Research Article

Synthesis, characterization, and swelling behaviors of chitosan-*g*-poly(acrylic acid)/poly(vinyl alcohol) semi-IPN superabsorbent hydrogels

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A series of granulated semi-interpenetrating polymer network (semi-IPN) superabsorbent hydrogels composed of chitosan-*g*-poly(acrylic acid) (CTS-*g*-PAA) and poly(vinyl alcohol) (PVA) were prepared by solution polymerization using ammonium persulfate (APS) as an initiator and *N,N'*-methylenebisacrylamide (MBA) as a crosslinker. The effects of reaction conditions such as the concentration of MBA, the weight ratio of AA to CTS, and the content of PVA on water absorbency were investigated. Infrared (IR) spectra and differential scanning calorimetry (DSC) analyses confirmed that AA had been grafted onto CTS backbone, and PVA semi-interpenetrating into CTS-*g*-PAA networks. SEM analyses indicated that CTS-*g*-PAA/PVA has improved porous surface and PVA was uniformly dispersed in CTS-*g*-PAA network. The semi-IPN hydrogel containing 10 wt% PVA shows the highest water absorbency of 353 and 53 g g^{-1} in distilled water and 0.9 wt% NaCl solution, respectively. Swelling behaviors revealed that the introduction of PVA could improve the swelling rate and enhance the pH stability of the superabsorbent hydrogel. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: superabsorbent; semi-IPN; chitosan; poly(vinyl alcohol); swelling

INTRODUCTION

Superabsorbents are slightly crosslinked hydrophilic polymers that can absorb huge volumes of aqueous fluids and can retain the absorbed water even under certain pressure. By right of the excellent performance superior to traditional absorbents (cotton, sponge, pulp, etc.), superabsorbents have found potential application in various fields including healthcare products,[1] agriculture and horticulture,[2,3] wastewater treatment,[4,5] coal dewatering,[6] drug-delivery system,[7] and so on. However, the further application of superabsorbent was limited because that the currently available superabsorbents are mainly expensive synthetic polymer derived from petroleum-based monomers. Their production depends on the consumption of petroleum resource and their usage may cause some environment problem. Thus, the further research was directed to the multicomponent superabsorbents containing natural macromolecules because such materials exhibited low cost, improved performance, and environmental friendly characteristics.[8–11]

Chitosan (CTS) is derived by the deacetylation of natural chitin and is the world's second most abundant natural hydrophilic biomacromolecule with highly reactive hydroxyl and amino groups. CTS can be easily modified through various chemical or physical methods such as grafting copolymerization with hydrophilic vinyl monomers,[12] polymer blending,[13,14] and compounding with other functional components.[15,16] Like with other natural biomacromolecules, CTS has attractive biocompatibility, biodegradability, and nontoxicity, and so CTS and their derivatives have been extensively applied in drug carrier, biomedical materials, and absorbents.[17] Therefore, to extend the application of CTS and

design novel biopolymer-based superabsorbents by a new technique has attracted considerable interests.

Recently, interpenetrating polymer network (IPN) and semi-interpenetrating polymer network (semi-IPN) was developed as a technique of preparing multicomponent polymer materials, and was also frequently used in the design and synthesis of various hydrogels because they provide a convenient route to modify the properties of hydrogels.[18–20] Semi-IPN is a way of blending two polymers where only one is crosslinked in the presence of another to produce a fine mixture, and the additional noncovalent interaction between the two polymers would affect the properties of the resultant semi-IPN hydrogel.[21,22] Poly(vinyl alcohol) (PVA) is a nonionic hydrophilic polyhydroxy linear polymer, which have excellent water solubility, nontoxicity,

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biodegradability, and compatibility. Because PVA is compatible with other polymers, it was considered as a suitable component for the preparation of semi-IPN hydrogel.[23,24] Also, introducing PVA into hydrogel network can enhance its hydrophilicity, gel strength, and other properties. It is expected that the effective combination of CTS with PVA through semi-IPN technique can constitute new superabsorbent with improved structure and performance, and the granular semi-IPN hydrogels based on CTS and PVA which could be directly formed in aqueous solution have not been reported by far. Therefore, the formation of semi-IPN superabsorbent hydrogel based on CTS and PVA can synchronously improve the performance of materials and the synthesis process.

Based on above description and our work about CTS-based superabsorbents,[16,25–28] in this paper, the series of granular chitosan-g-poly(acrylic acid) (CTS-g-PAA)/PVA semi-IPN superabsorbent hydrogels were synthesized by the graft copolymerization reaction in aqueous solution. The effects of polymerization conditions on the water absorbency of CTS-g-PAA/PVA were investigated. The granular semi-IPN superabsorbent hydrogels were characterized by infrared (IR) spectra, scanning electron microscope (SEM), and differential scanning calorimetry (DSC). In addition, the swelling kinetics and swelling behaviors of the semi-IPN hydrogels in solutions with different pHs and in various cationic saline solutions were also investigated systematically.

