

Study on Superabsorbent Composites. XXI. Synthesis, Characterization and Swelling Behaviors of Chitosan-g-poly(acrylic acid)/Organo-Rectorite Nanocomposite Superabsorbents

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ABSTRACT: A novel chitosan-g-poly(acrylic acid)/organo-rectorite (CTS-g-PAA/OREC) nanocomposite superabsorbent was synthesized by aqueous polymerization using *N, N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator. Rectorite was organified with four different degree of hexadecyltrimethyl ammonium bromide, and the organification of rectorite was proved by FTIR and XRD. The effect of organification degree of rectorite on water absorbency of CTS-g-PAA/OREC with different organo-rectorite content was investigated. The swelling behaviors in distilled

water and various pH solutions were also studied. The results from IR spectroscopy and XRD data show that acrylic acid had been grafted polymerization with chitosan and organo-rectorite and formed nanocomposite. Introducing organo-rectorite into the CTS-g-PAA polymeric network can improved water absorbency and swelling rate of CTS-g-PAA/OREC. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 678–686, 2008

Key words: nanocomposite superabsorbent; chitosan; rectorite; water absorbency; swelling rate

INTRODUCTION

Superabsorbents are moderately crosslinked hydrophilic polymer material, which can imbibe and retain a large amount of aqueous solution. Owing to their excellent properties, superabsorbents have received considerable research and have been used in many fields such as healthcare products, agriculture and horticulture, wastewater treatment, medicine for drug-delivery systems and other numerous applications.^{1–3} Recently, superabsorbents prepared through chemical modification of natural polymers such as starch,⁴ chitin, and its derivatives chitosan,⁵ alginate,⁶ and pectin⁷ have attracted extensively investigated. Chitosan (CTS), the most abundant natural amino polysaccharide with specific structure and properties, has highly reactive hydroxyl and

amino groups distributed on its chains, which allow it to modify easily through various chemical modifications.⁸ Grafted copolymerization of hydrophilic vinyl monomers onto CTS is considered to be an efficient approach to prepare biodegradable superabsorbents.^{9,10}

In recent years, the polymer/clay superabsorbent composites have also attracted great attention, which can not only reduce production cost, but also exhibit excellent water-absorbing and water-retention capabilities.^{11–17} However, swelling rate of superabsorbent composites could be little enhanced and even reduced due to the phase separation when inorganic clay particles were added.^{18,19} Organic-modified clay through ion-exchange reaction can render hydrophilic layered silicate organophilic, which can improve adhesion of inorganic and polymer matrix and result in a larger interlayer spacing simultaneously.²⁰ Zhang et al. have reported that the water absorbency of polyacrylamide/organo-attapulgite superabsorbent composite was greatly enhanced by introducing organo-attapulgite in comparison with superabsorbent composite based on attapulgite.²¹

Rectorite (REC) is a kind of layered silicate, with the structure and characteristics much like that of bentonite. It is a sort of regularly interstratified clay mineral with alternate pairs of dioctahedral mica-like layer (nonexpansible) and dioctahedral smectite-

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like layer (expansible) existing in 1 : 1 ratio.²² So, REC can easily be organized by ion-exchange reaction between REC and hexadecyltrimethyl ammonium bromide in the solution. Up to now, there is no report has used REC and organo-rectorite (OREC) for the preparation of superabsorbent composites. Therefore, in this article, the chitosan-*g*-poly (acrylic acid)/organo-rectorite (CTS-*g*-PAA/OREC) nanocomposite superabsorbents were prepared through graft-copolymerization and the effect of organification degree of OREC on water absorbency and swelling rate of CTS-*g*-PAA/OREC nanocomposite superabsorbents was investigated. The effect of various pH solutions on water absorbency for CTS-*g*-PAA/OREC nanocomposite superabsorbents with different organification degree of OREC was also studied.

EXPERIMENTAL

Materials

Chitosan (CTS, degree of deacetylation is 0.90, average molecular weight is 30×10^4) was purchased from Golden-shell Biochemical (Zhejiang, China). Acrylic acid (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 (Shanghai, China) and hexadecyltrimethyl ammonium bromide (HDTMABr) was supplied by Beijing Chemical Reagents Company (Beijing, China). Calcium rectorite (Ca^{2+} -REC, simply rectorite, milled through 320-mesh screen before use) was provided by Hubei Mingliu (Wuhan, China). Other agents used were all of analytical grade and all solutions were prepared with distilled water.

