# Synthesis and Swelling Behavior of a New Superabsorbent Hydrogel Network Based on Polyacrylamide Grafted onto Salep

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**ABSTRACT:** Synthesis and swelling behavior of a new superabsorbent hydrogel based on natural salep grafted with polyacrylamide is described. The new superabsorbent hydrogel biopolymer was synthesized via radical crosslinking and graft copolymerization of acrylamide monomer onto salep backbones. Regarding to the water absorption of hydrogel, the best synthesis condition is reported. FTIR spectroscopy and thermogravimetric analysis were used to confirm the structure of the final product and a mechanism

for superabsorbent hydrogel formation was also suggested. After preparing the desired hydrogels based on optimum condition, several factors affecting the swelling behavior of hydrogel including pH of medium, sensitivity to the salt solution, and mixture of solvents were studied. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 2625–2633, 2009

**Key words:** acrylamide; graft copolymers; salep; superabsorbent

#### **INTRODUCTION**

Hydrogel is a macromolecule network which can absorb pure water up to hundred or thousand times of its dried weight. The hydrophilicity, swelling in aqueous media, nonsoluble nature in aqueous fluids, and ionic aspect (which is responsible for charge repulsion in the network) are basic requirements of a good hydrogel. Because of their unique properties, polymeric hydrogels have a great potential of applications in various systems.<sup>1–8</sup> For example, since the hydrogel could absorb water in the rainy season and slowly releases it for plants in dry season, it would help them to survive under dry condition and increase the survival rate of afforestation.<sup>9,10</sup> Among commonly used types of hydrogels, natural-based superabsorbent ones have received a great deal of attention. Because of the presence of polysaccharides as the main part of the natural-based superabsorbent hydrogels, the biocompatibility, biodegradability, and nontoxicity of these polymers are assured. 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 biopolymer-based networks.11-13 This polymerization method has been used for the synthesis of various polysaccharide-based superabsorbent hydrogels. The synthesis of various hydrogels using different polysaccharides and vinyl monomers has been reported. In a series of our papers, the synthesis and characterization of cericinitiated acrylonitrile grafted onto chitosan and carboxymethylcellulose, graft copolymerization of mixtures of acrylic acid and acrylamide onto chitosan and persulfate-induced graft copolymerization of acrylamide, acrylic acid, and methacrylic acid onto  $\kappa$ carrageenan was described.<sup>14–18</sup> Herein, the synthesis of a novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylamide onto salep is reported.

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.<sup>19,20</sup> In addition, to giving the preferred aroma and flavor smell to product, it could be also used as a thickening and stabilizing agent.<sup>21</sup> For instance, it is utilized in medicines, drinks and ice-creams. Salep is a composite of several compounds and can be referred as a good source of glucomannan (16-60%).<sup>19</sup> 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 was chosen for this study.<sup>22</sup> Glucomannans are natural, neutral, and water-soluble fibers, which can assist to normalize blood sugar, relieve stress on the pancreas and discourage blood

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Figure 1 A portion of the glucomannan repeating unit.

sugar abnormalities, such as hypoglycemia.<sup>23</sup> They also act as a preventative of chronic disease<sup>24</sup> and a weight control agent.<sup>25,26</sup> As well they can be used in treatment of chronic constipation in adult patients.<sup>27</sup> Figure 1 shows a typical structure of glucomannan. The polysaccharide consists of glucose (G) and mannose (M) which joined by  $1\beta \rightarrow 4$  linkages. It is reported<sup>19</sup> that salep contains starch (2.7%), nitrogenous substance (5%), moisture (12%), and ash (2.4%).<sup>19</sup> Hoping to find more applications for salep, the synthesis of salep-based superabsorbent hydrogel could be very important for further studies.

