

Preparation and Swelling Properties of Semi-IPN Hydrogels Based on Chitosan-*g*-Poly(acrylic acid) and Phosphorylated Polyvinyl Alcohol

Jianghua Liu,^{1,2} Yian Zheng,¹ Wenbo Wang,^{1,2} Ai Qin Wang¹

¹Center for Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

²Graduate University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Received 1 December 2008; accepted 10 April 2009

DOI 10.1002/app.30592

Published online 8 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The phosphorylated poly(vinyl alcohol) (P-PVA) samples with various substitution degrees were prepared through the esterification reaction of PVA and phosphoric acid. By using chitosan (CTS), acrylic acid (AA) and P-PVA as raw materials, ammonium persulphate (APS) as an initiator and *N,N*-methylenebisacrylamide as a crosslinker, the CTS-*g*-PAA/P-PVA semi-interpenetrated polymer network (IPN) superabsorbent hydrogel was prepared in aqueous solution by the graft copolymerization of CTS and AA and followed by an interpenetrating and crosslinking of P-PVA chains. The hydrogel was characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) techniques, and the influence of reaction variables, such as the substitution degree and content of P-PVA on water absorbency were also investigated. FTIR and DSC results confirmed that PAA had been grafted

onto CTS backbone and revealed the existence of phase separation and the formation of semi-IPN network structure. SEM observations indicate that the incorporation of P-PVA induced highly porous structure, and P-PVA was uniformly dispersed in the polymeric network. Swelling results showed that CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogel exhibited improved swelling capability (421 g·g⁻¹ in distilled water and 55 g·g⁻¹ in 0.9 wt % NaCl solution) and swelling rate compared with CTS-*g*-PAA/PVA hydrogel (301 g·g⁻¹ in distilled water and 47 g·g⁻¹ in 0.9 wt % NaCl solution) due to the phosphorylation of PVA. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 643–652, 2009

Key words: chitosan; phosphorylated poly(vinyl alcohol); superabsorbent hydrogel; semi-interpenetrated polymer network; swelling

INTRODUCTION

Superabsorbent hydrogels are crosslinked hydrophilic polymers, which can imbibe and retain large quantities of aqueous fluids. Because of the particular advantages over traditional absorbents, these materials have been potentially used in various fields, such as healthcare product,¹ agriculture, and horticulture,^{2,3} wastewater treatment,^{4,5} and medicine for drug-delivery systems.^{6,7} However, most of the superabsorbent used as disposable articles is expensive synthetic polymer, their production consumes a lot of petroleum resource and their usage also causes a nonnegligible environmental problem.⁸ Thus, the further research was directed to the design

and synthesis of multicomponent superabsorbents based on natural materials due to their low cost, improved performance, and better environmental friendly characteristics.^{9–13}

Chitosan (CTS) is the world's second most abundant natural biopolymer with highly reactive hydroxyl and amino groups. CTS can be easily modified through various chemical or physical means, such as grafting copolymerization with hydrophilic vinyl monomers,¹⁴ polymer blending,^{15,16} and compounding with other functional components.^{17,18} Because of the nontoxicity, excellent biodegradability and biocompatibility, CTS, and their derivatives have been extensively applied in drug carrier, biomedical materials, and absorbents.¹⁹ Therefore, to extend the application of CTS and design novel biopolymer-based superabsorbents by a new means has become the subject of great interest.

Recently, interpenetrating polymer network (IPN) and semi-IPN provided a convenient route to modify the properties of natural polymer-based hydrogels.²⁰ IPNs and semi-IPNs are unique "alloys" of crosslinked polymers,²¹ in which at least one network is synthesized and/or crosslinked in the

Correspondence to: A. Wang (aqwang@lzb.ac.cn).

Contract grant sponsor: Western Action Project of CAS; contract grant number: KGCX2-YW-50.

Contract grant sponsor: "863" Project of the Ministry of Science and Technology, People's Republic of China; contract grant numbers: 2006AA03Z0454, 2006AA100215.

presence of the other. The formed “double network” IPN or semi-IPN systems usually exhibited surprising properties that are superior to either of the two single networks alone. Therefore, this means would be a better choice to meet the divergent demand in terms of both properties and performance. Poly (vinyl alcohol) (PVA) is a familiar hydrophilic, biodegradable, and commercially available linear polymer. By virtue of the excellent hydrophilic characteristics and gelling capability, PVA has been extensively used as water-soluble matrix polymer for preparing IPN and semi-IPN hydrogels.²² However, incorporation of PVA into superabsorbent network can only improve the water absorbency to a limited degree due to its strong hydrogen bonding interaction with gel network. It is desired that the further modification of PVA can improve the performance of superabsorbent more remarkably. Phosphorylation has been approved to be an effective method for modifying multihydroxyl polymer and improving the properties of superabsorbents,²³ and PVA can be easily phosphorylated like polysaccharide due to the existence of large amounts of —OH groups on its chains. Also, the phosphorylated PVA (P-PVA) also exhibited improved hydrophilicity, anionic properties and molecular electrostatic repulsion, and retained the bulk morphological features, compatible property, and solution stability of PVA.²⁴ The introduction of P-PVA into superabsorbent and its combination with CTS through semi-IPN technique was expected to derive a novel superabsorbent, and the granular semi-IPN hydrogels based on CTS and P-PVA which could be directly formed in aqueous solution have not been reported up to now.

Based on earlier description, in current work, a series of granular CTS-g-poly[acrylic acid (AA)]/CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogels were prepared by using CTS, AA, and P-PVA as raw materials. The structure and morphology of the developed hydrogel was characterized by means of Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) techniques. In addition, the effects of polymerization variables on the water absorbency of the semi-IPN hydrogels were studied and the swelling kinetics and swelling behavior in various pH solutions were evaluated systematically.

EXPERIMENTAL

Materials

CTS (degree of deacetylation is 0.90, average molecular weight is 30×10^4) was purchased from Golden-shell Biochemical Co. (Zhejiang, China). AA (distilled under reduced pressure before polymerization), 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). PVA (degree of polymerization is 1700 ± 50 , alcoholysis degree is 99%) was supplied by Lanzhou New-West Vinylon Co. (Lanzhou, China). Other reagents used were all of analytical grade, and all solutions were prepared with distilled water.

