

Synthesis, characterization and swelling behavior investigation of gelatin-g-poly(acrylic acid-co-itaconic acid)

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Abstract

A novel pH-responsive superabsorbent hydrogel based on gelatin was prepared through crosslinking copolymerization of poly (acrylic acid) and poly (itaconic acid). The copolymerization conditions including monomers, initiator, gelatin and crosslinker concentration, reaction temperature, and neutralization percent were systematically optimized to achieve a hydrogel with swelling capacity as high as possible. The hydrogels structure was confirmed using Fourier-transform infrared, thermogravimetric analysis, differential scanning calorimetric and scanning electron microscopy. The swelling of the superabsorbing hydrogel was examined in buffer solutions with pH ranged 3-12. Moreover, the swelling of the hydrogel was conducted in 0.15 M aqueous solutions of NaCl, CaCl₂, and AlCl₃. Due to the high swelling capacity in salt solutions, the hydrogel may be referred to as "low-salt sensitive" superabsorbent.

Key words: Superabsorbent; hydrogel; acrylic acid; itaconic acid; swelling behavior.

Introduction

The modification of natural polymers is a promising method for the preparation of new materials. In recent years, much interest has

been shown in the development of the synthesis of natural-based superabsorbent hydrogels [1-4]. These networks are specially soft and flexible polymeric materials that can

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absorb large quantities of water, saline or physiological solutions while the absorbed solutions are not removable even under pressure [5].

Because of their non-toxicity, biocompatibility and biodegradability, natural-based hydrogels have attracted attention in many fields such as personal hygiene and cosmetics [6-8]. Among hydrogels, however, a considerable research attention has focused on so-called "smart" hydrogels which can transfer their volume in response to environmental stimuli [9,10].

Graft polymerization of vinylic monomers onto their backbones in the presence of crosslinkers is an efficient approach to modify natural polymers [11-13]. Hence, in this work, we describe the preparation and characterization of a gelatin-g-poly(acrylic acid-co-itaconic acid) hydrogel as a new natural-based polymer with pH and salt-responsiveness properties.

Experimental

General

The gelatin (Merck) was used as received. Acrylic acid (AA, Merck) and itaconic acid (IA) were used after vacuum distillation. Methylene bisacrylamide (MBA), from Fluka, was employed after crystallization in acetone. Ammonium persulfate (APS, Merck) was used without purification. All other chemicals were of analytical grade.

Hydrogel preparation

A certain amount of gelatin (0.5-5.0 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 23 mL double distilled water. The reactor was immersed in a thermostated water bath preset at 70-75 °C. Then, variable amounts of AA and IA (AA 4-10 mL, IA 0.40–1.85 g) were added simultaneously to the gelatin solution. After 10 min, a definite amount of APS solution (0.13-0.35 g, dissolved in 1 mL H₂O) was added to the solution. After adding APS, methylene bisacrylamide solution (0.01–0.90 g, dissolved in 1 mL H₂O) was added to the reaction mixture. After 60 min, the reaction product was allowed to cool to ambient temperature and neutralized to pH 8 by addition of 4N sodium hydroxide solution. The hydrogel was poured to excess non-solvent ethanol (200 mL) and kept for 3 h to remove its absorbed water. Then ethanol was decanted and the product scissored to small pieces. Again, 100 mL fresh ethanol was added and the hydrogel was stored for 24 h. Finally, the filtered hydrogel was dried in oven at 60°C for 10 h. After grinding by mortar, the powdered superabsorbent was stored by protecting from moisture, heat and light.

Swelling measurements

An accurately weighed sample (0.5 ± 0.001 g) of the dried hydrogel was immersed in dis-

tilled water (200 mL) and allowed to soak for 30 min at room temperature. The equilibrium swelling (ES) capacity was measured twice at room temperature using the following formula:

$$\text{Equilibrium Swelling (g/g)} = \frac{W_2 - W_1}{W_1} \quad (1)$$

Where W_1 and W_2 are the weights of dry and swollen gel, respectively.