#### EXPERIMENTAL

### Materials

The palmate-tuber salep (PTS) was purchased from a supplier in Kordestan, Iran ( $M_n = 1.17 \times 10^6$  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 s from GPC results). Methylenebisacrylamide (MBA, from Merck, Darmstadt, Germany) as a crosslinker, ammonium persulfate (APS, from Fluka, St. Louis, MO) as a water soluble initiator, and acrylamide (AAm from Merck) as a monomer, were analytical grades 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. 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 a N<sub>2</sub> purge (25 mL/min) using sample weights of 5–10 mg over a temperature range 25–750°C at a scan rate of 20°C/min. The mass of the sample pan was continuously recorded as a function of temperature.

# Hydrogel preparation

In the rest of this manuscript, we use salep instead of its polysaccharide contents such as glucommanan. Certain amounts of water (35 mL) and salep (1.0 g) were added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021), while stirring (200 rpm). The reactor was placed in a thermostated water bath preset at desired temperature (80°C) for 20 min. After homogenization, the AAm monomer (in 5 mL water) and the MBA crosslinker (in 5 mL water) were simultaneously added and the reaction mixture was stirred for further 15 min. Then the APS initiator (in 5 mL water) was added and a gel-like product was observed after around 20 min. Finally, the reaction mixture was cooled to room temperature. The product was poured into 100 mL of ethanol, remained for 2 h and then chopped to small pieces for further drying. To remove the sol fraction of mixture (uncrosslinked and not grafted PAAm, uncrosslinked salep and possibly also some unreacted monomer), the dewatered hydrogel was allowed to completely swell for overnight in plenty of distilled water (400 mL) and then dewatered in ethanol (200 mL, 2 h). The nonsolvent ethanol was decanted and then 100 mL fresh ethanol was added. The chopped particles were remained for 24 h in ethanol to completely dewater. The dewatered gel particles were filtered and dried in oven (at 50°C) for 24 h. After grinding, the powdered superabsorbent hydrogel was stored in the absence of moisture, heat, and light.

#### Water absorption 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  $\pm$  0.001 g) with average particle sizes between 40 and 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:

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

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

### Measurement of absorption under load

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 dry hydrogel sample (weight  $0.5 \pm 0.01$  g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A  $\sharp$ Teflon cylindrical solid load ( $d = 60 \text{ mm}_{2}$ variable height) freely slipping in a glass cylinder (d = 60 mm, h = 50 mm) was placed on the dry hydrogel particles. 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. Whole set was covered to prevent surface evaporation and probable change in the saline concentration. After 1 h, the swollen particles were weighed again, and absorption under load (AUL) 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 ( $50^{\circ}$ C, 24 h). The gel content was calculated as the remaining weight (%) of the initial crude product.

# Effect of salt solution on the swelling

The procedures for these experiments are same as those described in "Water absorption measurement" section, except that we used salt solution instead of pure water. Several salt solutions including NaCl, CaCl<sub>2</sub>, and AlCl<sub>3</sub> were used. The swelling behavior of hydrogel in various concentrations of NaCl was measured too.

# Swelling variation with pH

The procedures for these experiments are same as those described in "Water absorption measurement" section. The pH dependent of hydrogel swelling was evaluated by considering certain amounts of the hydrogel samples ( $0.5 \pm 0.001$  g) in solutions (200 mL) with different pH. The various solutions were adjusted to the desired pH value by addition of diluted HCl or NaOH.

## Swelling measurements in mixture of solvents

The procedures for these experiments are same as those described in "Water absorption measurement" section. The 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 polyacrylamide onto backbone of salep was carried out in an aqueous medium using APS and MBA (as a free radical initiator and crosslinking agent, respectively). A simple scheme for polymerization process of entitled system is suggested in Scheme 1. The sulfate anion-radical produced from thermal decomposition of APS, abstracts hydrogen from the salep backbone (from OH or CH) to form corresponding radicals. Then the resulting macroradical, initiates graft copolymerization of AAm. Since MBA crosslinking agent is present in the reaction mixture, a three-dimensional network results.

