Carbohydrate Polymers 98 (2013) 1624–1630

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Synthesis and characterization of novel stimuli-responsive hydrogels based on starch and L-aspartic acid

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ARTICLE INFO

Article history:
Received 16 November 2012
Received in revised form 20 July 2013
Accepted 8 August 2013
Available online 14 August 2013

Keywords:
Starch
L-Aspartic acid
Hydrogel
Stimuli-responsive
Superabsorbent

ABSTRACT

Starch is a hydrophilic biopolymer that is desirable in synthesizing new hydrogels. L-Aspartic acid is a multifunctional amino acid that can be used to modify starch in order to introduce new functional groups on its chains. In this research, a series of novel natural hydrogels based on starch and L-aspartic acid have been synthesized. These hydrogels exhibited temperature-responsive swelling behavior, pH sensitivity and superabsorbency properties. They were characterized by Nuclear Magnetic Resonance (NMR), Infra-Red Spectroscopy (IR), and X-ray Diffraction (XRD). The thermal properties of the hydrogels were evaluated using Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetery (DSC). Swelling studies were carried out at various temperatures and pHs. All of the hydrogels exhibited a high swelling ratio; in aqueous media, this value was greater at higher pH than at lower pH. These properties introduce a novel carrier having applications in delivery systems.

1. Introduction

Superabsorbent hydrogels are polymers with hydrophilic functional groups that absorb a large amount of water to form a gel with a three-dimensional structure without dissolving. In addition, these polymer chains need to be held together through physical or chemical crosslinking in order not to dissolve in water (Saber-Samandari, Gazi, & Yilmaz, 2012; Wöhl-Bruhn, Bertz, Harling, Menzel, & Bunjes, 2012; Laftah, Hashim, & Ibrahim, 2011). Hydrogels load low molecular weight molecules in their aqueous matrix and release them gradually (Bejenariu, Popal, Le Cerf, & Picton, 2008). The role of hydrogels is scientifically important due to their wide range of applications, notably in biomaterials and drug delivery systems (Hamidi, Azadi, & Rafiei, 2008; Ismail, Irani, & Ahmad, 2013; Liu, Gan, & Chen, 2011).

Some hydrogels, referred to as "intelligent materials", respond to changes in the condition of the surrounding media. Among these intelligent materials are stimuli-responsive hydrogels, including pH-sensitive hydrogels (Arizaga, Ibarz, & Piñol, 2010; Du, Zhao, Liu, & Jie, 2013; Khurma & Nand, 2008). The presence of certain polar functional groups along the backbones of polymers results in this specification; for example, carboxylic acid functional groups provide not only bioadhesion properties, but also pH-sensitivity to these polymers.

pH-sensitive hydrogels exhibit new properties which help to achieve goals in drug delivery, including the loading and releasing of drugs at various pHs. In addition, carbohydrates are important compounds in pharmaceutical applications because of their biocompatibility, biodegradability, and low toxicity, and because they are sometimes available at low cost. Recently, starch and chitosan were used to synthesize new hydrogels (Qu, Wirse'n & Albertsson, 2000; Saboktakin, Maharramov, & Ramazanov, 2009; Safaei Nikouei & Lavasanifar, 2011; Sadeghi & Hossenzadeh, 2008). Hence, starch is a hydrophilic biomaterial that is useful for producing new hydrogels (Spagnol et al., 2012; Li, Shimei, Wang, Chen, & Feng, 2009; Xiao, 2013). L-Aspartic acid is a desired amino acid which has been applied to synthesize novel polymers due to its multifunctionality (Vakili, Zahmatkesh, Jafarizadeh, & Panahiyan, 2012). In this study, starch and L-aspartic acid were used to synthesize novel superabsorbent hydrogels with high accumulation of carboxylic acid functional groups on the modified starch hydrogel. The hydrogels were characterized by NMR, FT-IR, XRD, TGA, and DSC. In addition, the swelling properties of the hydrogels were investigated.

2. Experimental

2.1. Materials and instruments

L-Aspartic acid, starch native from wheat (Merck, 111685) and other chemicals (Merck) were used as received without any further purification. NMR spectra were recorded on a Bruker Avance 400 MHz instrument using DMSO-d_6 and D_2O. FT-IR spectra

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http://dx.doi.org/10.1016/j.carbpol.2013.08.016

were recorded on a Tenssor 27 instrument, using KBr pellets. Thermo-gravimetric analyses were recorded on a Mettler TA4000 instrument with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. DSC analyses were performed on a Shimadzu DSC-50 instrument with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Wide-angle X-ray diffraction measurements were performed at room temperature on a Bruker –D8 X-ray diffractometer (operating at 40 kV and 30 mA) with graphite monochromatized Cu Kα radiation (λ = 1.54118 Å). The scanning rate was 2°/min.

