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Synthesis and swelling behavior of acrylatedstarch-g-poly (acrylic acid) and acrylatedstarch-g-poly (acrylamide) hydrogels

A. Pourjavadi [a,*], P. Eftekhar Jahromi [a], F. Seidi [a], H. Salimi [b]

[a] *Polymer Research Laboratory, Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran*
[b] *Iran Polymer and Petrochemical Institute, Tehran, Iran*

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ABSTRACT

In the present work, synthesis and swellability of acrylatedstarch-based hydrogels was investigated. Acrylic groups were introduced onto starch backbone by a homogeneous synthesis to produce starch monomers with three different degree of substitution (DS). The radical copolymerization of acrylatedstarch (AST) with acrylic acid (AA) and acrylamide (AAm) was carried out in aqueous solution using ammonium persulfate (APS) as an initiator. Infrared spectroscopy (FT-IR) and TGA thermal analysis were carried out to confirm the chemical structure of the hydrogel. Moreover, morphology of the samples was examined by scanning electron microscopy (SEM). Their equilibrium swelling degree was evaluated in various conditions. The absorbency under load (AUL) of the hydrogel was also determined by using an AUL tester at various applied pressures. Finally, dynamic swelling kinetics of the hydrogel was studied.

1. Introduction

Covalent (or chemical) polymer networks are three-dimensional polymers in which the polymer chains are interconnected by chemical crosslinks (Flory, 1953; Yoshihito & Khokhlov, 2005). These networks are composed of homopolymers or copolymers and are insoluble in all solvents, but, depending on their compatibility with the solvent, they can absorb and hold a considerable volume of liquids. The most common hydrogels are polyelectrolyte gels: their high degree of swelling in water is due to the exerting osmotic pressure of counterions. Such gels can acquire up to several hundredweight parts of water per one part of a dry polymer. However, some neutral gels—e.g., based on polyacrylamide or poly(ethylene oxide)—also have high affinity to water, but their degree of swelling is always much lower than that of charged gels (Bajpai & Giri, 2003; Branca et al., 2006).

Hydrogels are used extensively as superabsorbents. For this application high swelling capacity is the most important property. However, there are a number of other areas of use for hydrogels as functional materials (e.g., carriers for controlled drug release (Peppas, Bures, Leobandung, & Ichikawa, 2000), artificial muscles (Lee & Mooney, 2001), membranes with regulated permeability (Dole, Joly, Espuche, Alric, & Gontard, 2004), and sensor devices (Yew, Ng, Li, & Lam, 2007)). For these purposes, high cooperativity of response to the change in external conditions and developed internal microstructure of the gels is required. Therefore, in addition to high swelling capacity, it is necessary to have a counteracting tendency, which favors the gel contraction.

Another important property of hydrogels is their response to external stimuli such as temperature, pH, presence of solutes, electric and magnetic fields, resulting in the absorption or release of water and solutes (Peppas et al., 2000; El-Naggar, Abd Alla, & Said 2006). Usually, these hydrogels are prepared by free-radical copolymerization of the acidic or basic monomers and a chemical crosslinker such as *N*,*N*′-methylenebis(acrylamide) (Omidian, Rocca, & Park 2005).

Because of the wide range of unique combinations of polymer backbone and crosslinking agent, properties such as hydrogel swelling/degradation, mechanical strength and swelling kinetics are interrelated in a complex and dynamic fashion. However, these characteristics could potentially be tailored to meet a specific biomedical application by modulating hydrogel compositions.

Biodegradable polymers are the youngest members of the materials family with increasing applications in pharmaceutical, medical and biomedical engineering (Bernkop-Schnurch & Kast, 2001; Jayakumar, New, Tokura, & Tamura, 2007; Vandamme, Lenourry, Charrueau, & Chanumeil, 2002). Starch is the main reserve polysaccharide of higher plants where it occurs as water insoluble granules. Starch is readily isolated from plant crops, and major commercial sources include maize, wheat, potato, and rice. The isolated starch finds a very wide range of commercial application, including use in the food, pharmaceutical, paper and packaging industries (Dumitriu, 2005).

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* Corresponding author.
E-mail addresses: purjavad@sharif.edu, kachal.vay@gmail.com (A. Pourjavadi).

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The present study reports on (i) the synthesis and characterization of acrylated starch (AST) with three different DS; (ii) the synthesis and characterization of AST-based hydrogels, carried out by radical graft copolymerization of AST with acrylic acid (AA) and acrylamide (AAm); (iii) investigation of swelling properties of the hydrogels in various conditions. As a matter of fact, according to the literature survey based on Chemical Abstract Service, there are some reports on synthesis of acrylate substituted starches itself without any crosslinking. Moreover, there are some reports on preparation of novel acrylate substituted starch-based hydrogels with different crosslinking systems. In the present study, we synthesize novel hydrogels with new type of crosslinking, and investigate their swelling behaviors in various media. According to the basic knowledge of SAP hydrogels (Buchholz & Graham, 1998), "small amounts of crosslinkers play a major role in modifying the properties of SAPs". Recently, some research groups have taken into consideration to study of the chemical nature of crosslinker (Kabiri, Mirzadeh, & Zohuriaan-Mehr, 2008; Metz & Theato, 2009; Ramazani-Harandi, Zohuriaan-Mehr, Yousefi, Ershad-Langroudi, & Kabiri, 2009) and showed that it has a great influence on key parameters such as absorbency under load (Ramazani-Harandi et al., 2009), and also temperature and time of the hydrogel drying (Kabiri et al., 2008).

