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Polysaccharide-based superporous hydrogels with fast swelling and superabsorbent properties

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ABSTRACT

Most dried hydrogels (xerogels) require a long time to reach equilibrium swelling due to the slow absorption of water by diffusion. Superporous hydrogels (SPHs) have been developed to demonstrate fast swelling and superabsorbent properties, and thus attracted much attention for various biomedical applications. In this study, we have developed and evaluated a new polysaccharide-based SPH that can absorb a significant amount of water instantaneously by a capillary mechanism and swell to equilibrium quickly, regardless of their dimension and size. Here, starch was chemically modified to have hydrophilic sulfate groups and reactive vinyl groups and used as a water-soluble, biodegradable building block for making three-dimensional networks. Starch-based SPHs were prepared by a radical crosslinking reaction and gas-blowing foaming process to generate an interconnected pore structure. These new biodegradable, starch-based, superabsorbent SPHs with fast swelling could be useful for pharmaceutical and biomaterial applications.

1. Introduction

Hydrogels are three-dimensional networks of hydrophilic polymers connected by chemical and/or physical crosslinking. They can swell to an equilibrium state that retains a significant amount of water. This swelling (water absorbent or retentive) property has been extensively utilized in various biomedical fields, including drug delivery and tissue engineering. However, most dried hydrogels (i.e., xerogels) swell very slowly and may take hours or days to reach equilibrium due to slow water absorption by diffusion into a glassy polymer matrix. This slow swelling can be limiting in some applications.

SPHs are novel hydrogel materials that can exhibit both fast swelling and superabsorbent properties (Omidian, Rocca, & Park, 2005). SPHs can quickly absorb water volumes that exceed 95% of the total weight (or volume) (Park, 2002) because interconnected pores with diameters of several hundred microns create open channels that allow for capillary action (Chen, Park, & Park, 1999). The superporous structure is fabricated by a simultaneous reaction of gelation and gas-blowing (Chen & Park, 1999; Kim & Park, 2004) to give a homogeneous pore structure because of the acid-induced decomposition of a bicarbonate compound.

Polysaccharide-based hydrogels have attracted much attention as biomaterials due to their excellent biocompatibility and biodegradability. Polysaccharides such as starch, chitosan, cellulose, and their derivatives (guar gum, sodium alginate, etc.) have been investigated as useful hydrogel materials for bio-applications (Berger et al., 2005; Bhuniya, Rahman, Satyanand, Gharia, & Dave, 2003; Chen et al., 2004; Coviello et al., 2005; Reis et al., 2008). Starch is one of the most abundant polysaccharides, composed of a mixture of amylose and amylopectin, that is low-cost, abundant, biocompatible, and biodegradable, and has many functional groups for chemical modification (Karlsson, Leeman, BjÖrck, Inger, & Eliasson, 2007; Kuakpetoon & Wang, 2007; Sandhu & Singh, 2007).

In this study, we evaluated a new biodegradable, starch-based SPH with fast swelling and superabsorbent properties. Our previous works on SPHs focused on inducing fast swelling kinetics via chemical and physical modifications (Choi et al., 2007) and improving mechanical strength by introducing interpenetrating network (IPN) structures (Omidian, Rocca, & Park, 2006). This is the first report of a biodegradable and biocompatible polysaccharide-based SPH system. Here, a water-soluble starch sulfate derivative with reactive vinyl groups was synthesized by a series of chemical modifications of corn starch and used as a building block for making SPHs. Various starch-based SPHs were synthesized and their physico-chemical properties were characterized, especially in terms of chemical composition, swelling ratio, swelling kinetics, pore structure, and enzymatic degradation.

2. Experimental

2.1. Materials

Corn starch, pyridine (99+%), acryloyl chloride (AC, 98%), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, 99%), ammonium

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persulfate (APS, 98+%), and sodium bicarbonate were purchased from Sigma–Aldrich. Chlorosulfuric acid and sodium hydroxide were purchased from Kanto Chemical Co., Inc., and Duksan Pharmaceutical Co., Ltd., respectively. *N*,*N*-Dimethylformamide (DMF) was from Mallinckrodt Chemicals. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (PF127) and acrylic acid (AA, 99%) were obtained from BASF and Fluka. Calcium chloride and acetic acid (glacial) were from Junsei Chemical Co., Ltd. Dialysis membrane (MWCO: 6–8 k, 32 mm) was from Spectrum Laboratories, Inc. α-amylase (E.C.1.1, type: VI-B, 28 units/mg solid) was purchased from Sigma. All other reagents were used as received.

