

Enhanced Swelling Properties of a Novel Sodium Alginate-Based Superabsorbent Composites: NaAlg-g-poly(NaA-co-St)/APT

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ABSTRACT: A novel alginate-based superabsorbent composite with enhanced swelling properties was synthesized by simultaneously grafted copolymerization partially neutralized acrylic acid (NaA), styrene (St) onto the sodium alginate (NaAlg) backbones in the presence of attapulgit (APT). The structure and morphology of the synthesized superabsorbent composites were characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible (UV-vis) spectra and Field emission scanning electron microscope (FESEM). Major factors affecting the swelling ratio according to Flory's theory were discussed. The superabsorbent composite synthesized under optimum reaction conditions exhibits the maximum swelling ratio of 587 g/g in distilled water and 73 g/g in 0.9 wt %

NaCl solution. Compared with NaAlg-g-PNaA hydrogel, the simultaneous introduction of tiny amount of St and APT not only enhanced the swelling ratio but also increased the initial swelling rate. In addition, the effects of salt and pH medium on the swelling behaviors were investigated, and the results indicated that the composite showed smart swelling behavior in multivalent salt solution and better pH-responsivity in the pH 2.2 and 7.4 solutions, which makes it promising for drug delivery application. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1822–1832, 2012

Key words: sodium alginate; styrene; superabsorbent composite; enhanced swelling properties

INTRODUCTION

In recent years, the natural polymer-based superabsorbents have been widely developed because of their abundant resources and eco-friendly properties.^{1–5} Among them, the polysaccharides-based superabsorbent composites fabricated by grafting vinyl monomers onto polysaccharide backbones and crosslinking to construct 3D network structure were especially concerned, and such materials have found extensive application in biomedical and biotechnological fields,⁶ chemical engineering,⁷ pharmaceuticals,^{8,9} hygienic productions,¹⁰ food industry,¹¹ agriculture and horti-

culture,^{12,13} wastewater treatment,¹⁴ etc. In contrast to the traditional fully petroleum-based superabsorbents, which may have serious environment impact, polysaccharides-based superabsorbent composites have good commercial and environmental values with the advantages of low cost, biocompatibility, and biodegradability. Many natural polysaccharides, such as chitosan,¹⁵ cellulose,¹⁶ starch,¹⁷ alginate,^{18–20} and gelatin²¹ have been used to prepare polysaccharides-based superabsorbent composites.

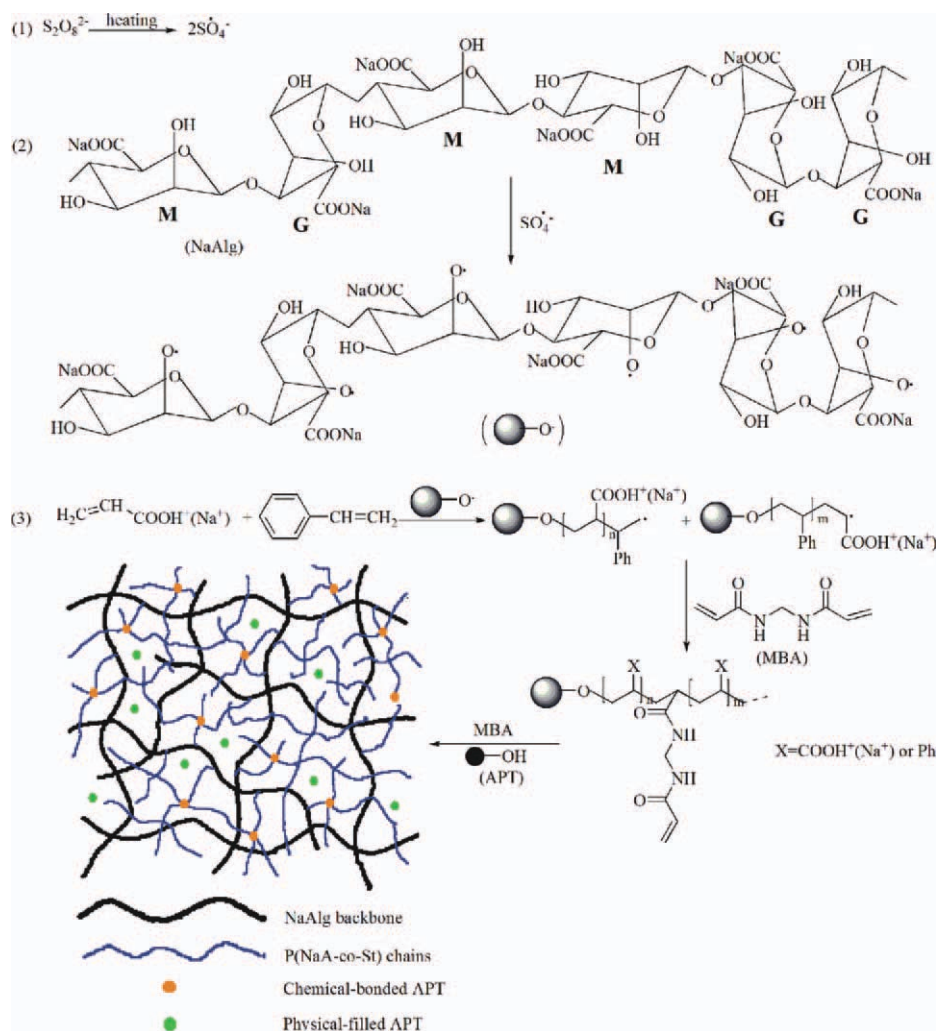
Alginate, extracted from brown algae, is a linear anionic polysaccharide composed of 1,4-linked β -D-mannuronic acid (M block) and α -L-guluronic acid (G block) units arranged in an irregular blockwise pattern of varying proportions of GG, MG, and MM blocks (Scheme 1). Alginate has plentiful free hydroxyl and carboxyl groups distributed along the backbone, and it may be utilized as hydrophilic building blocks chemically tailor to offer unique properties.²² Till now, more and more researches have reported that the graft alginate with multifunctional vinyl monomers to prepare hydrogels.^{23–25} As the interest in this field is growing, many methods are being attempted to manipulate the chemical composition and improve the absorption properties and