The synthesis of OREC

OREC with different organification degree was synthesized as follows: four different amounts of HDTMABr were dissolved in 25 mL distilled water, respectively, and then 2.50 g REC was suspended in the above solution. The suspension was stirred vigorously at room temperature for 2 h, and then OREC was formed. The separated OREC was washed with large volume of distilled water to remove excess HDTMABr (until no bromide can be detected by 0.1M AgNO_3 solution in the filtrate), and then dried in an oven at 60°C for several hours until the weight was constant. The product was milled to 160 mesh size for further use.

Preparation of CTS-*g*-PAA/OREC nanocomposite superabsorbents

A series of CTS-*g*-PAA/OREC nanocomposite superabsorbents were prepared through grafted polymer-

ization according to the following procedure. An appropriate amount of CTS was dissolved in 30 mL 1% (v/v) acetic acid solution in a 250 mL four-neck flask, equipped with a mechanical stirrer, a reflux condenser, a funnel, and a nitrogen line. After being purged with nitrogen to remove the dissolved oxygen, the solution was heated to 60°C. Then 0.0953 g APS was added to CTS solution, and it was gently stirred for 10 min to generate radicals. The mixed solution of AA (3.60 g), MBA (0.0953 g) and certain amount of OREC were added to the flask. The polymerization reaction was carried out at 65°C and reaction mixture was under constant stirred for 3 h. The reaction product was allowed to cool to ambient temperature and neutralized to pH 7 by adding 1M NaOH solution. The swollen product was dewatered with methanol. After complete dewatering, the sample particles were spread on a dish and dried at 60°C. The product was milled and all samples used for test had a particle size in the range of 40–80 mesh. CTS-*g*-PAA/REC was prepared according to the same procedure.

The measurement of organification degree of OREC

The organification degree (denotes the weight percent of organic cation of HDTMABr in the OREC) of OREC was determined by thermogravimetric analysis according to our previous reported method.²¹ OREC (0.50 g) with different organification degree and REC was accurately weighted to the crucible, respectively, and then put into muffle. The muffle was heated to 800°C for several hours until those samples were calcined to constant weight. After transferring into desiccator and cooling to room temperature, those samples were weighed and organification degree of OREC was calculated according to the following equations:

$$\text{OD} = (h - p)/h \times 100\% \quad (1)$$

$$h \text{ or } p = m_1 - m_2 \quad (2)$$

where OD is organification degree of OREC; *h* and *p* are the weight loss of REC and OREC, respectively; *m*₁ and *m*₂ are the weight of the samples before and after calcining, respectively. The relationship of dosage of HDTMABr and the organification degree of OREC is shown in Table I.

The measurements of water absorbency and swelling rate in distilled water

0.05 g of sample was immersed in excess distilled water (50 mL) at ambient temperature for 4 h to reach swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering through 100-mesh screen under gravity for 10 min

TABLE I
The Dosage of HDTMABr and the Resultant Organification Degree

m_{HDTMABr} (g)	Organification degree (wt %)
0.1154	2.33
0.2886	7.31
0.5772	10.72
1.1544	16.73

with no blotting of samples. Water absorbency of nanocomposite superabsorbents (W_{eq}) in distilled water was measured twice and calculated using the following equation:

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

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

Swelling rate of nanocomposite superabsorbents in distilled water was measured according to the following method: 0.05 g of sample with various organification degree or various OREC content was immersed into 100 mL of distilled water of 500 mL beakers. At certain time intervals, the water absorbency of swollen samples was measured according to the aforementioned method.

Measurement of water absorbency in various pH solutions

The pH of external solutions was adjusted using 1M NaOH or HCl aqueous solutions. The method used

was the same as the water absorbency in distilled water.

Characterization

IR spectra of samples were taken as KBr pellets using a Thermo Nicolet NEXUS TM spectrophotometer. The micrographs of samples were taken using SEM (JSM-5600LV, JEOL). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. XRD patterns were gotten using an X'Pert PRO diffractometer. The test was performed using Cu K α radiation under a voltage of 40 kv and a current of 30 mA, scanning from 1.5° to 10° at room temperature.

