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Synthesis and super-swelling behavior of a novel low salt-sensitive protein-based superabsorbent hydrogel: collagen-*g*-poly(AMPS)

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Superabsorbent polymers are obtained by the graft copolymerization of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) monomer onto collagen, using ammonium persulfate as a free radical initiator in the presence of methylene bisacrylamide as a crosslinker. Infrared spectroscopy and TGA thermal analysis were carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy (SEM). The effect of reaction variables on swelling capacity was investigated to achieve a hydrogel with improved water absorbency. Under the optimized conditions concluded, maximum capacity of swelling in distilled water was found to be 268 g/g. The swelling ratio in various salt solutions was investigated in detail. Since this hydrogel exhibited a very high absorptivity in saline, it may be referred to as a low salt-sensitive superabsorbent. The collagen-*g*-AMPS hydrogel also showed cation exchange properties. The swelling kinetics of the synthesized hydrogels with various particle sizes was also preliminarily investigated.

Key Words: Collagen, hydrogel, swelling, 2-acrylamido-2-methylpropanesulfonic acid

Introduction

The market for superabsorbent polymers (SAPs) has increased by a factor of 5 over the past 10 years. These materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, or saline or

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physiological solutions.[1,2] The absorbed fluids are difficult to remove even under some pressure. They are widely used in various applications such as hygiene, foods, cosmetics, and agriculture.[2–4] This accounts for the increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450,000 tons in 1996.[1] Nowadays, the worldwide production of SAPs is more than 1 million tons per year. Hence, the synthesis and investigation of specific and new superabsorbent hydrogels with high absorbency, mechanical strength, and initial absorption rate is the main goal of the several research groups worldwide.[5–10]

The properties of the swelling medium (e.g. pH, ionic strength and the counter ion and its valency) affect the swelling characteristics. SAPs responding to external stimuli such as heat, pH, electric field, and chemical environments are often referred to as "intelligent" or "smart" polymers. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs. Therefore, these hydrogels have important applications in the field of medicine, pharmacy, and biotechnology.[11,12]

Natural-based superabsorbent hydrogels have attracted much interest from the viewpoint of improving the tissue tolerance of synthetic polymers and the mechanical properties of natural polymers. The presence of the natural parts guarantees biodegradability of the superabsorbing materials. Because of their biocompatibility, biodegradability, and non-toxicity, natural polymers, i.e. polysaccharides and proteins, are the main part of these biopolymers. One of the best methods for the synthesis of these superabsorbent hydrogels is graft copolymerization of vinylic monomers onto natural polymers. Monomers such as acrylonitrile (AN), acrylic acid (AA), and acrylamide (AAm) have been graft copolymerized onto polysaccharides such as starch, cellulose, and their derivatives.[13–15] The first industrial superabsorbent hydrogel was synthesized using this method via ceric-induced graft copolymerization of acrylonitrile onto starch followed by alkaline hydrolysis of the resulting graft copolymer.[16]

Proteins are widely distributed in nature and are synthesized mainly in animals, i.e. collagen, keratin, gelatin, etc., and in a few plants such as soya. In general, proteins are high molecular weight polymers and their solubility in aqueous solutions is difficult. Two efficient methods for the preparation of aqueous soluble proteins are alkaline and enzymatic hydrolysis. According to the literature survey based on the Chemical Abstract Service, a few studies have been reported in the case of protein-based hydrogels.[17–19] Hence, the objective of the present paper is to describe the preparation and characterization of a hydrolyzed collagen-*g*-poly(2-acrylamido-2-methylpropanesulfonic acid) hydrogel as a new natural-based polymer with salt-responsiveness properties.

Experimental

Materials

Hydrolyzed collagen (Parvar Novin-E Tehran Co.) was industrial grade, which is available on the market, and has nearly 25% insoluble phosphate salt. 2-Acrylamido-2-methylpropanesulfonic acid (Merck, Darmstadt, Germany), N′,N′-methylene bisacrylamide, and ammonium persulfate (Fluka, Buchs, Switzerland) were of analytical grade and used without further purification. Double distilled water was used for the hydrogel preparation and swelling measurements.

Preparation of hydrogel

A pre-weighed amount of hydrolyzed collagen (1.0-4.0 g) was dissolved in 40 mL of degassed distilled water and filtered to remove its insoluble salt. The solution was added to a 1-L 3-neck reactor equipped with a mechanical stirrer (RZR 2021, a 3-blade propeller type, Heidolph, Schwabach, Germany) and the reactor was immersed in a thermostated water bath preset at a desired temperature (80 °C). Then 2-acrylamido-2-methylpropanesulfonic acid (2.0-8.0 g) was added to the reactor. After stirring for 10 min, ammonium persulfate (0.01-0.40 g of APS in 5 mL of H_2O) and methylene bisacrylamide (0.05-0.20 g in 5 mL of H_2O) were added simultaneously to the reaction mixture. The temperature was maintained at 80 °C and the reaction mixture was stirred continuously (300 rpm) for 1 h. At the end of the propagation reaction, the gel product was poured into ethanol (200 mL) and was dewatered for 12 h. Then the product was cut into small pieces, washed with 200 mL of ethanol, and filtered. The particles were dried in an oven at 50 °C for 12 h. After being ground, the powdered superabsorbent hydrogel was stored in the absence of moisture, heat, and light.

