Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly(sodium acrylate) and polyvinylpyrrolidone

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ABSTRACT

A pH-sensitive semi-interpenetrating polymer network (semi-IPN) superabsorbent hydrogel composed of sodium alginate-g-poly(sodium acrylate) (NaAlg-g-PNaA) network and linear polyvinylpyrrolidone (PVP) was prepared by free-radical solution polymerization in the presence of initiator ammonium persulfate (APS) and crosslinker N,N-methylene-bis-acrylamide (MBA). FTIR results revealed that PNaA had been grafted onto NaAlg macromolecular chains and PVP was penetrated throughout the NaAlg-g-PNaA network by a hydrogen binding action. The surface morphologies of the hydrogels were improved due to the incorporation of PVP as shown by SEM observation. The introduction of PVP and the formation of semi-IPN structure greatly improved the water absorption and swelling rate of the hydrogel. The hydrogel possesses remarkable sensitivity to external pH stimulus and shows reversible On–Off switching swelling characteristic. An intriguing time-dependent swelling behavior of the semi-IPN hydrogel was observed in multi-valence saline and cationic surfactant solutions, but the similar time-dependent behaviors are resulting from two distinct mechanisms.

1. Introduction

Superabsorbent hydrogels (SAHs) are moderately crosslinked 3-D hydrophilic network polymers that can absorb and conserve considerable amounts of aqueous fluids even under certain heat or pressure. Because of the unique properties superior to conventional absorbents, SAHs have found potential application in many fields such as agriculture (Karadağ, Saraydin, Çaldiran, & Güven, 2000; Liu, Liang, Zhan, Liu, & Niu, 2006; Puoci et al., 2008), hygiene products (Kosemund et al., 2009), wastewater treatment (Kaşgöz & Durmus, 2008; Kaşgöz, Durmuş, & Kaşgöz, 2008; Wang, Zhang, & Wang, 2008), sealing material (Vogt, Roehlen, & Tennie, 2005) and drug delivery system (Sadeghi & Hosseinzadeh, 2008), etc. Currently, the further extension of application domains of SAHs was limited because the practically available SAHs are mainly petroleum-based synthetic polymer with high production cost and poor environmental friendly properties (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002). Hence, the development of multi-component superabsorbents derived from natural polymer and eco-friendly additives become subject of great interest due to their unique commercial and environmental advantages (Kurita, 2001), and such materials have also been honored as the material families

of "in greening the 21st century materials world" (Ray & Bousmina, 2005). Thus far, many natural polymers such as starch (Lanthonga, Nuisinb, & Kiatkamjornwong, 2006; Li, Zhang, & Wang, 2007), cellulose (Suo, Qian, Yao, & Zhang, 2007), chitosan (Mahdavinia1, Zohuriaan-Mehr, & Pourjavadi1, 2004; Zhang, Wang, & Wang, 2007), guar gum (Wang & Wang, 2009) and gelatin (Pourjavadi, Hosseinzadeh, & Sadeghi, 2007), etc. have been utilized for fabricating multi-component superabsorbents, and it was concluded that the composition and preparation technologies of superabsorbents are the dominant factors affected the properties of SAHs.

Semi-interpenetrating polymer networks (semi-IPN) is a way of blending two polymers where only one is crosslinked in the presence of another to produce an additional non-covalent interaction between the two polymers (Sperling, 1981). Semi-IPNs have been developed as a convenient technique of preparing multi-component polymer materials and provided a convenient route to modify the properties of natural polymer-based hydrogels (Krishna Rao, Vijaya Kumar Naidu, Subha, Sairam, & Aminabhavi, 2006). Semi-IPN materials are unique "alloys" of crosslinked polymers, and the formed "double network" or semi-IPN systems usually exhibited surprising properties superior to either of the two single polymer alone (Myung et al., 2008). It was regarded as a facile and preferred technology to design multi-component materials based on natural macromolecules.

Sodium alginate (NaAlg) is an anionic natural macromolecule, which is composed of poly-β-1, 4-D-mannuronic acid (M units) and $\alpha - 1$, 4-L-glucuronic acid (G units) in varying proportions by 1–4 linkages. NaAlg can be extracted from marine algae or produced by bacteria, and so it is abundant, renewable, non-toxic, water-soluble, biodegradable and biocompatible. In addition, NaAlg can be easily modified through various chemical or physical methods such as grafting copolymerization with hydrophilic vinyl monomers (Işıklan, Kurşun, & İnal, 2010), polymer blending (Sæther, Holme, Maurstad, Smidsrød, & Stokke, 2008) and compounding with other functional components (Hua & Wang, 2009). By virtue of these advantages, NaAlg has received considerable attention in industrial and medical fields (Lin, Liang, Chung, Chen, & Sung, 2005; Yoo, Song, Chang, & Lee, 2006). Polyvinylpyrrolidone (PVP) is a non-ionic water-soluble linear polymer. It has been applied in medicine, pharmaceuticals, cosmetics, foods, printing inks, textiles, and many other fields due to its good solubility, excellent affinity to various polymers and resins, non-toxicity, biodegradability and compatibility (Robinson, Sullivan, Borzelleca, & Schwartz, 1990). By right of the compatibility, PVP was considered as a suitable component for the preparation of semi-IPN hydrogel (Jin, Liu, Zhang, Chen, & Niu, 2006). It is expected that the new type of SAHs with improved structure and performance can be developed by the effective combination of NaAlg with PVP through semi-IPN technique.

Based on above description, in this work, the highly swollen pH-sensitive sodium alginate-g-poly(sodium acrylate)/polyvinylpyrrolidone (NaAlg-g-PNaA/PVP) semi-IPN SAHs were synthesized by the free-radical graft copolymerization and semi-IPN technology. The structure and morphologies of the semi-IPN hydrogels were characterized by Fourier Transformation Infrared Spectra (FTIR) and Scanning Electron Microscope (SEM). And the effects of reaction conditions on the crosslinking density and water absorption of NaAlg-g-PNaA/PVP were investigated. In addition, the swelling kinetics, pH-sensitivity and the time-dependent swelling behaviors of the semi-IPN hydrogels in various media were also evaluated systematically.

