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Synthesis and super-swelling behavior of a novel protein-based superabsorbent hydrogel

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Summary

In this work, we synthesize a novel protein-based superabsorbent hydrogel and study its swelling behavior. The crosslinking graft copolymerization of acrylic acid (AA) onto the hydrolyzed collagen as a protein backbone was carried out in a homogeneous medium. Potassium persulfate (KPS) as an initiator and N,N'-methylene bisacrylamide (MBA) as a crosslinker were used. The product's structure was established using FTIR spectroscopy. We were systematically optimized the certain variables of the graft copolymerization (i.e. the monomer, the initiator, and the crosslinker concentration) to achieve a hydrogel with maximum swelling capacity. Under this condition, maximum capacity of swelling in distilled water was found to be 920 g/g. Morphology of the optimized sample was examined by scanning electron microscopy (SEM). The swelling ratio in various salt solutions was also determined. Additionally, the swelling of superabsorbing hydrogels was measured in solutions with pH ranged from 1 to 13. The synthesized hydrogel exhibited a pH-responsiveness character so that a swelling-collapsing pulsatile behavior was recorded at pH 2 and 8.

Introduction

Superabsorbent polymers (SAPs) are crosslinked hydrophilic networks that can absorb water in the amount from 10% up to thousands of times their dry weight [1]. Although hydrogels made from synthetic polymers, such as polyacrylate, posses excellent water-absorbing properties, their toxicity and non-biodegradability might pose long-time environmental problems and limit their use in drug delivery systems and consumer products [2-4]. Natural-based SAPs have attracted much attention in medical and pharmaceutical interests because of their non-toxicity, biocompatibility and biodegradability. Recently, attention has been focused on employing natural polymers such as cellulose [5], starch [6], gelatin [7], chitosan [8], carrageenan [9] and protein [10] to produce hydrogels with a specific response to a biological environment.

An efficient approach to modify of natural polymers, in order to synthesis of natural-based SAPs, is graft polymerization of vinylic monomers onto their backbones in the presence of crosslinkers. Free radical graft copolymerization with various monomers can carried out with different initiator systems. Proteins are widely distributed in nature and are synthesized mainly in animals, i.e. collagen, keratin, gelatin and 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 preparation of aqueous soluble proteins are alkaline and enzymatic hydrolysis. Only a few studies have been reported in the case of protein-based SAPs [10,11].

In the present report, to modify the hydrolyzed collagen, the grafting of acrylic acid (AA) onto protein chains in the presence of a crosslinking agent was performed in a homogeneous system. The effect of reaction variables affecting the water absorbency of the hydrogel and swelling behavior in various salt and pH solutions was investigated.

Experimental

Material

Hydrolyzed collagen (from Parvar Novin-E Tehran Co.), N,N$'$-methylene bisacrylamide (MBA, from Fluka), potassium persulfate (KPS, from Fluka), acrylic acid (AA, from Merck) were of analytical grade and used without further purification. All other chemicals were also analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Preparation of hydrogel

Hydrolyzed collagen (1.33g) was dissolved in 50 mL distilled water and filtered to remove its insoluble salt (approximately 25%). Then the solution was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm) and was immersed in a thermostated water bath at a desired temperature (80^{o}C). Then the initiator solution (0.01-0.35 g KPS in 5 mL H_2O) were added to the mixture. After stirring for 10 min, certain amounts of 70 mol % neutralized AA (1.5-8.0 g in 5 mL H_2O) and MBA (0.1-0.2 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 hydrogel was remained for 24 h. Finally, the filtered hydrogel 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 2 h at room temperature. The sample particle sizes were 40 to 60 meshes (250-400 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:

$$ES\,(g\,/\,g) = \frac{Weight\ \ of\ \ swollen\ \ gel - Weight\ \ of\ \ dried\ \ gel}{Weight\ \ of\ \ dried\ \ gel} \qquad \mathbf{(1)}$$

The accuracy of the measurements was ±3%.

Swelling in various salt solutions

Absorbency of the 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 of NaCl, $CaCl_2$, and $AlCl_3$ salt solutions.

