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Swelling Behaviour of a Novel Protein-Based Super Absorbent Hydrogel Composed of Poly(methacrylic Acid) and Collagen

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In this paper, a novel protein-based super absorbent hydrogel was synthesized through crosslinking graft copolymerization of methacrylic acid onto collagen, using ammonium persulphate as a free radical initiator in the presence of methylenebisacrylamide as a crosslinker. The hydrogel structure was confirmed by 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 the optimized conditions concluded, maximum capacity of swelling in distilled water was found to be 415 g/g. The swelling kinetics of the synthesized hydrogels with various particle sizes was preliminarily investigated. Absorbency in aqueous chloride salt solutions indicated that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. The swelling of super absorbing hydrogels was also measured in solutions with pH ranged from 1-13. The synthesized hydrogel exhibited a pH-responsiveness character so that a swelling-collapsing pulsatile behaviour was recorded at pHs 2 and 7. This behaviour makes the synthesized hydrogels as an excellent candidate for controlled delivery of bioactive agents.

Key Words: Collagen, Protein, Methacrylic acid, Hydrogels, Graft copolymers, Swelling.

INTRODUCTION

Synthesis and characterization of super absorbent hydrogels is the main goal of the several research groups[1-4]. These materials are defined as hydrophilic, three-dimensional networks with ability to absorb large values of water, saline solution or physiological fluids[5]. The absorbed fluids are hardly removable even under some pressure. They are widely used in various applications such as hygienics, foods, cosmetics and agriculture[6-8]. This accounts for increase in the worldwide production of super absorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996[5]. Nowadays, the worldwide production of super absorbent polymers is more than one million tons in year. Hence, synthesis and investigation of specific and

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new super absorbent hydrogels with high absorbency, mechanical strength and initial absorption rate is important.

The properties of the swelling medium (*e.g.*, pH, ionic strength and the counter ion and its valency) affect the swelling characteristics. Super absorbent polymers responding to external stimuli such as heat, pH, electric field, chemical environments, *etc.*, 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[9,10].

Natural-based super absorbent 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 super absorbing 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 super absorbent hydrogels is graft copolymerization of vinylic monomers onto natural polymers. Monomers such as acrylonitrile (AN), acrylic acid (AA), acrylamide (AAm) have been graft copolymerized onto polysaccharides such as starch, cellulose and their derivatives[11-15]. The first industrial super absorbent hydrogel was synthesized using this method *via* ceric-induced graft copolymerization of acrylonitrile onto starch followed by alkaline hydrolysis of the resulted graft copolymer[16].

Proteins are relatively new polysaccharides to synthesize of natural-based super absorbent polymers. Only a few studies have been reported in the case of protein-based SAPs[17,18]. Proteins are widely distributed in nature and are synthesized mainly in animals, *i.e.*, collagen, keratin, gelatin, ant *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. In the present report, to modify the hydrolyzed collagen, the grafting of methaacrylic acid (MAA) onto protein chains in the presence of a crosslinking agent was performed in a homogeneous system. Optimization of the grafting variables affecting on the swelling capacity as well as the salt- and pH-sensitivity of the hydrogels were investigated in detail.

EXPERIMENTAL

Hydrolyzed collagen (from Parvar Novin-E Tehran Co.), N,N'-methylene bisacrylamide (MBA, from Fluka), ammonium persulphate (APS, from Fluka), methacrylic acid (MAA, 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: Synthesis of the hydrogel, collagen-g-PMAA, was carried out using ammonium persulfate (APS) as an initiator and N,N′-methylene *bis*acrylamide (MBA) as a crosslinker in an aqueous medium. A general procedure for crosslinking graft copolymerization of methacrylic acid (MAA) onto collagen was conducted as follows. Hydrolyzed collagen (1.50 g) was dissolved in 35 mL distilled water and filtered to remove its insoluble salt. Then the solution was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 400 rpm). The reactor was immersed in a thermostated water bath preset at a desired temperature (70 ºC). Then 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 70 % neutralized MAA (2.0-8.0 g in 5 mL H_2O) and MBA (0.05-0.20 g in 5 mL H_2O) were simultaneously added to the reaction mixture. After 1 h, 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 *ca.* 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 ºC for 10 h. After grinding, the powdered super absorbent 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 (0.5000 ± 0.001 g) with average particle sizes between 40-60 mesh (250-350 μm) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrated swelling (ES) was measured twice using the following equation:

$$\text{Equilibrated swilling (g/g)} = \frac{\text{Weight of swollen gel - Weight of dried gel}}{\text{Weight of dried gel}} \quad (1)$$

The accuracy of the measurements was ± 3 %.