2. Experimental

2.1. Materials

Sodium alginate (NaAlg) was from Shanghai chemical reagents Co., Shanghai, China. Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, China) and N,N-methylene-bis-acrylamide (MBA, chemically pure, Shanghai Chemical Reagent Corp., China) was used as received. Polyvinylpyrrolidone (PVP, AR grade, the average molecular weight $M_r = 10,000$) was purchased from Tianjin Kermel Chemical Reagents Development Center. Cetyltrimethylammonium bromide (CTAB) was supplied by Beijing Chemical Reagents Company (Beijing, China). All other chemicals were of analytical reagent grade and solutions were prepared with purified water.

2.2. Preparation of NaAlg-g-PNaA/PVP semi-IPN SAHs

A calculated amount of NaAlg powder (1.03 g) and PVP (0.17–2.09 g) was dissolved in 30 mL purified water in a 250-mL four-necked flask equipped with a mechanical stirrer, a reflux condenser, a nitrogen line and a thermometer to form a sticky solution. The solution was heated to 60 °C with an oil bath and purged with N_2 for 30 min to remove the dissolved oxygen. Then, a 5 mL of aqueous solution of initiator APS (0.0576 g) was dropwise

added under continuous mechanical stirring and kept at 60 °C for 10 min to generate radicals. A 7.2 g of acrylic acid (AA) was neutralized using 7.6 mL 8.8 mol/L NaOH solutions to reach a total neutralization degree of 65%, and then 18 mg crosslinker MBA was dissolved in the partially neutralized acrylic acid (NaA) under magnetic stirring. After cooled the reactants to 50 °C, the mixture solution of NaA and MBA was added into the flask and the temperature was slowly risen to 70 °C and kept for 3 h to complete polymerization. Continuous purging of nitrogen was used throughout the reaction period. Finally, the resultant gel products were dried to constant weight at 70 °C, and the dried gels were ground and passed through 40–80 mesh sieve (180–380 μm). NaAlg-g-PNaA SAH was prepared according to a similar procedure except without addition of PVP.

2.3. Measurements of equilibrium water absorbency and swelling kinetics

The SAH particles (0.05 g) with the size of 180–380 μm was soaked in excess of aqueous solutions at room temperature for 4 h to reach a swelling equilibrium. The swollen gels were filtered by 100-mesh screen and drained on the screen for 10 min until no free water remained. After weighing the swollen gels, the equilibrium water absorption of the SAHs can be calculated using Eq. (1).

$$Q_{eq} = (w_s - w_d)/w_d \tag{1}$$

Q_{eq} is the equilibrium water absorption calculated as grams of water per gram of superabsorbent sample; w_d and w_s are the weights of the dry sample and swollen sample, respectively.

The swelling kinetics of SAHs in each solution was measured according to following procedure: 0.05 g of sample was contacted with aqueous solutions in 500 mL beakers at set intervals (1, 3, 5, 8, 10, 20, 30, 60, 120 and 240 min), and then the swollen SAHs were filtered using a sieve and drained for 10 min. After weighting the swollen gels, the water absorption of SAHs at a given moment can be calculated according to Eq. (1). In all cases three parallel measurements were carried out and the averages were reported in this paper.

2.4. Evaluation of pH-sensitivity

The buffer solutions with various pH values were prepared by combining KH_2PO_4, K_2HPO_4, H_3PO_4, NaCl and NaOH solution properly. Ionic strengths of all the buffer solutions were adjusted to 0.1 M with NaCl solution. The pH values were determined by a pH meter (DELTA-320). The equilibrium water absorption (Q_{eq}) in various pH solutions was determined by a method similar to that in distilled water. The pH reversibility of the SAHs was investigated in terms of its swelling and deswelling in pH buffer solution of phosphate between pH 7.2 and 2.0. The consecutive time interval is 15 min for each cycle.

2.5. Network parameter Mc

For each superabsorbent hydrogel, the crosslinking density was expressed as the average molar mass among the crosslink points, Mc, and Mc values can be determined according to a previously developed method (Li, Lin, & Wu, 2000; Li, Xu, Wang, Chen, & Feng, 2009). Mc is reversibly proportional to crosslinking density.

2.6. Characterizations

FTIR spectra were recorded on a Nicolet NEXUS FTIR spectrometer in 4000–400 cm^{-1} region using KBr pellets. The morphologies of the samples were examined using a JSM-5600LV SEM instrument (JEOL) after coating the sample with gold film.

3. Results and discussion

3.1. Synthesis of NaAlg-g-PNaA/PVP semi-IPN SAHs

The semi-IPN SAHs can be formed in aqueous solution by a synchronous chemical and physical process involved with the graft of NaA onto NaAlg, the crosslinking reaction of MBA and the interpenetration of linear PVP chains (Scheme 1). The initiator APS was firstly decomposed under heating to generate sulfate anion-radicals. These radicals striped down the hydrogen of —OH groups on NaAlg chains to form macro-radicals. After added NaA monomers, the active radical sites on NaAlg may initiate vinyl of the monomers to process chain propagation. During the chain propagation, the end vinyl groups of crosslinker MBA may react synchronously with different polymer chains to form polymeric network, and the linear PVP also combined and interpenetrated with this network through hydrogen-bonding interaction.