In conclusion, crosslinker type and concentration has a great influence on the physical properties of SAPs. Therefore, new types of crosslinkage should be investigated systematically to achieve hydrogels with improved properties. This new practical research represents deeper physicochemical studies on the structure–property relation in SAP hydrogels.

2. Experimental

2.1. Materials

Acrylic acid (AA, from Merck) as ionic monomer distilled before use. Starch (ST) was obtained from Merck Chemical. Ammonium persulfate (APS, from Merck) as a water soluble initiator, acrylamide (AAm, from Merk), acryloyl chloride (from Merk) were of analytical grade and used without further purification. The solvents (all from Merck) were used as received. All other chemicals were also analytical grades. Double distilled water was used for the hydrogel preparation and swelling measurements.

2.2. Instrumental analysis

^{1}H-NMR spectra were obtained using a Bruker DPX 500 MHz spectrometer with D_2O as solvents. The extent of the esterification was determined from the ^{1}H-NMR.

Thermogravimetric analyses (TGA) of synthesized hydrogels were performed using Polymer Laboratories systems at a heating rate of 20 °C/min under nitrogen atmosphere.

FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer. Morphology of the dried gel structures was studied by scanning electron microscopy (SEM). Dried superabsorbent powder was coated with a thin layer of gold and was imaged in a SEM instrument (Philips, XL30).

2.3. Acryloyloxystarch (AST) Synthesis

Twenty grams of dried starch was dissolved in 75 mL dimethyl sulfoxide (DMSO) in 100 °C. After cooling to room temperature 20 mL *N*,*N*-dimethylformamide (DMF) and an appropriate amount (1–2.6 mL) of pyridine were added. Then the reaction medium cooled to 0 °C and a suitable amount (1–2.6 mL) of ACOCl diluted in 5 mL DMF was added dropwise to the reaction medium under stirring. After addition was completed, the derivatization reaction developed 2 h in 0 °C and 3 h in room temperature. The product was precipitated and washed thoroughly by acetone, and then dried in air at r.t. The DS was determined by the ^{1}H–NMR spectroscopy.

2.4. Hydrogels synthesis

(a) With acrylic acid (AA):

A 200-mL, three-necked, round-bottomed flask, equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 200 rpm) is charged with 40 mL of water and 1.4 g of AST and the mixture is stirred for 10 min at r.t. until a clear solution is obtained. The reactor was immersed in a thermostated water bath preset at 75 °C. Then, 40% neutralized acrylic acid (AA, 5.0 g) dissolved in 10 mL H_2O was added. After 5 min, ammonium persulfate (APS, 0.07 g) in 5 mL H_2O was added. After 10–15 min obtained gel was cooled at room temperature and poured to excess non-solvent acetone (200 mL) and remained for 3 h to dewater. Then, acetone was decanted and the product was cut into small pieces (diameter ~5 mm). Again, 200 mL fresh acetone was added and the hydrogel remained for 48 h. Finally, the filtered gel was dried in oven at room temperature for 48 h. After grinding, the powdered hydrogel was stored away from moisture, heat and light.

(b) With acrylamide (AAm):

It is similar to the method mentioned above; just the amount of AST is 1 g, the amount of AAm is 3 g and APS is 0.05 g.

2.5. Measurement of monomer conversion

To determine monomer conversion values, a weighed, dried, and powdered sample was washed with non-solvent methanol several times. After filtration, the sample was dried, and reweighed. Monomer conversion was calculated by following equations:

(a) AAm-based hydrogel: monomer conversion % = $\left(\frac{m_f - 1}{3}\right) \times 100$,

(b) AA-based hydrogel: monomer conversion % = $\left(\frac{m_f - 1.4}{5.6}\right) \times 100$,

where m_f stands for final weight of sample after several washing. 1 and 1.4 values are related to weights of AST were used. 3 and 5.6 values are related to amounts of acryl amide and total weights of acrylic acid and sodium acrylate, respectively.

The results are as follows:

Sample	Monomer conversion %
AST-g-poly (AA) (DS = 0.08)	82
AST-g-poly (AA) (DS = 0.15)	80
AST-g-poly (AA) (DS = 0.24)	79
AST-g-poly (AAm) (DS = 0.08)	94.66
AST-g-poly (AAm) (DS = 0.15)	95.3
AST-g-poly (AAm) (DS = 0.24)	93

2.6. Swelling measurements

The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.1 ± 0.001 g) was immersed entirely in 200 ml distilled water or 0.15 M of NaCl solution and allowed to soak for 1 h at room temperature. The sample particle sizes were 40–60 meshes (250–400 μm). The tea bag was hung up for 15 min in order to remove the excess water. The equilibrium swelling (ES) was calculated according to following equation:

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

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

2.7. Absorbency at various values of pH

Individual solutions with acidic and basic values of pH were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions to achieve pH $\geqslant$ 6.0 and pH $\leqslant$ 6.0, respectively. Then, 0.1 (±0.001) g of the dried hydrogel was used for the swelling measurements according to Eq. (1).