RESULTS AND DISCUSSION

IR spectra analysis

Figure 1 shows the IR spectra of REC and OREC of different organification degree. As can be seen, in comparison with REC, a batch of new peaks at 2917, 2849, and 1469 cm^{-1} appeared in OREC with different organification degree, which belong to $-\text{CH}_3$ and $-\text{CH}_2$ asymmetrical stretching vibration, symmetrical stretching vibration and bending vibration. In addition, vibration strength of these new absorption peaks also enhanced as increasing organification degree of OREC. The results indicate organic cations of HDTMABr have been exchanged with the inter-layer Ca^{2+} of REC.²²

Figure 2 shows the IR spectra of CTS, CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite

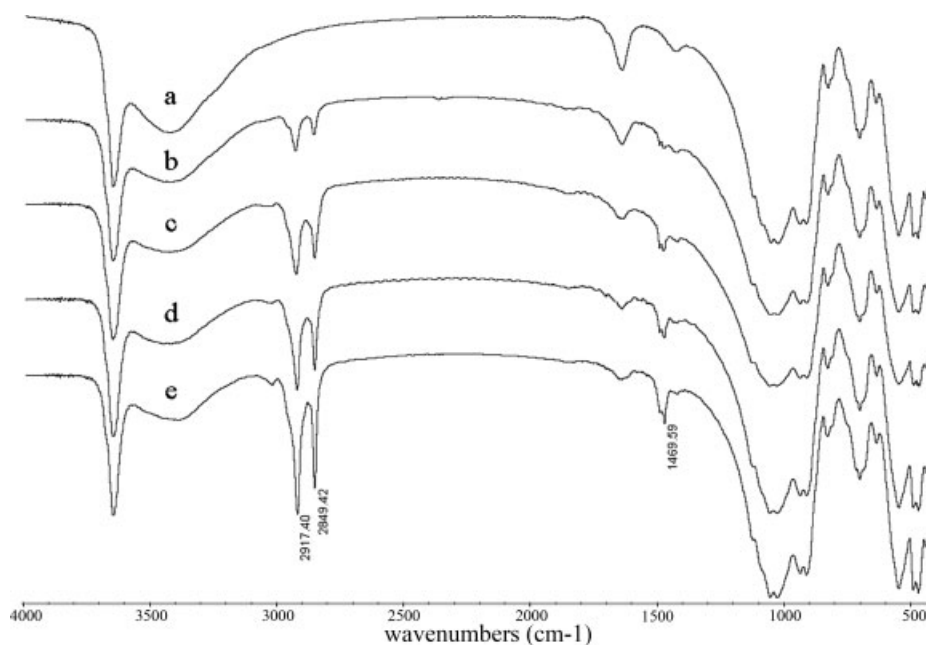


Figure 1 IR spectra of REC (a) and OREC with different organification degree of (b) 2.33 wt %, (c) 7.31 wt %, (d) 10.72% and (e) 16.73%.

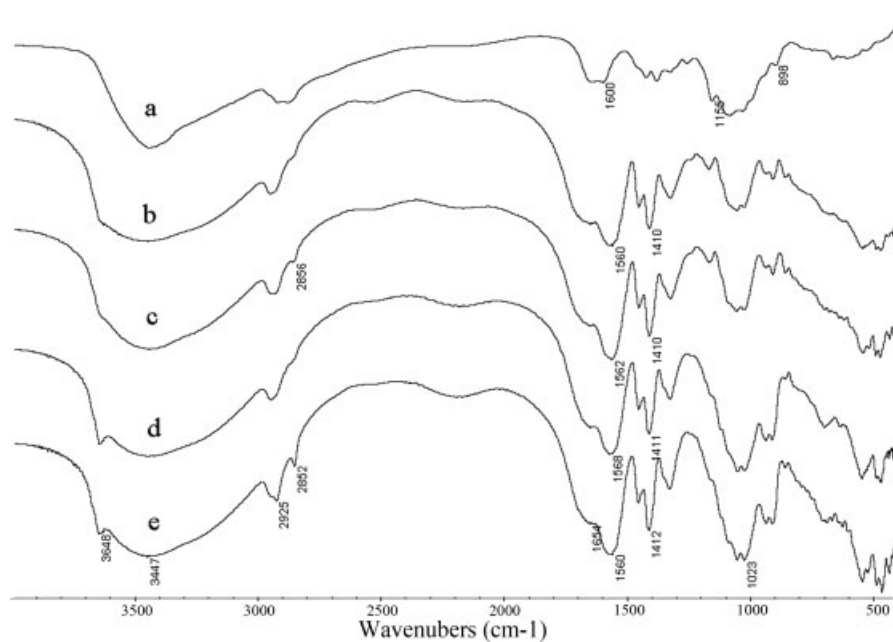


Figure 2 IR spectra of (a) chitosan, (b and d) CTS-g-PAA/REC nanocomposite superabsorbents (10 wt % and 30 wt % REC), and (c and e) CTS-g-PAA/OREC nanocomposite superabsorbents with 16.73 wt % organification degree of OREC (10 and 30 wt % OREC).

