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γ-Irradiation Synthesis of a Smart Hydrogel: Optimization Using Taguchi Method and Investigation of Its Swelling Behavior

A. Pourjavadi[1,*], **R. Soleyman**[1], **Gh.R. Bardajee**[2] **and F. Seidi**[1]

Abstract. *In the current work, synthesis of an environmental-sensitive superabsorbent hydrogel using γ-rays is described. Grafted polyacrylonitrile onto a homogeneous solution of starch and kappa-Carrageenan hybrid backbones created a smart material with reversible behavior. The reaction parameters (i.e. acrylonitrile, starch and kappa-Carrageenan concentration, as well as γ-irradiation time) affecting the water absorbency of the hydrogel were optimized using the Taguchi method, in order to achieve a hydrogel with high swelling capacity. FTIR spectroscopy was used for confirming the structure of the final product and the morphology of the synthesized hydrogel was examined by a scanning electron microscope. The swelling behavior of the optimized hydrogel sample in various NaCl concentrations and swelling kinetics in distilled water were investigated. The pH-reversibility and on-off switching behaviors of entitled smart hydrogel make it a good candidate for consideration as a potential carrier for bioactive agents like drugs.*

Keywords: *Superabsorbent hydrogel; Taguchi method; γ-irradiation; Synthesis; Swelling behavior.*

INTRODUCTION

In recent decade, considerable research attention has been focused on intelligent polymer materials, especially hydrogels, which contain functional groups, and are able to alter their volume or other properties in response to environmental stimuli, such as pH [1], ionic strength [2], temperature, and electric fields [3-5]. Superabsorbent hydrogels are slightly crosslinked networks that can absorb large amounts of water and aqueous fluids in a short time and retain water under pressure. They are widely used in many fields, such as medicine for drug delivery systems [6], agriculture and horticulture [7-8], sealing composites [9], biosensors [10], artificial snow [11], drilling fluid additives [12] and so on. Hydrogels are promising materials for pharmacological applications. They provide time-independent and sustained release of bioactive agents [2]. On the other hand, considerable interest has been devoted to the preparation of hydrogels, based on biocompatible polysaccharides such as chitosan, starch, CMC, sodium alginate and carrageenan [13-15]. In order to synthesis polysaccharide-based superabsorbents, vinylic graft copolymerization can be carried out by different initiators and crosslinkers with different mechanisms.

The radiation technique seems an excellent method for the preparation of hydrogels, because a polymer in an aqueous solution, with a monomer dissolved in it, undergo crosslinking and graft copolymerization on irradiation to yield a hydrogel. Simple procedure control, no initiators, crosslinkers, no waste, and relatively low operating costs make an irradiation technique a suitable choice for the synthesis of hydrogels [16].

The Taguchi method [16] is a powerful experimental design tool developed by G. Taguchi. It provides a simple, efficient and systematic approach to optimize the designs for performance, quality and cost. The

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1. *Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, Tehran, P.O. Box 1155-9516, Iran.*
2. *Department of Chemistry, Payame Noor University, Iran.*
*. *Corresponding author. E-mail: purjavad@sharif.edu*

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parameter design is a key step in the Taguchi method to achieve high quality without increasing cost, and the same is adopted in this paper. The evaluation of results has been standardized by this method, which can easily be applied by researchers [17,18].

In our previous work, the crosslinking and graft copolymerization of polyacrylonitrile (PAN) onto starch and carrageenan via a thermal classic initiation system have been reported separately [19-21]. In the present study, the synthesis and swelling behavior of an environmental-sensitive superabsorbent hydrogel via graft copolymerization of polyacrylonitrile onto a homogeneous solution of starch and kappa-carrageenan using γ-rays is reported. The use of γ-rays as a clean energy source, initiator and crosslinker, instead of toxic reagents like APS and MBA, and shorter routes for the synthesis optimization, are advantages of the presented work.

