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Synthesis and absorbency of gelatin-*graft*-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel with salt- and pH-responsiveness properties

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Abstract: In this article, we synthesize a novel gelatin-based superabsorbent hydrogel via graft copolymerization of mixtures of acrylic acid (AA) and acrylamide (AAm) onto gelatin backbones. The polymerization reaction was carried out in an aqueous medium and in the presence of ammonium persulfate (APS) as an initiator and *N*,*N*′-methylene bisacrylamide (MBA) as a crosslinker. The hydrogel structures were confirmed by FTIR spectroscopy. The effect of grafting variables, i.e. concentration of MBA and APS, AA/AAm weight ratio, and reaction time and temperature, was systematically optimized to achieve a hydrogel with swelling capacity as high as possible. The swelling behavior of these absorbent polymers was also investigated in various salt solutions. Results indicated that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. Furthermore, 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 7.0. This on-off switching behavior makes the synthesized hydrogels an excellent candidate for controlled delivery of bioactive agents. Finally, the swelling kinetics of the synthesized hydrogels with various particle sizes was preliminarily investigated.

Introduction

Highly swelling polymers, i.e. superabsorbent hydrogels, are hydrophilic, three dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight [1]. They are widely used in various applications such as hygienics, 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 450000 tons in 1996 [1]. Nowadays, the worldwide production of SAPs is more than one million tons in a year. Hence, synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world [5-8].

The properties of the swelling medium (e.g. pH, ionic strength and the counter ion and its valency) affect the swelling characteristics [2, 9]. The hydrogels sharply and reproducibly responding to the medium conditions are referred to as “responsive”,

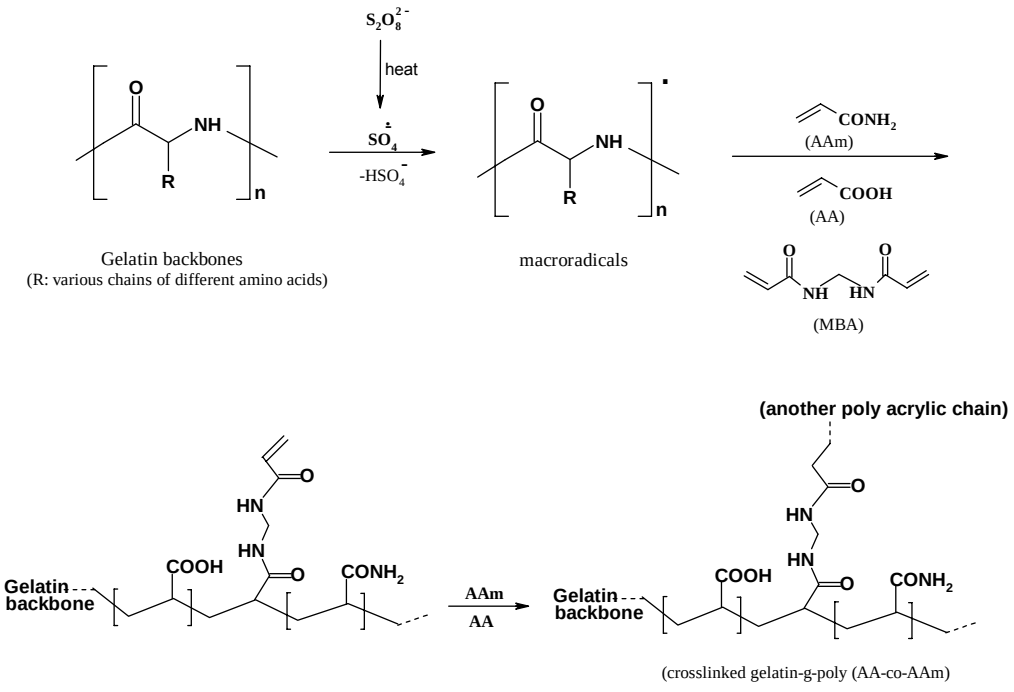
"smart" or "intelligent". Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs [10, 11].

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. Natural-based SAPs have attracted much attention in medical and pharmaceutical fields because of their non-toxicity, biocompatibility and biodegradability. Free radical vinyl graft copolymerization onto natural polymers is a well-known method for synthesis of natural-based superabsorbent hydrogels [12-15]. The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile was synthesized using this method [16].

Gelatin is a biomaterial with the above mentioned essential properties. Generally, crosslinking in gelatin is used in various purposes such as gelatin swelling, and gelatin hydrogels as biodegradable implants to deliver small and macromolecular drugs. Recently, attention has been focused on employing gelatin substrate to produce hydrogels with a specific response to a biological environment [17-21]. Therefore, following a continuous research on synthesis of natural-based superabsorbent hydrogels [22-25], in this paper we attempted the synthesis of a novel gelatin-based superabsorbing polymer. The swelling behavior in distilled water and various saline and pH solutions was investigated as well.

