Salt sensitivity, pH responsivity and kinetic study of chitosan-g-PAA hydrogel

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Abstract

Acrylic acid (AA) 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, AA and MBA concentrations, were studied. The polymer structures were characterized by FTIR spectroscopy. Maximum water absorbency of the optimized final product was found to be 434 gr/gr. Also, I studed manner swelling of product in different solution salty. results shown that the swelling capacity decreased with increasing of ionic strength. Farthermore, the swelling of superabsorbant hydrogel was measured in various Solutions with PH values ranging from 1 to 12. the hydrogels exhibited the highest swelling at PH 3 and8. also the swelling kinetics in distilled water investigated.

Keywords: chitosan, Superabsorbent, Hydrogel, Acrylic acid, swelling kinetics.

Introduction

The history of chitosan dates back to the 19th century,when Rouget[1] discussed the deacetylated forms of the parent chitin natural polymer in 1859. During the past 20 years, a substantial amount of work has been reported on chitosan and its potential use in various bioapplications. Chitosan is derived from naturally occurring sources, which is the exoskeleton of insects, crustaceans and fungi that has been shown to be biocompatible and biodegradable.[2] Chitosan polymers are semi-synthetically derived aminopolysaccharides that have unique structures, multidimensional properties, highly sophisticated functionality

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and a wide range of applications in biomedical and other industrial areas.[3-5] They have become interesting not only because they are made from an abundant renewable resource but because they are very compatible and effective biomaterials that are used in many applications.[6-8]

Loosely crosslinked hydrophilic polymers (hydrogels) being able to absorb and retain hundreds of their own weight of water are known as superabsorbents. They are mainly used in sanitary goods for absorbing the body fluids and in soil conditioning and improving water retention capability of soil in agriculture and horticulture.[9] They are also found to be valuable in some specialized applications, including controlled delivery of bioactive agents. Specifically engineered hydrogels may act intelligently, i.e., respond with large changes to small physical or chemical stimuli such as temperature and pH. These responsive or smart hydrogels have become an important area of research and development in the field of medicine, pharmacy and biotechnology.[10,11] Superabsorbing resins were first developed with a view to utilizing agricultural materials, and are typified by the hydrolyzed corn starch-*g*-poly(acrylonitrile), H-SPAN.[12,13] Since then, starches from different resources5 as well as other polysaccharides, for example, cellulose,[14,15] hydroxyethyl cellulose,[16,17] agar, sodium alginate,[18,19] and guar gum[20] were graft copolymerized to achieve water absorbing polymers. Polyacrylonitrile (PAN), polyacryamide, and poly(acrylic acid)[21] have been frequently grafted, mostly onto starch, using different initiators especially the cericsaccharide redox system.[22]

EXPERIMENTAL

Materials

The chitosan samples with different MWs (260, 1134, and 2227 kg mol_1) and constant DDA (48 wt%) were purchased from Fluka Chemical Company. Acrylic acid (AA) was purchased from from Merck Chemical Company. (Germany), and were distilled before use. Ammonium persulfate (APS) was used without purification. Methylenebisacrylamide (MBA, Fluka) was used as received. All other chemicals were of analytical grade.

Hydrogel preparation

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 65◦. 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 65◦. Following this, AA (2.0 g) 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 (250 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◦.

Infrared spectroscopy

IR spectra of samples were taken in KBr pellets using a ABB Bomem- MB-1000 FTIR spectrophotometer.

Absorbency measurements

A chitosan-g-PAA sample (0.1 g) was put into a weighed teabag and immersed in 100 mL 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 and hanging until no drop drained ~20 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency was calculated using the following equation:

$$\text{Absorbency} = (Ws\ \_Wd)/Wd \qquad (1)$$

where *Ws* and *Wd* are the weights of the swollen gel and the dry sample, respectively. So, 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(H3PO4/NaOH, 0.1 mol/L of H3PO4 was titrated with 0.1 M of NaOH solution to achieve pH 3), and pH 10 (NaHCO3/NaOH, 0.1 mol/L of NaHCO3 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-PAA hydrogels was evaluated in value different Aqueous solutions of NaCl, $CaCl_2$, and $AlCl_3$, according to the method described above for swelling measurements in distilled water.