Absorbency at various values of pH

Individual solutions ranging from pH 1 to 13 were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions to achieve pH≥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 (± 0.001) g of the dried hydrogel was used for the swelling measurements according to Eq. (1).

pH-sensitivity

Sensitivity of the hydrogel to pH was investigated in terms of swelling and deswelling of the final product at two basic (pH 8.0) and acidic (pH 2.0) solutions. Swelling capacity of the hydrogels at each pH was measured according to Eq. (1) at consecutive time intervals (10 min).

Swelling kinetics

For studying the rate of absorbency of the hydrogels, certain amount of samples (0.5 ± 0.001 g) with various particle sizes were poured into numbers of weighed tea bags and immersed in 200 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogels was measured according to the above mentioned method.

Centrifuge retention capacity (CRC)

Approximately 20-30 mg of dried superabsorbent with average particle sizes of 225 μm were dispersed in 50 mL of distilled water for 30 min. The swollen particles were placed on a 300-mesh wire gauze fixed in centrifuge tubes, then centrifuged at 2800 rpm at different times, unless otherwise specified, weighed, and CRC was calculated using the above Eq. (1).

Absorbency under load (AUL)

AUL was measured using a piston assembly allowing addition of weights on top of the superabsorbent sample [12]. A macro-porous sintered glass filter plate (porosity 0, d=80 mm, h=7 mm) was placed in a Petri dish (d=118 mm, h=12 mm), and weighted dried SAP sample (0.5±0.01g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid load (Teflon, d=60 *mm*, variable height) is put on the dry SAP particles while it can be freely slipped in a glass cylinder (d=60 *mm, h*=50 *mm*). Desired load (applied pressure 2068, 4137, and 6205 Pa) was placed on the SAP sample. Then, 0.9% saline solution was added so that the liquid level was equal to the height of the sintered glass filter. Whole of the set was covered to prevent surface evaporation and probable change in the saline concentration. After 60 min, the swollen particles were weighted again, and AUL was calculated according to Eq. (1).

Instrumental analysis

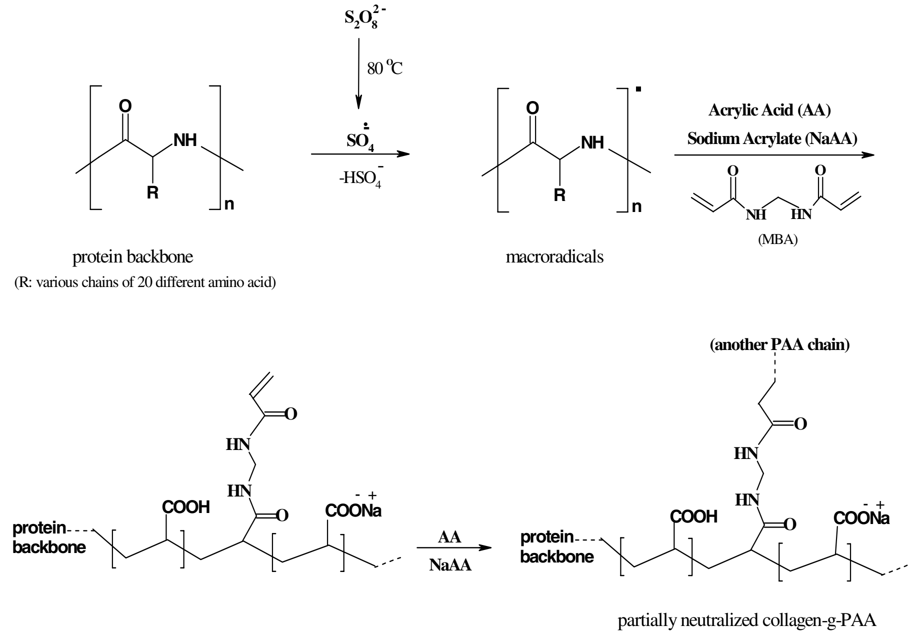
FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer. The surface morphology of the gel was examined using scanning electron microscopy (SEM). Dried superabsorbent powder were coated with a thin layer of palladium gold alloy and imaged in a SEM instrument (Leo, 1455 VP).