EXPERIMENTAL

Materials

Chitosan (CTS, degree of deacetylation is 0.90; average molecular weight is 30×10^4) was purchased from Golden-Shell Biochemical Co, Ltd (Zhejiang, China). Acrylic acid (AA, distilled under reduced pressure before use), ammonium persulfate (APS, AR grade, used as received), and N,N′-methylenebisacrylamide (MBA, CR grade, used as received) were supplied by Shanghai Regent Corp. (Shanghai, China) and PVA ($M_w = 72{,}600$–$77{,}000$, alcoholysis degree is 99%) was supplied by Lanzhou New-West Vinylon Co, Ltd (Lanzhou, China). All other reagents were of analytical grade and all solutions were prepared with distilled water.

Preparation of CTS-g-PAA/PVA semi-IPN superabsorbent hydrogels

A series of CTS-g-PAA/PVA semi-IPN superabsorbent hydrogels were prepared by solution polymerization according to the following procedure: a predetermined amount of PVA was added into 30 ml deoxygenated acetic acid solution (1 vol%) in a 250 ml four-neck flask equipped with a mechanical stirrer, a reflux condenser, a funnel and a nitrogen line. The resulting mixture was heated at 95°C for 30 min to obtain transparent PVA solution. After the solution was cooled to 80°C, variable amount of CTS was added into the solution with vigorous stirring for 30 min to achieve a homogenous solution. Then, 0.0953 g APS was introduced into the solution and was vigorously stirred for 10 min to generate radicals. The mixed solution of AA (3.60 g), 10 ml distilled water, and calculated amount of MBA was added to the flask. After the polymerization reaction was carried out at 80°C for 3 hr with continuous stirring, the granular gel product (Scheme 1) can be obtained. The granular product was cooled to
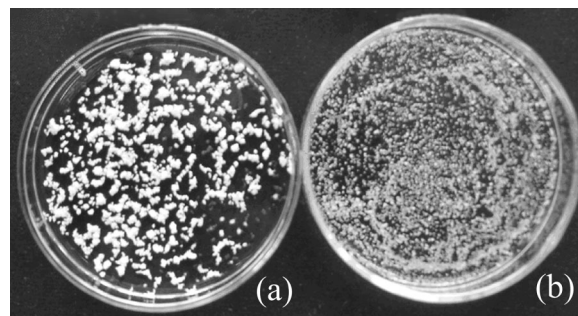
Scheme 1. Digital photographs of granular products for (a) CTS-g-PAA/PVA (10 wt%) and (b) CTS-g-PAA/PVA (20 wt%).

room temperature and neutralized to pH 7 using 1 mol/l NaOH solution. The swollen granular gel was put into 250 ml methanol for 24 hr, and then the hardened gel particles were filtered and dried at 60°C to constant weight. The product was ground and all samples used for test had a particle size in the range of 40–80 mesh (180–380 μm). Preparation procedure of CTS-g-PAA is similar to that of CTS-g-PAA/PVA superabsorbent hydrogel except without PVA. The feed compositions of all samples are listed in Table 1.

Measurement of equilibrium water absorbency

Sample (0.05 g) was immersed in excess aqueous solution at ambient temperature for 4 hr to reach swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering through 100-mesh screen under gravity for 10 min. After weighing the swollen samples, the water absorbency of the sample (W_{eq}) was calculated using the following equation:

$$W_{eq}(g\,g^{-1}) = \frac{m_2 - m_1}{m_1} \qquad (1)$$

W_{eq}, the water absorbency calculated as grams of water per gram of the sample, which is the average of three measurements; m_1

Table 1. Feed composition of CTS-g-PAA/PVA semi-IPN superabsorbent hydrogel

No.	AA	MBA	CTS	PVA
MBA1	3.60	0.0475	0.50	0.48
MBA2	3.60	0.0712	0.50	0.48
MBA3	3.60	0.0953	0.50	0.48
MBA4	3.60	0.1200	0.50	0.48
MBA5	3.60	0.1466	0.50	0.48
CTS1	3.60	0.0953	0.40	0.48
CTS2	3.60	0.0953	0.50	0.48
CTS3	3.60	0.0953	0.60	0.48
CTS4	3.60	0.0953	0.72	0.48
CTS5	3.60	0.0953	0.90	0.48
PVA0	3.60	0.0953	0.50	0
PVA1	3.60	0.0953	0.50	0.09
PVA2	3.60	0.0953	0.50	0.23
PVA3	3.60	0.0953	0.50	0.48
PVA4	3.60	0.0953	0.50	0.76
PVA5	3.60	0.0953	0.50	1.07

and m_2 are the weight of the dry superabsorbents and the swollen samples, respectively. All samples were carried out three times repeatedly and the average values are reported in this paper.

Measurements of water absorbency in various pH solutions and swelling kinetics in distilled water

The pH of external solutions was adjusted using 1 mol/l NaOH or HCl aqueous solutions. The determination method of water absorbency in various pH solutions was similar with that described above and the water absorbency was also calculated using eqn (1).

