

Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgitite superabsorbent composites

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Abstract

A novel chitosan-g-poly(acrylic acid)/attapulgitite superabsorbent composite with water absorbency of 159.6 g g⁻¹ in distilled water and 42.3 g g⁻¹ in 0.9 wt% NaCl solution was prepared by graft polymerization with chitosan, acrylic acid and attapulgitite in aqueous solution, using *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator. Factors influencing water absorbency of the superabsorbent composite were investigated, such as average molecular weight of chitosan, weight ratio of acrylic acid to chitosan, dewatering method, the amount of crosslinker and attapulgitite. The result from FTIR spectra showed that –OH of attapulgitite, –OH, –NHCO and –NH₂ of chitosan participated in graft polymerization with acrylic acid. The introduced attapulgitite enhanced thermal stability of the chitosan-g-poly(acrylic acid) superabsorbent and formed a loose and more porous surface. Introducing a small amount of attapulgitite also enhanced water absorbency of the chitosan-g-poly(acrylic acid) superabsorbent.

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1. Introduction

Superabsorbents are crosslinked networks of hydrophilic polymers that can absorb and retain a lot of aqueous fluids, with the absorbed water hardly removable even under some pressure. Due to their excellent properties relative to traditional water absorbing materials (such as sponge, cotton and pulp, etc.), superabsorbents are widely used in many fields, such as hygienic products, horticulture, gel actuators, drug-delivery systems and coal dewatering (Buchholz & Graham, 1998; Dorkoosh et al., 2000; Ende, Hariharan, & Peppas, 1995; Raju, Raju, & Mohan, 2003; Shiga, Hirose, Okada, & Kurauchi, 1992). However, most of these examples are synthetic polymers, which are poor in degradability, with potential for inherent environmental issues.

Extensive attention has been directed toward superabsorbent polymers prepared through graft copolymerization of vinyl monomers onto the chain of such natural polymers as starch (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002), cellulose (Farag & Al-Afaleq, 2002) and chitosan (Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004). Chitosan, a high molecular weight polysaccharide from chitin, is one of the most abundant biomass sources in the world. Reactive –NH₂ and –OH of chitosan are convenient for graft polymerization of hydrophilic vinyl monomers, making this is an efficient way to acquire hydrogels with novel properties. It has been reported previously that superabsorbent from chitosan has antibacterial activities and is thus suitable in infant diapers, feminine hygiene products and other special fields (Dutkiewicz, 2002; No, Park, Lee, Hwang, & Meyers, 2002). Chitosan has been widely used in the fabrication of biomedical materials owing to its biocompatibility and antibacterial properties (Chen & Tan, 2006). Thus, a novel superabsorbent polymer prepared through graft polymerization of acrylic

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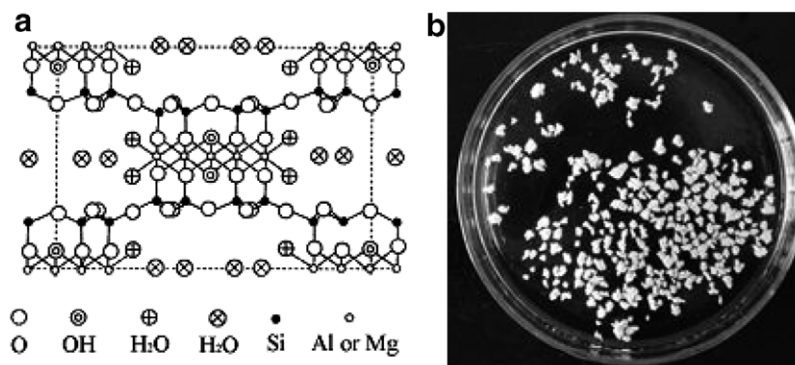


Fig. 1. Schematic structure of APT (a) and digital photo of granular CTS-g-PAA/APT superabsorbent composite (b).

acid onto the chitosan chain, not only improves biodegradability of its corresponding superabsorbent materials, but also reduces dependence on petrochemical-derived monomers.