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Scheme 1 Proposed preparation mechanism for the NaAlg-g-P(NaA-co-St)/APT superabsorbent composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

widen the application fields of the alginate-based superabsorbents.^{26,27} The use of clay mineral for the synthesis of polysaccharides-based superabsorbents could enhance mechanical, thermal, and barrier properties of the superabsorbents as well as reduce the production cost.^{5,7} Attapulgite (APT) is a natural nanoscale crystalline hydrated octahedral layered magnesium aluminum silicate with reactive hydroxyl groups on its surface. Because of its hydrophilic property and abundant resource, APT is an ideal inorganic component for added superabsorbent network to improve the swelling properties.²⁸

By the incorporation of APT into polysaccharide-based superabsorbents, the stiffness APT could weak the strong hydrogen-bonding interaction and reduce some physical intertwining between the polymeric chains, which is beneficial to improve the swelling properties.²⁹ However, some physical filled APT often blocks some free network voids for holding water. It was reported that the incorporation of the proper amount of hydrophobic segments into the

hydrophilic matrix could alter the physical properties and control the hydration and diffusion of the swelling media into the matrix network.^{30–32} However, so far, few investigations have been done with respect to the effect of inorganic clay and hydrophobic monomer on the swelling properties of the superabsorbents. On the basis of our previous work about polysaccharides-based superabsorbents,^{27,29,33} as an effort to improve their swelling performance and explore the synergistic effect of tiny amount of hydrophobic comonomers and clay mineral on the polymeric network, in this study, a novel sodium alginate-g-poly(sodium acrylate-co-styrene)/attapulgite (NaAlg-g-P(NaA-co-St)/APT) superabsorbent composite was synthesized by the simultaneous introduction of St and APT in aqueous solution, and the network structures of the composites were characterized by FTIR, UV-vis, and FESEM techniques. The optimized synthesis conditions were examined in detail to obtain the maximum swelling ratio. The synergistic influence of St and APT on the swelling

ratio and swelling kinetics were also discussed. Finally, the effects of salt and pH medium on the swelling behaviors were investigated in order to expand its potential application for agriculture and drug delivery system.

EXPERIMENTAL SECTION

Materials

Sodium alginate (NaAlg) was purchased from Shanghai chemical reagents Corp. (Shanghai, China). Attapulgite clay micropowder (APT, Jiuchuan Nanomaterial Technology, Jiangsu, China) was milled and passed through a 200-mesh screen prior to use. Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Styrene (St, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China). Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) and *N,N'*-methylene-bis-acrylamide (MBA, chemically pure, Shanghai Chemical Reagent, Shanghai, China) was used as received. All other chemicals were of analytical grade and all solutions were prepared with distilled water.

Synthesis of NaAlg-g-P(NaA-co-St)/APT superabsorbent composites

Totally, 1.2 g NaAlg was dissolved in 30-mL distilled water in a 250-mL four-necked flask equipped with mechanical stirrer, reflux condenser, gas inlet tube, and thermometer. The resultant viscous solution was stirred at 60°C for 1 h and purged with N₂ to remove the dissolved oxygen. Then, an aqueous solution of initiator APS (0.100 g in 5 mL H₂O) was added and kept at 60°C for 15 min to generate radicals. After cooling the reactants to 40°C, the desired amount of AA (partially neutralized by NaOH solution), St and APT was added, the mixture was stirred vigorously for 10 min, then MBA was added. The reaction temperature was slowly risen to 70°C and maintained for 3 h to complete polymerization. Continuous purging of nitrogen was used throughout the reaction period. Finally, the obtained gel products were oven-dried at 70°C to constant weight, and the dried gels were milled and passed through 40–80 mesh sieve (particle size is 180–380 μm). The St and APT-free hydrogels were prepared according to a similar procedure except without addition of St and APT.

Equilibrium swelling ratio measurement

Swelling properties of the superabsorbent composites in various media were measured at 25°C

according to the following process. A total of 0.05 g xerogels were immersed in 200-mL swollen media and kept for 3 h to reach swelling equilibrium. The swollen gels were filtered by a 100-mesh sieve and kept for 10 min until no drop drained. The equilibrium swelling ratio, Q_{eq} (g/g), was calculated from the mass change of the gels before and after swollen [see Eq. (1)].

$$Q_{eq} = (\text{Wt. of the swollen gels} - \text{Wt. of the dried gels}) / \text{Wt. of the dried gels} \quad (1)$$

In all cases three parallel measurements were carried out to obtain a mean value of Q_{eq} and the \pm SD is less than 3%.

Swelling kinetics measurement

Different swelling rate for the NaAlg-g-P(NaA-co-St)/APT superabsorbent composite was achieved by immersing 0.05 g xerogels with the particle size of 180–380 μm into 200 mL various swelling media. At consecutive time intervals (1, 3, 5, 7, 10, 15, 20, 30, 60, 120 min), the swelling ratio of the composites was measured according to the method described above.

pH-responsivity measurement

Individual solution with pH 2–13 was prepared by dilution of NaOH (pH = 13.0) or HCl (pH = 1.0) solutions, respectively. The buffer solutions with pH 2.2 and 7.4 were prepared by mixing NaH₂PO₄, Na₂HPO₄, H₃PO₄, NaCl, and NaOH solution properly. The pH values of all the solutions were determined by a pH meter (Mettler Toledo, accuracy 6 ± 0.1). The equilibrium swelling ratio (Q_{eq}) in individual pH solution was measured by a method similar to that in distilled water. The pH-reversibility of the composite was investigated in terms of swelling and deswelling in two buffer solution with pH 7.4 and 2.2, respectively. The consecutive time interval for each swelling–deswelling cycle is 30 min.

