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Hydrolyzed salep/gelatin-g-polyacrylamide as a novel micro/nano-porous superabsorbent hydrogel: Synthesis, optimization and investigation on swelling behavior

R. Soleyman[a], G. Rezanejade Bardajee[b,*], A. Pourjavadi[c,*],
A. Varamesh[a] and A.A. Davoodi[a]

a. *Polymer Science and Technology Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran.*
b. *Department of Chemistry, Payame Noor University, Tehran, P.O. Box 19395-3697, Iran.*
c. *Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran, P.O. Box 11155-9516, Iran.*

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Abstract. A novel micro/nano-porous superabsorbent hydrogel was synthesized via graft copolymerization of acrylamide (AAm) onto salep (a polysaccharide mixture) and a gelatin (a protein) hybrid backbone, after hydrolysis of this system. The Taguchi method was applied for the experiments, and standard 18 Orthogonal Arrays (OA), with seven factors and three levels for each factor, were the proposed trial conditions. Considering the results of 18 trials, according to the analysis of variance (ANOVA), optimum conditions were suggested. In addition, swelling kinetics, swelling in various organic solvents, the Absorbency Under Load (AUL) and On-Off switching behavior were investigated. Also, the hydrogel formation was confirmed by Fourier transform infrared spectroscopy (FTIR). The surface morphology of the synthesized hydrogels was assessed by Scanning Electron Microscopy (SEM) and showed a micro/nano-porous structure. Also, the surface area and total pore volume of the optimized hydrogel were measured using the Brunauer-Emmett-Teller (BET) technique.

1. Introduction

Hydrogels are multipurpose water-swollen polymeric materials that maintain a distinct three-dimensional structure [1]. Conventional hydrogels are limited by their slow swelling and deswelling rates [2], and new methods to prepare them have been investigated to enhance these rates. One of the best approaches is the synthesis of comb-like hydrogels by graft copolymerization. The grafted hydrogel shows advantageous swelling kinetics in comparison with conventional hydrogels, owing to the free mobility of the grafted chains [3-7].

Superporous hydrogels (SPHs) represent a fast-swelling class of hydrogel with pore sizes much larger than the typical mesh size of a conventional hydrogel. They were originally developed as novel gastric retention devices, increasing the residence time of drugs in the stomach [8,9]. The swelling kinetics of SPHs is much faster than that of conventional hydrogels [8].

Natural-based hydrogels have attracted medical and pharmaceutical interest due to their non-toxicity, biocompatibility and biodegradability [10]. Salep [11,12] is a polysaccharide composite and can be referred to as a good source of glucomannan. It can be obtained from dried tubers of certain nat-

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[*] *Corresponding authors. Fax: +98 21 66165356*
E-mail addresses: rezanejad@pnu.ac.ir (G. Rezanejade Bardajee); purjavad@sharif.ir (A. Pourjavadi)

ural terrestrial orchids. Recently, we have developed highly swelling nanoporous hydrogels, based on salep, as a new superabsorbent hydrogel backbone [13]. Then, these nanoporous materials were utilized as a nano-reactor for the synthesis of Hematite nanoparticles [14].

As a biomaterial, gelatin displays several advantages: It is a natural polymer that has not shown antigenity; it is completely resorbable in vivo and its physicochemical properties can be suitably modulated [15,16]. Because of its unique gelling properties, gelatin is an attractive candidate as starting material for preparing hydrogels.

In this paper, we have developed a polysaccharide/protein based porous hydrogel by hydrolyzing after gel formation. Preparation of the hydrogels involved free radical graft copolymerization of a combination of salep, gelatin and acrylamide (AAm) in the presence of a crosslinking agent, called N,N'-methylene bisacrylamide (MBA). The Taguchi method, as a powerful experimental design tool, was used for optimized synthesis of our SPH [17-19].

2. Experimental

2.1. Materials

The palmate-tuber salep (PTS, $M_n = 1.17 \times 10^6$ g/mol, $M_w = 1.64 \times 10^6$ g/mol (high M_w), PDI = 1.39, eluent = water, flow rate = 1 mL/min, Acquisition interval = 0.43 sec from GPC results) was purchased from a supplier in Kordestan, Iran. N,N'-methylene bisacrylamide (MBA, from Merck, Darmstadt, Germany), ammonium persulfate (APS, from Merck), gelatin (from Merck) and acrylamide (AAm, from Merck), as a monomer, were used as received. All other chemicals were also analytical grade. Doubly distilled water was used for hydrogel preparation and swelling measurements.

2.2. Instrumental analysis

FTIR spectra of samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FTIR spectrophotometer. The morphology of the dry samples was examined using a scanning electron microscope, SEM, (Philips, XL30) operated at 20-25 kV after coating the samples with gold film. Brunauer-Emmett-Teller (BET) apparatus (Micromeritics ASAP^{TM} 2020 surface area and porosity analyzer) was used to investigate specific surface area and the total pore volume of the optimized hydrogel.

2.3. Experimental design

2.3.1. Selection of factors and their levels

The reaction variables, including salep, gelatin, AAm, MBA and APS amounts, as well as NaOH concentration and hydrolysis temperature, were selected. These are generally important factors in the synthesis of SPHs, and three levels for each factor were chosen as shown in Tables 1 and 2.

Table 1. Experimental layouts of an L_{18} orthogonal array according to Taguchi's suggestion (the numbers in each column indicate the levels for the specific factors).