Recently, clay has become the focus for the preparation of superabsorbent composite in order to improve swelling properties, enhance gel strength and reduce production cost of corresponding superabsorbents. Clays, including montmorillonite (Kabiri & Zohuriaan-Mehr, 2004), kaolin (Wu, Wei, & Lin, 2003), mica (Lee & Chen, 2005; Lin, Wu, Yang, & Pu, 2001), attapulgite (Li & Wang, 2005) and sericite (Wu, Lin, Zhou, & Wei, 2000), have already been incorporated into poly(acrylic acid) and polyacrylamide polymeric network. Attapulgite, a kind of hydrated octahedral layered magnesium aluminum silicate absorbent mineral (schematic structure was shown in Fig. 1(a)), has exchangeable cations and reactive –OH groups on its surface (Neaman & Singer, 2004). On the basis of our previous work with superabsorbent composite (Li, Liu, & Wang, 2005; Li & Wang, 2005; Li, Wang, & Chen, 2004; Zhang, Chen, & Wang, 2005; Zhang, Li, & Wang, 2006) and chitosan (Sun & Wang, 2006; Sun & Wang, 2006), a novel chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composite was synthesized. The graft reaction mechanism, thermal stability, surface morphology and factors influencing water absorbency of the composite were investigated in this paper.

2. Experimental

2.1. Materials

Acrylic acid (AA, distilled under reduced pressure before use), ammonium persulfate (APS, recrystallized from distilled water before use) and *N,N'*-methylenebisacrylamide (MBA, used as received) were supplied by Shanghai Reagent Corp. (Shanghai, China). Chitosan (CTS, degree of deacetylation is 0.85, average molecular weight is 90×10^4) was supplied by Zhejiang Yuhuan Ocean Biology Co. (Zhejiang, China). Attapulgite (APT, supplied by Linze Colloidal Co., Gansu, China) was milled through a 320-mesh screen and treated with 37% hydrochloric

acid for 72 h, followed by washing with distilled water until pH = 6 was achieved, and then dried at 105 °C for 8 h before use. Other agents used were all of analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of CTS with different average molecular weight

CTS (2.0 g) was dispersed in 40 ml distilled water, and then specific volumes of 30% H₂O₂ solution (0.3, 1.0, 3.7, 9.4 ml, respectively) were added to the suspension. Each suspension was stirred and kept at 50 °C for 2 h. After reaction, the solution was filtrated. The collected solid was washed with distilled water to pH = 7, and then dried under vacuum at 50 °C to a constant weight. Average molecular weight of CTS was determined by viscometry measurement (Kubota, Tatsumoto, Sano, & Toya, 2000).

2.3. Preparation of chitosan-g-poly(acrylic acid)/attapulgite (CTS-g-PAA/APT) superabsorbent composites

A series of superabsorbent composites from CTS, AA, and APT were synthesized according to the following procedure; an appropriate amount of CTS was dissolved in 30 ml acetic acid solution (1%) 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 for 30 min to remove the oxygen dissolved from the system, the solution was heated to 60 °C, and then 0.10 g APS was introduced to initiate CTS to generate radicals. Ten minutes later, the mixed solution of 3.55 g AA, specific amounts of MBA and APT (as noted) were added. The water bath was kept at 60 °C for 3 h. The resulting granular product (as shown in Fig. 1(b)) was transferred into sodium hydroxide aqueous solution (1 M) to be neutralized to pH = 7, and then dehydrated through oven drying or with various dewatering agents including methanol, ethanol and acetone. After wiping off excessive dewatering agents on the surface using filter paper, the samples were spread on a dish to dry overnight at room temperature.

The product was milled and all samples used for test had a particle size in the range of 40–80 mesh.

CTS-*g*-PAA (without APT) was prepared according to the same procedure to study the effect of introduced APT on properties of the superabsorbent composite. Uncrosslinked CTS-*g*-PAA/APT (without MBA) was exhaustively extracted with distilled water and ethanol to be free from homopolymer in order to investigate the graft polymerization mechanism.