Characterization

The FTIR spectra of the composites were obtained from a Nicolet NEXUS FTIR spectrometer in 4000–400 cm⁻¹ wavelength region using KBr pellets. The water-swollen composites were also characterized by UV-vis spectrophotometer (SPECORD 200, Analytik Jera AG) to determine the presence of polystyrene. To examine whether the presence of polystyrene homopolymer, the milled composites were firstly immersed in toluene for 24 h, then added methanol as nonsolvent for polystyrene to the toluene, but no precipitation was observed. The morphologies of the

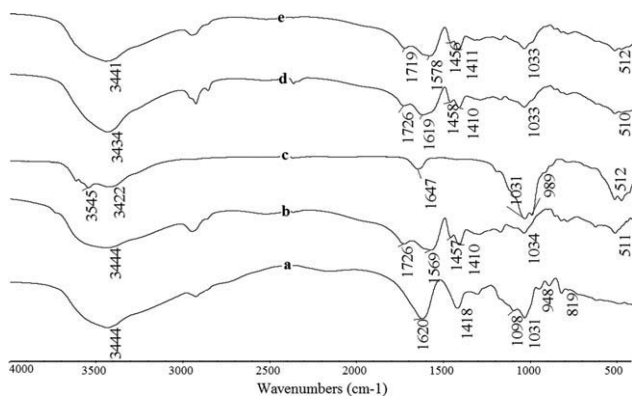


Figure 1 The FTIR spectra of (a) NaAlg, (b) NaAlg-g-PNaA, (c) APT, (d) NaAlg-g-PNaA/APT, and (e) NaAlg-g-P(NaA-co-St)/APT.

composites were examined using a S-4800 SEM instrument (Japan) after coating with a gold layer to provide proper surface conduction.

RESULTS AND DISCUSSION

Synthesis and spectral characterization

Aqueous-solution graft copolymerization of partially neutralized AA and St onto the NaAlg backbones was carried out using APS as the initiator and MBA as the crosslinker in the presence of APT as the inorganic component. A proposed formation mechanism of the superabsorbent network is schematically depicted in Scheme 1. Initially, the initiator APS was decomposed on heating to generate SO_4^- anionic-radicals and the radicals extract hydrogen from $-\text{OH}$ groups of NaAlg backbones to form alkoxy macroradicals.²² Then, the double bond of vinyl monomers, NaA/St, near the macroradicals was reacted with the macroradicals to form a covalent bond, and simultaneously the new radical sites that can propagate the graft chains were formed. In the process of chain propagation, the crosslinker (MBA) may participate in polymerization reaction by its two end vinyl groups and link the polymeric chains to form a 3D network. The inorganic APT particles may act as a crosslinker which combined with polymeric network through its reactive silanol groups during the chain propagation as well as hinder the polymeric chains growing by a chain transfer mechanism.

Figure 1 illustrates the FTIR spectra of (a) NaAlg, (b) NaAlg-g-PNaA, (c) APT, (d) NaAlg-g-PNaA/APT, and (e) NaAlg-g-P(NaA-co-St)/APT. As depicted in Figure 1(a,b), the characteristic absorption bands of NaAlg at 1098 and 1031 cm^{-1} (stretching vibration of C—OH groups) were obviously weakened after reaction, which indicate the $-\text{OH}$ groups of NaAlg participate in chemical reaction.²⁷ The hydrated surface (Si)O—H stretching vibration of APT at 3545 cm^{-1} disappears and the intensities of Si—O absorption

band at 1031 cm^{-1} weakened as shown in Figure 1(c,d). It confirms that APT participated in the grafting copolymerization reaction by its active silanol groups.²⁸ As shown in Figure 1(d), the absorption band at 1726 cm^{-1} can be assigned to C=O asymmetric stretching vibration. The bands at 1569 and 1457–1410 cm^{-1} were assigned to the asymmetric and symmetric stretching vibration of the $-\text{COO}^-$ groups, respectively. By comparing the absorption bands of Figure 1(d,e), it can be revealed that the spectrum of NaAlg-g-P(NaA-co-St)/APT shows no obvious variations for NaAlg-g-PNaA/APT composite, suggesting that the characteristic absorptions of St overlapped with the bulk $-\text{COO}^-$ absorption owing to its tiny content in the composites. To confirm the existence of St in the composites, the UV-vis spectra of (a) NaAlg-g-PNaA, (b) NaAlg-g-PNaA/APT, (c) NaAlg-g-P(NaA-co-St), and (d) NaAlg-g-P(NaA-co-St)/APT were determined Figure 2. The UV spectra of the composites containing St appeared the UV characteristic peak of E band of benzene ring (263 nm) indicating that St is existed in the polymeric network and took part in polymerization reaction.

MORPHOLOGICAL ANALYSIS

The SEM images of (a) NaAlg-g-PNaA, (b) NaAlg-g-PNaA/APT, (c) NaAlg-g-P(NaA-co-St), (d) NaAlg-g-P(NaA-co-St)/APT and (e, f) the magnification of a part of image (d) are depicted in Figure 3. Obviously, NaAlg-g-PNaA composite [Fig. 3(a)] shows a smooth and tight surface. However, the composites containing the appropriate amount of APT or St have the relative uneven surface [Fig. 3(b,c)]. Especially, the simultaneously corporation of APT and St generates an undulant and crapy surface [Fig. 3(d)].

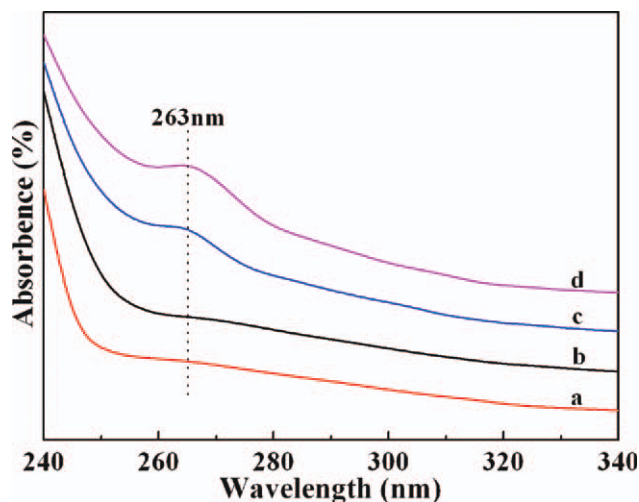


Figure 2 UV-vis spectra of (a) NaAlg-g-PNaA, (b) NaAlg-g-PNaA/APT, (c) NaAlg-g-P(NaA-co-St), and (d) NaAlg-g-P(NaA-co-St)/APT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

