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pH-responsive sodium alginate-based superporous hydrogel generated by an anionic surfactant micelle templating

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ABSTRACT

A novel sodium alginate-based superporous hydrogel (SPH) was prepared by the grafting copolymerization and micelle templating formed by the self-assembled anionic surfactant sodium *n*-dodecyl sulfonate (SDS). Fourier transform infrared (FTIR) spectra demonstrated that SDS was removed from the final hydrogel network. The formation mechanism of NaAlg-based SPH was proposed. Effect of SDS concentration on the morphologies and pore structure of the hydrogel was evaluated by Scanning Electron Microscopy (SEM), and the SDS-1.92 mM sample displays homogeneous and well-defined pores, which contribute to improve swelling ratio and swelling rate. The time-dependent swelling behaviors of the SDS-1.92 mM samples in various salt and pH solutions were investigated. The swelling in multivalent salt (Ca^{2+}, Al^{3+})/pH 2 solutions displayed a well-known “overshooting effect”, whereas, its swelling kinetics in Na^{+}/pH 3–12 solutions followed Schott’s pseudo second-order swelling kinetics model.

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1. Introduction

Hydrogels are lightly cross-linked polymeric network that are capable of swelling and absorbing large amounts of water without losing their physical dimension structure. Applications of hydrogels range from traditional agriculture to pharmaceutics (Almeida, Ferreira, Lopes, & Gil, 2011; Foungfung, Phattanarudee, Seetapan, & Kiatkamjornwong, 2011; Ozay, Ekici, Baran, Aktas, & Sahiner, 2009; Van Vlierberghe, Dubruel, & Schacht, 2011; Zohuriaan-Mehr, Omidian, Doroudiani, & Kabiri, 2010). Among them, superporous hydrogels (SPHs) are of particular interest and show great potential in various pharmaceutical and biomedical applications (Gils, Ray, & Sahoo, 2009; Jia, Young, & Moo, 2011; Yin et al., 2010). The advantageous fast swelling of SPHs is for a consequence of their interconnected open cellular structure. The superporous structure allows the faster diffusion of water molecules into the polymer network by reducing the transport resistance, and endows the hydrogels with additional space to hold more water. So, SPHs can generate rapid response to the external stimuli and possess higher total swelling capacity.

The creation of porosity in the hydrogels is the key to regulating the properties. Currently, available techniques for fabricating a porous hydrogel mainly include freeze-drying (Poursamara, Azamib, & Mozafari, 2011), gas-foaming (Park & Kim, 2006), water-soluble porogens (Delaney, Liberski, Perelaer, & Schubert, 2010) and phase-separation (Elbert, 2011). Among all of these techniques, the contradiction between the control of porosity and the convenience for pore-forming operation becomes a limiting factor. Emulsion templating is a facile approach for producing a well-defined and controllable pore structure (Busby, Cameron, & Jahoda, 2001; Cameron, 2005; Partap, Muthutantri, Rehman, Davis, & Darr, 2007; Partap, Rehman, Jones, & Darr, 2006). In aqueous solution, surfactants can self-assemble with each other to form micelles. These micelles can act as a template in the polymerization reaction to form porous materials with controlled pore size and applied in drug delivery system (Lee et al., 2010), tissue engineering (Barbetta, Barigelli, & Dentini, 2009; Ji, Khademhosseini, & Dehghani, 2011) and waste-water treatment (Chatterjee, Chatterjee, & Woo, 2010; Chatterjee, Lee, Lee, & Woo, 2010).

Recently, with the excessive consumption of petroleum resources and the increase in environmental pollution, natural polysaccharides have received great concerns as a renewable, biodegradable, non-toxic and biocompatible “green material”. Thus many polysaccharides including starch (Pang, Chin, Tay, & Tchong, 2011), cellulose (Chang, Duan, Cai, & Zhang, 2010), chitosan (Zhou, Ma, Shi, Yang, & Nie, 2011), alginate (Yang, Ma, & Guo, 2011) as well as the protein gelatin (Pourjavadi, Hosseinzadeh, & Sadeghi,

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2007) were utilized as starting materials for fabricating superabsorbent hydrogels. Sodium alginate (NaAlg) is a naturally occurred colloidal hydrophilic polysaccharide extracted from the brown seaweed (phaceophyceae) (Draget, SkjakBraek, & Smidsrod, 1997). It is a linear block copolymer consisting of (1,4)-α-L-glucuronic acid (G units) and (1,4)-β-D-mannuronic acid (M units), and was extensively used in foods, pharmaceuticals and agricultural areas (Augst, Kong, & Mooney, 2006). NaAlg with higher carboxylic content is expected to have superior hydrophilic properties and potential in absorbent applications. Many reports were available on the synthesis of superabsorbent hydrogels from NaAlg and multifunctional vinyl monomers (Cha, Kim, Kim, & Kong, 2011; Dumitriu, Mitchell, & Vasile, 2011; Sand, Yadav, Mishra, & Behari, 2010), but no substantial research on NaAlg-based SPHs preparing by micelle templating technique has been reported.

Based on our previous work for polysaccharides-based superabsorbent hydrogels (Shi, Wang, & Wang, 2011a; Shi, Wang, & Wang, 2011b), we prepared sodium alginate-*g*-poly(sodium acrylate-*co*-styrene)/attapulgite (NaAlg-*g*-P(NaA-*co*-St)/APT SPH using an anionic surfactant sodium *n*-dodecyl sulfonate (SDS) as the pore-forming templating. Fourier transform infrared (FTIR) spectra were used to confirm the successful synthesis of NaAlg-*g*-P(NaA-*co*-St)/APT hydrogel and removal of SDS from the final products by washing process. The effect of SDS concentration on the porosity of the hydrogel was investigated by Scanning Electron Microscopy (SEM). In addition, the effect of swelling medium (e.g. ionic strength and charge, pH) on the swelling kinetics of this SPH was investigated and analyzed by Schott's pseudo second-order swelling kinetics model.