Swelling measurements

An accurately weighed sample (0.2 ± 0.001 g) of the powdered superabsorbent with average particle sizes between 40 and 60 mesh (250-350 $\mu m \mu m$) was immersed in distilled water (200 mL) and allowed to soak for 3 h at room temperature. The equilibrium swelling (ES) capacity was measured twice at room temperature according to a conventional tea bag (i.e. a 100 mesh nylon screen) method and using the following formula:

$$ES(g/g) = \frac{Weight_o f_s wollen_g el - Weight_o f_d ried_g el}{Weight_o f_d ried_g el} \quad (1)$$

Swelling in various salt solutions

Absorbency of the optimized sample was evaluated in 0.15 M solutions of LiCl, NaCl, KCl, $CaCl_2$, $AlCl_3$, Na_2CO_3, $MgSO_4$, and $Al_2(SO_4)_3$ according to the earlier method described for swelling measurement in distilled water. In addition, swelling capacity of the hydrogel was measured in different concentrations of NaCl, $CaCl_2$, and $AlCl_3$ salt solutions.

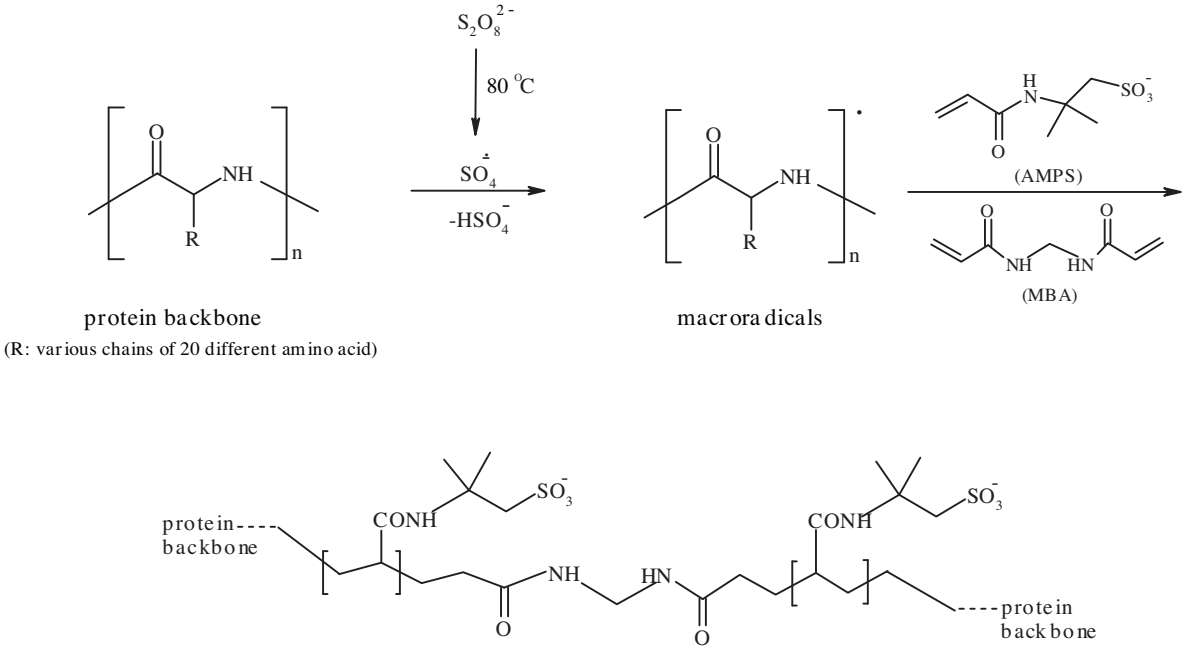
Instrumental analysis

Fourier transform infrared (FTIR) spectroscopy absorption spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature. To study the morphology of the hydrogel, the surface and cross-sectioned area of the hydrogel were examined using scanning electron microscopy (SEM). After Soxhlet extraction with methanol for 24 h and drying in an oven, superabsorbent powder was coated with a thin layer of gold and imaged in a SEM instrument (Leo, 1455 VP). Brunauer–Emmett–Teller (BET) analysis was used to determine the pore size of the hydrogels. Thermogravimetric analyses (TGA) were performed on a Universal V4.1D TA Instruments (SDT Q600) with 8-10 mg samples on a platinum pan under nitrogen atmosphere. Experiments were performed at a heating rate of 20 °C/min until 550 °C.

Results and discussion

Synthesis and spectral characterization

The mechanism for crosslinking graft copolymerization of AMPS onto collagen backbones in the presence of APS and MBA is shown in the Scheme. In the first step, the thermally dissociating initiator, i.e. APS, is decomposed under heating (80 °C) to produce sulfate anion-radicals. Then the anion-radicals abstract hydrogen from one of the functional groups (i.e. COOH, SH, OH, and NH_2) in side chains of the collagen backbones to form corresponding macro-initiators. These macroradicals initiate grafting of AMPS onto collagen backbones leading to a graft copolymer. A crosslinking reaction also occurred in the presence of the crosslinker, i.e. MBA.