Results and discussion

Synthesis and spectral characterization



Scheme 1. Proposed mechanistic pathway for synthesis of the gelatin-based hydrogels.

The mixture of monomers, acrylamide and acrylic acid, was simultaneously grafted onto gelatin backbones in a homogeneous medium using APS as a radical initiator and MBA as a crosslinking agent. A general reaction mechanism for gelatin-*g*-poly(NaAA-co-AAm) hydrogel formation is shown in Scheme 1. At the first step, the thermally dissociating initiator, i.e. APS, is decomposed under heating to produce sulfate anion-radical. Then, the anion-radical 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. So, these macroradicals initiated monomer grafting onto gelatin backbones led to a graft copolymer. In addition, crosslinking reaction was carried out in the presence of a crosslinker, i.e., MBA, so that a three dimensional network was obtained [26].

Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 1 shows the FTIR spectra of the gelatin substrate and the synthesized hydrogel. The band observed at 1634 cm^{-1} can be attributed to C=O stretching in carboxamide functional groups of substrate backbone (Figure 1a). The superabsorbent hydrogel product comprises a gelatin backbone with side chains that carry sodium carboxylate and carboxamide functional groups that are evidenced by peaks at 1558 and 1637 cm^{-1} respectively (Figure 1b). The characteristic band at 1558 cm^{-1} is due to asymmetric stretching in carboxylate anion that is reconfirmed by another peak at 1411 cm^{-1} which is related to the symmetric stretching mode of the carboxylate anion [27]. The stretching band of the grafted carboxamide groups overlapped with that of the gelatin portion of the copolymer.

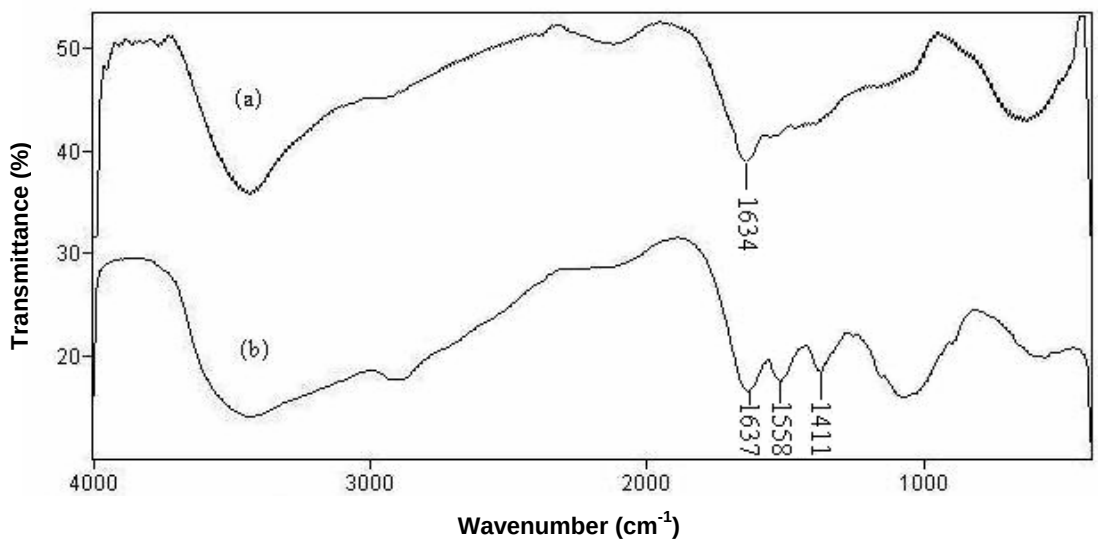


Fig. 1. FTIR spectra of gelatin (a) and gelatin-*g*-poly(NaAA-co-AAm) hydrogel (b).

To obtain an additional evidence of grafting, a similar polymerization was conducted in the absence of crosslinker. The resulted product was precipitated 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 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 gelatin-*g*-poly(sodium acrylate-co-acrylamide) was filtered, washed with ethanol and dried in oven at 50˚C to reach a constant weight. After

extracting the poly(NaAA-co-AAm) (3%), appreciable amount of grafted gelatin was concluded. The graft copolymer spectrum was very similar to Figure 1(b).

Optimization of the grafting conditions

Different variables affecting the ultimate swelling capacity (i.e. concentration of MBA and APS, AA/AAm weight ratio, and reaction time and temperature) were optimized to achieve superabsorbents with maximum water absorbency.