2.2. Synthesis of water-soluble starch sulfate (SS)

As shown in Fig. 1(a), SS was synthesized as previously reported with modified conditions (Cui, Liu, Wu, & Bi, 2009). The sulfating agent was prepared in a two-necked round bottom flask (500 mL) equipped with a dropping funnel, a condenser, and a magnetic stirrer. Off-gas absorption equipment must be fixed at the end of the condenser. The whole equipment was put into an ice-water bath. Pyridine (15 mL) was added into the flask. With slow magnetic stirring, chlorosulfonic acid (12.3 mL) was dropped very slowly to the reaction vessel and kept for 40–50 min to obtain the sulfur trioxide pyridine complex. The product was completely dissolved in DMF (70 mL) to make a yellow sulfating agent solution.

Corn starch (30 g) was dispersed in DMF (60 mL) in a three-necked round bottom flask (1000 mL) equipped with a dropping funnel, a condenser, and a thermometer. The mixture was kept in an oil bath with magnetic stirring and heated to 70 °C. Then, the sulfating agent solution was added dropwise over 1 h and the mixture was stirred for another 1 h. After the reaction, the product solution was poured into iced deionization (DI) water (100 mL) and neutralized to pH = 7.0–7.4 by adding NaOH solution (2.5 mol/L), followed by precipitation and washing with ethanol. The precipitate was dried in a vacuum oven at room temperature for 24 h, then dissolved again in DI water and centrifuged (10,000 rpm, 10 min) to obtain a clear supernatant solution of water-soluble SS. The solution was purified by a dialysis membrane for 48 h and lyophilized to obtain the final SS product as a white powder.

2.3. Synthesis of acryloyloxystarch sulfate (ASS)

In Fig. 1(b), water-soluble SS (1 g) was dissolved in DMF (40 mL) in a two-necked round bottom flask (250 mL) with a dropping funnel and a condenser. All the equipment was placed in an oil bath and heated to 60 °C, followed by addition of pyridine (0.5–1 mL) and AC (0.5–1 mL). The reaction was stirred for 30 min at 60 °C. The mixture solution was poured into acetone and the precipitate was washed two times, followed by drying in a vacuum oven at 40 °C for 24 h. The resulting product was dissolved in DI water and centrifuged (3500 rpm, 10 min) to make a transparent supernatant solution. The solution was purified by a dialysis membrane for 48 h and lyophilized to obtain water-soluble ASS as a white powder.

2.4. Synthesis of starch-based SPHs

All starch-based SPHs were prepared by crosslinking in the presence or absence of AA as a comonomer with gas-blowing technology (Fig. 1(c)). PF127 and acetic acid were added as a foam stabilizer and a foaming aid, respectively. All the reagents were dissolved in DI water and the pH was adjusted with NaOH (8 mol/L). The crosslinking reaction was initiated by adding APS (0.6%, w/v) and TEMED (0.4%, w/v) and accelerated by adding sodium bicarbonate. The time for harmonizing gelation and foaming reactions was controlled between 25 and 60 s. Once sodium bicarbonate interacted with the acid component of the system to produce CO_2 gas, the polymerization reaction proceeded rapidly, and the reaction mixture became viscous. The solution was kept for 15 min to ensure a complete reaction. The resultant SPHs were dehydrated and washed in ethanol, followed by drying in a vacuum oven for 12 h.

2.5. Characterization

2.5.1. ^1H NMR analysis

Proton nuclear magnetic resonance (^{1}H NMR, JNM-AL400 spectrometer, Jeol Ltd., Akishima, Japan) was used to confirm the chemical composition of SS (DMSO-d6 as solvent) and determine the substituent degree of acryloyl group (DA) of ASS (D_2O as solvent). The DA was calculated by the following equation:

$$\mathrm{DA} = \frac{5x}{3y}$$

where x is the peak area of protons obtained from acryloyl bonds and y is the peak area of protons obtained from anhydroglucose rings.