Scheme. Proposed mechanistic pathway for synthesis of collagen-*g*-poly(AMPS) hydrogel.

FTIR spectroscopy was used for identification of the hydrogel. Figure 1 shows the IR spectra of the collagen and the resulting hydrogel. The band observed at 1658 cm^{-1} can be attributed to C=O stretching in carboxamide functional groups of the substrate backbone (Figure 1-a). The broad band at 3200-3600 cm^{-1} is due to stretching of –OH groups of the collagen. The collagen-*g*-AMPS hydrogel comprises a collagen backbone with side chains that carry sulfate groups that are evidenced by a new characteristic absorption band at 1221 cm^{-1} (Figure 1-b). This peak is attributed to ester sulfate stretching of AMPS. The stretching band of –NH overlapped with the OH stretching band of the collagen portion of the copolymer.

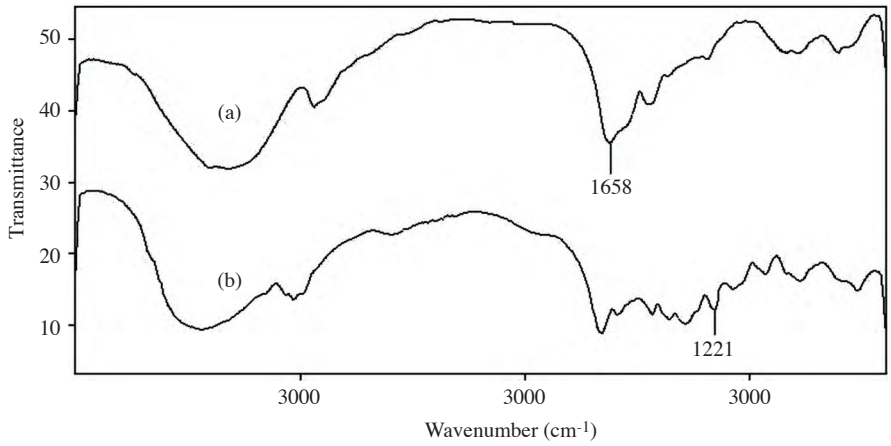


Figure 1. FTIR spectra of collagen (a) and collagen-g-poly(AMPS) hydrogel (b).

To obtain additional evidence of grafting, a similar polymerization was conducted in the absence of the crosslinker. After extracting the homopolymer and unreacted monomers using a cellophane membrane dialysis bag (D9402, Sigma–Aldrich), an appreciable amount of grafted collagen (87%) was observed. The graft copolymer spectrum was very similar to Figure 1-b. Moreover, according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.8 %. This fact practically proves that all AMPS are involved in the polymer network. Therefore, the monomers percentage in the network will be very similar to that of the initial feed of the reaction.

Scanning electron microscopy

One of the most important properties that must be considered is hydrogel microstructure morphologies. Figure 2 shows the scanning electron microscope (SEM) photographs of the surface (Figure 2A) and the cross-sectional area (Figure 2B) of the hydrogel with interconnected pores. These pictures verify that the synthesized polymer in this work has a porous structure, where the pores might be induced into the hydrogel by water evaporation resulting from reaction heat. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. The cross-sectional view of hydrogels (Figure 2B) also exhibited a large, open, channel-like structure.

The results of BET analysis showed that the average pore diameter of the synthesized hydrogel was 16.7 nm. In general, the size of the pores can be controlled by adjusting various factors such as the type and amount of surfactant, porosigens and gas forming agent during crosslinking polymerization, and the amount of diluent in the monomer mixture (i.e. monomer–diluent ratio).[20] For example, as the amount of diluent (usually water) in the monomer mixture increases, the pore size also increases up to the micrometer (μm) range.[21]

The porosity plays the multiple role of enhancing the total water sorption capability and the rate of response by reducing the transport resistance.[22,23] Therefore, creation of porosity in hydrogels has been considered an important process in many ways. The phase-separation technique,[24] the water-soluble porogens,[25] and the foaming technique[26,27] are 3 different methods for preparing porous hydrogel structures. In this paper, as mentioned above, however, the pores were simply produced from water evaporation resulting from reaction medium heat.