Absorbency at various pHs: Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions (0.1 M) to achieve pH = 6 and pH 6, respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ± 0.1). Then, 0.500 ± 0.001 g of the dried hydrogel was used for the swelling measurements according to eqn. 1.

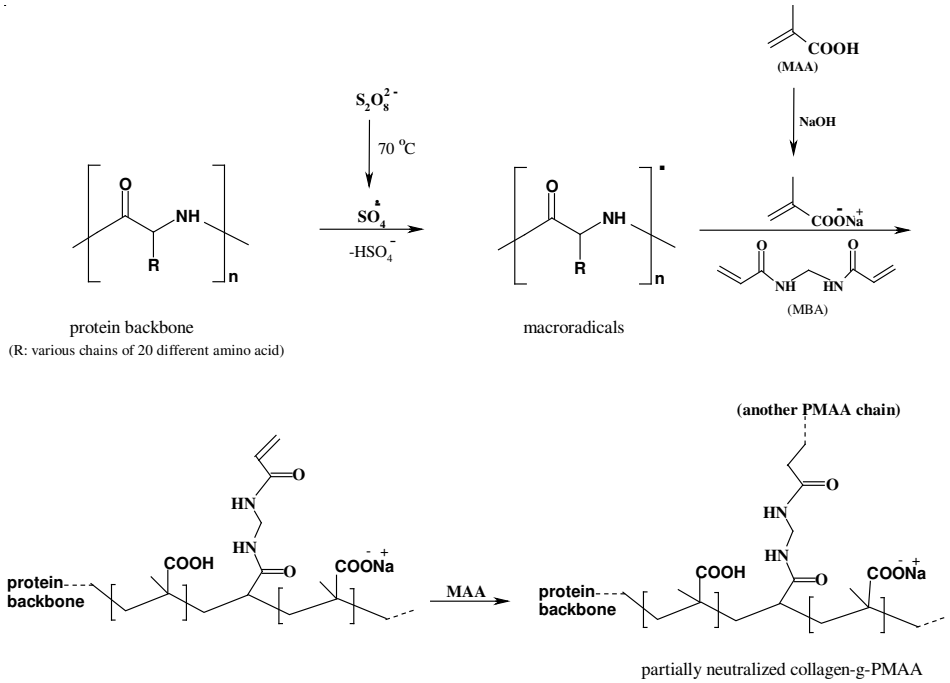
pH sensitivity: pH sensitivity of the hydrogel was investigated in terms of swelling and deswelling of the final product at two basic (pH 8) and acidic (pH 2) solutions, respectively. Swelling capacity of the hydrogels at each pH was measured according to eqn. 1 at consecutive time intervals (0.5 h).

Swelling kinetics: For studying the absorbency rate of the hydrogels, certain amount of samples (0.500 ± 0.001 g) was poured into numbers of weighed tea bags and immersed in distilled water (200 mL) or salt solution (100 mL). At consecutive time intervals, the equilibrium swelling capacity of the hydrogels was measured according to the above-mentioned method.

Infrared spectroscopy: FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Mechanism of hydrogel formation: A general reaction mechanism for crosslinking graft copolymerization of MAA onto collagen backbones in the presence of APS and MBA is shown in **Scheme-I**. The sulphate anion-radical produced from thermally decomposition of APS, abstracts hydrogen from one of the functional groups in side chains (*i.e.*, COOH, SH, OH and NH_2) of the substrate to form corresponding radical. Then the resulted macroradicals radically initiate graft copolymerization of neutralized MAA led to a graft copolymer so called collagen-g-PMAA. Since a crosslinking agent, *i.e.*, MBA, is presented in the reaction mixture, the crosslinked collagen-g-PMAA network is resulted.