Trial	A	B	C	D	E	F	G
1	1	1	1	1	1	1	1
2	1	2	2	2	2	2	2
3	1	3	3	3	3	3	3
4	2	1	1	2	2	3	3
5	2	2	2	3	3	1	1
6	2	3	3	1	1	2	2
7	3	1	2	1	3	2	3
8	3	2	3	2	1	3	1
9	3	3	1	3	2	1	2
10	1	1	3	3	2	2	1
11	1	2	1	1	3	3	2
12	1	3	2	2	1	1	3
13	2	1	2	3	1	3	2
14	2	2	3	1	2	1	3
15	2	3	1	2	3	2	1
16	3	1	3	2	3	1	2
17	3	2	1	3	1	2	3
18	3	3	2	1	2	3	1

Table 2. Experimental control factors and their levels.

Control factor	Level 1	Level 2	Level 3
Salep (g)	0.5	1.0	1.5
Gelatin (g)	0.5	1.0	1.5
AAm (g)	3.0	4.5	6.0
MBA (g)	0.03	0.06	0.09
APS (g)	0.03	0.06	0.09
NaOH (M)^{a}	1.0	2.0	3.0
T (°C)^{a}	70	80	90

^{a}: For hydrolysis.

2.3.2. Selection of orthogonal array and assignment of factors

Standard tables, known as Orthogonal Arrays (OA), are used for the design of the experiments in the Taguchi method. An OA with 3 levels and 7 factors are shown in Table 1. This OA is particularly designed with the symbol of L_{18}. Each row in the array represents a trial condition with the factor levels, which are indicated by the numbers in the row. The columns correspond to the factors specified in this study and each column contains three levels. Conditions (a total of 18 conditions) for the factors were assigned in Table 1. Evaluation of the results has been standardized by this method, which can easily be applied by other researchers. The software package, Qualitek-4 version 6.3, was used for selection of the orthogonal, optimum conditions and contribution of each factor.

2.4. SPH preparation

In general, certain amounts of salep (0.5-1.5 g) and gelatin (0.5-1.5 g), were added to 30 mL H_2O in a three-neck reactor equipped with a mechanical stirrer, while stirring (200 rpm). The reactor was immersed in a thermostated water bath preset at 80°C. After homogenizing the mixture, AAm (3.0-6.0 g) was added to the reaction mixture and stirred for a further 20 minutes. Then, MBA (0.03-0.09 g) in 5.0 mL H_2O, and, finally, certain amounts of APS (0.03-0.09 g) in 5.0 mL H_2O were added and the reaction started. After 30 min, a gel like material was prepared. The reaction product was kept in ethanol (200 mL) for 24 h to dewater. The completely hardened gel particles were filtered, washed with fresh ethanol (2 × 50 mL) and dried in an oven at 50°C for 10 h. Then, 0.40 g of dried gel was hydrolyzed in a thermostated water bath at different temperatures (70-90°C) with 30 mL of NaOH (1.0-3.0 M). The dried powdery superabsorbent hydrogel was stored away from moisture, heat and light for further experiments.

2.5. Water absorbency measurement

The degree of swelling was determined using a gravimetric method. The tea bag (i.e. a 100 mesh nylon screen), containing an accurately dried weighed powdered sample (0.1 ± 0.01 g), with average particle size between 40-60 mesh (250-400 μm), was immersed entirely in distilled water (400 mL) and allowed to soak for 60 min at room temperature. The Equilibrium Swelling (ES) capacity was measured twice at room temperature using the following formula:

$$\mathrm{ES}(g/g) = \frac{W_2 - W_1}{W_1}, \qquad (1)$$

where W_1 and W_2 are the weights of dried and swollen gels, respectively.

2.6. Swelling kinetics

For studying the rate of hydrogel absorbency, a certain amount of sample (0.1 ± 0.01 g), with average particle size between 40 and 60 mesh (250-400 μm), was poured into a weighed tea bag and immersed in 400 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogel was measured according to the earlier mentioned method.

2.7. Environmental sensitivity

2.7.1. pH sensitivity

The swelling pH dependency was performed by the interaction of certain amounts of hydrogel sample (0.5 ± 0.01 g) in solutions (500 mL) with different pHs. The various solutions were adjusted to the desired pH value by addition of diluted HCl or NaOH. The On-Off switching by pH was carried out at buffered solutions with pH 1.6 and pH 7.4, with 0.01 molar concentrations.

2.7.2. Salinity

The swelling capacity of the hydrogel was measured at different concentrations of various salt solutions.

2.7.3. Solvent-induced phase transition

The swelling of the optimized hydrogel sample (0.5 ± 0.01 g) in different mixtures of water soluble organic solvents and water was measured. The On-Off switching by the mixture of solvents was carried out at 20% acetone/water (swelling) and 60% acetone/water (deswelling).

2.8. Measurement of Absorbency Under Load (AUL)

A macroporous 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 a weighed dried hydrogel sample (0.9 ± 0.01 g) 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) was put on the dry hydrogel particles, while it can be freely slipped in a glass cylinder (d = 60 mm, h = 50 mm). The desired load (applied pressure 0.3 - 0.9 psi) was placed on the hydrogel sample. Then, 0.9% saline solution (NaCl) was added, so that the liquid level was equal to the height of the sintered glass filter. The whole set was covered to prevent surface evaporation and probable change in saline concentration. After the desired time, the swollen particles were weighed again, and AUL (absorbency under load) was calculated using Eq. (1).

