (MBA) as a crosslinking agent under an inert atmosphere. Two factors affecting the swelling capacity of the obtained hydrogel, AAm and MBA concentrations, were studied. The polymer structures were characterized by FTIR spectroscopy. Water absorbencies of the hydrogels were compared between before and after the alkaline hydrolysis treatment. Saponification of chitosan-g-poly(acrylamide) (chitosan-g-PAAm) with a hot sodium hydroxide solution gave rise to a high water absorbency. Swelling of the hydrogel samples in saline solution (0.15 mol/L NaCl, $CaCl_2$ and $AlCl_3$) was examined. Swelling capacity of the chitosan-g-PAAm hydrogels in $CaCl_2$ and $AlCl_3$ solutions was higher than that of its hydrolyzed chitosan-g-PAAm (H-chitosan-g-PAAm) hydrogels. It was also indicated that the chitosan-g-PAAm and H-chitosan-g-PAAm hydrogels had different swelling capacities in various pHs. The latter hydrogel showed a pH-reversible property between 3 and 10. The swelling kinetics of both hydrogels were found to obey second-order kinetics.

Key Words: Chitosan, polyacrylamide, hydrogel, superabsorbent, pH-reversibility, swelling behavior

Introduction

In recent years, there has been considerable interest in water-swellable superabsorbent polymers capable of absorbing and holding a large amount of water while maintaining the physical dimension structure. Superabsorbents are 3-dimensional networks of hydrophilic polymers held together by crosslinks of covalent bonds or ionic and/or secondary forces in the form of hydrogen bonds or hydrophobic interactions[1−3]. Their affinity for water makes them useful, especially for agriculture, personal hygiene products, industrial absorbents, medicine and cosmetics[4−6].

Because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels. Graft

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copolymerization of vinyl monomers onto polysaccharides is an efficient route for the preparation of hydrogels. The hydrogel forming ability through graft copolymerization of vinyl monomers onto polysaccharides such as starch, chitosan, sodium alginate, carrageenan, and cellulose has been well documented[7−11]. Because of the presence of certain functional groups along the polymer chains, hydrogels are often sensitive to the conditions of the surrounding environment, which are referred to as "intelligent materials" or "smart materials". For example, the water uptake of these materials may be sensitive to temperature, pH, or ionic strength of the swelling solutions, or even to the presence of a magnetic field or ultraviolet light[12]. These smart hydrogels are of general interest for biomedical applications, such as artificial muscles or switches, biomedical separation systems, and controlled release systems.

Chitosan is a linear natural polysaccharide composed of a partially deacetylated material of chitin. It is a basic polymer, having amine side groups[13]. Due to its excellent biocompatibility and biodegradability, chitosan and its derivatives were widely applied in the fabrication of biomedical materials, enzyme and cell immobilization, especially for drug delivery. Since chitosan is easily soluble in acidic solutions, crosslinking of chitosan to form a network is the only way to prepare chitosan hydrogels. Conventional chitosan crosslinking reactions have involved a reaction of chitosan with formaldehyde and dialdehydes, such as glutaraldehyde, diglycidyl ethers, or epoxides[13]. By crosslinking chitosan with dialdehydes, one can obtain a hydrogel with a swelling ability in acidic media. When an anionic monomer such as acrylic acid is grafted onto chitosan (in the presence of a divinyl crosslinking agent monomer), an ampholytic hydrogel containing both cationic and anionic charges is prepared. Therefore, by introducing anionic charges (-COO$^-$) onto chitosan, a hydrogel with swelling ability at various pHs is prepared. In our previous studies, we reported the synthesis of novel ampholytic hydrogels by hydrolysis of chitosan-g-poly(acrylonitrile),[14] and binary graft copolymerization of the acrylamide (AAm) and acrylic acid monomers onto chitosan[15]. The present work examined the synthesis and swelling behavior of chitosan-g-PAAm hydrogels. In the partial hydrolysis of the grafted PAAm, the $-CONH_2$ groups of PAAm could be converted to COO^- groups, which resulted in a hydrogel with ampholytic properties.

Experimental

Materials

The chitosan sample was prepared from chitin (extracted from shrimp shell) in our laboratory[16]. The degree of deacetylation (DD), as determined by titration, was 0.76. Acrylamide (AAm, Fluka) was used after recrystallization from acetone (for removal of inhibitor) below 30°. Ammonium persulfate (APS) was used without purification. Methylenebisacrylamide (MBA, Fluka) was used as received. All other chemicals were of analytical grade.

Synthesis of hydrogels

Chitosan solution was prepared in a 1-L reactor equipped with a mechanical stirrer and an inert gas inlet (argon). Chitosan was dissolved in degassed, distilled water containing 1 wt% of acetic acid. In general, 0.50 g of chitosan was dissolved in 30.0 mL of the acetic acid solution. The reactor was placed in a water bath preset at 60°. Then 0.10 g of APS (0.015 mol/L in solution) was added to the chitosan solution and the resulting mixture was stirred for 10 min at 60°. Following this, AAm (2.0 g, 0.94 mol/L in solution)

was added to the chitosan solution. MBA (0.05 g, 0.01 mol/L in solution) as a crosslinker was added to the reaction mixture after the addition of monomer, and the mixture was continuously stirred for 1 h under argon atmosphere. After 60 min, the reaction product was allowed to cool to ambient temperature. The shape of the resulting hydrogel was bulk gel cut into small particles. The resulting hydrogel was neutralized to pH 8 by the addition of 1 N NaOH solution. Then methanol (500 mL) was added to the gel product while stirring. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2 × 50 mL), and dried at 50°.