Swelling kinetics of superabsorbents in distilled water was measured according to the following method: a 0.05 g of sample was placed in 500 ml beakers, and then 100 ml of distilled water was poured into the beakers. At certain time intervals, the swollen samples were filtered out and weighed, and the water absorbency of samples was calculated according to eqn (1).

Characterization

The IR spectra were recorded on a Nicolet NEXUS FTIR spectrometer in 4000–400 cm^{-1} region using KBr pellets. The morphological structures of the samples were observed using a JSM-5600 SEM instrument (JEOL, Ltd). The thermal behaviors of CTS-*g*-PAA, CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogel, and PVA were investigated using DSC (DSC-7, Perkin Elmer Instrument, USA) using the hermetic aluminum pan and heating rate was 10°C/min in a N_2 atmosphere.

RESULTS AND DISCUSSION

Grafting polymerization and chemically crosslinking reaction of PAA and CTS backbone were simultaneously carried out in the aqueous solution using APS as an initiator and MBA as a crosslinker, and the proposed mechanism was depicted in Scheme 2. Firstly, the initiator APS can decompose under heating
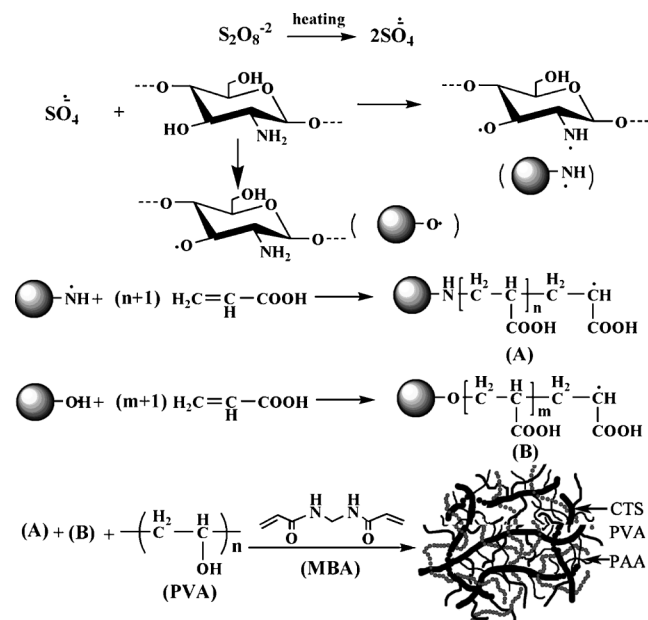
and generate sulfate anion-radicals. Then, these radicals may strip down the hydrogen of –OH or –NH_2 groups located on CTS macromolecular chains to form macroradicals. These macroradicals can act as the active sites during reaction and can initiate monomers to process chain propagation. During the chain propagation, the crosslinker MBA with vinyl groups take part in polymerization reaction and the linear PVA also combined with polymeric network through strong hydrogen bonding interaction and was distributed throughout the crosslinked networks of CTS-*g*-PAA/PVA to form semi-IPN hydrogels.

IR spectra analyses

IR spectra of (a) CTS, (b) CTS-*g*-PAA, (c) CTS-*g*-PAA/PVA with 10 wt% PVA, and (d) PVA are shown in Fig. 1. As can be seen from Fig. 1a, the absorption bands of CTS at 1647, 1593, 1380, 1094, and 1037 cm^{-1} are ascribed to C=O of amide I, –NH_2, –NHCO of amide III, C_3–OH, and C_6–OH of CTS, respectively. After reaction, the absorption bands of N–H (1593 and 1380 cm^{-1}) and C_3–OH (1094 cm^{-1}) disappeared (Fig. 1b), and the new absorption peaks at 1563 and 1407 cm^{-1} assigned to asymmetric stretching and symmetric stretching of –COO^- appeared in the spectrum of CTS-*g*-PAA. This information conformed that AA has been grafted on to CTS backbone and the –NH_2, –NHCO, and –OH groups of CTS participate in graft reaction.[16]