# 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 salep, polyacrylamide and synthesized hydrogel. In Figure 2(a), the broad band at 3400 cm<sup>-1</sup> is due to stretching of OH groups in the polysaccharide substrate. Another signal around 1628 cm<sup>-1</sup> can be attributed to the stretching band of C=O group in the glucomannan. As well, one can see the characteristic signals of polyacrylamide in Figure 2(b). The product, salep-g-PAAm, involves a salep (glucomannan) backbone with side chains carrying amide functional groups that are evidenced by a broad doublet peak around 1673 cm<sup>-1</sup> due to stretching band of C=O groups [Fig. 2(c)]. Although the stretching band of NH group in the amide function overlapped with the OH stretching band of the salep portion of the grafted copolymer, but the shape of the signal of OH groups around 3200-3400  $cm^{-1}$  [in Fig. 2(a)] and its change to a very broad doublet [in Fig. 2(c)], can be explained by the presence of an amide functional group in the hydrogel network.

# Characterization by TGA

To further investigate the grafting of acrylamide onto the salep backbone, the TGA data of the hydrogel (after removing sol fraction) obtained from optimum condition was compared with the TGA curve of salep. TGA curves are presented in Figure 3. As it is shown in Figure 3, the TGA curve for salep [Fig.



Scheme 1 Outline of the synthesis of Salep-g-PAAm superabsorbent hydrogel in thermal condition.

3(a)] is completely different than hydrogel sample. This difference in thermal behavior of our samples showed that the structure of hydrogel product is different from the salep.

Further observations about grafting of AAm onto salep can be obtained by very simple experiments. The desired hydrogel didn't dissolve in hot water or DMSO (80°C) after 12 h stirring. As well, the physical mixture of AAm and salep didn't absorb water in our experimental condition.

# Optimizing the parameters affecting swelling capacity

The relationship between the swelling ratio and network structure parameters is given by Flory<sup>28</sup> where



Figure 2 FTIR spectra of (a) salep, (b) polyacrylamide, and (c) salep-*g*-polyacrylamide synthesized in optimum condition.



**Figure 3** TGA curves of (a) salep and (b) salep-*g*-poly-acrylamide synthesized in optimum condition.

many variables can affect the ultimate swelling capacity. In this study, some of these variables like concentration of MBA, AAm, and APS were systematically optimized as follow.

#### Effect of crosslinker concentration

Figure 4 demonstrates the effect of MBA concentration on water uptake of the synthesized hydrogels. Different amount of MBA (0.02–0.08 g,  $1.3 \times 10^{-4}$  to  $5.2 \times 10^{-4}$  mol/L) was used where the maximum of swelling is achieved at  $1.3 \times 10^{-4}$  mol/L (0.02 g) of MBA. For smaller amount of MBA, a slimy gel is formed so that the strength of swollen gel is not sufficient as a real "superabsorbent hydrogel." According to the Figure 4, a reverse relation between swelling capacity and concentration of crosslinker was observed [eq. (2)].<sup>28</sup>

Swelling Capacity 
$$\approx K[MBA]^{-n}$$
 (2)

In eq. (2), *K* and *n* are constant values. A power law behavior of swelling versus [MBA], with K = 18.7 and n = 0.40, is obtained from the curve fitted with eq. (2). The *n* value represents the extent of the sensitivity of the hydrogel to the crosslinker content,



**Figure 4** Effect of crosslinker concentration on water absorption (abs or ES) in the presence and absence of load. Reaction conditions: salep 1 g, AAm 1.4 mol/L, APS  $5.5 \times 10^{-3}$  mol/L, 80°C, 20 min.

whereas the *K* value (constant for individual hydrogel) makes it possible to compare the extents of swelling for fixed crosslinker content.