EXPERIMENTAL

Materials

The polysaccharides, starch (Glucosan Co., Ghazvin, Iran) and kappa-Carrageenan (kC, from Condinson Co., Denmark) were used without further purification. Acrylonitrile (AN, Merck) was used as received. All other chemicals were also of analytical grade. Double distilled water was used for hydrogel preparation and swelling measurements.

Instrumental Analysis

FTIR spectra of samples in the form of KBr pellets were recorded on an ABB Bomem MB-100 FTIR spectrophotometer. Irradiation was carried out using gamma rays from a Co-60 source, in a Gammacell-220 (Nordion, Canada) with 1.5 kGy/h dose rate, under ambient condition. The morphology of the dried samples was examined using a scanning electron microscope, SEM, (Philips, XL30) operated at 20 kV after coating the samples with gold film.

Experimental Design

Selection of Factors and Their Levels

The reaction variables, including γ-irradiation time, acrylonitrile (AN), kappa-Carrageenan (kC) and starch concentration, were selected. These are, generally, important factors in the synthesis of superabsorbents, and three levels for each factor were chosen, as shown in Table 1.

Table 1. Experimental control factors and their levels.

Control Factor	**Level 1**	**Level 2**	**Level 3**
A (radiation dose (kGy))	1.5	6	11
B (starch (g))	0.4	0.6	0.8
C (k-Carrageenan (g))	0.4	0.6	0.8
D (acrylonitrile (mL))	1	2	3

Selection of Orthogonal Array and Assignment of Factors

A statistical method of Taguchi is proposed after identification of important, as well as effective, factors; usually through preliminary studies and experiments. The number of factors and their levels determine the Orthogonal Array (OA). The number of experiments and their performance conditions are set by the selected orthogonal array. For more explanation, important concepts in the OAs are described:

a) **Factor:** Main variables affecting the response of an experiment, which can be divided into qualitative and quantitative ones. The amount of monomer, the temperature and initiator concentration are among the quantitative factors. Various sorts of material and a study of the methodology are among the qualitative ones.

b) **Level:** Different values of factors are considered as the levels of that factor. For example, if the amount of monomer is assigned to four values (2, 4, 6 and 8 g), we have a four level factor. In the present study, an OA with 3 levels and 4 factors was chosen (Table 2). This OA is particularly designed with the symbol of L9. 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 9

Table 2. Experimental layouts of an L9 orthogonal array according to Taguchi's suggestion (the numbers in each column indicate the levels for the specific factors).

Trial	**A**	**B**	**C**	**D**
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

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. Software package Qualitek-4 version 6.3 was used for selection of the orthogonal, optimum conditions and the contribution of each factor [16].

Hydrogel Preparation

In general, certain amounts of starch (0.4-0.8 g), kC (0.4-0.8 g) and water (40 mL) were added to a 50 mL 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, AN (1-3 mL) was added to the reaction mixture and stirred for a further 20 minutes. The cold mixture was removed into a 250 mL aluminum tube, the inner wall of which was covered with aluminum foil. The tube was closed tightly with the foil and a paraffin film. The tube was then irradiated under γ-rays according to the desired total doses. 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. The final powdered superabsorbent hydrogel was stored away from moisture, heat and light for further experiments.

Water Absorbency Measurement

The degree of swelling was determined by the gravimetric method. The tea bag (for example a 100-mesh nylon screen) containing the powdered sample (0.5 ± 0.01 g) with average particle sizes between 40-60 mesh (250-350 μm) was immersed entirely in distilled water (400 mL) and allowed to soak for 60 minutes at room temperature. The Equilibrium Swelling (ES) capacity was measured twice at room temperature using the following formula:

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

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

Swelling Kinetics

For studying the rate of absorbency of the hydrogel, a certain amount of the sample (0.5 ± 0.01 g) with average particle sizes between 40-60 mesh (250-350 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.

Environmental Sensitivity

pH Sensitivity

The pH dependency of swelling was measured by the interaction of a certain amount of the hydrogel samples (0.5 ± 0.01 g) in solutions (400 mL) with different pH. The swelling behavior in each pH was determined at different times. The various solutions were adjusted to the desired pH value by the 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 (0.01 molar concentrations).