Results and discussion

The mechanism for graft copolymerization is shown in Scheme 1. At the first step, the thermally dissociating initiator, i.e. KPS, is decomposed under heating (80°C) to produce sulfate anion-radical [13]. Then the anion-radical abstracts hydrogen from one of the functional groups (i.e. COOH, SH, OH, and NH_2) in side chains of the substrate to form corresponding radical. So, these macroradicals initiate 70% neutralized acrylic acid grafting onto collagen backbones led to a graft copolymer. In addition, crosslinking reaction was occurred in the presence of a crosslinker, i.e., MBA, so that a three dimensional network was obtained.

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1 shows the FTIR spectra of the hydrolyzed collagen and the synthesized hydrogel. The band observed at 1654 cm^{-1} can be attributed to C=O stretching in carboxamide functional groups of substrate backbone (Fig. 1a). The broad band at 3200-3600 cm^{-1} is due to stretching of –OH groups of the collagen.

The hydrogel comprises a protein backbone with side chains that carry carboxylate functional groups which are evidenced by two new characteristic absorption bands at



Scheme 1. Proposed mechanistic pathway for synthesis of the partially neutralized collagen-*g*-PAA hydrogel.

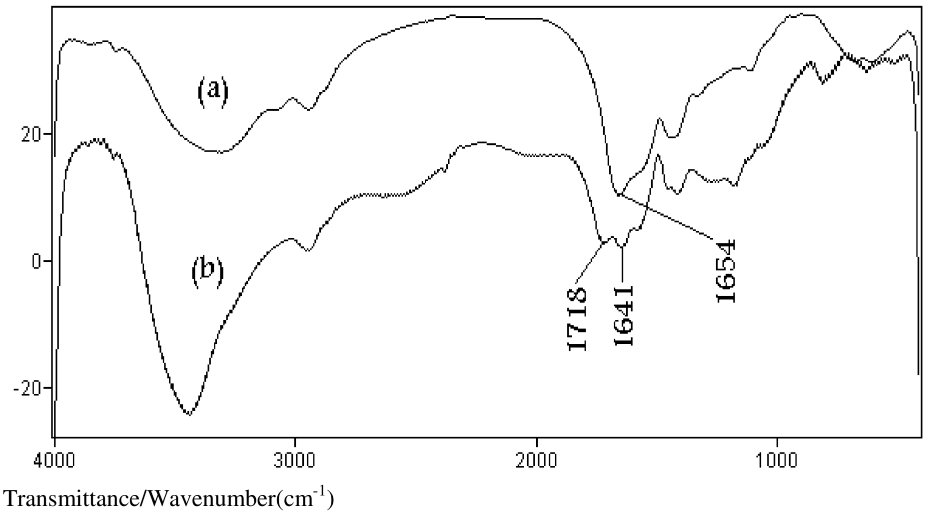


Figure 1. FTIR spectra of the hydrolyzed collagen (a) and the partially neutralized collagen-g-PAA hydrogel (b).

1641 and 1718 cm^{-1} (Fig. 1b). These peaks attributed to symmetric and asymmetric stretching modes of carboxylate anions, respectively [14].

Effect of MBA concentration

As shown in Fig. 2, the absorbency is diminished with increasing the MBA concentration. More crosslinking concentration causes to the higher crosslinking density and decreases the space between the copolymer chains and consequently, the resulted highly crosslinked rigid structure cannot be expanded and hold a large quantity of water. Such well-known behavior was reported by pioneering scientists [2,15,16]. Figure 2 exhibits a power law behavior of swelling-[MBA], with K=6.99 and n=0.91 which is obtained from the curve fitted with Eq.(2).

$$\text{Swelling capacity} \approx K\,[\text{MBA}]^{-n} \qquad (\mathbf{2})$$

where *K* and *n* are constant values for an individual superabsorbent. The n value represents the extent of the sensitivity of the hydrogel to the crosslinker content, while the K value gives an amount useful for comparing the extent of swelling versus fixed crosslinker content. According to Fig. 2, maximum swelling (347g/g) was obtained at 9.3 mmol/L of crosslinker concentration so that the hydrogels prepared with MBA concentration lower than 9.3 mmol/L do not posses good dimensional stability. Therefore the swollen gel strength is not sufficient to refer the hydrogels as "real superabsorbents".