The IR spectrum of PVA shows characteristic absorption bands of –OH groups at 3421 and 1096 cm^{-1} (Fig. 1d). The absorption bands of PVA at 2939 and 1419 cm^{-1} are attributed to the stretching vibration and bending vibration of C–H, respectively. In general, the spectrum of CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogel includes characteristic absorptions of CTS-*g*-PAA and PVA. As can be seen from Fig. 1c, the absorption bands of CTS-*g*-PAA/PVA at 1570 and 1409 cm^{-1} are from CTS-*g*-PAA. However, the characteristic absorption bands of PVA were not obviously found in the spectrum of CTS-*g*-PAA/PVA due to overlapping and smaller loading. By comparison with the spectrum of CTS-*g*-PAA, a broad absorption band of –OH in the range of 3421–3443 cm^{-1} appeared in the spectrum of CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogel. This is attributed to the formation of strong hydrogen bonds between PVA and CTS-*g*-
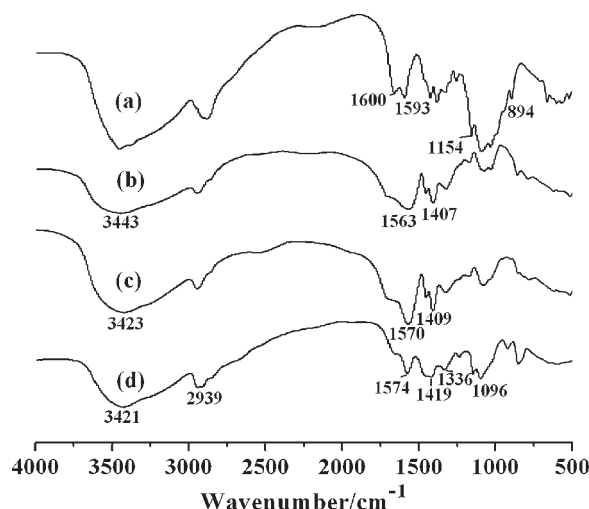

Scheme 2. Proposed mechanisms for the formation of semi-IPN superabsorbent hydrogel network.

Figure 1. IR spectra of (a) CTS, (b) CTS-*g*-PAA, (c) CTS-*g*-PAA/PVA with 10 wt% PVA, and (d) PVA.

PAA. These results indicate that CTS-g-PAA and PVA component coexisted in CTS-g-PAA/PVA superabsorbent hydrogel and formed a semi-IPN structure.

Morphological SEM analysis

SEM micrographs of (a) CTS-g-PAA and (b) CTS-g-PAA/PVA with 10 wt% PVA semi-IPN superabsorbent hydrogel were observed and are shown in Fig. 2. As can be seen, CTS-g-PAA shows a dense, nonporous, and relatively rough surface. After introducing PVA, the surface morphology of the superabsorbent hydrogel was greatly changed due to the formation of semi-IPN structure. As shown in Fig. 2b, the semi-IPN superabsorbent hydrogel shows loose and porous surface; the pores are equably distributed in the surface and the radius of the pores is in the range of 0.1–1 μm. Furthermore, this observation also gives a direct revelation that PVA are almost embedded within CTS-g-PAA and uniformly dispersed in the polymer matrix. The change in the surface morphology induced by introducing PVA into CTS-g-PAA may influence the penetration of water into the polymeric network, and then affects the swelling capabilities of superabsorbent hydrogels.

DSC analyses

Figure 3 shows the DSC thermogram of (a) CTS-g-PAA, (b) CTS-g-PAA/PVA with 10 wt% PVA semi-IPN superabsorbent hydrogel, and (c) PVA. As can be seen from Fig. 3c, PVA shows a small endothermic peak at 73°C, corresponding to glass transition temperature (T_g); and a broad and sharp peak at 248°C, corresponding to melting temperature (T_m). CTS-g-PAA exhibits an endothermic peak at 87°C (Fig. 3a). After incorporating PVA into CTS-g-PAA, the resultant CTS-g-PAA/PVA semi-IPN superabsorbent hydrogels show two endothermic peaks at 78 and 245°C, and the peak positions are close to the characteristic peaks
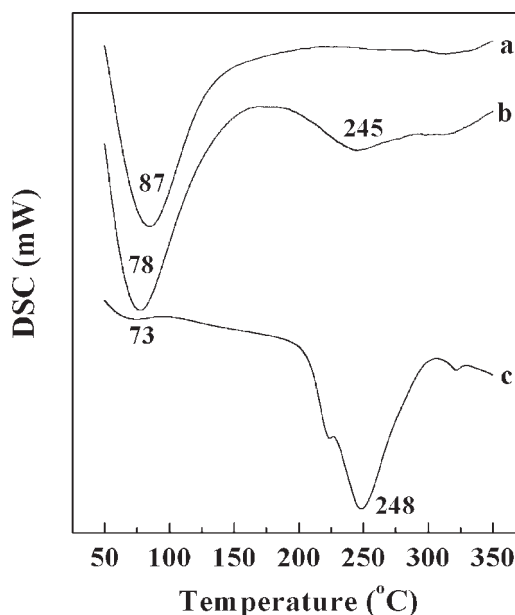

Figure 3. DSC thermograms for CTS-g-PAA (a), CTS-g-PAA/PVA with 10 wt% PVA (b), and PVA (c).

of PVA and CTS-g-PAA, respectively. Because no endothermic peak can be observed in the DSC curve of CTS-g-PAA in this region, the appearance of characteristic peak of PVA indicates that the linear PVA chains are not chemically bonded with gel network but are only combined with polymer network through hydrogen bonds, and the phase separation structure can be confirmed. Therefore, according to the change in DSC thermogram of hydrogel before and after reaction, it can be concluded that the two domains are coexisted in CTS-g-PAA/PVA semi-IPN superabsorbent hydrogels, and CTS-g-PAA and PVA formed a hydrogel with semi-IPN structure.