Salinity

The swelling capacity of the hydrogel was measured in different concentrations of NaCl solution. The on-off switching by ionic strength was carried out at solutions with distilled water/NaCl (0.1 M) or distilled water/$CaCl_2$ (0.1 M) or NaCl (0.1 M)/$CaCl_2$(0.1M).

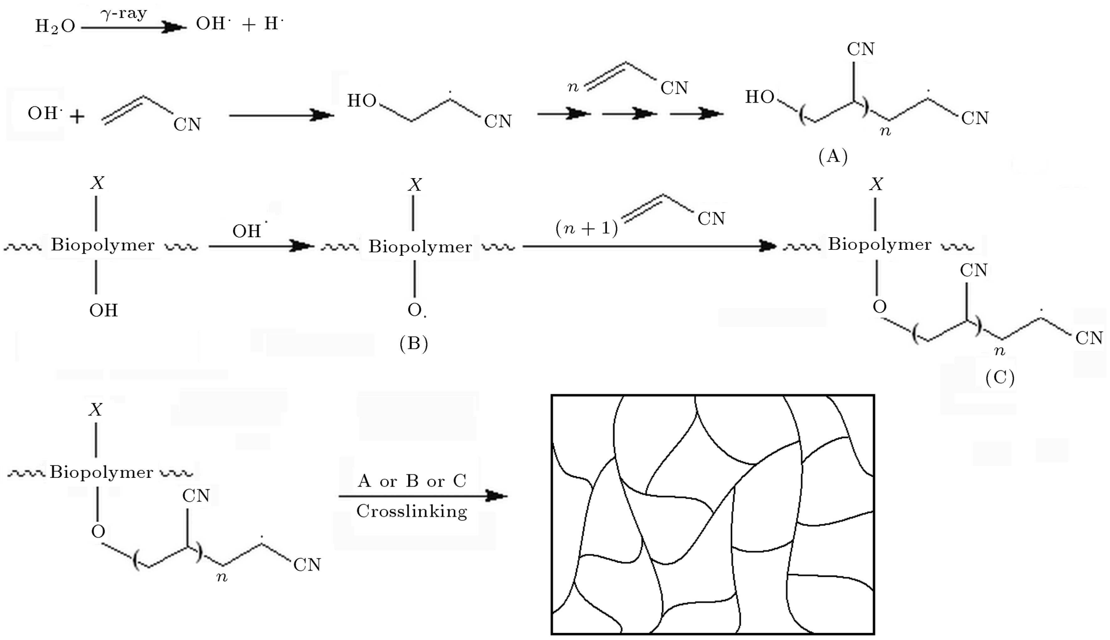
RESULTS AND DISCUSSION

Synthesis and Mechanism Aspects

The crosslinking and graft copolymerization of PAN onto the backbones of kC and starch substrates were carried out in an aqueous medium using γ-ray as a free radical initiator and crosslinking agent [21]. When homogeneous solutions of (starch/kC) polysaccharides and AN monomer are irradiated with γ-rays, one double bond of -C=C- on AN and one of C-H or O-H bonds of (starch/kC) are broken by irradiation and free radicals are generated. These free radicals react with each other, and (starch/kC)-g-PAN superabsorbent hydrogel is produced. The possible polymerization of an entitled system by γ-irradiation is suggested in Scheme 1. When AN, polysaccharides, and water ternary mixtures were irradiated, polymerization and crosslinking occurred simultaneously.

Spectral Characterization

The grafting was confirmed by comparing the FTIR spectra of the polysaccharide backbone before and after graft polymerization. Figure 1 shows the FTIR spectra of starch, kC and synthesized hydrogel (after removing the sol fraction). In the spectrum of starch (Figure 1a), the broad band, at 3200-3400 cm^{-1} , is due to stretching the vibrational mode of hydroxyl groups. Similar signals can be found in Figures 1b and 1c for OH groups in polysaccharides. The bands observed at 847, 916, 1025 and 1225 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage and ester sulfate stretching of kC, respectively (Figure 1b). The product, (starch/kC)-g-PAN comprises starch/kC backbone with side chains



Scheme 1. Proposed mechanism pathway for radiation synthesis of the (starch/kC)-g-PAN superabsorbent hydrogel.

