

Novel Superabsorbent Hydrogel Based on Natural Hybrid Backbone: Optimized Synthesis and its Swelling Behavior

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The synthesis of a novel superabsorbent hydrogel with natural hybrid backbone *via* graft copolymerization of acrylamide (AAm) onto kappa-carrageenan (kC, as a polysaccharide) and gelatin (as a protein) under classic thermal conditions is described. The Taguchi method as a strong experimental design tool was used for synthesis optimization. A series of hydrogels were synthesized by proposed conditions of Qualitek-4 Software. Considering the results of 9 trials according to analysis of variance (ANOVA), optimum conditions were proposed. The swelling behavior of optimum hydrogel was measured in various solutions with pH values ranging from 1 to 13. In addition, swelling kinetics, swelling in various organic solvents, various salt solutions and On-Off switching behavior were investigated. The hydrogel formation was confirmed by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Surface morphology of the synthesized hydrogels was assessed by scanning electron microscope (SEM).

Key Words: Superabsorbent hydrogel, Natural hybrid backbone, Swelling behavior, Taguchi method

Introduction

Hydrogels are polymeric networks, which absorb and retain large amounts of water.¹ The use of hydrogels as biomaterials has recently gained great importance in view of the low toxicity and high biocompatibility presented by many of them.^{2,3} The main hydrogel application areas today include:⁴ (i) topical applications as wound dressings, (ii) drug delivery systems, (iii) transdermal systems, (iv) dental applications, (v) injectable polymers, (vi) implants, (vii) ophthalmic applications, and (viii) stimuli-responsive systems.

Recently, natural materials (such as polysaccharides and proteins) have been used as the superabsorbent hydrogels backbone because of their exceptional properties, i.e., biocompatibility, biodegradability, renewability, and nontoxicity.⁵⁻⁸

Carrageenans are commercially important hydrophilic polysaccharides that occur in numerous species of seaweeds.⁹ These linear sulfated polymers are composed of d-galactose and 3,6-anhydrogalactose units. The types of carrageenans differ only in the position and number of ester sulfate groups.

Gelatin is a natural polymer, derived from collagen and due to its biodegradability^{10,11} and biocompatibility in physiological environments^{12,13} is commonly used for pharmaceutical and medical applications.

The Taguchi method 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 parameter design is the 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.¹⁴⁻¹⁷

The present article represents an optimized synthesis (by Taguchi method) of a novel biopolymer-based superabsor-

bent hydrogel *via* crosslinking graft polymerization of acrylamide (AAm) onto kappa-carrageenan/gelatin hybrid backbone, under thermal classic conditions.

Experimental Section

Materials. Kappa-carrageenan (kC, from Condinson Co., Denmark), gelatin (from Darnstadt, Germany, Merck), *N,N'*-methylenebisacrylamide (MBA, from Merck), ammonium persulfate (APS, from Merck) and acrylamide (AAm, from Merck) were used as received. All other chemicals were also analytical grade. Double distilled water was used for hydrogel preparation and swelling measurements.

Instrumental Analysis. FTIR spectra (KBr pellets) were recorded on ABB Bomem MB-100 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed using polymer laboratories systems at a heating rate of 20 °C/min under nitrogen atmosphere. The morphology of the dried samples was examined using a scanning electron microscope, SEM, (Philips, XL30) operated at 15 - 20 kV after coating the samples with gold film.

Experimental Design, Selection of Factors and Their Levels: The important factors in the synthesis of superabsorbent hydrogel including kC/gelatin weight ratio, AAm, MBA and APS amounts were selected as main factors. As well, three levels for each factor were chosen as shown in Tables 1 and 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 a 3 level and 4 factors are shown in Table 1. 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 conditions) for the factors were assigned in Table 1. Software package Qualitek-4 version 6.3 was used for selection of orthogonal, optimum conditions and contribution of each factor.