Characterization

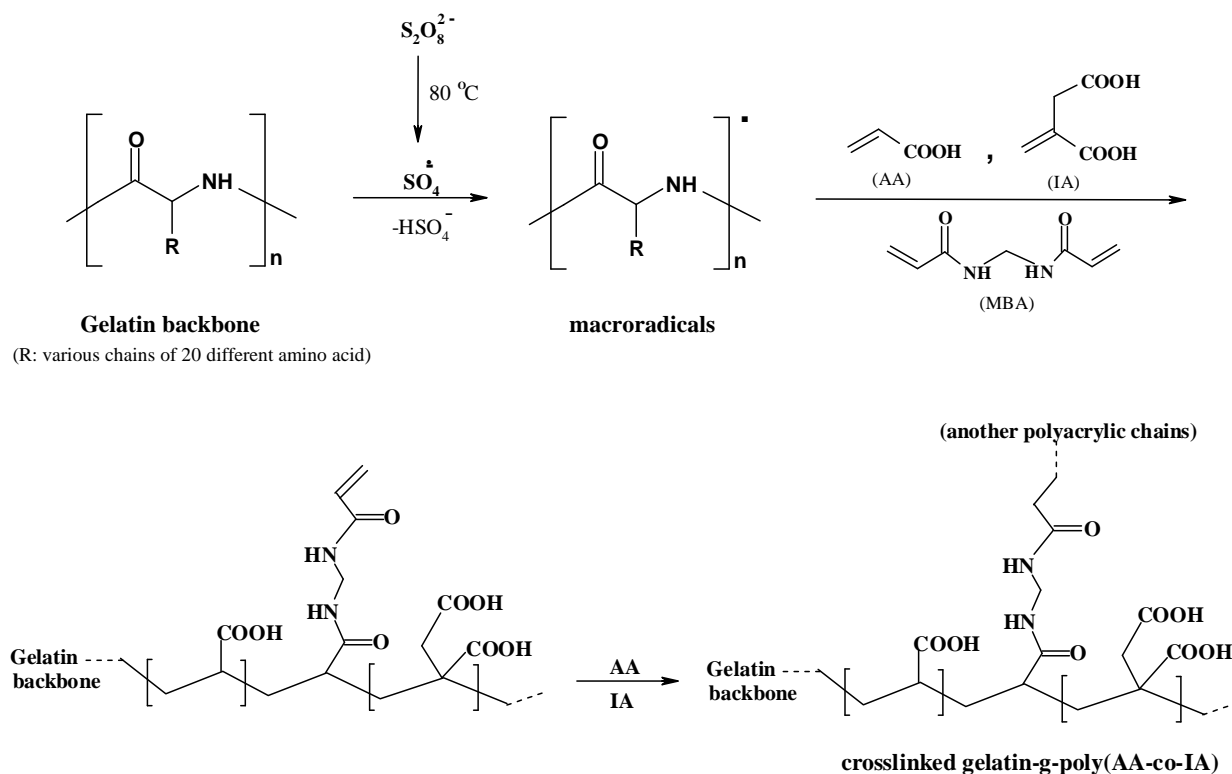
The Fourier transformation infrared (FTIR) spectra of gelatin and hydrogel samples were recorded on a FTIR spectrophotometer (ABB Bomem MB-100) using KBr. The grafted structural and morphological variations were observed using a scanning electron microscope (SEM). Dried superabsorbent powder were coated with a thin layer of palladium gold alloy and imaged in a SEM instrument (Leo, 1455 VP). Thermo gravimetric analyses (TGA) were performed on a Universal V4.1D TA Instruments (SDT Q600) with 8–10 mg samples on a platinum pan under ni-

trogen atmosphere. Experiments were performed at a heating rate of 10 °C/min to 600 °C. Differential scanning calorimetric (DSC) studies were carried out on DSC (TA Instruments, Model 2910, USA) under nitrogen atmosphere using 2-5 mg sample in a crimple aluminium pan with lid.

Results and discussion

Synthesis and mechanism aspects

Scheme 1 shows a simple structural proposal of the graft copolymerization of poly (acrylic acid-co-itaconic acid) onto gelatin backbones and crosslinking of the graft copolymer. In the first step, the thermally dissociating initiator (APS) is decomposed under heating to produce sulfate anion-radicals. Then the anion-radicals remove hydrogen from gelatin backbone to form the corresponding macroinitiators. These macroradicals initiate grafting of monomers onto gelatin backbone, leading to a graft copolymer. Crosslinking reactions also occurred in the presence of the crosslinker (MBA).