Scheme-I: Proposed mechanistic pathway for synthesis of the partially neutralized collagen-g-PMAA hydrogel

Spectral characterization: For identification of the hydrogel, infrared spectroscopy was used. Fig. 1 shows the FTIR spectra of the hydrolyzed collagen and the synthesized hydrogel. The band observed at 1655 cm^{-1} can be attributed to C=O stretching in carboxamide functional groups of substrate backbone (Fig. 1a). The broad band at 3600-3200 cm^{-1} is due to stretching of -OH groups of the collagen. The IR spectrum of the hydrogel, collagen-g-PMAA (Fig. 1b) shows three new

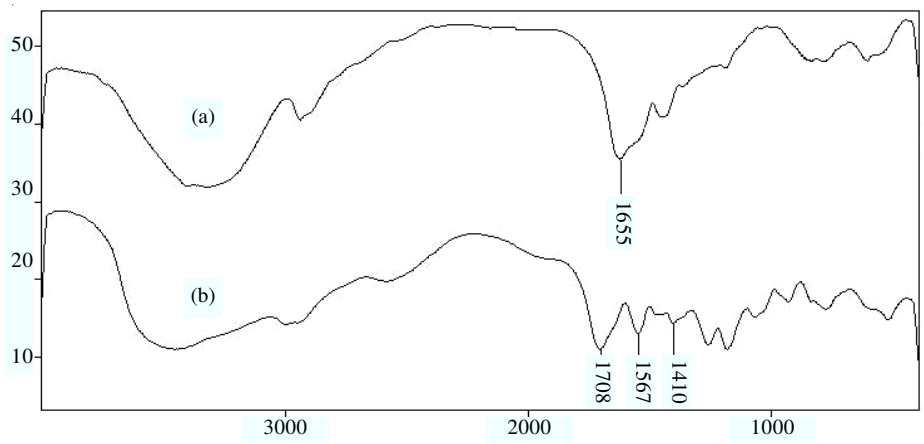


Fig. 1. FTIR spectra of hydrolyzed collagen (a) and collagen-g-PMAA hydrogel (b)

characteristic absorption bands at 1708, 1567 and 1410 cm^{-1} verifying the formation of graft copolymer product. These peaks attributed to carbonyl stretching of the carboxylic acid groups and symmetric and asymmetric stretching modes of carboxylate anions, respectively[19]. Combination of absorption of the carboxylate and alcoholic O-H stretching bands is appeared in the wide range of 3600-2550 cm^{-1}.

To obtain an additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. The resulted product was precipated by pouring the reaction mixture solution into 250 mL of ethanol and the precipitate was filtered and repeatedly washed with ethanol. Then, 0.5 g of the dried product was poured product in 50 mL of dimethyl formamide solution (a suitable solvent for homopolymer). The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the collagen-g-PMAA was filtered, washed with ethanol and dried in oven at 50 °C to reach a constant weight. After extracting the homopolymer (PMAA), appreciable amount of synthetic polymer percentage of the graft copolymer (85 %) were concluded. Since the FT-IR spectrum of the homopolymer and graft copolymer is similar, the homopolymer-free graft copolymer spectrum was compared with that of the hydrogel. The graft copolymer spectrum was very similar to Fig. 1b. Also according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.2 %. This fact practically proves that all MAA are involved in the polymer network. Therefore, the monomer per cent in the network will be very similar to that of the initial feed of reaction.

Optimization of the grafting variables: In this work, the main factors affecting on the grafting conditions (*i.e.*, concentration of MBA, MAA and APS) as well as the swelling behaviour of the resulted pH-responsive and low salt-sensitive super absorbent hydrogels were investigated.