Effect of AA concentration

The relationship between the monomer concentration and water absorbency values was studied by varying the AA concentration from 0.3 to 1.6 mol/L (Figure 3). It is observed that the absorbency is substantially increased with increasing in the AA concentration and then it is decreased. The initial increment in swelling values can be attributed to the higher hydrophilicity of the hydrogel and the greater availability of

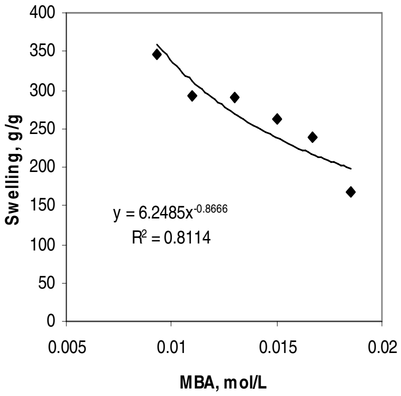


Figure 2. Swelling dependency of the partially neutralized collagen-*g*-PAA hydrogel on crosslinker concentration. Reaction conditions: Collagen 1.33 g, AA 0.6 mol/L, KPS 5.3 mmol/L, 80 °C, 60 min.

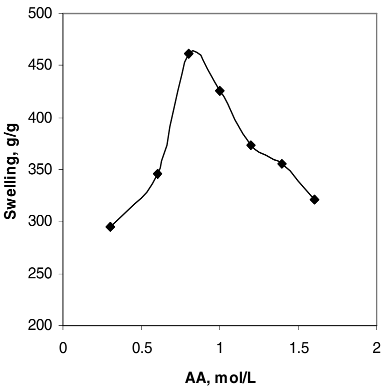


Figure 3. Swelling dependency of the partially neutralized collagen-*g*-PAA hydrogel as a function of monomer concentration. Reaction conditions: Collagen 1.33 g, MBA 9.3 mmol/L, KPS 5.3 mmol/L, 80 °C, 60 min.

AA molecules in the vicinity of collagen macroradicals. The swelling-loss after the maximum may be originated from (a) the increased chance of chain transfer to AA molecules, (b) increase in viscosity of the reaction which restricts the movement of the reactants and deactivates the macroradical growing chains soon after their formation, and (c) the enhanced homopolymerization reaction over graft copolymerization. Similar conclusions were reported by other investigators [17-19].

Effect of KPS concentration

The relationship between the initiator concentration and water absorbency values was studied by varying the KPS concentration from 0.53 to 19 mmol/L (Fig. 4). The maximum absorbency (920 g/g) is obtained at 2.6 mmol/L of the initiator. Less than that, the resulted polymers were completely soluble. Initial increment in water absorbency may be attributed to increased number of active free radicals on the protein backbone. Subsequent decrease in swelling is originated from an increase in terminating step reaction via bimolecular collision which, in turn, causes to enhance crosslinking density. This possible phenomenon is referred to as "self crosslinking" by Chen and Zhao [20]. In addition, the free radical degradation of collagen backbones by sulfate radical-anions is an additional reason for swelling-loss at higher KPS concentration [21,22].

Swelling in various salt solutions

The swelling ratio is mainly related to the characteristics of the external solution i.e. the charge number and ionic strength, as well as the nature of polymer, i.e. the, elasticity of the network, the presence of hydrophilic functional groups, and the extent of crosslinking density. 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 [15]. In addition, in the case of salt solutions with multivalent

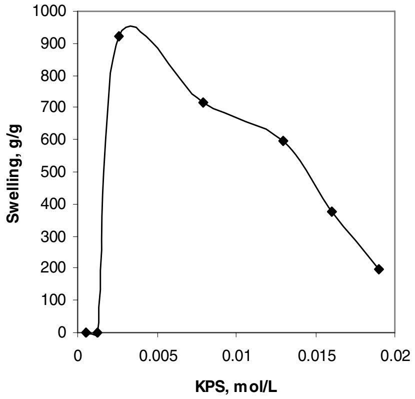


Figure 4. Effect of initiator concentration on swelling capacity of the partially neutralized collagen-*g*-PAA hydrogel. Reaction conditions: Collagen 1.33 g, AA 0.8 mol/L, MBA 9.3 mmol/L, 80 °C, 60 min.