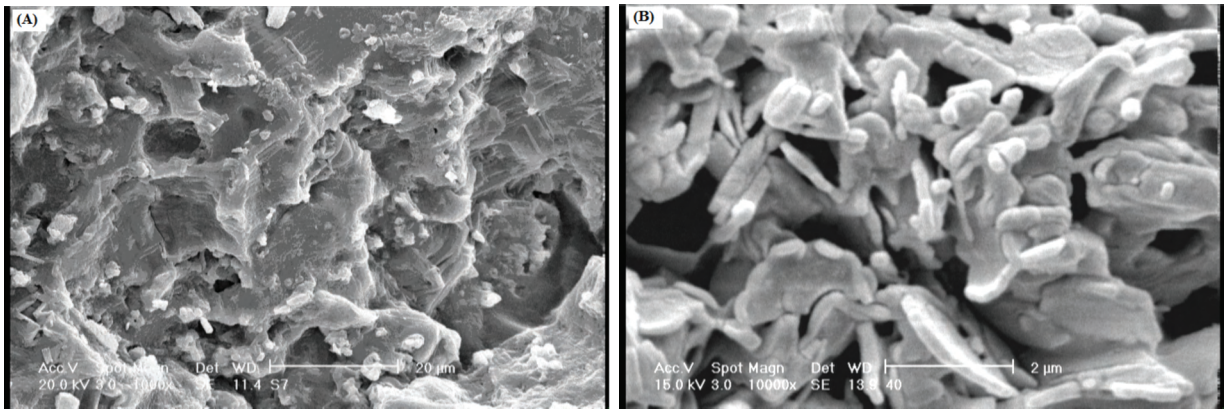


Figure 2. SEM photograph of the optimized superabsorbent hydrogel (collagen 3.0 g, MBA 0.008 mol/L, AMPS 0.68 mol/L, APS 0.015 mol/L, 80 °C, 60 min). (A) Surface of porous hydrogel; (B) Cross-sectional area of porous hydrogel. The average pore diameter of the synthesized hydrogel was 16.7 nm.

Thermal analysis

Thermogravimetric analysis (TGA) was employed to thermally characterize the hydrogel in comparison with the intact collagen (Figure 3). The thermal stability of the grafted collagen was improved as is obvious from the TGA curve. TGA of collagen (Figure 3-a) shows a weight loss in 2 distinct stages. The first stage ranges between 10 and 130 °C and shows about 17% loss in weight. This may correspond to the loss of adsorbed and bound water.[28] No such inflexion was observed in the TGA curve of collagen-*g*-poly(AMPS) hydrogel (Figure 3-b). This indicated that the grafted copolymers were resistant to moisture absorption. The second stage of weight loss starts at 230 °C and continues up to 300 °C during which there was 52% weight loss due to the degradation of collagen. In general, degradation of native collagen is faster than that of grafted collagen. About 60% weight loss takes place in the temperature range of 220-370 °C for collagen. In the collagen-g-poly(AMPS) sample, a residual weight of 77% was observed at 310 °C. The appearance of these stages indicates that the structure of collagen backbones has changed, which might be due to the grafting of poly(AMPS) chains. In general, the copolymer had a lower weight loss than collagen. This means that the grafting of collagen increases the thermal stability of collagen to some extent.

Optimization of the grafting variables

In this work, the main factors affecting the grafting conditions, i.e. concentration of MBA, AMPS, APS, and collagen, were systematically optimized to achieve a superabsorbent with maximum water absorbency.

Effect of MBA concentration

The effect of crosslinker concentration on the swelling capacity of collagen-*g*-poly(AMPS) was investigated. As shown in Figure 4, higher values of absorbency are obtained with lower MBA concentration as reported by pioneering scientists.[2,29] In fact, higher crosslinker concentrations decrease the free space between the copolymer

chains and consequently the resulting highly crosslinked rigid structure cannot be expanded and hold a large quantity of water. The maximum absorbency (121 g/g) was achieved at 0.008 mol/L of MBA.

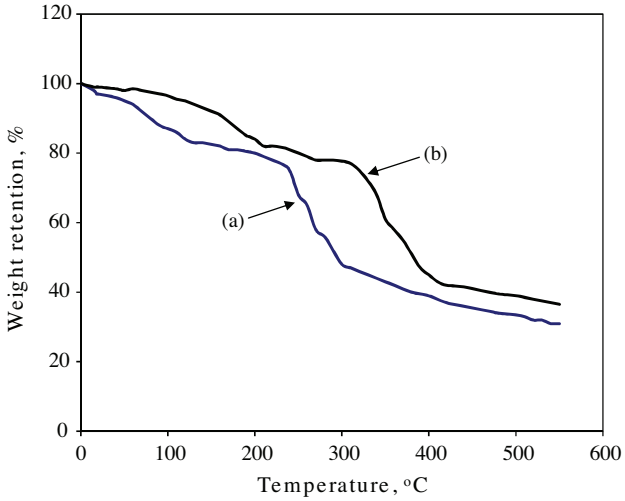


Figure 3. TGA of collagen (a) and collagen-*g*-poly(AMPS) hydrogel (b).

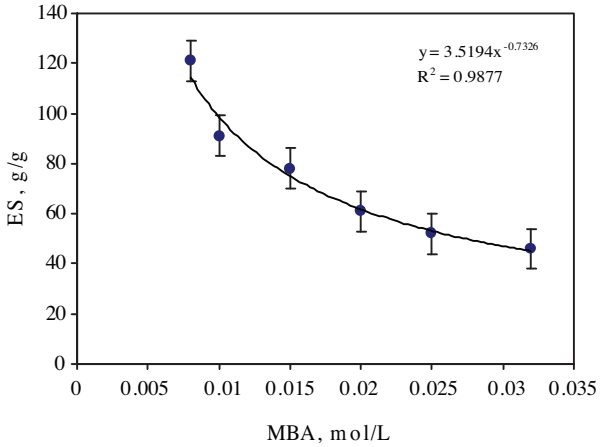


Figure 4. Effect of crosslinker concentration on swelling capacity. Reaction conditions: collagen 2.0 g, AMPS 0.58 mol/L, APS 0.01 mol/L, 80 ° C, 60 min.