2.8. Absorbency under load (AUL)

AUL was measured as reported earlier (Ramazani-Harandi, Zohuriaan-Mehr, Yousefi, Ershad-Langroudi, & Kabiri, 2006). A macroporous sintered glass filter plate (porosity 0, $d = 80$ mm, $h = 7$ mm) was placed in a Petri dish ($d = 118$ mm, $h = 12$ mm), and weighed, dried hydrogel (0.5 ± 0.01 g) was uniformly placed on the surface of a polyester gauze located on the sintered glass. A cylindrical solid weight (Teflon, $d = 60$ mm, variable height) which could slip freely in a glass cylinder ($d = 60$ mm, $h = 50$ mm) was used to apply the desired load (applied pressure 0.3 or 0.6 psi) to the dry hydrogel sample particles. Then 0.9% saline solution was added so that the liquid level was equal to the height of the sintered glass filter. The entire setup was covered to prevent surface evaporation and probable change in the saline concentration. After certain time intervals, the swollen particles were weighed again, and AUL was calculated according to Eq. (1).

2.9. Swelling kinetics

For studying the rate of absorbency of the composite, certain amount of sample (0.1 ± 0.001 g) with average particle sizes between 40 and 60 mesh (250–400 μm) was poured into a weighed tea bag and immersed in 400 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogel was measured according to the earlier mentioned method.

3. Results and discussions

3.1. Spectral characterization of acrylated starch

The FTIR spectra of the ST and AST are shown in Fig. 1. As can be seen, in the spectrum of AST as compared to the ST, the additional absorption bands appear at 1730 cm^{-1} and at 1635 cm^{-1} which can be ascribed to the bounds >C=O and to >C=C<, respectively. In addition, there is also a distinct absorption band within 3700–3140 cm^{-1} corresponding to the hydroxyl group.

The ^{1}H-NMR (D_2O, ppm) spectra of ST and AST are shown in Fig. 2. The spectrum of AST shows resonance signals at δ 7.6–8.8 ppm (3H) corresponding to the protons of –CO–CH=CH_2, δ 3.5–3.9 ppm (6H) corresponding to the protons of C6, C6′, C5, C4, C3, C2 and δ 5.3 (1H) corresponding to the proton of C1 in pyranose ring. The DS was calculated from the integral ratio of δ 7.6–8.8 and δ 5.3 ppm (it can also be calculated from the integral ratio of δ 7.6–8.8 and δ 3.5–3.9 ppm).

$$DS = \frac{(\text{Integral of the protons of } \text{—CO—CH=CH}_2)/3}{\text{Integral of the protons of C1}} \tag{2}$$

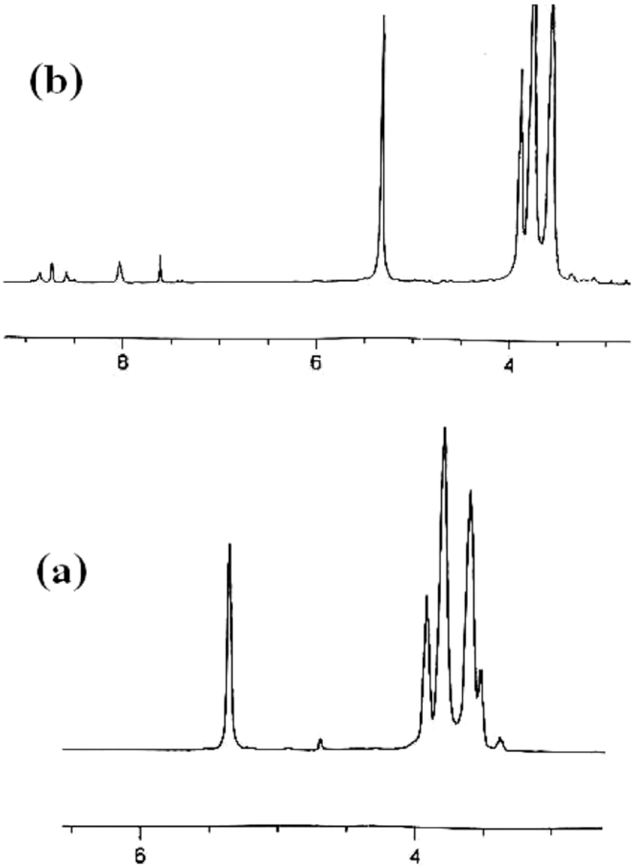


Fig. 2. ^{1}H-NMR spectra of (a) ST and (b) AST.

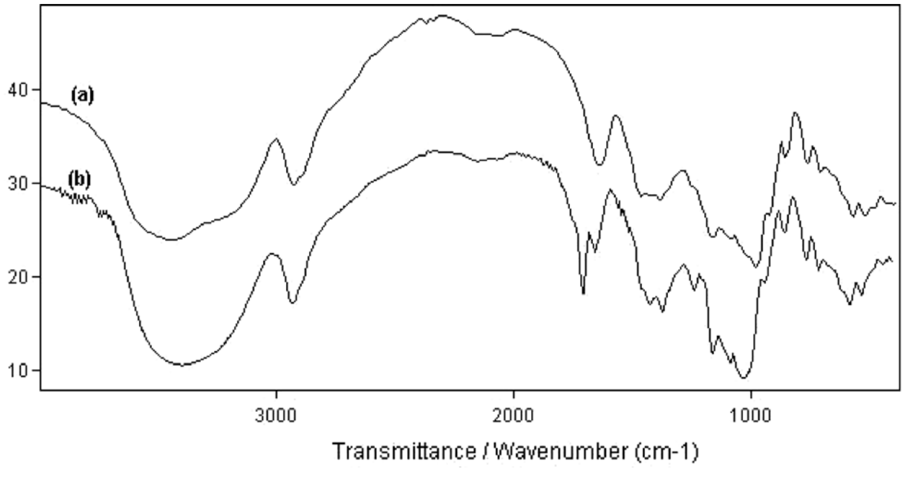


Fig. 1. FTIR spectra of (a) ST and (b) AST.