It is well known that a higher crosslinker concentration increases the extent of crosslinking of the polymeric chains which decreases the free spaces between them and consequently decreases the swelling capacity of the hydrogel.<sup>28</sup> Similar behaviors have been reported in literature as well.<sup>29</sup>

When superabsorbents are under load, the swelling capacity will decrease. The AUL is often defined and reported especially in technical data sheets. Since AUL is logically changing with mechanical strength of the swollen gel proportionally, it can be considered as a scale for superabsorbent hydrogel strength. Therefore, many efforts have been made to achieve superabsorbents with higher AUL or higher strength of swollen gel.<sup>30,31</sup> As shown in Figure 4, AUL for all of the samples is almost the same (35 g/ g) which means that AUL is independent of MBA concentrations in this range. The applied pressure for AUL experiments was 0.3 psi.

# Effect of monomer concentration

The effect of monomer concentration on water absorption of the hydrogel was investigated by varying the acrylamide concentration from 1.4 to 3.5 mol/L (2–5 g) whereas the amount of MBA was kept in optimum value ( $1.3 \times 10^{-4}$  mol/L or 0.02 g of MBA) from previous experiment. As show in Figure 5, increasing the monomer concentration up to 2.1 mol/L (3 g), the free swelling capacity is increasing initially and then it is considerably decreased with further increase in monomer amount. The maximum absorption (150 g/g) is obtained for monomer concentration 2.1 mol/L. Although AUL is much lower (36 g/g) than the free absorption, but their



**Figure 5** Effect of AAm concentration on swelling capacity in the presence and absence of load. Reaction conditions: salep 1 g, MBA  $6.5 \times 10^{-3}$  mol/L, APS  $5.5 \times 10^{-3}$  mol/L, 80°C, 20 min.

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**Figure 6** Effect of APS concentration on the swelling capacity in the presence and absence of load. Reaction conditions: salep 1 g, MBA  $6.5 \times 10^{-3}$  mol/L, AAm 2.1 mol/L, 80°C, 20 min.

behavior is the same. The initial increase in water absorption can be explained by the fact that an increase in monomer concentration led to more grafting of acrylamide onto Salep. This led to better formation of polymer networks; consequently the water absorption is increased. The swelling decreases after the maximum can be attributed to (a) increase in viscosity of the medium which hinders the movement of free radicals and monomer molecules and (b) the enhanced chance of chain transfer to monomer molecules. These factors prevent efficient network formation, which in turn causes a decrease in water absorbency. Such behaviors have been reported by us and other investigators.<sup>17,18,32</sup>

# Effect of initiator concentration

In this series of experiments, the swelling capacity was investigated as a function of initiator concentration (0.03–0.12 g, 5.5  $\times$  10 $^{-3}$  to 2.2  $\times$  10 $^{-2}$  mol/L) (Fig. 6). Maximum swelling (314 g/g) has been obtained at  $1.65 \times 10^{-2}$  mol/L (0.09 g) of APS. The gel content of the optimized sample with highest water absorption in thermal condition was 71%. A large number of active free radical sites were produced on the salep backbones with increasing APS content, which led to a higher chance of acrylamide graft copolymerization reaction onto the substrates. The reduction of swelling was observed at 1.65  $\times$  $10^{-2}$  mol/L (0.09 g) APS which may be attributed to increase of terminating step reaction by bimolecular collision (self crosslinking). Also a decrease in molecular weight of grafted PAAm in the hydrogel may also decrease the swelling value. In addition, the free radical degradation of salep backbones by sulfate radical-anions may cause a reduction in swelling at higher APS concentrations.<sup>33</sup> The maximum water absorption for synthesized hydrogel in optimum condition (in distilled water, 314 g/g) is much higher than water absorption for other polyacrylamide-g-polysaccharide reported in the literature (thermal condition ~ 100 g/g).<sup>33</sup> This higher water absorption can be attributed to the presence of salep in the copolymer networks. The AUL results showed a constant trend in these concentrations of APS. It means that disparity of hydrogel networks strength is not enough to make a significant change in AUL measurements.

