Gamma Irradiation Mediated Synthesis of a New Superabsorbent Hydrogel Network Based on Poly(acrylic acid) Grafted onto Salep

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A novel and smart biopolymer-based hydrogel was synthesized by graft copolymerization of acrylic acid onto the salep backbones. The new superabsorbent hydrogel was synthesized *via* simultaneous crosslinking and graft copolymerization of acrylic acid (AA) monomer onto salep backbones using radiochemical methods. In radiochemical methods, γ-rays as initiator, energy source and crosslinker are applied. In our experiments, the effects of reaction variables such as relative contents of salep and AA, as well as γ-rays total dose were examined. According to water absorbency of the entitled network, the best synthesis condition is reported. FTIR spectroscopy, SEM photograph and TGA analysis were used for confirming the structure of the final product and a mechanism for superabsorbent hydrogel formation is also suggested. Furthermore, in this research, several factors affecting the swelling behavior of hydrogel including pH of medium, sensitivity to the salt solution and mixture of solvents were studied.

INTRODUCTION

Smart materials including hydrogels, with unique properties such as swelling/deswelling, are key materials in biological applications. Since the initial work of Wichterle for the synthesis of crosslinked HEMA (2-Hydroxyethyl methacrylate) hydrogels, and due to their hydrophilic and biocompatible characters, hydrogels have been of great interest to biomaterial scientists in recent years [1]. The dominant work of Lim and Sun demonstrated the successful submission of calcium alginate microcapsules for

encapsulation. After a while, Yannas involved natural polymers such as collagen and shark cartilage into hydrogels for use as artificial burn dressings [1]. Hydrogels based on both natural and synthetic polymers have continued to be of interest for fields of encapsulation of cells, tissue engineering, drug delivery systems, separation/purification, gene therapy, catalysis and sensors [1-4].

Free radical graft copolymerization of vinyl monomers onto polysaccharide back-bones followed by crosslinking of their chains is a familiar method for the synthesis of these smart biopolymer-based networks [5-7]. Crosslinking can be introduced by either chemical reactions that form covalent bonds between chains or by physical aggregation of units from

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two or more chains. To crosslink a polymeric system *via* chemical reactions, ionizing radiation such as electron beams (EB) or gamma rays (γ) can be used [8-9]. Simple procedure control, no need for initiators and or crosslinkers, no waste, and relatively low operating costs, make irradiation technique as a promising tool for the synthesis of hydrogels.

Salep is a powder which can be obtained from dried tubers of certain natural terrestrial orchids, and has been used for many years because of its nutritive and demulcent properties. In addition to giving the preferred aroma and flavor smell to the product, it could also be used as a thickening and stabilizing agent [10-11]. Salep is a composite of several compounds and can be referred to as a good source of glucomannan (16-60%) [10]. In addition to glucomannan (16-60%) as a main constituent of salep, it also contains starch (2.7%), nitrogenous substance (5%), moisture (12%) and ash (2.4%). Indeed, there are two kinds of salep growing in Iran. The first one has branched or palmate (PTS), while the other one has rounded or unbranched tubers (RTS). The PTS type of salep contains more glucomannans (58%) and hence was chosen for the present study [12]. Glucomannans (Fig. 1) are natural, neutral and water-soluble fibers, which can assist to normalize blood sugar, relieve stress on the pancreas and discourage blood sugar abnormalities such as hypoglycemia [13]. They also act as a preventative of chronic diseases [14] and as a weight control agent [15-16]. Expecting to find some more applications for salep, herein, gamma irradiation mediated synthesis of a novel poly-saccharide-based superabsorbent hydrogel *via* graft copolymerization of acrylic acid onto salep is reported.

EXPERIMENTAL

Materials

The palmate-tuber salep (PTS) was purchased from a supplier in Kordestan, Iran ($Mn = 1.17 \times 10^6$ g mol^{-1}, $Mw = 1.64 \times 10^6$ g mol^{-1} (high Mw), PDI = 1.39, eluent = water, flow rate = 1 ml min^{-1}, Acquisition interval = 0.43 s from GPC results). Acrylic acid (AA from Merck) as a monomer, was analytical grade and used without further purification. All other chemicals were also 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 using an ABB Bomem MB-100 FTIR spectrophotometer. Irradiation was carried out using gamma rays from ^{60}Co source, in a Gammacell-220 (Nordion, Canada) with a dose rate of 1.5 kGy h^{-1} at room temperature. The dose rate was determined by the conventional Fricke dosimeter. The morphology of the dry samples was examined using a scanning electron microscope, SEM, (Philips, XL30) operated at 25 kV after coating the sol free dried samples with gold film. The dynamic weight loss tests were conducted on a TA Instrument 2050 thermogravimetric analyzer (TGA). All tests were conducted in an N_2 purge (25 ml min^{-1}) using sample weights of 5-10 mg over a temperature range 25-750 °C at a scan rate of 20 °C min^{-1}. The mass of the sample pan was continuously recorded as a function of temperature.