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

Spectral characterization

FTIR analysis

The grafting was confirmed by FT-IR spectroscopy. Figure 1 shows the IR spectra of the gelatin and the resulted hydrogel. The band observed at 1706 cm^{-1} can be attributed to C=O stretching in carboxamide functional groups of the substrate backbone (Figure 1-A). The broad band at $3200\text{-}3600\text{ cm}^{-1}$ is due to stretching of -OH groups of the gelatin. The superabsorbent hydrogel product comprises a gelatin backbone with side chains that carry sodium carboxylate functional groups that are evidenced by peak at 1546 cm^{-1} (Figure 1(B)). The characteristic band at 1546 cm^{-1} is due to asymmetric stretching in

carboxylate anion that is reconfirmed by another peak at 1461 cm^{-1} and, moreover, it is related to the symmetric stretching mode of the carboxylate anion.

Thermal analysis

The hydrogel structure was also supported by thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) technique (Figures 2 and 3). The comparison of TGA and DSC curves of intact gelatin and of the cross-linked hydrogel indicates that the structure of gelatin has been changed, which might be due to the crosslinking of chitosan chains. The percent residual mass of the hydrogel was higher than that observed for gelatin. In general, the hydrogel had lower

weight loss than gelatin. This means that the crosslinking increases the thermal stability of gelatin to some extent.