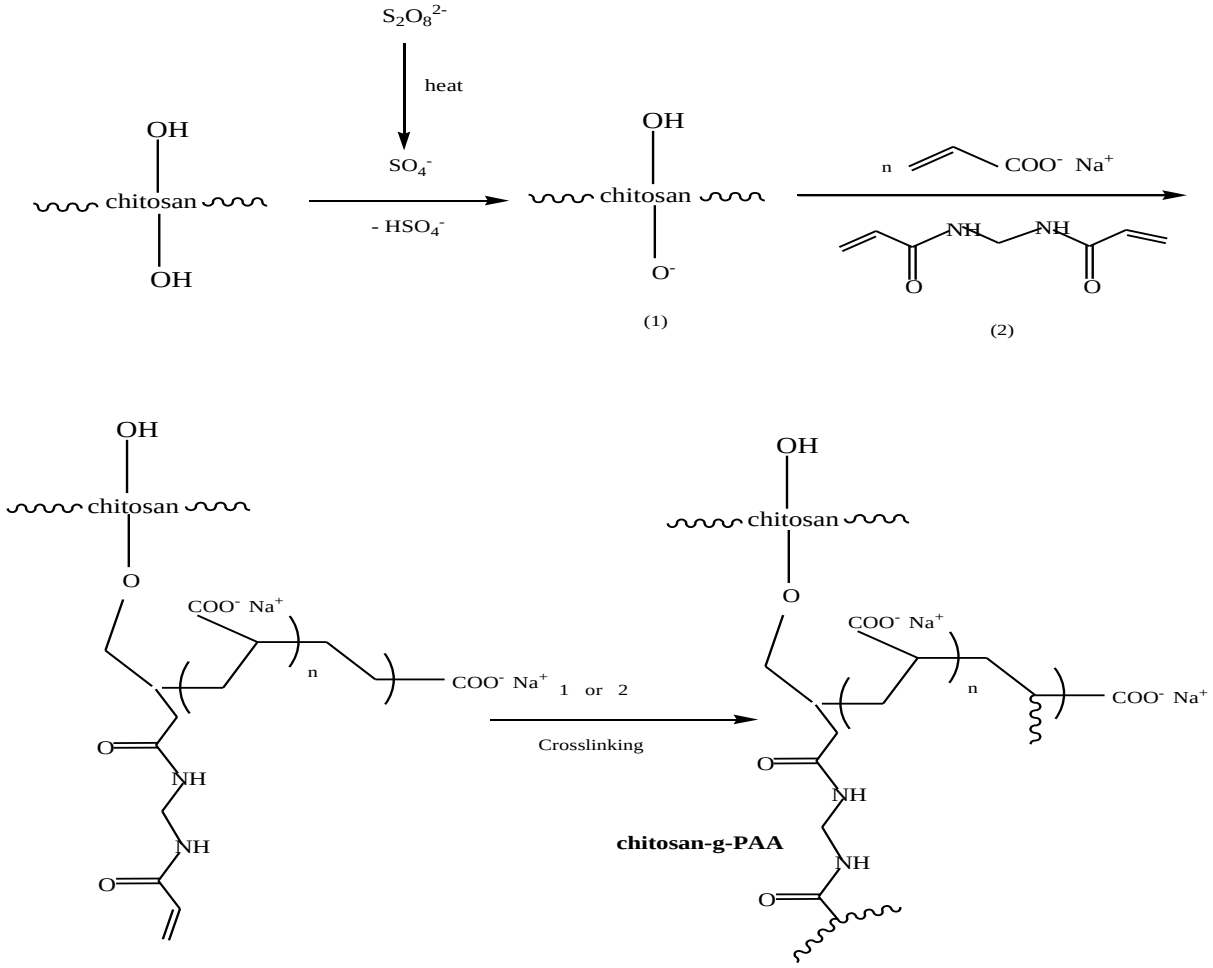

Figure 1. Proposed mechanism for APS-initiated graft copolymerization of acrylic acid onto chitosan in the presence of MBA.

Results and Discussion

Synthesis and characterization

Superabsorbent hydrogels were prepared by graft copolymerization of acrylic acid 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 AA 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 acrylic acid onto chitosan in the presence of MBA is shown in the(Figure 1). In the spectrum of chitosan-g-PAA (Figure2), 2 band peaks at 1564 and 1450 cm^{-1} correspond to the primary symmetric anion carboxylate and asymmetric anion carboxylate stretching vibrations, respectively.