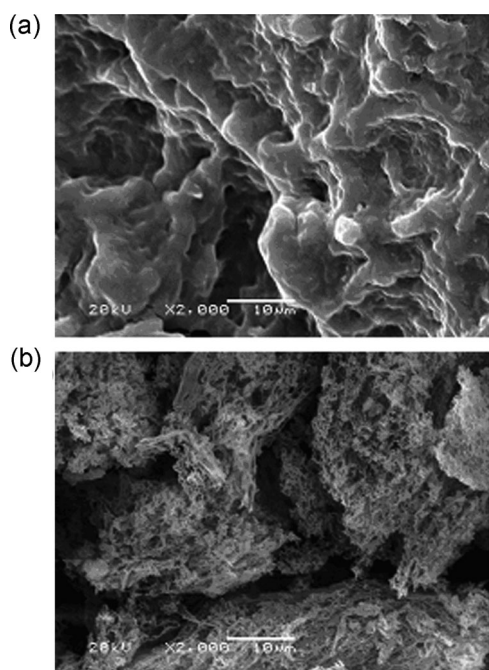## Effect of MBA content on water absorbency

The effect of MBA content on the water absorbency of CTS-g-PAA/PVA semi-IPN superabsorbent hydrogel is shown in Fig. 4. It can be seen that the water absorbencies of CTS-g-PAA/PVA in

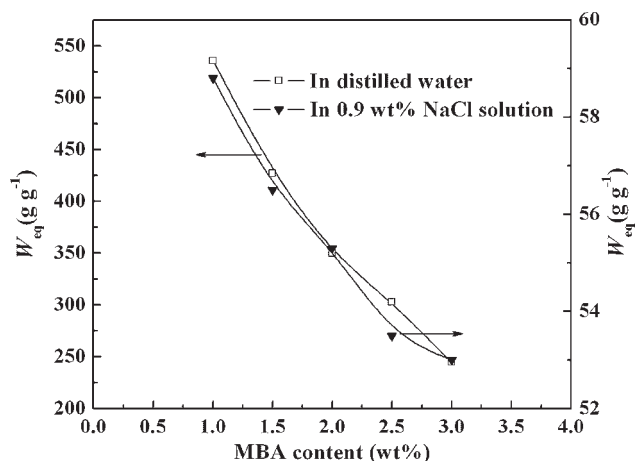**Figure 2.** SEM micrographs of (a) CTS-g-PAA and (b) CTS-g-PAA/PVA with 10 wt% PVA.

Figure 4. Water absorbency variation of CTS-g-PAA/PVA semi-IPN superabsorbent hydrogels with MBA content.

either of distilled water and 0.9 wt% NaCl solution decreased with increasing MBA content. This tendency was attributed to the fact that higher crosslinker concentration leads to the generation of more crosslink points in the polymeric network and the decrease of the free space between polymeric chains. As a result, the highly crosslinked rigid structure of polymeric network increased and the water absorbency decreased. Similar phenomena has also been observed in starch-*g*-poly(acrylic acid)/sodium humate[29] and carrageenan-*g*-poly(acrylamide)/poly(vinylsulfonic acid, sodium salt).[30]

Effect of the weight ratio of AA to CTS on water absorbency

The influence of weight ratio of AA to CTS on the water absorbency was studied and the results are shown in Fig. 5. It can be seen that the water absorbency increased almost linearly with increasing the weight ratio of AA to CTS. The increase in water absorbency with increasing the weight ratio of AA to CTS could be attributed to the following reasons: (i) as the weight ratio of AA to CTS increased, more available monomer molecules in the vicinity of chain propagation sites of CTS macroradicals could be grafted onto CTS backbone, which enhanced the grafting efficiency and improved the hydrophilicity of the corresponding superabsorbent, and then resulted in an increase in water absorbency; (ii) the molecular weight of polymer resulting from grafting PAA chains onto CTS backbone increased with enhancing the weight ratio of AA to CTS, which also can improve the water absorbency.[31]

Effect of PVA content on water absorbency

It is well known that the incorporation of hydrophilic polymer into crosslinked superabsorbent network contributes to enhance the water absorbency and improve the comprehensive properties of the resultant materials. In this section, the effect of PVA content on the water absorbency of CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogel was investigated and the results are shown in Fig. 6. As can be seen, the water absorbency of CTS-*g*-PAA/PVA in distilled water and in 0.9 wt% NaCl solution increased with the increase in PVA content, reached a maximum and then decreased. The semi-IPN superabsorbent hydrogel incorporating 10 wt% PVA give the best water absorbency of 353 g g^{-1} in distilled water and 53 g g^{-1} in 0.9 wt% NaCl solution. However,

Figure 6. Water absorbency variation of CTS-*g*-PAA/PVA superabsorbent hydrogels with PVA content.

with the further increase in PVA content, the water absorbency decreased. This behavior is due to the fact that the initial increase in the content of PVA leads to an increase in hydrophilicity of the semi-IPN superabsorbent hydrogel, and PVA molecules can act as dispersant during the polymerization process, which enhances dispersion of the reactants and improve the network structure of the superabsorbent, thus the water absorbency can be enhanced. However, a denser polymeric network was formed when the PVA content is higher than 10 wt%, which restricts the penetration of water molecules into the semi-IPN superabsorbent hydrogel.[32] Furthermore, the increase in the number of physical crosslinkages resulting from the entanglement between PVA and CTS-*g*-PAA may also result in the decrease of water absorbency.