Effect of AMPS concentration

The effect of monomer concentration on the swelling capacity of the hydrogel was studied by varying the AMPS concentration from 0.24 to 0.96 mol/L (Figure 5). Enhanced monomer concentration increases the diffusion of AMPS molecules into the collagen backbone, which consequently causes an increase in water absorbency. In addition, higher AMPS content enhanced the hydrophilicity of the hydrogel, causing a higher absorption of water. The swelling loss after the maximum may have originated from the increased chance of chain transfer to AMPS molecules and an increase in the viscosity of the reaction, which restricts the movement of the reactants.

Effect of APS concentration

The relationship between the initiator concentration and water absorbency values was studied by varying the APS concentration from 0.001 to 0.04 mol/L (Figure 6). It is observed that the absorbency is substantially increased with increasing in the APS concentration and then it is decreased. The initial increment in water absorbency may be attributed to the increased number of active free radicals on the collagen backbone. The subsequent decrease in swelling originates from an increase in the terminating step reaction via bimolecular collision, which, in turn, causes enhanced crosslinking density. This possible phenomenon is referred to as "self crosslinking" by Chen and Zhao.[30] In addition, the free radical degradation of collagen backbones by sulfate radical-anions is an additional reason for swelling loss at higher APS concentration. The proposed mechanism for this possibility is reported in a previous work.[31] A similar observation is reported by Hsu et al. in the case of degradation of chitosan with potassium persulfate.[32]

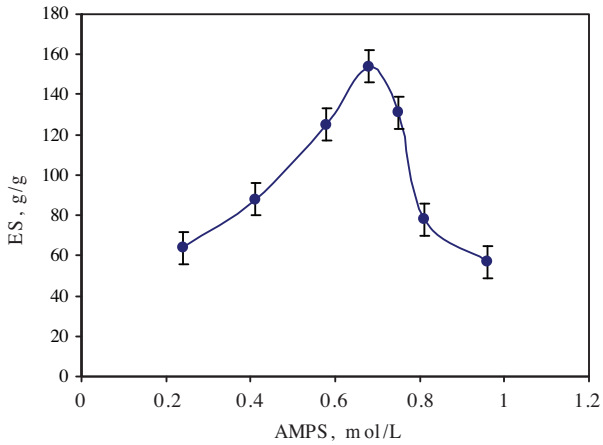


Figure 5. Effect of monomer concentration on swelling capacity. Reaction conditions: collagen 2.0 g, MBA 0.008 mol/L, APS 0.01 mol/L, 80 °C, 60 min.

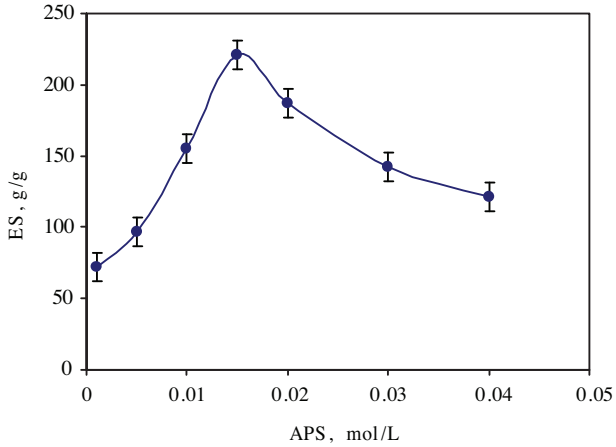


Figure 6. Effect of initiator concentration on swelling capacity. Reaction conditions: collagen 2.0 g, MBA 0.008 mol/L, AMPS 0.68 mol/L, 80 °C, 60 min.

Effect of collagen concentration

The effect of collagen weight on hydrogel swelling is shown in Figure 7. Maximum swelling (268 g/g) was observed at 3.0 g of collagen, while other factors including monomer, initiator, and MBA concentration were kept constant. Swelling capacity was increased by increasing the collagen weight from 1.0 to 3.0 g from 78 to 268 g/g. As the collagen weight was increased in the polymerization feed, the active sites can react easily with monomers. Increasing collagen content more than 3.0 g results in a high viscosity of the medium and a decrease in the diffusion of monomers to active sites to produce crosslinked hydrogels.

Swelling in various salt solutions

Swelling capacity in salt solutions is of prime significance in many practical applications such as personal hygiene products and water release systems in agriculture. The swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased compared 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.[29] Moreover, in salt solution the osmotic pressure resulting from the difference in the mobile ion concentration between gel and the aqueous phases is decreased and consequently the absorbency amounts are diminished. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at the surface of hydrogel particles causes an appreciable decrease in swelling capacity.

In this series of experiments, the swelling capacity was measured in various salt solutions. The effect of cation charge on swelling can be concluded from Figure 8. With increasing charge of cation, the degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency of the synthesized hydrogel is in the order $NaCl > CaCl_2 > AlCl_3$.