superabsorbents with 16.73 wt % organification degree of OREC. 1600 cm^{-1} absorption peak is assigned to amino characteristic peak of CTS [Fig. 2(a)]. After grafted copolymerization with OREC (REC) and AA, the amino characteristic peak of CTS disappears. Comparing with REC [Fig. 1(a)] and OREC [Fig. 1(b–e)], the absorption peaks at 3648 cm^{-1} attributed to stretching vibration of Si–OH became smaller after grafted copolymerization reaction, which implies that the –OH groups of REC and OREC participated in the reaction. The absorption peaks of REC and OREC at 1023 cm^{-1} contributed to Si–O–Si groups also appeared in the CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents [Fig. 2(b–e)], which demonstrated the existence of REC and OREC in the nanocomposite superabsorbents. In addition, CTS-g-PAA/REC superabsorbents have new peaks appearing at 1560 and 1410 cm^{-1} , respectively, which attributed to be asymmetric stretching and symmetric stretching absorption bands of $-\text{COO}^-$. Moreover, the absorption band of $-\text{COO}^-$ of CTS-g-PAA/OREC nanocomposite superabsorbents with 16.73 wt % organification degree of OREC shifts to 1568 and 1412 cm^{-1} . These information indicate that AA had been grafted copolymerization with CTS and OREC.

SEM analysis

Figure 3 shows the SEM pictures of CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents with different organification degree of

OREC. As can be seen, these pictures verify that both CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents with different organification degree show a porous and rough surface structure. However, the compatibility of polymer matrix and OREC with different organification degree is better than that of polymer matrix and REC particles and it is more evident especially for polymer matrix and OREC with higher organification degree. The surface morphology change by organification of clay may have some influence on water permeation regions and further influences water absorbency and swelling ability of corresponding nanocomposite superabsorbents.

The XRD analysis

XRD is commonly used to probe the nanocomposites structure for its easiness and availability, by which the intercalated or exfoliated nanocomposites can be ascertained. The XRD profiles of REC, OREC, CTS-g-PAA/REC, and CTS-g-PAA/OREC nanocomposite superabsorbent are shown in Figure 4. It can be seen from Figure 4 that the XRD of REC shows a characteristic peak (d_{001}) at 3.595° corresponding to a basic spacing of 2.458 nm [Fig. 4(a)]. After modification with HDTMABr, the d_{001} peak of OREC shifts towards lower angle ($2\theta = 2.129^\circ$) corresponding to an increasing in spacing from 2.458 to 4.149 nm [Fig. 4(b)]. It confirms that HDTMABr has been intercalated into the interlayer of REC.