3. Results and discussions

3.1. Synthesis and mechanism aspects

Crosslinking and graft copolymerization of PAAm onto backbones of salep and gelatin hybrid substrates were carried out in an aqueous medium using APS as a radical initiator and MBA as a crosslinking agent (Figure 1). The persulfate anions decompose by heating (at 80°C) and produce sulfate anion-radicals that abstract hydrogen atoms from the anomeric carbons or hydroxyl groups of salep and NH_2 groups of gelatin backbones. This redox system results in active centers capable of radically initiating the polymerization of acrylamide, leading to a graft copolymer. Since a crosslinking agent (MBA) is present in the system, the copolymer has a crosslinked structure. The entitled hydrogel was hydrolyzed under the desired temperature and molarity of NaOH (according to Taguchi method). During hydrolysis, the amide groups of polyacrylamide, MBA

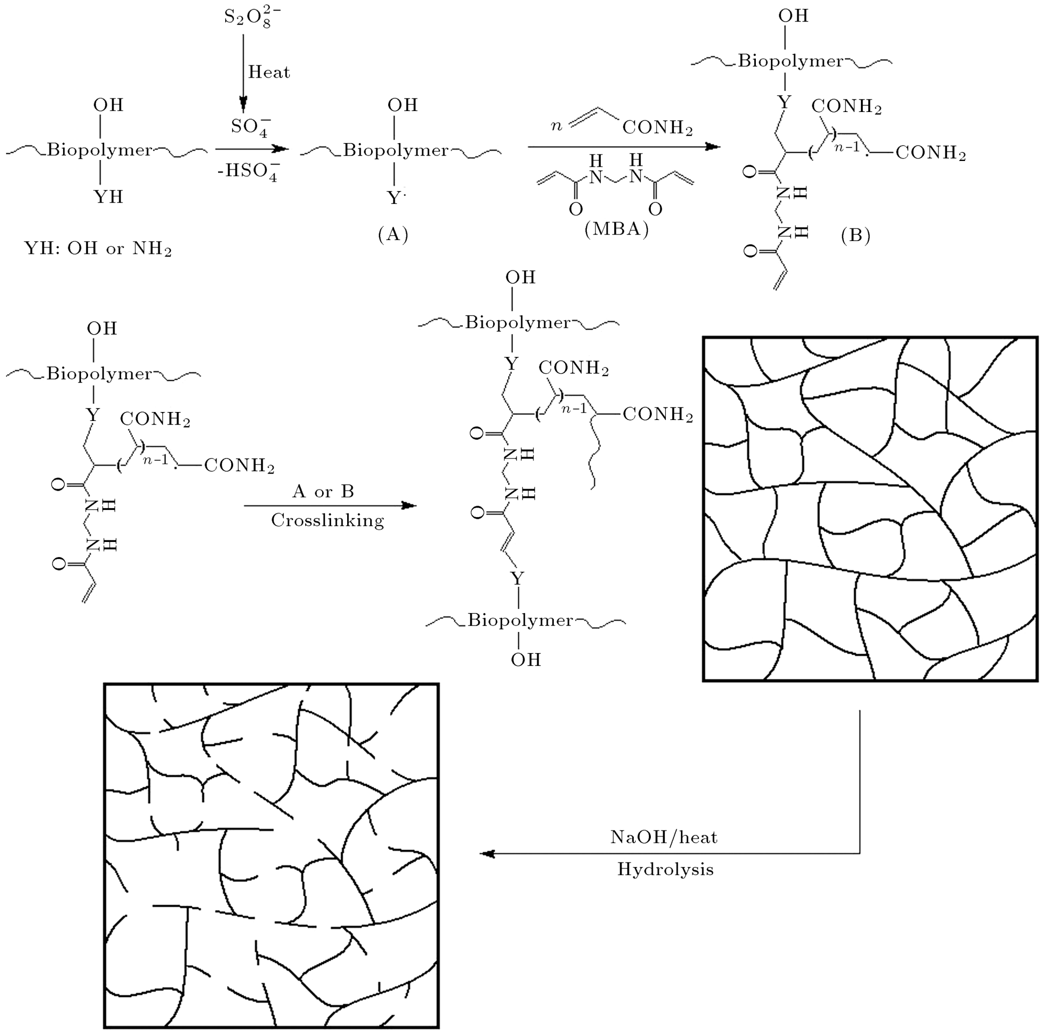


Figure 1. Proposed mechanism pathway for synthesis of the hydrolyzed (salep/gelatin)-g-PAAm hydrogel.

or gelatin are converted to carboxylate anions in basic media. Also, BET analysis showed that the total pore volume and specific surface area of the optimized hydrogel were 1.9 mL/g and 1750 m^2/g, respectively.

3.2. Spectral characterization

The FTIR spectra of the initial substrates and result materials are shown in Figure 2. Figure 2(a) shows the characteristic absorption band of salep around 1630 cm^{-1}, which is attributed to the carboxylate stretching mode of glucomannan. The broad band at 3200-3500 cm^{-1} is due to the stretching absorption of the hydroxyl groups of the salep. In the spectrum of gelatin (Figure 2(b)), the broad band at 3430 cm^{-1} is due to the stretching vibration modes of amino groups. Two indicated peaks, at 1545 and 1650 cm^{-1}, can be correlated to N-H bending vibration and the carbonyl stretching mode of peptide groups, respectively. Figure 2(c) indicated two series of peaks that confirm the amide groups in polyacrylamide. New patterns of peaks created in "d" spectra objectively confirmed the structure of the synthesized hydrogel before hydrolysis (Figure 2(d)). As one can see, after the hydrolysis of (salep/gelatin)-g-PAAm superabsorbent hydrogel, amide groups are converted to carboxyl groups, this is obvious due to the indicated peaks around 1720, 1650 and 1580 cm^{-1}.