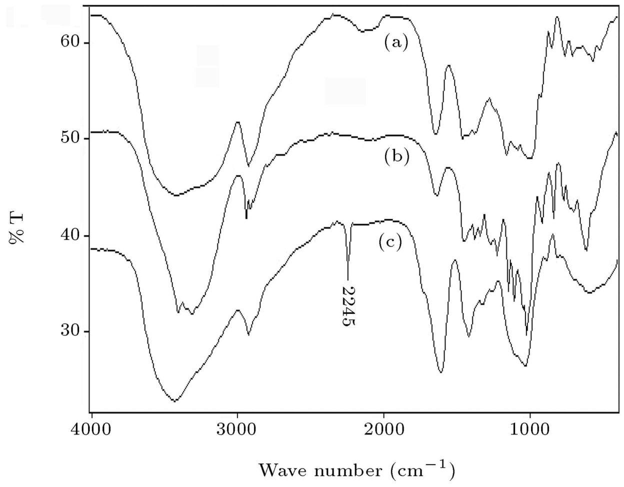


Figure 1. FTIR spectra of (a) starch, (b) kC and (c) (starch/kC)-g-PAN superabsorbent hydrogel.

that carry nitrile functional groups, which are evidenced by a sharp peak around 2245 cm^{-1} (Figure 1c).

Furthermore, the TGA data of the optimized hydrogel (after removing the sol fraction) was compared with the TGA curves of starch, kC and PAN. The TGA curves of starch, kC and PAN were completely different from the hydrogel sample. This can be attributed to the different structures for entitled samples. For the optimized hydrogel sample, the difference in degradation at higher temperatures is more obvious.

Additional observation about the grafting of acrylonitrile onto hybrid polysaccharides can be obtained by very simple experiments. In spite of starch and kC polysaccharides, the desired hydrogel (after removing the sol fraction) did not dissolve in hot water (80°C) after 12 h stirring. As well, the physical mixture of starch, kC and acrylonitrile did not absorb water under our experimental conditions.

Optimization of Water Absorbency

According to our previous work [16,20], the variables affecting the ultimate swelling capacity are AN, kC and starch concentrations, as well as gamma doses. After identification of the effective parameters (factors) in the reaction, based on past experience regarding the synthesis of hydrogels, the levels of factors were determined (Table 1). After the selection of factors and their levels, an orthogonal array appropriate for 4 factors, and 3 levels for each factor was applied. Software Qualitek-4, proposes the L9 OA (Table 2). The methods of performing the experiments were given in Table 3. After the synthesis of 9 hydrogels with conditions proposed by the Taguchi statistical method, results for the water absorbency of 9 samples are given in Table 4 (each measurement was repeated two times). Finding the optimum conditions and contribution of each factor was performed by ANOVA, neglecting the interaction between factors. According to analysis performed by software Qualitek-4, optimum conditions are shown in Table 5 (AN: 1 mL, gamma irradiation dose: 11 kGy, kC: 0.8 g and starch: 0.4 g).

Table 3. A three-level orthogonal array (L9).

Trial	**Radiation Dose (kGy)**	**Starch (g)**	***k*-Carrageenan (g)**	**Acrylonitrile (mL)**
1	1.5	0.4	0.4	1
2	1.5	0.6	0.6	2
3	1.5	0.8	0.8	3
4	6	0.4	0.6	3
5	6	0.6	0.8	1
6	6	0.8	0.4	2
7	11	0.4	0.8	2
8	11	0.6	0.4	3
9	11	0.8	0.6	1

Table 4. Experimental results for swelling of superabsorbents for 9 trials.