Preparation of P-PVA and determination of substitution degree

The phosphorylation of PVA using H_3PO_4 as esterification agent under the catalytic action of urea was carried out using a slightly improved procedure by previous report.²⁵ Typically, 10 g of PVA, 50 mL of phosphoric acid, and a calculated amount of urea were dissolved in 50-mL distilled water in a 250-mL three-neck flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer. The resultant solution was then heated to $90^\circ C$ under continuous mechanical stirring and maintained for 3 h to finish reaction. After the product was cooled to room temperature, an excess of anhydrous ethanol was slowly added into the reaction flask with vigorous stirring, and then a large amounts of floc was precipitated from the flask. The floc product was filtered out and washed with ethanol for several times until the pH value of washed solution reached 5–6. Finally, the product was dried to constant weight at $40^\circ C$ in a vacuum oven.

Substitution degree denotes substitutional degree of esterification per 100 hydroxy units. The measurement of substitution degree was carried out as follows: 30 mg of accurately weighed sample was decomposed with 10-mL mixed acid ($HNO_3 : HClO_4 = 1 : 1$), and then the resultant solution was thoroughly transferred into a 25-mL volumetric flask and diluted with distilled water to the scaleplate. A 5 mL of mixed solution prepared above, 5 mL ammonium metavanadate (0.25%), and 5 mL ammonium molybdate (5%) was added to another 25-mL volumetric flask and diluted to the scaleplate. Then the absorbency of the solution was determined by UV-Vis spectrophotometer at 395 nm. The potassium dihydrogen phosphate was used to prepare standard solution, and the concentration of phosphorus (c : mg/mL) was calculated according to the standard curve [$y = 4.1773x$ ($R = 1$)]. The substitution degree for P-PVA can be calculated according to the following equations:

$$m_p = c \times 25 \times 5 \text{ (mg)} \quad (1)$$

$$SD = \frac{m_p/31}{(30 - m_p \times 80/31)/44} \times 100\% \quad (2)$$

where m_p is the mass of phosphorus (mg), c is the concentration of phosphorus (mg/mL), and SD is

TABLE I
The Dosage of Urea and the Corresponding Substitution Degree of P-PVA

m_{urea} (g)	0.5	2.0	4.0	6.0
Substitution degree (%)	6.51	5.95	2.61	1.95

the degree of substitution of P-PVA. The dosages of urea and the corresponding substitution degree of P-PVA were listed in Table I.

Preparation of CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogel

A series of CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogels were prepared through graft polymerization according to the following procedure. An appropriate amount of P-PVA was added to 30-mL deoxygenated 1 vol% acetic acid solution in a 250-mL four-neck flask equipped with a mechanical stirrer, a reflux condenser, a funnel and a nitrogen line, and then the solution was heated to 95°C under stirring for 30 min to obtain transparent P-PVA solution. After the temperature fell to 80°C, CTS were added to the solution and the solution was vigorously stirred for 30 min to achieve a homogenous solution. Then 0.0902 g APS was added to the solution, and it was vigorously stirred for 10 min to generate radicals. The mixed solution of AA (3.60 g), distilled water, and certain amount of MBA were added to the flask, and the polymerization reaction was carried out at 80°C for 3 h. The resultant granular product was allowed to cool to ambient temperature and neutralized to pH = 7 using standard 1 mol/L NaOH solution. After swelling thoroughly

in distilled water, the swollen granular product was immersed in excess anhydrous methanol for 24 h. Finally, the dewatered sample were spread on a dish and dried to constant weight at 60°C, and the dried sample was milled and passed through a 40–80 mesh (180–380 μm) before test. CTS-*g*-PAA hydrogel was prepared according to the similar procedure except without P-PVA. The feed compositions of all samples were listed in Table II.

Measurements of water absorbency and swelling kinetics

A 0.05 g of sample was immersed in excess distilled water (200 mL) at ambient temperature for 4 h to reach swelling equilibrium. The swollen gel samples were then separated from unabsorbed water by filtering through 100-mesh screen under gravity for 10 min with no dropping. The equilibrium water absorbency (W_{eq}) of CTS-*g*-PAA/P-PVA in distilled water was measured thrice and calculated using the following equation:

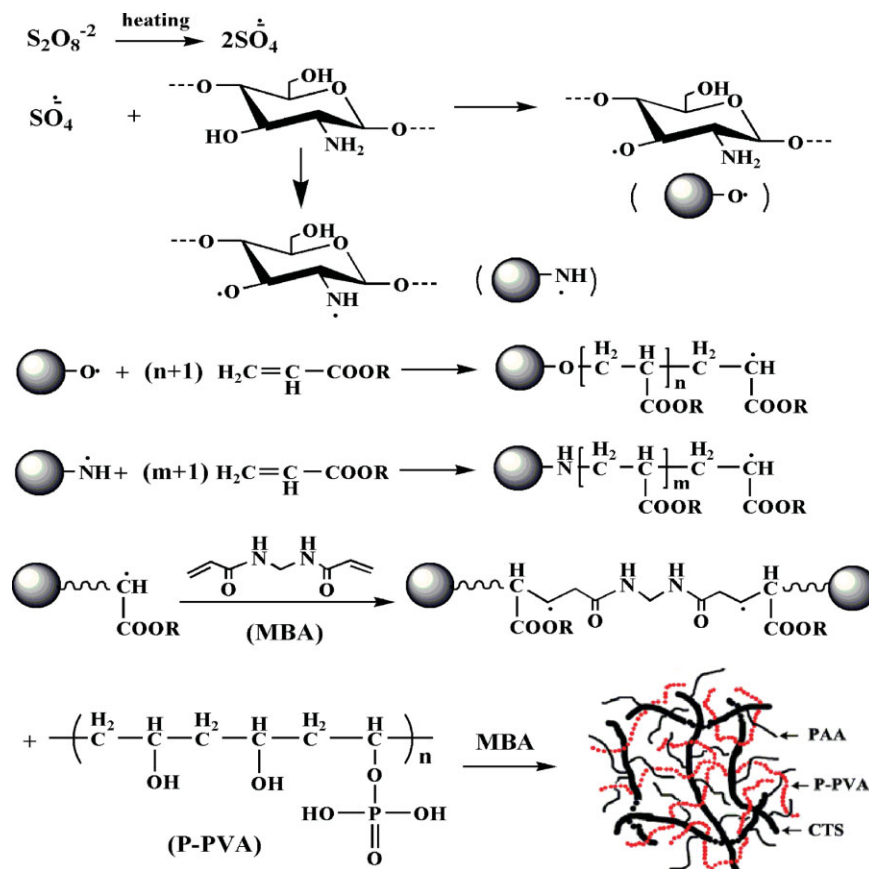
$$W_{\text{eq}} (\text{g} \cdot \text{g}^{-1}) = (m_2 - m_1)/m_1 \quad (3)$$

where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively.

Swelling kinetics of superabsorbent hydrogels was measured according to the following method: 0.05 g of sample was immersed into 200 mL of distilled water. At certain time intervals, the swollen gels were filtered out using a screen. After weighing the swollen gels, the water absorbency of the superabsorbent hydrogels can be calculated according to eq. (3).