Effect of N,N′-methylene bisacrylamide concentration: Crosslinks have to be present in a hydrogel in order to prevent dissolution of the hydrophilic polymer

chains in an aqueous environment. The crosslinked nature of hydrogels makes them insoluble in water. The efficiency of the incorporated crosslinker controls the overall crosslink density in the final hydrogel. Fig. 2 shows the influence of the crosslinking agent on the swelling capacity of collagen-g-PMAA hydrogel. As indicated in Fig. 2, the maximum absorbency is achieved at 0.008 mol/L of crosslinker MBA. Higher values of absorbency is obtained using lower crosslinker concentration (Cc). However, the hydrogels prepared do not posses good dimensional stability, so that the swollen gel strength is not sufficient to be referred as a real super absorbent. In fact, with Cc 0.002-0.004 mol/L no gel is prepared and with Cc 0.006 mol/L, slimy gel is formed. Fig. 2 exhibits a power law behaviour of absorbency-Cc. The relationship absorbency = $k \cdot Cc^{-n}$ with k = 13.89 and n = 0.53 is obtained from the fitted curve. Such a behaviour is well-known as reported by pioneering scientists[10,20]. Chen and Zhao[21] have also reported a similar behaviour for an acrylic-based super absorbent. Higher crosslinker concentration 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.

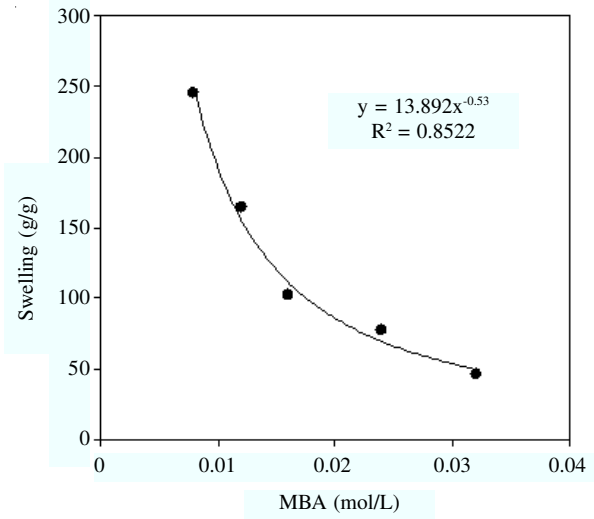


Fig. 2. Effect of crosslinker concentration on swelling capacity. Reaction conditions: collagen 1.50 g, MAA 0.80 mol/L, APS 0.01 mol/L, H_2O 50 mL, 70 °C, 1 h

Effect of methacrylic acid concentration: Fig. 3 demonstrates the effect of the monomer concentration on swelling capacity of collagen-g-PMAA product. The absorbency is increased *versus* increasing the MAA concentration from 0.40-1.02 mol/L and then, it is decreased with a further increase for MAA. The maximum absorbency (325 g/g) is obtained at 1.02 mol/L of the monomer, MAA. The initial increase in swelling values can be attributed to the higher the hydrophilicity of the hydrogel and the greater availability of MAA molecules near the collagen macroradicals. The swelling-loss after the maximum may be attributed to (a) preferential

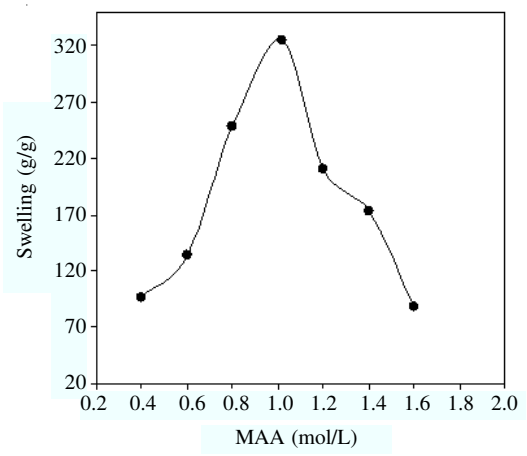


Fig. 3. Effect of monomer concentration on swelling capacity. Reaction conditions: collagen 1.50 g, MBA 0.008 mol/L, APS 0.01 mol/L, H_2O 50 mL, 70 °C, 1 h

homopolymerization over graft copolymerization, (b) increase in viscosity of the medium, which restricts the movement of free radicals and monomer molecules and (c) the enhanced chance of chain transfer to monomer molecules. Other investigators[22-24] reported similar conclusions.