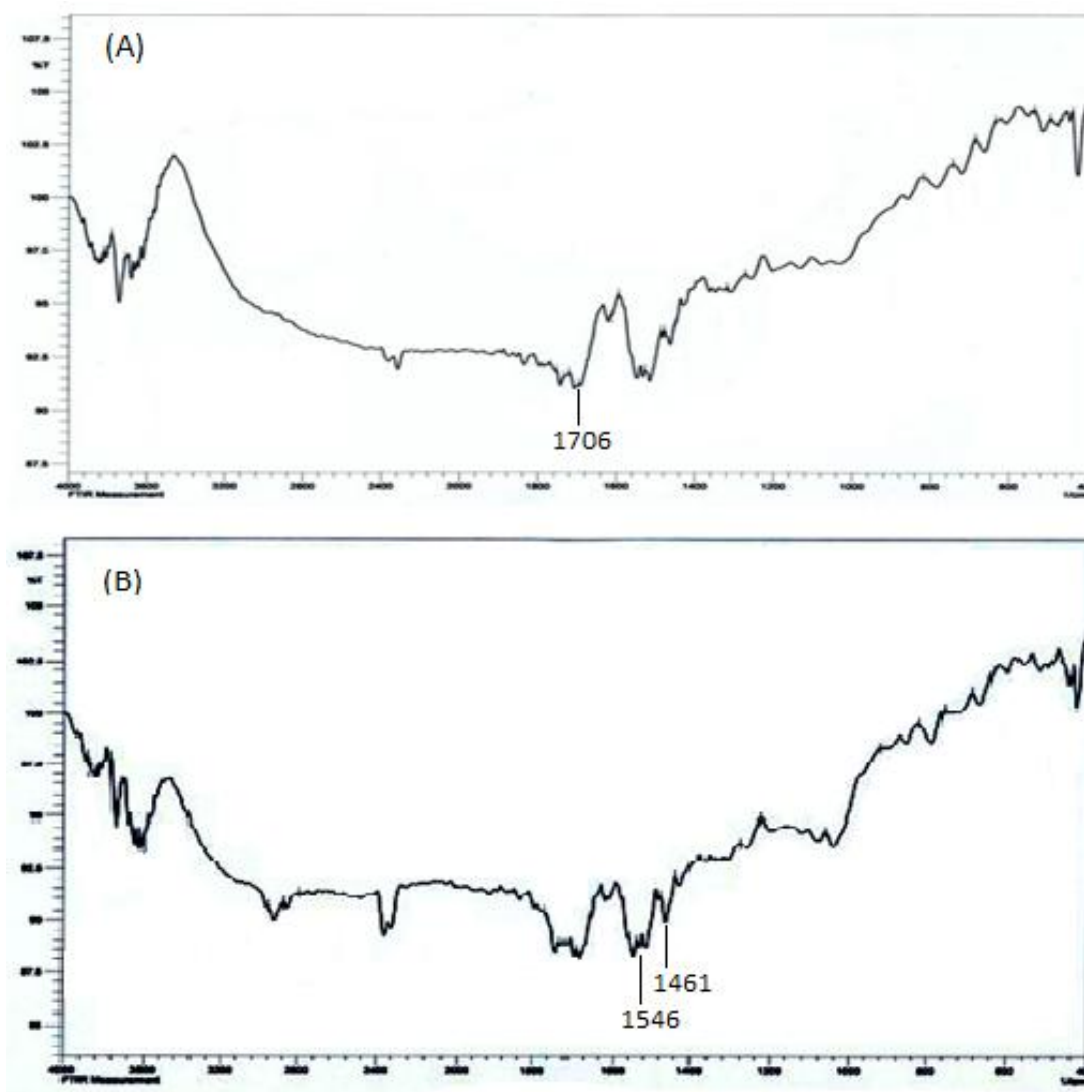


Figure 1. FT-IR spectra of gelatin (a) and gelatin-g-poly(AA-co-IA) hydrogel (b)

SEM analysis

It is known that the composition of hydrogels which affects its microstructure influences its swelling behaviour. The surfaces of the polymeric hydrogels were usually observed by scanning electron microscopy (SEM). The scanning electron micrographs of gelatin and gelatin-based hydrogel are shown in Figure

4. It can be observed in the SEM image that structures with a great penetration of the medium into the system with pores form connections (channels) with the interior of the structure. The capillary channels were clearly observed from SEM image and this may enable water to enter into the networks.

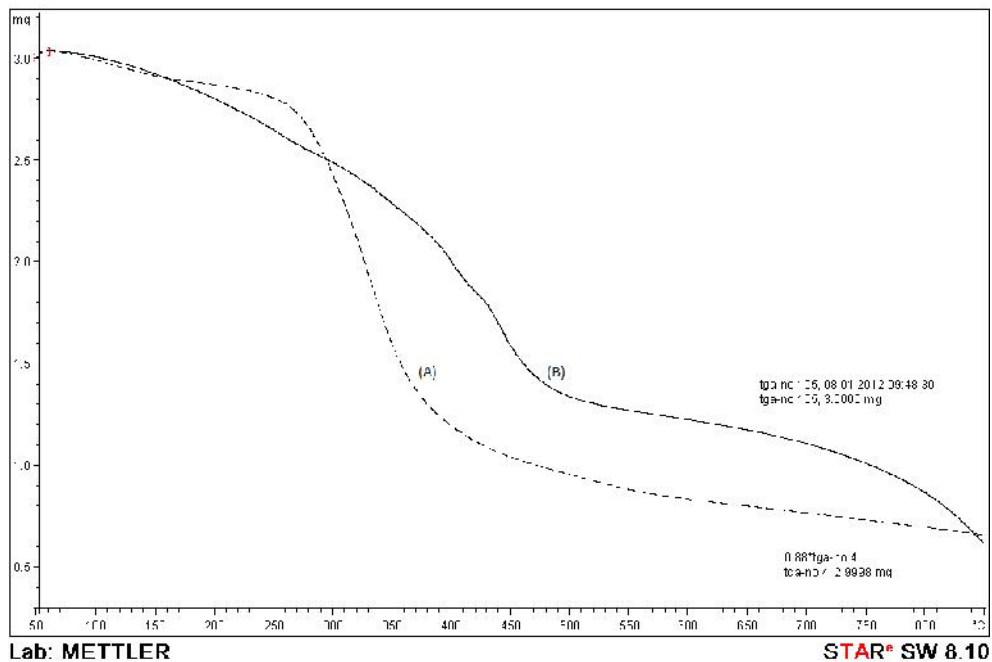


Figure 2. TGA thermograms of gelatin (A) and the gelatin-based hydrogel (B).