Hydrogel Preparation *via* Gamma Irradiation

Hereafter, we shall use salep instead of its polysaccharide contents such as glucomannan. Certain amount of salep (1.0 g) and water (40 ml) were added to a 50 ml three-neck reactor equipped with a mechanical stirrer (200 rpm). The reactor was immersed in a thermostated water bath preset at 80 °C. After homogenizing the mixture, AA (0.013-0.040 mol (1.0-3.0 ml)) was added to the reaction mixture and stirred for another 20 min. The cold mixture was removed into a 250 ml aluminum
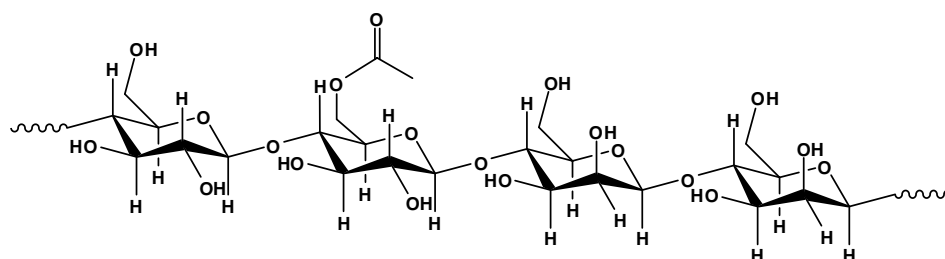

Fig. 1. A portion of the glucomannan repeating unit.

tube, where the inner wall was covered with aluminum foil. The tube was closed tightly with the foil and paraffin film and then irradiated under gamma-rays with the desired γ-rays total dose. To neutralize carboxylic acid groups of acrylic acid, an appropriate amount of NaOH (40% based on moles of acrylic acid monomer in 5 ml H_2O) was added and thoroughly mixed together. Finally, the product was poured into 100 ml of ethanol, left for 2 h and then chopped to small pieces for further drying. In order to remove the sol fraction of the mixture (uncrosslinked and not grafted PAA, uncrosslinked salep and possibly also some unreacted monomer), the dewatered hydrogel was allowed to totally swell (4 h) in distilled water and then dewatered in ethanol (200 ml, 2 h). The non-solvent ethanol was decanted and then 100 ml fresh ethanol was added on. The chopped particles were remained for 24 h in ethanol to completely dewater. The dewatered gel particles were filtered and dried in an oven (at 50 °C) for 24 h. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light.

Water Absorption (ES) Measurement

The degree of swelling was determined by gravimetric method. A tea bag (*i.e.* a 100 mesh nylon screen) containing an accurately dry powdered sample (0.5 ± 0.001 g) with average particle sizes between 40-60 mesh (250-350 μm) was immersed entirely in distilled water (200 ml) and allowed to soak for 3 h at the room temperature. The equilibrium swelling (ES) capacity was measured twice at the room temperature using the following formula:

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

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

Measurement of Absorption Under Load (AUL)

A macro-porous 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 dry hydrogel sample (weight 0.5 ± 0.01 g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A teflon cylindrical solid load (d = 60 mm, variable height) freely slipping in a glass cylinder (d = 60

mm, h = 50 mm) was placed on the dry hydrogel particles. A desired load (applied pressure 0.3 psi) was placed on the hydrogel sample. Then, 0.9% NaCl saline solution 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 a probable change in the saline concentration. After 3 h, the swollen particles were weighed again, and AUL (absorption under load) was calculated using Eq. (1).

Gel Content Determination

The weighed crude product particles (sol and gel) were dispersed for overnight in distilled water to swell completely at room temperature. The hydrogel was washed with distilled water frequently and then filtered, dewatered in excess ethanol for 48 h, and dried (50 °C, 24 h). The gel content was calculated as the remaining weight (%) of the initial crude product.

Swelling Kinetics

Hydrogel samples (40-60 mesh, 0.10 g) were poured into some of weighed tea bags and immersed in 100 ml distilled water. At consecutive time intervals, the water absorbency of the samples was measured according to Eq. (1).

Effect of Salt Solution on the Swelling

The procedures for these experiments were the same as those for "Water Absorption (ES) Measurement", except that NaCl solution instead of pure water was used. The swelling behavior of the hydrogel in various concentrations of NaCl was measured.

Swelling Variation with pH

The procedures for these experiments were the same as those for "Water Absorption (ES) Measurement". The pH dependence of hydrogel swelling was evaluated by considering certain amounts of the hydrogel samples (0.5 ± 0.001 g) in solutions (200 ml) with different pH. The various solutions were adjusted to the desired pH value by the addition of diluted HCl or NaOH.