2.4. Measurement of water absorbency

Sample (0.05 g) was immersed in excess distilled water (500 ml) at room temperature for 8 h to reach swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering through a 100-mesh screen under gravity for 30 min with no blotting of samples. Water absorbency in distilled water of the superabsorbent composite, Q_{eq} , was calculated using the following equation:

$$Q_{\text{eq}} = \frac{m_2 - m_1}{m_1} \quad (1)$$

where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. Q_{eq} is calculated as grams of water per gram of sample. Water absorbency of the sample in 0.9 wt% NaCl solution, Q_{eq}' , was tested according to the same procedure.

2.5. Characterization

IR spectra of samples as KBr pellets were taken using a Thermo Nicolet NEXUS TM spectrophotometer. The micrographs of samples were obtained using Scanning Electron Microscopy (SEM), (JSM-5600LV, JEOL, Ltd.).

Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. Thermal stability of samples was studied on a Perkin–Elmer TGA-7 thermogravimetric analyzer (Perkin–Elmer Cetus Instruments, Norwalk, CT), with a temperature range of 25–700 °C at a heating rate of 10 °C min⁻¹ using dry nitrogen purge at a flow rate of 50 ml min⁻¹.

3. Results and discussion

3.1. IR spectra

IR spectra of APT, uncrosslinked CTS-*g*-PAA/APT, CTS, CTS-*g*-PAA and CTS-*g*-PAA/APT are shown in Fig. 2. As can be seen, intensity of the absorption bands at 3616 cm⁻¹ and 3544 cm⁻¹ ascribed to –OH of APT was decreased in spectrum of uncrosslinked CTS-*g*-PAA/APT comparing with Fig. 2(a). A series of new absorption bands at 2928 cm⁻¹, 1712 cm⁻¹, 1456 cm⁻¹ and 1404 cm⁻¹ ascribed to C–H stretching, –COOH stretching, symmetric –COO⁻ stretching and C–H bending appeared in Fig. 2(b). The information from Fig. 2(a) and (b) indicates the participation of –OH group of APT in the graft reaction between APT and AA. As can be seen from Fig. 2(c), the absorption bands at 1647 cm⁻¹, 1598 cm⁻¹, 1380 cm⁻¹, 1094 cm⁻¹ and 1037 cm⁻¹ are ascribed to C=O of amide I, –NH₂, –NHCO of amide III, C₃–OH and C₆–OH of CTS, respectively. However, the absorption bands of N–H (1598 cm⁻¹ and 1380 cm⁻¹) and C₃–OH (1094 cm⁻¹) disappeared after the reaction with AA as shown in Fig. 2(d). This information reveals that –NH₂, –NHCO and –OH of CTS took part in graft reaction with AA. The absorption band at 1647 cm⁻¹ (C=O of amide I) was overlapped by asymmetric –COO⁻ stretching and resulted in a broad absorption band in the range of 1550 cm⁻¹ ~ 1650 cm⁻¹. The new