To obtain an additional evidence of grafting (or swelling) dependency to the monomer concentration, the percentage of grafting efficiency (Ge %) was evaluated with the following weight-basis equation as reported by Fanta[25]:

$$\text{Grafting efficiency (GE,\%)} = \frac{\text{PMAA grafted}}{\text{Monomer charged}} \times 100 \quad (2)$$

The Ge % stands for the grafted PMAA formed from initial monomer charged. The Ge % parameter was found to be increased (79-86 %) by enhancement of methacrylic acid concentration from 0.40-1.02 mol/L and then, it is decreased.

Effect of ammonium persulfate concentration: The effect of initiator content on swelling capacity of crosslinked collagen-g-PMAA was studied by varying the APS concentration from 0.001-0.040 mol/L (Fig. 4). As shown in the figure, swelling capacity is increased with increasing the APS concentration from 0.001-0.015 mol/L and then it is considerably decreased with a further increase in the concentration of APS. By increasing the APS concentration up to 0.015 mol/L, the number of active free radicals on the collagen backbone is increased which, in turn, resulting in higher graft polymerization extent and consequently higher final water absorbency. The APS concentrations higher than the optimum value, however, lead to low-swelling super absorbents. This swelling-loss may be attributed to an increase in terminating step reaction *via* bimolecular collision, which, in turn, causes to enhance crosslinking density. Chen and Zhao[21] refer to this possible phenomenon as "self-crosslinking". In addition, decrease in molecular weight (MW) of grafted PMAA of the hydrogel causes to decrease swelling value. The latter reason is due to the

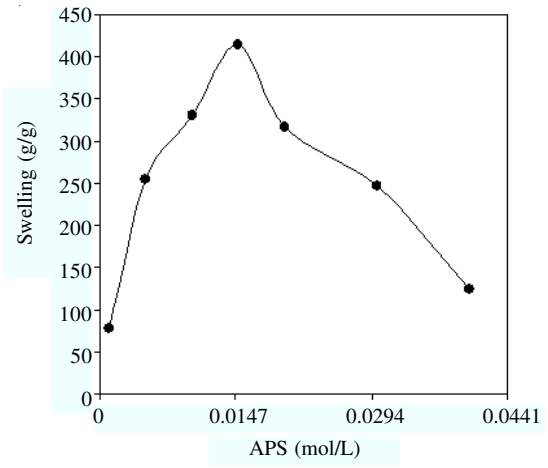


Fig. 4. Effect of initiator concentration on swelling capacity. Reaction conditions: collagen 1.50 g, MBA 0.008 mol/L, MAA 1.02 mol/L, H_2O 50 mL, 70 °C, 1 h

inverse relationship between molecular weight and initiator concentration[26]. Moreover, the free radical degradation of collagen backbones by sulphate radical-anions is an additional reason for swelling-loss at higher APS concentration. The proposed mechanism for this possibility is reported in the previous work[27]. Hsu *et al.*[28], recently report a similar observation in the case of degradation of chitosan with potassium persulphate.

Swelling kinetics: In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Buchholz[29] has suggested that the swelling kinetics for the super absorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer[29]. Fig. 5 represents the dynamic swelling behaviour of the super absorbent 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 *ca.* 0.5 h. A power law behaviour is obvious from Fig. 5. The data may be well fitted with a Voigt-based equation (eqn. 3)[30]:

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

where S_t (g/g) = swelling at time t, S_e = equilibrium swelling (power parameter, g/g); t = time (min) for swelling S_t and τ (min) stand for the "rate parameter". The rate parameters for super absorbent are found to be 0.88, 1.80 and 3.50 min for super absorbents with particle sizes of 100-250, 250-400 and 400-550 μm, respectively. It is well-known that the swelling kinetics for the super absorbent polymers is significantly influenced by particle size of the absorbents[31]. With a lower the 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.