Table 1
Substitution degree (DS) at different ACOCl/glucosidic unit ratios.

Sample	ACOCL/glucosidic unit (mol/mol)	Pyridine (mL)	DS
1	0.148 (1 mL)	1	0.082
2	0.296 (2 mL)	2	0.151
3	0.385 (2.6 mL)	2.6	0.244

The results are collected in Table 1.

3.2. Grafting of AA and AAm onto AST

After the substitution reaction, the double bond of vinyl groups on AST backbone became available for copolymerization with other vinyl monomers through traditional chain polymerization. The acrylated starch prepared previously was thus copolymerized with two different monomer (AA & AAm). The reaction route and the chemical structure of the product are shown in Scheme 1.

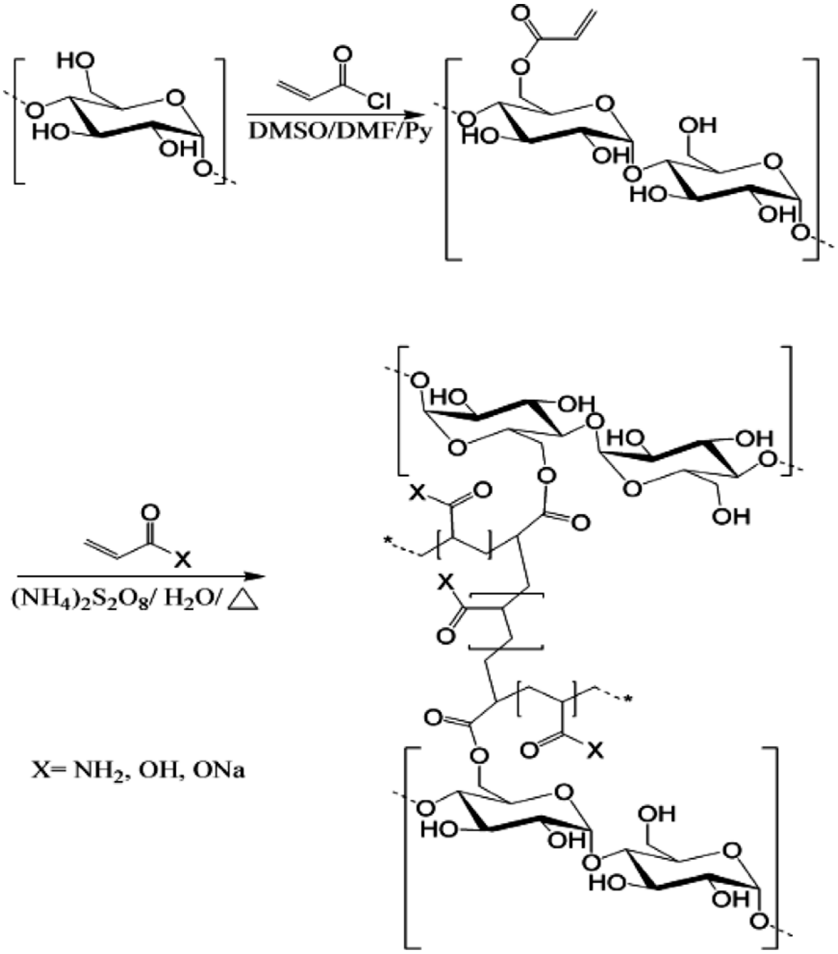
Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Fig. 3 shows the FTIR spectra of the AST-g-poly (AA) (Fig. 3a) and AST-g-poly (AAm) (Fig. 3b). The broad band at 3200–3500 cm^{-1} is due to stretching of hydroxyl groups of AST. In the spectrum of AST-g-poly (AA) (Fig. 3a) three peaks at 1712, 1602 and 1421 cm^{-1} are related to the stretching of COOH, asymmetrical and symmetrical stretching of $–COO^-$ groups, respectively. Finally, in the spectrum of AST-g-poly (AAm) (Fig. 3b) new peak at 1680 cm^{-1} is related to the stretching of Amide groups.

TGA and DTGA traces of AST-g-poly (AA) (Fig. 4a) and AST-g-poly (AAm) (Fig. 4b) are presented in Fig. 4. Better thermal stability of AST-g-poly (AAm) superabsorbent than AST-g-poly (AA) may be concluded from this figure and data summarized in Table 2. According to this Table, values related to the AST-g-poly (AAm) such as T_{20} (285 °C) and char yield at 700 °C (18.27%) are higher compared to that of the AST-g-poly (AA) hydrogel (T_{20} = 233 °C, Y = 16.27%).

Fig. 5 shows the SEM pictures of superabsorbent composite. As it is obvious from this figure, the hydrogel has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

3.3. Effect of the DS of AST on the hydrogel swelling

Acrylate groups on the starch backbone causes the crosslinking of polymer chains during graft copolymerization process. In other words, AST play as a macro-crosslinker in this process. Thus with increasing the acrylate groups on the starch backbone, crosslinking between chains increased too. Fig. 6(a and b) shows the swelling ratio as a function of DS in distilled water and in 0.15 M of NaCl solution. As shown in Fig. 6, the maximum absorbency is achieved at the lowest of DS. According to the literatures high values of absorbency are obtained with low concentrations of crosslinkers, leading to a low crosslinking density (Flory, 1953). Increasing the



Scheme 1. Proposed mechanistic pathway for synthesis of AST hydrogels.