Swelling Measurements in Mixture of Solvents

The procedures for these experiments were the same as those for "Water Absorption (ES) Measurement". The

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swelling behavior of hydrogels in various solutions of water/ethanol or water/acetone was measured.

RESULTS AND DISCUSSION

Synthesis and Mechanistic Aspect

Crosslinking and graft copolymerization of poly(acrylic acid) onto the backbone of salep was carried out in an aqueous medium using ionizing gamma radiation. A simple scheme for polymerization process of the entitled system is suggested in Scheme 1 (involving more important steps). First of all, it should be mentioned that during the irradiation of AA, salep and water ternary mixture, most of the energy is absorbed by water and only very small fraction by other components. Thus,

the initiation occurs mainly by an indirect effect. Hydroxyl radicals, formed during irradiation, add to one side of the acrylic acid double bond and lead to the formation of an unpaired spin on the other side of vinyl bond. In this way, homopolymerization of acrylic acid is initiated. Attack of OH radicals on salep would lead almost solely to the breakage of C-H bonds which is very well-known from radiation chemistry of alcohols and carbohydrates in aqueous solution. A more probable pathway is the addition of an acrylic acid molecule (not a radical) to the salep-based radical, followed by polymerization leading to the growth of a branched chain. These reactions should lead to the formation of poly(acrylic acid)-grafted-salep, but not necessarily to the formation of hydrogel. Thus, an alternative pathway would be the formation
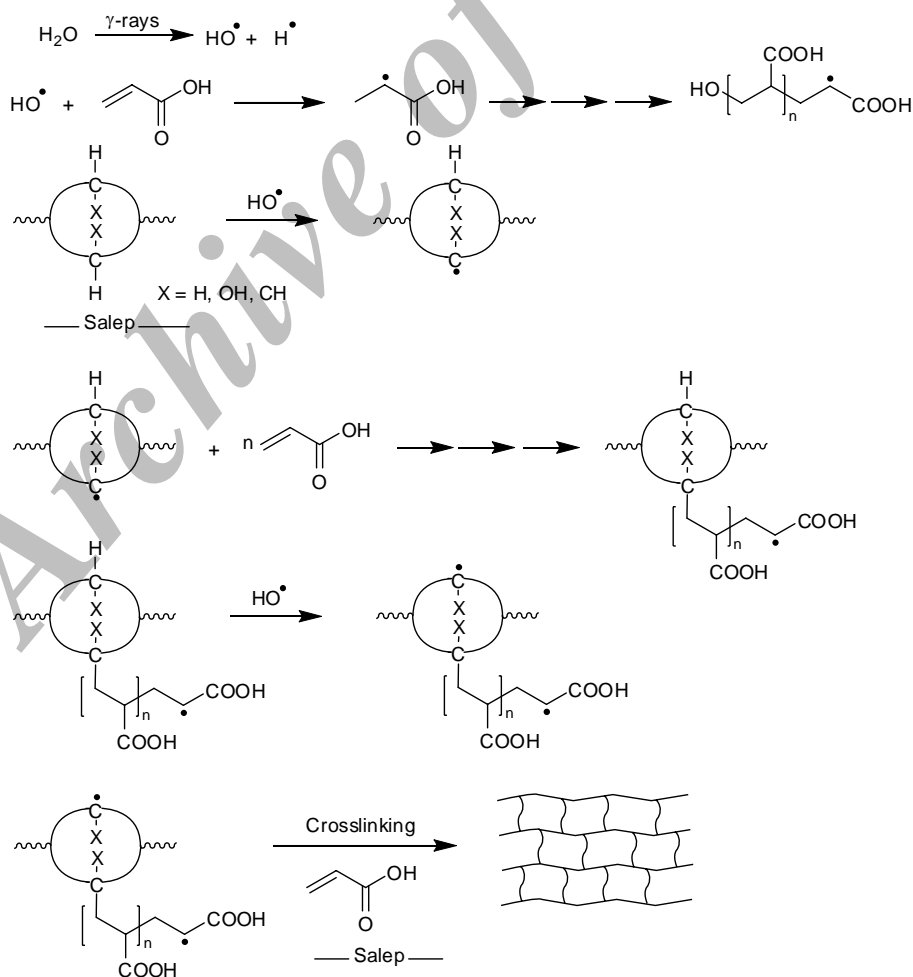
Scheme 1

of the network (gel) via crosslinking. Furthermore, another radiation-induced reaction in the studied system could include chain scission of the polysaccharide (probably the second most efficient process after the chain reaction of acrylic acid polymerization) as well as the formation and reactions of peroxy radicals.