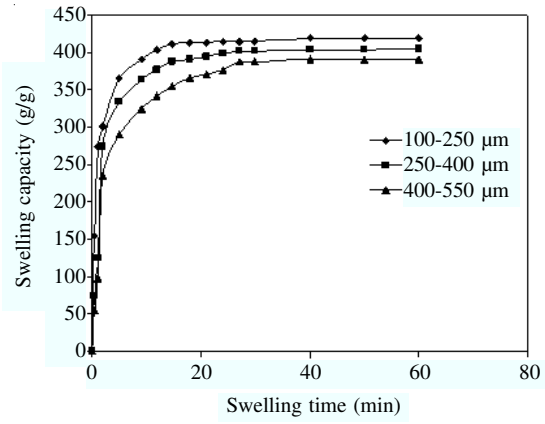


Fig. 5. Representative swelling kinetics of the hydrogel, collagen-g-PMAA, in distilled water with various particle sizes

Equilibrium swelling at various pH solutions: Ionic super absorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, equilibrium swelling for the synthesized hydrogels was measured in different pH solutions ranged from 1-13 (Fig. 6). 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) and HCl (pH 1) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (95 g/g) was obtained at pH 8. Under acidic pHs (≤ 4), most of the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling values are decreased. However, some sort of attractive interactions (H-O hydrogen bonding) lead to decreased absorbencies. At higher pHs (5-8), some of carboxylate groups are ionized and the electrostatic repulsion between COO^- groups causes an enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions (pH > 8) is "charge screening effect" of excess Na^+ in the swelling media, which shields the sulfonate and carboxylate anions and prevents effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems[32-35].

pH responsiveness behaviour of collagen-g-PMAA hydrogel: Since the synthesized hydrogel, collagen-g-PMAA, shows different swelling behaviours in acidic and basic pH solutions, we investigated the reversible swelling-deswelling behaviour of this hydrogel in solutions with pH 2 and 8 (Fig. 7). At pH 8, the hydrogel swells due to anion-anion repulsive electrostatic forces, while at pH 2, it shrinks within a few minutes due to protonation of the sulfonate and carboxylate anions. This swelling-deswelling behaviour of the hydrogels makes them as suitable candidate for designing drug delivery systems. Such on-off switching behaviour as reversible swelling and deswelling has been reported for other ionic hydrogels[36-39].

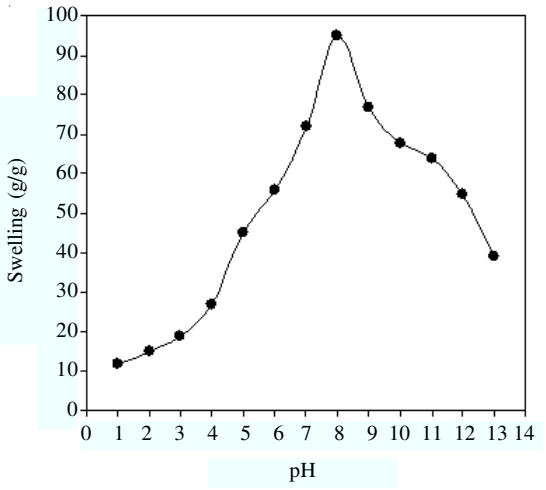


Fig. 6. Effect of pH of solution on swelling of collagen-g-PMAA super absorbent hydrogel

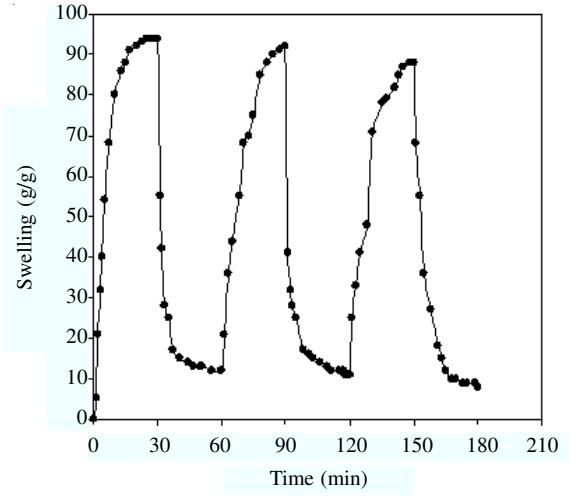


Fig. 7. On-off switching behavior as reversible pulsatile swelling (pH 8) and deswelling (pH 2) of the collagen-g-PMAA hydrogel. The time interval between the pH changes was 0.5 h