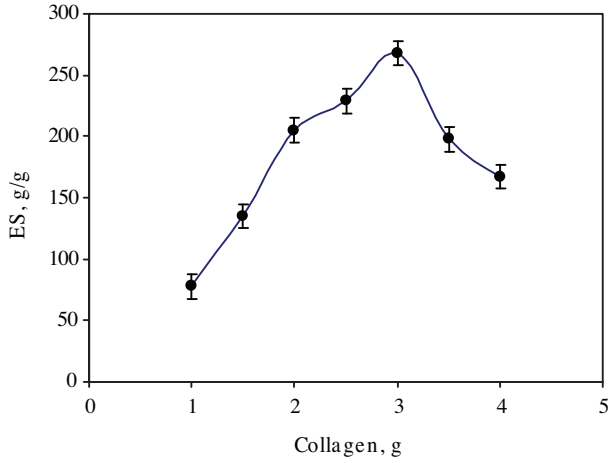


Figure 7. Effect of collagen amount on swelling capacity. Reaction conditions: MBA 0.008 mol/L, AMPS 0.68 mol/L, APS 0.015 mol/L, 80 °C, 60 min.

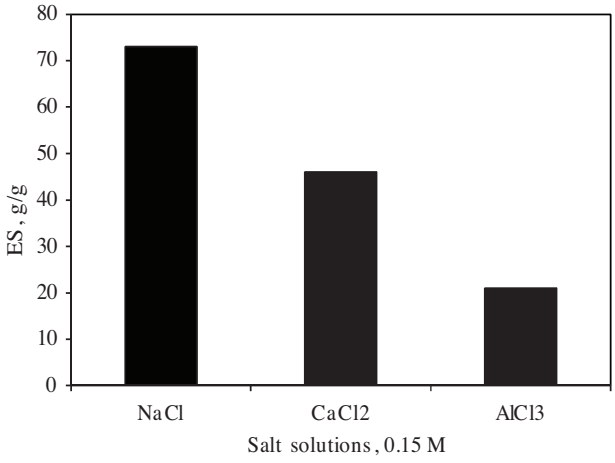


Figure 8. Swelling capacity of the hydrogel in different chloride salt solutions (0.15 M). Reaction conditions: collagen 3.0 g, MBA 0.008 mol/L, AMPS 0.68 mol/L, APS 0.015 mol/L, 80 °C, 60 min.

To study the effect of cation radius on swelling behaviors, the equilibrium swelling absorbency was measured in 0.15 M chloride salt solutions of Li^+, Na^+, and K^+ (Figure 9). A stronger interaction between sulfate groups and large cations has been observed by Pass et al. using measurement of activating coefficients of various cations in several salt solutions.[33] Thus, the collagen-*g*-poly(AMPS) has the highest affinity for crosslinking with K^+ among monovalent cations of the studied salt solutions. As a result, swelling of the synthesized hydrogels in KCl solution is lower than in LiCl and in NaCl solutions (LiCl > NaCl > KCl).

Figure 10 shows the swelling capacity of the hydrogel as a function of the salt concentration. These results reveal that the swelling ratio decreased with increasing salt concentration of the medium. The known relationship between swelling and concentration of salt solution is stated as the following equation:[29]

$$\text{swelling} = k[salt]^{-n}, \tag{2}$$

where k and n are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt and the n value is a measure of salt sensitivity. As shown in the Table, the k values were almost the same ($\sim$5) for the swelling in various salt solutions and the n values proportionally changed with the cation valence enhancement. These results imply that the effect of the ionic crosslinking acts as a more effective factor rather than the charge screening effect of the cation.

Table. Values k and n (as obtained from the curve fitting, Figure 10) for the synthesized hydrogel.

Swelling medium	k	n
$NaCl$	5.3	0.28
$CaCl_2$	5.6	0.44
$AlCl_3$	5.5	0.78

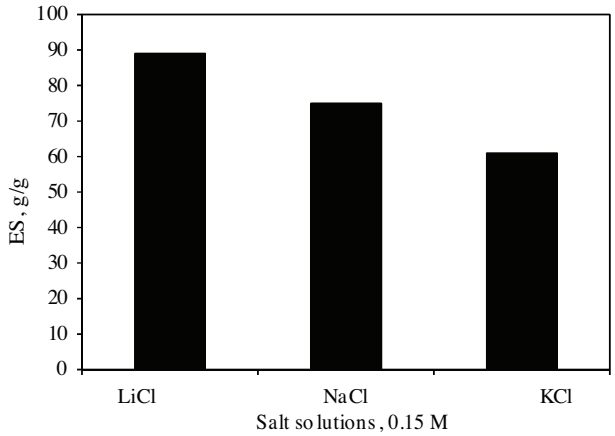


Figure 9. Swelling capacity of the hydrogel in various chloride salt solutions (0.15 M). Reaction conditions: collagen 3.0 g, MBA 0.008 mol/L, AMPS 0.68 mol/L, APS 0.015 mol/L, 80 °C, 60 min.