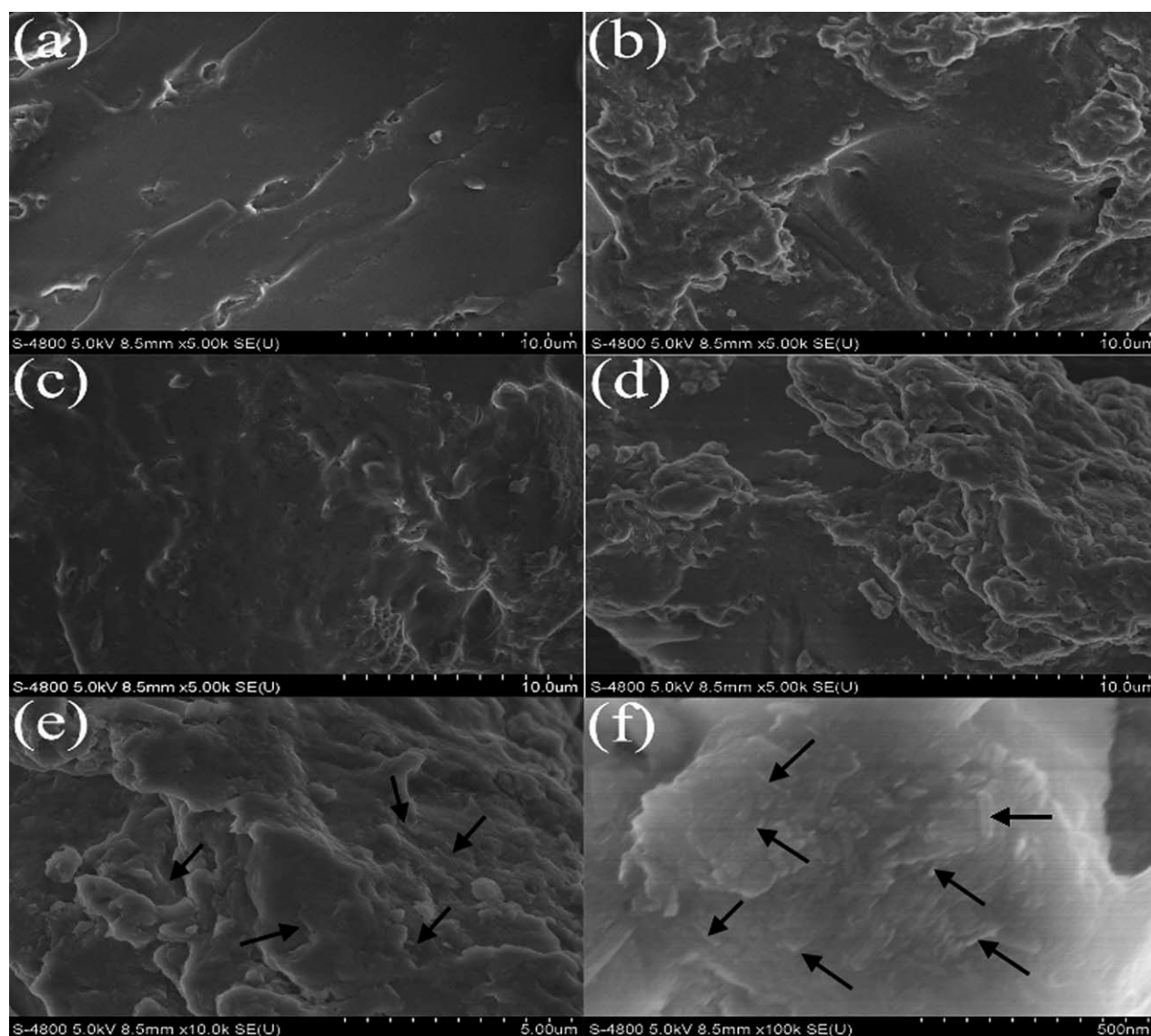


Figure 3 SEM images of (a) NaAlg-g-PNaA, (b) NaAlg-g-PNaA/APT, (c) NaAlg-g-P(NaA-co-St), and (d) NaAlg-g-P(NaA-co-St)/APT; Images (e) and (f) are the magnification of a part of image (d). The arrows in images (e) and (f) show dispersion of APT.

The uniform dispersion of APT in the polymer network was observed in the magnification of a part of image (d). The synergistic influence of APT and St could decrease the physical intertwisting of the polymer chains and benefit the dispersion of APT, all which to improve the composite network. The improved network structure and the coarse surface brings about an increased contact area that is convenient for the penetration of water into the polymeric network, and then may be beneficial to improve the swelling properties of the corresponding superabsorbents.³⁴

Optimization of the grafting condition

According to the Flory's theory,³⁵ the relationship between the swelling ratio and polymeric network

structure parameters is often described as the following:

$$Q^{5/3} = [(i/2V_u \cdot S^{1/2})^2 + (1/2 - X_1)/V_1]/(V_e/V_0) \quad (2)$$

where Q is the swelling ratio of the hydrogel; V_u is the volume of the structural unit and $i/2V_u$ is the fixed charges per volume of polymer; S is the ionic strength of external solution; $(1/2 - X_1)/V_1$ represents the affinity of the hydrogel with external solution and V_e/V_0 is the cross-linking density of polymer. It is obvious that the ionic osmotic pressure, cross-linking density, and affinity of hydrogel with water can affect the ultimate swelling capacity. In this study, some of these variables like the concentration of MBA, content of APT and St, mass ratio of

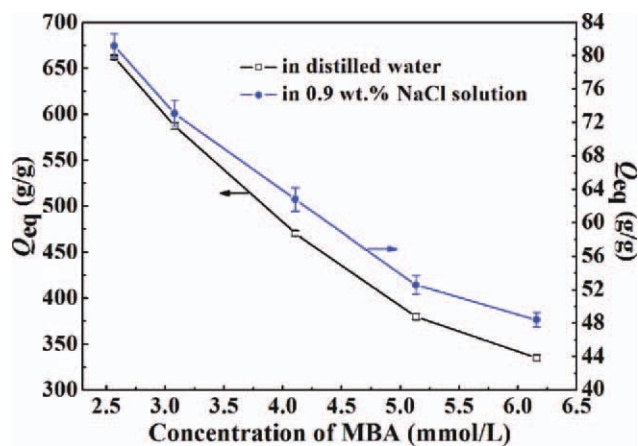


Figure 4 Effect of MBA concentration on the swelling ratio (mass ratio of AA/NaAlg = 6 : 1, neutralization degree of AA is 70%, APT and St content is 10 wt % and 1.5 wt %, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

AA/NaAlg, and neutralization degree of AA were systematically optimized as follows.