Trial	1	2	3	4	5	6	7	8	9
ES (g/g)	195	102	62	82	225	85	170	115	191

Swelling Kinetics

Figure 2 represents the swelling capacity of the hydrogel in distilled water at consecutive time intervals. Initially, the rate of water uptake sharply increases and then begins to level off. The equilibrium swelling was achieved after 30 minutes approximately. A power law behavior is obvious from Figure 2. The data may be well fitted with a Voigt-based equation (Equation 2) [22]:

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

where S_t (g/g) is swelling at time t, S_e is equilibrium swelling (power parameter, g/g), t is time (minute) for swelling and τ (minute) stands for the "rate parameter". To calculate the rate parameter, by using the above formula and a little rearrangement, one can plot $\ln(1 - \frac{St}{Se})$ versus time (t). The slope of the fitted straight line (slope $= -1/\tau$) gives the rate parameter. According to Figure 2 and using Equation 2, the rate parameter for the swelling of hydrogel in water is found to be 7.5 minutes. Since the τ value is a measure of swelling rate (i.e., the lower the τ value, the higher the rate of swelling), it can be used for comparative evaluation of the rate of water absorbency of hydrogels in conditions where the particle sizes of the comparing samples are the same or, at least, in the same range.

Table 5. Optimum conditions and performance.

Factor	**Level Description**	**Optimum Conditions**
Radiation dose (kGy)	3	11
Starch (g)	1	0.4
k-Carrageenan (g)	3	0.8
Acrylonitrile (mL)	1	1

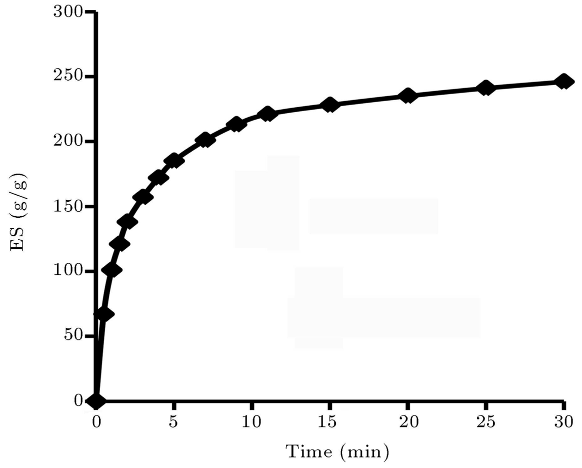


Figure 2. The swelling kinetics of optimized sample in distilled water.

Environmental Sensitivity

pH Sensitivity and On-Off Switching

The swelling behavior of the superabsorbent hydrogel was studied at room temperature at various pH values between 0 and 14 (Figure 3). To prepare the desired pH media, standard HCl (pH 0) and NaOH (pH 14) solutions were diluted with distilled water to reach the preferred acidic and basic pHs, respectively. The swelling of the hydrogel increased with increasing pH from 1 to 7, but it decreased in the pH range between 7 and 14. The maximum water absorbency of the hydrogel was achieved in weak basic media (pH 7-9). At this point, some of $-SO_3H$ groups were converted to $-SO_3^-$ anions resulting in high anion-anion repulsion

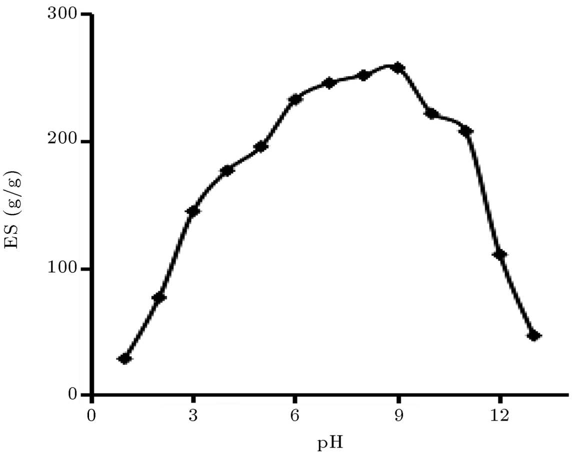


Figure 3. Swelling dependency of (starch/kC)-g-PAN on pH.

and a high swelling capacity. At pH greater than 9, the Na^+ cations from NaOH shielded the -SO_3^- groups and prevented the perfect anion-anion repulsion. Also, the ionic strength of the medium is increased and, consequently, the swelling is decreased. The low water absorbency in strong acidic media (pH = 1-3) can be attributed to the high ionic strength of the solutions. The optimally prepared 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 4). This repeatable behavior guarantees the smartness of our hydrogel, which has significant importance in the controlled delivery of drugs [1].