2.2. Acryloyl L- aspartic acid synthesis

The synthesis of acryloyl L-aspartic acid (ALA) has been reported in several articles, the first of them published in 1961 (Kulkarni & Morawetz, 1961; Xiea et al., 2004). This experimental method involves a modified approach to this synthesis. L-Aspartic acid (4.0 mmol) was dissolved in an aqueous solution of anhydrous sodium carbonate (4.0 mmol), and hydroquinone (0.004 g). Then, a solution of acryloyl chloride (5.0 mmol) in dried dichloromethane (3 mL) was added to the aspartic acid solution drop-wise for 30 min with stirring. This reaction is exothermic, therefore, the temperature of reaction is maintained at 0–5 °C in an ice bath for 2.5 h and 2 h at room temperature. The pH of the reaction solution was maintained at pH ∼ 8–9 through the addition of a solution of sodium bicarbonate (2M). Finally, concentrated hydrochloric acid was added to acidify the solution to pH ∼ 2–3. Then the product was extracted using ethyl acetate, and the solvent was distilled off under reduced pressure. The solid product was washed using a small amount of cooled ethyl acetate and put in a desiccator to dry. The isolated yield of this reaction was 87% (0.65 g), mp 160–163 °C.

FT-IR (KBr): 3400–2400, 1700, 1655, 1600–1630, 1535, 1189, 930, 834, 635 cm^{-1}.

^{1}H NMR (400 MHz, D_2O) δ: 2.80–2.90 (2H), 4.70 (1H), 5.7 (1H), 6.0–6.3 (2H) ppm.

^{13}C NMR (400 MHz, D_2O) δ: 35.45, 49.07, 128.40, 129.14, 168.16, 173.94, 174.23 ppm.

2.3. Preparation of superabsorbent hydrogels-graft copolymerization (St-g-ALA)

The amount of each chemical was determined according to Table 1. Starch was heated in an oven at 80 °C to dry completely and was weighed before use. Products were heated in a vacuum oven at 80 °C for 5 h.

2.3.1. Graft copolymerization by ceric ammonium nitrate

Graft copolymerization of ALA onto starch was carried out using ceric ammonium nitrate (CAN) as the initiator under a nitrogen atmosphere. Starch was dissolved in DMSO (2 ml) and placed in a round bottom flask. CAN and ALA were added to the solution. The reaction solution was stirred and heated at 80 °C for 1.5 h. The viscous solution was then poured into ethyl acetate to precipitate the synthesized copolymer. The product was washed completely with ethanol and dried.

2.3.2. Graft copolymerization by azobis(isobutyronitrile)

A solution of dried starch in DMSO (2 ml) was placed in a round bottom flask. Azobis(isobutyronitrile) (AIBN) and ALA were then added to that flask under nitrogen gas and stirred at 80 °C for 1.5 h. The viscous solution was poured into ethyl acetate to precipitate the solid product. The produced material was washed completely with ethanol and dried.

2.4. Measurement of equilibrium water content (EWC)

Individual solutions having basic and acidic pH were prepared by dilution of NaOH (pH 10.0) and HCl (pH 2.0) solutions to achieve pH >6.0 and pH <6.0, respectively.

Dried hydrogels were immersed in various solutions (pH 2–10) or NaCl (0.15 M) and maintained for 24 h until equilibrium swelling was reached. The swollen hydrogels were removed from the solution, the excess water on the grafted copolymers was wiped off using filter paper, and the swelled hydrogels were then weighed. Their equilibrium water content (EWC) was calculated from the following equation:

$$EWC(g/g) = [(W_s - W_d)/W_s]$$

where W_s and W_d are the weights of the grafted starch sample at the equilibrium swelling state and dry state, respectively.

2.5. Swelling kinetic

To study the rate of water uptake of the hydrogels, a certain amount of dried copolymer was immersed in aqueous media. At consecutive time intervals, the equilibrium swelling capacity of the hydrogels was measured according to the above-mentioned method (Pourjavadi, Harzandi, & Hosseinzadeh, 2005).

2.6. Determination of grafting parameters for St-g-ALA copolymer

For St-g-ALA copolymers, grafting parameters such as the percentage of grafting (%) and efficiency of grafting (%) were calculated as follows (Kim, Cho, Lee, & Kim, 2000).

$$\text{Percentage of grafting (PG\%)} = [(W_2 - W_1)/W_1] \times 100$$

$$\text{Efficiency of grafting (GE\%)} = [(W_2 - W_1)/W_3] \times 100$$

where W_1, W_2 and W_3 are the weight of initial starch, grafted starch and ALA, respectively.