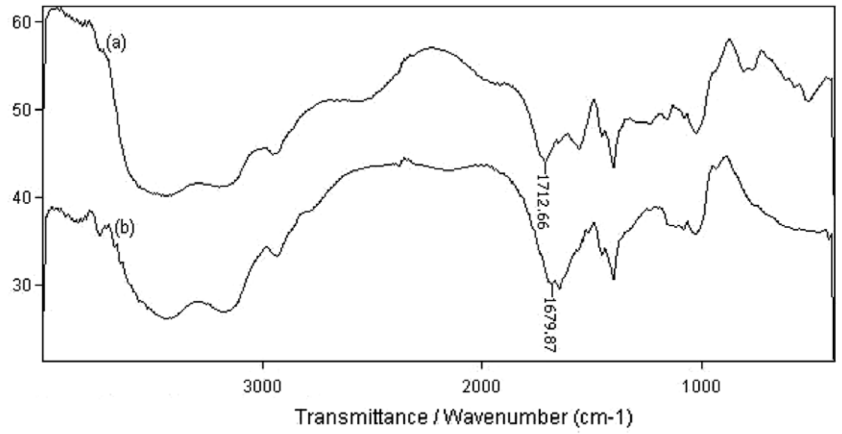


Fig. 3. FTIR spectra of (a) AST-g-poly (AA) and (b) AST-g-poly (AAm).

crosslinking agent and subsequently, the crosslinking density results in a highly crosslinked, rigid structure that cannot be expanded to hold a large quantity of water.

The swelling degree of the hydrogel in saline solutions was significantly decreased as compared with the values measured in deionized water. This result, commonly observed in the swelling of ionic hydrogels, is often attributed to a charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion, make the difference of osmotic pressure (ionic pressure) between the hydrogel network and the external decrease.

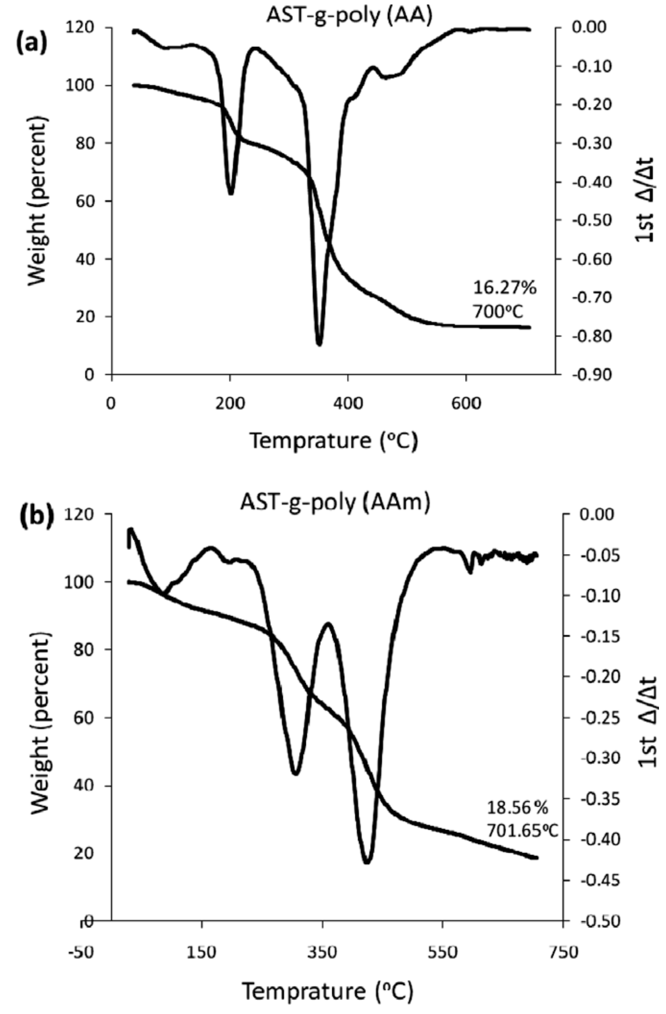


Fig. 4. TGA of (a) AST-g-poly (AA) and (b) AST-g-poly (AAm). Method: 20 °C/min to 700 °C, in (N2).

According to Fig. 6b, swelling of AST-g-poly (AAm) hydrogels decreased in saline solutions, because in saline solutions osmotic pressure of the external fluid is increased and migration of water into the hydrogel network decreased. Nevertheless, sensitivity of AST-g-poly (AAm) hydrogels to saline solutions is less than AST-g-poly (AA) hydrogels, because in AAm hydrogels ionic group has not exist and thus difference of the osmotic pressure between hydrogel network and external saline solution is still large, while ionic groups in AA hydrogels led to a decreased osmotic pressure difference between the hydrogel network and the external saline solution.

3.4. Effect of the pH on the hydrogel swelling

Water absorbency of the AST-g-poly (AA) hydrogel with DS = 0.08 was studied at various pH solutions ranged from 1.5 to 12.1. To prepare the pH media, the stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs. The results are illustrated in Fig. 7. As shown, maximum swelling was obtained at pH ~8.