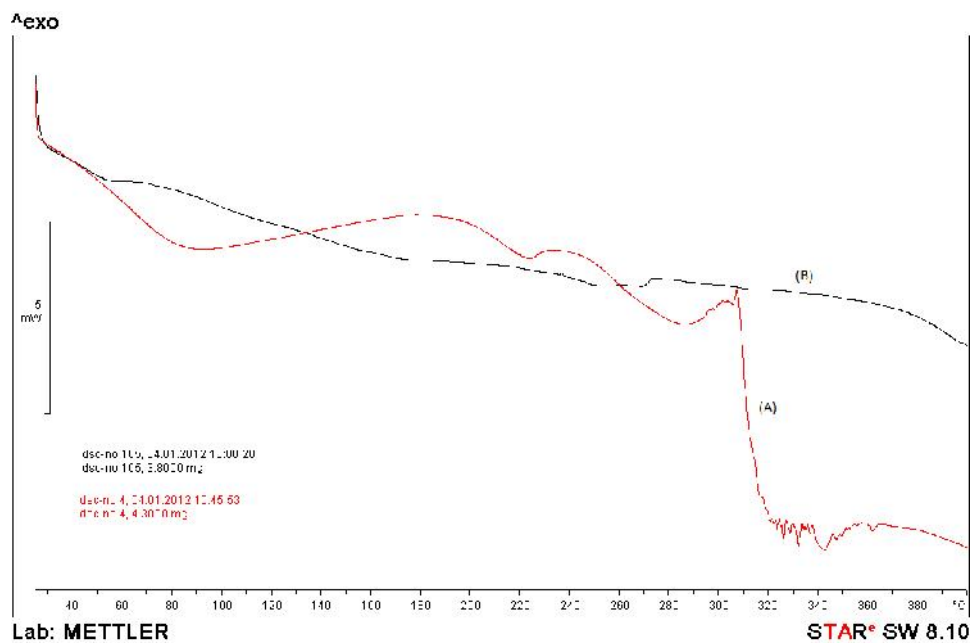


Figure 3. DSC curves of gelatin (A) and the gelatin-based hydrogel (B).

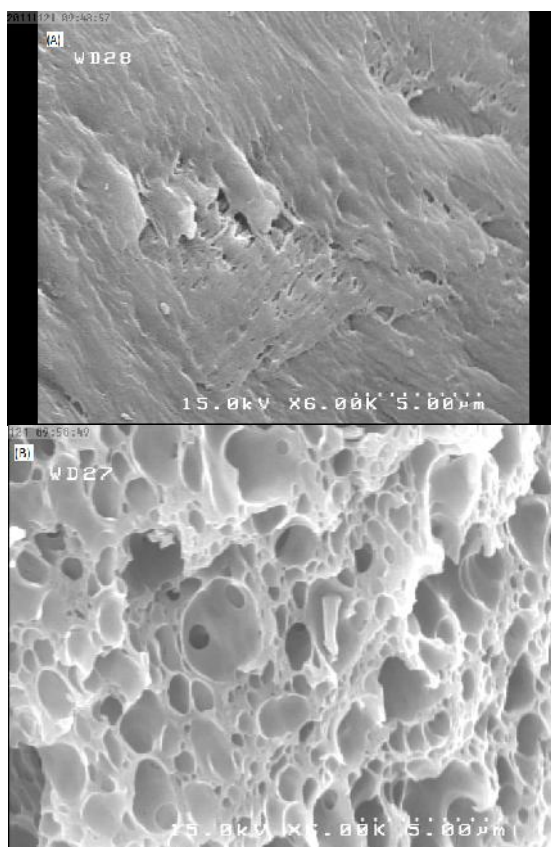


Figure 4. SEM photograph of gelatin (A) and the gelatin-based hydrogel (B)

Optimization of the hydrogel synthesis

Different variables affecting the ultimate swelling capacity were optimized to achieve hydrogels with maximum water absorbency.

Effect of AA Concentration on Swelling

The effect of acrylic acid concentration on the swelling capacity of the hydrogel was studied by varying the AA concentration from 2.53 to 6.33 mol/L (Figure 5). Maximum swelling (343 g/g) was obtained at 3.48 mol/L of monomer concentration. Enhanced monomer concentration increases the diffusion of AA molecules into the gelatin backbone which consequently causes an increase

in water absorbency. In addition, higher AA content which enhanced the hydrophilicity of the hydrogel caused a stronger affinity for more absorption of water. The swelling decrease after the maximum may be attributed to (a) preferential homopolymerization over graft copolymerization, (b) increase in viscosity of the medium which hinders the movement of free radicals and monomer molecules, (c) the enhanced chance of chain transfer to monomer molecules and (d) non-neutralized acid groups of grafted and non-grafted polyacrylic acid chains.

Effect of IA Concentration on Swelling

The swelling capacity of the hydrogel as a function of IA monomer concentration is illustrated in Figure 6. The effect IA amount on water absorbency and the reasons of increase and decrease of swelling capacities along with increasing the monomer concentration is similar to AA influence on absorbency.

Effect of crosslinker concentration

The concentration of crosslinker affects the porous structure, swelling characteristics and mechanical strength. By setting appropriate degree of crosslinking it is possible to prepare superporous hydrogel having desired characteristics.