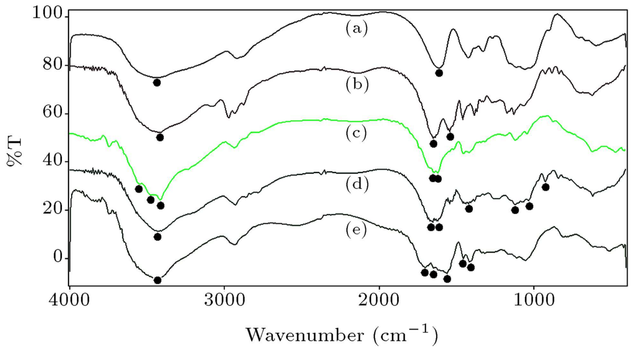


Figure 2. FTIR spectra of (a) salep, (b) gelatin, (c) PAAm, (d) (salep/gelatin)-g-PAAm, and (e) hydrolyzed (salep/gelatin)-g-PAAm hydrogel.

Furthermore, the TGA data of the optimized hydrogel before and after hydrolysis (after removing the sol fraction) were compared with the TGA curves of salep, gelatin and polyacrylamide. The TGA curves of the aforementioned samples were completely different from each other. This can be attributed to the different structures for the entitled samples. Additional observations about the grafting of polyacrylamide onto salep/gelatin backbone can be obtained by solubility experiments. Despite the starting materials, the desired hydrogel did not dissolve in hot water (80°C) after 12 h. Also, the physical mixture of the starting materials did not absorb water under our experimental conditions. The abovementioned data provides enough information for synthesis of the desired hydrogel.

3.3. Optimization of water absorbency

According to our previous work [10-13], the variables affecting the ultimate swelling capacity are salep, gelatin, AAm, MBA and APS amounts, molarities of NaOH and hydrolysis temperature. After identification of the effective parameters (factors) in the reaction, based on past experience about the synthesis of hydrogels, the levels of factors were determined (Table 2). After the selection of factors and their levels, an orthogonal array appropriate for 7 factors with 3 levels for each factor should be applied. Software Qualitek-4, proposes the L_{18} OA (Table 1). Methods of performing experiments are given in Table 3. After synthesis of 18 hydrogels with conditions proposed by the Taguchi statistical method, the results for the water absorbency of 18 samples are given in Table 4 (each measurement was repeated twice). Finding the optimum conditions and contribution of each factor was performed by ANOVA, neglecting interaction between factors. According to analysis performed by software Qualitek-4, optimum conditions are shown in Table 5 (salep: 1.0 g, gelatin: 0.5 g, AAm: 6.0 g, MBA: 0.09, APS: 0.06, NaOH molarity: 2M and T: 80°C).

Table 3. A three-level orthogonal array for seven factors (L_{18}).

Trial	Salep (g)	Gelatin (g)	AAm (g)	MBA (g)	APS (g)	NaOH (M)	T (°C)
1	0.5	0.5	3.0	0.03	0.03	1.0	70
2	0.5	1.0	4.5	0.06	0.06	2.0	80
3	0.5	1.5	6.0	0.09	0.09	3.0	90
4	1.0	0.5	3.0	0.06	0.06	3.0	90
5	1.0	1.0	4.5	0.09	0.09	1.0	70
6	1.0	1.5	6.0	0.03	0.03	2.0	80
7	1.5	0.5	4.5	0.03	0.09	2.0	90
8	1.5	1.0	6.0	0.06	0.03	3.0	70
9	1.5	1.5	3.0	0.09	0.06	1.0	80
10	0.5	0.5	6.0	0.09	0.06	2.0	70
11	0.5	1.0	3.0	0.03	0.09	3.0	80
12	0.5	1.5	4.5	0.06	0.03	1.0	90
13	1.0	0.5	4.5	0.09	0.03	3.0	80
14	1.0	1.0	6.0	0.03	0.06	1.0	90
15	1.0	1.5	3.0	0.06	0.09	2.0	70
16	1.5	0.5	6.0	0.06	0.09	1.0	80
17	1.5	1.0	3.0	0.09	0.03	2.0	90
18	1.5	1.5	4.5	0.03	0.06	3.0	70

Table 4. Experimental results for swelling of superabsorbent hydrogels for 18 trials.

Trial	1	2	3	4	5	6	7	8	9
ES (g/g)	340	686	75	320	186	725	500	98	214
Trial	9	10	11	12	13	14	15	16	18
ES (g/g)	300	565	155	612	480	585	322	428	112

Table 5. Optimum conditions and performances.