Table 1
Reaction conditions and results of grafting.

No.	Ratio[a]	Starch(g)	ALA (g)	Initiator	Product mass (g)	EG[b]	PG[c]
1	1:1	0.1620	0.1870	CAN	0.2430	43.32	50.00
				AIBN	0.2790	62.57	72.22
2	1:2	0.1620	0.3740	CAN	0.2510	23.79	54.94
				AIBN	0.2920	34.76	80.25
3	1:3	0.1620	0.5620	CAN	0.2020	7.11	24.69
				AIBN	0.2280	11.74	80.25
4	1:4	0.1620	0.7530	CAN	0.1990	4.91	22.84
				AIBN	0.2240	8.23	38.27
5	1:5	0.1620	0.9410	CAN	0.1970	3.72	21.60
				AIBN	0.2220	6.38	37.04

[a] Starch (an unit mass) to ALA (mole(s)).
[b] Efficiency of grafting(%).
[c] Percentage of grafting(%).

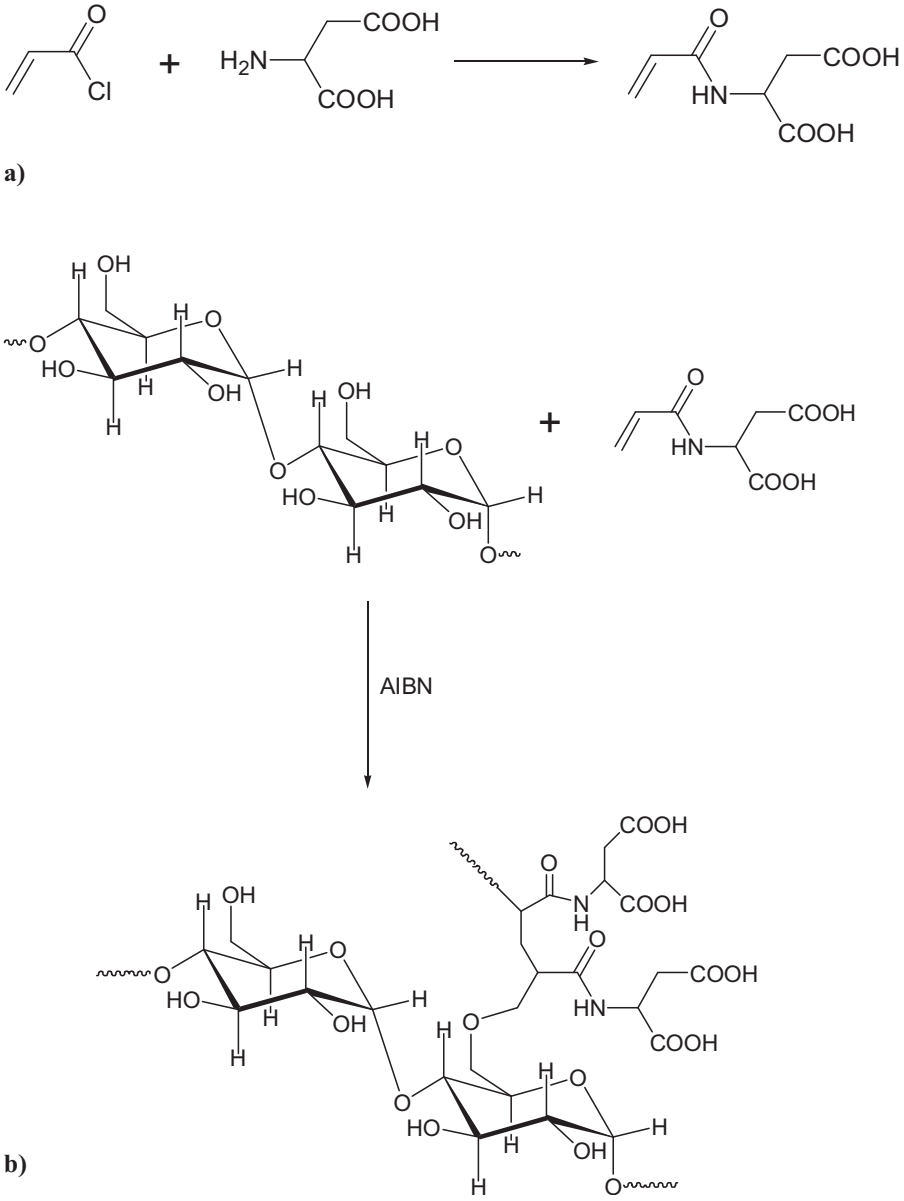
3. Results and discussion

3.1. Synthesis and characterization of acryloyl L-aspartic acid and its hydrogel

Biocompatibility for hydrogels which are used in biological systems is necessary. Natural compounds may play an important role in achieving this goal. Such compounds are beneficial because they are supplied from sustainable resources and may be inexpensive. In this study, two natural materials, starch and L-aspartic acid, were applied in order to fabricate novel stimuli-response superabsorbents. L-Aspartic acid is a multifunctional natural amino acid that bears two carboxylic acids and an amine group.