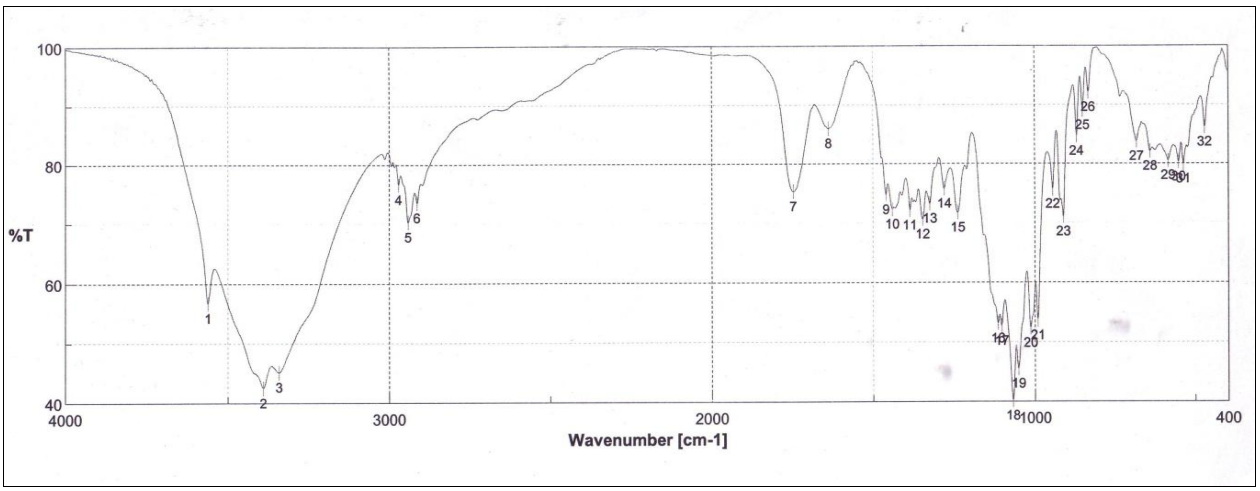

Figure 2. FTIR spectra of chitosan-g-PAA hydrogel

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-PAA hydrogels was examined by varying the MBA concentration from 0.001 to 0.1 mol /L. All the other parameters in these series of reactions were constantAs the concentration of MBA was increased, the water absorbency of both hydrogels decreased. The behavior is shown in Figure 3. 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 and other groups for other superabsorbent hydrogels.[23] At a MBA concentration of 0.003 mol/L, the swelling capacity of the hydrogel 94g/g.

Effect of the monomer concentration on swelling capacity

The dependence of the swelling capacity of hydrogels on AA concentration is illustrated in Figure 4.

In hydrogels, with an increase in the AA 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 AA content enhances the hydrophilicity of the hydrogel in chitosan-g-PAA 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.

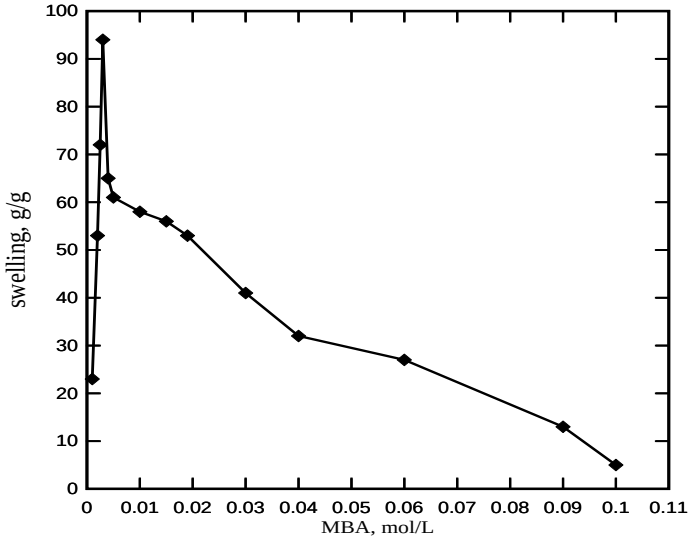

Figure 3. Effect of MBA concentration on the swelling of chitosan-g-PAA hydrogels.