Effect of crosslinker 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. Efficiency of the incorporated crosslinker controls the overall crosslink density in the final hydrogel. Figure 2 shows the influence of the crosslinking agent on the swelling capacity of gelatin-*g*-poly(NaAA-co-AAm) hydrogel. In this reaction series, the AA/AAm ratio in monomer feed was chosen to be 1. As indicated in Figure 2, the maximum absorbency is achieved at 0.043 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 superabsorbent. In fact, with Cc 0.01-0.02 mol/L no gel is prepared and with Cc 0.03 mol/L, slimy gel is formed. Figure 2 exhibits a power law behavior of absorbency-Cc. The relationship $absorbency = k.Cc^{-n}$ with k=11.65 and n=0.72 is obtained from the fitted curve. Such a behavior is well-known as reported by pioneering scientists [2, 11, 28]. Chen and Zhao have also reported a similar behavior for an acrylic-based superabsorbent [29]. 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.

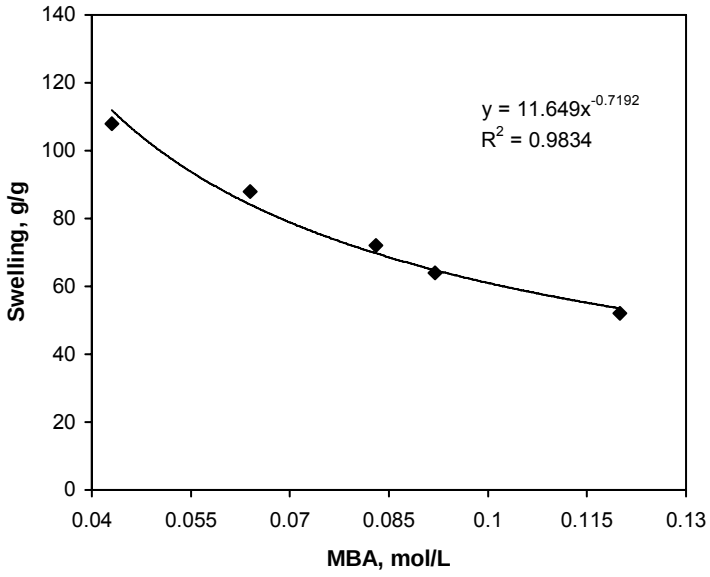


Fig. 2. Swelling dependency of the hydrogel on crosslinker concentration. Reaction conditions: Gelatin 1.0 g, AA= 1g, AAm= 1g, APS 0.016 mol/L, 60 °C, 90 min.

Effect of monomer ratio on swelling capacity

The swelling capacity of the hydrogels prepared with various ratios of monomers, is shown in Figure 3. In this series of experiments, both monomer concentrations were simultaneously changed from 0.4 to 1.6 g. Since pH of the polymerization mixture was adjusted at 8.0 after the reaction, the superabsorbency of gelatin-*g*-poly(NaAA-co-AAm) hydrogel is due to both functional groups of ionic carboxylate (from neutralized AA) and non-ionic carboxamide (from AAm). As shown in Figure 3, higher swelling capacities are obtained from employing higher initial ratios of AA/AAm. This behavior can be attributed to the formation of high carboxylate groups in samples. The ionic groups are more strongly solvated than non-ionic groups in the aqueous medium.

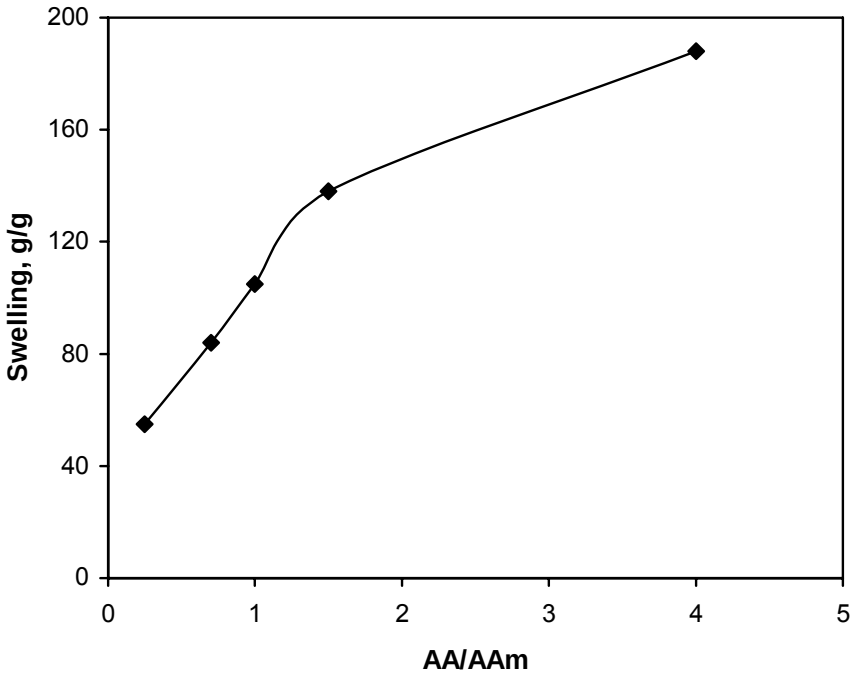


Fig. 3. Effect of monomer ratio on swelling capacity of the gelatin-based hydrogels. Reaction conditions: Gelatin 1.0 g, AA= 0.4-1.6 g, AAm= 1.6-0.4 g, MBA 0.043 mol/L, APS 0.016 mol/L, 60 °C, 90 min.