The main objective of this study was to introduce the two carboxylic acid functional groups and the amidic group from the monomer to the backbone of a starch molecule. The *St-g-ALA* hydrogels contain these functional groups with a high density of hydrogen bonding. Thus, the higher number of hydrophilic groups is responsible for absorbing more water, compared to the hydrogels of starch and acrylic acid derivatives. In addition, the monomer's carboxylic acid groups have suitable distance and orientation in relation to each other; they thus exhibit a new structure compared to the acrylic acid monomer. Hence, the structure might be useful for drug loading into the hydrogel. The hydrogels were synthesized in two stages. First, acryloyl chloride was reacted with aspartic acid (Scheme 1a), and second, free radical polymerization was carried out in the presence of two types of initiators, cerium ammonium nitrate (CAN) and azobis(isobutyronitrile) (AIBN) (Scheme 1b).

The monomer was characterized by NMR and IR spectroscopy. The FT-IR spectrum of the monomer exhibited characteristic absorptions at 2200–3600 cm^{-1} (O–H, carboxylic acid), 1700 cm^{-1} (C=O, carboxylic acid), 1665 cm^{-1} (C=O, amide), 3299 cm^{-1} (N–H stretching of amide group), 1600 cm^{-1} (C=C stretching). The ^{1}H NMR spectrum of the monomer (D_2O, δ in ppm) showed two aliphatic peaks at 2.88 (2H), a hydrogen on the chiral center which was overlapped by solvent peak at 4.7 (1H), and three alkene hydrogen atoms at 5.6 (1H), and 6.1 (2H). The ^{13}C NMR spectrum of the monomer (D_2O, δ in ppm) indicated: 35.45, 49.07 (two aliphatic carbons), 128.43, 129.14 (C=C carbons), 168.16, 173.94, and 174.23 (carbonyl groups).



Scheme 1. The monomer and hydrogel synthesis. (a) Synthesis of acryloyl L-aspartic acid, (b) Graft copolymer synthesis.