The chitosan-g-PAAm (0.50 g) was then saponified using 20 mL of aqueous 1.0 N NaOH solution in a loosely stoppered 100-mL flask at 100° for 60 min. The hydrolyzed chitosan-g-PAAm (H-chitosan-g-PAAm) product was then allowed to cool to ambient temperature and neutralized to pH 8 by addition of 10 wt% acetic acid solutions. Methanol (200 mL) was added to the gel product while stirring. After complete dewatering (for 3 h), the yellow product was filtered, washed with fresh methanol (2 × 50 mL) and dried in an oven at 50°.

Infrared analysis

The dried samples were crushed with KBr to make pellets. Spectra were obtained on an ABB Bomem MB-100 FTIR spectrophotometer.

Swelling measurements

For determination of the water absorbency of the hydrogels, the particles were used with 40-60 meshes of amorphous shape. A chitosan-g-PAAm sample (0.10 g) was put into a weighed teabag and immersed in 100 mL of distilled water and allowed to soak for 2 h at room temperature. The equilibrated swollen gel was allowed to drain by removing the teabag from water ($\sim$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:

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

where W_s and W_d are the weights of the samples swollen in water and in dry state, respectively. Thus, absorbency was calculated as grams of water per gram of resin (g/g). The accuracy of the measurements was ±3%.

Swelling in buffer solutions

Two buffers with pH 3 and 10 were used to study of pH-reversibility of hydrogels. The following buffer solutions were used: pH 3 (H_3PO_4/NaOH, 0.1 mol/L of H_3PO_4 was titrated with 0.1 M of NaOH solution to achieve pH 3), and pH 10 ($NaHCO_3$/NaOH, 0.1 mol/L of $NaHCO_3$ was titrated with 0.1 M of NaOH solution to achieve pH 10). The pH values were checked precisely by a pH-meter (Metrohm/820, accuracy ±0.1). Then 0.10 g of dried sample was used for the swelling measurements in both buffers according to the above-mentioned method.

Swelling in salt solutions

Absorbency of chitosan-g-PAAm and H-chitosan-g-PAAM hydrogels was evaluated in 0.15 M aqueous solutions of NaCl, CaCl$_2$, and AlCl$_3$, according to the method described above for swelling measurements in distilled water.
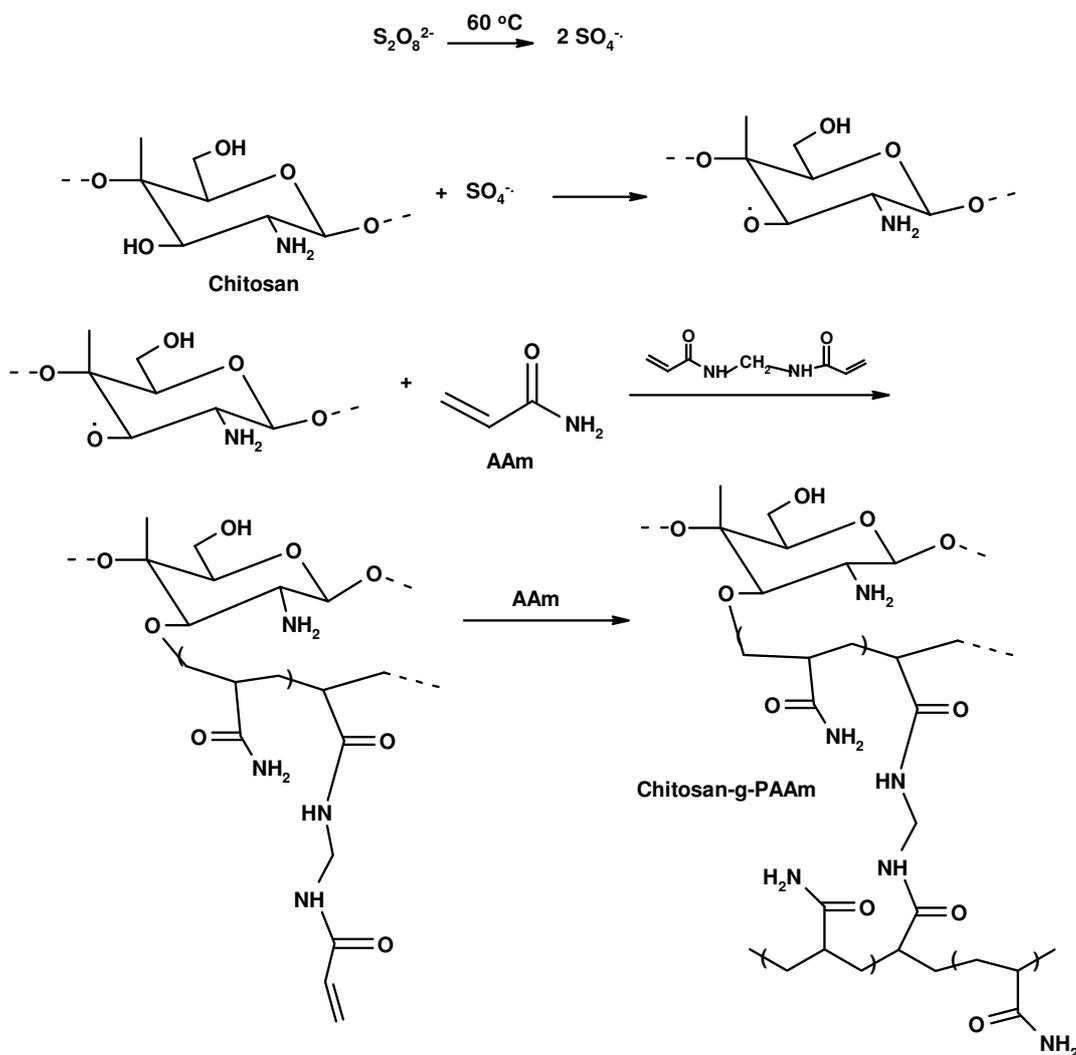
Scheme. General mechanism for APS-initiated graft copolymerization of acrylamide onto chitosan in the presence of MBA.