2.5.2. Elemental analysis

Elemental analysis (Flash EA 1112 series, Thermo Fisher Scientific International Inc.) was used to determine the substituent degree of sulfate groups (DS) of SS. The DS was calculated as follows:

$$\mathrm{DS} = \frac{162[\mathrm{S}]}{3200£ - 102[\mathrm{S}]}$$

where [S] is the sulphur content (%) of SS obtained from elemental analysis.

2.5.3. FT-IR analysis

The chemical compositions of corn starch, SS, and ASS were characterized by Fourier transform infrared spectroscopy (FT-IR, Magna 560 spectrometer, Nicolet, USA) using the KBr disc pressing method.

2.5.4. Morphological study

The surface and inner pore structure of dried SPHs were observed by a scanning electron microscope (SEM, S-2460N, Hitachi, Tokyo, Japan) at 100×.

2.5.5. Contact angle measurements

The surface hydrophilicity of SPHs was confirmed by contact angle measurement. Contact angles were measured by a drop shape analyzer (DSA 100, KrÜss, Germany) by the Sessile drop method. Since SPHs are not directly available for measurements because of the porous structure, the non-porous hydrogel samples with the same chemical compositions were made as a film without foaming for comparison.

2.5.6. Swelling ratio measurements

The SPH samples were cut into discs (about 15 mm in diameter and 2 mm in thickness) and then dried under vacuum for 24 h at room temperature. These samples were immersed in DI water and weighed at predetermined times after removal of excess surface water by lightly tapping on a filter paper. The weight swelling ratio (S) of SPHs was calculated by this equation:

$$\mathrm{S} = \frac{W_\mathrm{s} - W_\mathrm{d}}{W_\mathrm{d}}.$$

where W_s and W_d are the weights of swollen and dried SPHs, respectively.

