



Synthesis, characterization and swelling behaviors of sodium alginate-g-poly(acrylic acid)/sodium humate superabsorbent

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ABSTRACT

A novel sodium alginate-g-poly(acrylic acid)/sodium humate superabsorbent was prepared by graft copolymerization with sodium alginate, acrylic acid and sodium humate in aqueous solution, using *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate as an initiator. The effects of crosslinker, sodium alginate and sodium humate content on water absorbency of the superabsorbent were studied. The swelling behavior in solutions of various pH and the swelling kinetics in saline solutions (5 mmol/L NaCl and CaCl₂) were also investigated. The results from IR analysis showed that both sodium alginate and sodium humate react with the acrylic acid monomer during the polymerization process. The introduction of sodium humate into the sodium alginate-g-poly(acrylic acid) system could enhance the water absorbency and the superabsorbent containing 10 wt% sodium humate acquired the highest water absorbency (1380 g/g in distilled water and 83 g/g in 0.9 wt% NaCl solution).

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1. Introduction

Superabsorbents are three-dimensional polymeric networks that can absorb and retain large volumes of water. Because of superior properties compared to traditional absorbents (such as sponge, cotton and pulp, etc.), superabsorbents are widely used in many fields, such as hygienic products, horticulture, gel actuators, drug-delivery systems, as well as water-blocking tapes and coal dewatering (Lokhande & Varadarajan, 1992; Yu et al., 2005). Recently, the research on the use of superabsorbents as water managing materials for the renewal of arid and desert environment has attracted great attention, and encouraging results have been observed as they can reduce irrigation water consumption, lower the death rate of plants and increase plant growth rate (Raju, Raju, & Mohan, 2003). However, the growth of plants and their quality are mainly a function of the quantity of fertilizer and water. So, researches in superabsorbent have been contributed to the development of the superabsorbent containing fertilizer, such as N, P, K and humic substances (Guo, Liu, Zhan, & Wu, 2005; Liang, Liu, & Wu, 2007; Zhang, Liu, Li, & Wang, 2006b). The results proved that the superabsorbent could enhance the water-holding capacity of the soil and was endowed with slow-release fertilizer properties.

Sodium humate (SH) can regulate plant growth, accelerate root development, enhance photosynthesis, improve soil cluster structures and benefit the absorption of nutrient elements. SH also con-

tains a large number of functional groups, such as carboxylates and phenolic hydroxyls (Senesi, Miano, Provenzano, & Brunetti, 1989; Stevenson & Goh, 1971). So, we paid our attention to the synthesis and characterization of polymer/humate superabsorbents by introducing SH into poly (acrylic acid) or poly(acrylic acid-co-acrylamide) systems and studied the slow-release behavior of SH from the superabsorbents (Li, Zhang, & Wang, 2005; Zhang, Li, & Wang, 2006a; Zhang et al., 2006b).

In recent years, a number of studies have greatly paid attention to the preparation and utilization of polysaccharidic superabsorbents because of their biodegradability, biocompatibility, renewability and nontoxicity (Guilherme et al., 2005; Murthy, Mohan, Sreeramulu, & Raju, 2006; Pourjavadi, Barzegar, & Mahdavinia, 2006; Zhang, Wang, & Wang, 2007). In particular, sodium alginate (NaAlg) is a renewable and biodegradable natural polymer that is used in a variety of commercial applications because of its capacity for gelatinization. Alginates are linear anionic polysaccharides of (1, 4)-linked α -L-guluronate and β -D-mannuronic acid residues and are obtained mainly from brown algae belonging to the *Phaeophyceae*. Alginates and their derivatives are widely used in food, cosmetic, drug delivery (Babu, Sairam, Hosamani, & Aminabhavi, 2007; Pongjanyakul & Puttipipatkachorn, 2007) and agriculture applications (Mishra, Bajpai, & Bajpai, 2004).

In order to obtain multifunctional superabsorbent with biodegradable and slow release fertilizer properties, on the basis of our previous work on superabsorbent composites (Li et al., 2005; Liu, Wang, & Wang, 2007; Zhang et al., 2006a), a novel sodium alginate-g-poly(acrylic acid)/sodium humate (NaAlg-g-PAA/SH) super-

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absorbent was synthesized by graft cross-link copolymerization of NaAlg and AA in the presence of SH. The swelling behaviors of the superabsorbent were also investigated.