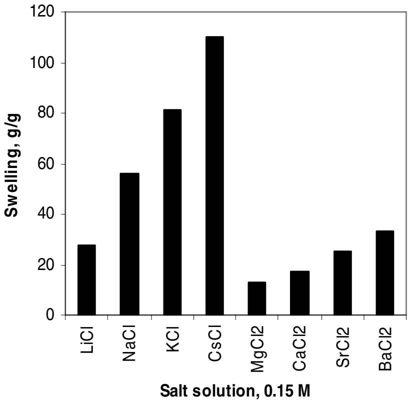


Figure 5. Swelling capacity of the partially neutralized collagen-g-PAA hydrogel in different chloride salt solutions (0.15M).

cations, "ionic crosslinking" at surface of particles causing an appreciably decrease in swelling capacity. In this series of experiments, the swelling capacity was measured in various salt solutions (Figs. 5, 6).

It is obvious that swelling decrease is strongly depended on the "type" and "concentration" of salt added to the swelling medium. The effect of cation type (cations with different radius and charge) on swelling behavior is shown in Fig. 5. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency for the hydrogel in the studied salt solutions is in the order of monovalent > divalent> trivalent cations. The effect of cation radius on swelling may also been observed from Fig. 5. As reported by Pass et al. [23], the carboxylate anion interacts with small cations, e.g. Li^+, stronger than with large cations, e.g. Cs^+. The stronger interactions of carboxylate-small cation have been observed using measurement of activating coefficients of various cations in several salt solutions. As a result, the absorbency in monovalent and divalent cation salt solutions is in the order of CsCl>KCl>NaCl>LiCl and $Ba^{2+}>Sr^{2+}>Ca^{2+}>Mg^{2+}$, respectively. Fig. 6 illustrates a reverse and power law relationship between concentration of salt solutions (NaCl, $CaCl_2$, and $AlCl_3$) and swelling capacity of the hydrogel. Again, charge screening effect and ionic crosslinking are the main explanations for the intense loss of swelling. The known relationship between swelling and concentration of salt solution is stated as following equation [15]:

$$\text{Swelling} = k\,[\text{salt}]^{-n} \qquad \textbf{(3)}$$

where *k* and *n* are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity. Figure 6 indicates that changing of the salt concentrations higher than ~0.2 M has no appreciable influence on superabsorbency of the superabsorbent. The k values are almost the same (~9) for the swelling in various salt solutions. The n values are proportionally changes with the cation valency enhancement (0.52 for NaCl, 0.67 for $CaCl_2$ and 0.81 for $AlCl_3$). Here, the effect of the ionic crosslinking acts as more effective factor against swelling rather than the charge screening effect of the cation.

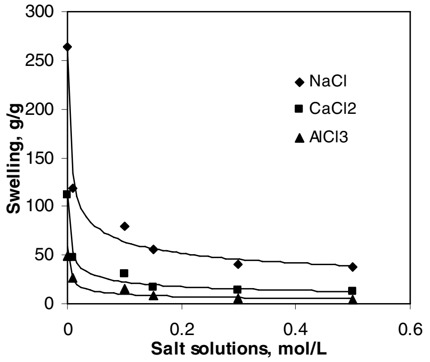


Figure 6. Swelling capacity variation of the partially neutralized collagen-g-PAA hydrogel in saline solutions with various concentrations.

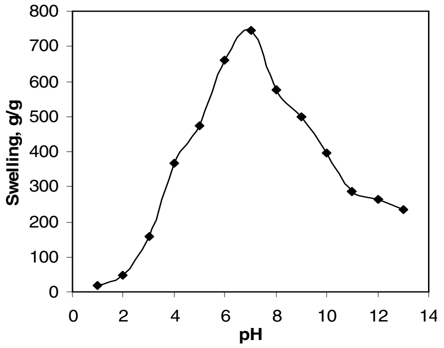


Figure 7. Effect of pH of solutions on swelling capacity of the partially neutralized collagen-*g*-PAA hydrogel.