Effect of MBA concentration on swelling ratio

Figure 4 illustrated the effect of MBA concentration on the equilibrium swelling ratio of the composites in distilled water and 0.9 wt % NaCl solution. As can be seen, the swelling ratio greatly decreases with increasing MBA concentration from 2.57 to 6.16 mmol/L. When the crosslinker concentration is lower than 2.57 mmol/L, the three-dimensional network of the superabsorbent composites cannot be formed efficiently and the swelling ratio of the composite is lower. Whereas, it is obvious from Eq. (2), increasing crosslinker concentration could increase crosslinking density (V_e/V_0) of the polymeric network and decrease the network void for holding water, and consequently, the swelling ratio of the composite is decreased both in distilled water and 0.9 wt % NaCl solution. The optimum concentration of MBA in this system is 2.57 mmol/L.

Effect of AA/NaAlg mass ratio on swelling ratio

The effect of the mass ratio of AA to NaAlg on the swelling ratio was investigated and illustrated in Figure 5. The swelling ratio increased initially with enhancing the mass ratio of AA/NaAlg and reached a maximum swelling ratio (587 g/g, in distilled water; 73 g/g, in 0.9 wt % NaCl solution) at 6 : 1, and then decreased. The increase of AA dosage certainly increased the number of hydrophilic group in the polymer network, which enhances the hydrophilicity of the corresponding superabsorbent composites and improves the swelling ratio. In addition, one of the driving forces of swelling, osmotic pres-

sure, was increased with increasing the AA amount due to neutralized AA generated more mobile Na^+ ion in the polymeric network. However, as the ratio of AA/NaAlg became larger, the rate of the chain transfer to polymer increases, the amount of self-crosslinking reactions increased and more copolymers of NaA was formed due to the comparatively deficiency in the sites on the NaAlg backbones. The tangle of PNaA chains increased the crosslinking density of polymeric network, and thus decreased the swelling ratio. These results are in agreement with the results obtained by Wang during the investigation of carboxymethyl cellulose-based superabsorbent composites.²⁹

Effect of neutralization degree of AA on swelling ratio

The investigation of the effect of neutralization degree of AA on the swelling ratio also was carried out. Figure 6 shows the equilibrium swelling ratio of the NaAlg-*g*-P(NaA-*co*-St)/APT superabsorbent composites with different neutralization degrees of AA in distilled water and 0.9 wt % NaCl solution. It is observed that the swelling ratio tends to increase from 50 to 70% and decrease with the further increase of neutralization degree; the optimum neutralization degree is 70%. This tendency may be interpreted as the collaborative absorbing effect between carboxylic acid and carboxylate groups. When AA was neutralized with NaOH, the amount of fixed charges on the polymer chain is increased and the electrostatic repulsive forces that tend to expand the network elasticity also enhanced, which were helpful to improve the swelling ratio. Beyond a certain range of neutralization degree, more Na^+ in the polymeric network would screen the negative

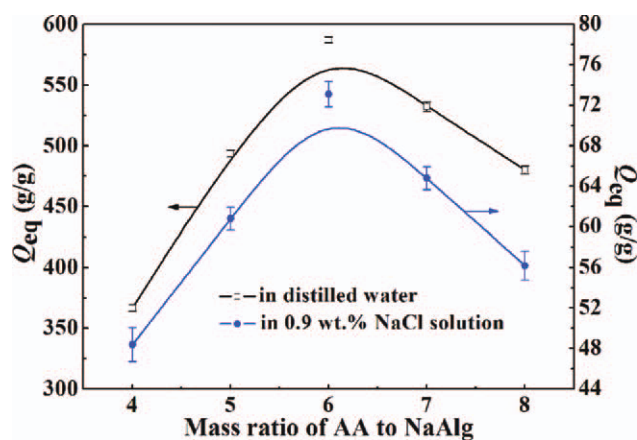


Figure 5 Effect of mass ratio AA to NaAlg on the swelling ratio (concentration of MBA = 2.57 mmol/L, neutralization degree of AA is 70%, APT and St content is 10 and 1.5 wt %, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

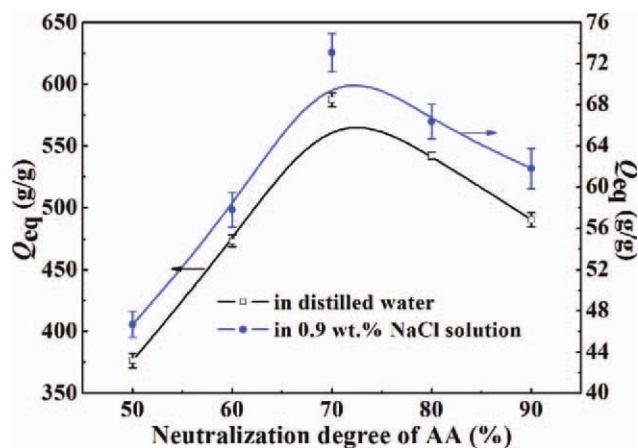


Figure 6 Effect of neutralization degree of AA on the swelling ratio (concentration of MBA = 2.57 mmol/L, mass ratio of AA/NaAlg = 6 : 1, APT and St content is 10 and 1.5 wt %, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

charges of carboxylate groups and reduce the electrostatic repulsion, which resulting in the decrease of swelling ratio. Similar observations were previously reported by others.³⁷

Effect of APT content on swelling ratio

To study the effect of APT content on swelling ratio of the superabsorbent composite, the swelling ratio of the composites with the variable content of APT (0–20 wt %) in distilled water and 0.9 wt % NaCl solution was evaluated. As shown in Figure 7, the tendency of the equilibrium swelling ratio of the composites with different APT content was similar, all which increased with increasing APT content and reached a maximum at 10 wt %. It was reported that inorganic clay interferes with poly-

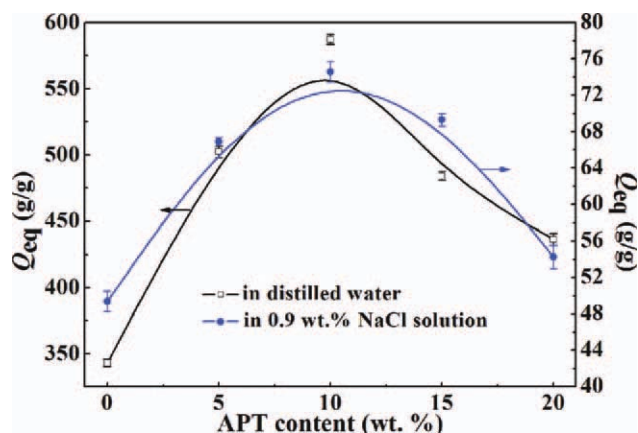


Figure 7 Effect of APT content on the swelling ratio (concentration of MBA = 2.57 mmol/L, mass ratio of AA/NaAlg = 6 : 1, neutralization degree of AA is 70% and St content is 1.5 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