Spectral Characterization

The grafting process was confirmed by comparing the FTIR spectra of the salep before and after copolymerization reaction while the sol fraction of hydrogels was removed. Figure 2 shows the FTIR spectra of poly(acrylic acid), salep and synthesized hydrogel *via* gamma irradiation. In Fig. 2b, the broad band at 3200-3500 cm^{-1} is due to the stretching of OH groups in the polysaccharide substrate. The other signal around 1630 cm^{-1} can be attributed to the stretching band of C=O group in glucomannan. The product, salep-*g*-PAA, involves a salep (glucomannan) backbone with side chains that carry carboxylic acid functional groups which are evidenced by a broad doublet peak around 1630 cm^{-1} due to stretching band of C=O groups (Fig. 2c). Although the stretching band of C=O function in the carboxylic acid groups overlapped with the C=O stretching band of the salep portion of the copolymer, the shape of the signal of C=O groups around 1630 cm^{-1} (in Fig. 2b) and its change to a very broad signal (in Fig. 2c), can be explained by the presence of a carboxylic acid function in

the biopolymer network.

Characterization by TGA

In order to further investigate the grafting of acrylic acid onto the salep backbone, the TGA data of the hydrogels (after removing sol fraction) obtained from the optimum condition of gamma irradiation was compared with the TGA curve of the salep. TGA curves are presented in Fig. 3. As it is shown in Fig. 3, the TGA curve for salep (Fig. 3a) is totally different from the hydrogel samples. This may be indicative of the fact that something has happened during the polymerization process. For the sample prepared in the optimum condition of gamma irradiation (Fig. 3b), the difference in degradation at higher temperatures is more obvious. This difference can be attributed to the release of CO_2 during TGA analysis. Likewise, the TGA curve of the entitled hydrogel sample is quite different from the poly(acrylic acid) which is synthesized according to the optimum condition. It was also noticed that degradation temperature for the synthesized hydrogel was sufficiently high for different applications.

Further observation about the grafting of AA onto the salep can be made by some very simple experiments. In spite of the salep being there, the desired hydrogel didn't dissolve in hot water (80 °C) after 12 h of stirring. Likewise, the physical mixture of AA and the salep did not absorb water in our experimental conditions.
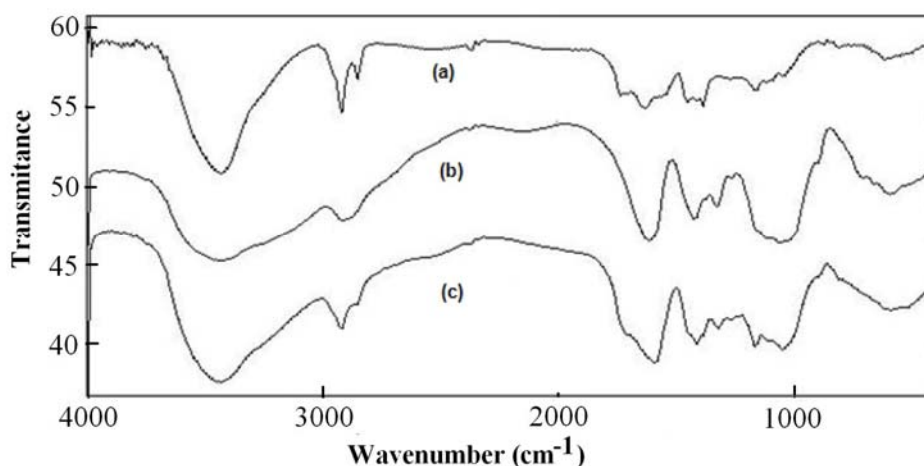

Fig. 2. FTIR spectra of (a) poly(acrylic acid), (b) salep and (c) salep-*g*-poly(acrylic acid) synthesized *via* gamma irradiation in optimum condition.
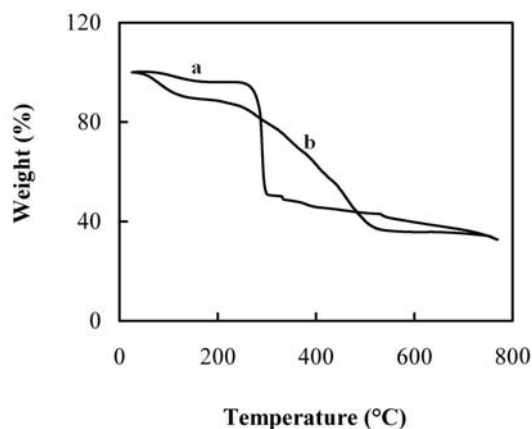
Fig. 3. TGA curves of (a) salep and (b) salep-*g*-poly(acrylic acid) synthesized under optimized gamma irradiation condition.
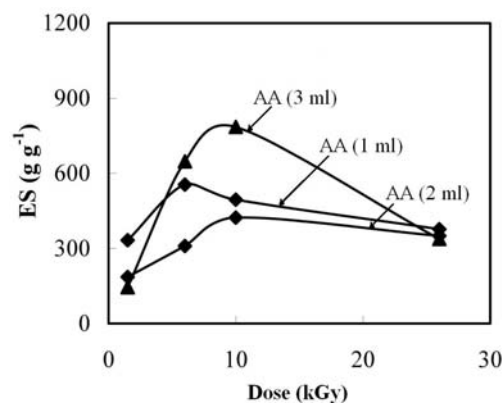