3.2. FTIR spectra analysis

FTIR spectra of NaAlg, PVP, NaAlg-g-PNaA, NaAlg-g-PNaA/PVP (15 wt.%) and the physical mixture of NaAlg with PNaA are depicted in Fig. 1. It can be noticed that, (i) the characteristic absorption bands of NaAlg at 1098 and 1031 cm^{-1} (stretching vibration of C—OH groups) were obviously weakened after reaction, but these bands can be observed in the spectrum of the physical mixture of NaAlg and PNaA with a certain intensity (Fig. 1(e)). The new bands at 1704 cm^{-1} (asymmetric stretching vibration of —COOH groups), 1571 cm^{-1} (asymmetric stretching vibration of —COO$^-$ groups), 1454 and 1409 cm^{-1} (symmetric stretching vibration of —COO$^-$ groups) were observed in the spectrum of NaAlg-g-PNaA (Fig. 1(b)), which indicate that PNaA chains have been grafted onto the NaAlg backbone; (ii) the characteristic absorption bands of NaAlg at 1620 cm^{-1} (asymmetrical stretching vibration of —COO$^-$ groups), 1419 cm^{-1} (symmetrical stretching vibration of —COO$^-$ groups) were overlapped with the —COO$^-$ absorption of PNaA in this range; (iii) the C=O absorption band of PVP at 1653 cm^{-1} and the —COOH absorption band of NaAlg-g-PNaA at 1704 cm^{-1} shifted to 1663 cm^{-1} after forming SAH, which suggested strong hydrogen-bonding interaction between —COOH and —C=O groups (Lin, Guan, Zhang, Xu, & Zhu, 2009); (iv) the characteristic absorption bands of PVP centered at 1494, 1463 and 1422 cm^{-1} (C—N) and 1289 cm^{-1} also appeared in the spectrum of semi-IPN SAH. These information indicate that the linear PVP polymer chains were existed in the network of semi-IPN SAHs, and combined with the NaAlg-g-PNaA network by hydrogen-bonding interaction.

3.3. Morphological analyses

For investigating the change of surface morphology of the SAHs resulting from the incorporation of PVP, the SEM micrographs of NaAlg-g-PNaA and NaAlg-g-PNaA/PVP (5, 15 and 20 wt.%) semi-
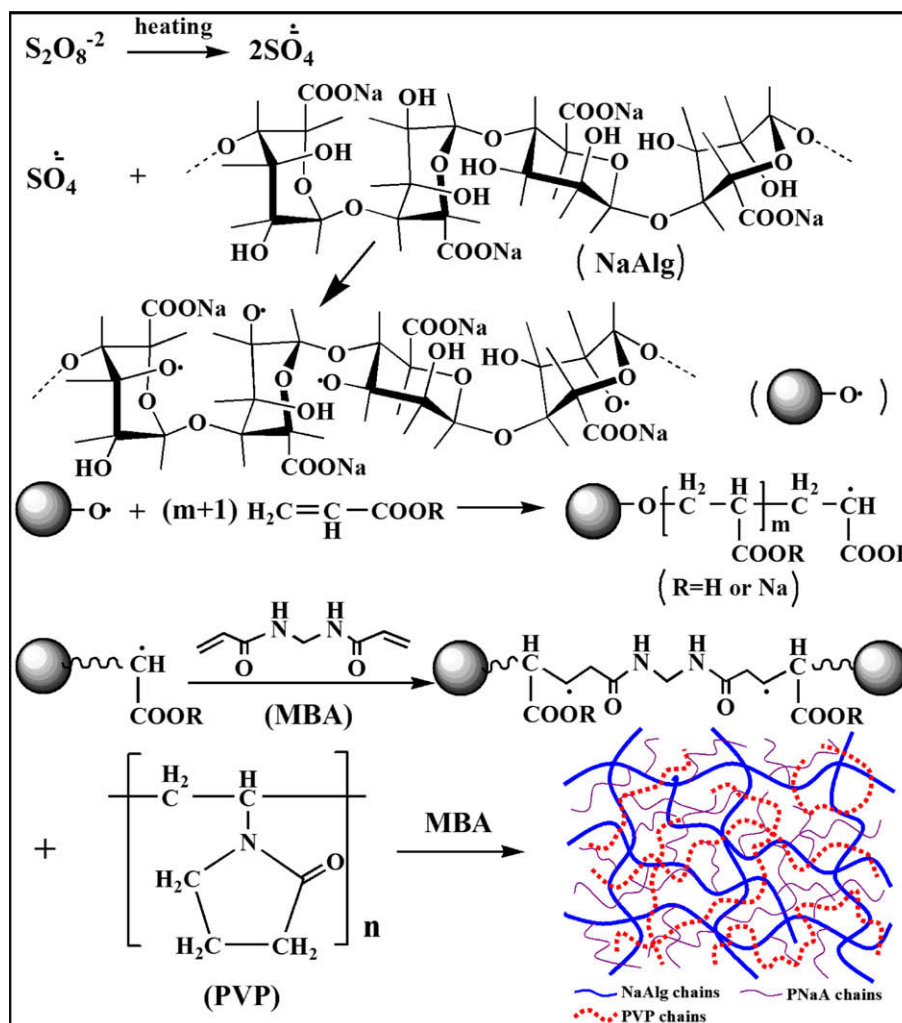
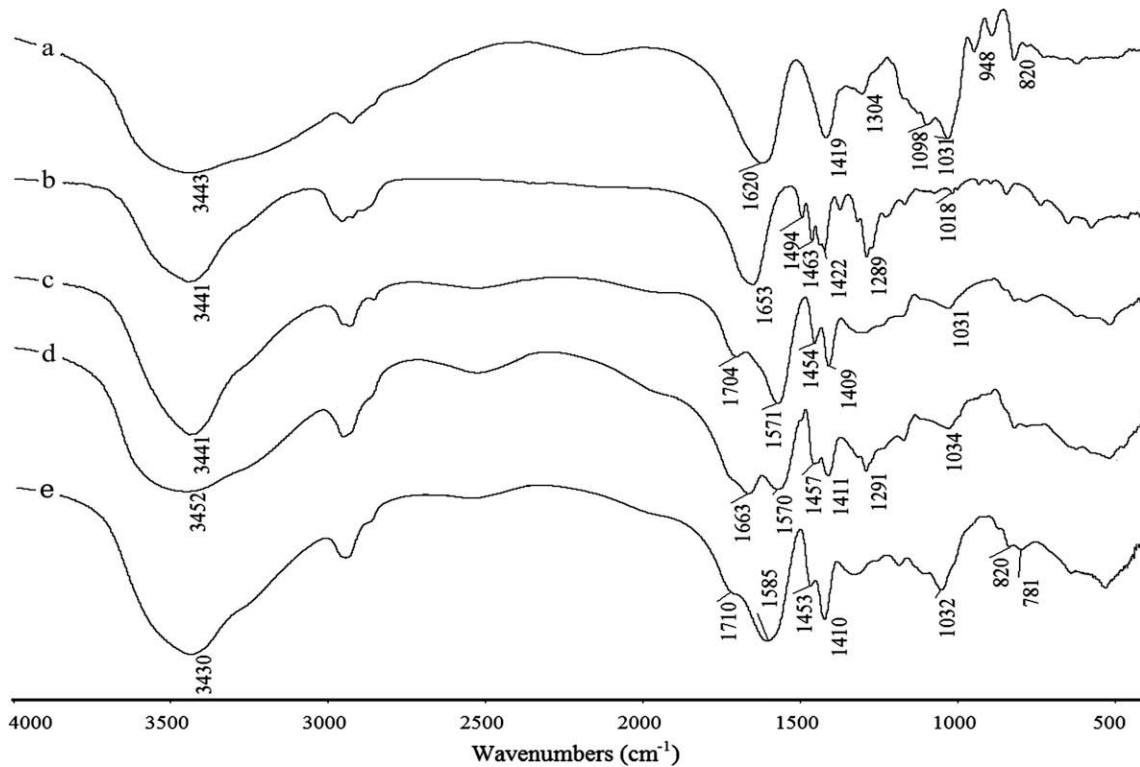**Scheme 1.** Proposed reaction mechanism for the formation of semi-IPN SAHs.