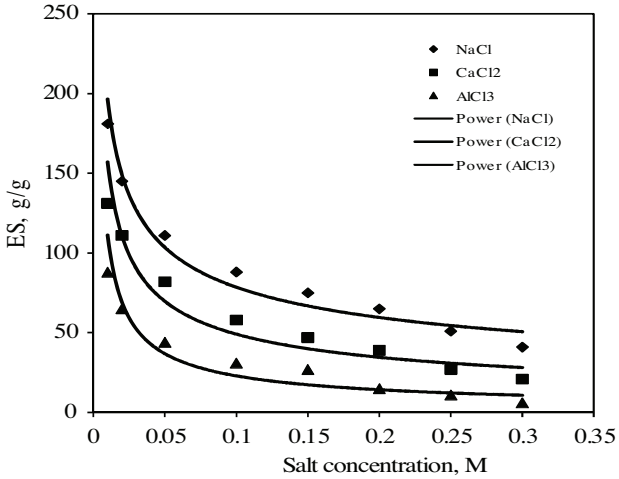


Figure 10. Swelling capacity variation of the hydrogel in saline solutions with various concentrations. Reaction conditions: collagen 3.0 g, MBA 0.008 mol/L, AMPS 0.68 mol/L, APS 0.015 mol/L, 80 °C, 60 min.

The results shown in Figure 11 indicate that the absorbency for the hydrogels in various salt solutions decreased with increasing ionic strength of the salt solution. The effect of the ionic strength on water absorbency has been determined using the relation suggested by Hermans:[34]

$$Q^{5/3}(eq) = A + B^2/I \tag{3}$$

where Q(eq) is the equilibrium water absorbency, I is the ionic strength of the external solution, and A and B are the empirical parameters. At low ionic strengths, the concentration of charges within the hydrogel network exceeds the concentration of salt in the external solution, and a large ion-swelling pressure causes the hydrogel to expand, thereby lowering the concentration of ions within the hydrogel. As the external salt concentration rises, the difference between the internal and external ion concentration decreases and the hydrogel deswells. The hydrogel continues to deswell with increasing external salt concentration until the mobile-ion concentrations inside and outside are approximately equal. These phenomena can also be explained on the basis of repulsion between fixed charged groups on the hydrogel. As the ionic strength increases, electronic repulsion is shielded and the hydrogels deswell (charge screening effect).

In our collagen-modified hydrogels, however, the swelling in salt solutions, especially in salt solutions with monovalent cations, was considerable. The reason for this low salt-sensitivity behavior seems to be the presence of AMPS sulfate groups. The synthesized hydrogels in this work comprise many "non-ionic" amide groups and "low salt-sensitive" sulfate anions. Since the sulfate ions do not have counter cations in their vicinity, the "charge screening effect" is not a factor. Thus, the resulting swelling loss is less. A similar conclusion was reported by Lim et al.[35] in the case of sodium starch sulfate-g-poly(acrylonitrile) superabsorbent (SSS). They developed a superabsorbent with high water and saline absorbency of 1510 and 126.4 g/g, respectively, compared with 820 and 61.5 g/g for a hydrolyzed starch-g-poly(acrylonitrile). They attributed the enhanced absorbency to increased charge density and ionization tendency brought about by the introduction of sulfate

anions in SSS superabsorbent. Similarly, Barbucci et al. achieved considerable water absorbency in the case of a sulfated carboxymethyl cellulose hydrogel.[36]

Since the collagen-based hydrogels comprise sulfate groups, they exhibit various swelling capacities in different salt solutions with the same concentrations. These swelling changes are due to valency difference of salts. The networks contain poly(AMPS) chains with sulfate groups that can interact with cations. As given in Figure 8, the swelling capacity of the hydrogels in $CaCl_2$ solution is lower than that in NaCl solutions. As mentioned above, in the presence of the bivalent calcium ions, the crosslinking density increases because of a double interaction of $CaCl_2$ with sulfate groups, leading to ionic crosslinking. The swelling–deswelling cycle of the hydrogel in sodium and calcium salts is shown in Figure 12. In sodium solution, swelling of the hydrogel increases with time. When this hydrogel is immersed in calcium chloride solution, it deswells to a collapsed form. When the shrunken hydrogel is immersed in sodium chloride solution again, the calcium ions are replaced by sodium ions. This ion exchange disrupts the ionic crosslinks, leading to swelling enhancement. As a result, when hydrogel is treated alternatively with NaCl and $CaCl_2$ solutions of equal molarity, the swelling reversibility of hydrogel is observed. This chemical behavior of hydrogel results from the ion exchange ability of the sulfate groups.

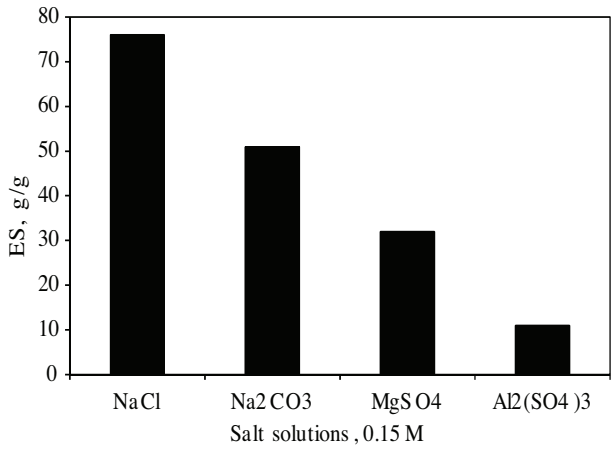


Figure 11. Swelling capacity of the hydrogel as a function of ionic strength of the salt solution. Reaction conditions: collagen 3.0 g, MBA 0.008 mol/L, AMPS 0.68 mol/L, APS 0.015 mol/L, 80 °C, 60 min.