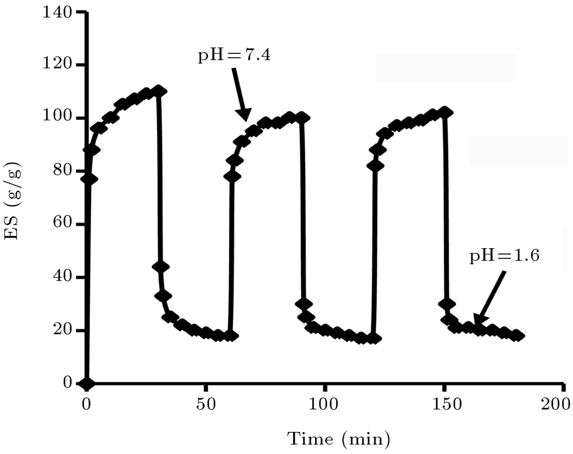


Figure 4. On-off switching behavior of the optimized hydrogel in 0.01 M buffered solutions with pH = 7.4 and pH = 1.6.

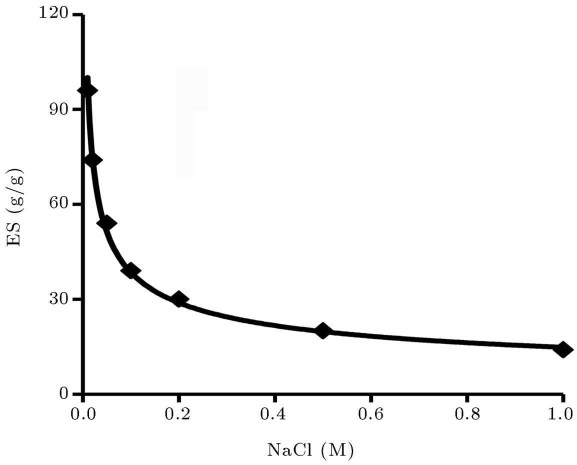


Figure 5. The swelling capacity variation of (starch/kC)-g-PAN in various concentrations of NaCl solution.