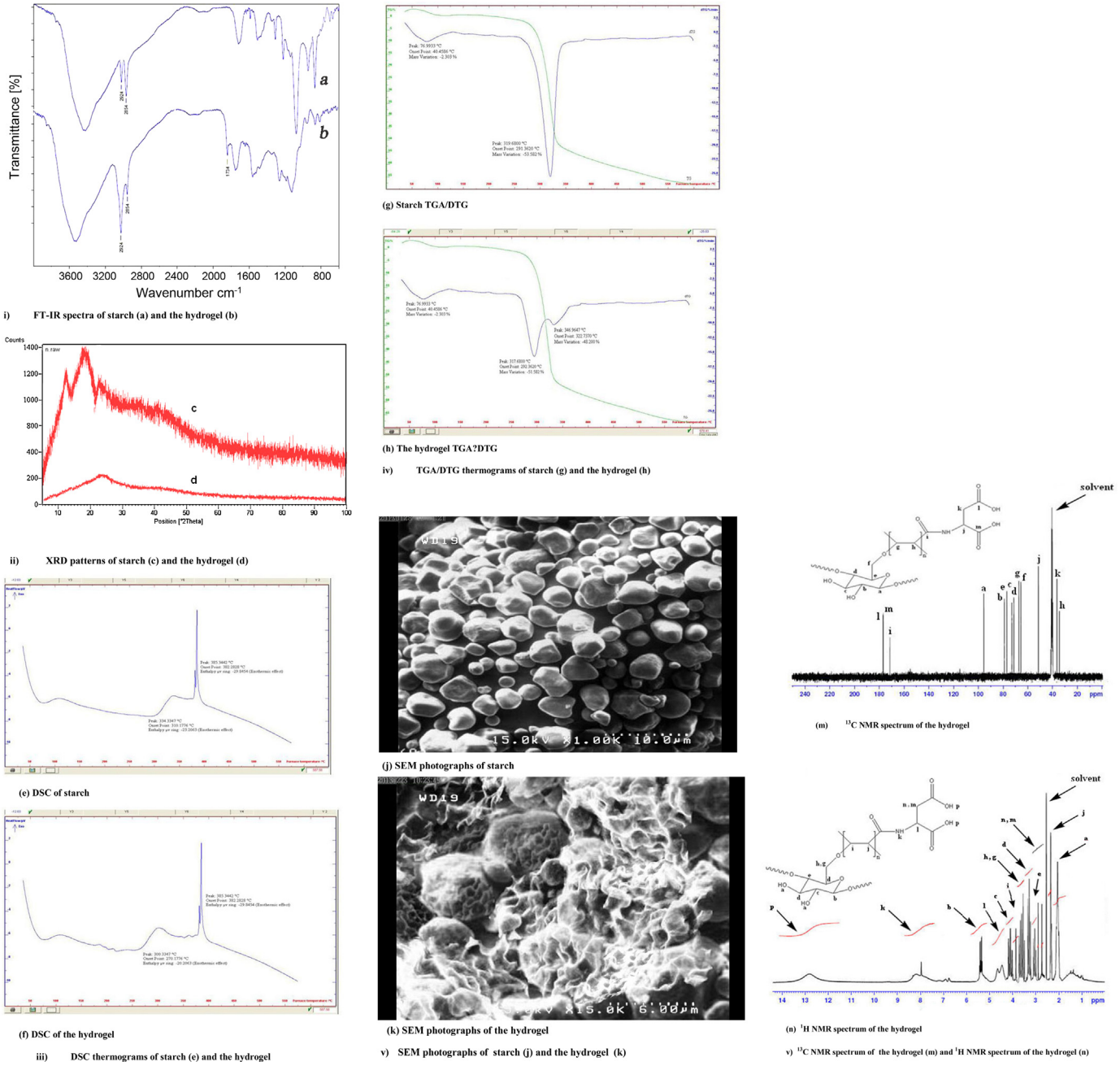


Fig. 1. FT-IR spectra, XRD patterns, DSC, TGA/DTG of starch and the hydrogel product and ^{13}CNMR of the hydrogel, ^{1}H NMR of the hydrogel.
(i) FT-IR spectra of starch (a) and the hydrogel (b).
(ii) XRD patterns of starch (c) and the hydrogel (d).
(iii) DSC thermograms of starch (e) and the hydrogel (f).
(iv) TGA/DTG thermograms of starch (g) and the hydrogel (h).
(v) SEM photographs of starch (j) and the hydrogel (k).
(vi) ^{13}C NMR spectrum of the hydrogel (m) and ^{1}H NMR spectrum of the hydrogel (n).

The process of grafting ALA on starch molecule was carried out using radical polymerization, which is a simple and reasonable method. To characterize these polymers, techniques such as FT-IR, NMR, TGA, DSC, and XRD were used. The FT-IR spectra of the untreated and treated starch are depicted in Fig. 1a and b respectively. The characteristic absorption bands of the starch are 3423 cm^{-1} for O–H stretching and 1043 cm^{-1} for C–O stretching. The modified starch exhibited an additional peak at 1734 cm^{-1} (C=O, stretching) which is characteristic of absorption for carboxylic acids of L-aspartic acid. The other peaks of the grafted units overlap with starch absorption peaks (Huang, Yu, & Xiao, 2007; Singh, Tiwari, Pandey, & Singh, 2006; Zhang, Wang, & Wang, 2006).

The ^{13}C NMR and ^{1}H NMR (DMSO-d_6, ppm) spectra agree well with the proposed structures of these two compounds. In particular, the ^{13}C NMR spectrum (Fig. 1m) of the hydrogel showed three peaks of carbonyl groups at 173.96, 174.23 and 177.23 ppm, in addition to the starch absorption peaks.

SEM photographs of starch and the hydrogel (St-g-ALA4) are shown in Fig. 1j and k, respectively. The hydrogel was particulate. Thus, the morphology of the dry hydrogel is formed from spherical granules. The swelling process destroyed and altered the granular

structure of the dried hydrogel. The texture of the swelled hydrogel after drying was fluffy which was confirmed by SEM. The SEM photograph of the dried hydrogel after swelling exhibited some pores in the dried hydrogel.

3.2. XRD study of the hydrogel

The XRD pattern of unmodified starch (Fig. 1c) showed three sharp peaks at 13°, 19° and 23° (2θ). However, the hydrogel XRD pattern (Fig. 1d) indicated only a sharp peak at 23° (2θ). Comparing the two XRD patterns shown, the degree of crystallinity in the hydrogel product decreased. Upon grafting of starch with the monomer, the number of counts of starch dropped sharply from about 1200 counts for starch to about 200 counts for the hydrogel. This could be a result of breaking of the inter-chain hydrogen bonding in starch. As a result, the crystallinity was reduced upon grafting of the monomer onto starch. In fact, the crystalline region of starch is also involved in grafting (Fares, El-faqeeh, & Osman, 2003).