Effect of initiator concentration

The swelling ratio as a function of initiator concentration, for gelatin-*g*-poly(NaAA-co-AAm) hydrogel was investigated (Figure 4). The absorbency is increased versus increasing the APS concentration from 0.005 to 0.02 mol/L and then, it is decreased considerably with a further increase in the amount of APS. The maximum absorbency (210 g/g) is obtained at APS 0.02 mol/L. The number of active free radicals on the gelatin backbone is increased in terms of the initiator levels lower than 0.02 mol/L. This accounts for the initial increment in swelling up to a certain amount of APS. The swelling decrease after the maximum may be attributed to increased number of produced radicals which leads to terminating step via bimolecular collision resulting in enhanced crosslink density. This possible

phenomenon is referred to as "*self crosslinking*" by other workers [29]. An additional reason for decreasing the absorbency can be related to decreasing molecular weight (MW) of the grafted monomers at high levels of APS concentration. Since MW inversely depends on initiator concentration, [I], higher [I] results in lower MW and, in turn, lower swelling capacity of the hydrogel [30]. On the other hand, free radical degradation of gelatin substrate is also possible at high APS levels. A similar observation is recently reported by Hsu et al. in the case of degradation of chitosan with potassium persulfate [31].

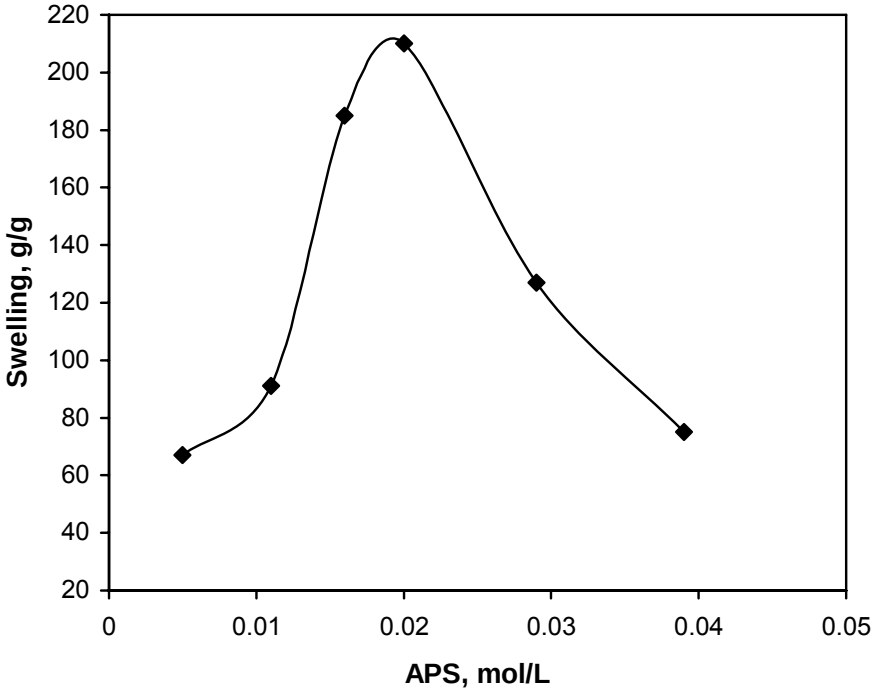


Fig. 4. Effect of initiator concentration on swelling capacity. Reaction conditions: Gelatin 1.0 g, MBA 0.043 mol/L, AA= 1.6 g, AAm= 0.4 g, 60 °C, 90 min.

Effect of reaction temperature

The swelling capacity of the hydrogels prepared with various reaction temperatures is shown in Figure 5. Higher temperatures favor the rate of diffusion of the monomers to the gelatin macroradicals as well as increase the kinetic energy of radical centers. In addition, higher temperatures increase the rate of decomposition of the thermally dissociating initiator, APS [32]. The temperatures higher than the optimum value (60°C), however, lead to low-swelling superabsorbents. This swelling loss may be attributed to (a) oxidative degradation of gelatin chains by sulfate radical-anions, (b) increasing the rate of termination and chain transfer reactions, and (c) decomposition of APS to give O_2 (a radical scavenger), which reacts with primary free radicals [Eqs. (1) and (2)] [33] resulting in decreased molecular weight and decreased swelling (the sulfate radical anions may react with water to produce hydroxyl radicals, Eq. (1), and finally oxygen, Eq. (2)).