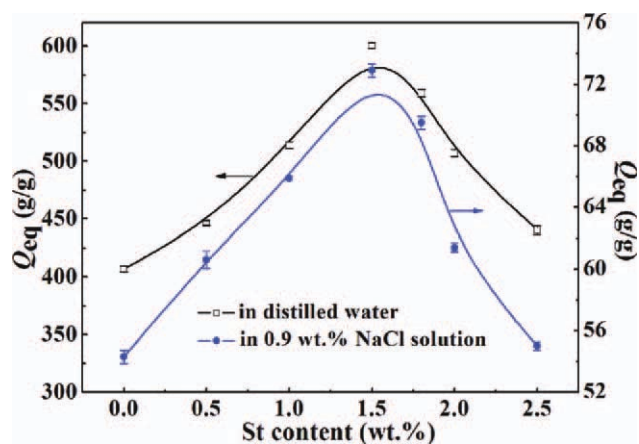


Figure 8 Effect of St content on the swelling ratio (concentration of MBA = 2.57 mmol/L, mass ratio of AA/NaAlg = 6 : 1, neutralization degree of AA is 70% and APT content is 10 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

merization by increasing the viscosity of the reacting medium,²⁸ and restrain the efficiency of the crosslinking reaction. Another reason is the rigid APT could weaken the strong hydrogen-bonding interaction and other physical intertwining between the polymeric chains. So, the dependence of swelling ratio on APT content is equivalent to reduce the actual crosslinking density of the polymeric networks, which are extremely facilitated to improve the swelling ratio. However, on increasing APT content further, the excessive APT particles will plug up some network voids and hinder the diffusion of water into the polymer. Furthermore, the hydrophilicity of APT is lower than that of AA. Consequently, with the increasing of APT content over 10 wt %, the equilibrium swelling ratio displayed a decreasing tendency.

Effect of St content on swelling ratio

As shown in Figure 8, St content has an important influence on the swelling ratio of the superabsorbent composite. By increasing St content from 0 to 1.5 wt %, the equilibrium swelling ratio increases from 407 to 587 g/g in distilled water and from 54 to 73 g/g in 0.9 wt % NaCl solution. The observed results can be explained by the fact that incorporation of tiny amount of St as comonomer into the hydrophilic system introduced hydrophobic monomeric units phenyl group that did not participate in the hydrogen bonding, and the hydrogen bonding interaction among polymeric chains was weakened.³² Furthermore, the flexible polystyrene chain segments generate a steric repulsion among the macromolecular chains, which may remedy some defects of the composite's network resulting from the rigid APT and widen the interstitial volume per unit mass

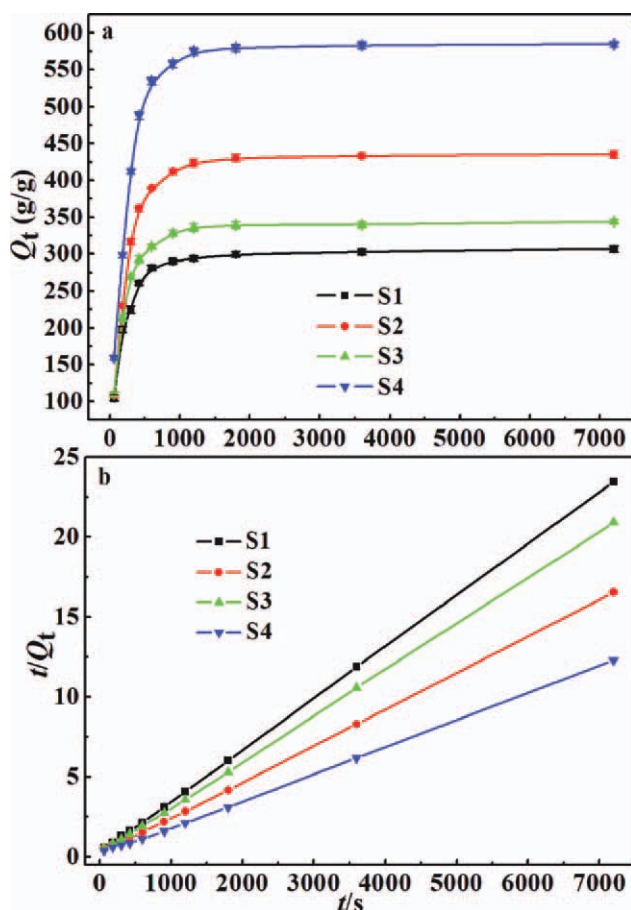


Figure 9 Swelling kinetic curves (a) and t/Q_t vs. t graphs (b) of the composites in distilled water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the composites. So the synergistic influence of St and APT can efficiently alter physical properties of the polymeric network and ultimately enhance the swelling ratio both in distilled water and 0.9 wt % NaCl solution. However, the excess hydrophobic monomers in the gel matrix often decreased the hydrophilic degree of the gel network, which makes it difficult for water molecules to penetrate inside the hydrogel.³² As a result, the swelling ratio was reduced. In this system, the optimum content of St is 1.5 wt %.

Synergistic effect of St and APT on the swelling kinetics

To examine the synergistic influence of St and APT on the swelling kinetics, the profiles of the swelling ratio in distilled water as a function of swelling time for the NaAlg-based composites are presented in Figure 9. As expected, the swelling ratio of the composites increased rapidly during a short time and leveled off to equilibrium swelling almost within the initial 900 s. Once again, the data from the presented

swelling curves were analyzed by using the Schott's second-order swelling kinetics³⁸:

$$t/Q_t = A + Bt \quad (3)$$

where Q_t is the swelling ratio at time t ; A is the reciprocal of the initial swelling rate, that is, $A = 1/K_{is}$; $B = 1/Q_\infty$ (where Q_∞ represents the theoretical equilibrium swelling ratio). The plots of t vs. t/Q_t gives straight lines with the linear correlation coefficients larger than 0.999, indicating that it is reasonable to model the kinetics with the Schott's second-order theoretical swelling model and to determine the swelling kinetics parameters, K_{is} and Q_∞ , from the slopes and intercepts of straight lines. The obtained values for Q_{eq} , Q_∞ , and K_{is} are listed in Table I.