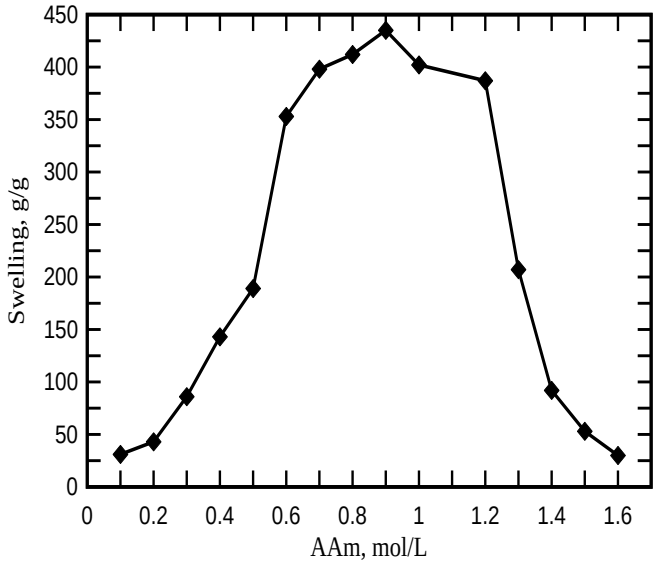

Figure 4. Effect of monomer concentration on the swelling capacity of chitosan-g-PAA hydrogels.

Swelling in salt solutions

The swelling capacity of superabsorbent hydrogels could be significantly affected by various factors of the external solutions such as its valencies and salt concentration. The presence of ions in the swelling medium has a profound effect on the absorbency behaviour of the superabsorbent hydrogels. Many theories were reported in the case of swelling behaviour of ionic hydrogels in saline solutions. The simplest one of the theories is Donnan equilibrium theory. This theory attributes the electrostatic interactions (ion swelling pressure) to the difference between the osmotic pressure of freely mobile ions in the gel and in the outer solutions. The osmotic pressure is the driving force for swelling of superabsorbents. Increasing the ionic mobile ion concentration difference between the polymer gel and external medium which, in turn, reduces the gel volume, *i.e.* the gel shrinks and swelling capacity decreases (charge screening effect). In addition, in case of salt solutions with multivalent cations, ionic crosslinking at surface of particles causing an appreciably decrease in swelling capacity. For example, Castel *et al*. reported that calcium ion can drastically decrease the swelling capacity for a hydrolyzed starch-graftpolyacrylonitrile, due to the complexing ability of the carboxylate group to include the formation of intra- and inter-molecular complexes. The effect of charge of cation on swelling can be concluded from Fig. 5. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency of the synthesized hydrogel is in the order of NaCl > $CaCl_2$ > $AlCl_3$. Fig. 5 also shows the swelling capacity of the hydrogel [chitosan-g-PAA], as a function of the salt concentration for NaCl, $CaCl_2$ and $AlCl_3$ solutions. The results reveal that the swelling ratio decreases as the salt concentration of the medium increases.

Effect of pH on equilibrium swelling

Figure 6 represents pH dependence of the equilibrium swelling for chitosan-g-PAA 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. In addition, it has been reported that the swelling properties of polybasic gels are influenced by buffer composition (composition and p*Ka*). 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. The effective pKa for chitosan is 6.5 and that for carboxylic acid groups is ~4.7. In the case of

chitosang- PAA, 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. In Figure 6, the dependence of the equilibrium swelling of the chitosan-g-PAA 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 chitosan-g-PAA 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 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 inhigh 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.

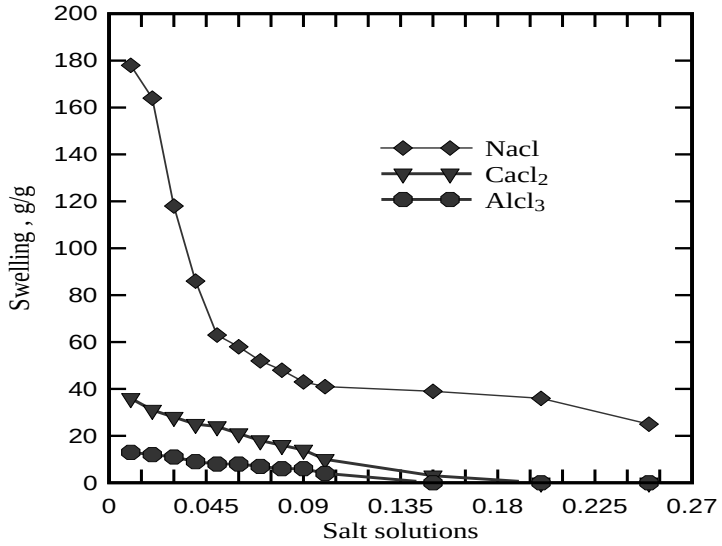

Figure 5. Swelling capacity of hydrog in salt solutions with different size of catio