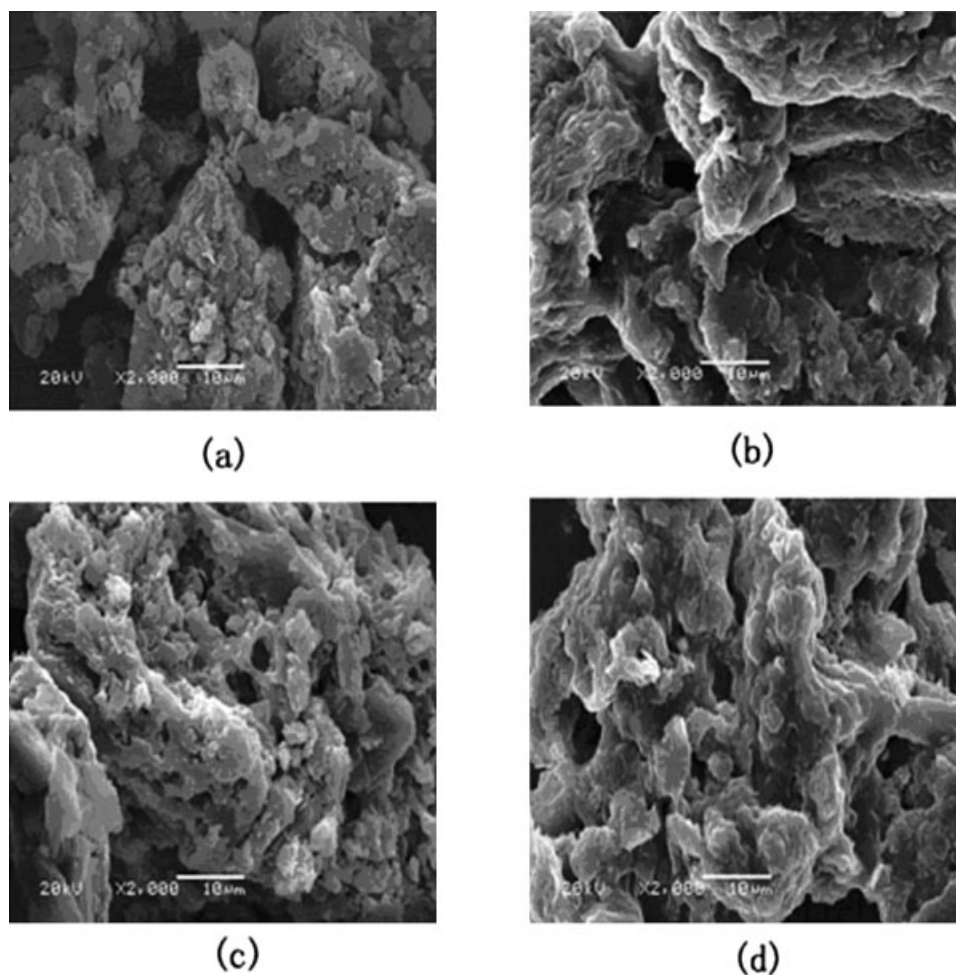


Figure 3 SEM images of CTS-g-PAA/REC (10 wt % REC) (a) and CTS-g-PAA/OREC nanocomposite superabsorbents (10 wt % OREC) with different organization degree [(b) 2.33 wt %; (c) 7.31 wt %, and (d) 16.73 wt %].

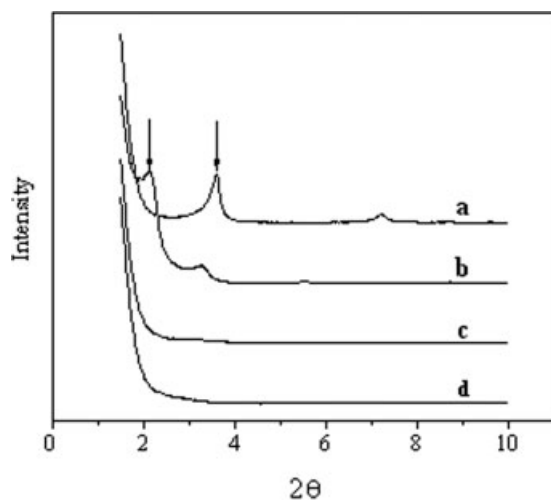


Figure 4 The XRD patterns of (a) REC, (b) OREC with 16.73 wt % organization degree, (c) CTS-g-PAA/REC (10 wt % REC), and (d) CTS-g-PAA/OREC nanocomposite superabsorbents with 16.73 wt % organization degree of OREC (10 wt % OREC).

The XRD profiles of CTS-g-PAA/REC (10 wt % REC) and CTS-g-PAA/OREC nanocomposite superabsorbent with 16.73 wt % organization degree of OREC (10 wt % OREC) are presented in Figure 4(c and d). It has been found that the CTS chains can insert into REC and OREC, and formed the intercalated nanocomposites.²² However, after polymerization of CTS and REC and OREC with AA, the typical diffraction peak of REC and OREC cannot be detected as shown in Figure 4(c and d), which indicates the formation of exfoliated nanocomposite superabsorbent. This may be because CTS could first intercalate into layers of REC and OREC, and then formed the nanocomposite through graft-polymerization with AA. In acidic solutions, CTS shows an extended structure that may facilitate its intercalation into layers of REC and OREC. In addition, $-\text{NH}_2$ of CTS was protonated in acidic solution, and then the extended and protonated CTS could intercalate into layers of REC and OREC through a cation-exchange process or be adsorbed in the

TABLE II
Variation of Water Absorbency for CTS-g-PAA/OREC
Nanocomposite Superabsorbents with Organification
Degree and OREC Content

Samples	Organification degree (wt %)	W_{eq} (g g ⁻¹)		
		10 wt %	20 wt %	30 wt %
SA0	0	229.7	201.5	174.3
SA1	2.33	255.4	212.0	174.6
SA2	7.31	261.1	230.6	182.8
SA3	10.72	262.9	231.0	186.3
SA4	16.73	265.2	245.7	187.5

acetate salt form.²³ OREC have shown better intercalation effect, which will be favorable for greatly improving the material properties.