2. Experimental

2.1. Materials

Sodium alginate (NaAlg) was obtained from Shanghai chemical reagents Co., Shanghai, China. Acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS, analytical grade, supplied by Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water before use. *N,N'*-methylenebisacrylamide (MBA, chemically pure, supplied by Shanghai Chemical Reagent Corp., Shanghai, China) was used as purchased. Sodium humate (SH) (supplied by Shuanglong Ltd, Xinjiang, China) was milled and passed through 320-mesh screen. Other agents used were all analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of NaAlg-g-PAA/SH and NaAlg-g-PAA superabsorbents

A series of the samples with different amounts of crosslinker, NaAlg and SH were prepared according to the following procedure. 1.0 g NaAlg was charged into 30 mL distilled water under vigorous stirring in a 250 mL four-necked flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. The solution was kept at 60 °C for 30 min under nitrogen atmosphere, and then 0.05 g of APS was added. After 15 min, the mixture solution of 7.0 g AA (partially neutralized by 10 mL 6 mol/L NaOH solution, 60% neutralization degree), 0.01 g MBA, 1.0 g SH and 5 mL distilled water was charged into the flask dropwise. The water bath was heated slowly to 70 °C and kept for 3 h. The resulting product was dried at 70 °C to a constant weight. The dried black product was milled and screened. All samples used for test had a particle size in the range of 40–80 mesh. The feed compositions of all samples were listed in Table 1.

Sodium alginate-g-poly(acrylic acid) (NaAlg-g-PAA) superabsorbent was prepared according to a similar procedure except without SH.

2.3. Water absorbency measurement

0.05 g NaAlg-g-PAA/SH superabsorbent powder was immersed in excess of distilled water (400 mL) at room temperature for 4 h to reach the swelling equilibrium. The swollen sample was then separated from unabsorbed water by filtering through a 100-mesh

screen. The water absorbency of the superabsorbent, Q_{eq} , was calculated using the following equation:

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

where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. The Q_{eq} value was calculated as grams of water per gram of sample.

2.4. Measurement of water absorbency in solutions of various pH and swelling kinetics in saline solutions

The pH of external solutions was adjusted using 1 mol/L NaOH or HCl aqueous solutions. The method used was the same as the water absorbency measured in distilled water.

The swelling kinetics of the superabsorbent was measured according to the following process. Sample (0.05 g) was poured into 250 mL 5 mmol/L NaCl or CaCl₂ solutions. At certain time intervals, the water absorbency of the sample, Q_t , was measured according to Eq. (1). The measurement condition was the same as the equilibrium water absorbency measured in distilled water.

2.5. Characterization

IR spectra of samples were taken as KBr pellets using a Thermo Nicolet NEXUS TM spectrophotometer. 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 25–800 °C at a heating rate of 10 °C/min using dry nitrogen purge at a flow rate of 50 mL/min. The micrographs of samples were taken using SEM (JSM-5600LV, JEOL, Ltd.). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold.

3. Results and discussions

3.1. IR spectra

The IR spectra of the SH, NaAlg-g-PAA, NaAlg-g-PAA/SH superabsorbent with 10 wt% SH and NaAlg are shown in Fig. 1(a–d), respectively. Comparing with the IR spectrum of NaAlg (Fig. 1(d)), the absorption bands at 1612 and 1417 cm⁻¹ for the -COO⁻ group shift to 1567 and 1452 cm⁻¹, respectively, and the absorption bands at 947 and 892 cm⁻¹ disappeared in the IR spectrum of NaAlg-g-PAA (Fig. 1(b)), suggesting the grafting reaction of AA on NaAlg. Comparing with the IR spectrum of SH (Fig. 1(a)), the absorption bands at 1708 cm⁻¹ (C=O stretching of carboxylic group of SH), 1611 cm⁻¹ (-COO⁻ asymmetric stretching of SH) and 1250 cm⁻¹ (phenolic C-O stretching of SH) almost disappeared in the spectrum of NaAlg-g-PAA/SH

Table 1
Feed compositions of NaAlg-g-AA/SH superabsorbent

Samples code	AA(g)	MBA(g)	NaAlg(g)	SH(g)	APS(g)
MBA ₁	7	0.010	1	1	0.05
MBA ₂	7	0.012	1	1	0.05
MBA ₃	7	0.015	1	1	0.05
MBA ₄	7	0.018	1	1	0.05
MBA ₅	7	0.020	1	1	0.05
NaAlg ₁	7	0.010	0.25	1	0.05
NaAlg ₂	7	0.010	0.50	1	0.05
NaAlg ₃	7	0.010	1.00	1	0.05
NaAlg ₄	7	0.010	1.50	1	0.05
NaAlg ₅	7	0.010	2.00	1	0.05
SH ₁	7	0.010	1	0	0.05
SH ₂	7	0.010	1	0.43	0.05
SH ₃	7	0.010	1	1.00	0.05
SH ₄	7	0.010	1	1.43	0.05
SH ₅	7	0.010	1	2.00	0.05