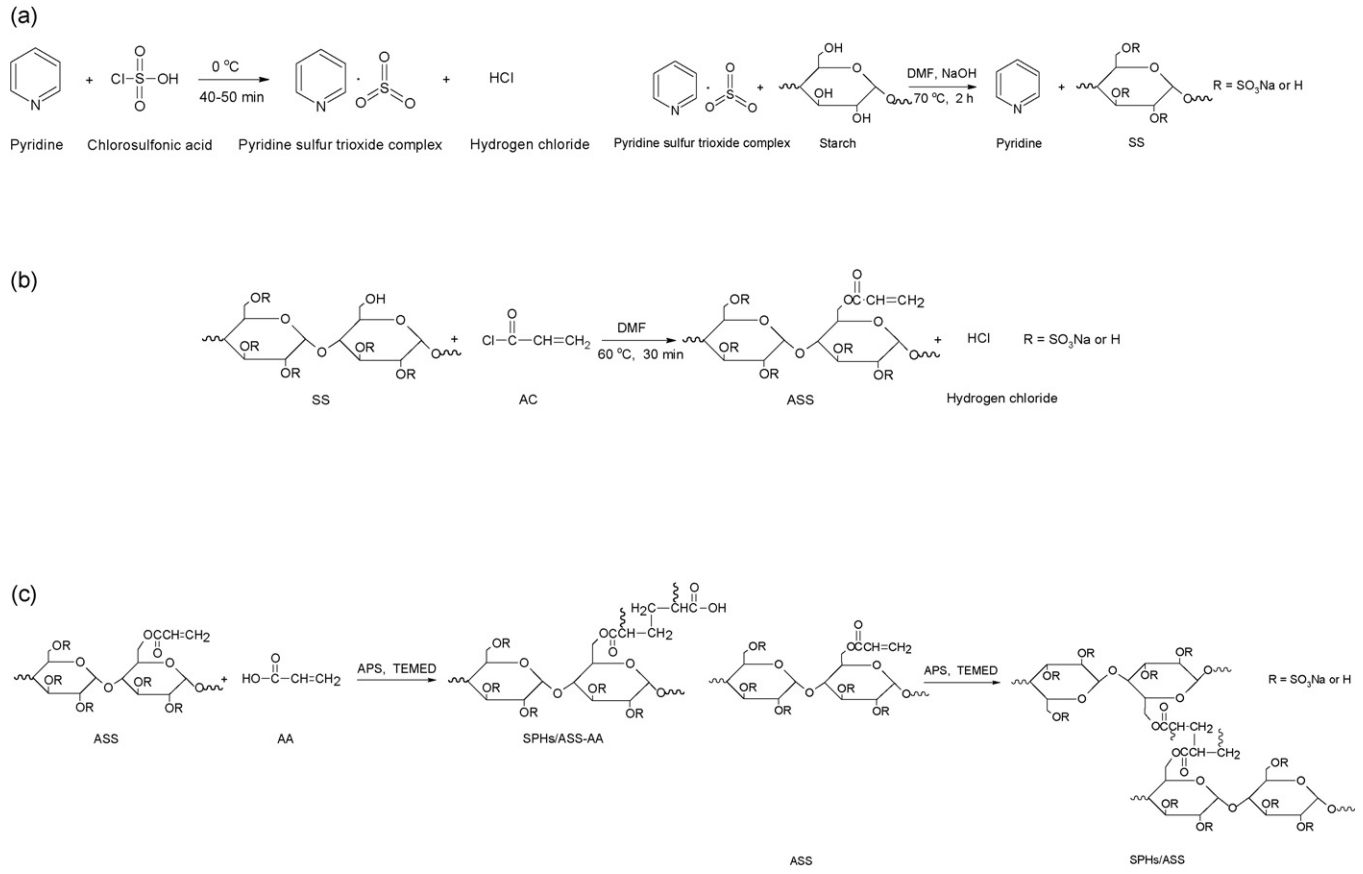

Fig. 1. Synthetic procedure of sulfating agent (a), SS (b), ASS (c), SPH/ASS (d), and SPH/ASS-AA (e).

2.5.7. Enzymatic degradation test

An enzymatic degradation test was performed in phosphate buffered saline solution (PBS, 1000 mL, pH = 7.4, including 0.1 g/L calcium chloride as an enzymatic stabilizer and activator) at 37 °C with 280 Units α-amylase per 1 g SPH. The mass loss of swollen SPHs was monitored at pre-established intervals. The degradation level is determined with the following relation:

$$\text{Mass loss}\,(\%) = \frac{W_t}{W_{eq}} \times 100$$

where W_t and W_{eq} represent the weights of SPHs at degraded and original equilibrium swollen states, respectively.

3. Results and discussion

3.1. Synthesis of water-soluble starch sulfate (SS)

The fast swelling and superabsorbent properties of typical SPHs depend on the hydrophilicity of the polymer composition and the superporous structure of the hydrogels. Due to its limited water solubility, starch required a chemical modification to enhance hydrophilicity and prepare SPHs with good swelling properties. The sulfuric derivative of starch has high hydrophilicity and excellent physiological and biological activities. The sulfation reagents used for starch were mostly $ClSO_3H$ in pyridine or sulfur trioxide complexes with amines, such as pyridine or triethylamine, or with DMF. Here, we synthesized SS by a two-step chemical reaction. We first prepared the sulfur trioxide pyridine complex as a sulfating agent, which is as strong a sulfating agent as chlorosulfonic acid but does not cause significant dehydration or carbonization of starch granules (Cui et al., 2009). The next reaction at 70 °C could destroy the granule structure of the corn starch and increase the activity of the acid groups to accelerate the reaction rate without obvious starch depolymerization.

The ^{1}H NMR spectrum of starch (Fig. 2(a)) showed proton peaks at a range of 3.2–4.0 ppm, corresponding to C2, C3, C5, and C6

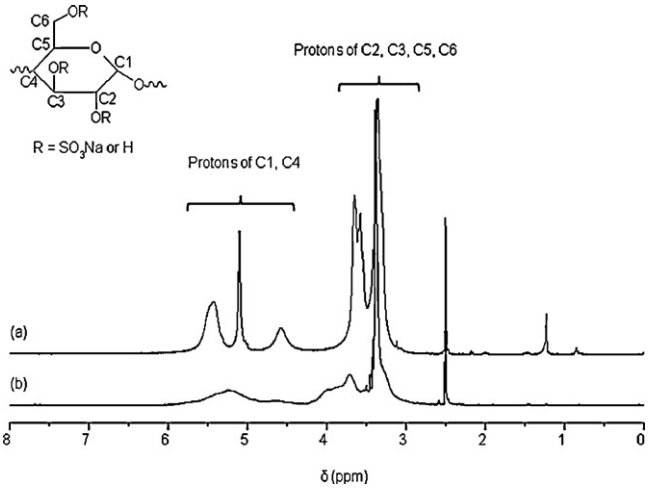

Fig. 2. The ^{1}H NMR spectra of starch (a) and SS (b).