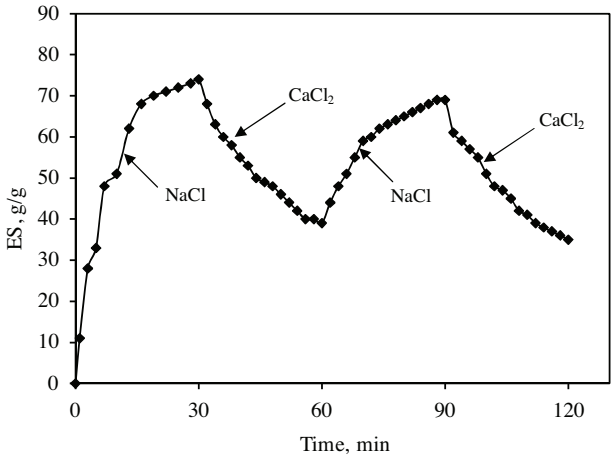


Figure 12. Reversible cation exchange ability of the collagen-*g*-poly(AMPS) hydrogel.

Swelling kinetics

In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate. Buchholz has suggested that the swelling kinetics for the superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area, and composition of polymer.[37] Figure 13 represents the dynamic swelling behavior of the superabsorbent samples with various particle sizes in water. Initially, the rate of water uptake sharply increases and then begins to level off. The equilibrium swelling capacity was achieved after $\sim$40 min. A power law behavior is obvious from Figure 13. The data may be fitted

well to a Voigt-based equation (Eq. 3):[38]

$$S_t = S_e(1 - e^{-t/\tau}) \tag{4}$$

where S_t (g/g) is swelling at time t, S_e is equilibrium swelling (power parameter, g/g;, t is time (min) for swelling S_t, and τ (min) stands for the "rate parameter". The rate parameters for superabsorbent are found to be 0.57, 2.4, and 4.6 min for superabsorbents with particle sizes of 100-250, 250-400, and 400-550 μm, respectively. It is well known that the swelling kinetics for the superabsorbent polymers is significantly influenced by the particle size of the absorbents.[39] With a lower particle size, a higher rate of water uptake is observed. An increase in the rate of absorption would be expected from the increase in surface area with decreasing particle size of hydrogel.

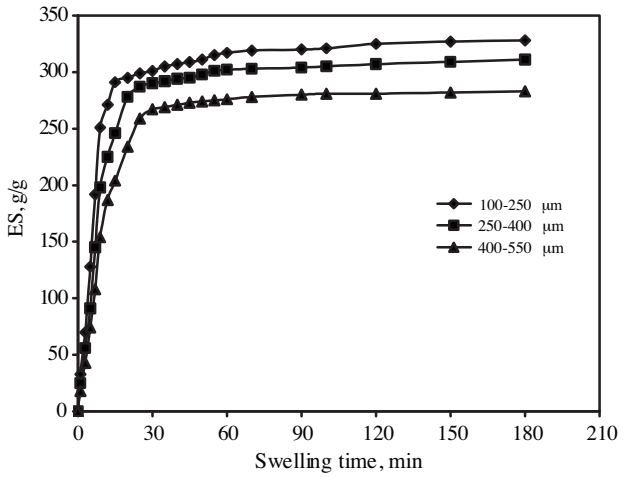


Figure 13. Representative swelling kinetics of the hydrogel, collagen-*g*-poly(AMPS), in distilled water with various particle sizes.

Conclusion

A novel protein-based superabsorbent hydrogel was synthesized via graft copolymerization of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto collagen backbones in an aqueous solution using a persulfate initiator and a hydrophilic crosslinker. The FTIR spectra and thermogravimetric analysis show that graft copolymerization does takes place. The optimum reaction conditions to obtain maximum water absorbency (286 g/g) were found to be: MBA 0.008 mol/L, AMPS 0.68 mol/L, APS 0.015 mol/L, and collagen 3.0 g. Swelling measurements in various salt solutions showed that the synthesized hydrogels are low salt-sensitive due to the presence of anti-salt sulfate groups in the AMPS parts of the network. However, swelling loss in salt solutions, in comparison with distilled water, can be attributed to the charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. The swelling capacity in $CaCl_2$ is much lower than that in NaCl solution and distillated water. The swelling–deswelling process of the hydrogel alternatively carried out in $CaCl_2$ and NaCl solutions results in a high capability of ion exchanging of the collagen-based hydrogel. Finally, dynamic swelling kinetics of the hydrogels shows that the rate of absorbency increases with decreasing particle size of superabsorbing samples.

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