Results and Discussion

Synthesis and characterization

Superabsorbent hydrogels were prepared by graft copolymerization of acryl amide onto chitosan in the presence of MBA as a crosslinking agent. Ammonium persulfate was used as an initiator. The persulfate was decomposed under heating and produced sulfate anion-radicals that remove hydrogen from –OH groups of chitosan backbones. Therefore, this persulfate-saccharide redox system results in active centers capable

of radically initiating polymerization of AAm leading to graft copolymer. Since the crosslinking agent, MBA, is present in the system, the copolymer comprises a crosslink structure. A possible mechanism of the polymerization of acrylamide onto chitosan in the presence of MBA is shown in the Scheme.

To obtain a hydrogel with a high swelling capacity, the chitosan-g-PAAm hydrogel copolymer was hydrolyzed with NaOH solution, the hydrolyzed chitosan-g-PAAm being termed H-chitosan-g-PAAm. During the saponification, ammonia evolves and amide groups are converted to carboxylate salts. This reaction can be shown as below:
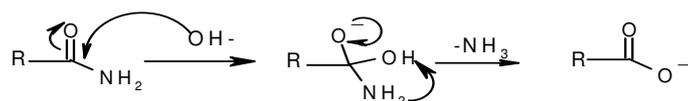
The absorbency, pH-sensitivity, and salt-sensitivity of these hydrogels were investigated. Figure 1 shows FTIR spectra of chitosan-g-PAAm and H-chitosan-g-PAAm hydrogels (in dried state). In the spectrum of chitosan-g-PAAm (Figure 1a), 2 band peaks at 3206 and 1660 cm^{-1} correspond to the primary amides and amide –NH stretching vibrations, respectively. Under saponification conditions, the amide groups were converted to carboxylate groups. In the hydrolyzed hydrogel (Figure 1b), the very intense characteristic band at 1566 cm^{-1} is due to C=O asymmetric stretching in the carboxylate anion that is reconfirmed by another sharp peak at 1406 cm^{-1}, which is related to a symmetric stretching mode of the carboxylate anion. A combination of absorptions of the carboxylate and alcoholic O-H stretching appears in the wide range of 2550–3500 cm^{-1} [17].
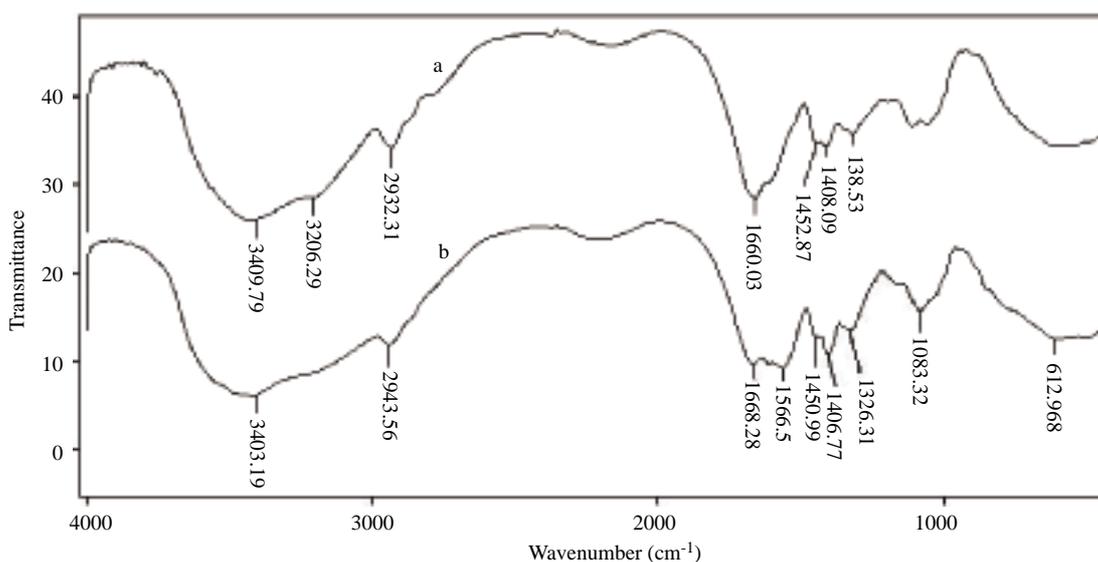

Figure 1. FTIR spectra of (a) chitosan-g-PAAm and (b) H-chitosan-g-PAAm.