In AST-g-poly (AA) hydrogel, under acidic pHs, most of the –COO$^-$ groups are protonated, thus the main anion–anion repulsive forces are eliminated and as a result swelling capacity values are considerably decreased. The swelling-loss in the highly basic solutions can be attributed to the "charge screening effect" of excess Na in the swelling media, which, in turn, shields the carboxylate anions and prevents effective anion–anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogels systems (Pourjavadi, Farhadpour, & Seidi, 2008a; Pourjavadi, Seidi, Salimi, & Soleyman, 2008b).

Table 2
Thermal properties of the samples of AST-g-poly (AA) (a) and AST-g-poly (AAm) (b) with the DS = 0.08. Heating rate 205 °C/min, under N2.

Polymer	Temperature (°C) at weight loss			Y^a (wt.%)
	20%	40%	60%	
AST-g-poly (AAm)	285	378	436	18.27
AST-g-poly (AA)	233	347	377	16.27

[a] Char yield at 700 °C in nitrogen.

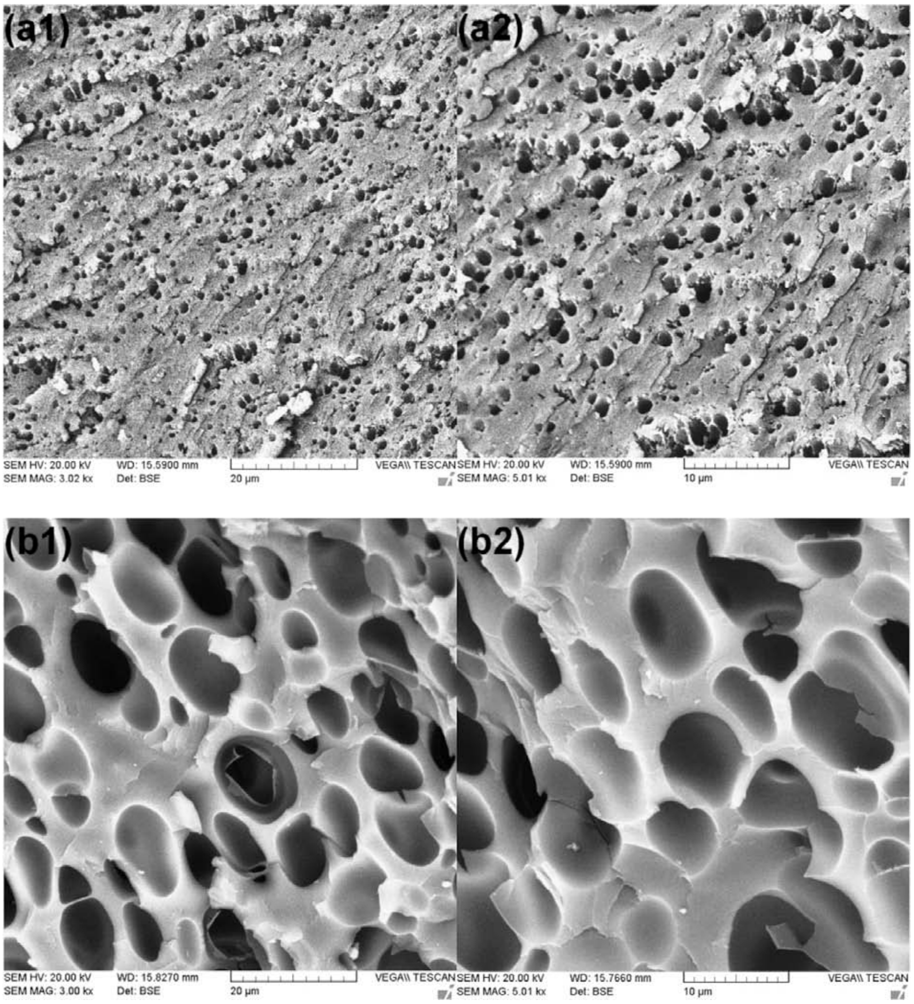


Fig. 5. SEM photographs of (a) AST-g-poly (AA) and (b) AST-g-poly (AAm). Surfaces were taken at a magnification of (a_1,b_1) 30,000× and (a_2,b_2) 50,000×.

AST-g-poly (AAm) hydrogels is not very sensitive to pH because there is no acidic or basic group in their structures.

3.5. Absorbency under load (AUL)

The AUL is an effective factor to investigate the swollen gel strength in the practical application of superabsorbents, which is usually given in the patent literature and technical data sheets offered by industrial hydrogel manufacturers. The AUL of hydrogel samples is determined by using an AUL tester according to a procedure reported earlier (Ramazani-Harandi et al., 2006). Fig. 8 represents the AUL of the hydrogels in saline solution (NaCl 0.15 M) at r.t. under the desired load [applied pressure 0.3, and 0.6 psi (2068 and 4137 Pa)].

In Table 3, swelling in 0.15 M NaCl solution has been compared with absorbency under load at 0.3 psi. This table shows, that when we measure the absorbency under load in AST-g-poly (AA) hydrogels, swelling reaches to ~77% of the swelling in 0.15 M NaCl solution and in AST-g-poly (AAm) hydrogels, swelling reaches to ~82.5% of the swelling in 0.15 M NaCl solution. This result shows that strength of AST-g-poly (AAm) hydrogels is more than AST-g-poly (AA) hydrogels.

3.6. Swelling kinetics

Fig. 9(a1 and b1) represents the dynamic swelling behavior of all the hydrogel samples with certain particle sizes (40–60 mesh) in water. Initially, the rate of water uptake sharply increases and then begins to level off.