Superabsorbent Hydrogel Preparation. In general, certain amount of kC (0.5 - 1.0 g, according to Table 3) and gelatin (0.5 - 1.0 g, according to Table 3), were added to 30 mL H₂O at 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, according to Table 3) was added to the reaction mixture and stirred for further 20 minutes. Then, MBA (0.03 - 0.09 g, according to Table 3) in 5.0 mL H₂O and finally, certain amount of APS (0.03 - 0.09 g, according to Table 3) in 5.0 mL H₂O were added, respectively. After 30 min, the gel like material was separated and immersed in ethanol (200 mL) for 24 h. 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.

Table 1. 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

Table 2. Experimental control factors and their levels

Control factor	Level 1	Level 2	Level 3
kC/gelatin (g/g)	0.5 / 1.0	0.75 / 0.75	1.0 / 0.5
AAm (g)	3.0	4.5	6.0
MBA (g)	0.03	0.06	0.09
APS (g)	0.03	0.06	0.09

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

Trial	kC/gelatin (g/g)	AAm (g)	MBA (g)	APS (g)
1	0.5 / 1.0	3.0	0.03	0.03
2	0.5 / 1.0	4.5	0.06	0.06
3	0.5 / 1.0	6.0	0.09	0.09
4	0.75 / 0.75	3.0	0.06	0.09
5	0.75 / 0.75	4.5	0.09	0.03
6	0.75 / 0.75	6.0	0.03	0.06
7	1.0 / 0.5	3.0	0.09	0.06
8	1.0 / 0.5	4.5	0.03	0.09
9	1.0 / 0.5	6.0	0.06	0.03

Water Absorbency Measurement. The degree of swelling was determined by gravimetric method. The tea bag (i.e. a 100 mesh nylon screen) containing the powdered sample (0.1 ± 0.01 g) with average particle sizes between 40 - 60 mesh (250 - 400 μm) was immersed entirely in distilled water (400 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:

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

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

Swelling Kinetics. To investigate the rate of absorbency of the hydrogel, certain amount of the sample (0.1 ± 0.01 g) with average particle sizes between 40 - 60 meshes (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.

The Environmental Sensitivity, pH Sensitivity: The procedures for these experiments are the same as section 2.5. pH dependency of swelling was measured by interaction of certain amounts of the hydrogel samples (0.5 ± 0.01 g) in solutions (500 mL) with different pH. 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.

Salinity: Swelling capacity of the hydrogel was measured in various salt solutions with different concentrations according to section 2.5.

Solvent-induced Phase Transition: The procedures for these experiments are also the same as section 2.5 except that instead of distilled water, mixture of solvents was used. The On-Off switching by mixture of solvents was carried out at acetone/water: 20% (swelling) and acetone/water: 60% (deswelling).

Results and Discussion

Synthesis and Mechanism Aspects. Crosslinking and graft copolymerization of PAAm onto backbones of kC and gelatin hybrid substrates were carried out in an aqueous medium using APS as a radical initiator and MBA as a crosslinking agent. The persulfate decomposes on heating (at 80 °C) and produces sulfate anion-radicals that abstract hydrogen atoms from the OH groups of kC or NH₂ groups of gelatin backbones. This redox system results in active centers capable of initiating the radical polymerization of AAm, leading to a graft copolymer. Since a crosslinking agent (MBA) is present in the system, the copolymer contains a crosslinked structure (Figure 1).

Spectral Characterization. The grafting was confirmed by comparing the FTIR spectra of polysaccharide and protein backbones before and after graft polymerization. Figure 2 shows the FTIR spectra of gelatin, polyacrylamide, kC and synthesized hydrogel, respectively. In the spectrum of gelatin (Figure 2a), the broad band at 3430 cm⁻¹ is due to stretching