As depicted in Table I, the results clearly revealed that the incorporation of single St or APT could improve the initial swelling rate (K_{is}) of the composites. However, the significant enhancement of K_{is} values could be obtained by the simultaneous introduction of the appropriate amount of St and APT. These results are in agreement with the above discussion that the synergistic influence of St and APT could regulate the physical crosslinking and elastic repulsion of the constituent macromolecular chain of the composite, which is favorable to increase the diffusion and capillary action and then enhance the swelling ratio and swelling rate.

Effect of external salt solution on the swelling behaviors

To investigate the effect of salt solution on the swelling behavior, we studied the equilibrium swelling ratio of the samples S1, S2, S3, and S4 in NaCl, CaCl₂, and AlCl₃ solution with different concentration. As shown in Figure 10(a–c), the decreasing tendency of swelling ratio for all composites is strongly dependent on the type and concentration of salt, and the swelling ratio in each concentration

TABLE I
Equilibrium Swelling Ratio and Swelling Kinetic Parameters of the NaAlg-Based Superabsorbent Composites

Samples	Q_{eq} (g g ⁻¹)	Q_∞ (g g ⁻¹)	K_{is} (g g ⁻¹ s ⁻¹)	R
St, 0 wt %; APT, 0 wt % (S1)	307	311	3.5826	1
St, 0 wt %; APT, 10 wt % (S2)	435	444	4.1824	0.9998
St, 1.5 wt %; APT, 0 wt % (S3)	344	348	4.2378	0.9999
St, 1.5 wt %; APT, 10 wt % (S4)	585	595	5.8858	0.9998

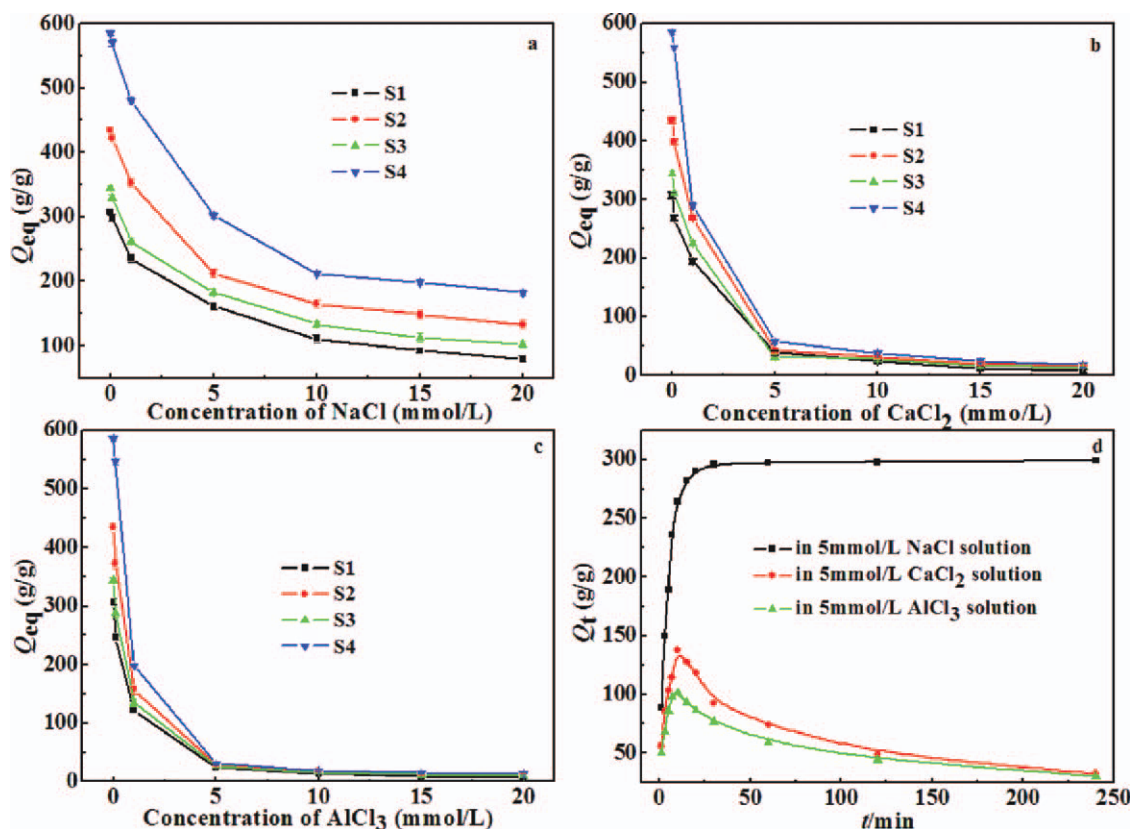


Figure 10 Effect of salt concentration on swelling ratio of the composites [10(a–c)] and swelling kinetics of the optimized composite in 5 mmol/L salt solutions [10(d)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

follows the order of $NaCl > CaCl_2 > AlCl_3$. For the ionic-type hydrogels, swelling and deswelling behaviors are mainly determined by the Donnan osmotic pressure and the elasticity of the gel network. With increasing ionic strength of the external solution, the additional cations screen the $-COO^-$ groups which induced the reduction of the Donnan osmotic pressure. In addition, in multivalent salt solution, the extra ionic crosslinking between multivalent cations and $-COO^-$ groups may reduce the elastic retractile force of the hydrogel and cause the decrease of swelling ratio. Moreover, the order of swelling ratio in all salt solutions is: $S4 > S2 > S3 > S1$, which is in agreement with the order in distilled water [Fig. 10(a–c)]. The enhancement of swelling ratio in salt solutions for S4 compared with S1 confirmed that the synergistic influence of St and APT could enhance the deformation flexibility of the polymeric network and improve the salt-resistance of the composite.