Fig. 1. The FTIR spectra of (a) NaAlg, (b) PVP, (c) NaAlg-g-PNaA, (d) NaAlg-g-PNaA/PVP (15 wt.%) and (e) the physical mixture of NaAlg and PNaA.

IPN SAHs were observed and are shown in Fig. 2. As can be seen, NaAlg-g-PNaA shows a smooth and dense surface, whereas NaAlg-g-PNaA/PVP semi-IPN SAHs exhibited a comparatively loose and coarse surface. The surface roughness increased with increasing the content of PVP, and some pores and gaps can be observed on the surface of semi-IPN SAHs with 15 and 20 wt.% PVP
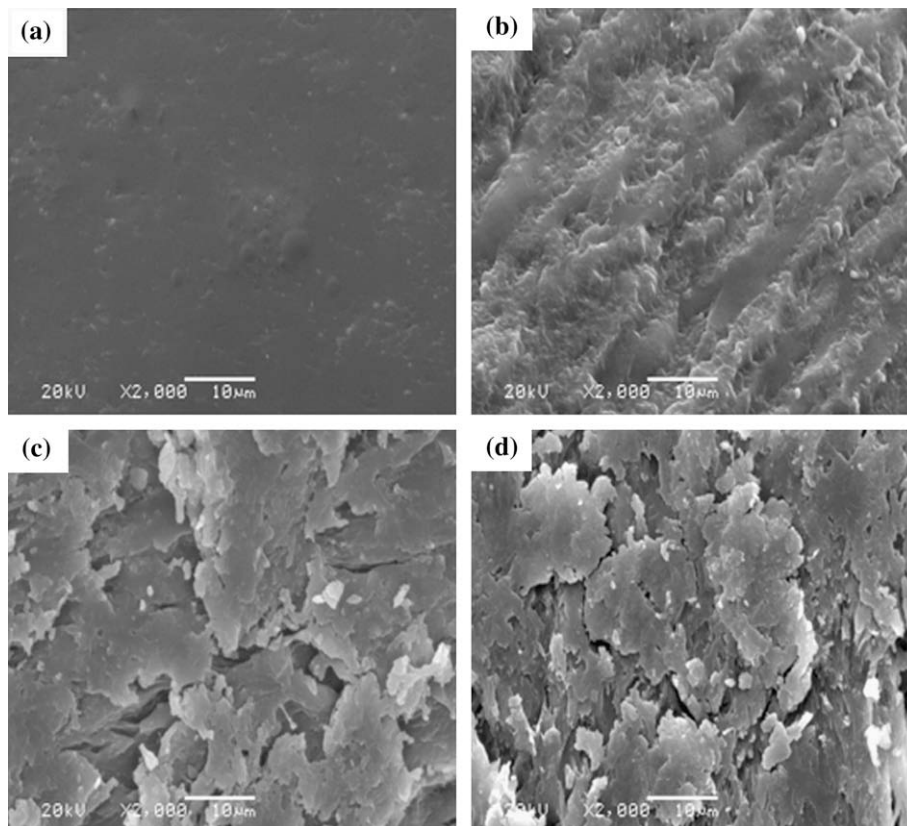

Fig. 2. SEM micrographs of (a) NaAlg-g-PNaA, (b–d) NaAlg-g-PNaA/PVP semi-IPN SAHs containing 5, 15 and 20 wt.% of PVP, respectively.

compared with NaAlg-g-PNaA and NaAlg-g-PNaA/PVP (5 wt.%) (Fig. 2(b and c)). This observation revealed that the introduction of PVP facilitates to improve the surface and network structure of SAH and the improved surface is convenient for the penetration of water into the polymeric network and is favorable to the enhancement of water absorption. Moreover, this observation also gives a direct revelation that PVP are almost embedded and dispersed within NaAlg-g-PNaA matrix without coacervation.

3.4. Effects of NaAlg content on Mc and water absorption

As shown in Fig. 3(a), the Mc of the semi-IPN hydrogel increased with increasing the content of NaAlg until a maximum value of 5, 369, 160 was reached at 11.08 wt.% of NaAlg, and then Mc decreased. Similarly, the variation of water absorption with increasing content of NaAlg showed the same tendency (Fig. 3(a′)), and the highest water absorption was achieved at the content of NaAlg at 11.08 wt.%. This result indicates that NaAlg content affected the crosslinking density and the water absorption. In the reaction