Effect of PVA content on swelling kinetics

Figure 7 represents the swelling kinetics of the CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogels with different PVA content in distilled water. Initially, the swelling rate of CTS-*g*-PAA and CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogels with 5 and 10 wt% PVA sharply increases and reaches 93.8, 94.2, and 96.7% of their equilibrium water absorbency in 5 min, respectively. Then the curves become level off and the swelling equilibrium was achieved after 10 min. For evaluating the mechanism of the swelling process and the effect of PVA content on swelling kinetics of the superabsorbent hydrogels, the second order swelling kinetics model[33,34] was adopted to test the experimental data. The second order swelling kinetic model can be expressed as follows:

$$\frac{t}{W} = A + Bt \qquad (2)$$

where W is the water absorbency at time t, $B = 1/W_{eq}$ is the inverse of equilibrium water absorbency and $A = 1/K_s W_{eq}^2$ is the reciprocal of the initial swelling rate of the superabsorbents, and K_s is swelling rate constant. The final form of the eqn (2) can be written as follows:

$$\frac{t}{W} = \frac{1}{K_s W_{eq}^2} + (1/W_{eq})t \qquad (3)$$

Based on the experimental data, the graphs of t/W versus t for CTS-*g*-PAA and CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogels give perfect straight lines with good linear correlation coefficient (Fig. 7b), indicating that the swelling processes of the
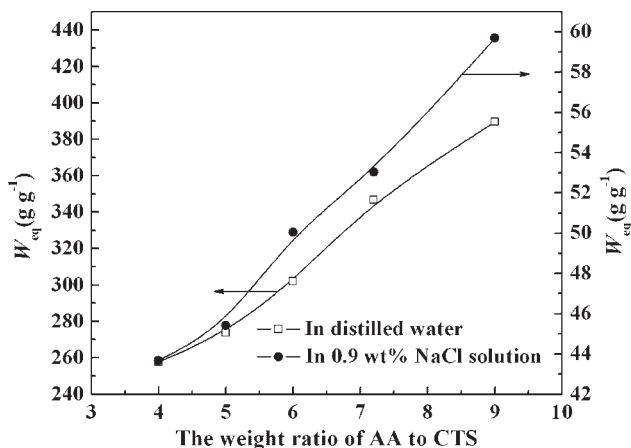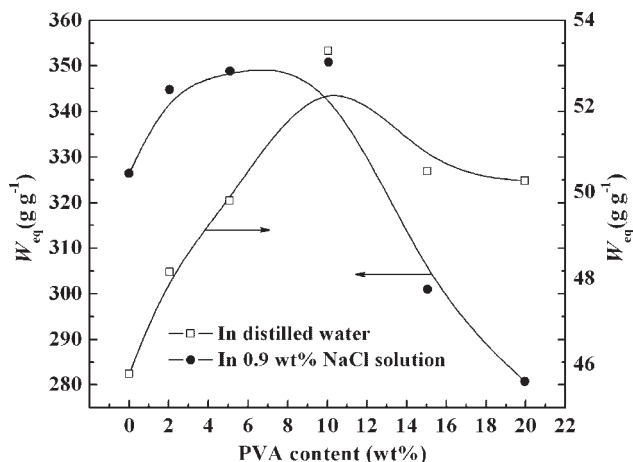

Figure 5. Water absorbency variation of CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogels with the weight ratio of AA to CTS.

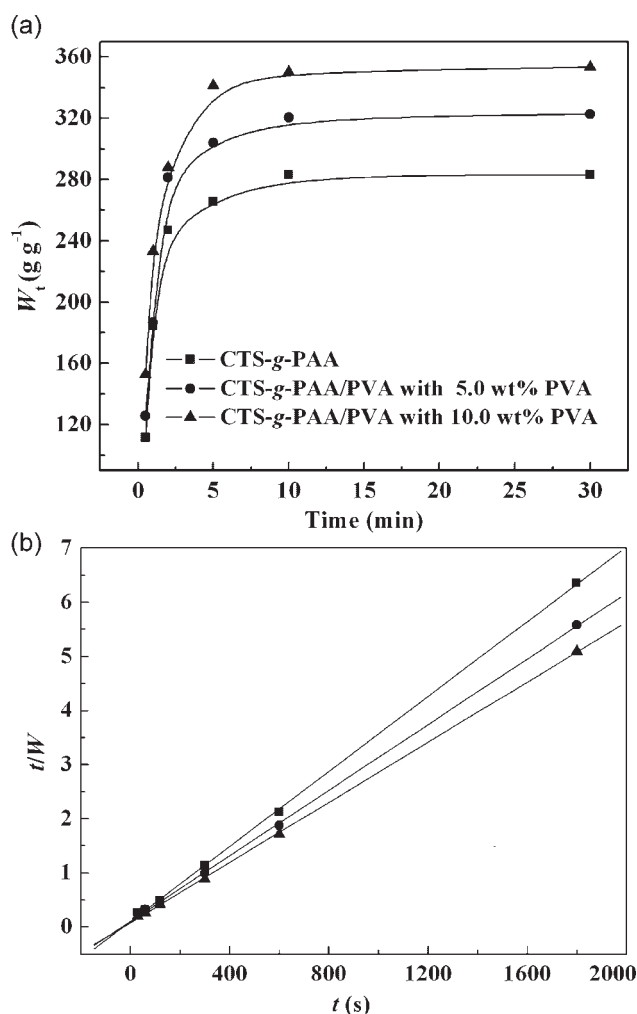 View this article online at wileyonlinelibrary.com