### Surface morphology of hydrogels

The surface structure of the hydrogels was observed using SEM. The SEM photographs of different samples are presented in Figure 7. The SEM photograph of the optimized hydrogel sample is compared with salep as starting material in this synthesis. In spite of salep-g-poly(acrylamide) sample, the SEM photograph of salep doesn't show any porous structure. SEM photographs are also indicated the relation between porosity and water absorption of our samples in distilled water. For the salep-g-poly (acrylamide) sample prepared under optimum condition, the porosity is high and gives a macroporous structure in size. The water absorption of this sample can be attributed to its morphology. Because



**Figure 7** SEM photograph of (a) the salep-*g*-polyacrylamide synthesized under optimized condition and (b) salep.

TABLE I The Relation Between δ and Swelling Capacity of Hydrogel in Different Media

Solvent	$\delta$ (or $\delta_{mix}$ )	Abs (g/g)
Water	23.4	314
Ethanol	12.7	_
Acetone	9.9	_
Ethanol/water (30 : 70)	20.2	222
Acetone/water (30 : 70)	19.3	186

of the formation of polymer networks during the polymerization reaction (and in the presence of MBA as a crosslinker), a porous structure is predictable.

### Swelling behavior

It is recognized that the swelling behavior of superabsorbents is significantly influenced by factors such as swelling media, size distribution of powder particles, specific size area, and composition of polymer (Table I). In previous sections, the water absorption of entitled hydrogel sample in distilled water was measured. In the remaining of this report, the effect of some other parameters (such as salt solution, pH, and solvent) will be studied.

## Effect of salt solution on the swelling

In continue, the effect of various salt solutions on the swelling behavior of hydrogels was investigated. Generally, the swelling capacity of ionic hydrogels in salt solutions was significantly decreased comparing to the absorption values in distilled water. This phenomenon for charged hydrogels can be explained on the basis of osmotic pressure developed due to unequal distribution of ions in the medium and the polymer network. The ions attached to the polymer network are immobile and considered to be separated from the external solution by a semipermeable 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 (e.g., NaCl), the development of osmotic pressure is much lower because the external solution contains Na<sup>+</sup> and Cl<sup>-</sup>. Therefore the swelling is drastically reduced. There is a well-known relationship between swelling and concentration of salt solution that is stated as following equation in the literature<sup>28</sup>:

$$Swelling = k[salt]^{-n}$$
(3)

where k and n are constants 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.

In the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of the particles is another factor for appreciable decrease in swelling capacity. According to Figure 8, decrement in swelling amounts is strongly dependent on the type and concentration of salt added to the swelling medium. For example, the water absorption of hydrogel is very susceptible to the presence of NaCl in the solution [Fig. 8(a)]. In Figure 8(b), at constant concentrations of salt solutions, the absorption is decreased as the charge of the metal cations increases from Na<sup>+</sup> to  $Ca^{2+}$  and  $Al^{3+}$ . With increasing the cation charge, the ionic strength of the medium and the degree of crosslinking is increased whereas the swelling capacity consequently decreased. The role of AlCl<sub>3</sub> salt in decreasing the pH of solution is an additional reason for lower water uptake of entitled hydrogel.



**Figure 8** The swelling capacity variation of salep-*g*-poly (AAm) hydrogel (synthesized according to optimum condition) (a) in various concentration of NaCl solutions, (b) in 1*M* solutions of NaCl, CaCl<sub>2</sub> and AlCl<sub>3</sub>. The optimum condition is as follows: Optimum condition: Salep 1 g, MBA  $6.5 \times 10^{-3}$  mol/L, AAm 2.1 mol/L, APS  $1.65 \times 10^{-2}$  mol/L, 80°C, 20 min.