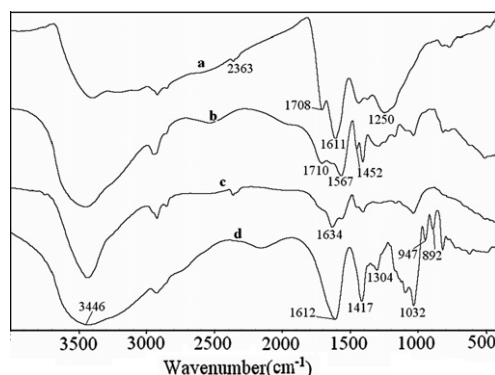


Fig. 1. IR spectra of (a) SH, (b) NaAlg-g-PAA, (c) NaAlg-g-PAA/SH incorporated with 10 wt% SH and (d) NaAlg.

superabsorbent with 10 wt% SH (Fig. 1(c)). The results obtained from IR analysis showed that the reaction of both NaAlg and SH with AA monomer took place during the polymerization process. Fig. 2 shows the schematic representation of the NaAlg-g-PAA/SH superabsorbent. The free radicals on NaAlg initiated the polymerization of AA and SH, and then formed the superabsorbent polymeric network.

3.2. Thermal stability

The thermogravimetric analysis (TGA) of NaAlg-g-PAA and NaAlg-g-PAA/SH superabsorbent are shown in Fig. 3. As the temperature increased from room temperature to 387 °C, the weight loss of NaAlg-g-PAA and NaAlg-g-PAA/SH superabsorbents were associated with a complex process, including the evaporation of water present in the samples, dehydration of saccharide rings and breaking of C–O–C bonds in the chain of NaAlg (Laurienzo, Malinconico, Motta, & Vicinanza, 2005). The sharp weight losses at 387 and 445 °C are suggested to be due to the thermal decomposition of the carboxyl groups of PAA chain and the breakage of the chains of PAA (Chen & Tan, 2006). Comparing with NaAlg-g-PAA, NaAlg-g-PAA/SH superabsorbent showed lower total weight loss within this temperature range. The results indicated that the introduction of SH into the NaAlg-g-PAA polymeric network enhanced thermal stability of the superabsorbent. This may be attributed to the generation of chemical bonds between SH and the NaAlg-g-PAA polymeric network as mentioned above.

3.3. Morphology

SEM micrographs of NaAlg-g-PAA and NaAlg-g-PAA/SH incorporated 10 wt% SH superabsorbent were observed and shown in Fig. 4. Obviously, the surface morphology of NaAlg-g-PAA/SH superabsorbent is different from that of NaAlg-g-PAA. NaAlg-g-PAA has a smooth and tight surface (Fig. 4(a)), however, the sample doped with SH present an undulant and coarse surface (Fig. 4(b)). This surface is convenient for the penetration of water into the polymeric network, and then may be of benefit to water absorbency of corresponding superabsorbent.

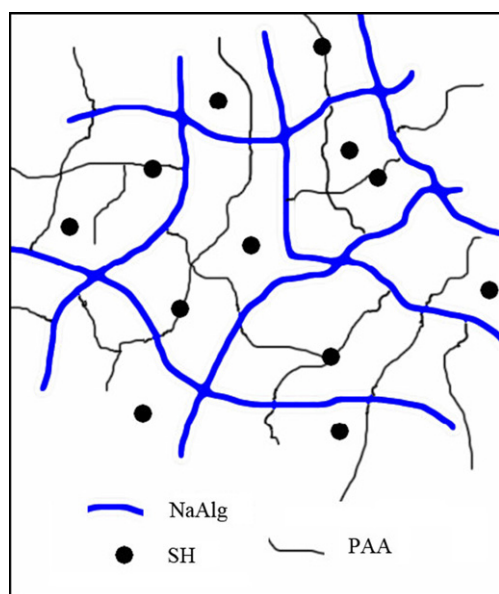


Fig. 2. Schematic representation of the NaAlg-g-AA/SH superabsorbent.