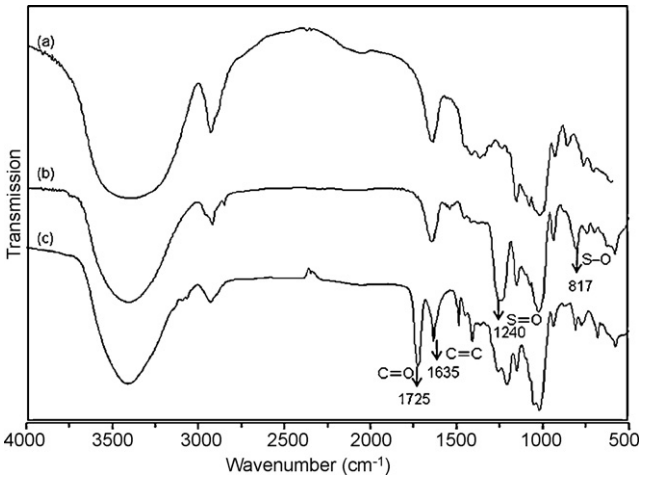

Fig. 3. The FT-IR spectra of starch (a), SS (b), and ASS (c).

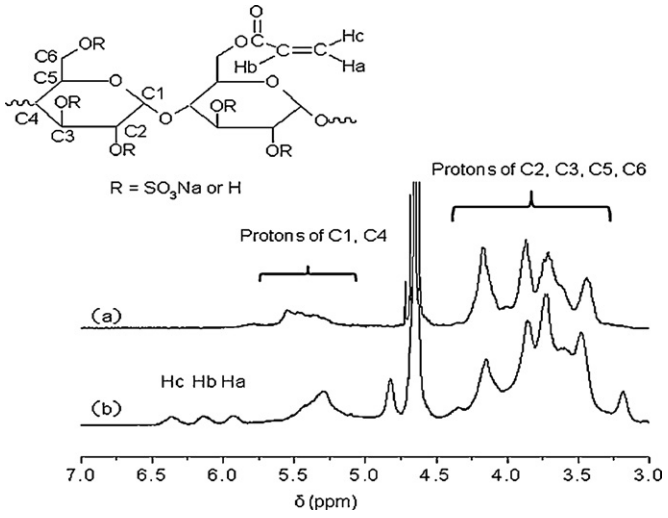

Fig. 4. The ^{1}H NMR spectra of SS (a) and ASS (b).

positions of the anhydroglucose units of starch, and an equatorial proton shift existed at 4.6–5.5 ppm (Graaf, de Lammers, Janssen, & Beenackers, 1995). As sulfate groups were successfully created at the C2, C3, C5, or C6 positions of starch, the proton peaks shifted to a higher frequency (downfield) due to increased electron density. The resonance frequency decreased at 3.5–5.5 ppm, indicating that the –OH groups of starch were partially substituted with $-OSO_3Na$ groups. In addition, the proton peaks from the α-anomer carbon (5.27 ppm) and β-anomer carbon (4.68 ppm) of the reducing end groups of the anhydroglucose rings disappeared, indicating that the OH groups at these positions were replaced by $-OSO_3Na$ groups.

The sulphur content measured by elemental analysis was 9.59% and the DS was calculated to be 0.69, indicating that there existed average 69 sulfate groups per 100 anhydroglucose units after sulfation.

3.2. Synthesis of acryloyloxystarch sulfate (ASS)

Modified starch components of SPHs should have high water solubility and vinyl groups available for the crosslinking reaction. Esterification of starch in the presence of acryloyl chloride after starch gelatinization and dispersion in inert solvents at 100 °C can produce reactive vinyl groups (Fang, Fowler, & Hill, 2005; Stawski & Jantas, 2003). However, the reaction does not give a high substituent degree of esters, mainly due to the insolubility of starch in