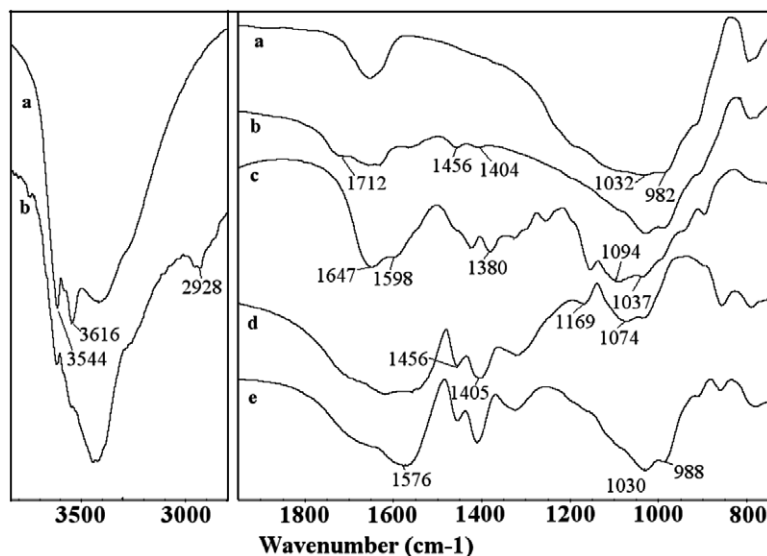


Fig. 2. IR spectra of (a) APT, (b) uncrosslinked CTS-*g*-PAA/APT, (c) CTS, (d) CTS-*g*-PAA and (e) CTS-*g*-PAA/APT. Weight ratio of AA to CTS is 7.2; average molecular weight of CTS is 22.9×10^4 ; MBA content is 2.94 wt%; APT content is 10 wt%; dewatered with methanol.

absorption bands at 1456 cm^{-1} (C–H), 1405 cm^{-1} (symmetric COO^- stretching), 1169 cm^{-1} and 1074 cm^{-1} indicate the existence of PAA chains. After incorporating APT into the polymeric network, intensity of absorption band at 1576 cm^{-1} ascribed to asymmetric COO^- stretching increased, which indicates that the chemical environment of COO^- has changed, which may have some influence on the absorbing ability of the corresponding superabsorbent composite. Absorption bands of APT at 1030 cm^{-1} and 988 cm^{-1} ascribed to Si–OH also appeared in Fig. 2(e), which shows the existence of APT in the composite. It can be concluded from Fig. 2 that graft reaction has taken place among AA, APT and CTS.

3.2. Thermal stability

The effect of introduced APT on thermal stability of CTS-g-PAA was investigated by TGA in this section. TGA curves of CTS-g-PAA and CTS-g-PAA/APT incorporated with 10 wt% APT were shown in Fig. 3. As can be seen from Fig. 3, both CTS-g-PAA and CTS-g-PAA/APT exhibit a three-stage thermal decomposition process. As the temperature increased to $381.7\text{ }^\circ\text{C}$, the weight of samples decreased gradually implying a loss of moisture, dehydration of saccharide rings and breaking of C–O–C glycosidic bonds in the main chain of CTS (Douglas & Sergio, 2004). There is a sharp weight loss with increasing temperature from 381.7 to $391.9\text{ }^\circ\text{C}$ and 21% of sample was lost in this temperature range. There was no obvious difference between CTS-g-PAA and CTS-g-PAA/APT as the temperature was below $391.9\text{ }^\circ\text{C}$. With further increasing temperature to $501.6\text{ }^\circ\text{C}$, CTS-g-PAA exhibits a second step decomposition implying the decomposition of carboxyl groups of PAA chains. Similar thermal behavior has been reported by Chen et al. for carboxymethylchitosan-g-poly(acrylic acid) (Chen & Tan, 2006). During this period, the onset of CTS-g-PAA was at $470.9\text{ }^\circ\text{C}$, however, the onset of CTS-g-PAA/APT was not obvious. The sharp weight losses of CTS-g-PAA and CTS-g-PAA/APT at

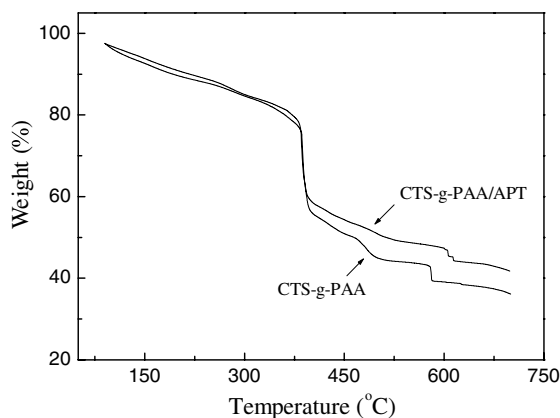


Fig. 3. TGA curves of CTS-g-PAA and CTS-g-PAA/APT. Weight ratio of AA to CTS is 7.2; average molecular weight of CTS is 22.9×10^4 ; MBA content is 2.94 wt%; APT content is 10 wt%; dewatered with methanol.