Effect of crosslinker concentration on swelling of hydrogels

Crosslinking is necessary to form a superabsorbent hydrogel in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. The effect of MBA concentration on the water absorbency of the chitosan-g-PAAm and its hydrolyzed chitosan-g-PAAm hydrogels was examined by varying the MBA concentration from 0.0025 to 0.063 mol/L. All the other parameters in these series of reactions were constant.

As the concentration of MBA was increased, the water absorbency of both hydrogels decreased. The behavior is shown in Figure 2. This is due to a decrease in the space between the polymer chains as the crosslinker concentration is increased. This decreasing trend is similar to the cases found by us[15] and other groups for other superabsorbent hydrogels[18]. At a MBA concentration of 0.0025 mol/L, the swelling capacity of the hydrogel before and after hydrolyzing is 80 and 232 g/g, respectively.
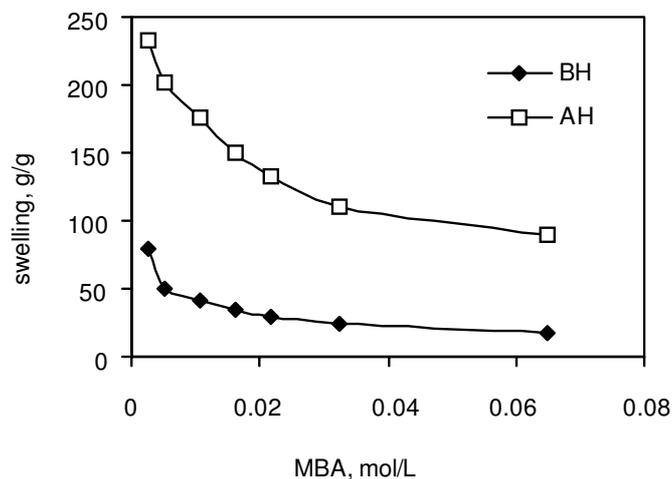

Figure 2. Effect of MBA concentration on the swelling capacity of chitosan-g-PAAm and H-chitosan-g-PAAm hydrogels. (AAm = 0.94 mol/L, APS = 0.015 mol/L, and the reaction volume was 30 mL). BH, before hydrolysis; AH, after hydrolysis.

Effect of the monomer concentration on swelling capacity

The dependence of the swelling capacity of hydrogels on AAm concentration is illustrated in Figure 3. In both hydrogels, before and after hydrolysis, with an increase in the AAm concentration their swelling capacity increased, reaching the maximum value of swelling capacity. The increase in swelling capacity in the initial stage may originate from the greater availability of monomer molecules in the vicinity of the chain propagating sites of chitosan macroradicals. In addition, higher AAm content enhances the hydrophilicity of the hydrogel in chitosan-g-PAAm and carboxylate salt in the H-chitosan-g-PAAm hydrogel that, in turn, causes a stronger affinity for more absorption of water. A further increase in monomer concentration, however, results in decreased absorbency. This is probably due to (a) preferential homopolymerization over graft copolymerization, (b) an increase in the viscosity of the medium, which hinders the movement of free radicals and monomer molecules, (c) the enhanced chance of chain transfer to monomer molecules, and (d) non-hydrolyzed amide groups of grafted and ungrafted PAAm chains.

Swelling in salt solutions

The swelling behavior of both hydrogels ([AAm] = 0.7 mol/L, [MBA] = 0.0025 mol/L) in aqueous solutions of 0.15 mol/L NaCl, $CaCl_2$ and $AlCl_3$ is shown in Figure 4. The swelling of the absorbents in saline solutions was appreciably decreased compared to the values measured in distilled water. This well-known phenomenon, commonly observed in the swelling of ionic hydrogels,[7] is often attributed to a screening effect of the additional cations causing a non-perfect anion-anion electrostatic repulsion, leading to a decreased

osmotic pressure (ionic pressure) difference between the hydrogel network and the external solution. The swelling capacity increases with a decrease in the charge of the metal cation ($Al^{3+} < Ca^{2+} < Na^+$). This may be explained by complexing ability arising from the coordination of the multivalent cations with carboxylate groups present in the hydrolyzed hydrogel. This ionic crosslinking mainly occurs at the surface of particles and makes them rubbery and very hard when they swell in Ca^{2+} or Al^{3+} solution. As shown in this figure, the swelling capacity of chitosan-g-PAAm in $CaCl_2$ and $AlCl_3$ solutions is higher than that of the hydrolyzed hydrogel. This phenomenon is due to the absence of ionic groups in chitosan-g-PAAm hydrogel, but in the hydrolyzed hydrogel the carboxylate groups cause complexing between ionic groups, so that the crosslink density increases and swelling capacity decreases.
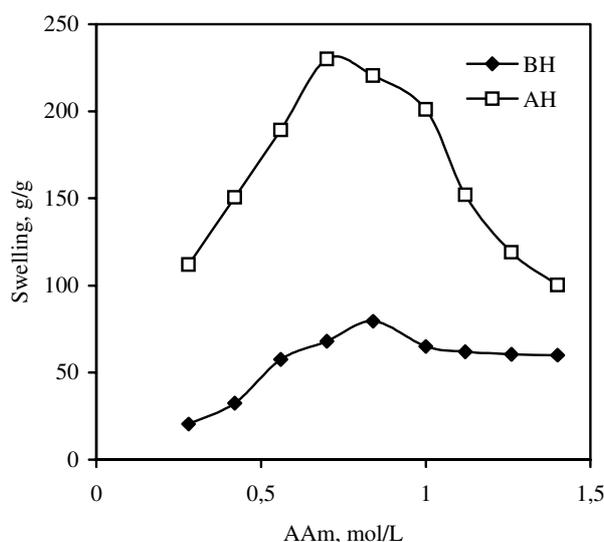