Effect of organification degree on water absorbency

Organic-modified REC enlarged interlayer spacing and enhanced compatibility with polymeric matrix, which would further have great influence on water absorbency of nanocomposite composites. The effect of organification degree on water absorbency of CTS-g-PAA/OREC nanocomposite superabsorbents with different OREC content is displayed in Table II. As can be seen, water absorbency of CTS-g-PAA/OREC nanocomposite superabsorbents with different OREC content continuously increases with increasing organification degree. This phenomenon can be explained as follows: For one hand, HDTMABr has long hydrophobic chains, which can not only enlarge interlayer spacing of REC and enhance compatibility with polymeric matrix, but also can reduce interaction of hydrophilic groups. As a result, the introduction of OREC with different organification degree formed looser polymeric network during polymerization progress and improve water absorbency. For the other hand, the OREC with long hydrophobic chains may have some influence on the degree of crosslinking. The long hydrophobic chains can act as obstructers for the reaction between propagating radicals and monomeric double bond, which results in increasing intramolecular cyclization reactions of MBA.²⁴ Therefore, the crosslinking efficiency of MBA reduces and equilibrium swelling increases.

Effect of pH on water absorbency

The swelling behavior of CTS-g-PAA/REC (10 wt % REC) and CTS-g-PAA/OREC nanocomposite superabsorbents with different organification degree (10 wt % OREC) are investigated in various pH solutions ranged from 2 to 13, and the results are shown in Figure 5. CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents with different organification degree of OREC show almost the

same trend for the swelling change in various pH solutions. The water absorbency roughly maintains a constant from pH 5 to 10 and drastically decreases from pH 5 to 2 and from pH 10 to 13. The water absorbency of CTS-g-PAA/OREC nanocomposite superabsorbents increases with increasing organification degree of OREC and all higher than that of CTS-g-PAA/REC nanocomposite superabsorbent from pH 5 to 10. CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents are polyelectrolytical superabsorbent composites containing carboxyl of grafted PAA chains, which play the main role in swelling behavior and result in water absorbency changes through different interaction species in various pH solutions. In the range of pH from 5 to 10, the water absorbency keeps almost the same because of buffer action of $-\text{COOH}$ and $-\text{COO}^-$ with weak acid or weak base. However, the water absorbency sharply decreases from pH 5 to 2 and from pH 10 to 13, which indicates that the buffer action has vanished. In addition, in comparison with CTS-g-PAA/REC and other CTS-g-PAA/OREC nanocomposite superabsorbents with different organification degree, the water absorbency for CTS-g-PAA/OREC nanocomposite superabsorbent with 16.73 wt % organification degree decreases more sharply at pH < 5 and pH > 10. This phenomenon can be explained as follows: the interlayer of REC possesses larger amounts of Ca^{2+} , which can enhance osmotic pressure of polymeric network for nanocomposite superabsorbent. However, after ion-exchange reaction, more amounts of interlayer Ca^{2+} can be exchanged by organic cations of HDTMABr as increasing organification degree of OREC. As a result, osmotic pressure difference between polymeric network for CTS-g-PAA/OREC nanocomposite superabsorbent with

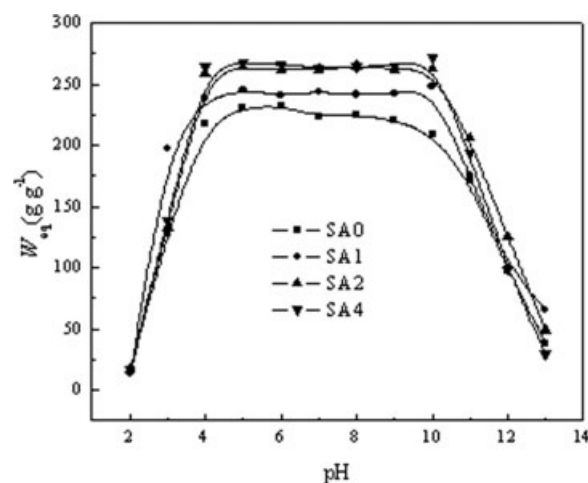


Figure 5 The swelling behaviors in various pH solutions for CTS-g-PAA/REC (10 wt % REC) and CTS-g-PAA/OREC nanocomposite superabsorbents (10 wt % OREC) with different organification degree.