system, the amount of initiator APS is definite and the number generated by the decomposition of APS is also invariable. When the dosage of NaAlg is less, the radical reactive sites on NaAlg chains were distributed thick and fast. After some monomers being grafted on the active sites, the formed graft chains generated a steric hindrance and prevent the grafting of other monomers in these grafting sites. These superfluous NaA monomers tend to copolymerize and accelerate the free-radical polymerization reaction, forming a dense polymeric network. As a result, the Mc increased with increasing the dosage of NaAlg due to the formation of more branched multiple side chains (Peng, Xu, Peng, Wang, & Zheng, 2008). So the water absorption was also greatly improved with increasing the content of NaAlg from 8.02 to 11.08 wt.%. However, when the content of NaAlg increased beyond 11.08 wt.%, the viscosity of NaAlg solution sharply increased and the initiation efficiency decreased, and the reactive sites on NaAlg can not be adequately formed. Consequently, both grafting efficiency and the molecular weight of the grafted PNaA chains decreased, which also results in a decreased Mc and reduced water absorption (Reyes, Syz, Huggins, & Russell, 1968). These
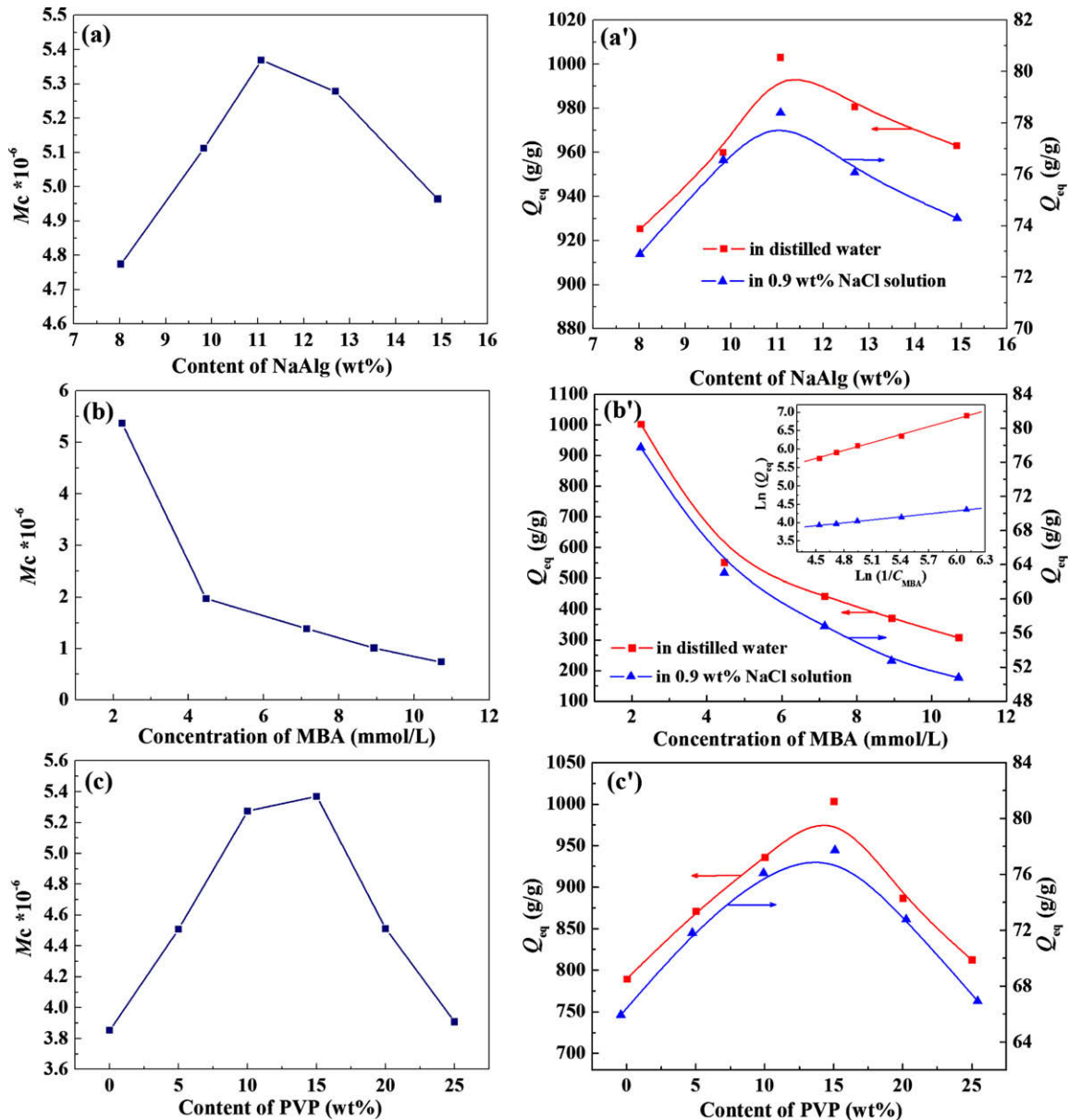

Fig. 3. Effect of NaAlg content on Mc (a) and water absorption (a′); Effect of MBA concentration on Mc (b) and water absorption (b′), the inset illustration in (b′) is the plots of $Ln(Q_{eq})$ versus $Ln(1/C_{MBA})$; and Effect of PVP content on Mc (c) and water absorption (c′).

results indicate that only introducing moderate amounts of NaAlg is favorable to improve the swelling properties of the semi-IPN superabsorbent hydrogel.

3.5. Effects of MBA concentration on Mc and water absorption

Fig. 3(b and b′) depicted the effects of MBA concentration on Mc and water absorption, respectively. As can be seen, the Mc of the semi-IPN hydrogel decreased with increasing MBA concentration. The same tendency was also observed in the effect of MBA concentration on water absorption (Fig. 3(b′)), in which the water absorption sharply decreased with increasing the MBA concentration from 2.23 to 10.72 mmol/L. This is because that higher concentration of crosslinker MBA produces a larger degree of polymer chains branching and generates an additional network (Peng et al., 2008). As a result, the Mc decreased and the water absorption reduced. As described previously (Kabiri, Omidian, Hashemi, & Zohuriaan-Mehr, 2003), the relation between equilibrium water absorption (Q_{eq}, g/g) and MBA concentration (C_{MBA}, mol/L) follows a power law as shown in Eq. (2) and its logarithmic form Eq. (3).

$$Q_{eq} = kC_{MBA}^{(-n)} \tag{2}$$
$$Ln(Q_{eq}) = Lnk + nLn(1/C_{MBA}) \tag{3}$$

k and n are constant for an individual SAH. The plots of $Ln(Q_{eq})$ versus $Ln(1/C_{MBA})$ gives perfect straight line with better linear correlation coefficient (Inset illustration in Fig. 3(b); $R > 0.9982$), and so the k and n values can be calculated through the slope and intercept of the straight lines. For the NaAlg-g-PNaA/PVP (15 wt.%) semi-IPN SAH, the effect of MBA concentration on equilibrium water absorption follows the relation $Q_{eq} = 12.37\ C_{MBA}^{(-0.7180)}$ in distilled and $Q_{eq} = 14.79\ C_{MBA}^{(-0.2707)}$ in 0.9 wt.% NaCl solution.