Figure 7. (a) Swelling kinetic curves of CTS-*g*-PAA and CTS-*g*-PAA/PVA semi-IPN superabsorbent with 5 wt% and 10 wt% PVA in distilled water, and (b) *t/W* versus *t* graph for CTS-*g*-PAA and CTS-*g*-PAA/PVA with 5 wt% and 10 wt% PVA.

superabsorbents observes the Scott's swelling theoretical model. The swelling kinetic parameters including swelling rate constant (K_s), the theoretical equilibrium water absorbency (W_{eq}), and the initial swelling rate ($K_{is} = K_s \times W_{eq}^2$) can be calculated by fitted the experimental data using eqn (3) and the results are given in Table 2.

Table 2. The swelling kinetics parameters of CTS-*g*-PAA and CTS-*g*-PAA/PVA

Samples	W_{eq}^a	W_{eq}^b	K_s^c	K_{is}^d
PVA0	282	289	11.8×10^{-5}	9.83
PVA2	320	330	9.18×10^{-5}	10.00
PVA3	353	360	9.84×10^{-5}	12.73

[a] Experimental equilibrium swelling.
[b] Theoretical equilibrium swelling; g_{water}/g_{gel}.
[c] Swelling rate constant (g_{gel}/g_{water})/sec.
[d] Initial swelling constant (g_{water}/g_{gel})/sec.

It can be noticed that from Table 2 that the values of theoretical equilibrium water absorbency (W_{eq}) are almost equal to the experimental equilibrium water absorbency, and the initial swelling rate constant (K_{is}) for CTS-*g*-PAA/PVA is obviously larger than that of CTS-*g*-PAA. This may be attributed to looser and porous structure of CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogel, which is favorable to the penetration of water molecules into the superabsorbent networks. However, the swelling rate constant (K_s) for CTS-*g*-PAA/PVA is less than that of CTS-*g*-PAA. This is because that the introduction of PVA into CTS-*g*-PAA network has greatly improved the equilibrium water absorbency of the resulting hydrogels, the polymer chains, and the network space need relatively longer time to reach the equilibrium, and so the time to achieve swelling equilibrium was prolonged and the swelling rate was slowed. As described above, it can be concluded that the initial swelling rate for CTS-*g*-PAA/PVA was improved due to the incorporation of PVA and the swelling process was greatly affected by PVA content.

Effect of pH on water absorbency

The swelling behaviors of CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogels with various amounts of PVA as well as CTS-*g*-PAA in various pH solutions were studied and the results are shown in Fig. 8. As can be noticed, the water absorbency almost maintains constant in the pH range of 4–9 for CTS-*g*-PAA, 4–10 for CTS-*g*-PAA/PVA with 5 wt% PVA, and 4–11 for CTS-*g*-PAA/PVA with 10 wt% PVA semi-IPN superabsorbent hydrogel, respectively. According to previous report,[35,36] this behavior is attributed to the buffer action of –COOH and –COO⁻ groups with weak acid or weak base. In comparison with CTS-*g*-PAA, the adaptive range of CTS-*g*-PAA/PVA to pH was widen and the widen degree increases with increasing the content of PVA, which indicate that the introduction of nonionic PVA and the formation of semi-IPN structure enhanced the buffer action of –COOH and –COO⁻ groups and improved the pH-stability of the superabsorbent hydrogels, and the adaptive range of the hydrogels can also be controlled by altering the content of PVA. However, the buffer action vanished and the water absorbency sharply decreased when pH < 4 or pH > 9 for CTS-*g*-PAA, pH > 10 for CTS-*g*-PAA/PVA with 5 wt% PVA and pH > 11 for CTS-*g*-PAA/PVA with 10 wt% PVA.
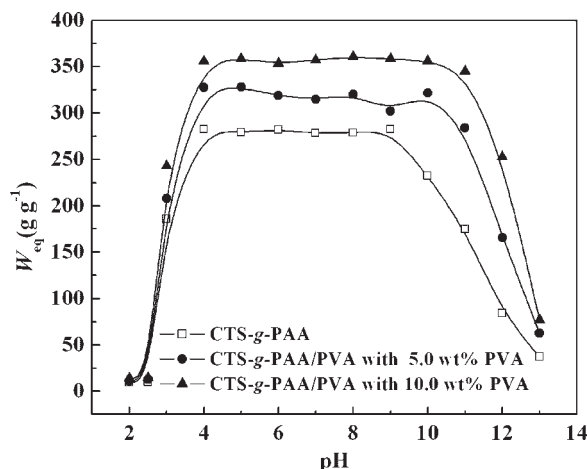