TABLE II
The Reaction Conditions for CTS-*g*-PAA/P-PVA

No.	AA (g)	MBA (g)	CTS (g)	P-PVA (g)	Substitution degree of P-PVA (%)
MBA1	3.60	0.0673	0.50	0.23	5.95
MBA2	3.60	0.0902	0.50	0.23	5.95
MBA3	3.60	0.1133	0.50	0.23	5.95
MBA4	3.60	0.1367	0.50	0.23	5.95
MBA5	3.60	0.1520	0.50	0.23	5.95
CTS1	3.60	0.0902	0.45	0.23	5.95
CTS2	3.60	0.0902	0.50	0.23	5.95
CTS3	3.60	0.0902	0.60	0.23	5.95
CTS4	3.60	0.0902	0.72	0.23	5.95
CTS5	3.60	0.0902	0.90	0.23	5.95
P-PVA0	3.60	0.0902	0.50	0	–
P-PVA1	3.60	0.0902	0.50	0.09	5.95
P-PVA2	3.60	0.0902	0.50	0.13	5.95
P-PVA3	3.60	0.0902	0.50	0.23	5.95
P-PVA4	3.60	0.0902	0.50	0.37	5.95
SD0	3.60	0.0902	0.50	0.23	0
SD1	3.60	0.0902	0.50	0.23	1.95
SD2	3.60	0.0902	0.50	0.23	2.61
SD3	3.60	0.0902	0.50	0.23	5.95
SD4	3.60	0.0902	0.50	0.23	6.51



Scheme 1 Proposed mechanisms for the formation of semi-IPN superabsorbent hydrogel network. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Measurement of water absorbency in various pH solutions

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 in distilled water.

Characterization

The FTIR spectra were recorded on a Nicolet NEXUS FTIR spectrometer in 4000–400 cm^{-1} region using KBr pellets. The surface morphologies of the samples were examined using a JSM-5600 scanning electron microscope (JEOL, Tokyo, Japan) after coating the sample with gold film. The thermal behaviors of CTS-g-PAA, CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogel, and P-PVA were investigated on a Perkin Elmer DSC-7 (Perkin-Elmer, Norwalk, CT) instrument at a heating rate of 10°C/min using dry nitrogen purge at a flow rate of 50 mL/min.

RESULTS AND DISCUSSION

Synthesis of the CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogel

The semi-IPN superabsorbent hydrogel network for CTS-g-PAA/P-PVA can be formed through the graft-

ing polymerization of CTS with PAA followed by a semi-interpenetration of P-PVA in the presence of initiator APS and crosslinker MBA. The proposed mechanism was depicted in Scheme 1. At the initial step, the sulfate anion radicals was generated after the thermal decomposition of initiator APS, and then these radicals strip down the hydrogen of –OH or –NH₂ groups on CTS chains to form radicals. These radicals can act as the active centers during polymerization and can initiate monomers to process chain propagation. In the course of the chain propagation, the crosslinker MBA containing vinyl groups participated in reaction and the linear P-PVA also combined with polymeric network through strong hydrogen bonding interaction.

FTIR spectra analyses

FTIR spectra of CTS, PAA, CTS-g-PAA, CTS-g-PAA/P-PVA with 5 wt % and 8 wt % of P-PVA are shown in Figure 1. As can be seen from Figure 1(a), the absorption bands of CTS at 1659, 1593, 1381, 1088, and 1033 cm^{-1} are ascribed to the stretching vibration of C=O of amide I, –NH₂, –NHCO of amide III, C₃–OH and C₆–OH of CTS, respectively. After reaction, the characteristic absorption bands of CTS

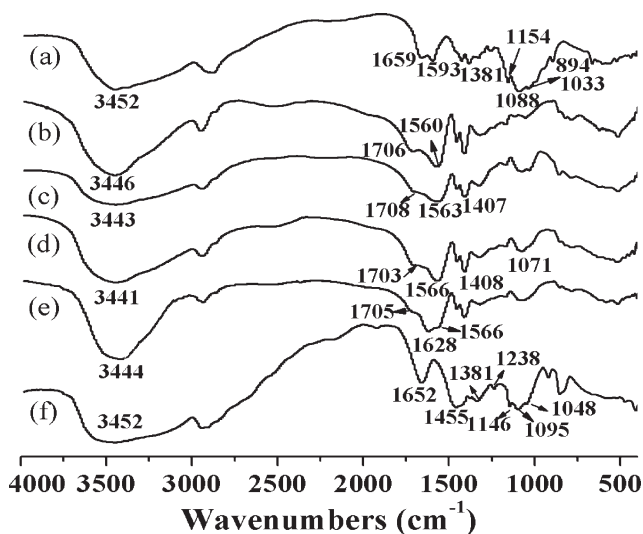


Figure 1 FTIR spectra of (a) CTS, (b) PAA, (c) CTS-g-PAA, (d) CTS-g-PAA/P-PVA (5 wt %), (e) CTS-g-PAA/P-PVA (8 wt %) semi-IPN hydrogels, and (f) P-PVA.

appeared in the FTIR spectrum of CTS-g-PAA [Fig. 1(c)], but their intensity was obviously weakened. Also, the new bands at 1563 and 1407 cm^{-1} assigned to the asymmetric stretching and symmetric stretching of $-\text{COO}^-$ groups were observed in the spectrum of CTS-g-PAA and are very close to the characteristic absorption of PAA [Fig. 1(b)], which reveals that the graft copolymerization reaction took place among $-\text{NH}_2$, $-\text{NHCO}$, $-\text{OH}$ groups of CTS and AA.¹⁸ As shown in Figure 1(f), the FTIR spectrum of P-PVA showed characteristic absorption bands of $\text{P}=\text{O}$ at 1652 cm^{-1} and $\text{P}-\text{O}-\text{C}$ at 1048 cm^{-1} . However, the $\text{P}=\text{O}$ band at 1652 cm^{-1} can be clearly observed in the spectrum of CTS-g-PAA/P-

PVA (8 wt %), which shifted to 1628 cm^{-1} due to the hydrogen bonding interaction of P-PVA with polymer chains. This gives direct evidence that the linear P-PVA was existed in the semi-IPN hydrogels, and combined with CTS-g-PAA gel network by only some hydrogen bonding interaction among them.