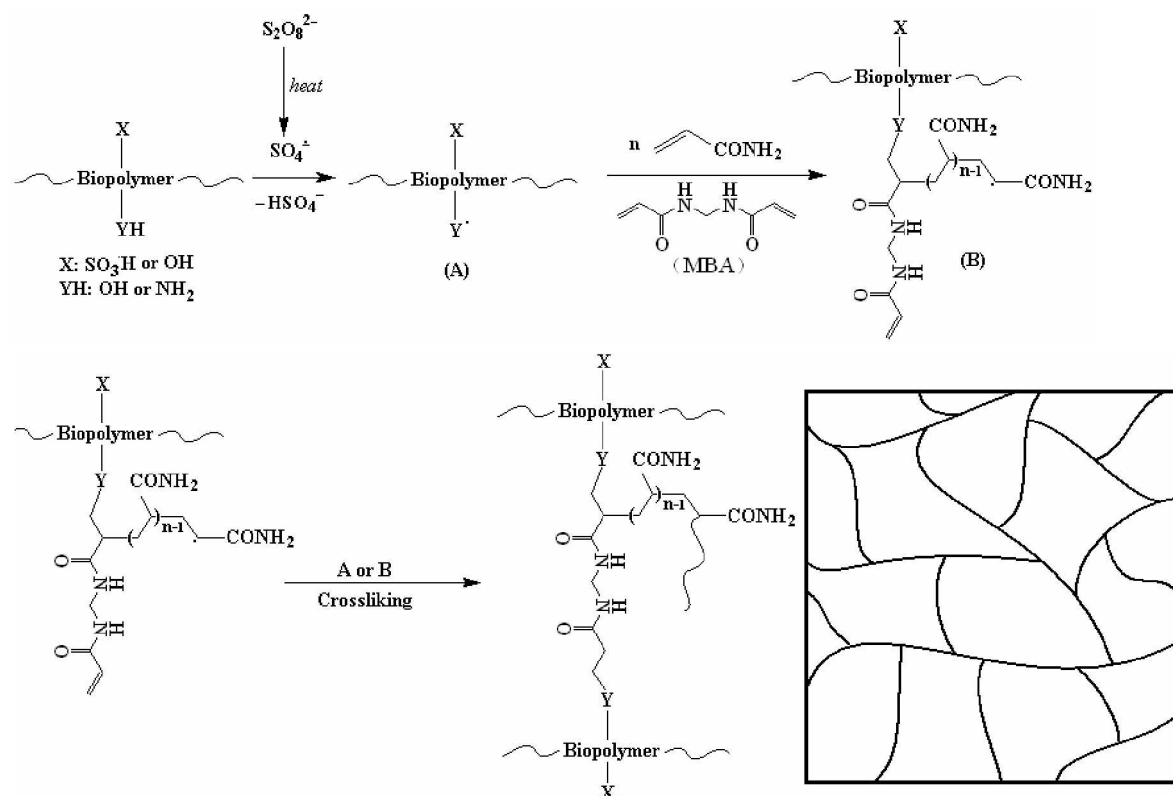


Figure 1. Proposed mechanism pathway for synthesis of the (kC/gelatin)-g-PAAm superabsorbent hydrogel.