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# Swelling variation with pH

To investigate the sensitivity of the hydrogel to pH, the ES (ultimate absorption) of the hydrogel was studied at various pH ranged from 1.0 to 13.0 (Fig. 9). No additional ions (through buffer solution) were added to medium for setting pH, due to the effect of ionic strength on the absorption of a superabsorbent. Therefore, stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pH, respectively. According to Figure 9, the maximum water absorbency is observed in distilled water (at pH 7). As we know, the amide function (CONH<sub>2</sub>) is not enough reactive to absorb a proton  $(CONH_3^+)$  or deprotonate (CONH<sup>-</sup>) in our reaction condition and generate an ionic network. Although it may be happen in very acidic or basic pH, but the ionic strength of medium makes a decrease in water absorption of entitled network. Furthermore, due to the moderate change of ionic strength of the medium at the pH close to 7, the water absorbency of our hydrogel decreases more slowly relative to higher pH.

# Swelling behavior of superabsorbent hydrogel 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 acetone were investigated. In Figure 10, the absorption of hydrogel dropped from 314 to 7, when the ethanol concentration was increased from 0 to 75%. As well the absorption of



**Figure 9** Swelling dependency of salep-*g*-polyacrylamide superabsorbent (synthesized according to optimum condition) on pH.



**Figure 10** Effect of the ethanol or acetone concentration on the water absorption of superabsorbent hydrogel (synthesized according to optimum condition).

entitled hydrogel in the mixture of water and acetone reduced from 314 to 2, when the acetone concentration was increased from 0 to 75%. As one can see, the swelling behavior of our hydrogel in mixture of water and acetone or ethanol 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.<sup>34,35</sup>

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

In eq. (4),  $\Delta H_m$  is the enthalpy change on mixing of a polymer and a solvent,  $\Phi_1$  and  $\Phi_2$  are the volume fractions for the solvent and the polymer, V is the whole volume of the solution, and  $\delta_1$  and  $\delta_2$  are the solubility parameters for the solvent and the polymer, respectively. This equation clearly indicates that to dissolve a polymer in a solvent, the  $\delta$  values must be close to each other. As a consequence, to predict the solubility of a polymer,  $\delta$  values should be calculated. As swelling capacity of the synthesized hydrogel in water is maximum, the  $\delta$  value of water [23.4 (cal/cm<sup>3</sup>)<sup>1/2</sup>] can be regarded as the solubility parameter of it. The solubility parameter for solvent-water mixtures ( $\delta_{mix}$ ) can be calculated using eq. (5):

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

where  $\Phi_1$  and  $\Phi_2$  are the volume fraction, and  $\delta_1$ and  $\delta_2$  are the solubility parameters of the two solvents. According to these eqs. (4) and (5), with increasing of  $\delta_{mix}$  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  $\delta_{mix}$  is close to water.

# CONCLUSIONS

The synthesis and swelling characteristics of a new superabsorbent hydrogel based on polyacrylamide grafted onto natural salep is described. To our knowledge, we are the first group who use the salep in the synthesis of superabsorbent hydrogels. The entitled hydrogel was synthesized via both crosslinking and graft copolymerization of AAm monomer onto salep backbones in a homogeneous aqueous solution. The initiation step can be performed by using APS as a water soluble initiator and MBA was used as a suitable crosslinking agent. Different parameters including MBA, APS, and AAm were studied and the hydrogel with highest water absorption was obtained. The maximum water absorption for the sample in optimized condition was around 314 g/g which is an unusual swelling capacity in comparison with other polysaccharide-gpolyacrylamide superabsorbent hydrogels. Studying the surface morphology of hydrogels using SEM showed a macroporous structure. Furthermore several factors affecting the swelling behavior of hydrogel including pH of medium, sensitivity to the salt solution and mixture of solvents were studied and a normal behavior was observed.

#### References

- Buchholz, F. L.; Peppas, N. A. In Superabsorbent Polymer: Science and Technology, ACS Symposium Series 573; American Chemical Society: Washington DC, 1994.
- 2. Park, T. G. Biomaterials 1999, 20, 517.
- 3. Park, K.; Qiu, Y. Adv Drug Deliv Rev 2001, 53, 321.
- 4. Holtz, J. H.; Asher, S. A. Nature 1997, 389, 829.
- 5. Adhikari, B.; Majumdar, S. Prog Polym Sci 2004, 29, 699.