Morphological analyses

Aqueous solution polymerization is the common method for the preparation of superabsorbent hydrogels. Because most of the hydrogels prepared through solution polymerization are gelatinous products, the granular hydrogels that can be directly formed in aqueous solution have long been desired. Based on the previous report,¹⁸ the granular semi-IPN superabsorbent hydrogels derived from CTS and P-PVA were obtained in aqueous solution and their digital photographs were shown in Figure 2. It can be observed that the CTS-g-PAA and CTS-g-PAA/P-PVA hydrogels all exhibited granular shape. However, serious agglomeration of hydrogel granules was appeared for CTS-g-PAA, and the CTS-g-PAA/P-PVA semi-IPN hydrogel granules may restrain this agglomeration and exhibited better dispersion. For studying the surface morphology of the granular hydrogels, the SEM micrographs of CTS-g-PAA and CTS-g-PAA/P-PVA with 5 wt % and 8 wt % P-PVA semi-IPN superabsorbent hydrogels were observed and shown in Figure 3. As can be observed from Figure 3(a), CTS-g-PAA shows a rough surface with fewer pores, whereas CTS-g-PAA/P-PVA semi-IPN hydrogels exhibited a comparatively coarse and porous structure [Fig. 3(b,c)]. This observation indicates that the incorporation of P-PVA contributes to improve the surface morphologies of hydrogels. In

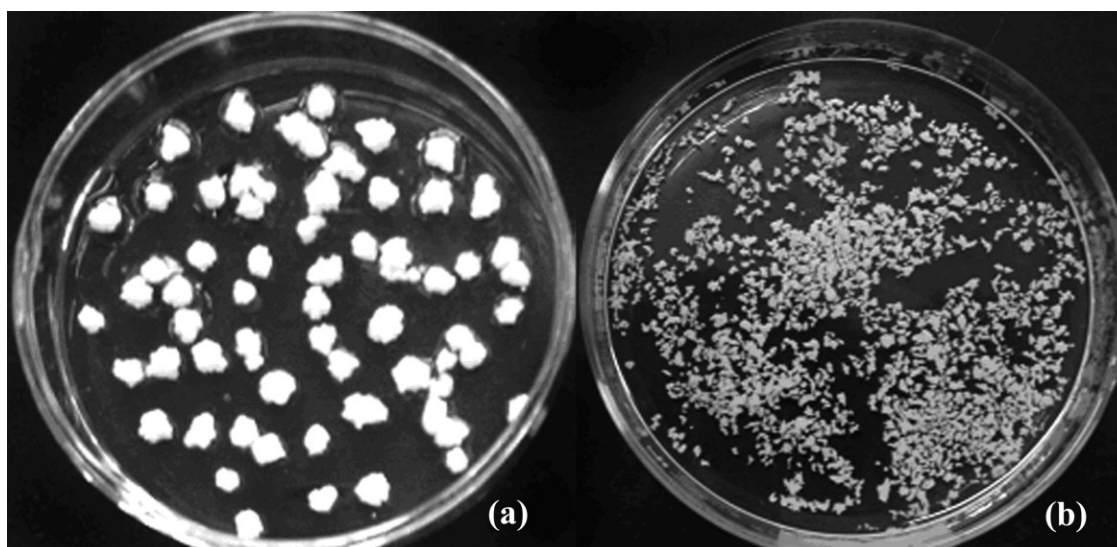


Figure 2 Digital photos of granular products of (a) CTS-g-PAA and (b) CTS-g-PAA/P-PVA (5 wt %) semi-IPN superabsorbent hydrogel.

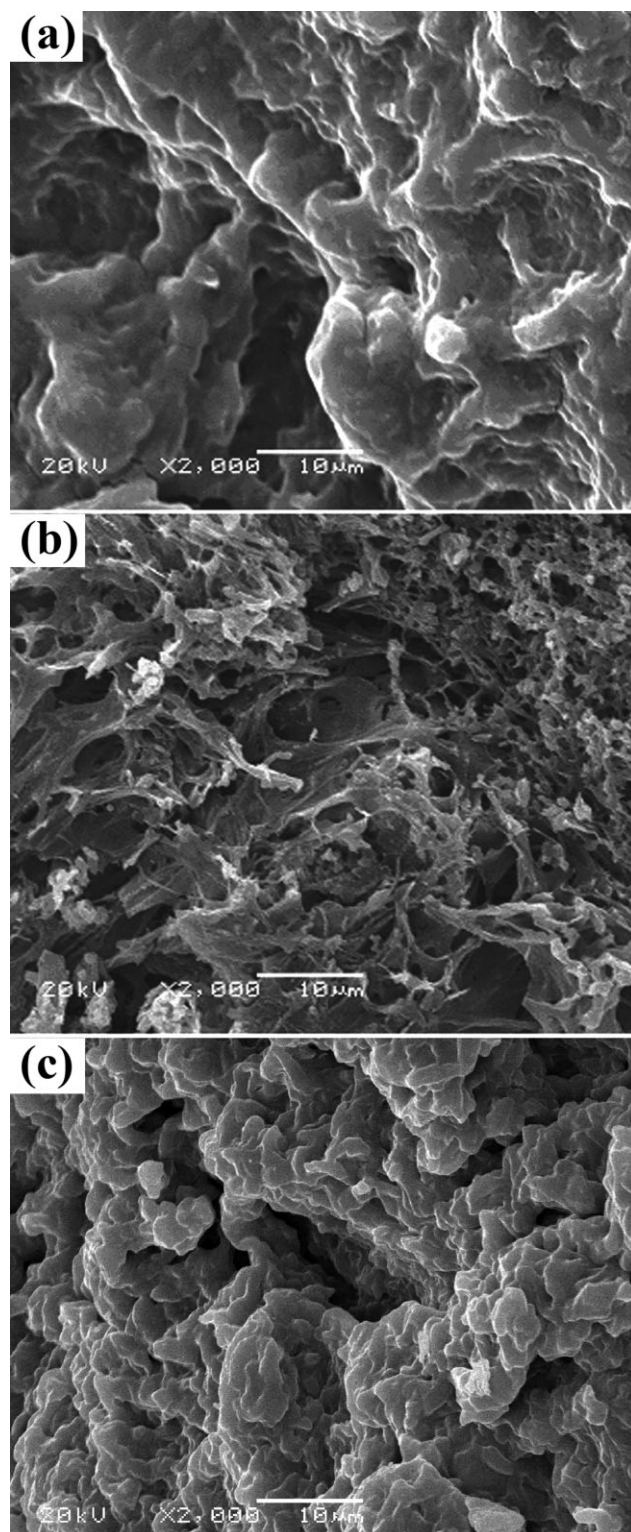


Figure 3 SEM micrographs of (a) CTS-g-PAA, (b) CTS-g-PAA/P-PVA (5 wt %), and (c) CTS-g-PAA/P-PVA (8 wt %).

comparison with Figure 3(b,c), it can be depicted that the CTS-g-PAA/P-PVA (5 wt %) hydrogel showed better porous network structure than CTS-g-PAA/P-PVA (8 wt %), and the surface of CTS-g-

PAA/P-PVA (8 wt %) was denser than that of CTS-g-PAA/P-PVA (5 wt %).