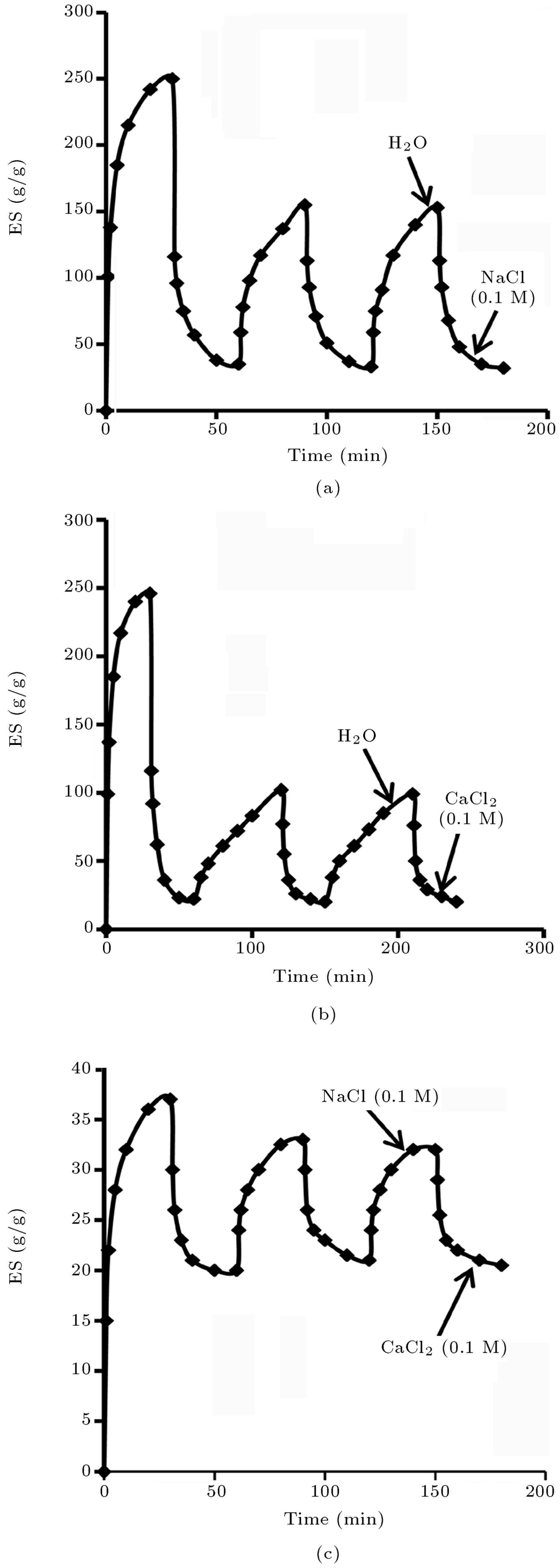
Salinity and On-Off Switching

The ionic strength of the environment affects the swelling capacity of superabsorbents. Figure 5 shows the effect of various concentrations of NaCl on the water absorbency of the superabsorbent hydrogel. A decrease in the swelling capacity of the hydrogel is attributed to the osmotic pressure difference between the hydrogels and the aqueous phase. Another factor influencing the swelling capacity in salt solutions is the charge screening effect or shielding effect in which perfect anion-anion repulsion is prevented by cations [23]. The well-known relationship between swelling and salt solution concentration is stated in Equation 3 [24]:

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

where k and n are constants for an individual superabsorbent. The k value is swelling at a high concentration of salt and the value of n is a measure of the dependence of swelling on salt concentration.

The swelling of the superabsorbent hydrogel hybrids in saline solutions appreciably decreases, compared to the values measured in deionized water [1]. This phenomenon, commonly observed in the swelling of all ionic hydrogels, is often attributed to the screening effect of the additional cations causing a non efficient anion-anion electrostatic repulsion, leading to a decreased osmotic pressure (ionic pressure) difference between the hydrogel network and the external solution [2]. An optimum sample was tested to be swollen and de-swollen alternatively in distilled water and a 0.10 M sodium chloride solution. As shown in Figure 6a, the sorption-de-sorption behavior is quite repeatable. Interestingly, a similar capability was observed when a $CaCl_2$ solution with the same molar concentration was used (Figure 6b). According to previous studies on the starch-acrylic superabsorbent hydrogels, these particles, which had once been immersed in the multivalent cations solution, will not be re-swollen in water [2]. A similar observation in the case of poly(vinyl alcohol)/poly(acrylic acid) hydrogel fibers has also been reported [4]. The nonreversible phenomenon has been explained by a complexing ability arising from a coordination of multivalent



(a)

(b)

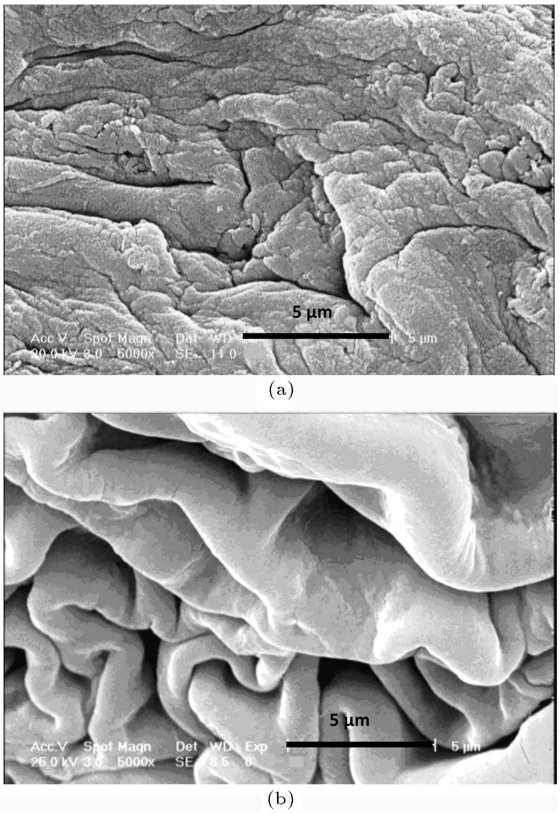
(c)