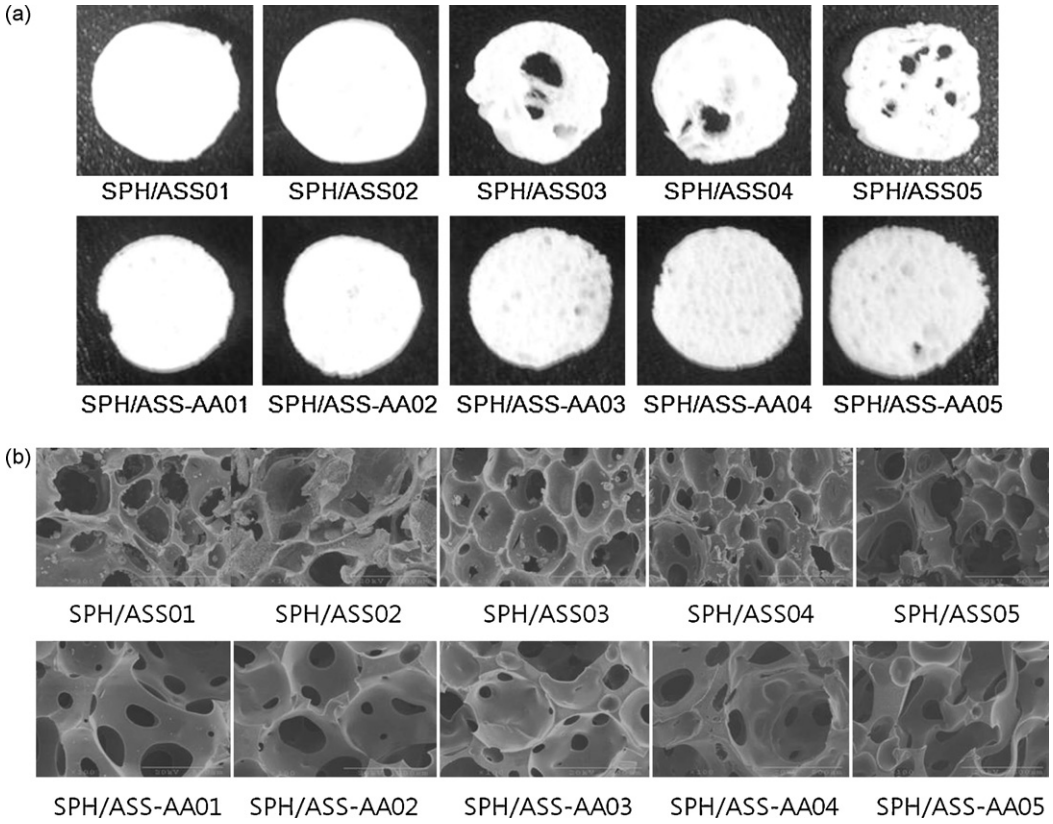

Fig. 5. Photographs (a) and SEM micrographs (b) of dried starch-based SPHs.

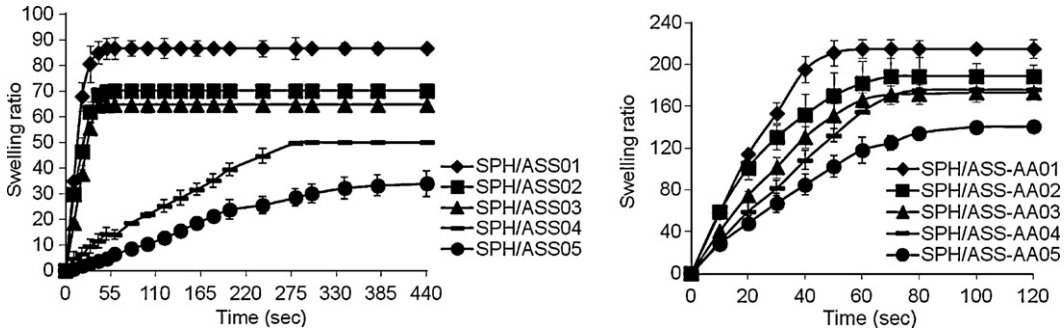

Fig. 6. Swelling ratios of starch-based SPHs.

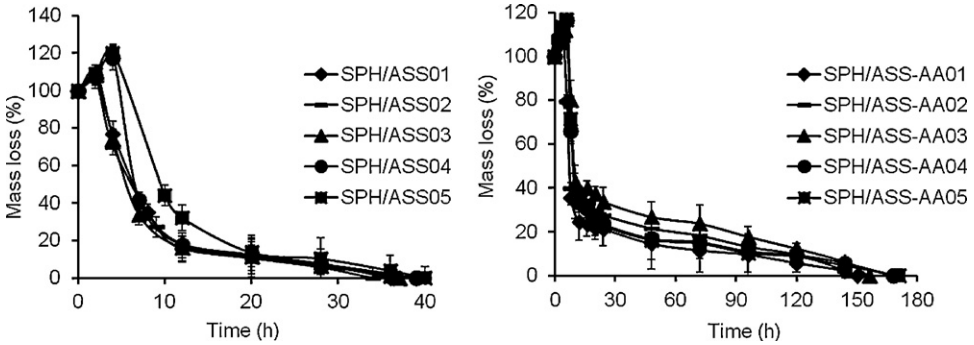

Fig. 7. Enzymatic degradation results of starch-based SPHs.

