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Effect of pH, and Salinity onto Swelling Properties of Hydrogels Based on H-alginate-g-poly(AMPS)

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To following synthesis of a novel superabsorbent hydrogel based on alginate, the swelling of superabsorbing hydrogels was examined in solutions with pH values ranging between 1.0 and 13.0. It showed a reversible pH-responsive behavior at pHs 2.0 and 8.0. The swelling measurements of the hydrogels were also conducted in aqueous solutions of LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, and $AlCl_3$. Results indicated that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. Due to the high swelling capacity in salt solutions, the hydrogels may be referred to as anti-salt superabsrbents.

Key words: Alginate, hydrogel, pH-responsive, anti-salt.

The term hydrogel is used to describe materials that are three-dimensional, hydrophilic, polymeric networks capable of imbibing large amounts of water or biological fluids. These hydrogels exhibit a thermodynamic compatibility with water that allows them to swell in aqueous media. Hydrogels are best considered as polymeric materials, which are able to swell in water and retain a significant fraction of water within their structure, but do not completely dissolve in water[1-3]. Hydrogels have received considerable interest due to their variety of biomedical and biotechnological applications.

The hydrogels based on synthetic polymers such as poly(acrylamide) and poly(sodium acrylate) have large amount swelling capacity, but hydrogels based natural polymers have a greater demand in industry due to their low cost and also because of the large amount of natural polymers in these hydrogels which render them biodegradable and thus environmental friendly[4]. The polysaccharides (natural polymer) are widely distributed in nature. Of the many kind of polysaccharides, alginate is once of the most important biomass resource. Graft copolymerization of vinylic monomers is an efficient rout to modification of the polysaccharides to results in new materials with different properties. In this work, we attempted to that water absorbency in saline solutions and various pHs was studied.

EXPERIMENTAL

Materials

Sodium alginate (chemical grade, MW 50000), N',N'-methylene bisacrylamide (MBA, from Fluka), ammonium persulfate (APS, from

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Fluka), 2-acrylamido-2-methylpropanesulfonic acid (AMPS, from Merck) were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Procedure to Graft Copolymerization

Synthesis of the hydrogel, H-alginte-g-poly(AMPS), was carried out using APS as an initiator and MBA as a crosslinker in an aqueous medium. A general procedure for crosslinking graft copolymerization of AMPS onto alginte was conducted as follows. alginate (0.25-1.00 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 40 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at desired temperature (45-85 ^{o}C). After complete dissolution of alginte, various amounts of the initiator solution (0.01-0.40 g APS in 5 mL H_2O) were added to the mixture. After stirring for 10 min, certain amounts of monomer (0.2-1.4 g in 5 mL H_2O) and MBA (0.08-0.15 g in 5 mL H_2O) were simultaneously added to the reaction mixture. After 60 min, the produced hydrogel was poured to excess non-solvent ethanol (200 mL) and remained for 3 h to dewater. Then ethanol was decanted and the product scissored to small pieces (diameter ~5 mm). Again, 100 mL fresh ethanol was added and the composite hydrogel was remained for 24 h. Finally, the filtered composite is dried in oven at 60 ^{o}C for 10 h. After grinding, the powdered superabsorbent was stored away from moisture, heat and light.

Swelling Measurements Using Tea Bag Method

The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) was immersed entirely in 200 mL distilled water and allowed to soak for 3 h at room temperature. The sample particle sizes were 40 to 60 meshes (250-350 µm). The tea bag was hung up for 15 min in order to remove the excess solution. The equilibrium swelling (*ES*) was calculated according to following equation:

$$ES\ (g/g) = \frac{Weight\ of\ swollen\ gel - Weight\ of\ dried\ gel}{Weight\ of\ dried\ gel} \quad ...(1)$$

Swelling in Various Salt Solutions

Absorbency of the alginate-g-poly(AMPS) hydrogel was evaluated in 0.15 M solutions of LiCl, NaCl, KCl,CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ according to the above method described for swelling measurement in distilled water. In addition, swelling capacity of the hydrogel was measured in different concentration (0.005-0.25 M) of $BeCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ salt solutions.