Factor	Level description	Optimum conditions
Salep (g)	2	1.0
Gelatin (g)	1	0.5
AAm (g)	3	6.0
MBA (g)	3	0.09
APS (g)	2	0.06
NaOH (M)	2	2.0
T (°C)	2	80

3.4. Swelling kinetics

In practical applications, not only is a higher swelling capacity required, but also a higher swelling rate is needed. Buchholz has suggested that the swelling kinetics for superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer [20]. Figure 3 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 equilibrium swelling capacity was achieved after about 5 min. A power law behavior is obvious from Figure 3. The data may be well fitted with a Voigt-based equation (Eq. (2)) [21]:

$$S_t = S_e(1 - e^{-t/\tau}), \tag{2}$$

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, and τ (min) stands for the “rate parameter”. To calculate the rate parameter, using the above formula and a little rearrangement, one can plot Ln $(1 - S_t/S_e)$ versus time (t). The slope of the straight

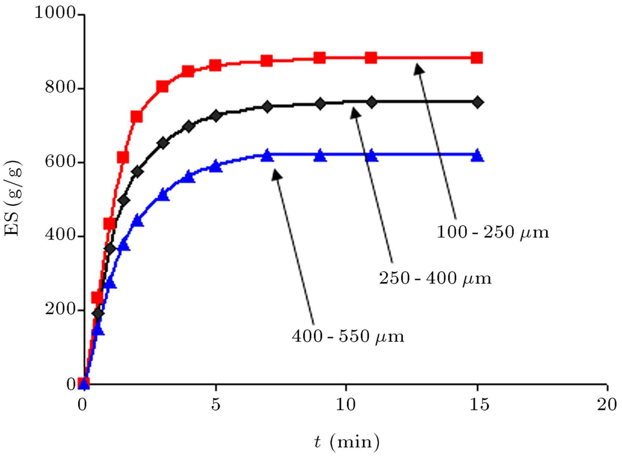


Figure 3. The swelling kinetics of optimized sample in distilled water with various particle sizes.

line fitted (slope $= -1/\tau$) gives the rate parameter. The rate parameters for the superabsorbent are found to be 1.12, 1.32, and 1.52 min for the superabsorbent with particle sizes of 100-250, 250-400 and 400-550 μm, respectively. It is well-known that the swelling kinetics for the superabsorbent polymers is significantly influenced by the particle size of the absorbents [22]. 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 the decreasing particle size of the hydrogel.

3.5. Absorbency Under Load (AUL)

When the superabsorbents are under load, the swelling capacity is considerably decreased. So, AUL is often defined and reported, especially in technical data. Since AUL values are logically changed with the mechanical strength of the swollen gel, proportionally, AUL can be considered as a measure of the gel strength of the superabsorbent composite. So, many efforts have been made to achieve superabsorbents having higher AUL or higher strengths of the swollen gel [23,24]. To determine the swollen gel strength, we used superabsorbent samples under different loads in saline solution. As shown in Figure 4, the minimum time needed for the highest AUL, in the case of each load, is estimated to be 60 minutes. After this time, AUL values were almost unchanged. In addition, the AUL decreases with increasing the amount of loading. Maximum swelling was found to be 71, 65 and 57 (g/g) for applied pressures, 0.3, 0.6 and 0.9 psi, respectively. It means that our synthesized composite is very resistant against applied pressure increase.

3.6. Environmental sensitivity

3.6.1. pH sensitivity and On-Off switching behavior

The swelling behavior of the superabsorbent hydrogel was studied at room temperature, at various pH values between 1 and 13 (Figure 5(a)). To prepare the pH media standard HCl (pH 1) and NaOH (pH 13) solutions, they were diluted with distilled water to reach the desired acidic and basic pHs, respectively. The swelling of the hydrogel increased with increasing the pH from 1 to 5, but decreased in the pH range between 7 and 13. At pH=5, all the -NH_2 groups of gelatin were converted to -NH_3^+; at pH=7, all the -COOH groups were converted to -COO^-. Because of these conversions and ion-ion repulsions, two maxima were observed in this figure (pHs 5 and 7). In an acidic solution, the ionic strength of the medium is increased and the charge of the -COO^- anions is shielded by counter ions, which prevented efficient repulsion. At pHs greater than 7, the Na^+ cations from NaOH shielded the -COO^- groups and prevented perfect anion-anion repulsion. Also, the ionic strength of the medium is increased and, consequently, the swelling is decreased. The optimally prepared pH-sensitive hydrogel showed a reproducible On-Off switching behavior when the environmental pH of the sample was alternatively changed between 7.4 and 1.6 (Figure 5(b)). This responsive behavior may be of significant importance in the controlled delivery of drugs to the colon, having an alkaline medium.

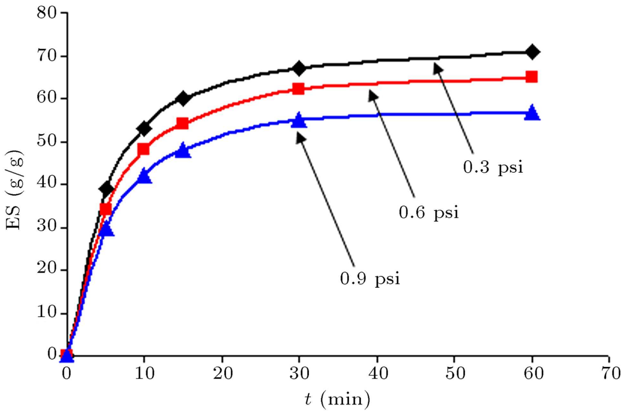


Figure 4. Time dependence of the AUL values for optimized sample.