Figure 3. Effect of monomer concentration on the swelling capacity of chitosan-g-PAAm and H-chitosan-g-PAAm hydrogels. (MBA = 0.01 mol/L and APS = 0.015 mol/L, and the reaction volume was 30 mL). BH, before hydrolysis; AH, after hydrolysis.
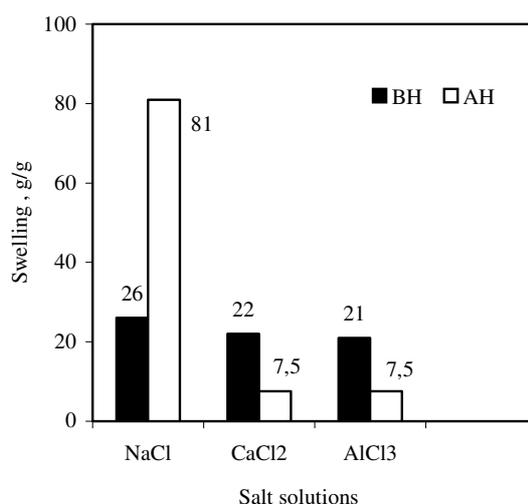

Figure 4. Swelling capacity of hydrogels in salt solutions (0.15 mol/L) before and after hydrolysis. AH, after hydrolysis; BH, before hydrolysis.

To make a comparative measure of the sensitivity of the hydrogels to the sort of aqueous fluid, we defined a dimensionless swelling factor, f, as follows:

$$f = 1\text{-(Absorption in a given fluid/Absorption in deionized water)} \tag{2}$$

The f values are given in Figure 5. The effect of increasing cation charge on the ultimate absorption for the chitosan-g-PAAm and hydrolyzed chitosan-g-PAAm hydrogels can be found from the values, so that the lower the cation charges, the lower the salt sensitivity.
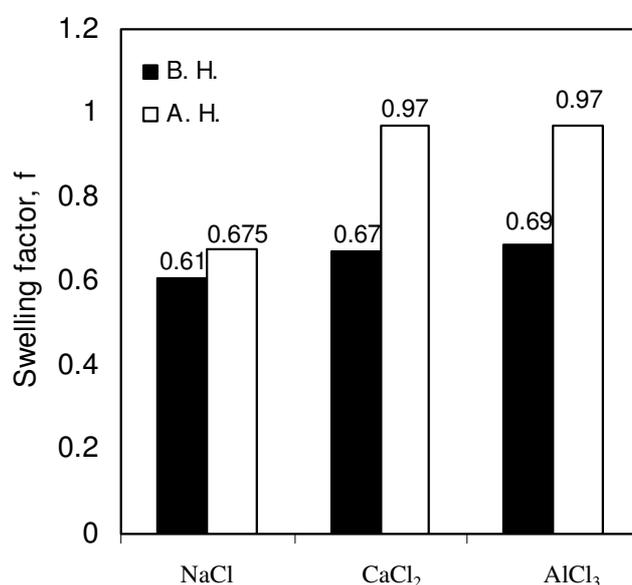

Figure 5. Dependence of the dimensionless salt sensitivity (f) for non-hydrolyzed and hydrolyzed chitosan-g-PAAm hydrogels on the valance of the metal cation (0.15 molar solutions). AH, after hydrolysis; BH, before hydrolysis.

Effect of pH on equilibrium swelling

Figure 6 represents pH dependence of the equilibrium swelling for chitosan-g-PAAm and H-chitosan-g-PAAm hydrogels at ambient temperature (25° C). The equilibrium swelling (ultimate absorbency) of the hydrogels was studied at various pHs ranging from 1.0 to 13.0. No additional ions (through buffer solution) were added to the medium for setting pH because the absorbency of a superabsorbent is strongly affected by ionic strength[4]. In addition, it has been reported that the swelling properties of polybasic gels are influenced by buffer composition (composition and pK_a)[19]. Therefore, stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach the desired basic and acidic pHs, respectively.
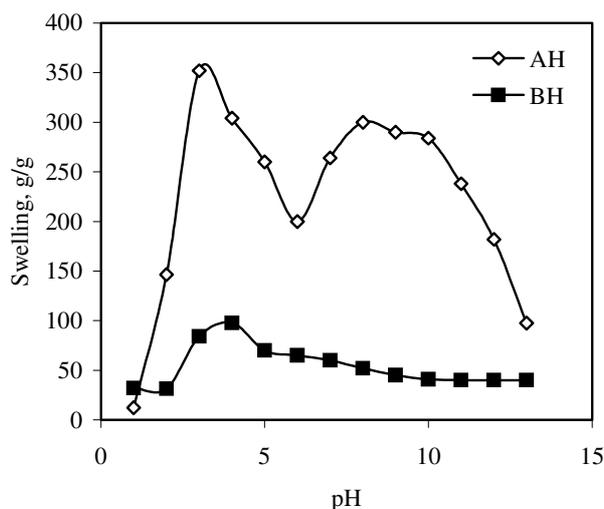
Figure 6. Swelling behavior of chitosan-g-PAAm and H-chitosan-g-PAAm at various pHs. AH, after hydrolysis; BH, before hydrolysis.