Absorbency at Various pHs

Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 10.0) and HCl (pH 1.0) solutions to achieve pHe"6.0 and pH<6.0, respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ±0.1). Then, 0.5 g (± 0.001 g) of the dried hydrogel was used for the swelling measurements according to Eq. 1.

pH-sensitivity

pH-sensitivity of the hydrogel was investigated in terms of swelling and deswelling of the final product at two basic (pH 8.0) and acidic (pH 2.0) solutions, respectively. Swelling capacity of the hydrogels at each pH was measured according to Eq. 1 at consecutive time intervals (30 min).

RESULTS AND DISCUSSION

Swelling in Salt Solutions

The swelling capacity of "ionic" absorbents is significantly affected by various factors of the external solution. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing to the swelling values in distilled water. This well-known undesired swelling-loss is often attributed to a "charge screening effect" of the additional cations causing a non-perfect anion-anion electrostatic repulsion[5-6]. Therefore, the osmotic pressure resulted from the mobile ion concentration difference between the gel and aqueous phases decreased and consequently the absorbency amounts decreased. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciably decrease in swelling capacity. It is obvious that swelling decrease is strongly depended on the "type" and "concentration" of salt added to the swelling medium.

To study the effect of cation radius on swelling behaviors, the equilibrium swelling absorbency was measured in two series of 0.15

M chloride salt solutions of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}. As a result, swelling of the synthesized hydrogels in KCl solution is lower than in LiCl and in NaCl solutions (swelling capacity in LiCl and NaCl solutions is almost equal but in KCl solution decrease in absorbency is observed). Similar results are also observed in the case of chloride solutions of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} (Fig. 1-2). The stronger interaction between sulfunate groups of AMPS monomers and large cations have been observed by Pass *et al.,*[10]. Therefore, swelling capacity of these hydrogels in salt solutions was not significantly decreased in comparison with water absorbency values.This anti-salt behavior is due to presence of lots of sulfunate groups in AMPS parts with high ionization tendency and low salt-sensitivity characteristics. Since the sulfonate ions do not keep cations in their vicinity, the "charge screening effect" is not so effective. Similar results were obtained in previous work[11].

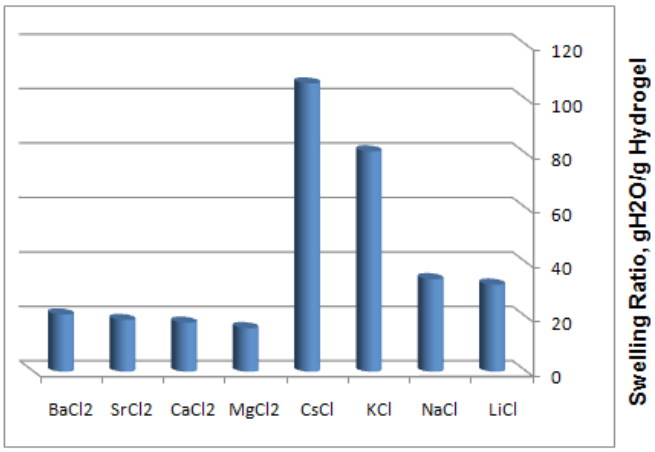

Fig. 1. Swelling capacity of the H-gelatin-g-poly(AMPS) hydrogel in different chloride salt solutions (0.15M)

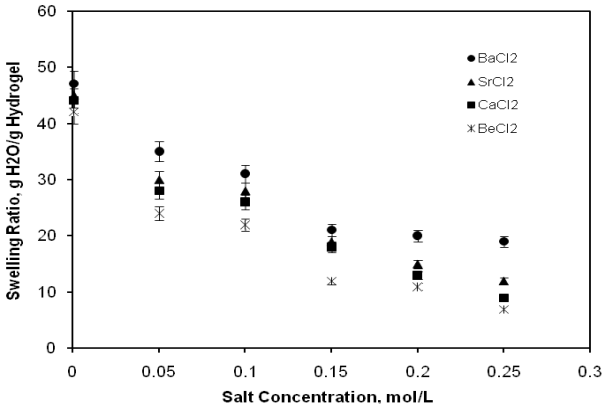

Fig. 2. Swelling capacity variation of superabsorbent hydrogel in different saline solutions with various concentrations in divalent cations