an unsuitable medium, but caused severe depolymerization after exposure to high temperatures. We prepared a simpler and more efficient method for esterification of starch with AC. Hydrophilic sulfate groups can increase starch solubility in water at room temperature. SS with a DS value of more than 0.69 could be dissolved in both water and DMF. Here, we used DMF to make a homogenous reaction solution of SS. SS was acryloylated directly and efficiently at a lower temperature, with no starch depolymerization. Pyridine was added as a nucleophilic acryloylation catalyst and a reaction accelerating base. The DA could be adjusted by varying the feed ratio of AC to obtained ASS with different DA contents (DA = 0.03–0.23).

The FT-IR spectra of starch (a), SS (b), and ASS (c) are shown in Fig. 3. Bands resulting from S=O and S–O stretching were observed at 1247 and 819 cm^{-1}, respectively, verifying SS synthesis. The absorption intensity of the –OH bond from anhydroglucose rings of starch at 3400 cm^{-1} decreased after substitution with sulfate groups. As indicated in spectrum (c), two main absorption peaks were changed in acryloylated starch with the presence of strong carbonyl peaks (C=O) at the region of 1725 cm^{-1} and the carbon double bond (C=C) at the region of 1635 cm^{-1}. The lack of absorbance at 1770 cm^{-1}, which is associated with the carbonyl stretch of the acryloylating reagent, indicated no contaminating acryloyl chloride. Thus, the esterification between SS and AC occurred, and the vinyl groups were successfully introduced onto SS without self-polymerizing.

The ^1H NMR analysis of ASS shows peaks at 5.92, 6.14, and 6.36 ppm from nonequivalent protons of the acryloyl groups (Fig. 4). Peaks at 4.5–4.7 ppm are due to the protons and deuterium exchange resonance of D_2O (HOD). Peaks at 3.2–4.2 ppm shifted to a lower frequency (upfield) after esterification because the acryloyl groups on the anhydroglucose rings shielded electrons and changed the resonance frequency. DA was calculated by the quantitative peak area of the ^1H NMR spectrum of ASS.

3.3. Preparation and characterization of starch-based SPHs

3.3.1. Preparation of starch-based SPHs

SPHs were fabricated under different synthetic conditions. An APS/TEMED-coupled initiator system initiated the polymerization reaction within 20–60 s at a range of pH = 5.0–5.5. Homogeneous pore structure requires control of AA as a comonomer, the monomer composition, the DA of ASS, the pH of reaction solution, and the initiation time for gas foaming. The synthetic results for SPHs were presented in Table 1 and photographs of the dried state were given in Fig. 5(a). No SPHs with good pore structure were obtained from ASS alone (without comonomer AA), but good pore structure was formed with AA. The best pore structure, in which the pores were interconnected to form the open channels essential for fast water absorption, was found from SPHs/ASS-AA01.

The pore structure and distribution in SPHs are important for determining swelling behaviors. SPHs with homogeneous pores show fast water absorption by capillary force. As shown in Fig. 5(b), SEM images of the inner pore structures showed that all the SPHs had many pores with diameters on the micron scale. However, the SPHs/ASS series had a more heterogeneous pore size and distribution than SPHs/ASS-AA series. SPHs prepared without AA were too brittle and fragile due to the intrinsic nature of starch itself, providing an explanation for the debris around the cutting plane in SEM images from the SPHs/ASS series. SPHs prepared with AA (SPHs/ASS-AA series) showed better physical properties in both the dried and swollen state.

3.3.2. Swelling properties of starch-based SPHs

As the concentration of ASS increased, the equilibrium swelling ratio of SPHs significantly decreased (Fig. 6), probably because high polymer concentration increased the degree of crosslinking in the polymer networks and restricted the chain relaxation process, causing a low equilibrium swelling ratio with a slow swelling rate.