Figure 7 shows the influence of the crosslinking agent on the swelling capacity of

gelatin-g-poly(AA-co-IA) hydrogel. As indicated in Figure 7, higher crosslinker concentration decreases the space between the copolymer chains and, consequently, the highly crosslinked rigid structure cannot be expanded and hold a large quantity of water.

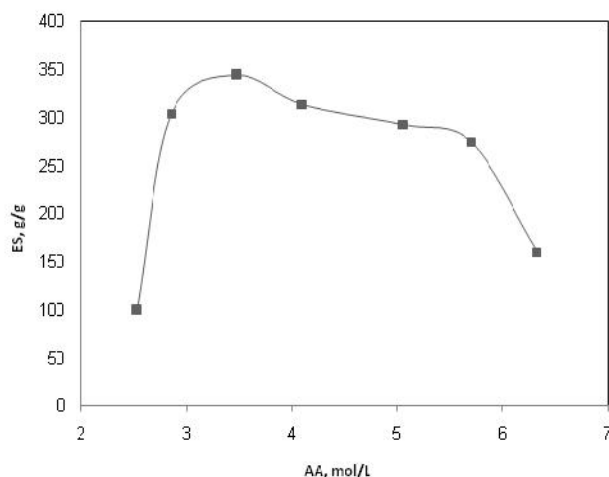


Figure 5. Swelling dependency of the hydrogel on AA concentration

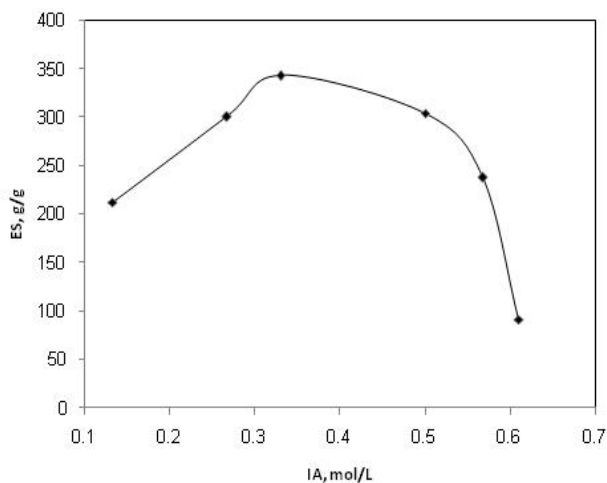


Figure 6. Swelling dependency of the hydrogel on IA concentration

Effect of initiator concentration on swelling

The swelling ratios of the hydrogel for various initiator concentrations are shown in Figure 8. By increasing the APS content, a large number of free radicals were produced. It led to more chain ends in the network and short average of kinetic chain length. Accordingly, swelling capacity will be increased. Subsequent decrease in water absorbency can be attributed to increased number of produced radicals. This led to terminating step via bimolecular collision [14]. Moreover, decreasing molecular weight of the grafted hydrogel [15] results in shortening the chains and reducing the available free volumes within the hydrogel.

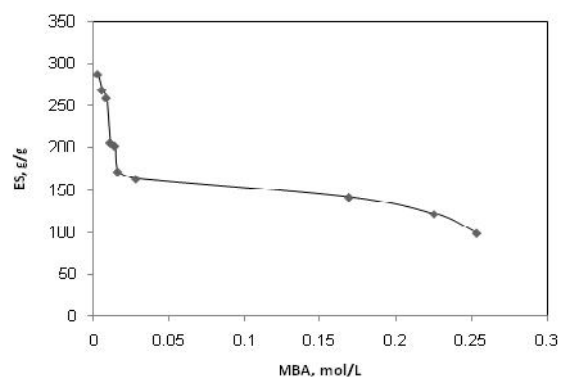


Figure 7. Swelling dependency of the hydrogel on crosslinker concentration.

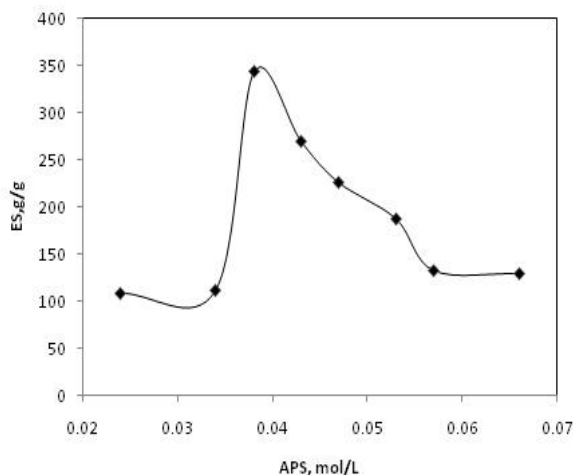


Figure 8. Swelling dependency of the hydrogel on the initiator concentration.