3.3. Optimizing of grafting condition

In this study, ceric ammonium nitrate (CAN) and azobis(isobutyronitrile) (AIBN) were used as initiators for the graft copolymerization onto starch. Ceric ammonium nitrate (CAN) is a redox initiator for free radical polymerization. The cerium ion reacts with the starch molecules and forms a starch–ceric complex. The Ce (IV) ion in the complex is then reduced to a Ce (III) ion. As a result, a free radical is formed onto starch, while the bond between carbon atoms 2 and 3 of the glucopyranose unit is broken. The polymeric starch free radical so formed may react with the monomer to initiate graft copolymerization (Rahman et al., 2000). AIBN is decomposed to produce isobutyl radicals during initiation. The radicals abstract hydrogen atoms from the starch backbone (mostly from primary hydroxyl groups) and form active radical sites that could start the graft copolymerization.

Efficiency of grafting (GE) and percentage of grafting (PG) were measured for five ratios of starch-to-ALA by mass for two types of initiators. As shown in Table 1, the maximum amount of PG was 54.94% and 80.25% for the ratio of 1:2 (starch to ALA) in presence of CAN and AIBN, respectively. Thus, the maximum grafting was done while the starch-to-ALA ratio was 1:2 using AIBN. Using more ALA in this reaction may have resulted in the production of more homopolymers. As a result, the efficiency was less for ratios greater than 1:2. Based on these results, AIBN was the desired initiator for this reaction. In fact AIBN is a more efficient initiator than CAN. AIBN abstracts hydrogen of primary hydroxyl group from starch. The radical represents less steric hindrance compared to glucopyranose ring radical which is created by CAN. To find the best amount of AIBN, six reactions (Table 2) were run using the best ratio of starch-to-ALA (1:2). The results of PG in Table 2 reveal that 0.00060 g (3.7% of starch mass) of AIBN with a starch-to-ALA ratio of 1:2 creates the maximum percentage of grafting (100%). It was confirmed using ^{1}H NMR spectroscopy (Fig. 1n) that the ratio of integration of the anomeric proton (5.4 ppm, 1H) of starch to the hydrogen of the chiral center of ALA (4.3 ppm, 1H) was equal to one. This hydrogel was selected for further characterization and for the investigation of its properties.

3.4. Thermal properties

The thermal properties of the grafted starch and starch were evaluated by means of TGA/DTG and DSC under nitrogen gas at a heating rate of 10 °C min^{-1}. These polymers showed similar decomposition behavior. TGA and DTG thermograms (Fig. 1g, h) showed that the temperatures of 10% weight loss for pure unmodified starch and its hydrogel were 296.4 °C and 292.8 °C, respectively. The residual weights for the modified starch and starch were 33.8% and 34.0% at 600 °C, respectively. The DTG of starch showed a peak at 319.6 °C, while the DTG of the hydrogel indicated two peaks at 317.7 and 322.7 °C. These results showed that the thermal stability of the starch and the modified starch were similar. Two opposite factors influence the thermal stability of the hydrogel. The replacement of the hydrogen of the starch primary hydroxyl group with the grafted monomer may enhance thermal stability of the polymer. However, grafting process decreased the degree of crystallinity according to XRD data. Decreasing crystallinity degree might decrease thermal stability. As a result, the hydrogel and starch showed similar thermal stability.

DSC thermograms of starch and the hydrogel are depicted in Fig. 1e and f, respectively. The DSC thermogram of starch exhibited three exothermic peaks because of thermal degradation at 334.3 °C, and a pair of sharp peaks at about 385 °C. It showed no glass transition temperature due to the low moisture content of starch. A previous study revealed that glass transition temperature of starch was extremely sensitive to the percentage of moisture present. The transition was too broad below 13% moisture (Zeleznak & Hoseney, 1987). The DSC of the hydrogel product indicated a glass transition temperature at 190 °C. The transition may be due to the presence of the grafted polymer on the hydrogel. This thermogram also showed three exothermic degradation peaks at 300.3, 380 and 385 °C.