Table 1
Synthetic results of starch-based SPHs.

Samples	ASS (%, w/v)	DA (%)	Acetic acid (%, w/v)	AA (%, w/v)	T^a (s)	Contact angles (°)	$S_{eq}{}^b$
SPH/ASS01	35	5.33	15	–	60	18.8	70
SPH/ASS02	35	2.16	15	–	60	18.5	87
SPH/ASS03	35	6.84	15	–	60	19.3	65
SPH/ASS04	45	5.33	15	–	300	17.7	50
SPH/ASS05	55	5.33	15	–	440	11.1	34
SPH/ASS-AA01	6	5.33	–	30	60	57.9	215
SPH/ASS-AA02	6	2.16	–	30	80	54.8	189
SPH/ASS-AA03	6	6.84	–	30	100	64.9	173
SPH/ASS-AA04	12	5.33	–	30	100	50.3	176
SPH/ASS-AA05	18	5.33	–	30	120	47.4	140

Other chemicals were fixed as: PF127 = 0.5%, w/v, sodium bicarbonate = 5%, w/v, APS = 0.6%, w/v, TEMED = 0.4%, w/v. The pH was adjusted to a range of 5.0–5.5.
[a] Time required for equilibrium swelling.
[b] Equilibrium swelling ratios.

While the SPHs/ASS series showed slow swelling kinetics with a low swelling ratio, the SPHs/ASS-AA series swelled to their equilibrium state within 1 min and showed a much higher swelling ratio (more than 200 for SPH/ASS-AA01). Capillary force is directly affected by the surface hydrophilicity and the pore structure, so we measured contact angles of the non-porous hydrogel films with the same chemical composition as the SPH sample (Table 1). All SPHs had a hydrophilic surface, and hydrophilicity changed according to the concentration and DA of ASS and the presence of AA. The SPH/ASS series showed very low contact angles (below 20°), indicating extreme hydrophilicity, indicating why starch sulfate-based SPHs showed fast swelling despite poor pore structure and a lower equilibrium swelling ratio. The SPH/ASS-AA series showed higher contact angles (47–64°). Increasing hydrophilic ASS concentrations decreased the contact angle slightly. SPHs from ASS with higher DA had lower contact angles. SPH/ASS-AA01 demonstrated both fast swelling and superabsorbent properties despite a high contact angle, indicating that homogeneous pore structure and surface hydrophilicity are critical for capillary water absorption.

3.3.3. Enzymatic degradation test

Biodegradability of polysaccharide-based hydrogels is often required for biomedical applications (Spiridon, Popescu, Bodârlău, & Vasile, 2008). Generally, the glycosidic linkages in the polysaccharide chain are degradable by microorganisms and hydrolytic enzymes. α-Amylase (1,4-α-D-glucan glucanohydrolase) is an enzyme that hydrolyzes (1→4) linkages between α-D-glucopyranosyl residues in an endo action randomly within the polysaccharide chain. Ultimately, starch is converted to maltose and D-glucose. Starch-based SPHs could be completely degraded by α-amylase (Fig. 7). Immersion of SPHs at equilibrium into PBS containing the enzyme caused swelling ratios to slightly increase and then drastically decrease. The initial increase in the hydrogel mass results from the decrease in crosslinking density induced by enzymatic degradation of the hydrogels. After 10 h of enzymatic treatment, only about 20% of the original hydrogel mass remained and only hydrogel fractures were observed, followed by slow degradation due to the abundance of non-degradable chemical components in the fractures. All the SPHs with or without AA were completely degradable and were totally solubilized in aqueous media.

4. Conclusions

We prepared novel, biodegradable, starch-based SPHs by radical polymerization of starch sulfate containing vinyl groups (ASS) in the presence or absence of AA as a comonomer, accompanied by a gas blowing process. First, the starch was chemically modified to introduce hydrophilic sulfate groups without significant depolymerization. Second, the vinyl groups were coupled onto the starch through a simple and efficient method. Third, SPHs with different chemical compositions were prepared and compared. The SPH prepared with 30% AA and 6% ASS of DA = 5.33 had the best pore structure and showed fast swelling and superabsorbent properties. All SPHs could be degraded enzymatically. These biodegradable polysaccharide-based SPHs could be useful for various applications, including biomedical and other industrial fields.

Acknowledgements

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