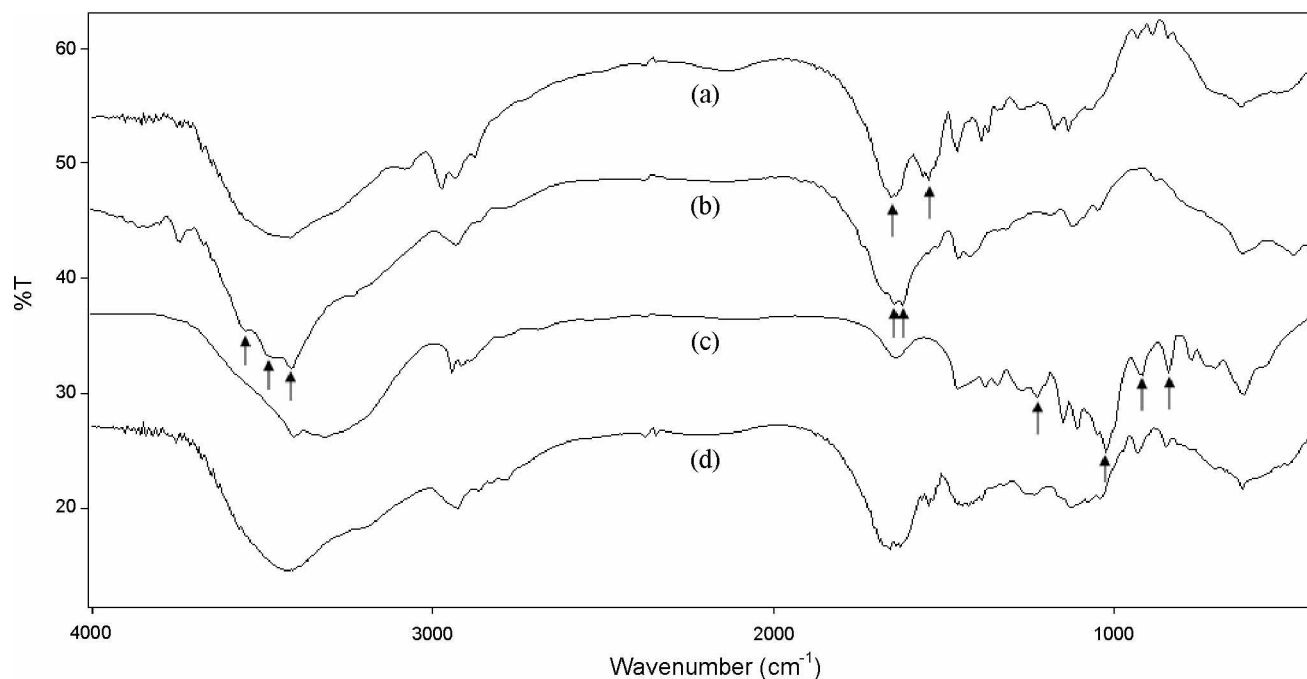


Figure 2. FTIR spectra of (a) gelatin, (b) PAAm, (c) kC and (d) (kC/gelatin)-g-PAAm superabsorbent hydrogel synthesized under optimized conditions, respectively.

vibration modes of amino groups. Two bands at 1545 and 1650 cm^{-1} can be attributed to N–H bending vibration and amide group, respectively. The bands observed at 840, 917, 1022 and 1227 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 2c). All indicated peaks in prior spectra were objectively repeated in the spectrum of final hydrogel (Figure 2d).

TGA traces of (a) superabsorbent hydrogel and (b) physical mixture of kC/gelatin/PAAm are presented in Figure 3. This Figure and the data summarized in Table 4, shows the improvement of the thermal stability of superabsorbent hydrogel. According to Table 4, the related values of the superabsorbent hydrogel such as T_{10} (282.8 °C) and char yield at 550 °C (37.5%) are higher compared to that of the physical mixture of kC/gelatin/PAAm (T_{10} = 247.1 °C, Y = 30.1%). As one can see, this sample is found to be the most thermally stable one studied. The ionic and crosslinked structure in the network may act as heat barriers and as a consequence enhance the overall thermal stability of the superabsorbent hydrogel.

Optimization of Water Absorbency. According to previous works,^{17,21} the factors and corresponding levels affecting the ultimate swelling capacity of the entitled hydrogel were selected

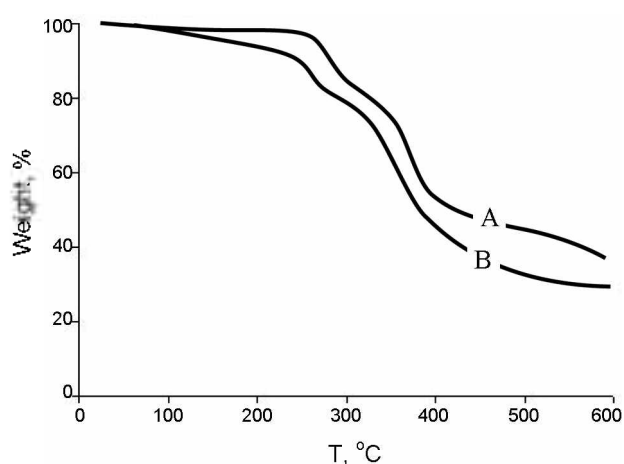


Figure 3. TGA of (a) superabsorbent hydrogel and (b) physical mixture of kC/gelatin/PAAm.

Table 4. Thermal properties of the optimized (kC/gelatin)-g-PAAm and physical mixture of kC/gelatin/PAAm

Polymer	Temperature (°C) at weight loss			Y ^a (wt%)
	10%	30%	50%	
A	282.8	364.1	419.0	37.5
B	247.1	337.2	385.1	30.1

^aChar yield 550 °C in nitrogen.