3.6. Effects of PVP content on Mc and water absorption

In this section, the effect of PVP content on the Mc and water absorption of NaAlg-g-PNaA/PVP semi-IPN SAH was investigated and is shown in Fig. 3(c and c′), respectively. With increasing the content of PVP, the Mc of the semi-IPN SAH firstly increased and then decreased. Also, the water absorption of the semi-IPN SAH enhanced with increasing PVP content until a maximum absorption (1004 g/g in distilled water and 78 g/g in 0.9 wt.% NaCl solution) was achieved at 15 wt.% of PVP. This result indicates that the water absorption of the semi-IPN hydrogel is dependent on the crosslinking density. In addition, the great increase of water absorption can be ascribed to the fact that, (i) PVP molecules can act as dispersant during the polymerization reaction, which enhances dispersion of the reactants and improve the network structure of the superabsorbent; (ii) the incorporation of non-ionic PVP chains also increased the number of non-ionic groups in polymeric network. According to previous report (Wu, Lin, Li, & Wei, 2001), the collaborative absorption effect of —C=O(N), —COOH and —COO⁻ groups is superior to either of single groups; (iii) the hydrophobic alkyl chain ends of PVP may form a tiny hydrophobic regions and facilitate to the formation of a regular polymeric network. However, the excess of PVP may tangle with the graft polymeric chains, and the physical crosslinking was formed when the PVP content exceeding 15 wt.%. This restricts the penetration of water molecules into the semi-IPN SAH and decreased water absorption.

3.7. Swelling kinetics

The incorporation of PVP and the formation of semi-IPN structure can not only affect the water absorption of the SAHs, but also can influence their swelling kinetics. As shown in Fig. 4, the swelling rate of the semi-IPN SAHs with various amounts of PVP is faster within 1200 s

and then reached a plateau. For evaluating the dynamic swelling properties of the SAHs, the Schott's pseudo second order kinetics model was adopted and can be expressed as Eq. (4) (Schott, 1992).

$$t/Q_t = 1/K_{is} + (1/Q_\infty)t \tag{4}$$

Q_t (g/g) is the water absorption at swelling time t (s); Q_∞ (g/g) is the power parameter, denoting the theoretical equilibrium water absorption; K_{is} is the initial swelling rate constant (g/g·s). According to Eq. (4), the plots of t/Q_t versus t give a perfect straight line with good linear correlation coefficient (Fig. 4(b)). This indicates that the pseudo second order model is suitable for evaluating the swelling kinetics of the SAHs. In addition, the K_{is} and Q_∞ values can be calculated through the slope and intercept of above straight lines. The K_{is} values are 9.0843, 9.9950, 10.8542, 7.9409 and 7.0827 g/g·s, Q_∞ values are 800, 870, 943, 1012 and 893 g/g for NaAlg-g-PNaA, NaAlg-g-PNaA/PVP (5 wt.%), NaAlg-g-PNaA/PVP (10 wt.%), NaAlg-g-PNaA/PVP (15 wt.%) and NaAlg-g-PNaA/PVP (20 wt.%), respectively. By analysing the values of K_{is} and Q_∞ for each SAH, it can be concluded that the initial swelling rate decreased as the order: NaAlg-g-PNaA/PVP (10 wt.%) > NaAlg-g-PNaA/PVP (5 wt.%) > NaAlg-g-PNaA > NaAlg-g-PNaA/PVP (15 wt.%) > NaAlg-g-PNaA/PVP (20 wt.%). This result indicates that the incorporation of moderate amount of PVP is favorable to enhance the swelling rate, but the excessive addition of PVP decreased it.

3.8. pH-sensitivity

Fig. 5(a) depicted the dependence of water absorption for NaAlg-g-PNaA/PVP semi-IPN SAH on pH of external buffer solution
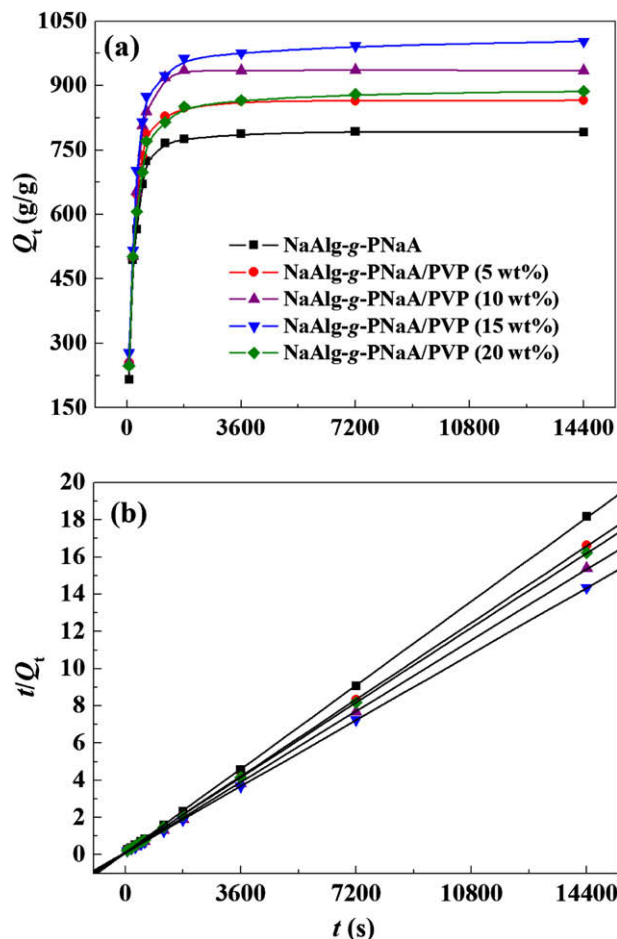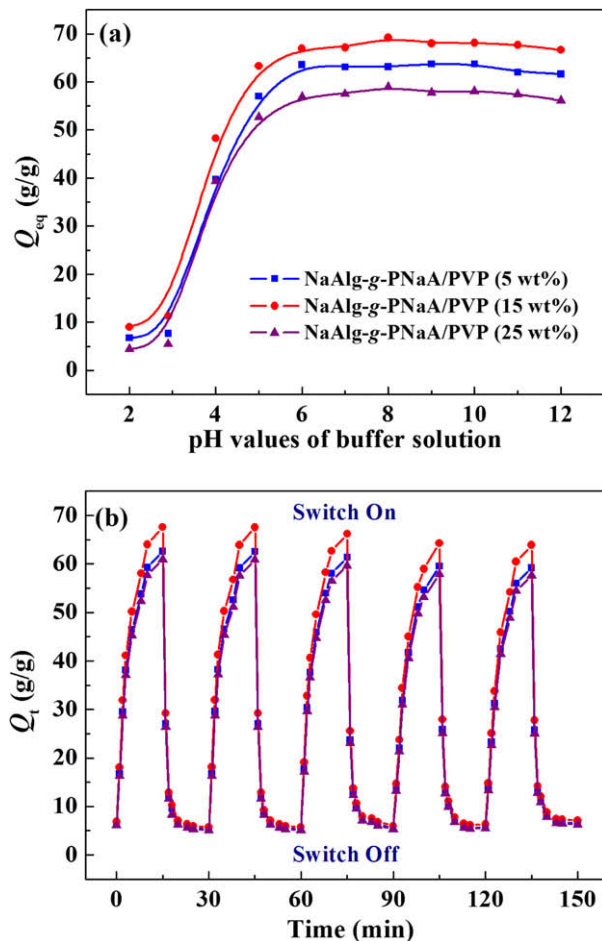