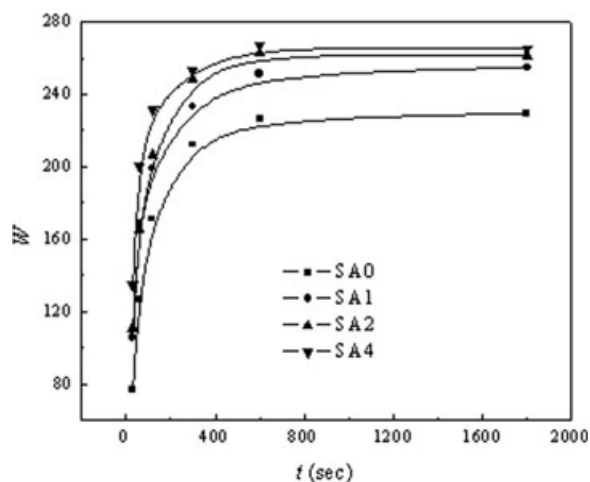


Figure 6 Swelling rate curves of CTS-g-PAA/REC (10 wt % REC) and CTS-g-PAA/OREC nanocomposite superabsorbents (10 wt % OREC) with different organization degree.

16.73 wt % organization degree of OREC and external solution increases more seriously at pH < 5 and pH > 10.

Effect of organization degree of OREC and OREC content on swelling rate

Figure 6 shows swelling rate of nanocomposite superabsorbents with different organization degree of OREC in distilled water. As shown in Figure 6, the swelling rate of CTS-g-PAA/OREC nanocomposite superabsorbents increases with increasing organization degree of OREC comparing with that of CTS-g-PAA/REC nanocomposite superabsorbent. In addition, the initial swelling rate prominently increases in 2 min as organization degree of OREC increase. This result indicates that introducing OREC into the CTS-g-PAA polymeric network can improve the initial swelling rate.

Figure 7 shows the swelling rate of CTS-g-PAA/REC nanocomposite superabsorbents with 10 wt % REC and CTS-g-PAA/OREC nanocomposite superabsorbents with different content of OREC provided with 16.73 wt % organization degree. The results show that CTS-g-PAA/OREC nanocomposite superabsorbents prepared with higher OREC content exhibits a higher initial swelling rate, a lower saturated water absorbency and a shorter time to reach swelling equilibrium. In addition, the CTS-g-PAA/OREC nanocomposite superabsorbents incorporated with 20 wt % OREC shows higher water absorbency than that of CTS-g-PAA/REC nanocomposite superabsorbents with 10 wt % REC and can even reach equilibrium in 5 min. We can infer from the above results that CTS-g-PAA/OREC nanocomposite super-

absorbents with higher content of OREC also show excellent properties such as the initial swelling rate.

On the basis of the above the experimental results, the second-order swelling kinetics model equation was applied to study the organization degree and OREC content on the swelling kinetics.^{25,26}

$$t/W = A + Bt \quad (4)$$

where W is water uptake at time t , $B = 1/W_{eq}$ is the inverse of maximum or equilibrium swelling and $A = 1/K_s W_{eq}^2$ the reciprocal of the initial swelling rate of the superabsorbents, and k_s swelling rate constant. The final form of equation will be as follows:

$$t/W = 1/K_s W_{eq} + 1/W_{eq}^2 t \quad (5)$$

The swelling kinetics curves of CTS-g-PAA/OREC nanocomposite superabsorbents are shown in Figures 8 and 9 by means of eq. (5), where t/W is plotted against time t to give a straight line with good correlation coefficients for swelling results. From the slope and intercept of lines of Figures 8 and 9, the parameters of swelling rate constant (K_s), the theoretical equilibrium swelling (W_{eq}) and the initial swelling rate ($K_{is} = K_s W_{eq}^2$) were calculated and the results are listed in Table III.

From the data of Table III, the theoretical equilibrium swelling is similar to the experimental equilibrium swelling of nanocomposite superabsorbents. As organization degree of OREC increases, the swelling rate constant K_s and the initial swelling rate K_{is} increase. The initial swelling rate of superabsorbent

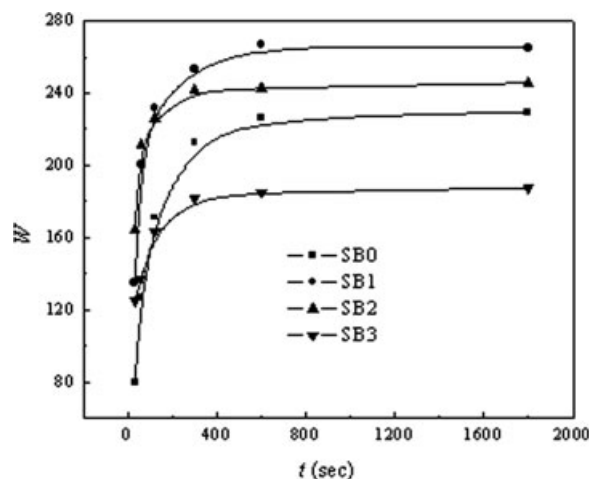


Figure 7 Swelling rate curves of CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents with different OREC content (SB0: CTS-g-PAA/REC with 10 wt % REC; SB1, SB2, SB3: CTS-g-PAA/OREC nanocomposite superabsorbents with 10, 20, and 30 wt % OREC, respectively, organization degree: 16.73 wt %).