Table 5. Experimental results for swelling of superabsorbents for 9 trials

Trial	1	2	3	4	5	6	7	8	9
ES (g/g)	70	32	10	30	68	90	48	74	50

Table 6. Optimum conditions and performance

Factor	Level description	Optimum conditions
kC/gelatin (g/g)	2	0.75 / 0.75
AAM (g)	2	4.5
MBA (g)	1	0.03
APS (g)	1	0.03

(Tables 1-2). After selection of factors and their levels, an orthogonal array appropriate for 4 factors with 3 levels for each factor (L9 OA) was applied (Tables 1 and 3). The results for the synthesis of 9 hydrogels with conditions proposed by Taguchi statistical method are given in Table 5 (each measurement was repeated two times). Finding the optimum conditions and contribution of each factor was found by using ANOVA, neglecting the interaction between factors. According to analysis performed by software Qualitek-4, optimum conditions are shown in Table 6.

Swelling Kinetics. Figure 4 represents the dynamic swelling behavior of the superabsorbent in water. The time required to reach the equilibrium swelling capacity was achieved after about 10 min. The data may be well fitted with a Voigt-based equation.¹⁹

The rate parameter of our superabsorbent is 1.7 min for sizes between 250 - 400 μm.

The Environmental Sensitivity. pH Sensitivity: The swelling behavior of the superabsorbent hydrogel was studied at room temperature at various pH values between 1 and 13 (Figure 5a).²² To prepare the pH media standard HCl (pH 1) and NaOH (pH 13) solutions were diluted with distilled water to reach the desired acidic and basic pHs, respectively. The swelling of the hydrogel increased with increasing pH from 1 to 5, but it is decreased in the pH range between 7 and 13. In the range between 5 and 7, a minimum was observed. At pH = 5, all the -NH₂ groups of gelatin were converted to -NH₃⁺, and at pH = 7, all the -SO₃H groups of kC were converted to -SO₃⁻. Because of these conversions and ion-ion repulsions, two maximum were observed in this Figure. In acidic solution, ionic strength of the medium increases and the charges of the -SO₃⁻ anions are shielded by the counter ions so that prevent efficient repulsion. At the pHs greater than 7, the Na⁺ cations from NaOH shield the -SO₃⁻ groups and prevent the 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

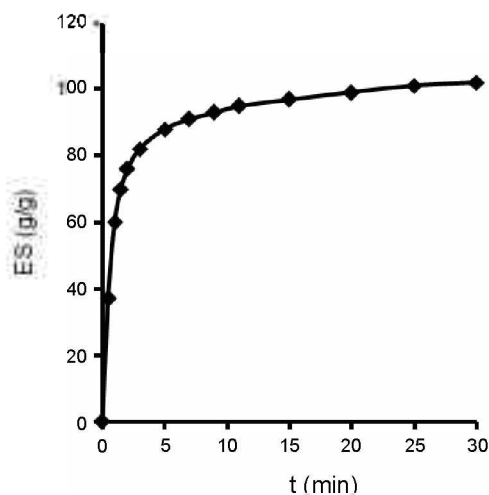


Figure 4. The swelling kinetics of optimized sample in distilled water.