3.6.2. Salinity

Swelling ratio is mainly related to the characteristics of the external solution, such as charge number, ionic strength and polymer nature, i.e. network elasticity, presence of hydrophilic functional groups, and extent of crosslinking density. For instance, the swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased compared to the swelling values in distilled water. This well-known undesired swelling-loss is often attributed to the "charge screening effect" of the additional cations, causing a non-perfect anion-anion electrostatic repulsion [25]. Therefore, the osmotic pressure resulted from the difference in mobile ion concentration between gel and aqueous phases is decreased and, consequently, the absorbency

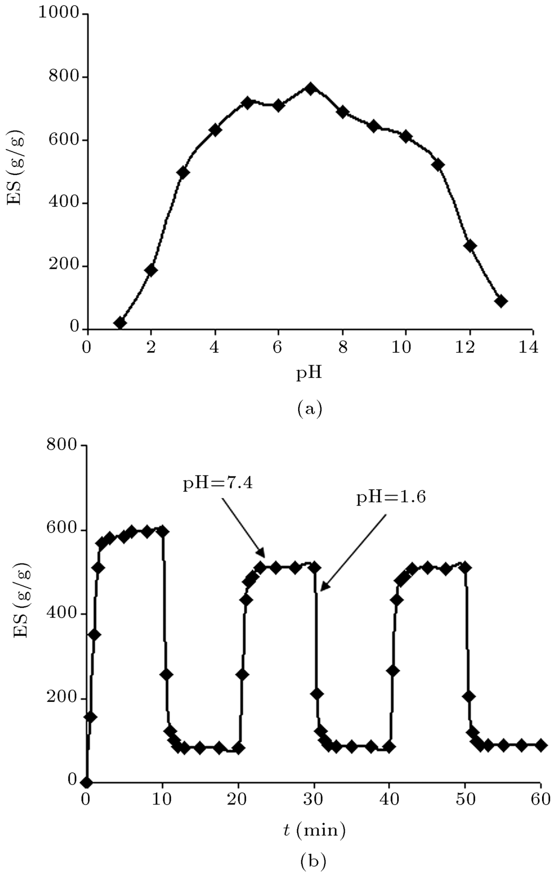


Figure 5. (a) Swelling dependency of optimized sample on pH. (b) On-Off switching behavior of the optimized SPH in 0.01 molar buffered solutions with pH= 7.4 and pH= 1.6.

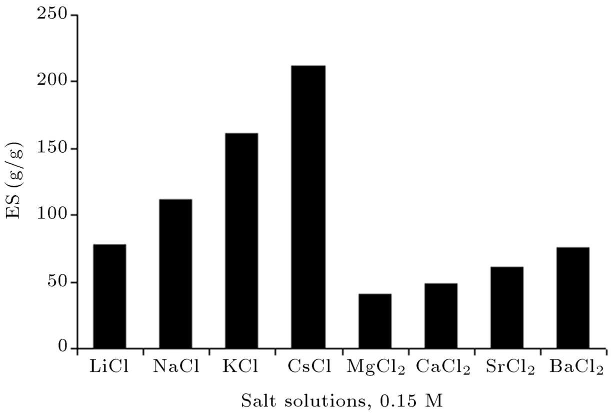


Figure 6. Swelling capacity of the superabsorbent hydrogel in different chloride salt solutions (0.15 M).

amounts are diminished. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at the surface of the particles caused an appreciable decrease in swelling capacity. In this series of experiments, the swelling capacity was measured in various salt solutions (Figure 6). It is obvious that swelling decrease is strongly dependent 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 6. By increasing the charge of cation, the 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 be observed from Figure 6. As reported by Pass et al. [26], the carboxylate anion interacts with small cations, e.g. Li^+, more strongly 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.

Figure 7 illustrates a reverse and power law relationship between the concentration of salt solutions (NaCl, $CaCl_2$, and $AlCl_3$) and swelling capacity of the hydrogel. Again, charge screening effects and ionic crosslinking are the main explanations for the intense loss of swelling. The known relationship between swelling and the concentration of salt solution is stated as in the following equation [25]:

$$\text{Swelling} = k[\text{salt}]^{-n}, \tag{3}$$

where k and n are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt, and the n value is a measure of salt sensitivity. Figure 7 indicates that changing salt concentrations higher than about 0.5 M has no appreciable influence on the swelling of the superabsorbent. The k and n values for NaCl solutions are 70.7 and 0.24, respectively. The value of n is a measure of the dependence of swelling on salt concentration and proportionally changes with the cation valence

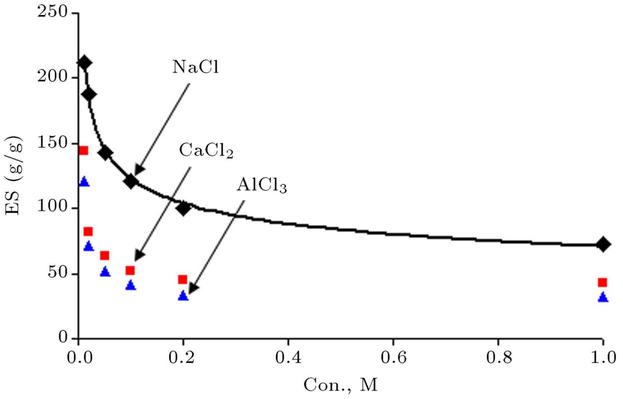


Figure 7. The swelling capacity variation of optimized sample in various concentrations of NaCl, $CaCl_2$ and $AlCl_3$ solution.

enhancement (0.25 for $CaCl_2$ and 0.28 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.