DSC analyses

Figure 4 exhibits the DSC thermograms of CTS-g-PAA, CTS-g-PAA/P-PVA semi-IPN hydrogel, and P-PVA. As is shown in Figure 4(c), PVA exhibited an endothermic peak at 73°C corresponding to the glass transition temperature (T_g) and a strong endothermic peak at 248°C corresponding to the melting transition (T_m) of PVA.^{26,27} After phosphorylation, the T_g of P-PVA become un conspicuous and the T_m peak shifted to 235°C. The crosslinked CTS-g-PAA showed an endothermic peak at 87°C, which was ascribed to the removal of water molecules retained inside the polymeric structure. The DSC curve of CTS-g-PAA/P-PVA appeared the characteristic T_m peak of P-PVA at 249°C [Fig. 4(b)], which shifted to higher temperature contrast to that of P-PVA due to the hydrogen bonding interaction between P-PVA

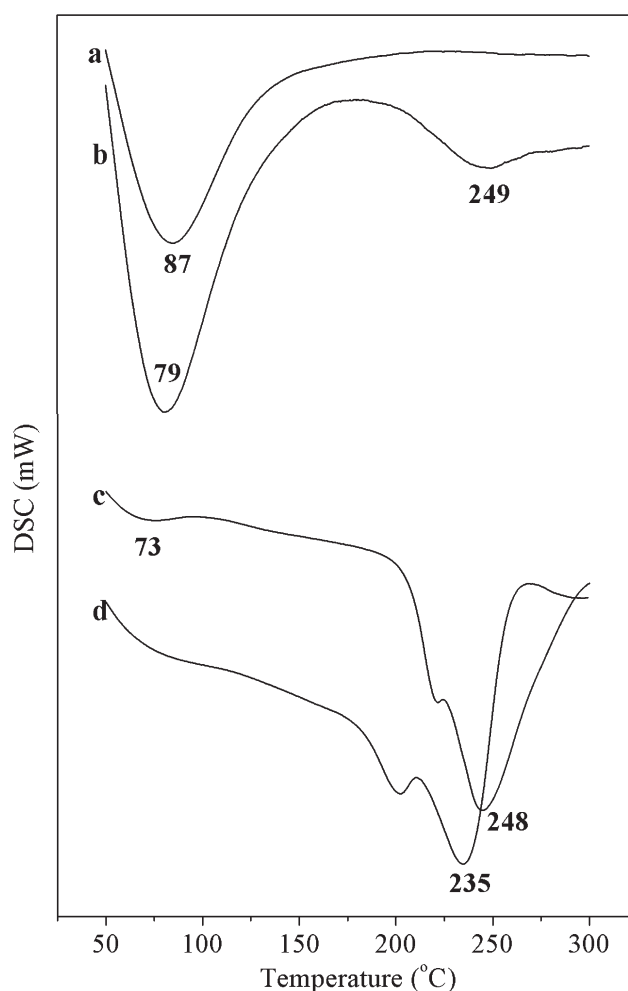


Figure 4 DSC thermograms of (a) CTS-g-PAA, (b) CTS-g-PAA/P-PVA (5 wt %) semi-IPN superabsorbent hydrogel, (c) PVA, and (d) P-PVA.

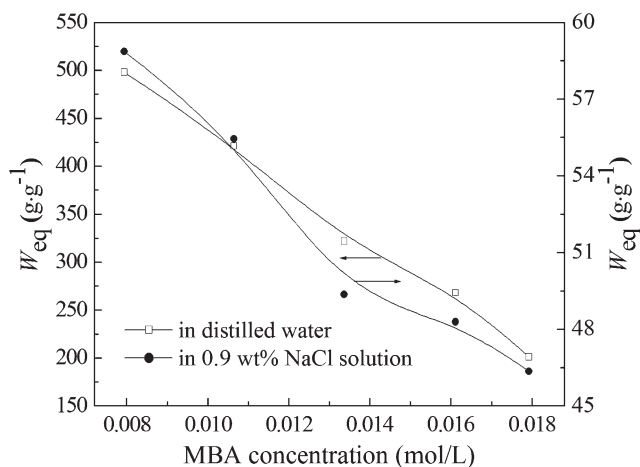


Figure 5 Effect of MBA content on water absorbency in distilled water and in 0.9 wt % NaCl solution.

and hydrogel network. Because that no endothermic peak can be observed in the DSC curve of CTS-*g*-PAA in this region, the appearance of characteristic peak of P-PVA indicates that the linear P-PVA chains are not chemically bonded with gel network but are only combined with polymer network through hydrogen bonds. By comparing the change of samples in DSC curves before and after reaction, the phase separation between CTS-*g*-PAA and P-PVA as well as the formation of semi-IPN structure can be confirmed.

Effect of MBA content on water absorbency

It is well known that the concentration of crosslinker usually exhibits more remarkable influence on the water absorbency than others. Figure 5 shows the effect of MBA concentration on the water absorbency of CTS-*g*-PAA/P-PVA in distilled water and in 0.9 wt % NaCl solution. As can be seen, the water absorbency decreases abruptly with increasing MBA concentration. This is because higher crosslinker concentration produced more crosslinking points in the polymeric network, which resulted in the generation of highly crosslinked rigid structure and the shrinkage of polymeric network space used for holding water. As a result, the water absorbency decreased. A power law behavior between water absorbency and crosslinker content was calculated according to the following equation from eq. (4).²⁸

$$W_{\text{eq}} = kC_{\text{MBA}}^{(-n)} \quad (4)$$

C_{MBA} is the concentration of crosslinker MBA. k and n are constant values for an individual superabsorbent: n value represents the extent of the sensitivity of the hydrogel to the crosslinker content, whereas k value gives an amount useful for comparing the extent of swelling versus fixed crosslinker content.