The swelling kinetic profiles of the optimized composite S4 in 5 mmol/L NaCl, $CaCl_2$, and $AlCl_3$ solution as a function of time was shown in Figure 10(d). Its dynamic swelling curve in NaCl medium is similar to that in distilled water, but exhibits a remarkable “overshoot effect” in $CaCl_2$ and $AlCl_3$ medium. First, the sample rapidly increases its swell-

ing ratio to a maximum (138 g/g in $CaCl_2$ solution and 101 g/g in $AlCl_3$ solution) within 10 min, and then it deswells until an equilibrium value is reached. We attributed this feature to the consequence of a swell–deswelling process because of the diffusion of Ca^{2+} and Al^{3+} ions into the polymeric network and the “cooperative ionic crosslinking” of carboxyl groups of the hydrogel with Ca^{2+} and Al^{3+} , which leads to the expelling of the absorbed water during the dynamic swelling measurements. The swelling–deswelling process of the hydrogel renders it sensitive to multivalent salt.

Effect of external pH on the swelling ratio and pH-responsive characteristics

Figure 11(a) presents the swelling profiles of the composites in various pH solutions ranged from 2 to 13. The order of swelling ratio for the four composites in various pHs was similar to that in salt solutions. This further confirmed that the synergistic influence of St and APT could alter physical properties of the polymeric network and improve the swelling properties of the composites. For all the composites, the degree of swelling depends on external pHs. In $pH < 4$ solutions, most of the carboxylate anions were protonated, which restricts the electrostatic

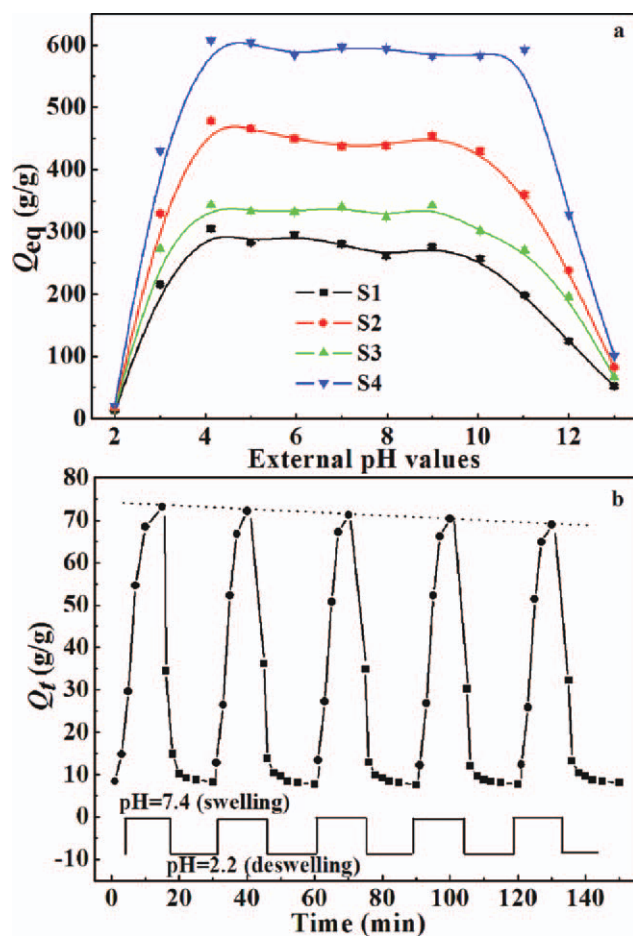


Figure 11 Effect of external pH on swelling ratio of the composites (a) and pH-responsiveness for the optimized composite (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

repulsion and strengthen the hydrogen-bonding interaction among the polymer chains. So, the network tends to contract and expel water from the gel network and the swelling ratio is lower. In basic medium (pH > 10), the dominated electrostatic-bonding between $-\text{COO}^-$ and excess Na^+ clearly reduced the osmotic pressure of the polymer network, and thus decreased the swelling ratio of the composites. The swelling ratio of the S1, S2, and S3 composites exhibits an almost constant value in the range of pH 4–9, but the range is pH 4–11 for S4. The greater difference in pH stable range indicates that the synergistic influence of St and APT also could reduce the electrostatic-screening effect and increase the pH-stability in the basic medium.

To expand the potential application of the composite, the pH-responsivity of the optimized composite S4 in 0.1 mol/L buffer solution of phosphate was characterized between pH 2.2 and 7.4. As shown by Figure 11(b), the hydrogel displayed a repetitive oscillating swelling–deswelling with a constant time period, and the amplitude of the swelling

was mainly affected by the elastic retractive force exerted by the anion–anion electrostatic repulsion in the polymeric network. It is obvious that, after five swelling–deswelling reversibilities, the amplitude of the swelling only decreases a little, which proves that the composite has better pH-responsivity and can potentially be used as a drug-deliver vehicle in biomedical engineering.

CONCLUSION

A novel swelling enhanced NaAlg-*g*-P(NaA-*co*-St)/APT superabsorbent composite was synthesized by using APS as a radical initiator and MBA as a cross-linker in aqueous solution. The results of FTIR and UV-*vis* spectra shown that NaA and St comonomers have been grafted onto NaAlg backbones, and APT participated in copolymerization reaction, all which comprise of a three-dimensional crosslinking structure. FESEM observation revealed that the surface morphology of the composite was obviously improved after simultaneously introducing St and APT. The synergistic influences of St and APT on the swelling ratio and swelling rate were observed and the optimum condition for the synthesis of the composite is: $C_{\text{MBA}} = 3.08$ mmol/L, mass ratio of AA/NaAlg = 6 : 1, neutralization degree of AA = 70%, weight content of St and APT = 1.5 and 10%, respectively. The investigation of the effect of salts on the swelling behaviors shows that the swelling in NaCl solution was controlled by osmotic pressure and expressed by Donnan equilibrium. Whereas, in CaCl_2 and AlCl_3 solution, the composite undergoes a swelling–deswelling process which was induced by stronger binding action between $-\text{COO}^-$ and $\text{Ca}^{2+}/\text{Al}^{3+}$ ion. The swelling ratio of the composite also showed good buffer action in an extended pH value range from 4 to 11, and exhibited a smart responsive characteristics in 0.1 mol/L buffer solution with pH 2.2 and 7.4. These smart swelling properties in multivalent cationic and pH media contribute to extend the application of the NaAlg-based superabsorbent composite such as using for drug delivery carrier.³⁹

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