Fig. 4. Effect of total gamma dose and different ratio of salep/AA on the water absorption (ES) of hydrogels. The amount of salep (1 g) was kept the same in all of the samples.

Optimizing the Parameters Affecting Swelling Capacity

In order to optimize the water absorption of hydrogels synthesized by using gamma rays, two important factors, that is, monomer (AA) concentrations and γ-rays total dose were considered.

Effect of Monomer Concentration and γ-Rays Total Dose

The effect of monomer concentration on the swelling of the superabsorbents was investigated by varying the acrylic acid concentration. Three samples with different amounts of acrylic acid (1 ml, 2 ml and 3 ml (0.013-0.040 mol)) were prepared while the concentration of salep was kept constant (1 g). The different samples were irradiated under gamma rays. The water absorption (ES) of hydrogels as a function of γ-rays total dose is shown in Fig. 4. The ES of the hydrogels increased with increasing of the total dose of γ-rays up to around 10 kGy, and above that the absorption leveled off. The water absorption of samples was thoroughly dependent on the amount of acrylic acid and γ-rays total dose. As shown in Fig. 4, for the salep: acrylic acid ratio of 1:1 (w/v), the maximum water absorption was 555 g/g which was obtained at irradiation total dose of 6.0 kGy. According to these series of experiments, the highest water absorption (786 g/g) was achieved in total dose of 10.0 kGy with the ratio of the salep to acrylic acid 1:3 (w/v).

Effect of Neutralization Percentage

In this series of experiments, after the completion of the reaction in optimized condition (salep/AA: 1 g/3 ml, total gamma dose 10.0 kGy), the carboxylic acid groups of the grafted and nongrafted PAA 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 (Fig. 5). According to Fig. 5, the best neutralization percent was found to be 55%. In higher neutralization percent of the carboxylic acid groups, reduced swelling are observed due to different phenomena that is related to 'charge screening effect' of excess Na^+ ions in the swelling media [17]. The excess cations shield the carboxylate anions and prevent effective anion-anion repulsion (screening/ shielding effect). Similarly, with 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.

Additionally, the effect of salep on acrylic acid ratio as well as total gamma irradiation dose on the AUL were investigated. The AUL results are presented in Table 1. The highest AUL (0.3 psi) of these samples is 59 g/g which belongs to the sample with the highest water absorption in the absence of load. The special morphology of the optimized
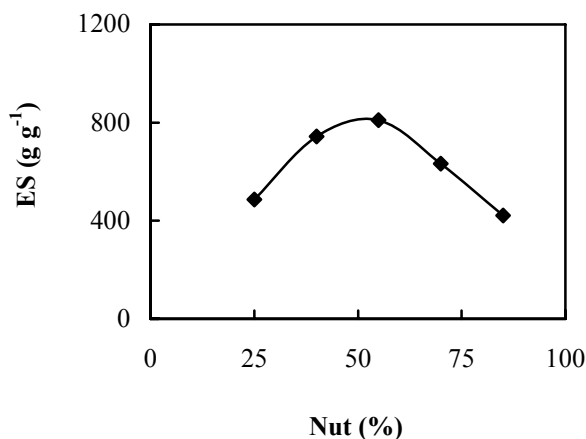
Fig. 5. Effect of neutralization percentage on swelling (reaction condition: salep/AA: 1 g/3 ml, total gamma dose 10.0 kGy).

Table 1. Effect of the Salep to AA Ratio and Total Gamma Irradiation Dose on the AUL (0.3 psi) in the Graft Copolymerization of Acrylic Acid onto Salep (Neutralization = 55%)

Salep/AA ratio [w/v]	Total gamma irradiation dose [kGy]			
	1.5	6.0	10.0	27.0
1:1	41	53	50	44
1:2	33	36	48	43
1:3	30	56	59	40

sample guaranteed both the highest AUL and normal water absorption.

Table 2 shows the variation of gel content of poly(acrylic acid) grafted-salep hydrogels with respect to the total dose and the amount of acrylic acid in the hydrogels. The gel fraction of the hydrogels increases with the increase of the dose up to around 27.0 kGy. These results indicate that hydrogels with high gel fraction of 95% could be produced even in the presence of salep and under gamma irradiation. The gel content of the optimized gamma irradiation sample was 60% which is good enough regarding its water absorption.