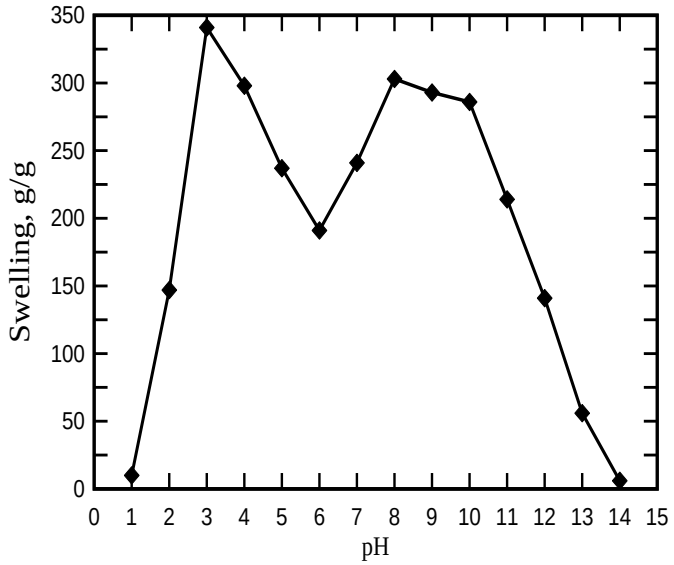

Figure 6. Swelling behavior o chitosan-g- PAA at various pHs

Swelling kinetics

A preliminary study was conducted on the hydrogel swelling kinetics. Figure 7 represents the dynamic

swelling behavior of chitosan-g-PAA 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 (100- 400 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:

$$St = Se(1 - e^{-t/\tau}) \qquad (2)$$

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 Sτ), min. The rate parameters for the

hydrogels are found to be 2.8 and 1.6 m in, 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.

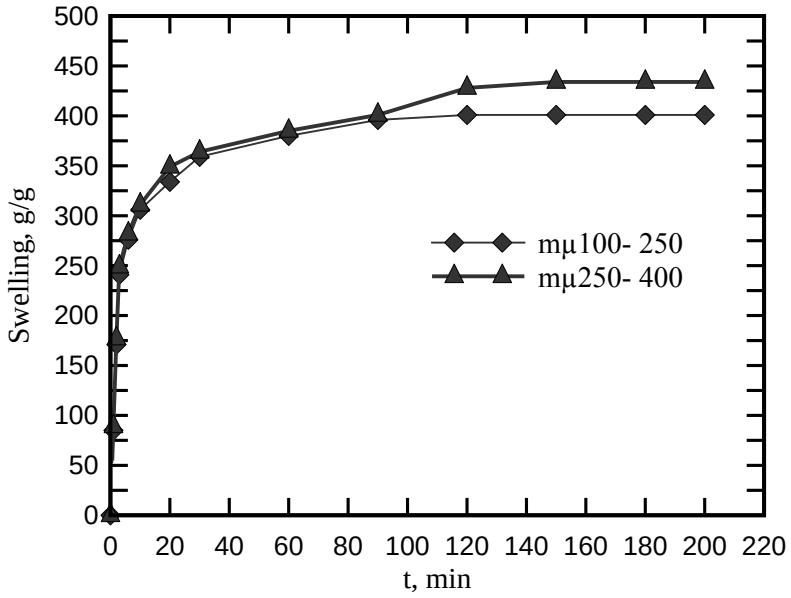

Figure 7. Swelling ratio as a function of time for chitosan-g-PAA hydrogel with different particle size

Conclusion

Superabsorbent hydrogels, Chitosan-g-PAA were synthesized through grafting of AA onto chitosan. 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-PAA versus small pH variations. Ionic repulsion of protonated groups in acidic solutions causes volume change. 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. TheThis 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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