578.4 and $604.3\text{ }^\circ\text{C}$, respectively, are suggested to be due to the thermal decomposition of the PAA chain backbone.

As can be seen, CTS-g-PAA/APT showed a lower weight loss rate and smaller total weight loss within the temperature of 391.9 – $700\text{ }^\circ\text{C}$ comparing with CTS-g-PAA. This result indicates that the incorporation of APT is helpful for the improvement of thermal stability of CTS-g-PAA. The role of APT in the polymeric network may be the main reason for the difference in TGA curves. APT acts as heat barrier, thus delaying the diffusion of volatile thermo-oxidation products to gas, and gas to the composite. This enhances thermal stability of the system. Similar effect of clay on thermal stability of composite materials has been reported previously (Ray & Okamoto, 2003).

3.3. Morphological analysis

SEM micrographs of APT, CTS-g-PAA and CTS-g-PAA/APT superabsorbent composite were observed and are shown in Fig. 4. As can be seen, APT shows a fibrous surface. CTS-g-PAA shows a tight surface, however, the introduction of APT forms a relatively loose and fibrous surface. This surface morphology change by introducing APT may influence the penetration of water into the polymeric network, and then may have some influence on swelling ability of corresponding superabsorbent composites.

3.4. Effect of average molecular weight of CTS on water absorbency

Many previously reports from the literature focused on the effects of external factors, such as initiator, monomer concentration and ratio of CTS to monomer, on water absorbency and graft polymerization between CTS and monomers (Chen & Tan, 2006; Ge, Pang, & Luo, 2006; Huang, Jin, Li, & Fang, 2006). No information about the effect of average molecular weight of CTS on water absorbency can be seen, to the best of our knowledge. The effect of this factor was investigated in this section and shown in Fig. 5. Water absorbency of CTS-g-PAA/APT in distilled water and in 0.9 wt% NaCl solution increased evidently with decreasing average molecular weight of CTS. This may be attributed to the fact that CTS solution of smaller average molecular weight has lower viscosity, which would facilitate the penetration of AA to CTS and enhance graft efficiency, and then the improvement of water absorbency. CTS of higher average molecular weight could restrict the graft reaction by factors such as steric hindrance, and then the decrease of water absorbency.

3.5. Effect of MBA content on water absorbency

According to Flory's network theory (Flory, 1953), crosslinking density is a key factor influencing water absorbency of superabsorbents and water absorbency is in inverse proportion to crosslinking density. Water absorbency can