Surface Morphology of Hydrogels

The surface structure of the hydrogels was observed using

Table 2. Effect of the Salep to AA Ratio and Total Gamma Irradiation Dose on the Gel Content (%) in the Graft Copolymerization of Acrylic Acid onto Salep

Salep/AA ratio [w/v]	Total gamma irradiation dose [kGy]			
	1.5	6.0	10.0	27.0
1:1	36	42	50	55
1:2	40	48	55	80
1:3	44	52	60	95

scanning electron microscopy (SEM). The SEM photographs of the different samples are presented in Fig. 6. The SEM photograph of the optimized hydrogel sample prepared under gamma irradiation is compared with salep as starting material in this synthesis. In spite of salep-*g*-poly(acrylic acid) sample, the SEM photograph of salep doesn't show any porous structure. The sample prepared under optimized condition of gamma irradiation (maximum water absorption, 785 g/g) has extremely macroporous and cellular structure. The interesting point about these SEM photographs is the relationship between porosity and water absorbency of samples in distilled water.

Swelling Behavior

It is familiar to chemists that the swelling behavior of super-absorbents is significantly influenced by factors such as swelling media, size distribution of powder particles, specific size area, and composition of polymer. In the previous sections, the water absorption of different hydrogel samples synthesized under various conditions in distilled water was measured. In the remaining part of this report, the effects of some other parameters (such as salt solution, pH, and solvent) are studied. The sample which was obtained under optimized condition was chosen for further investigations.

Swelling Kinetic

Figure 7 represents the dynamic swelling behavior of the superabsorbent sample with certain particle size (40-60 mesh) in water. Initially, the rate of water uptake sharply increased
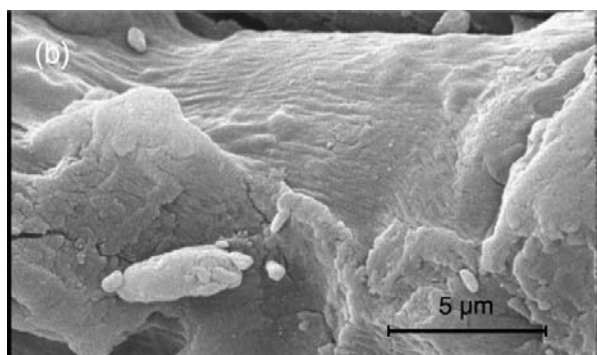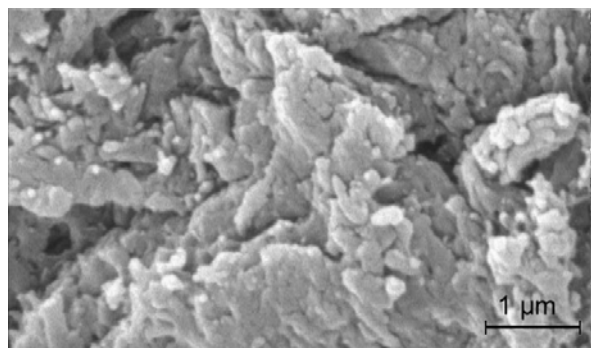
Fig. 6. SEM photograph of (a) salep-*g*-poly(acrylic acid) synthesized under optimized condition of gamma irradiation and (b) salep.
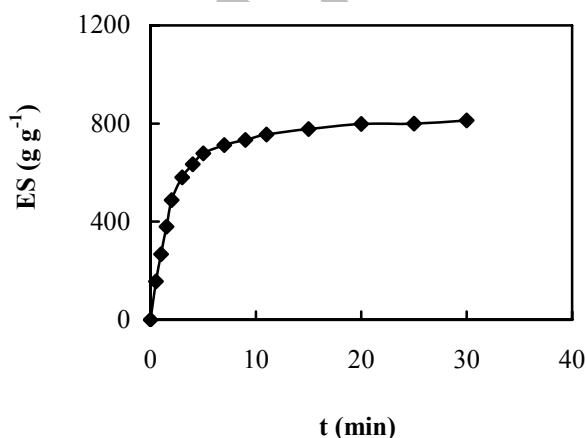

Fig. 7. Swelling kinetic as a function of time.

and then began to level off. The equilibrium swelling was almost achieved after 10 min. Power law behaviors are obvious from Fig. 7. The data may be well-fitted with a Voigt-based equation (Eq. (2)) [18].

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

In this equation, S_t is swelling at time t (g/g), S_e is equilibrium swelling (g/g), t is time (s) for swelling S_t, and τ stands for the ''rate parameter'' (s). The small τ value of the entitled hydrogel makes it suitable for different applications.