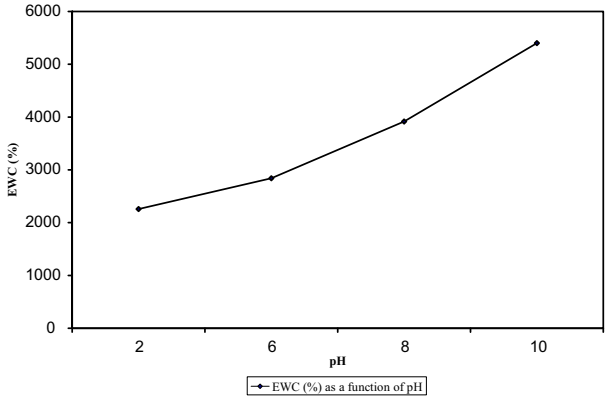
3.5. Equilibrium swelling

Equilibrium swelling of St-g-ALA4 was studied at various pH solutions, ranging in value from 2 to 10. The swelled hydrogel was stable and uniform. Under alkaline pHs, most carboxylic acid functional groups are ionized; as a result, these functional groups bear negative charges and induce repulsion. Consequently, the maximum level of the EWC occurred at pH 10. Indeed, at a lower pH, the hydrogel carries more protonated carboxylic acid functional groups which promote physical cross-linking through hydrogen bonding (Yan Baoa, Jianzhong, & Lib, 2011). Consequently, the hydrogel absorbed less water at an acidic pH (Fig. 2a). EWC at pH 8 was almost 1.4 times greater than EWC at pH 6. This revealed that this hydrogel was responsive to pH changes.

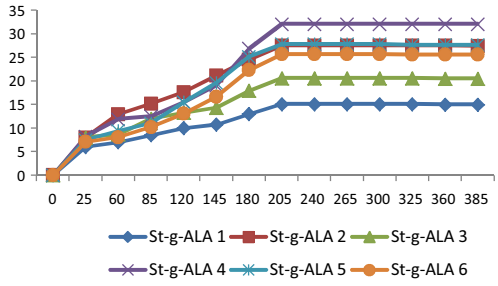
Table 2
Reaction conditions and results of grafting in present of various amounts of azobis(isobutyronitrile).

No.	Starch (g)[a]	ALA (g)[a]	Initiator AIBN (g)	Product mass (g)	EG[b]	PG[c]	EWC[d]
St-g-ALA1	0.1620	0.3740	0.0270	0.2900	34.22	79.01	791.67
St-g-ALA2	0.1620	0.3740	0.0170	0.2900	34.76	80.25	1108.33
St-g-ALA3	0.1620	0.3740	0.0130	0.3120	40.11	92.59	2041.67
St-g-ALA4	0.1620	0.3740	0.0060	0.3240	43.32	***100.0***	2491.67
St-g-ALA5	0.1620	0.3740	0.0030	0.3020	37.43	86.42	1875.00
St-g-ALA6	0.1620	0.3740	0.0010	0.2990	36.63	84.57	1508.33

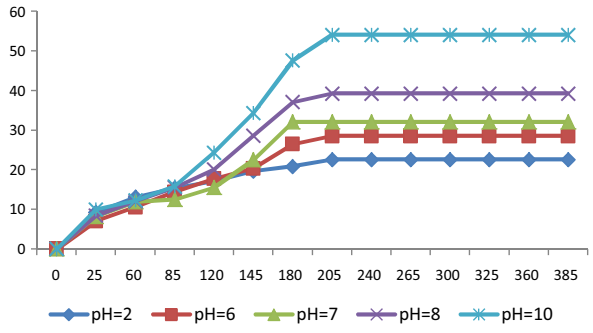
[a] Ratio of starch (an unit) to ALA(moles) is 1:2.
[b] Efficiency of grafting (%).
[c] Percentage of grafting (%).
[d] EWC (%) in 0.15 M of NaCl at 35 °C.



a) Equilibrium Water Content (%) *vs.* pH at 35 °C (St-g-ALA4)



b) Swelling ratio (g/g) *vs.* time (min) of synthesized hydrogels



c) Swelling ratio (g/g) *vs.* time (min) at various pH

Fig. 2. Equilibrium swelling studies of hydrogels. (a) Equilibrium water content (%) *vs.* pH at 35 °C, (b) Swelling ratio (g/g) *vs.* time (min) of synthesized hydrogels, (c) Swelling ratio (g/g) *vs.* time (min) at various pH.

Equilibrium swelling also was measured in the solution of NaCl (0.15 M). Table 2 indicates the value of EWC for the hydrogels; St-g-ALA4 showed the maximum value of EWC (entry 4). Therefore, the product of ratio 2:1, ALA to starch and AIBN (initiator), was the best choice in this investigation. In another study, methacrylic acid was grafted onto starch molecules in order to prepare corresponding hydrogels. Equilibrium swelling of this hydrogel was less than 250% at pH 8 (El-Hag Ali & Al Arifi, 2009). In the current study, however, the value of EWC is less than 4000% (Fig. 2a) at the same pH for St-g-ALA4. In fact, a molecule of acryloyl L-aspartic acid bears two carboxylic groups, whereas methacrylic or acrylic acid contains one carboxylic acid functional group. As a result, the accumulation of hydrogen-bonding on the St-g-ALA hydrogels is more extensive than in hydrogels based on acrylic and methacrylic acids.