Effect of pH on equilibrium swelling

Ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pH values. Therefore, in this series of experiments, equilibrium swelling for the synthesized hydrogels was measured in different pH solutions ranged from 1.0 to 13.0 (Fig. 7). 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 13.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pH values, respectively.

Maximum swelling (746g/g) was obtained at pH 7. Under acidic pH values, most of the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling values are decreased. At higher values of pH (5-7), some of carboxylate groups are ionized and the electrostatic repulsion between COO^- groups causes an enhancement of the swelling capacity. Again, a charge-screening effect of the counter ions (cations) limits the swelling at pH>7. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems [24-27].

pH-responsiveness behavior of the hydrogel

Since the present hydrogels show different swelling behaviors in various pH solutions, we investigated the pH reversibility of these hydrogels in 0.01 M solutions with pH 2 and pH 8 (Fig. 8). At pH 8.0, the hydrogel swells up to 537 g/g due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to protonation of carboxylate groups. This sharp swelling-deswelling behavior of the hydrogels makes them a suitable candidate for controlled drug delivery systems. Such on-off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels [28-31].

Swelling kinetics

In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Buchholz has suggested that the swelling kinetics for

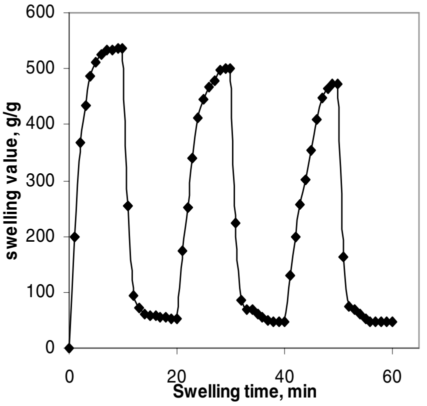


Figure 8. On-off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of the partially neutralized collagen-*g*-PAA hydrogel. The time interval between the pH changes was 10 min.

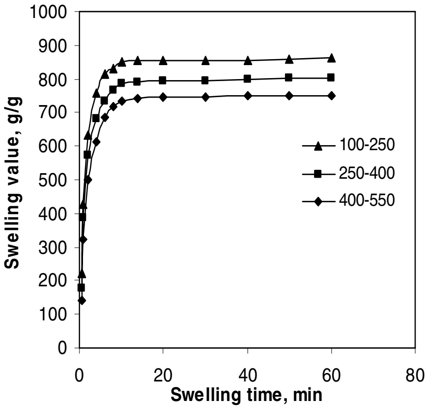


Figure 9. Representative swelling kinetics of the partially neutralized collagen-*g*-PAA hydrogel with various particle sizes.

the superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer [32]. Figure 9 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 time required to reach the equilibrium swelling capacity was achieved after ~20 min. A power law behavior is obvious from Fig. 9. The data may be well fitted with a Voigt-based equation (Eq. (4)) [33]:

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

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) stand for the "rate parameter". The rate parameters for superabsorbent are found to be 1.41, 1.54, and 1.75 min for superabsorbents with particle sizes of 100-250, 250-400 and 400-550 µm, respectively. 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 [34].

Absorbency under load

AUL is an important factor in the practical application of superabsorbents to determine of the swollen gel strength. The absorbencies measured under different loads are shown in Figure 10. As shown, the minimum time needed for the highest AUL in the case of each load was determined to be 180 minutes. After this time, the AUL values were unchanged. In addition, the curves expectedly exhibit that AUL decreases with increasing the amount of loading.

Water retention value

For showing the water retention power, we used CRC method. The CRC and weight of water lost by swollen superabsorbents on centrifuging at different times are

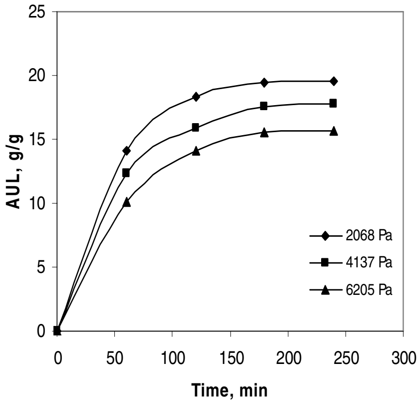


Figure 10. Time dependence of the AUL values for optimized sample swollen in saline solution.