Fig. 4. Swelling kinetic curves of the semi-IPN SAHs in distilled water (a) and the plots of t/Q_t against t for each hydrogel (b).

(0.10 mol/L). It can be clearly observed that the SAH almost does not swell at pH 2, but it sharply swell as enhancing external pH values until a plateau was reached (pH > 4). The evident change of water absorption with altering the pH of external buffer solution confirmed the excellent pH-sensitive behavior of NaAlg-g-PNaA/PVP semi-IPN SAH. The intriguing behavior of the semi-IPN SAH can be ascribed to the following reason. As an anionic polymer, the semi-IPN SAH contains numerous hydrophilic —COO$^-$ and —COOH groups that can convert with each other. In extreme acid medium (pH 2), the —COO$^-$ groups transformed into —COOH groups. On the one hand, the hydrogen-bonding interaction among —COOH groups was strengthened and the additional physical crosslinking was generated; on the other hand, the electrostatic repulsion among —COO$^-$ group was restricted, and so the SAH network tends to shrink. As increasing external pH, the ratio of —COO$^-$ groups in polymer network increased. Consequently, the hydrogen-bonding interaction was broken and the electrostatic repulsion among negatively charged polymer chains increased, and so the polymer network tends to swell more. For evaluating the pH reversibility of the SAH, the swelling–deswelling behavior was investigated in 0.1 mol/L buffer solution of phosphate between pH 2 and 7.2 (Fig. 5(b)). It can be noticed that the SAH exhibited higher swelling capability at pH 7.2, but the swollen gel rapidly shrinks at pH 2 and the intriguing On–Off switching effect was observed. After five On–Off cycles, the SAH still has better sensitivity, indicating that the semi-IPN SAH possess excellent pH reversibility.
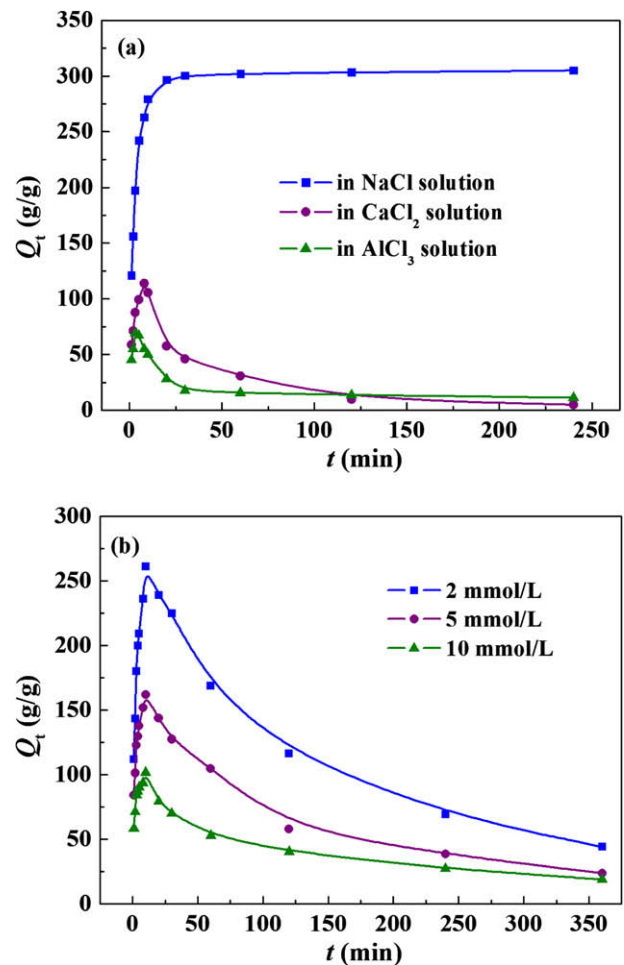
3.9. Time-dependent swelling behaviors in saline solution

As shown in Fig. 6(a), the water absorption of the semi-IPN SAH in CaCl$_2$ and AlCl$_3$ solutions increased with prolonging contact time, reached a maximum absorption and then decreased with further prolonging contact time until swelling almost disappeared; however, no similar behaviors can be observed in NaCl solution. The intriguing time-dependent swelling effect can be attributed to the following reasons. In multi-valence saline solution, Ca^{2+} and Al^{3+} may complex with hydrophilic —COO$^-$ groups to form an additional crosslinking (Hua & Wang, 2009; Pourjavadi, Amini-Fazl, & Hosseinzadeh, 2005), and so the crosslinking degree of SAH network increased with prolonging the contact time. As a result, the swollen SAH network gradually collapsed and the initially absorbed water was squeezed out of the network under this action. Because Na$^+$ has no complexing action with —COO$^-$ groups, there is no time-dependent swelling effect in NaCl solution.