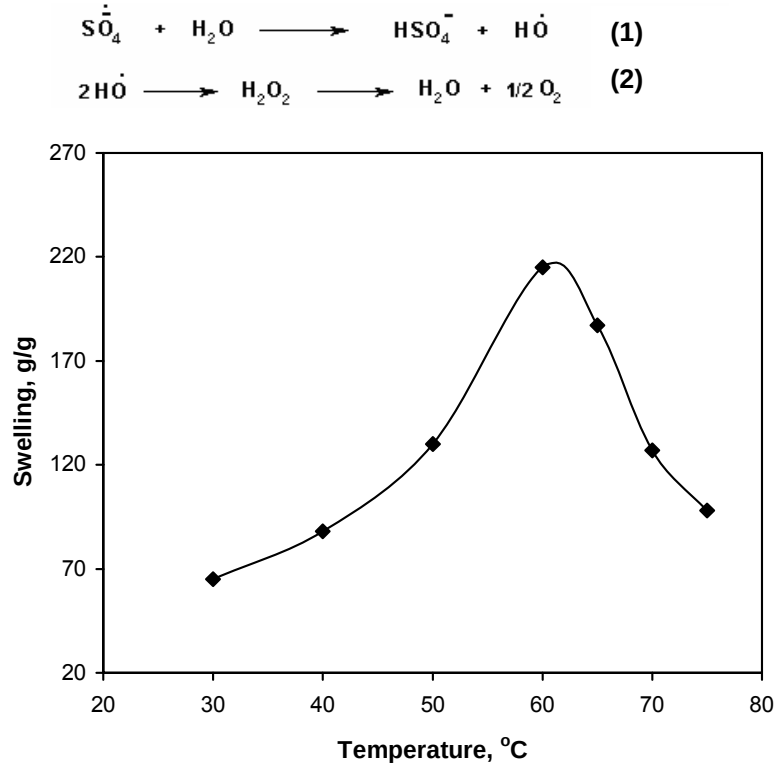


Fig. 5. Effect of reaction temperature on swelling capacity. Reaction conditions: Gelatin 1.0 g, MBA 0.043 mol/L, APS 0.02 mol/L, AA= 1.6 g, AAm= 0.4 g, 90 min.

Effect of reaction time

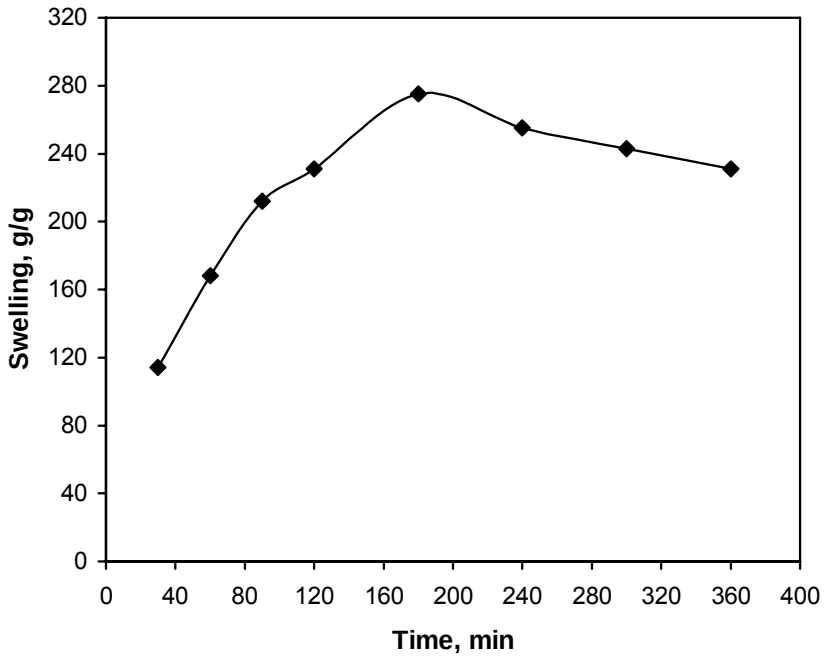


Fig. 6. Effect of polymerization time on swelling capacity. Reaction conditions: Gelatin 1.0 g, MBA 0.043 mol/L, APS 0.02 mol/L, AA= 1.6 g, AAm= 0.4 g, 60 °C.

Figure 6 demonstrates the effect of the reaction time on swelling of gelatin-*g*-poly(NaAA-co-AAm) product. The reaction period (the time after addition of monomers and crosslinker to the mixture) was varied from 30 to 360 min. The water absorbency intensely increased versus time up to 180 min and then, it is gradually decreased. It is obvious that with increasing the reaction time, more collision of monomers and gelatin macroradicals causes a higher graft copolymer and, in turn, higher water absorbency of the final gelatin-*g*-poly(NaAA-co-AAm). The absorbency loss after 180 min can be ascribed to (a) the degradation of gelatin with remained sulfate ion-radicals, (b) decrease in activity and concentration of APS and monomers with progress of reaction, (c) increase in viscosity and steric hindrance due to production of long grafted chains and (d) reaction between water and sulfate radical-anion to produce hydroxyl radicals and oxygen scavenging the propagation macroradicals [33].