The initial swelling rate can be calculated using Voigt-based equation (Eq. (3)) (Omidian, Hashemi, Sammes, & Meldrum, 1998).

$$S_t = S_e(1 - e^{-t/\tau}) \tag{3}$$

where $S_t(g/g)$ is swelling at time t, $S_e(g/g)$ is equilibrium swelling; t (min) is time for swelling S_t, and τ (min) stand for the “rate parameter”.

To find the rate (τ) and power (S_e) parameters for superabsorbent samples, the data obtained from swelling of the hydrogels at consecutive time intervals were fitted into Eq. (3), using Origin 6.1 software. The results are summarized in Table 4. The values of swelling rate (SR, grams/gram second) for the individual samples were determined from the following equation (Kabiri & Zohuriaan-Mehr, 2004; Pourjavadi & Salimi, 2008):

$$SR = S_{m\tau}/\tau_{\min} \tag{4}$$

where $S_{m\tau}$ stands for swelling at the time related to the minimum rate parameter $\tau_{\min}$ (120 s in this work) obtained from superabsorbents from a set of similar experiments (Table 4).

It can be concluded from Table 4, the welling rate of AA-based hydrogels are higher than AAm-based ones. This behavior can be attributed to the increase in ionic groups existing in copolymer chains, which allows polymer coils to expand more easily.

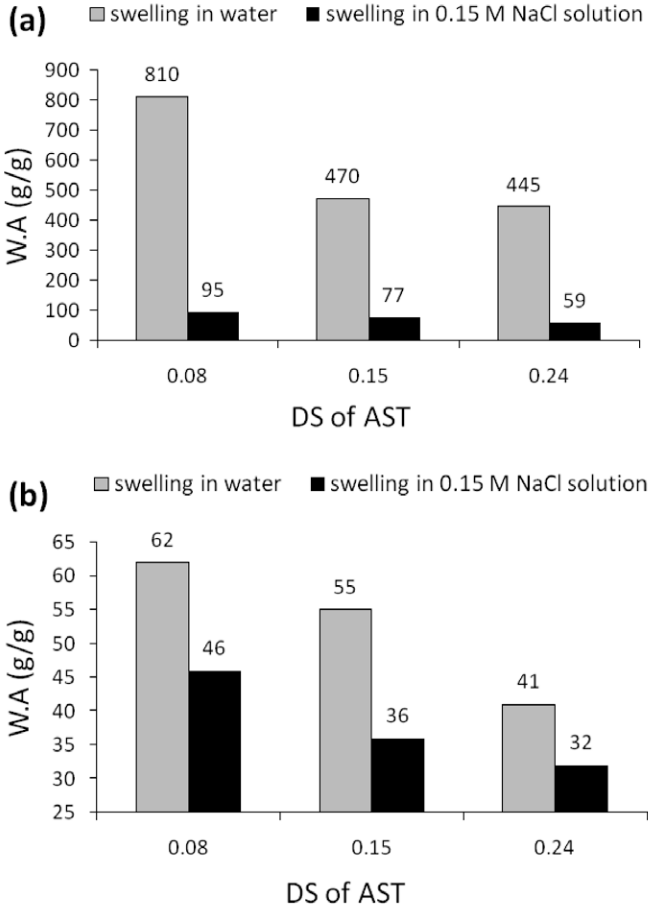


Fig. 6. Effect of DS on swelling. (a) AST-g-poly (AA) and (b) AST-g-poly (AAm).

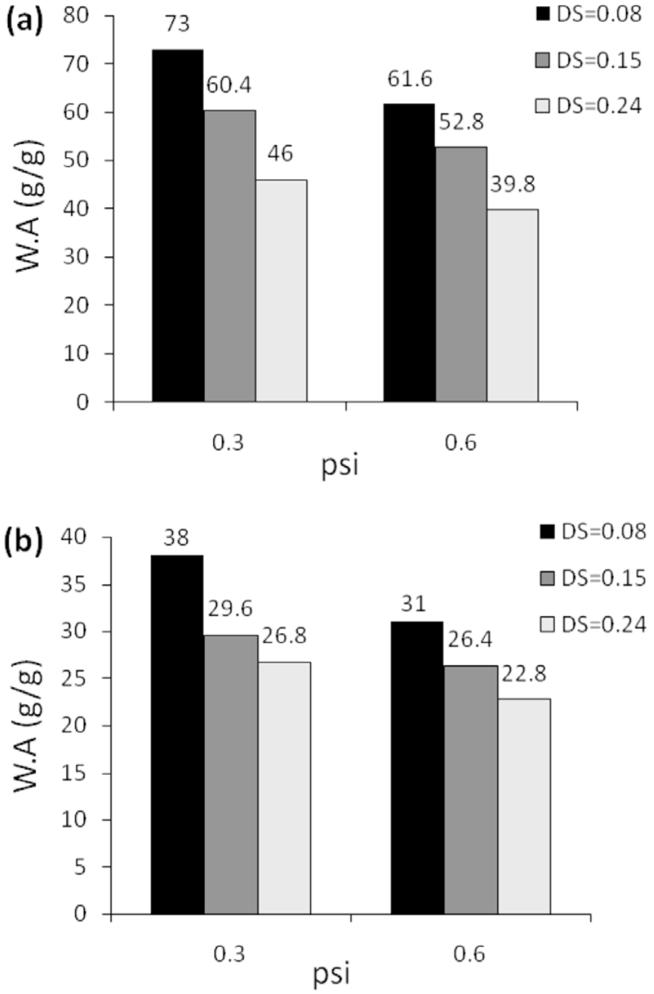


Fig. 8. AUL values for hydrogels swollen in saline solution. (a) AST-g-poly (AA) and (b) AST-g-poly (AAm).