Effect of substrate content on swelling

The swelling dependency on gelatin amount is shown in Figure 9. Maximum swelling (343 g/g) has been observed at 2 g of gelatin, while other factors were kept constant. Swelling of hydrogel is considerably increased by increasing the gelatin value from 0.5 to 2 g. This behavior is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher gelatin concentration. However, upon further increase in the substrate concentration, increase in the reaction medium viscosity restricts the movements of macroradicals, thereby decreases the grafting ratio and the swelling capacity. It may also be attributed to deactivation of the macroradical growing chains (*e.g.*, by transfer reactions, combination and/or interaction

with the primary radicals) soon after their formation.

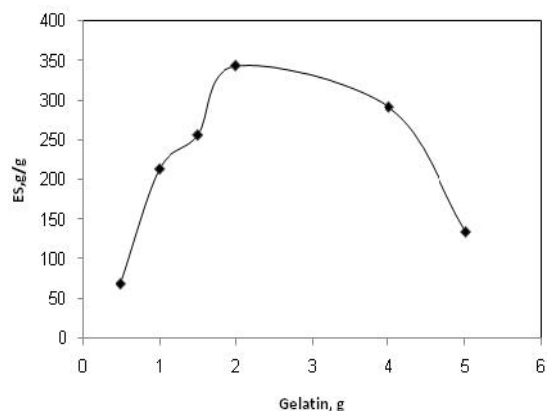


Figure 9. Swelling dependency of the hydrogel on the gelatin content.

Effect of the reaction bath temperature

The effect of temperature on water absorbency was studied by varying temperatures of the water bath from 60 to 90 °C (Figure 10). As it is obvious from the figure, the temperature leading the hydrogel with highest absorbency is around 70 °C. Since APS is a thermally dissociating initiator, it does not completely act at the temperature lower than its dissociation temperature, *i.e.* 70 °C [16]. So, the lower initiating radicals diminished the extent of polymerization (Scheme 1). In addition, the rate of diffusion of monomers to gelatin macroradicals as well as the kinetic energy of radical centers is decreased at lower temperatures which, in turn, result in lower graft polymerization extent and consequently lower final water absorbency. Subsequent decrease in water absorbency can be ex-

plained on the basis of (a) increasing the rate of termination and chain transfer reactions, and (b) decomposition of APS to give O_2 (a radical scavenger), which reacts with primary free radicals [17], resulting in decreased molecular weight and decreased swelling.

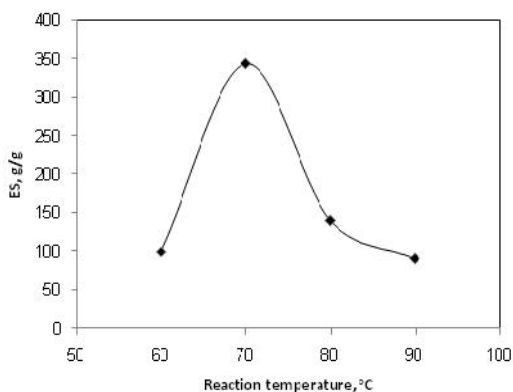


Figure 10. Swelling dependency of the hydrogel on the reaction bath temperature

Effect of neutralization percentage

In this series of experiments, after the completion of the reaction, the carboxylic acid groups of grafted PAA and PIA were neutralized to carboxylate anions by NaOH solution. Without the neutralization stage, the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently the water absorbency is decreased (Figure 11). According to Figure 11, the best neutralization percent was found to be 80%. In high neutralization percent of the carboxylic acid groups, reduced swelling is observed due to different phenomena that is related to "charge screening effect" of

excess Na^+ ions in the swelling media [18]. The excess cations shield the carboxylate anions and prevent effective anion-anion repulsion (screening/shielding effect). Also, by increasing the NaOH concentration, the ionic strength of the swollen solution is increased. As a result, the osmotic pressure between the aqueous and the gel phases is reduced and the swelling is consequently decreased.