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[20]. Therefore, the

osmotic pressure resulted from the mobile ion concentration difference between the gel and aqueous phases decreased and consequently the absorbency amounts diminished. In addition, in the case of salt solutions with multivalent 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. 8 and 9). 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 behaviour is shown in Fig. 8. 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 cations. The effect of cation radius on swelling may also been observed from Fig. 8. As reported by Pass *et al.*[40], the carboxylate anion interacts with small cations, *e.g.*, Li^+, stronger than with large cations, *e.g.*, K^+. 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 KCl > NaCl > LiCl and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$, respectively.

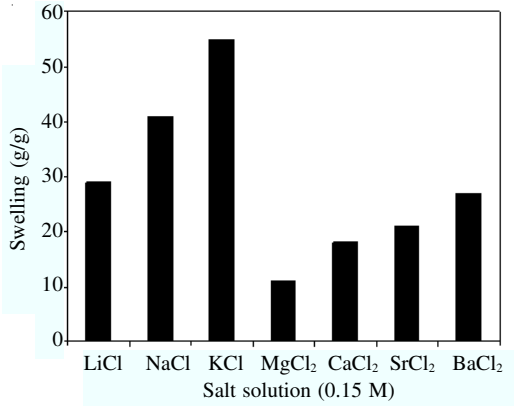


Fig. 8. Swelling capacity of the hydrogel, collagen-g-PMAA, in different chloride salt solutions (0.15 M)

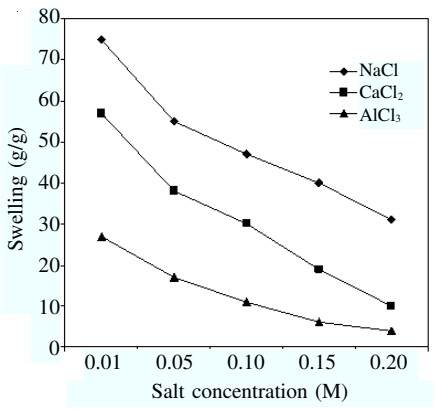


Fig. 9. Swelling capacity variation of the hydrogel in saline solutions with various concentrations

Fig. 9 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[20]:

$$\text{Swelling} = k[\text{salt}]^{-n} \quad (4)$$

where k and n are constant values for an individual super absorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity. As shown in Table-1, the k values were almost the same (*ca.* 6) for the swelling in various salt solutions. The n values proportionally changed with the cation valence enhancement. Here, the ionic crosslinking was a more effective factor against swelling than the charge-screening effect of the cation.

TABLE-1
VALUES k AND n (AS OBTAINED FROM THE CURVE FITTING, FIG. 9)
FOR THE SYNTHESIZED HYDROGEL

Swelling medium	k	n
NaCl	6.4	0.42
$CaCl_2$	6.2	0.56
$AlCl_3$	6.3	0.78

Conclusion

The super absorbent hydrogel, collagen-g-PMAA, was synthesized by graft copolymerization of methacrylic acid onto collagen, in a homogeneous medium. The maximum water absorbency (415 g/g) was achieved under the optimum conditions that found to be MAA 1.02 mol/L, MBA 0.008 mol/L and APS 0.015 mol/L. The super absorbent hydrogels exhibited high sensitivity to pH, so that, several swelling changes of the hydrogel were observed *in lieu* of pH variations in a wide range (1-13). Ionic repulsion between charge groups incorporated in the gel matrix by an external pH modulation could be assumed as the main driving force responsible for such abrupt swelling changes. Furthermore, the reversible swelling-deswelling behaviour in solutions with acidic and basic pH makes the hydrogels as a suitable candidate for controlled drug delivery systems. Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in solutions with monovalent cations. 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. Finally, dynamic swelling kinetics of the hydrogels shows that the rate of absorbency is increased with decreasing the particle size of super absorbing samples.

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