4. Conclusion

In the present study, acrylatedstarchs (ASTs) were made by esterification of the hydroxyl group of starch with the acryloyl chloride. Then we prepared a novel natural based hydrogel by graft copolymerization of acrylic acid (AA) and acrylamide (AAm) onto AST. Effect of (i) salinity and (ii) pH of solutions on the swelling of hydrogels was investigated, results was showed that AST-g-poly (AAm) hydrogels are less sensitive to these factors in compared with AST-g-poly (AA) hydrogels. Results of TGA as well as AUL showed that AST-g-poly (AAm) hydrogels has a stronger network than AST-g-poly (AA) hydrogels. Finally, dynamic swelling kinetics of the hydrogel was also determined.

In conclusion, crosslinker type and concentration has a great influence on the physical properties of SAPs.

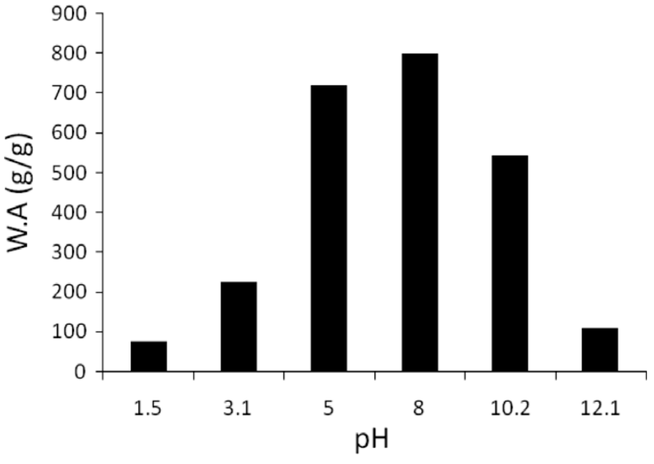


Fig. 7. Effect of pH of solutions on swelling capacity of the AST-g-poly (AA) hydrogel with the DS = 0.08.

Table 3
Comparison between strength of AST-g-poly (AA) and AST-g-poly (AAm) hydrogels according to their decreased swelling under load.

	Swelling in 0.15 M NaCl solution	AUL[a]	Ratio of AUL to swelling in saline solution (%)
AST-g-poly (AA) (DS = 0.08)	95	73	76.8
AST-g-poly (AA) (DS = 0.15)	77	60.4	78.4
AST-g-poly (AA) (DS = 0.24)	59	46	77.9
AST-g-poly (AAm) (DS = 0.08)	46	38	82.6
AST-g-poly (AAm) (DS = 0.15)	36	29.6	82.2
AST-g-poly (AAm) (DS = 0.24)	32	26.8	83.7

[a] Under 0.3 psi in 0.15 M NaCl solution.

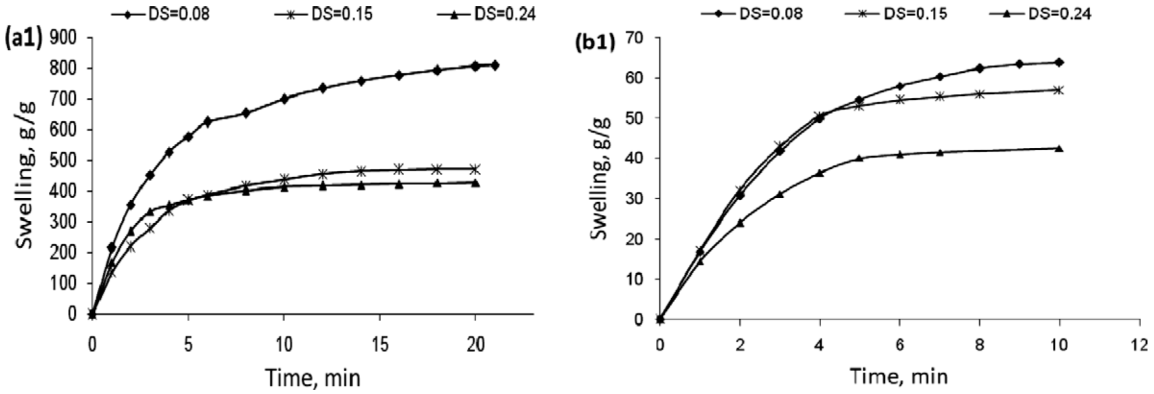


Fig. 9. Representative swelling kinetics of AST-g-poly (AA) hydrogels (a1) and AST-g-poly (AAm) hydrogels (b1).

Table 4
Rate parameters (τ) and swelling rates (SR) of the hydrogels.

Sample	DS	τ (sec)	S_e (g/g)	$S_{m\tau}$ (g/g)	*SR* (g/g sec)
AST-g-poly (AAm)	0.08	186	67.5	32.1	0.3
AST-g-poly (AAm)	0.15	144	59	33.3	0.3
AST-g-poly (AAm)	0.24	144	44.3	25	0.2
AST-g-poly (AA)	0.08	222	784	327.4	2.7
AST-g-poly (AA)	0.15	192	467.6	217.3	1.8
AST-g-poly (AA)	0.24	120	417.8	264.1	2.2

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