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.

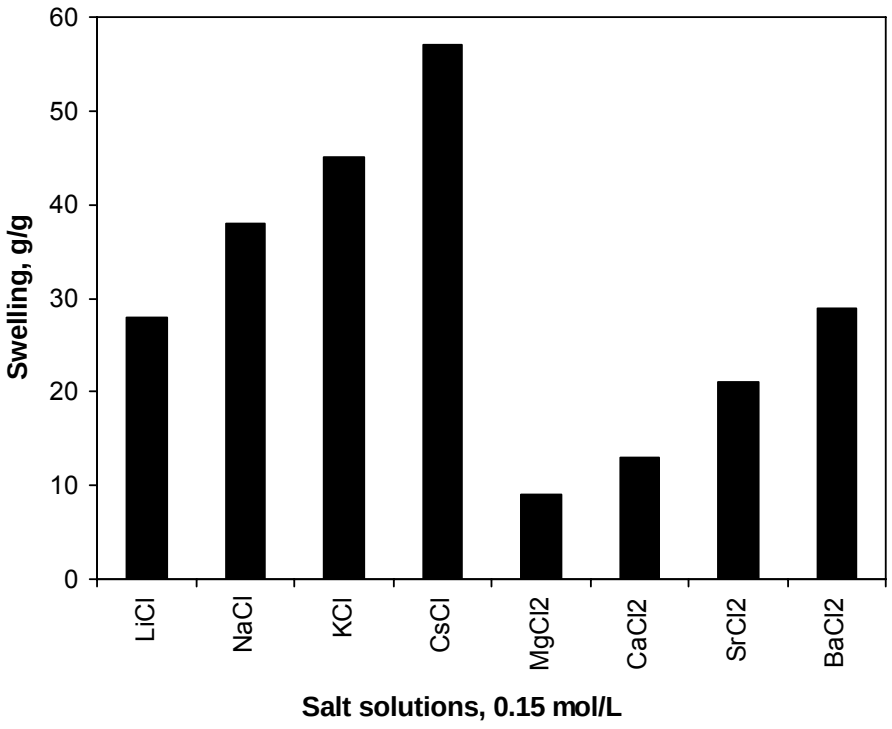


Fig. 7. Swelling capacity of the hydrogel in different chloride salt solutions (0.15M).

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 [28]. 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 causes an appreciable decrease in swelling capacity.

In this series of experiments, the swelling capacity was measured in various salt solutions (Figures 7, 8). It is obvious that swelling decrease 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 Figure 7. 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 Figure 7. As reported by Pass et al. [34], 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.

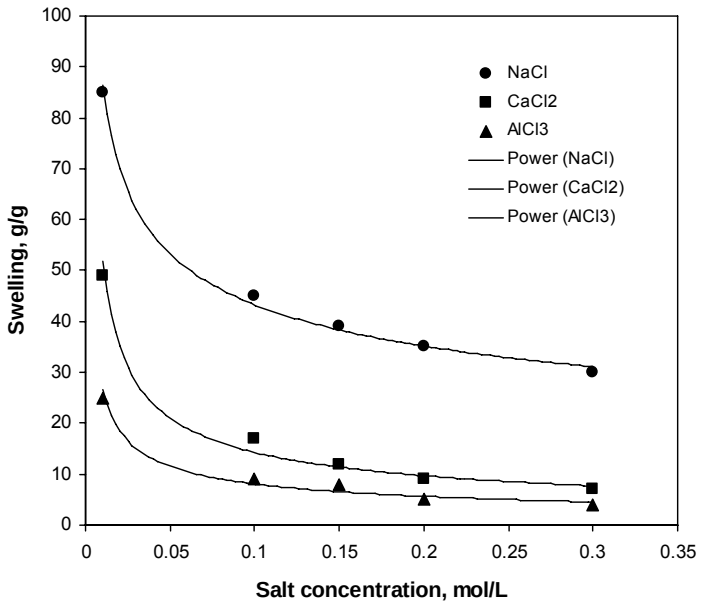


Fig. 8. Swelling capacity variation of the hydrogel in saline solutions with various concentrations. Hydrogel composition: AA= 1.6 g, AAm= 0.4 g.

Figure 8 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 [28]:

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

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 8 indicates that changing of the salt concentrations higher than ~0.2 M has no appreciable influence on superabsorbency of the superabsorbent.