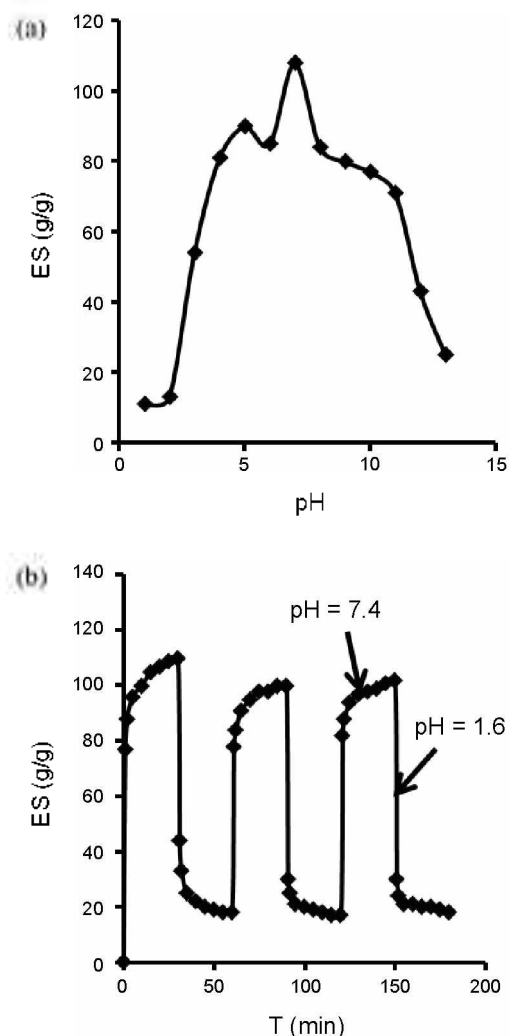


Figure 5. (a) Swelling dependency of (kC/gelatin)-g-PAAm on pH and (b) On-Off switching behavior of the optimized superabsorbent hydrogel in 0.01 molar buffered solutions with pH = 7.4 and pH = 1.6.

1.6 (Figure 5b). This responsiveness behavior may be of significant importance in controlled delivery of drugs to colon having alkaline medium.

Salinity: In these experiments, the swelling capacity was measured in various salt solutions. It is obvious that swelling decrease is strongly depended on the "type" and "concentration" of salt added to the swelling medium.²³⁻²⁵ The effect of cation type (cations with different radius and charge) on swelling behavior is shown in Figure 6. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency for the hydrogel in the mentioned salt solutions is in the order of monovalent > divalent cations. The effect of cation radius on swelling is shown in Figure 6. As reported by Pass *et al.*,²⁶ 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 $\text{CsCl} > \text{NaCl} >$

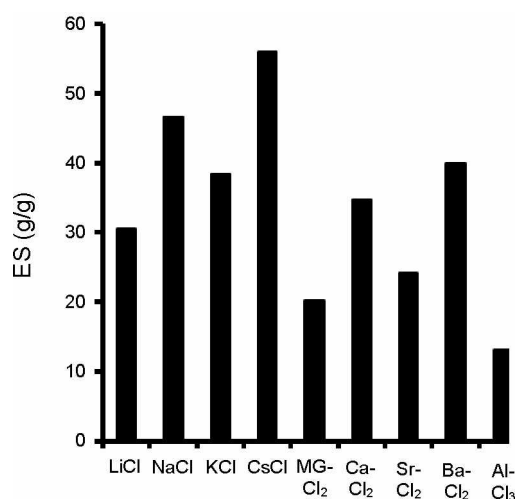


Figure 6. Swelling capacity of the superabsorbent hydrogel in different chloride salt solutions (0.15 M).

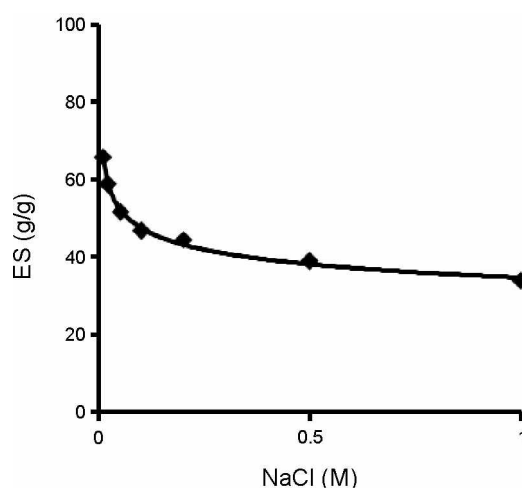


Figure 7. The swelling capacity variation of (kC/gelatin)-g-PAAm in various concentrations of NaCl solution.