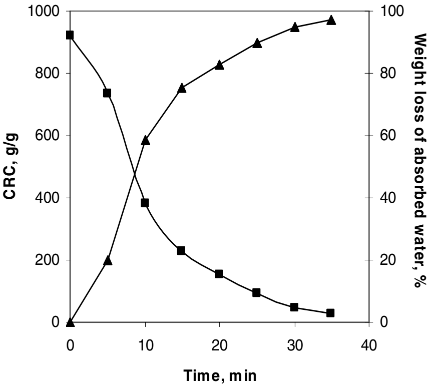


Figure 11. Time dependence of the CRC values and weight of water lost for optimized sample swollen in distilled water.

shown in Figure 11. According to a previous study [35], the water in a hydrogel can be classified into bound water, half-bound water, and free water. Compared to bound water and half-bound water, the free water in a hydrogel has high mobility and can easily be lost.

The percentages of bound water and half-bound water content in swollen gel are related to the number of hydrophilic groups (COOH and COONa) in a unit volume in superabsorbent.

Scanning electron microscopy

Figures 12 and 13 showed the scanning electron microscopic pictures of the hydrolyzed collagen and the optimized hydrogel. These pictures verify that graft copolymers have a porous structure. 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.

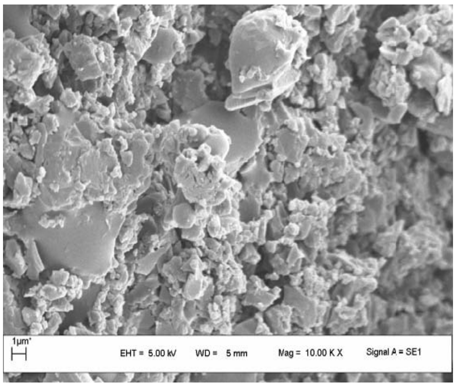


Figure 12. SEM photograph of hydrolyzed collagen.

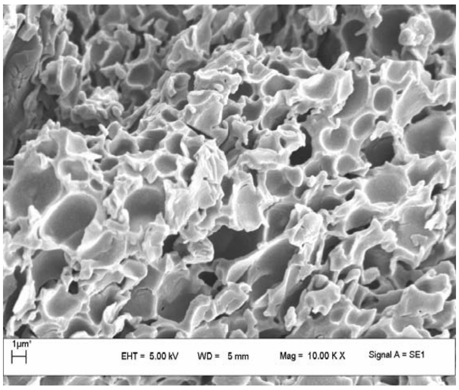


Figure 13. SEM photograph of optimized superabsorbent hydrogel.

Conclusion

In the present study, a novel superabsorbent hydrogel was prepared by crosslinking graft copolymerization of AA onto a hydrolyzed collagen. The optimum reaction conditions to obtain maximum water absorbency (920 g/g) were found to be: MBA 9.3 mmol/L, AA 0.8 mol/L, and KPS 2.6 mmol/L. Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in CsCl and KCl solutions. However, swelling loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively.The absorbency under load (AUL) and centrifuge retention capacity (CRC) data are usually given in the patent literature and technical data sheets offered by industrial SAP manufacturers. Also the superabsorbent hydrogels exhibited high sensitivity to pH, so that, several swelling changes of the hydrogel were observed as a function of pH variations in a wide range (1-13). Furthermore, the reversible swelling-deswelling behavior in solutions with acidic and basic pH makes the hydrogels a suitable candidate for controlled drug delivery systems. In addition, because of the use of protein as a natural backbone, it is expected that the resulted SAPs show more compatibility with body when they use as drug delivery systems. Finally, dynamic swelling kinetics of the hydrogels shows that the rate of absorbency is increased with decreasing the particle size of superabsorbing samples.

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