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 (Figure 9). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by the addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 10.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (51 g/g) was obtained at pH 8. In acidic media, most carboxylate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio. At higher pHs (3– 8), some carboxylate groups are ionized and the electrostatic repulsion between carboxylate groups causes an enhancement of the swelling capacity. The reason of the swelling loss for the highly basic solutions is the charge screening effect of excess Na^+ in the swelling media, which shield the carboxylate anions and prevent effective anion–anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems [35-37].

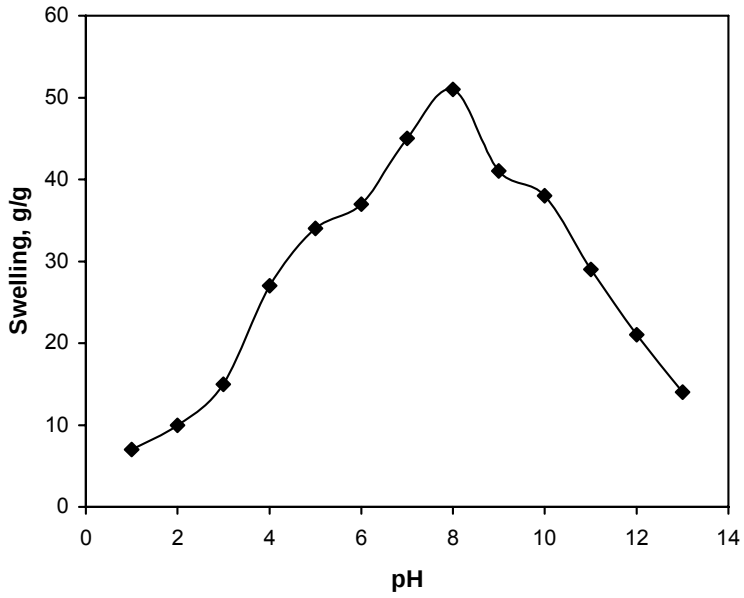


Fig. 9. Effect of pH of solutions on swelling capacity of the hydrogel. Hydrogel composition: AA= 1.6 g, AAm= 0.4 g.

pH-responsiveness behavior of the hydrogel

Since the hydrogels show different swelling behaviors at various pHs, we investigated their pH-reversibility in the solutions buffered at pHs 2.0 and 7.0 (Figure 10). The figure shows a stepwise reproducible swelling change of the hydrogel at 25 ^oC with alternating pH between 2.0 and 7.0. At pH 7.0, the hydrogel swells up to 44 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 suitable candidates for controlled drug delivery systems. Such on–off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels [38–41].

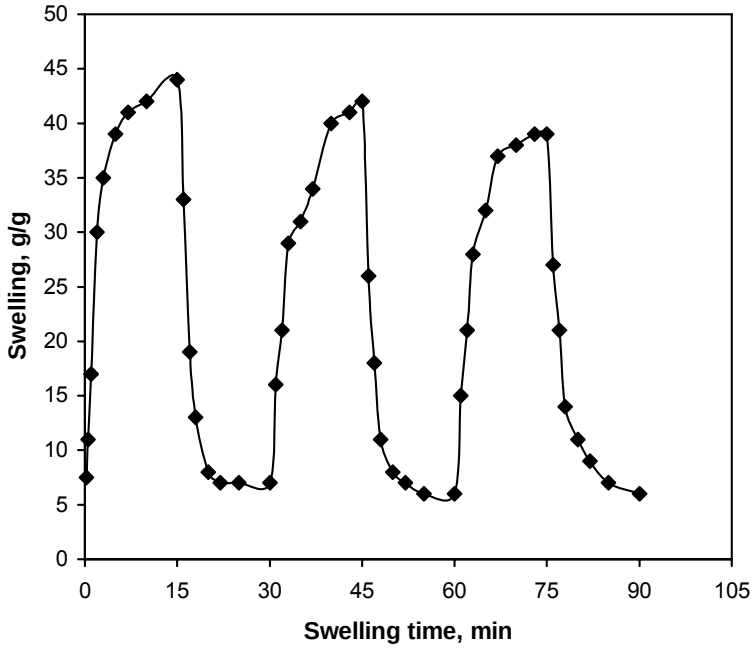


Fig. 10. On-off switching behavior as reversible pulsatile swelling (pH 7.0) and deswelling (pH 2.0) of the hydrogel. The time interval between the pH changes was 15 min.

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 the superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer [42].