2. Materials and methods

2.1. Materials

Sodium alginate (NaAlg) was purchased from Shanghai Chemical Reagents Corp. (Shanghai, China). Attapulgite clay (APT, milled and passed through a 200-mesh screen prior to use) was supplied by Gaojiawa Colloidal Co. (Jiangsu, China). Acrylic acid (AA, CP) and styrene (St, CP) were purchased from Shanghai Wulian Chemical Factory (Shanghai, China). Ammonium persulfate (APS, AR) was purchased from Xi'an Chemical Reagent Factory (Xi'an, China). *N,N'*-methylene-*bis*-acrylamide (MBA, AR) was purchased from Shanghai Chemical Reagent Corp. (Shanghai, China). Sodium *n*-dodecyl sulfonate (SDS) was also obtained from Shanghai Chemical Reagent Corp. (Shanghai, China) and used as received. Other agents used were all analytical grade, and all solutions were prepared with distilled water.

2.2. Preparation of NaAlg-g-P(NaA-co-St)/APT SPHs

NaAlg (1.20 g) was dissolved in 20 mL distilled water in a 250 mL four-necked flask under stirred at 60 °C. Then, a certain amount of SDS aqueous solution (0, 0.96, 1.92, 2.88 and 3.84 mM) was added and the mixture was stirred for 30 min to form a homogenous solution. The solution was purged with nitrogen to remove the dissolved oxygen, and 5 mL aqueous solution of initiator APS (0.100 g) was introduced and kept at 60 °C for 15 min to generate radicals. Afterward, the reaction system was cooled to 40 °C, and the mixture solution containing AA (7.20 g, 70% neutralized degree), St (0.150 g), crosslinker MBA (0.0216 g) and APT (0.928 g) was added. The reaction temperature was increased to 70 °C and maintained for 3 h to complete the polymerization reaction. The hydrogel product was firstly washed with ethanol/water (*v*/*v*, 7:3) to remove SDS, and then dehydrated by absolute ethanol. The dried product was ground and passed through 40–80 meshes (the particle size is 180–380 μm).

2.3. Measurement of swelling ratio

A conventional gravimetric method was adopted to determine the swelling ratio of the SPHs. Typically, 0.050 g of dry sample was immersed in 200 mL swelling medium at room temperature for 2 h to reach swelling equilibrium. The swollen hydrogel was filtrated from the unabsorbed water by a 100-mesh sieve, and drained for 10 min until no droplet drip down. The swelling ratio (S_{eq}, g/g) of the superporous hydrogel was calculated according to Eq. (1).

$$S_{eq} = \frac{m_s - m_d}{m_s} \tag{1}$$

Here, m_d is the mass of dried sample (g), and m_s is the mass of swollen hydrogel (g). The data points represent mean ± SD from three repeated experiments.

2.4. Measurement of swelling kinetics

0.050 g dry sample was soaked in 200 mL swelling medium. At certain time intervals, the swelling ratio at t (s) moment (S_t, g/g) was calculated according to Eq. (1), correlating the mass of the swollen hydrogel (m_t) at given time to the dry sample (m_d).

2.5. Characterizations

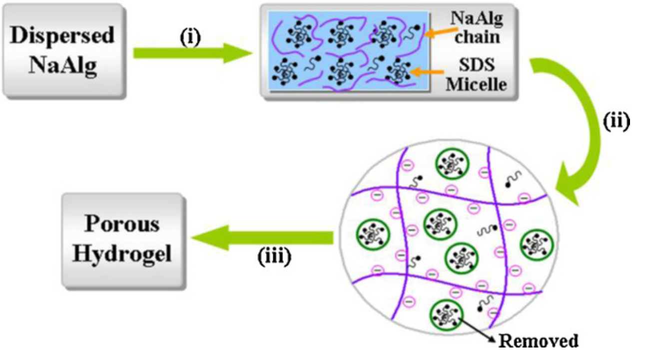
Fourier transform infrared spectroscopy (FTIR) of the dry samples was taken on a Nicolet NEXUS FTIR spectrometer in the wave-number region of 4000–400 cm^{-1} using KBr pellet. For investigating the effect of SDS concentration on the porosity of the hydrogels, the surface morphologies of the xerogels were recorded by an S-4800 Scanning Electron Microscopy (SEM) after sputter-coating the specimens with gold film.

3. Results and discussion

3.1. Preparation and characterization of NaAlg-g-P(NaA-co-St)/APT SPHs

A proposed mechanism for the formation of NaAlg-*g*-P(NaA-*co*-St)/APT SPHs by an anionic surfactant SDS micelle templating is shown in Scheme 1. In NaAlg solution, the self-assembly of SDS can form spherical micelles. In the process of grafting copolymerization and crosslinking, these micelles may be enclosed in the network and act as a template for pore-forming. After removed SDS micelles by a washing process, the superporous structure was generated.

FTIR spectroscopy was employed to verify the chemical structure of NaAlg-*g*-P(NaA-*co*-St)/APT hydrogel and removal of SDS



Scheme 1. Proposed reaction scheme for the synthesis of NaAlg-based SPHs using SDS micelle templating.

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