LiCl and $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, respectively. In this case, there is an exception on K^+ cation. This unexpected behavior could be rationalized to chelating property of K^+ cation with kC, so a behavior similar to ionic crosslinking of divalent cations was observed. In fact, aqueous solutions of kC with specific cations, especially K^+ , form physically crosslinked thermoreversible polyelectrolyte gels. The stronger interaction between sulfate groups of kC molecules and large cations have also been observed by Pass *et al.* using measurement of activating coefficients of various cations in several salt solutions. Thus, kC has the highest affinity for crosslinking with K^+ among monovalent cations of the studied salt solutions. As a result, swelling of the synthesized hydrogels in KCl solution is lower than in LiCl and in NaCl solutions. Similar results are also observed in the case of chloride solutions of Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} (Figure 6).

Figure 7 illustrates a reverse and power law relationship between concentration of NaCl solutions and swelling capacity of the hydrogel. Charge screening effect is the main explanations for the intense loss of swelling. The known relationship

between swelling and concentration of salt solution is stated as following equation:²⁴

$$\text{Swelling} = k [\text{salt}]^{-n} \quad (2)$$

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 7 indicates that increasing the concentrations of salt to higher than about 0.5 M has no appreciable influence on absorbency of the superabsorbent. The k and n values for NaCl solutions are 34.7 and 0.137, respectively.

Solvent-induced Phase Transition: In the present study, the swelling changes of the optimized hydrogel were examined in various water-solvent systems (Figure 8a). The swelling-loss in these mixtures can be attributed to the change of the solubility parameter of the solvent-water mixture.^{28,29} Anionic

groups are easily solvated by water molecules, but the organic solvent molecules (ethanol or acetone) can not solvate the anionic groups. As a consequence, the swelling capacities are considerably decreased.

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%. In literature, M. J. Zohuriaan-Mehr and *et al.*³⁰ reported that optimum hydrogel of Gum Arabic-acrylic swollen highly in a solvent-water mixture (solvent: ethanol, methanol, DMSO, ethylene glycol and glycerol). Our superabsorbent hydrogel, similar to mentioned hydrogel showed a reproducible swelling-deswelling behavior when the environmental medium was changed alternatively between the acetone-water mixtures 20 wt% and 60 wt% (Figure 8b). The collapse of the gel is a result of the total depletion of water

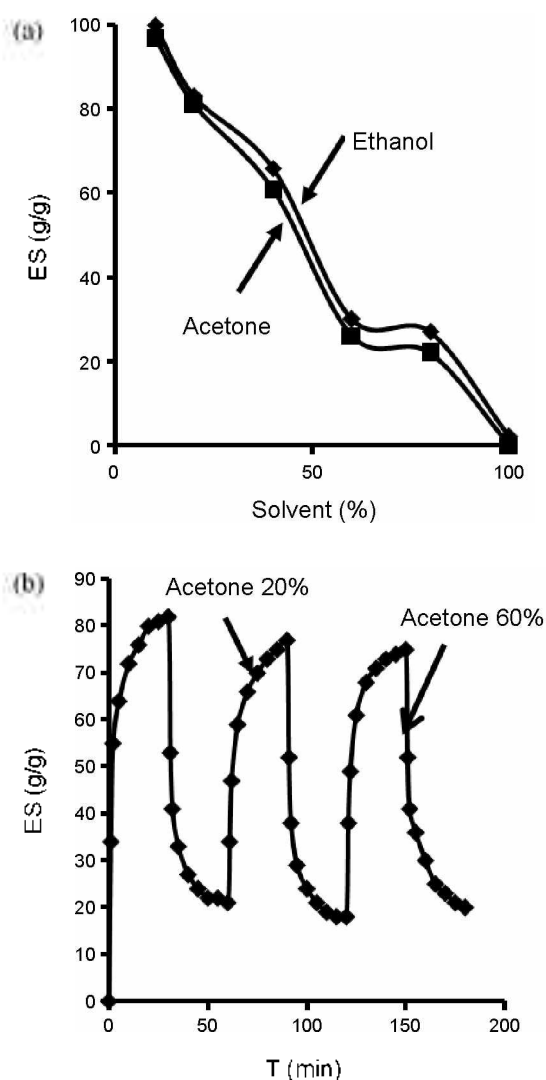


Figure 8. (a) Effect of organic solvents (ethanol, acetone) on the water absorbency of superabsorbent hydrogel and (b) On-Off switching behavior of the optimized superabsorbent hydrogel, in acetone/water: 20 wt% (swelling), acetone/water: 60 wt% (deswelling).