Effect of Salt Solution on the Swelling

In this part, the swelling capacity variation of entitled hydrogel in different concentrations of NaCl solution was investigated. Generally, the swelling capacity of ionic hydrogels in salt solutions is significantly decreased compared to the absorbency values in distilled water. This well-known phenomenon [19], is often attributed to a decreased osmotic pressure difference between the hydrogel network and the external solution. The ions attached to the polymer network are immobile and considered to be separated from the external solution by a semi-permeable membrane. When the hydrogels are placed in water, the maximum osmotic pressure is developed and hence the maximum swelling is achieved. When the polymer is in salt solution (for example, NaCl), the development of osmotic pressure is much lower because the external solution contains Na^+ and Cl^-. Therefore, the swelling is drastically reduced. In the case of salt solutions with multivalent cations, 'ionic crosslinking' at the surface of the particles is another reason for appreciable decrease in swelling capacity. There is a familiar relationship between the swelling and concentration of salt solution that is stated in the literature [8] as follows:

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

where k and n are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity. Figure 8 illustrates a power law relationship between swelling and saline concentration ($k \sim 45$, $n \sim 0.38$). It indicates that changing the NaCl concentration to higher than ~0.1 M has no
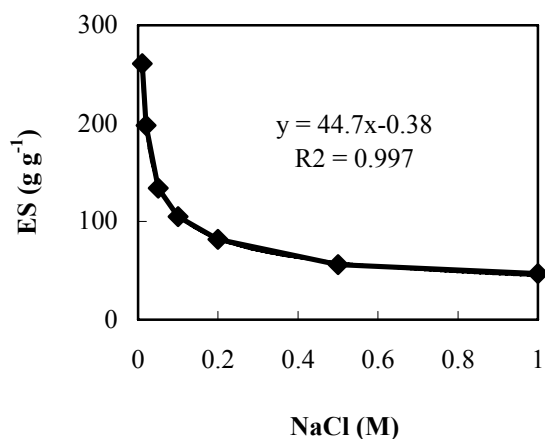
Fig. 8. Swelling capacity variation of salep-*g*-poly(AA) hydrogel in various concentrations of NaCl solution.
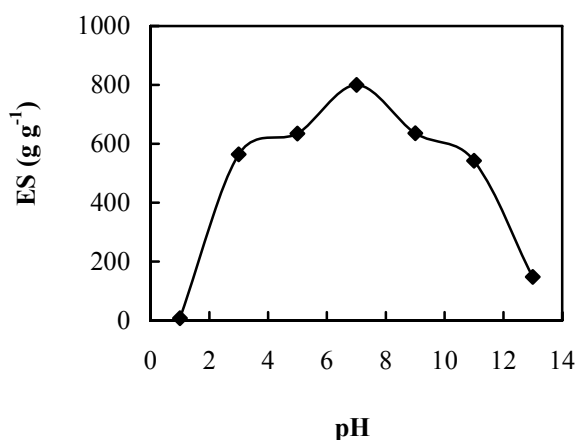

Fig. 9. Swelling dependency of salep-*g*-poly(acrylic acid) superabsorbent on pH.

appreciable influence on the water absorption of the superabsorbent.

pH Sensitivity and Pulsatile Behavior

To investigate the sensitivity of the hydrogel to pH, the equilibrium swelling (ultimate water absorption) of the hydrogel was studied at various pHs ranging from 1.0 to 13.0 (Fig. 9). No additional ions (through buffer solution) were added to the medium for setting pH, due to the effect of ionic strength on the absorption of a superabsorbent. Therefore,
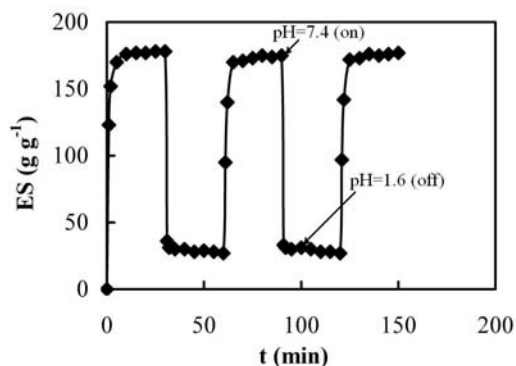

Fig. 10. The pH-responsiveness (on-off switching) behavior of salep-g-poly(acrylic acid) hydrogel in buffer solutions (pH 7.4 and 1.6).

stock NaOH (pH 13.0) and HCl (pH 2.0) solutions were diluted with distilled water to reach the desired basic and acidic pHs, respectively. The presence of carboxylic acid groups (COOH) in the hydrogel network makes them susceptible to pH changes in the medium. According to Fig. 9, the maximum water absorbency was observed in distilled water (at pH 7). Although the ionization may happen in basic condition, the ionic strength of the medium is responsible for the decrease in water absorption of the entitled network at different pHs. Also, it should be noted that the network in our optimized hydrogel sample (neutralization percent = 55%) was already ionized. Due to this neutralization percent, in this experiment the maximum water absorption was achieved around pH 7 (not higher pHs). Furthermore, due to the lesser change in ionic strength of the medium at pHs close to 7, the water absorption of our hydrogel decreases rather slowly relative to far-off pHs.