Effect of pH on Equilibrium Swelling

In this series of experiments, swelling ratio for the synthesized hydrogels was measured in different pH solutions ranged from 1.0 to 13.0 (Fig. 3). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 10.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (95 g/g) was obtained at pH 8. In acidic media,

the most of solfunate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio[7-8]. At higher pHs (5-8), some of solfunate groups are ionized and the electrostatic repulsion between SO_3^- groups causes an enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions is "charge screening effect" of excess Na^+ in the swelling media which shield the solfunate anions and prevent effective anion-anion repulsion.

pH-reversibility

The synthesized hydrogel, alginate-g-poly(AMPS), shows different swelling behaviors in acidic and basic pH solutions. So, we investigated the reversible swelling-deswelling behavior of this hydrogel in solutions with pH 2.0 and 8.0 (Fig. 4). At pH 8.0, the hydrogel swells up to 95 g/g due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to protonation of solfunate groups. This sharp swelling-deswelling behavior of the hydrogels makes them as suitable candidate for controlled drug delivery systems. Such on-off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels[12].

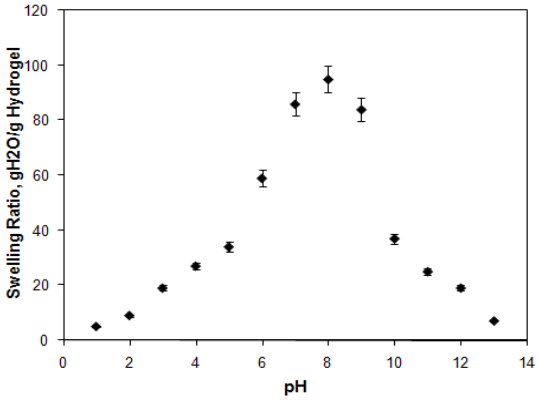

Fig. 3. Effect of pH of buffered solution on swelling of H-gelatin-g-poly(AMPS)hydrogel.

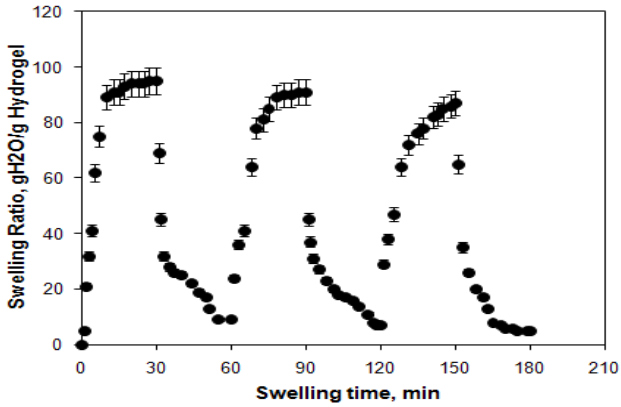

Fig. 4. On-off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of the hydrogel

CONCLUSIONS

To following synthesis of a novel superabsorbent hydrogel based on alginate, the swelling measurement in various salt solutions was examined. The results showed that the synthesized hydrogels are low salt-sensitive due to presence of anti-salt sulfunate groups in the AMPS parts of the network. However, swelling-loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect nd ionic crosslinking for mono- and multi-valent cations,

respectively. Swelling capacity of alginate-g-AMPS hydrogel in various pH solutions (1-13) as well as swelling-deswelling behavior of the product exhibited high absorbency at basic pHs and reversible pH-responsiveness property. Therefore, the synthesized hydrogels in this work, with anti-salt and high pH-sensitivity may be considered as an excellent candidate for various applications, such as designing the novel drug delivery systems.

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