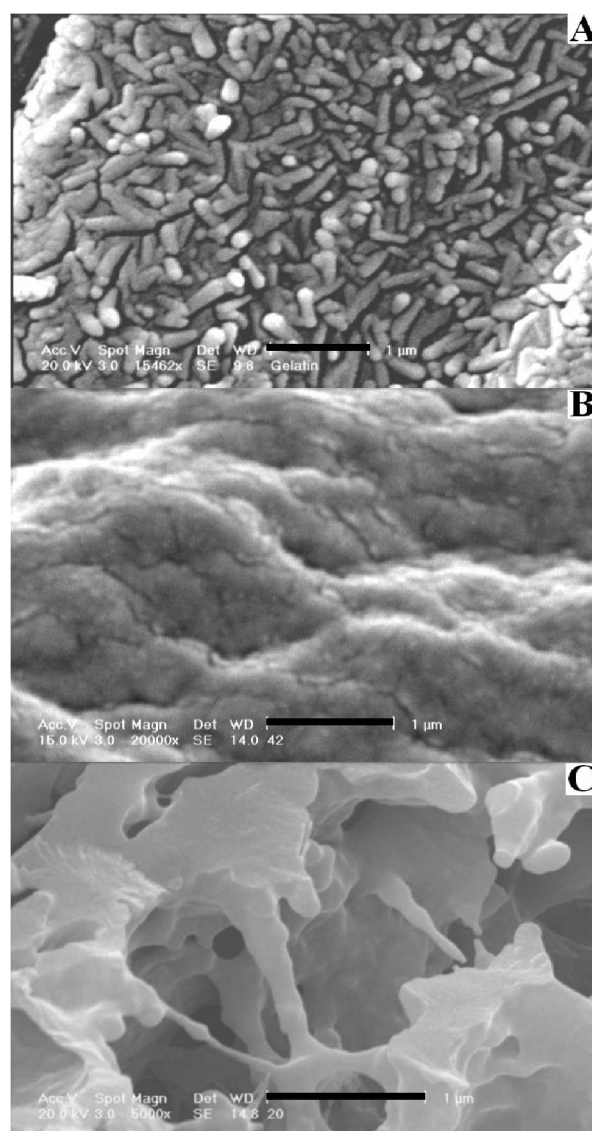


Figure 9. SEM photographs of (a) gelatin, (b) kC and (c) (kC/gelatin)-g-PAAm superabsorbent hydrogel synthesized under optimized conditions.

from the solvated polymer network. In higher percents of acetone, the capability of the hydrogen bonding formation between the molecules of the acetone-water and the hydrogel macromolecular network is decreased. The nonsolvent 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 water content.³⁰

Surface Morphology of Hydrogels. Figure 9 shows the scanning electron microscopic (SEM) pictures of the (a) gelatin (b) kC and (c) synthesized hydrogel under optimum conditions. 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. These pictures verify that superabsorbent hydrogel has porous structure, but started materials (kC and gelatin) have no porosity in their structures.

Conclusion

In the present work, we prepared a novel superabsorbent hydrogel by crosslinking graft copolymerization of acrylamide onto polysaccharide/protein hybrid backbone. The optimum reaction conditions to obtain maximum water absorbency (103 g/g) were found to be: kC/gelatin: 1 (0.75/0.75 g/g), AAm: 4.5 g, MBA: 0.03 g and APS: 0.03 g. Swelling measurement of the hydrogels in different salt solutions showed appreciable swelling capacity, especially in CsCl and BaCl₂ solutions. Also the superabsorbent hydrogels exhibited high sensitivity to pH, so that, several swelling changes of the hydrogel were observed in lieu of pH variations in a wide range (1 - 13). Furthermore, the reversible swelling-deswelling behavior in solutions with acidic and basic pH makes the hydrogels as a suitable candidate for controlled drug delivery systems. In addition, it is expected that the resulted superabsorbent polymers show more compatibility with body when they are used as drug delivery systems, because of polysaccharide/protein as a natural hybrid backbone.

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