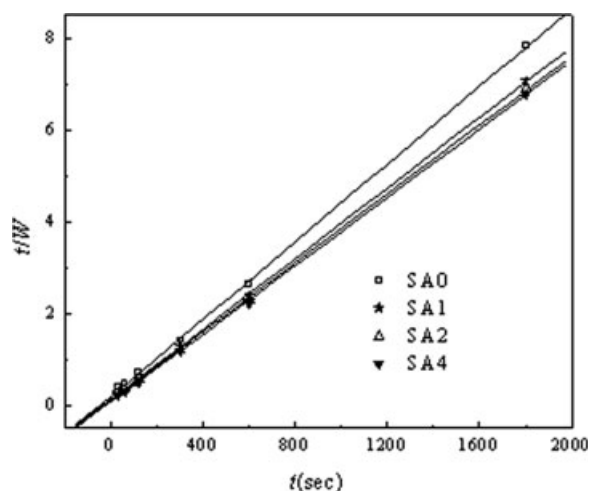


Figure 8 t/W and t graph of CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents with different organification degree.

is subject to capillarity and diffusion. This result indicates OREC can improve capillarity and diffusion of superabsorbent in distilled water and further improves the initial swelling rate in comparison with REC. As the OREC content increases, the swelling rate constant K_s and the initial swelling rate K_{is} increase and then decrease when the OREC content exceeds 20 wt %. Those results indicated that the swelling rate process is greatly affected by organification degree and OREC content.

CONCLUSIONS

A series of CTS-g-PAA/OREC nanocomposite superabsorbents were synthesized by graft-copolymeriza-

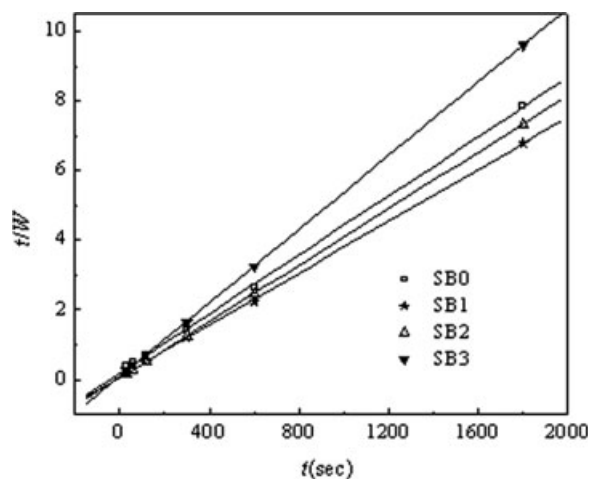


Figure 9 t/W and t graph of CTS-g-PAA/REC and CTS-g-PAA/OREC nanocomposite superabsorbents with different OREC content.

TABLE III
Role of Organification Degree and OREC Content on Swelling Kinetics

Sample	W_{eq}^a	W_{eq}^b	$K_s^c (10^{-4})$	K_{is}^d
SA0	229.7	236.4	0.922	5.15
SA1	255.4	260.4	1.10	7.47
SA2	261.1	266.6	1.24	8.80
SA4	265.2	268.8	1.92	13.90
SB0	229.7	236.4	0.922	5.15
SB1	265.2	268.8	1.92	13.90
SB2	245.7	247.5	3.68	22.52
SB3	187.5	189.3	3.10	11.12

^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.

tion in aqueous solution. The FTIR data indicated that PAA chain had been grafted onto CTS and hydroxyl groups of OREC also participated in the graft-copolymerization. XRD data suggested CTS-g-PAA/OREC nanocomposite superabsorbents showed an exfoliated nanostructure. The water absorbency for CTS-g-PAA/OREC increased with increasing organification degree of OREC and all higher than that of corresponding to CTS-g-PAA/REC. The second-order swelling kinetics mode provided a good estimation of swelling rate and the results show that the swelling rate constant and the initial swelling rate increase with increasing organification degree. This is mainly because the compatibility of polymer matrix and OREC is better than that of polymer matrix and REC particles, which results in a looser polymeric network and improves swelling behaviors.

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