The effective pKa for chitosan is 6.5 and that for carboxylic acid groups is ~4.7. In the case of chitosan-g-PAAm, which contains amine groups, the maximum degree of swelling of the hydrogel was attained at pH 3, this being due to the complete protonation of amine groups of chitosan at this pH value. With the saponification of chitosan-g-PAAm hydrogel, the amide groups are converted to carboxylate groups. In Figure 6, the dependence of the equilibrium swelling of the H-chitosan-g-PAAm hydrogel is characterized by a curve with 2 maxima at pH 3 and 8. The remarkable swelling changes are due to the presence of different interacting species depending on the pH of the swelling medium. It can be assumed that H-chitosan-g-PAAm includes chitosan, poly(acrylic acid) (PAA) and poly(acrylamide) structures. The structures of chitosan and PAA are unsizable. Therefore, based upon pK_a of PAA (~4.7) and pK_a of chitosan (6.5), the species involved are NH_3^+ and COOH (at pH 1-3), NH_2 and COO^- (at pH 7-13) and NH_3^+ and COO^- or NH_2 and COOH (at pH 4-7). Under acidic conditions, the swelling is controlled mainly by the amino group (NH_2) on the C-2 carbon of the chitosan component. It is a weak base with an intrinsic pK_a of about 6.5,[19] and so it gets protonated and the increased charge density on the polymer should enhance 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. However, under very acidic conditions (pH < 3), a screening effect of the counter ion, i.e. Cl^-, shields the charge of the ammonium cations and prevents an efficient repulsion. As a result, a remarkable decrease in equilibrium swelling is observed (gel collapsing). At pH > 4.7, the carboxylic acid component comes into action as well. Since the pK_a of the weak polyacid is about ~4.7, its ionization occurring above this value may favor enhanced absorbency. However, under pH 6.4, or in a certain pH range, 4-7, the majority of the base and acid groups are as NH_3^+ and COO^- or NH_2 and COOH forms, and therefore ionic interaction of NH_3^+ and COO^- species (ionic crosslinking) or hydrogen bonding between amine and carboxylic acid (and probably carboxamide groups) may lead to a kind of crosslinking followed by decreased swelling. At pH 8, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes an increase in swelling. Again, a screening effect of the counter ions (Na^+) limits the swelling at pH 9-13. In fact, at high and low pHs, the presence of high concentrations of the ions results in

high ionic strength. When the ionic strength of the solution is increased, the difference in osmotic pressure between the hydrogel and the medium is decreased. Thus the swelling capacity of the hydrogel is decreased.

The pH-dependent swelling reversibility of the H-chitosan-g-PAAm hydrogel was examined in buffered solutions. A typical result of the pulsatile reversible swelling of H-chitosan-g-PAAm is shown in Figure 7. The figure demonstrates the hydrogel reversibility to absorb water upon changing the pH in acidic and basic regions (3↔ 10).
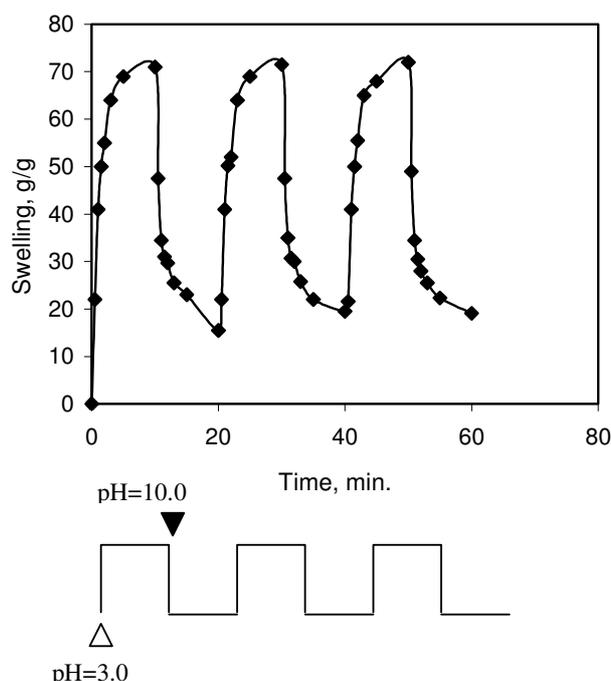

Figure 7. On-off switching behavior as reversible pulsatile swelling (pH 3.0) and deswelling (pH 10.0) of the pH-responsive hydrogel, H-chitosan-g-PAAm.