The k and n values can be calculated by fitting the experimental data using eq. (4). For semi-IPN superabsorbent hydrogel CTS-*g*-PAA/P-PVA (5 wt %), the relation between W_{eq} and C_{MBA} follows the equations $W_{\text{eq}} = 4.88C_{\text{MBA}}^{(-0.9638)}$ in distilled water and $Q_{\text{eq}} = 15.66C_{\text{MBA}}^{(-0.7559)}$ in 0.9 wt % NaCl solution. The similar tendency can be observed in superabsorbents CTS-*g*-poly(AA-*co*-acrylamide)²⁹ and guar gum-*g*-poly(sodium acrylate)/sodium humate.³⁰

Effect of weight ratio of AA to CTS on water absorbency

The effect of weight ratio of AA to CTS on water absorbency was shown in Figure 6. As can be seen, the water absorbency increased almost linearly with increasing the weight ratio of AA to CTS. Because that the dosage of initiator APS is definite, the number of free radicals generated by the decomposition of APS did not vary in reaction systems. Thus, the dosage of monomer may directly determine the reaction rate and the amount of hydrophilic groups in superabsorbents. As the increase in the weight ratio of AA to CTS, more AA molecules are available in the vicinity of active sites of CTS and participate in polymerization reaction more easily.³¹ As a result, the hydrophilicity of the superabsorbent was improved due to the polymerization of AA. Moreover, the osmotic pressure difference derived from the neutralization of PAA chains and the repulsive interaction derived from the negative $-\text{COO}^-$ groups also increased with increasing the dosage of AA, which is also responsible for the enhancement of the water absorbency.¹⁸

Effect of P-PVA content on water absorbency

The effect of P-PVA content in the feed system of CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogel was investigated and the result was shown in

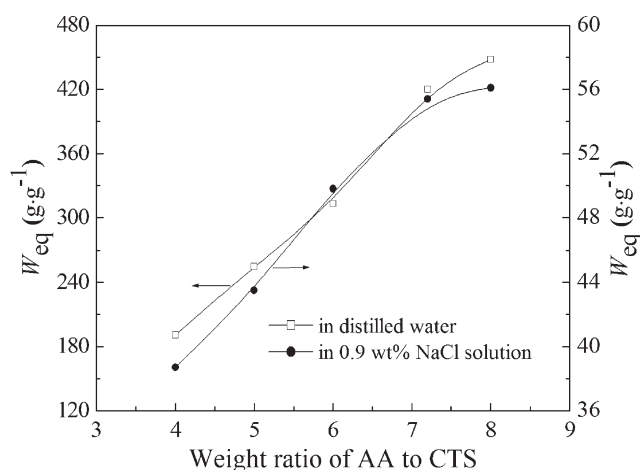


Figure 6 Effect of weight ratio of AA to CTS on water absorbency in distilled water and in 0.9 wt % NaCl solution.

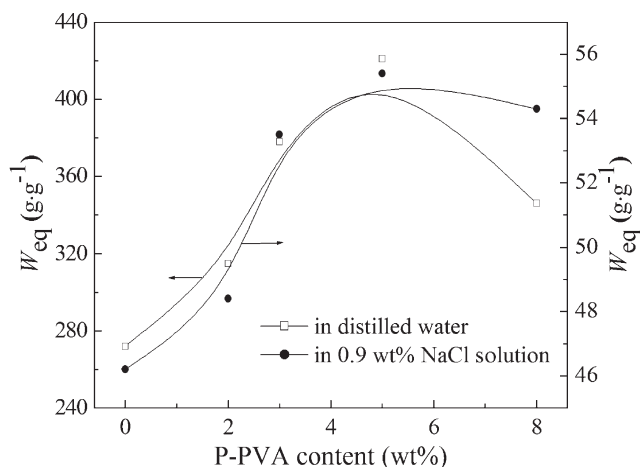


Figure 7 Effect of P-PVA content on the water absorbency.

Figure 7. The water absorbency of CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogel increased dramatically with the increase of P-PVA content, reaching a maximum at the content of 5 wt % P-PVA and then decreased. The semi-IPN hydrogel obtained under the optimum condition shows the best water absorbency of 421 g.g⁻¹ in distilled water and 55.4 g.g⁻¹ in 0.9 wt % NaCl solution. And the optimum water absorbency of CTS-g-PAA/P-PVA in distilled water almost increased twofold comparing that of sample without P-PVA. The initial increase in the content of P-PVA leads to an increase in hydrophilicity of semi-IPN superabsorbent hydrogel, which results in enhancement of water absorbency. However, the further increase of P-PVA content in semi-IPN superabsorbent hydrogel induces the increase of dense of macromolecular chains, which restricts the penetration of water molecules into semi-IPN polymeric network.³² Also, the numbers of physical crosslinking points resulting from the entanglement between P-PVA and CTS-g-PAA network also increased, which increased the crosslink density and decreased the water absorbency of the superabsorbent hydrogel.

Effect of substitution degree of P-PVA on water absorbency

Table III depicts the water absorbency of CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogel as a function of substitution degree of P-PVA. As shown in Table III, CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogels with different substitution degree all exhibited higher water absorbency than CTS-g-PAA/PVA, indicating that the phosphorylation of PVA is favorable to the enhancement of water absorbency of the resultant hydrogels. It can be obviously observed that the water absorbency rapidly increased with the augment of substitution degree of P-PVA,

reaching a maximum at 5.95% and then decreased. This tendency can be attributed to the fact that (i) after being phosphorylated, the orderly arrangement of hydrogen bonds among PVA chains was destroyed due to the substitution of phosphate groups to part of the —OH groups; (ii) the P—OH can disassociate in solution to form negative P—O⁻ groups, which increased the repulsive interaction among P-PVA and negative PAA chains and then enhanced the water absorbency; (iii) the introduction of phosphate groups with stronger hydrophilicity generally improved the affinity of superabsorbent network to water, which is responsible for the enhancement of water absorbency.²⁴ However, the water absorbency decreases appreciably when substitution degree is higher than 5.95%. This is because more —OH groups from phosphates groups may also form hydrogen bonds with CTS-g-PAA in the network; the physical crosslinking was strengthened and the expanding of polymeric network was also restricted. As a result, the water absorbency was reduced.

Effect of external pHs on water absorbency

In the practical application, the sensitivity of superabsorbent hydrogel to the pHs of external aqueous media is also a nonnegligible factor. In this section, the swelling properties of CTS-g-PAA and CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogel are investigated in various pH solution ranged from 2 to 13, and the results are shown in Figure 8. It can be noticed that CTS-g-PAA and CTS-g-PAA/P-PVA shows similar swelling behaviors in various pH solutions. The water absorbency roughly maintains a constant pH from 4 to 11 and drastically decreases in the range of pH < 4 or pH > 10, and the water absorbency for CTS-g-PAA/P-PVA is always higher than that of CTS-g-PAA. The almost constant water absorbency of superabsorbent in the range of pH from 4 to 11 can be ascribed to the buffer action of —COOH and —COO⁻ with weak acid or weak base.³³ In acidic medium (pH < 4), increasing the pH of external solution may enhance the ionized degree of hydrophilic groups, which can induce an increase

TABLE III
Effect of the Substitution Degree on Water Absorbency of the Semi-IPN Superabsorbent Hydrogel