3.10. Time-dependent swelling behaviors in surfactant solutions

Fig. 6(b) represented the dependence of water absorption of the semi-IPN SAH on time in various surfactant solutions at different concentrations. It can be obviously observed that the SAH exhibited time-dependent swelling behavior in aqueous solution of cationic surfactant CTAB at each concentration. In addition, the required time reaching the maximum swelling in high concentra-

Fig. 5. (a) Variation of water absorption for NaAlg-g-PNaA/PVP (5, 15 and 25 wt.%) semi-IPN SAHs at the buffer solution of various pH values, and (b) the On–Off switching behavior as reversible pulsatile swelling (pH 7.2) and deswelling (pH 2.0) of the semi-IPN SAHs.

Fig. 6. (a) Kinetic swelling curves of the semi-IPN hydrogel in 5 mmol/L saline solution with various valence; (b) kinetic swelling curves of NaAlg-g-PNaA/PVP (15 wt.%) in 2, 5 and 10 mmol/L CTAB solutions.
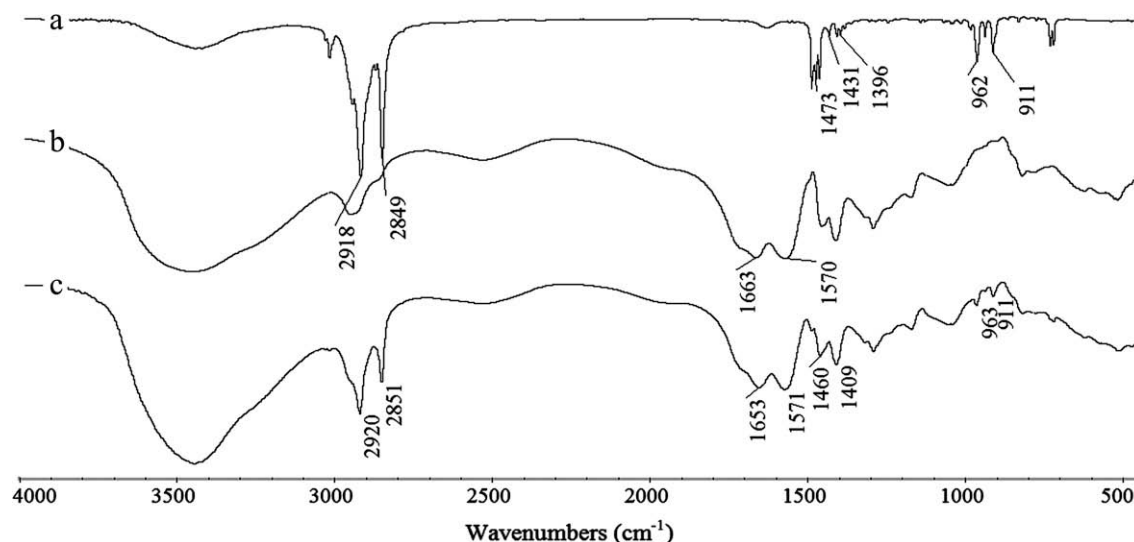
Fig. 7. FTIR spectra of (a) CTAB, (b) the NaAlg-g-PNaA/PVP semi-IPN SAH before swelling and (c) the NaAlg-g-PNaA/PVP semi-IPN SAH after swelling in 5 mmol/L CTAB solution.

tion of CTAB is less than that in low concentration. Different from the chemical crosslinking in multi-valence saline solution, the time-dependent swelling of the SAH in CTAB is arisen from the collaborative effects of three physical actions: (i) the hydrogen-bonding interactions among the —COOH, —COO⁻, —OH and R − NH₄⁺ cations generated an additional physical crosslinking to make the network shrink; (ii) the electrostatic screen of positively charged quaternary ammonium cations to negatively charge —COO⁻ groups screened the negative changes of —COO⁻ groups and weakened the repulsion among polymer chains; (iii) the hydrophobic interaction of long alkyl chains in crosslinked network. In this process, the entrance of CTAB with long alkyl chains into the polymer network decreased its hydrophilicity, which is also responsible for the deswelling of the semi-IPN SAH. FTIR spectra (Fig. 7) showed the change of functional groups of NaAlg-g-PNaA/PVP after swelling in 5 mmol/L CTAB solution. The characteristic absorption bands of CTAB can be clearly observed in the spectra of the SAH after swelling in CTAB solution. This indicates that the CTAB has entered into polymer network during swelling. Compared with the spectrum of SAH before swelling, the —COOH and —COO⁻ absorption bands of the SAH after swelling shifted from 1663 to 1653 cm⁻¹ (for —COOH) and from 1570 to 1571 cm⁻¹ (for —COO⁻), which confirmed that some hydrogen-bonding interaction occurred among —COOH and quaternary ammonium cations.

4. Conclusions

As an effort to develop new kinds of SAHs with improved structure and environmental friendly property, to reduce the excessive consumption of petroleum resource and minimize the pollution resulting from the industrial polymers, new type of semi-IPN SAHs composed of NaAlg-g-PNaA and PVP were synthesized by free-radical graft copolymerization and semi-interpenetrating techniques. FTIR analysis confirmed that the PNaA chains had been grafted onto the macromolecular chains of NaAlg, and PVP chains were interpenetrated throughout the polymer network and combined with the network by hydrogen-bonding interaction. After forming semi-IPN SAH, the surface morphologies, swelling capabilities and swelling rate were greatly improved. The semi-IPN SAH exhibited excellent pH-sensitive behavior and On–Off switching swelling characteristics with better reversibility. The intriguing time-dependent swelling behaviors were observed in multi-valence sal-

ine and cationic surfactant solution, which is caused by additional chemical crosslinking in saline solution and is induced by strong physical crosslinking action in cationic surfactant solution. The semi-IPN SAHs based on renewable and biodegradable natural NaAlg and biocompatible PVP exhibited satisfactory swelling properties and pH-sensitivity, which can be used as potential candidate for water-manageable materials or drug delivery system.

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