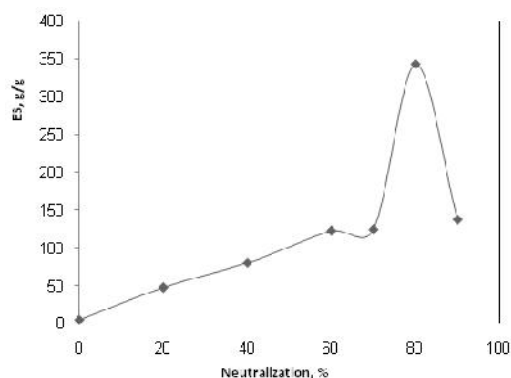


Figure 11. Effect of neutralization percentage on swelling capacity

Swelling in salt solutions

To investigate the effect of saline, as well as the cation type, equilibrium swelling was measured in 0.15 molar solutions of NaCl, $CaCl_2$ and $AlCl_3$ for the synthesized hydrogels. The swelling data triply measured in these solutions are given in Table 1. In general, all swelling values in saline media are expectedly decreased. The reason is usually attributed to the reduction of osmotic pressure between the gel and the aqueous phase. Osmotic pressure, the driving force for swelling, is originated from anion-anion repul-

sion. In the presence of excess cations, cations can shield the anions and prevent efficient electrostatic repulsion. This phenomenon is often referred to as charge "screening effect". An additional reason is the increasing

electrostatic attraction between anionic sites of chains and multi-valent cations leading to increased ionic crosslinking degree and consequent loss of swelling.

Table 1. Swelling of gelatin-based hydrogels in water and different salt solutions (0.15 M)

Swelling medium	H ₂ O	NaCl	CaCl ₂	AlCl ₃
Swelling capacity (g/g)	343	25	13	10

Table 2 shows a comparison between the equilibrium swelling capacity of the gelatin-based hydrogel prepared in the present work with some gelatin-based hydrogels prepared by other researchers and also with some

known commercial/reported superabsorbing hydrogels. On the contrary, the hydrogels synthesized in this work had acceptable water absorbency.

Table 2. The equilibrium swelling (ES) capacity of the hydrogel prepared in this work and other hydrogels.

Hydrogel	ES (g/g)
Gelatin-P(SA/AM) ^a	182
Gelatin-P(PL) ^b	74
Gelatin-P(-PGA) ^c	28
SuperAB A200 ^d	176
Sanwet IM-815A ^e	304
GS-3000H ^f	310
Gelatin-P(AA/IA) ^g	343

^aGelatin-g-Poly(Sodium Acrylate-co-Acrylamide) [19]

^bGelatin-g-Polylysine [20]

^cGelatin-g- Poly(-Polyglutamic Acid) [21]

^dAn agricultural hydrogel from Rahab Resin Co., Iran.

^eA hygienic hydrogel from Sanyo Chemical Co., Japan.

^fA hygienic hydrogel from Kolon Co., Korea.

^gHydrogel prepared in this work.

Swelling at various pH solutions

In this series of experiments, the swelling ratio for the synthesized hydrogels was measured in different pH solutions ranged from 3 to 12 (Table 3). Maximum swelling (60 g/g) was obtained at pH 8. In acidic media, most of the carboxylate groups are protonated, so decreased repulsion of anionic groups lead to a decreased swelling ratio. 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 for the swelling-loss in the highly basic solutions is the charge screening effect of excess Na⁺ in the swelling media, which shields the carboxylate anions and prevents effective anion-anion repulsion.

Conclusion

Crosslinking graft copolymerization of acrylic acid/itaconic acid mixtures onto gelatin was performed in an aqueous medium using a persulfate initiator and a bifunctional hydrophilic crosslinker. The synthesis of superabsorbent hydrogel was optimized by varying the reaction parameters affecting the ultimate swelling capacity of the final product.

Swelling capacity of gelatin-g-poly(AA-co-IA) hydrogels in various pH solutions exhibited high pH-sensitivity. Swelling measurements of the synthesized hydrogels in different salt solutions also showed appreciable swelling capacity, especially in sodium chloride solution.

Table 3. Effect of pH of solution on swelling of gelatin-g-poly(AA-co-IA) hydrogel

pH	3	4	5	6	7	8	9	10	11	12
Swelling capacity (g/g)	2	4	28	40	44	60	32	23	21	19

Acknowledgments

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