Substitution degree of P-PVA (%)	W _{eq} (g.g ⁻¹)	
	In distilled water	In 0.9 wt % NaCl solution
0	301	46.8
1.95	392	51.1
2.61	399	53.8
5.95	421	55.4
6.51	363	53.9

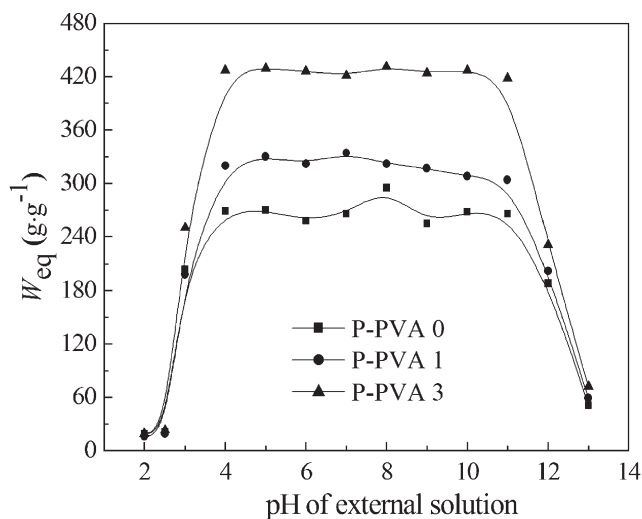


Figure 8 Effect of external pH on water absorbency for CTS-g-PAA and CTS-g-PAA/P-PVA superabsorbent hydrogels.

in the osmotic swelling pressure as well as the electrostatic repulsion among $-\text{COO}^-$ groups.³⁴ Thus, the polymeric network was more easily to expand and hold more water. When pH of external solution exceeds 11, the increased ionic strength of the external solution causes the rapid decrease of osmotic swelling pressure and ultimately reduces the equilibrium swelling capacity of the superabsorbent.³⁵

Swelling kinetics

The swelling kinetics of CTS-g-PAA and CTS-g-PAA/P-PVA semi-IPN superabsorbent hydrogel with various amounts of P-PVA in distilled water was evaluated. As shown in Figure 9(a), the water absorbency of CTS-g-PAA and CTS-g-PAA/P-PVA sharply increased within 5 min and then becomes level off, and the swelling equilibrium can be reached after 10 min. In this section, the swelling kinetics of the superabsorbent hydrogel in distilled water was expressed by the Scott's second-order swelling kinetics model [eq. (5)].^{36,37}

$$t/W_t = 1/K_s W_\infty^2 + 1/W_\infty t \quad (5)$$

W_t is the water absorbency at a given time t ; $1/W_\infty$ is the inverse of equilibrium water absorbency; $1/K_s W_\infty^2$ is the reciprocal of the initial water-absorbing rate of the superabsorbent, and K_s is swelling rate constant. As shown in Figure 9(b), the plots of t/W_t versus t give perfect straight lines with good linear correlation coefficient (>0.99), indicating that the swelling of superabsorbent hydrogels observes the Scott's swelling theoretical model. Also, by fitting experimental data using eq. (5), the swelling kinetic parameters for CTS-g-PAA and CTS-g-PAA/P-PVA

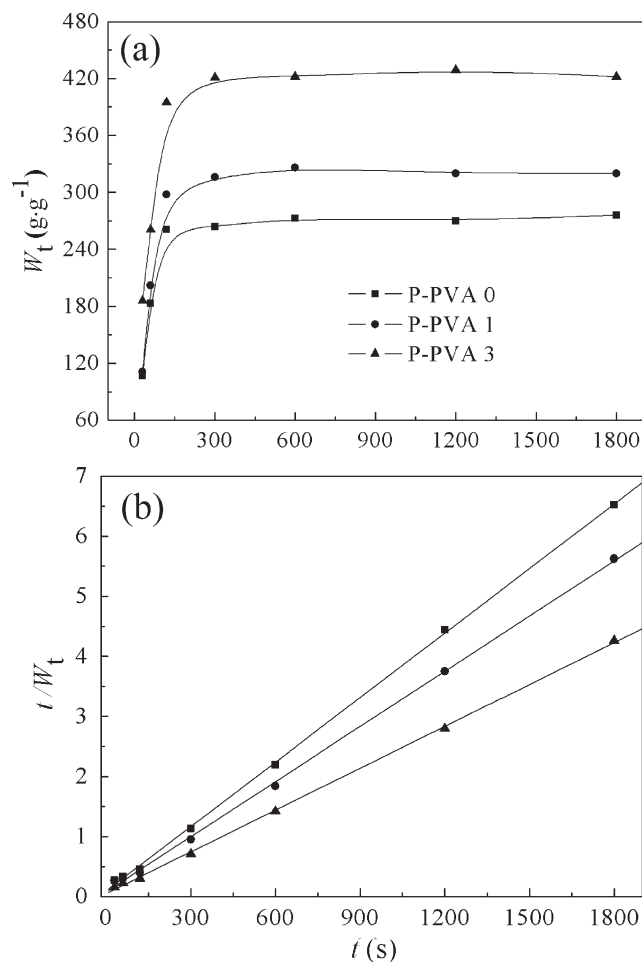


Figure 9 (a) Swelling kinetic curves of CTS-g-PAA (SA0) and CTS-g-PAA/P-PVA with various P-PVA content; (b) t/W_t and t graph of CTS-g-PAA and CTS-g-PAA/P-PVA with various P-PVA content.

semi-IPN superabsorbent hydrogel, including the swelling rate constant (K_s), the theoretical equilibrium water absorbency (W_∞), and the initial swelling rate ($K_{is} = K_s W_\infty^2$) can be calculated by the slope and intercept of lines [Fig. 9(b)], and the results were listed in Table IV. It can be concluded from the swelling parameters that the theoretical equilibrium water absorbency of superabsorbent hydrogels is almost equal to the experimental values. The

TABLE IV
Swelling Kinetic Parameters of CTS-g-PAA and CTS-g-PAA/P-PVA with Various P-PVA Content

Sample	^a W_{eq}	^b W_{eq}	^c K_s	^d K_{is}
P-PVA0	273	279	1.36×10^{-4}	10.64
P-PVA1	320	326	1.19×10^{-4}	13.70
P-PVA3	421	431	1.06×10^{-4}	19.73

^a Experimental equilibrium swelling.

^b Theoretical equilibrium swelling: g_{water}/g_{gel} .

^c Swelling rate constant: $(g_{gel}/g_{water})/s$.