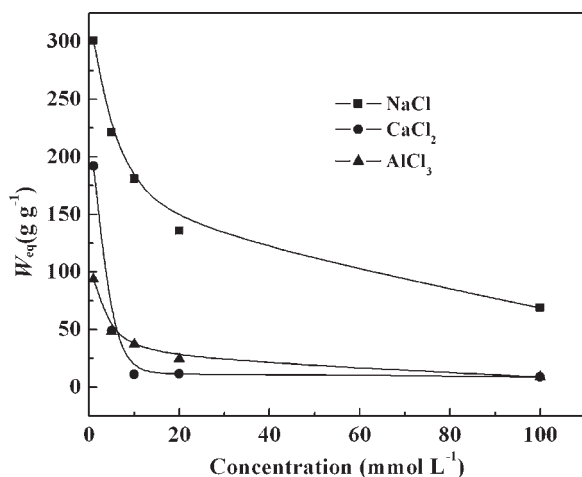Figure 8. Effect of the pHs of external solution on the water absorbency of CTS-*g*-PAA and CTS-*g*-PAA/PVA.

Figure 9. Effect of cationic salt solutions on the water absorbency of CTS-*g*-PAA/PVA with 10 wt% PVA.

Swelling behavior in saline solutions

The effect of saline on the water absorbency of superabsorbent is especially significant to its practical application in each field. In this section, the influence of saline solutions with different cations (Na^+, Ca^{2+}, Al^{3+}) and common anion (Cl^-) on the water absorbency of CTS-*g*-PAA/PVA with 10 wt% PVA semi-IPN superabsorbent hydrogel was investigated and the result is depicted in Fig. 9. As can be seen, the water absorbency degreased with increasing the concentration of external salt solutions. In addition, the water absorbency of the semi-IPN superabsorbent hydrogel in multivalent cationic salt solutions is always lower than that in monovalent cationic salt solution, and the water absorbency in multivalent salt solution at a high concentration is almost close to zero, but the water absorbency in monovalent cationic salt solution is greatly higher than that in multivalent salt solution even at a high concentration. As well known, the sensitivity of ionic superabsorbent hydrogels to monovalent saline has been mainly attributed to the reduction of osmotic pressure difference between gel networks and the salt-containing swelling medium. For the salt solution containing multivalent cations, the ionic sites of superabsorbent hydrogels can complex with multivalent cations, which reduced the negative charges in polymeric chains and produces denser crosslinking network. As a result, the expanding of polymeric network was restricted and the water-holding capabilities of the superabsorbents were remarkably decreased.

CONCLUSIONS

As part of the efforts to minimize the consumption of petroleum resource and the negative effect to environment resulting from the industrial polymers, the naturally occurred CTS and linear biodegradable PVA were utilized as raw materials for fabricating novel granular CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogels through aqueous solution polymerization. The developed semi-IPN superabsorbent hydrogel gives the best absorption of 353 g g^{-1} in distilled water and 53 g g^{-1} in 0.9 wt% NaCl solution. The results from IR spectra revealed that the characteristic absorption bands of CTS-*g*-PAA and PVA

appeared in the spectrum of CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogel. DSC results showed the characteristic T_m peak of PVA appeared in the DSC curve of CTS-*g*-PAA/PVA semi-IPN hydrogel, and this gives direct evidence that PVA existed in the semi-IPN hydrogel and combined with CTS-*g*-PAA network through hydrogen bonding interaction, and the semi-IPN structure was formed. The CTS-*g*-PAA/PVA semi-IPN superabsorbent hydrogel exhibited a looser and porous surface structure contrast to CTS-*g*-PAA hydrogel as shown by SEM observation, indicating that the incorporation of PVA greatly improved the surface morphologies of the hydrogels. The content of PVA can not only affect the water absorbency of the semi-IPN hydrogel, but also can control the size of the granular products. The kinetic swelling behaviors of the semi-IPN hydrogels obey second order swelling kinetics model, and the fitted kinetic parameters indicated that the initial swelling rate of the semi-IPN hydrogel was improved contrast to CTS-*g*-PAA hydrogel due to the incorporation of PVA. Moreover, the pH stability of the superabsorbent hydrogels was improved after introducing PVA and forming semi-IPN network structure, and the pH adaptability of the superabsorbent hydrogels can also be controlled by altering the content of PVA.

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