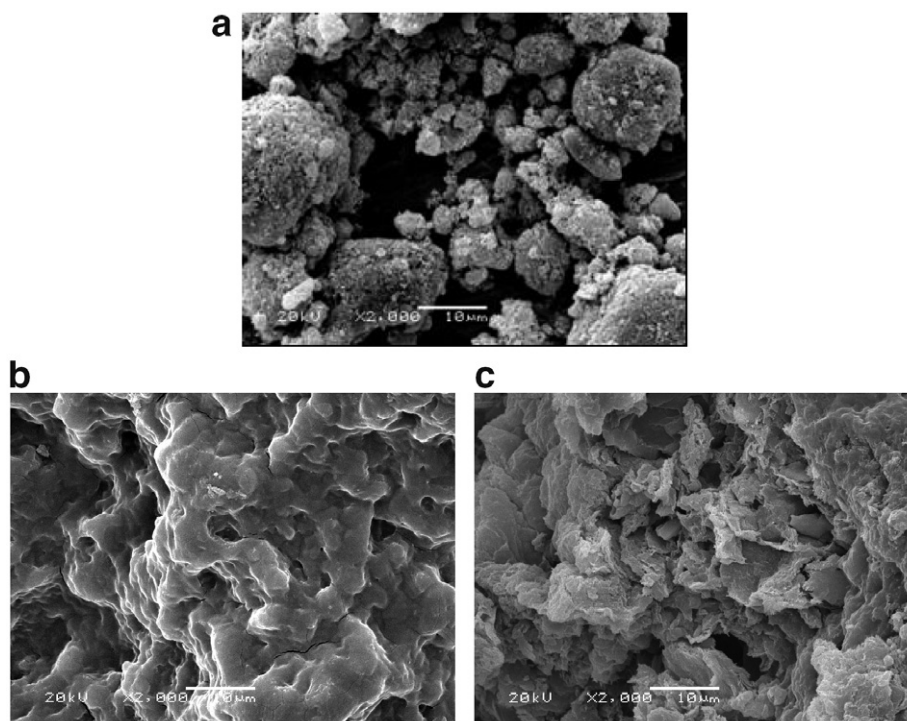


Fig. 4. SEM micrographs of (a) APT, (b) CTS-g-PAA and (c) CTS-g-PAA/APT superabsorbent composite. Weight ratio of AA to CTS is 7.2; average molecular weight of CTS is 22.9×10^4 ; MBA content is 2.94 wt%; APT content is 10 wt%; dewatered with methanol.

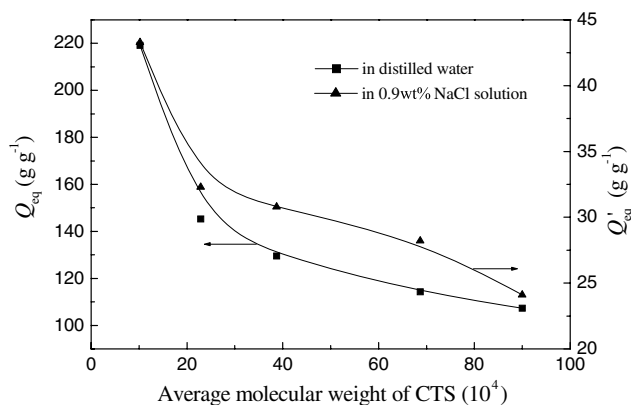


Fig. 5. Variation of water absorbency for the CTS-g-PAA/APT superabsorbent with average molecular weight of CTS. Weight ratio of AA to CTS is 7.2; MBA content is 2.94 wt%; APT content is 10 wt%; dewatered with methanol.

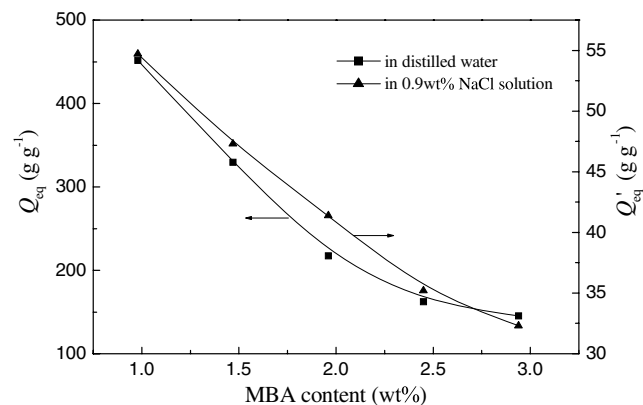


Fig. 6. Variation of water absorbency for the CTS-g-PAA/APT superabsorbent composite with MBA content. Weight ratio of AA to CTS is 7.2; average molecular weight of CTS is 22.9×10^4 ; APT content is 10 wt%; dewatered with methanol.

be influenced greatly even with a relatively small change of crosslinker content. The effect of MBA content on water absorbency of CTS-g-PAA/APT superabsorbent composite is shown in Fig. 6. As can be seen, water absorbency of the composite in distilled water and in 0.9 wt% NaCl solution decreases with increasing MBA content from 0.98 wt% to 2.94 wt%. This tendency was attributed to the fact that crosslinking density of the composite increased with increasing MBA content, and then elasticity of polymer chains of the CTS-g-PAA/APT superabsorbent composite decreased, which resulted in the decrease of water absorbency. Similar phenomena have been previous-

ly reported by Chen (Chen & Zhao, 2000) and Mizutani (Mizutani, 1996) on the poly(acrylic acid) network, and is in conformity with Flory's network theory.