3.6. Swelling kinetics

The swelling of hydrogels (St-g-ALA1-6 g/g) as a function of time (min) is shown in Fig. 2b. Among these synthesized hydrogels, the greatest swelling ratio (32g/g) occurred in St-g-ALA4. Swelling rate and kinetic parameters of prepared hydrogels (Table 3) were calculated using a Voigt-based equation (Eq. (1)).

Table 3
Swelling rate and kinetic parameters of synthesized hydrogels.

Sample	τ (s)	S_e (g/g)	$S_{m\tau}$ (g/g)	SR (g/g s)
St-g-ALA1	100.9	15.8	10.0	0.09
St-g-ALA2	105.1	29.2	18.0	0.18
St-g-ALA3	105.6	21.8	13.4	0.13
St-g-ALA4	165.2	38.0	17.4	0.17
St-g-ALA5	141.3	31.6	16.1	0.16
St-g-ALA6	156.5	30.0	14.2	0.14

$$S_t = S_e\left(1 - e^{\frac{-t}{\tau}}\right) \quad (1)$$

S_e (g/g) is the "power parameter" or equilibrium swelling, S_t(g/g) is swelling at time t; t (min) is time for swelling and τ is the parameter of swelling rate. To calculate the power and rate parameters for the hydrogels, the swelling data of the samples at consecutive time intervals were fitted well with Eq. (1), using Origin 8 software. Swelling rate values (SR g/g s.) for the individual samples were determined based on the following equation (2):

$$\mathrm{SR} = \frac{S_{mt}}{\tau_{\min}} \quad (2)$$

where S_{mt} is swelling at the time related to the minimum rate parameter τ_{min} (100.9 s) obtained from superabsorbents from a set of similar experiments (Table 3) (Pourjavadi, Eftekhar Jahromi, Seidi, & Salimi, 2010). These results also showed that the S_e (g/g) of St-g-ALA4 was the largest, with a swelling rate of 0.17 g/g s.

As a result, the St-g-ALA4 hydrogel was selected for further kinetic study. Fig. 2c depicts the swelling ratio (g/g) vs. time (min) for this sample at pH ranging from 2 to 10, and at 35 °C. Initially, the rate of water absorption sharply increases and then levels off at about 205 min to achieve maximum swelling ratios of 22.6, 28.5, 32.1, 39.3, and 54.1 g/g at pH 2, 6, 7, 8, and 10, respectively. This superabsorbent was sensitive to pH changes; in fact, increasing the pH caused the hydrogels to absorb more aqueous solution. The swelling rates were calculated using EqS. (1) and (2) noted above. The results are summarized in Table 4. It can be concluded, based on Table 4, that the swelling rate of the hydrogel at pH 10 was higher than at the other pHs.

Furthermore, the swelling rate of this hydrogel was investigated as a function of temperature. Table 5 indicates the value of the swelling rate at various temperatures. This hydrogel showed temperature-responsive swelling behavior due to the association and/or dissociation of hydrogen bonding by carboxylic acid and amide groups (Kim, Park, & Kim, 2003). The maximum value of S_e and swelling rate were 36.8(g/g) and 0.19(g/g sec) at 35°C.

Table 4
Swelling rate and kinetic parameters of St-g-ALA4 at various pHs.

pH	τ (s)	S_e (g/g)	$S_{m\tau}$ (g/g)	SR (g/g s)
2	70.3	22.8	14.4	0.21
6	122.7	31.4	13.7	0.19
7	143.2	36.8	14.3	0.20
8	162.3	46.2	16.2	0.23
10	197.6	68.9	20.6	0.29

Table 5
Swelling rate and kinetic parameters of St-g-ALA4 at pH 7 and various temperatures.

Temperature (°C)	τ (s)	S_e (g/g)	$S_{m\tau}$ (g/g)	SR (g/g s)
35	143.2	36.8	17.8	0.19
15	94.6	21.0	13.2	0.14
45	116.9	25.3	14.0	0.15

4. Conclusions

In this study, a series of novel superabsorbents based on aspartic acid and starch were synthesized. These hydrogels were also characterized by NMR, FT-IR, XRD, TGA, and DSC. The hydrogels exhibited temperature-responsive swelling behavior and pH sensitivity. The swelling ratio in alkaline aqueous media was greater than that in acidic media. The EWC (%) of the selected hydrogel was more than 5000, and the swelling rate was equal to 0.29 (g/g s) at pH 10.

Acknowledgements

The authors would like to thank Dr Ashan Shooshtarian for her valuable contributions to this study. This work has been supported by Firoozabad Branch, Islamic Azad University.

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