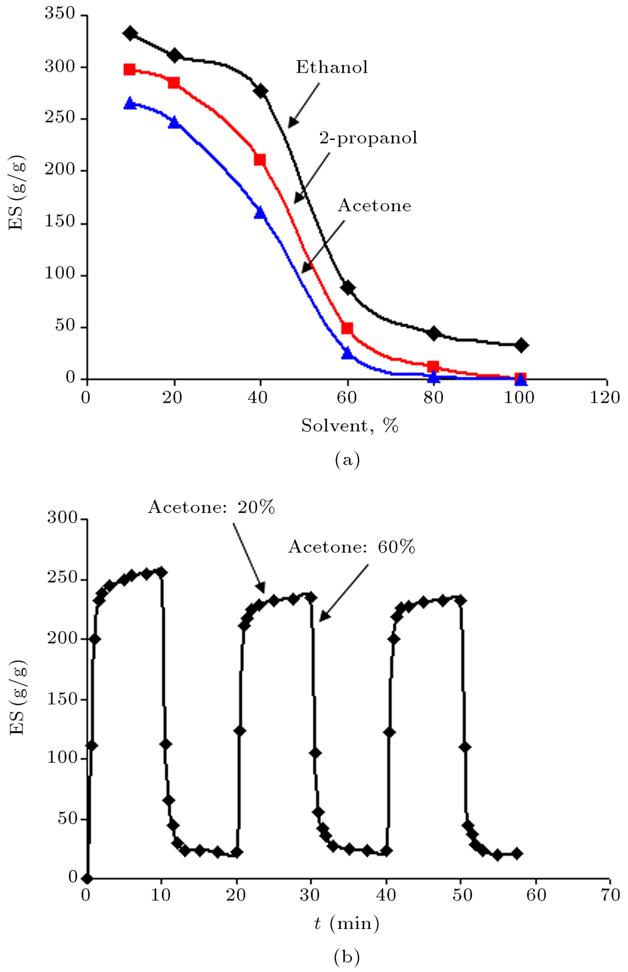
3.6.3. Solvent-induced phase transition

In the present study, the swelling changes of the optimized SPH were examined in various water-organic solvent systems. The swelling-loss in these mixtures can be easily explained. Anionic groups are easily solvated by water molecules. However, it is widely restricted in these organic solvent-water systems because the organic solvent molecules (EtOH, 2-propanol, acetone) cannot solvate the anionic groups. As a consequence, the swelling capacities are considerably decreased.

It can also be concluded from Figure 8(a) that in a fixed ratio of solvent-water (e.g., a 30:70 w/w solvent-water mixture), the swelling is increased in the order of ethanol> 2- propane> acetone. This can be explained using the Hildebrand equation [27]:

$$\Delta H_m/(V\Phi_1\Phi_2) = (\delta_1 - \delta_2), \tag{4}$$

where ΔH_m is the enthalpy change during the mixing of a polymer and a solvent, Φ_1 and Φ_2 are the volume fractions for the solvent and the polymer, V is the whole volume of the solution, and δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively.



(a)

(b)

Figure 8. (a) Effect of organic solvents (ethanol, 2-propanol and acetone) on the water absorbency of SPH. (b) On-Off switching behavior of the optimized SPH in acetone/water: 20 wt% (swelling), acetone/water: 60 wt% (deswelling).

This equation clearly indicates that to dissolve a polymer in a solvent, the δ values must be close to each other. As a consequence, to predict the solubility of a polymer, δ values should be calculated. As the swelling capacity of the synthesized hydrogel in water is maximum, the δ value of water (23.4 $(\text{cal/cm}^3)^{1/2}$) can be regarded as its solubility parameter. The solubility parameter for solvent-water mixtures (δ_{mix}) can be calculated using the following equation [28]:

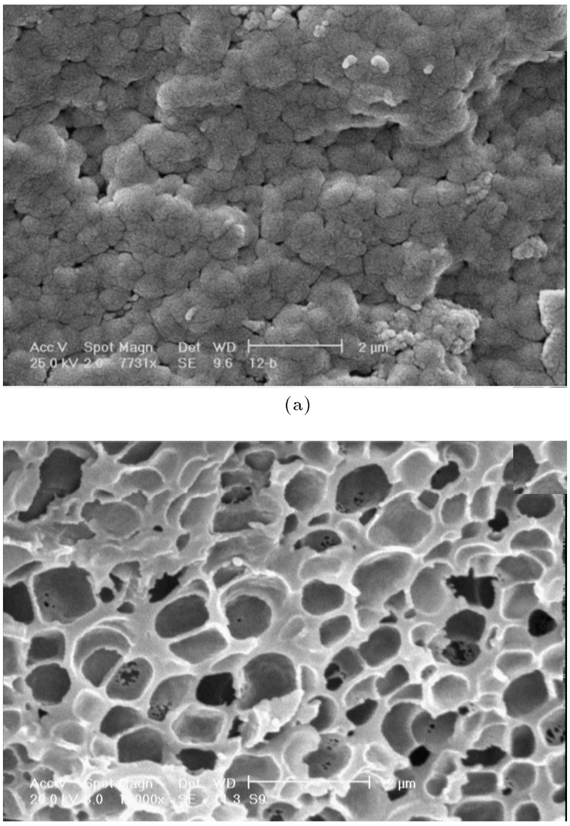
$$\delta_{\text{mix}} = \delta_1\Phi_1 + \delta_2\Phi_2, \tag{5}$$