Figure 6. On-off switching behavior of the optimized hydrogel: a) swelling in distilled water and deswelling in NaCl (0.1 M), b) swelling in distilled water and deswelling in $CaCl_2$ (0.1 M) and c) swelling in NaCl (0.1 M) and deswelling in $CaCl_2$ (0.1 M).

cations with carboxylate pendant groups. This ionic crosslinking mainly occurs at the surface of particles and makes them rubbery and very hard when they swell in multivalent cation solutions. In the case of our hydrogel, however, the sulfate-Ca^{2+}-sulfate bridges are weak enough to break and the network re-swells in distilled water. It can primarily be attributed to highly branched(starch/kC) sections of the hybrid network. The steric hindrances of the branches disfavor the formation of stable ionic crosslinks. Based on a similar possible reason, the hydrogel hybrid shows a good ion-exchange capability, i.e. it can repeatedly be swelled and collapsed when its swelling medium is alternatively changed between two media of the chloride solutions of Na^+ and Ca^{2+} with the same molarity (Figure 6c). This repeatable salt sensitivity is another evidence to guarantee the smartness of our hydrogel.

Surface Morphology of Hydrogels

The surface structure of the hydrogels was observed using a Scanning Electron Microscope (SEM). The SEM photographs of two samples are presented in Figure 7. The SEM photograph of the optimized hydrogel sample is compared with (starch/kC) as the starting material. It is supposed that pores are the regions of water



(a)

(b)

Figure 7. SEM photograph of a) starch/kC and b) (starch/kC)-g-PAN synthesized under optimized conditions.

permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers. These pictures verify that superabsorbent hydrogel has a porous structure, while started materials (the physical mixture of kC and gelatin) have no porosity in their structures.

CONCLUSIONS

(Starch/kC)-g-PAN hydrogel was synthesized in an aqueous medium using gamma irradiation as an initiator and a crosslinking agent at the same time. By applying this method, the toxic initiator and crosslinking agents are deleted and a more echo-friendly procedure is developed. γ-rays bring about cleaner and more non-toxic hydrogels. The synthesis of superabsorbent hydrogel was optimized by the Taguchi method. The maximum water absorbency (225 g/g) was achieved under optimum conditions, which are as follows: kC, starch and acrylonitrile 0.8 g, 0.4 g and 1 mL, respectively, as well as γ-ray at the optimum total dose (11 kGy). The Taguchi method was found to be a promising tool for obtaining the optimum condition. The synthesis of superabsorbent hydrogel was optimized by varying the reaction parameters affecting the ultimate swelling capacity of the final product. The on-off switching behavior of our hydrogel put it as a smart material for further applications.

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BIOGRAPHIES

Ali Pourjavadi has been a Professor at the Chemistry Department of Sharif University of Technology, Tehran, Iran, since 1983. He earned a DS from Pierre et Marie Curie University (Paris VI) in France. His teaching and research specializations include: Synthesis and Characterization of New Polymers.

Rouhollah Soleyman earned his BS in Pure Chemistry and MS in Organic Chemistry from Sharif University of Technology, Tehran, Iran where he is now a PhD student in the Department of Chemistry.

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

F. Seidi earned his BS in Pure Chemistry from Tabriz University, Iran, and his MS in Organic Chemistry from Sharif University of Technology, Tehran where he is now a PhD student in the Department of Chemistry.