The entitled hydrogel further exhibited reproducible swelling-deswelling cycles as demonstrated in Fig. 10. The buffer solutions were used for the adjustment of different pHs. At pH 7.4, the hydrogel swelled up to 178 g/g due to anion-anion repulsive electrostatic forces, while at pH 1.6 it shrank within a few minutes due to the Hydrogen bond-type attractive forces. This sudden and sharp swelling-deswelling behavior at different pH values makes the system highly pH-responsive and suitable for tailoring pulsatile (on-off swelling) drug-delivery systems. It is well-known that smart materials are the ones that have one or more properties that could be

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significantly altered in a controlled fashion by external stimuli such as stress, temperature, moisture, pH, electric or magnetic fields. In brief, the hyrogel in question is taking shape in our mind as a truly smart material.

Swelling Behavior in the Mixtures of Water and Hydrophilic Solvents

The swelling behaviors of superabsorbent hydrogel in the mixtures of water and hydrophilic solvents, including ethanol and 2-propanol were investigated. In Fig. 11, the absorption of hydrogel dropped from 384 g/g to 3 g/g, when the 2-propanol concentration was increased from 10 to 80%. Likewise, the absorption of the entitled hydrogel in the mixture of water and ethanol reduced from 574 g/g to 4 g/g, when the ethanol concentration was increased from 10 to 80%. As one can see, the swelling behavior of our hydrogel in mixture of water and ethanol or 2-propanol is almost the same. By adding these solvents to water, the absorption decreased gradually to zero. According to the Hildebrand Eq. (4), this phenomenon can be attributed to the change of the solubility parameter of the solvent-water mixture [20-22].

$$\Delta H_m / (V\Phi_1\Phi_2) = (\delta_1 - \delta_2)^2 \qquad (4)$$

In Eq. (4), ΔH_m is the enthalpy change on 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. 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 swelling capacity of the synthesized hydrogel in water is maximum, the δ value of water (23.4 (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 Eq. (5):

$$\delta_{mix} = \delta_1\Phi_1 + \delta_2\Phi_2 \qquad (5)$$

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 these Eqs. (4 and 5), with increasing of δ_{mix} values toward 23.4, the hydrogel can be highly swollen as in pure water. In other
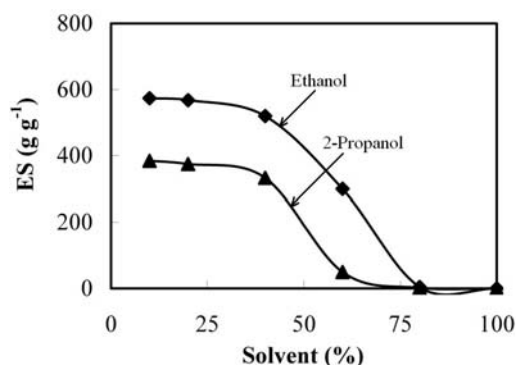

Fig. 11. Effect of the 2-propanol and ethanol percent on the water absorption of superabsorbent hydrogel.

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 water.

CONCLUSIONS

The synthesis and swelling characteristics of a new smart superabsorbent hydrogel based on natural salep grafted with poly(acrylic acid) is described. The entitled hydrogel was synthesized *via* both crosslinking and graft copolymerization of acrylic acid (AA) monomer onto salep backbones in a homogeneous aqueous solution. The initiation step was taken using γ-rays as an initiator, energy source and crosslinker, at the same time. In continue, the synthesis of superabsorbent hydrogel was optimized by varying the reaction parameters affecting the ultimate swelling capacity of the final product. Different parameters including the amount of AA and total dose of γ-rays were studied and the hydrogel with the highest water absorption was obtained. The maximum water absorption for the optimized sample was around 785 g/g. The study of the surface morphology of the optimized hydrogel using scanning electron microscopy (SEM) revealed a macroporous and cellular structure which was responsible for hydrogel water absorption. Furthermore, to show the smartness of our hydrogel, several factors affecting the swelling behavior of the superabsorbent including pH of medium, sensitivity to the salt solut ion and mixture of solvents were studied and a normal behavior was observed. The use of a cheap and local polysaccharide source (salep), γ-

rays as clean energy supplier, initiator and crosslinker instead of toxic reagents like APS and MBA, and shorter routes for the synthesis optimization are advantages of the current work.

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