- 6. Tanaka, H.; Kambayashi, T.; Sugiyama, Y.; Nagai, T.; Nagata, K.; Kubota, K.; Hirano, K. Eur. Pat. 501,482 (1992).
- 7. Walker, C. O. U.S. Pat. 4,816 (1987).
- 8. Athawale, V. D.; Lele, V. Starch/Staerke 2001, 53, 7.
- 9. Zhou, W. J.; Yao, K. J.; Kurth, M. J. J Appl Polym Sci 1996, 62, 911.
- 10. Yao, K. J.; Zhou, W. J. J Appl Polym Sci 1994, 53, 1533.
- 11. Yazdani-Pedram, M.; Retuert, J.; Quijada, R. Macromol Chem Phys 2000, 201, 923.
- 12. Sugahara, Y.; Takahisa, O. J Appl Polym Sci 2001, 82, 1437.
- Patel, G. M.; Patel, C. P.; Trivedi, H. C. Eur Polym J 1999, 35, 201.
- Pourjavadi, A.; Mahdavinia, G. R.; Zohouriaan-Mehr, M. J. J Appl Polym Sci 2003, 90, 3115.
- Pourjavadi, A.; Zohuriaan-Mehr, M. J.; Ghasempoori, S. N.; Hossienzadeh, H. J Appl Polym Sci 2007, 103, 877.
- Mahdavinia, G. R.; Pourjavadi, A.; Hosseinzadeh, H.; Zohouriaan-Mehr, M. J. Eur Polym J 2004, 40, 1399.
- 17. Pourjavadi, A.; Harzandi, A. M.; Hosseinzadeh, H. Eur Polym J 2004, 40, 1363.
- Bardajee, G. R.; Pourjavadi, A.; Sheikh, N.; Amini-Fazl, M. S. Radiat Phys Chem 2008, 77, 131.
- 19. Kaya, S.; Tekin, A. R. J Food Eng 2001, 47, 59.
- 20. Ktistis, G.; Georgakopoulos, P. P. Pharmazie 1991, 46, 55.
- 21. Kayacier, A.; Dogan, M. J Food Eng 2006, 77, 261.
- 22. Farhoosh, R.; Riazi, A. Food Hydrocolloids 2006, 20, 660.
- Hozumi, T.; Yoshida, M.; Ishida, Y.; Mimoto, H.; Sawa, J.; Doi, K.; Kazumi, T. Endocrine J 1995, 42, 187.
- 24. Vuksan, V.; Jenkins, D. J.; Spadafora, P.; Sievenpiper, J. L.; Owen, R.; Vidgen, E. Diabetes Care 1999, 22, 913.
- Reffo, G. C.; Ghirardi, P. E.; Forattani, C. Curr Ther Res 1990, 47, 753.
- 26. Walsh, D. E.; Yaghoubian, V.; Behforooz, A. Int J Obes 1984, 8, 289.
- Marzio, L.; Bianco, R. D.; Donne, M.; Pieramico, O.; Cuccurullo, F. Am J Gastroenterol 1989, 84, 888.
- Flory, P. J. In Principles of Polymer Chemistry; Cornell University Press: New York, 1953.
- 29. Chen, J.; Zhao, Y. J Appl Polym Sci 2000, 75, 808.
- Riccardo, P. J Macromol Sci-Rev Macromol Chem Phys 1994, 34, 607.
- Kabiri, K.; Zohuriaan-Mehr, M. J. Polym Adv Technol 2003, 14, 438.
- 32. Athawale, V. D.; Lele, V. Carbohydr Polym 1998, 35, 21.
- Pourjavadi, A.; Ghasemzadeh, H.; Hosseinzadehe, H. e-Polymers 2004, 27.
- 34. Chen, J.; Shen, J. J Appl Polym Sci 2000, 75, 1331.
- 35. Li, A.; Wang, A.; Chen, J. J Appl Polym Sci 2004, 94, 1869.