Swelling kinetics

A preliminary study was conducted on the hydrogel swelling kinetics. Figure 8 represents the dynamic swelling behavior of chitosan-g-PAAm and H-chitosan-g-PAAm hydrogel samples. The particle size of hydrogel affects the kinetics of water uptake, and so the rate of swelling of hydrogels was examined with samples with certain particle size (40-60 mesh). Initially, the rate of water uptake sharply increases and then begins to level off. A power law behavior is obvious from Figure 8. The data may be well fitted with a Voight-based equation:[20]

$$S_t = S_e(1 - e^{-t/\tau}) \tag{3}$$

where S_t is swelling at time t (g/g), S_e is the equilibrium swelling ("power parameter", g/g), t is time (min) for swelling S_t, and τ stands for a "rate parameter" (time for S_τ), min. The rate parameters for the non-hydrolyzed and hydrolyzed gels are found to be 2.5 and 1.3 min, respectively. Since τ is a measure of the resistance to water permeation, the lower the τ value, the higher the rate of water uptake will be.
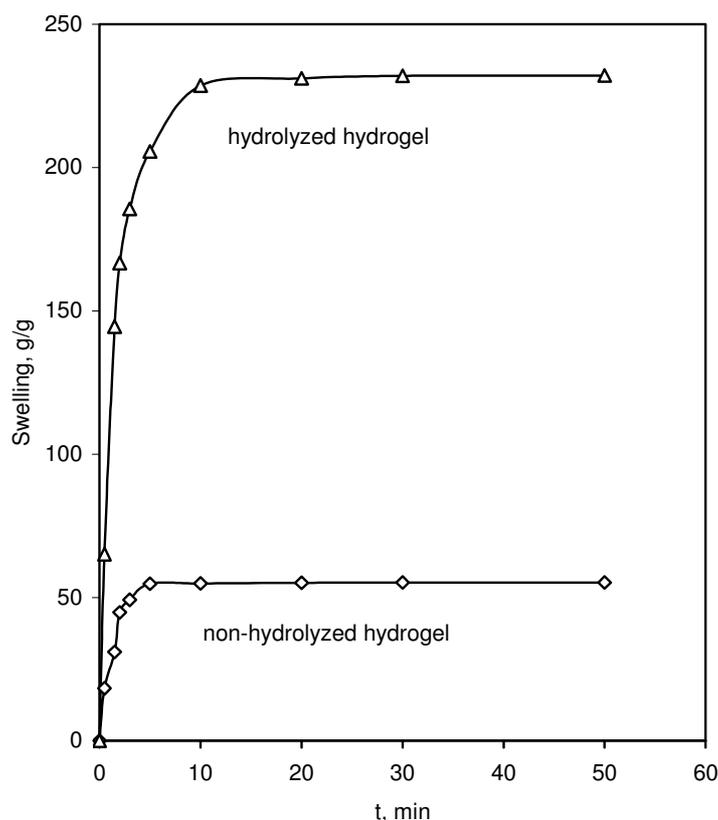
Figure 8. Swelling ratio as a function of time for chitosan-g-PAAm hydrogel before and after hydrolysis.

The rate of water uptake in the hydrolyzed hydrogel is higher than that of the non-hydrolyzed hydrogel, according to the smaller τ value of the hydrolyzed hydrogel; it swells faster than its non-hydrolyzed counterpart. This difference can originate from more hydrophilic groups (COO^-) in the hydrolyzed hydrogel. In addition, it may also be attributed to a possible porosity of particles, originating from the alkaline hydrolysis. In the course of the hydrolysis, the reaction mixture becomes gelly or pasty, which prevents the removal of the evolved NH_3 and water vapors from the pasty medium (see Experimental). Therefore, the removed vapors create porosity in the gel. The porosity favors faster water diffusion through the hydrogel network.

We analyzed the swelling kinetics to see whether the swelling follows first-order or second-order kinetics. We adopted the procedure proposed by Quintana et al.[21]. For first-order kinetics, the rate of swelling at any time t is directly proportional to the water content that the hydrogel has to obtain before the equilibrium water content $W\infty$ is reached. The swelling is then expressed as

$$\frac{dW}{dt} = K(W_\infty - W) \qquad (4)$$

where W is the water content of the hydrogel at time "t", and K is the proportionality constant between the swelling rate and the unrealized swelling capacity W_∞-W.

Upon integration of Equation 4 between the limits t = 0 to t and W = 0 to W, the following expression can be obtained:

$$\ln \frac{W_\infty}{W_\infty - W} = Kt \qquad (5)$$

If the swelling process of the hydrogel considered follows first-order kinetics, the plot of the variation of ln $(W_\infty/W_\infty-W)$ as a function of time should give a straight line. However, none of the swelling studied distilled water followed Equation 5, as is clear from Figure 9.
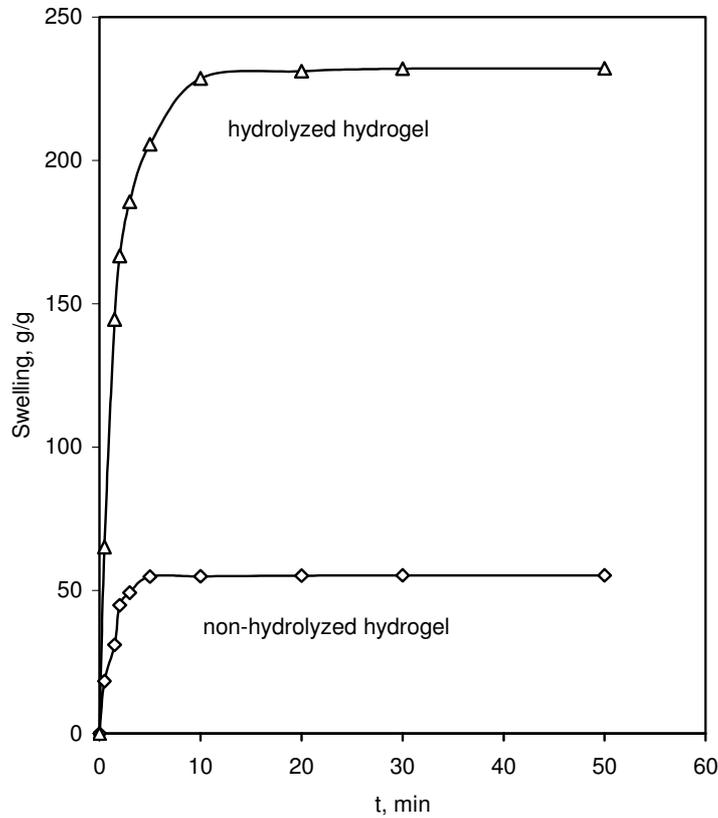

Figure 9. A plot of water content W and time according to Equation 5 (first-order kinetics) for both hydrogels.

Considering second-order kinetics, the swelling rate at any time may be expressed as

$$\frac{dW}{dt} = K(W_\infty - W)^2 \tag{6}$$

Integration of Equation 6 with the limits $t = 0$ to t and $W = 0$ to W and after rearrangement, Equation 7 is obtained:

$$\frac{t}{W} = \frac{1}{KW_\infty^2} + \frac{1}{W_\infty}t \tag{7}$$

According to this equation, the swelling data must fit a straight line with a slope of $1/W_\infty$ and an ordinate intercept of $1/KW_\infty^2$. The variation of t/W against time is plotted in Figure 10 for hydrogel samples of chitosan-g-PAAm and H-chitosan-g-PAAm. It was found that the swelling data for both hydrogels give a straight line. Therefore, the swelling behaviors of both hydrogels obey second-order kinetics.
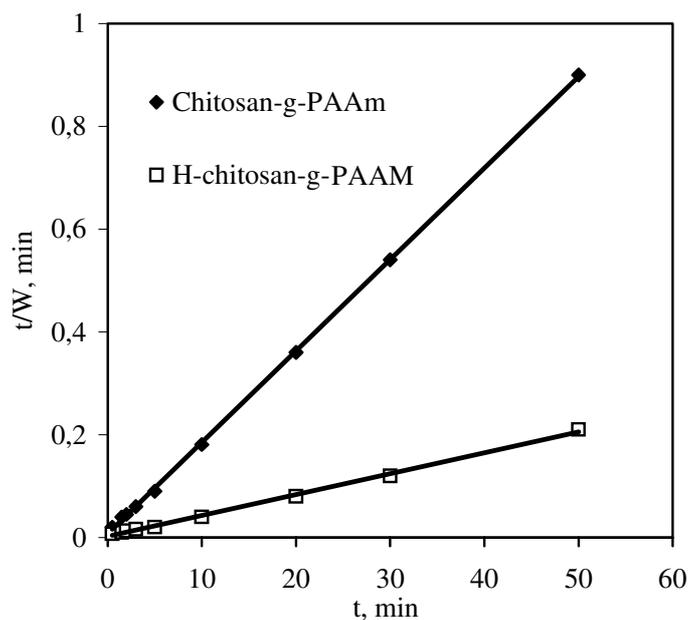
Figure 10. Water content W versus time t plotted according to Equation 7 (second-order kinetics) for 2 hydrogel samples.

Conclusion

Superabsorbent hydrogels, Chitosan-g-PAAm and H-chitosan-g-PAAm, were synthesized through grafting of AAm onto chitosan and saponification of chitosan-g-PAAm, respectively. Swelling capacity of the hydrogels was found to be affected by monomer and crosslinker concentrations. The swelling of the hydrogels exhibited a high sensitivity to pH. The net effect of H^+/OH^- concentration was examined at various pHs in the absence of any buffer solution. One large, sharp volume change was observed for chitosan-g-PAAm versus small pH variations. Ionic repulsion of protonated groups in acidic solutions causes volume change. In the hydrolyzed hydrogel 2 sharp volume changes were observed. The hydrolyzed hydrogel has both amine and carboxylic groups. Ionic repulsion between charged groups incorporated in the gel matrix by an external pH modulation could be assumed to be the main driving force responsible for such abrupt swelling changes. They also exhibited ampholytic nature of pH-responsiveness in swelling behavior. We investigated their swelling in different salt solutions and in media with a wide range of pHs. The pH-reversibility of the hydrolyzed hydrogel (swelling/deswelling process) at pH 3.0 and 10 was also studied. This hydrogel polyampholytic network intelligently responding to pH may be considered an excellent candidate for the design of novel drug delivery systems.

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