3.6. Effect of weight ratio of AA to CTS on water absorbency

The effect of weight ratio of AA to CTS on water absorbency of the CTS-g-PAA/APT superabsorbent composite was investigated and the results are shown in Fig. 7. It can be seen from Fig. 7 that the water absorbency increases continuously with increasing the weight ratio of AA to CTS. The increasing water absorbency with the increase

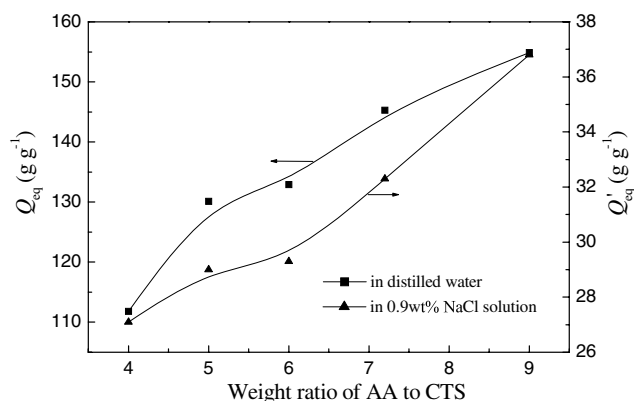


Fig. 7. Variation of water absorbency for the CTS-g-PAA/APT superabsorbent composite with weight ratio of AA to CTS. Average molecular weight of CTS is 22.9×10^4 ; MBA content is 2.94 wt%; APT content is 10 wt%; dewatered with methanol.

of weight ratio can be explained as follows. As the weight ratio of AA to CTS increases, more AA molecules could be grafted onto the backbone of CTS, which enhances hydrophilicity of corresponding superabsorbent composite, and then the water absorbency is improved. In addition, more mobile Na^+ ions are generated in the polymeric network owing to the neutralization of PAA chains of the composite. Consequently, osmotic pressure difference between polymeric network and external solution increase. Moreover, molecular weight of grafted PAA chains increases which also contributes to the improvement of water absorbency (Reyes, Syz, Huggins, & Russell, 1968).

3.7. Effect of APT content on water absorbency

The influence of APT content on water absorbency of the CTS-g-PAA/APT superabsorbent composite was shown in Fig. 8. It is obviously that APT content is another important factor influencing water absorbency of the superabsorbent composite. Water absorbency of the

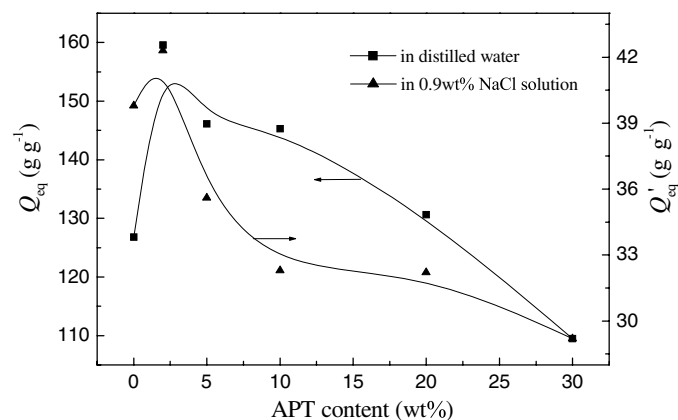


Fig. 8. Variation of water absorbency for the CTS-g-PAA/APT superabsorbent composite with weight ratio of AA to CTS. Weight ratio of AA to CTS is 7.2; average molecular weight of CTS is 22.9×10^4 ; MBA content is 2.94 wt%; dewatered with methanol.

composite increased with increasing APT content when APT content was less than 2 wt%. According to our previous study (Li et al., 2005; Li et al., 2004) and the above investigation, $-\text{OH}$ on the surface of APT could react with acrylic acid, which could improve the polymeric network, and then enhance the water absorbency. In addition, APT contains a lot of cations and they are easily ionized and dispersed into the superabsorbent composite polymeric network, which enhances hydrophilicity of composite and makes it swell more. Further increasing APT content to 30 wt% resulted in a sharp decrease of water absorbency. The decreasing tendency of water absorbency with increasing APT content may be attributed to the following facts. APT could react with AA and there are lots of $-\text{OH}$ groups on the surface of APT, thus, APT particles act as crosslinking points in the network. Consequently, higher APT content results in the generation of more crosslink points in the polymeric network, and then elasticity of the polymer chains decreases. Additionally, the content of hydrophilic groups is lower at a higher APT content, which also results in shrinkage of the composite.