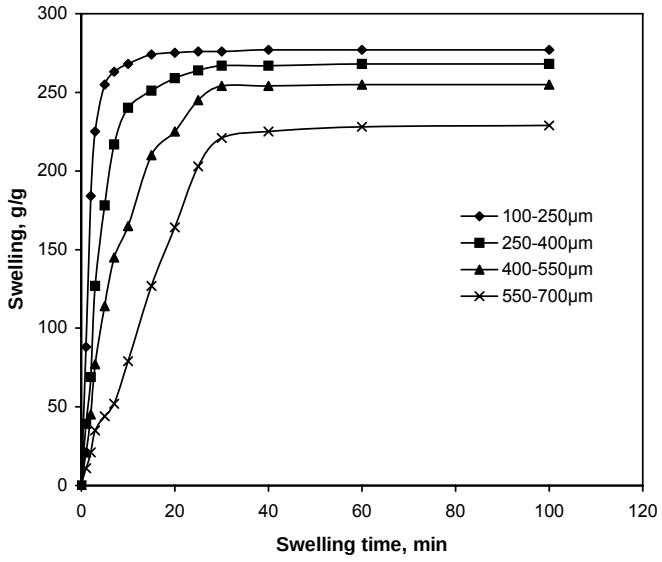


Fig. 11. Representative swelling kinetics of the superabsorbent hydrogel with various particle sizes.

Figure 11 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 ~30 min. A power law behavior is obvious from Figure 11. The data may be well fitted with a Voigt-based Eq. (Eq. 4) [43]:

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

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 1.4, 4.2, 9.8, and 17.3 min for superabsorbent with particle sizes of 100-250, 250-400, 400-550, and 550-700 μm, respectively. It is well-known that the swelling kinetics for the superabsorbent polymers is significantly influenced by particle size of the absorbents [44]. 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. Additionally, the ultimate degree of absorption increased as the particle size became smaller. This is attributed to more water being held in the volume between the particles.

Conclusions

Gelatin-*g*-poly(NaAA-co-AAm) hydrogel was synthesized through simultaneous crosslinking and graft polymerization of acrylic acid/acrylamide mixtures onto gelatin. The optimum reaction conditions to obtain maximum water absorbency (275 g/g) were found to be: MBA 0.043 mol/L, AA 0.49 mol/L, AAm 0.13 mol/L, APS 0.02 mol/L, reaction temperature 60 ^{o}C, and reaction time 180 min. The superabsorbent hydrogels exhibited high sensitivity to pH, so that, several swelling changes of the hydrogel were observed in pH variations of a wide range (1-13). Ionic repulsion between charged 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 behavior in solutions with acidic and basic pH makes the hydrogels 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 superabsorbing samples.

Experimental part

Infrared spectroscopy

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

Materials

The Gelatin (Merck) was used as received. Acrylic acid (AA, Merck), was used after vacuum distillation. Acrylamide (AAm, Fluka), was used after crystallization in acetone. Ammonium persulfate (APS, Merck) was used without purification.

Methylene bisacrylamide (MBA, Fluka), was used as received. All other chemicals were of analytical grade.

Preparation of hydrogel

A general procedure for chemically crosslinking graft copolymerization of AA and AAm onto gelatin backbones was conducted as follows. Gelatin (1.0 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at a desired temperature (30-75 ^{o}C). Then a definite amount of APS solution (0.05-0.40 g in 5 mL H_2O) was added to gelatin solution and was allowed to stir for 10 min. After adding APS, variable amounts of AA and AAm (AA 0.40–1.60 g, AAm 0.40–1.60 g) were added simultaneously to the gelatin solution. MBA solution (0.03–0.08 g in 5 ml H_2O) was added to the reaction mixture after the addition of monomers and the mixture was continuously stirred. After certain time (30-360 min), the reaction product was allowed to cool to ambient temperature and neutralized to pH 8 by addition of 1N sodium hydroxide solution. The hydrogel, gelatin-*g*-poly(NaAA-co-AAm), was poured to excess non solvent ethanol (200 mL) and kept 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 kept for 24 h. Finally, the filtered hydrogel is dried in oven at 60 ^{o}C for 10 h. After grinding using mortar, 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 triple according to Eq. 5:

$$ES(g/g) = \frac{Weight\ of\ swollen\ gel - Weight\ of\ dried\ gel}{Weight\ of\ dried\ gel} \tag{5}$$

So, absorbency was calculated triple as grams of water per gram of resin (g/g). The accuracy of the measurements was ±3%. The standard deviation (s) for a sample of data that is of limited size is given by the following equation:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(X_i - \overline{X})^2}{N-1}} \tag{6}$$

where $(X_i - \overline{X})$ is deviation from average of *i*th measurement and N is number of replicates of each measurement (here N=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 pHs

Individual solutions (50 ml) with acidic and basic pHs were prepared by dilution of NaOH (pH 10.0) and HCl (pH 1.0) solutions (0.1 M) 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. 5.

pH-sensitivity

pH-sensitivity of the hydrogel was investigated in terms of swelling and deswelling of the final product at two basic (pH 7.0) and acidic (pH 2.0) solutions, respectively. Swelling capacity of the hydrogels at each pH was measured according to Eq. 5 at consecutive time intervals (15 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 a number 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.

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