^d Initial swelling constant $(g_{water}/g_{gel})/s$.

swelling rate constant K_s for CTS-*g*-PAA/P-PVA decreased but the initial swelling rate constant K_{is} increased as increasing the content of P-PVA. By comparison with CTS-*g*-PAA, CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogels exhibit higher initial swelling rate and equilibrium water absorbency. This may be attributed to that (i) the improved network structure and porous morphologies resulting from the formation of semi-IPN network because the porous structure is favorable to the penetration of water molecules into the superabsorbent networks; (ii) the phosphorylation of PVA introduced more hydrophilic and ionizable phosphate groups, which exhibited better affinity to water and is more beneficial to the expanding of superabsorbent network faster. As a result, the swelling rate was enhanced.

CONCLUSIONS

A series of semi-IPN superabsorbent hydrogels composed of CTS-*g*-PAA and P-PVA was prepared through graft copolymerization of AA onto CTS with APS as an initiator and MBA as a crosslinker in the present of P-PVA. The results obtained by FTIR spectra and DSC analyses of the samples proved the formation of semi-IPN structure. SEM analysis indicates the better porous structure of the semi-IPN hydrogel. A better water absorbency was obtained for CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogel in comparison with CTS-*g*-PAA, and the water absorbency was greatly affected by the content and substitution degree of P-PVA. CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogel with various substitution degrees in distilled water and in 0.9 wt % NaCl solution all absorbs more water than CTS-*g*-PAA/PVA, indicating that the phosphorylation of PVA contributes to enhance the water absorbency of the resultant superabsorbent hydrogel. The swelling kinetic curves of semi-IPN superabsorbent hydrogel are well fitted to second-order swelling kinetics model. CTS-*g*-PAA/P-PVA semi-IPN superabsorbent hydrogels exhibit a higher initial swelling rate, which may find potential applicability in various applications.

References

1. Malowanec, K. D. U.S. Pat. 6,414,216 B1 (2002).
2. Karada, E.; Saraydin, D.; Caldiran, Y.; Güven, O. *Polym Adv Technol* 2000, 11, 59.
3. Chu, M.; Zhu, S. Q.; Li, H. M.; Huang, Z. B.; Li, S. Q. *J Appl Polym Sci* 2006, 102, 5137.
4. Guilherme, M. R.; Reis, A. V.; Paulino, A. T.; Fajardo, A. R.; Muniz, E. C.; Tambourgi, E. B. *J Appl Polym Sci* 2007, 105, 2903.
5. Kaşgöz, H.; Durmus, A.; Kaşgöz, A. *Polym Adv Technol* 2008, 19, 213.
6. Hoare, T. R.; Kohane, D. S. *Polymer* 2008, 49, 1993.
7. Sadeghi, M.; Hosseinzadeh, H. J. *Bioact Compat Polym* 2008, 23, 381.
8. Kiatkamjornwong, S.; Mongkolsawat, K.; Sonsuk, M. *Polymer* 2002, 43, 3915.
9. Cao, L. Q.; Xu, S. M.; Feng, S.; Wang, J. D. *J Appl Polym Sci* 2005, 96, 2392.
10. Pourjavadi, A.; Ghasemzadeh, H.; Soleyman, R. *J Appl Polym Sci* 2007, 105, 2631.
11. Ibrahim, S. M.; El Salmawi, K. M.; Zahran, A. H. *J Appl Polym Sci* 2007, 104, 2003.
12. Li, A.; Liu, R. F.; Wang, A. Q. *J Appl Polym Sci* 2005, 98, 1351.
13. Ray, S. S.; Bousmina, M. *Prog Mater Sci* 2005, 50, 962.
14. Pourjavadi, A.; Mahdavinia, G. R.; Zohuriaan-Mehr, M. J. *J Appl Polym Sci* 2003, 90, 3115.
15. Chen, X.; Liu, J. H.; Feng, Z. C.; Shao, Z. Z. *J Appl Polym Sci* 2005, 96, 1267.
16. Jia, Y. T.; Gong, J.; Gu, X. H.; Kim, H. Y.; Dong, J.; Shen, X. Y. *Carbohydr Polym* 2007, 67, 403.
17. Mahdavinia, G. R.; Zohuriaan-Mehr, M. J.; Pourjavadi, A. *Polym Adv Technol* 2004, 15, 173.
18. Zhang, J. P.; Wang, Q.; Wang, A. Q. *Carbohydr Polym* 2007, 68, 367.
19. Rinaudo, M. *Prog Polym Sci* 2006, 31, 603.
20. Pourjavadi, A.; Ghasemzadeh, H. *Polym Eng Sci* 2007, 47, 1388.
21. Suthar, B.; Xiao, H. X.; Klempner, D.; Frisch, K. C. *Polym Adv Technol* 1996, 7, 221.
22. De Melo-Junior, M. R.; Alves, L. C.; Dos Santos, F. B.; Beltrão, E. I. C.; De Carvalho, L. B., Jr. *React Funct Polym* 2008, 68, 315.
23. Zhang, J. P.; Li, A.; Wang, A. Q. *Carbohydr Polym* 2006, 65, 150.
24. Sreenivasan, K. *J Appl Polym Sci* 2004, 94, 651.
25. Lin, Y.; Chen, B. Q. *Chem Res Appl (China)* 1996, 8, 547.
26. Strawhecker, K. E.; Manias, E. *Chem Mater* 2000, 12, 2943.
27. Yua, Y. H.; Lina, C. Y.; Yeha, J. M.; Lin, W. H. *Polymer* 2003, 44, 3553.
28. Kabiri, K.; Omidian, H.; Hashemi, S. A.; Zohuriaan-Mehr, M. J. *Eur Polym J* 2003, 39, 1341.
29. Mahdavinia, G. R.; Pourjavadi, A.; Hosseinzadeh, H.; Zohuriaan, M. J. *Eur Polym J* 2004, 40, 1399.
30. Wang, W. B.; Wang, A. Q. *J Appl Polym Sci* 2009, 112, 2102.
31. Chen, Y.; Tan, H. M. *Carbohydr Res* 2006, 341, 887.
32. Mohan, Y. M.; Murthy, P. S. K.; Sreeramulu, J.; Raju, K. M. *J Appl Polym Sci* 2005, 98, 302.
33. Lee, W. F.; Wu, R. J. *J Appl Polym Sci* 1996, 62, 1099.
34. Kiatkamjornwong, S.; Chomsaksakul, W.; Sonsuk, M. *Radiat Phys Chem* 2000, 59, 413.
35. Li, A.; Wang, A. Q.; Chen, J. M. *J Appl Polym Sci* 2004, 92, 1596.
36. Schott, H. *J Macromol Sci B* 1992, 31, 1.
37. El-Hamshary, H. *Eur Polym J* 2007, 43, 4830.