3.8. Effect of dewatering agent on water absorbency

According to some previous reports, dewatering method of superabsorbent also has great influence on water absorbency (Kabiri, Omidian, & Zohuriaan-Mehr, 2003; Kabiri & Zohuriaan-Mehr, 2004; Zhang, Wang, & Wang, 2006). The effect of dewatering agent on water absorbency of the CTS-g-PAA/APT superabsorbent composite was investigated in this section and shown in Fig. 9. As can be seen, the composites dewatered with methanol and ethanol almost have the same water absorbency in distilled water, however, the composite dewatered with methanol has lower water absorbency in 0.9 wt% NaCl solution. The composite dewatered with acetone has lower water absorbency comparing with those of dewatered with methanol and ethanol. It also can be seen from Fig. 9 that there was an evident difference of water absorbency between composite dewatered by oven drying and those of dewa-

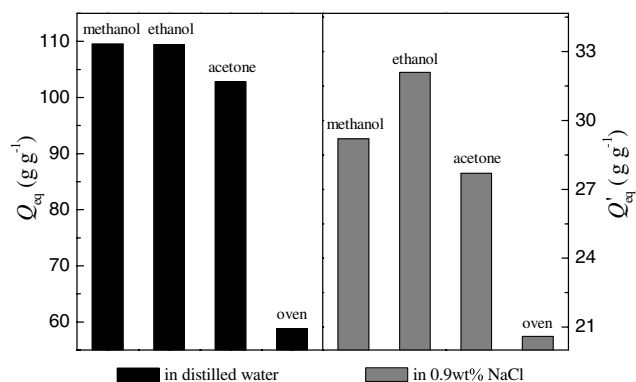


Fig. 9. Variation of water absorbency for the CTS-g-PAA/APT superabsorbent composite with dewatering agents. Weight ratio of AA to CTS is 7.2; average molecular weight of CTS is 22.9×10^4 ; MBA content is 2.94 wt%; APT content is 30 wt%.

tered by organic agents (methanol, ethanol and acetone). Dewatering the composite with methanol, ethanol and acetone could enhance water absorbency greatly comparing with that of oven drying. This result may be attributed to protection effect of organic agents on porous structure of the superabsorbent composite. The composites dewatered with organic agents have porous structure as shown in Fig. 4(b), which is convenient for the penetration of water molecules, and then the improvement of water absorbency. For the composite dewatered through oven drying, polymer chains of the composite interact with each other, which would result in collapse of the porous structure and the increase of effective crosslinking density, and then the decrease of water absorbency. Another reason for the composites dewatered with organic agents have higher water absorbency is that the porous structure endowed the superabsorbent composites additional space to hold more water.

4. Conclusions

A novel superabsorbent composite was obtained through graft polymerization with CTS, AA and APT in aqueous solution, and then neutralized with NaOH solution. $-\text{OH}$, $-\text{NH}_2$ and $-\text{NHCO}$ of CTS and $-\text{OH}$ of APT participated in graft polymerization with AA. Investigation of thermal stability and surface morphology of the superabsorbent composite reveals that the introduced APT could improve thermal stability of the CTS-*g*-PAA polymeric network and generate a loose and more porous surface at the same time. Various factors including average molecular weight of chitosan, weight ratio of acrylic acid to chitosan, dewatering method, the amount of crosslinker and attapulgite have great influence on water absorbency of the CTS-*g*-PAA/APT superabsorbent composite. Introducing a small amount of APT could improve water absorbency of the CTS-*g*-PAA superabsorbent.

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