where Φ_1 and Φ_2 are the volume fraction, and δ_1 and δ_2 are the solubility parameters of the two solvents. According to data summarized in Table 6, by increasing δ_{mix} values toward 23.4, the hydrogel can be highly swollen, as in pure water. In other words, the swelling capacity of the hydrogel in the solvent-water mixture will be close to that in pure water if δ_{mix} is close to δ_{water}. The optimally prepared environmental-sensitive superabsorbent composite showed a reproducible On-Off switching behavior when the environmental mixture of the sample was alternatively changed between acetone/water: 20 wt% and acetone/water: 60 wt%. The collapse of the gel is a result of the total depletion of water from the solvated polymer network. The non-solvent acetone dissociates the water-hydrogel hydrogen bonding, and, as a result, the hydrogel is collapsed at a certain concentration of acetone-water. The contracted gel is reswollen when it is located in another acetone-water mixture with higher δ_{mix} [29].

Table 6. The solvent-water concentrations in which the superabsorbent hydrogel exhibits volume-phase transition.

Solvent	**δ (or δ_{mix})^a**	**ES (g/g)**
Water	23.4	762
Ethanol	12.7	33
2-Propanol	11.5	-
Acetone	9.9	-
Ethanol/water (30:70)	20.2	305
2-propanol/water (30:70)	19.8	255
Acetone/water (30:70)	19.3	208

[a]: Symbols δ and δ_{mix} $[(\text{cal/cm}^3)^{1/2}]$ are the solubility parameters for the solvent and the solvent-water mixture, respectively.



(a)

(b)

Figure 9. SEM photographs of (a) hydrolyzed (salep/gelatin)-g-PAAm SPH with 5000X magnification, and (b) (salep/gelatin)-g-PAAm superabsorbent hydrogel with 5000X magnification, synthesized under optimized conditions.

3.7. Surface morphology of hydrogels

It is supposed that the pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. Figure 9 shows the Scanning Electron Microscopic (SEM) pictures of the optimized hydrogel (a) after and (b) before gel hydrolysis. These pictures verify that our superabsorbent hydrogel shows a micro/nano porous structure after hydrolysis. The pores might be inducted into the hydrogel by water evaporation resulting from neutralization heat or the delivery of NH_3 gas due to the hydrolysis of acrylamide groups.

4. Conclusions

In the present work, a novel SPH was prepared by crosslinking the graft copolymerization of acrylamide onto the polysaccharide/protein hybrid backbone after hydrolysis. The optimum reaction conditions to obtain maximum water absorbency (762 g/g) were found to be: salep 1.0 g, gelatin 0.5 g, AAm 6.0 g, MBA 0.09 g, APS 0.06 g, NaOH 2 M and T 80°C. It was found that the neutralization process after gel formation incredibly influenced the morphology of the produced hydrogel. The swelling measurements of the optimally synthesized hydrogel in different salt solutions showed appreciable swelling capacity, especially in CsCl and KCl solutions. Also, the superabsorbent hydrogel exhibits a 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). Furthermore, the reversible swelling-deswelling behavior in solutions with acidic and basic pH makes the hydrogels suitable candidates for controlled drug delivery systems. In addition, it is expected that the resulted superabsorbent polymer will show more compatibility with the body when they are used in drug delivery systems, because of the use of polysaccharide/protein as a natural hybrid backbone. Finally, the dynamic swelling kinetics of the hydrogels shows that the rate of absorbency is increased by decreasing the particle size of superabsorbent samples.

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Biographies

Rouhollah Soleyman obtained his BS and MS degrees in Pure Chemistry and Organic Chemistry (Polymer) in 2006 and 2008, respectively, from Sharif University of Technology (SUT), Tehran, Iran, where he also obtained his PhD degree, in 2012, specializing in shape-controlled synthesis of silver nanoparticles and evaluation of their biomedical properties. Presently, he is a senior researcher in the polymer science and technology division at the Research Institute of the Petroleum Industry (RIPI).

Ghasem Rezanejade Bardajee earned his BS degree in Pure Chemistry from Shiraz University, Iran, his MS degree in Organic Chemistry from the University of Tehran, Iran, and his PhD degree from Sharif University of Technology, Tehran, Iran.

Ali Pourjavadi obtained his DSC from Pierre et Marie Curie (Paris VI) University, France, and is currently Professor in the Chemistry Department at Sharif University of Technology, Tehran, Iran. His teaching and research specializations include synthesis and characterization of new polymers.

Akbar Varamesh obtained his BS and MS degrees in Pure and Organic Chemistry from Tabriz University, Iran, in 2003 and 2006, respectively. In 2007, he joined the polymer science and technology division of the Research Institute of the Petroleum Industry (RIPI) as a senior researcher.

Ali Asghar Davoodi obtained his BS in chemical engineering in 2004. Then, he completed his MS degree (2008) in Chemical Engineering with specialty in thermodynamic and kinetic at Iran University of Science & Technology. Next, he worked in CAPE consulting company as senior process engineer for two years. After that, in 2010, he joined to the polymer science and technology division of Research Institute of Petroleum Industry (RIPI) as a project manager. His current research interests include synthesis, phase equilibriums, and adsorption.