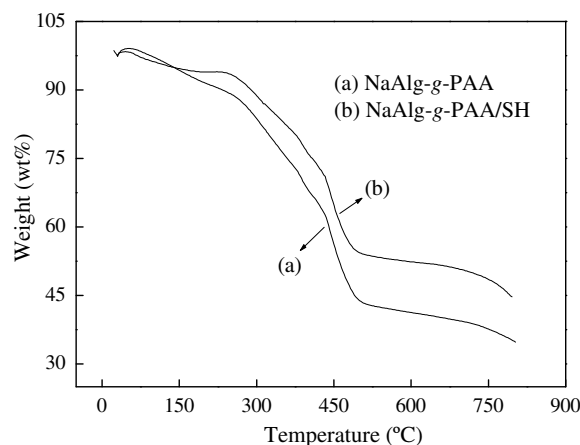


Fig. 3. TGA curves of NaAlg-g-PAA and NaAlg-g-PAA/SH incorporated 10 wt% SH.

3.4. Effect of MBA content on water absorbency

According to Flory's network theory (Flory, 1953), the crosslinking density is a key factor influencing water absorbency of superabsorbents and water absorbency is in inverse proportion to crosslinking density. The effect of crosslinker content on water absorbency of NaAlg-g-PAA/SH superabsorbent is shown in Fig. 5. As can be seen, the water absorbency decreased with the increase of crosslinker content from 0.11 to 0.22 wt%. This tendency was attributed to the fact that crosslinking density of the superabsorbent increased with increasing MBA content, and the elasticity of the polymeric network of the superabsorbent decreased, which resulted in the decrease of water absorbency. Similar phenomena have been previously reported by Zhang et al. (Zhang et al., 2007) on the chitosan-g-poly(acrylic acid)/attapulgit superabsorbent composite.

3.5. Effect of NaAlg content on water absorbency

The effect of NaAlg content on water absorbency of the superabsorbents is shown in Fig. 6. It can be seen that the water absorbency increased with increasing the amount of NaAlg from 3 to 11 wt% and decreased with further increase in NaAlg content. The maximum water absorbency was obtained with a NaAlg content of 11 wt%. When the amount of NaAlg was low, the monomer was superfluous in the reaction system. The superfluous AA turned to be a homopolymer, which cannot contribute to the water absorbency. The homopolymer content decreased with the increase of NaAlg content at fixed crosslinking density (Finkenstadt & Willett, 2005). However, when the amount of NaAlg was above 11 wt%, both grafting ratio and the molecular weight of the grafted PAA chains decreased, also resulting in a decrease of the water absorbency (Reyes, Syz, Huggins, & Russell, 1968). Comparing with the chitosan-g-poly(acrylic acid)/sodium humate superabsorbent reported by Liu et al. (Liu et al., 2007), the introduction of natural polysaccharide NaAlg can obtain much higher water absorbency (the highest water absorbency of chitosan-g-poly(acrylic acid)/sodium humate in distilled water was 183 g/g), which may be attributed to the presence of hydrophilic carboxylate moiety on the C₆ of NaAlg sugar ring.

3.6. Effect of SH content on water absorbency

To confirm the introduction of SH could benefit the swelling capacity of the superabsorbent, a reference sample NaAlg-g-PAA was synthesized under the same condition for comparison. The relationship between water absorbency and SH content is shown

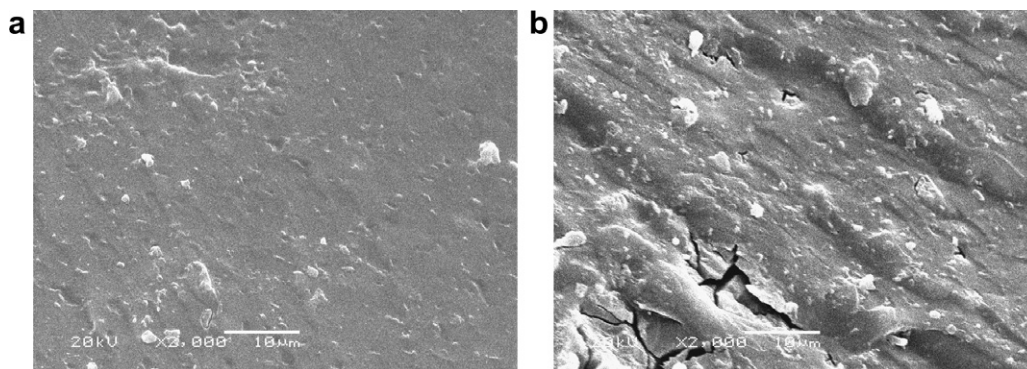


Fig. 4. Scanning electron micrographs for dried superabsorbents: (a) NaAlg-g-PAA, (b) NaAlg-g-PAA/SH incorporated 10 wt% SH.

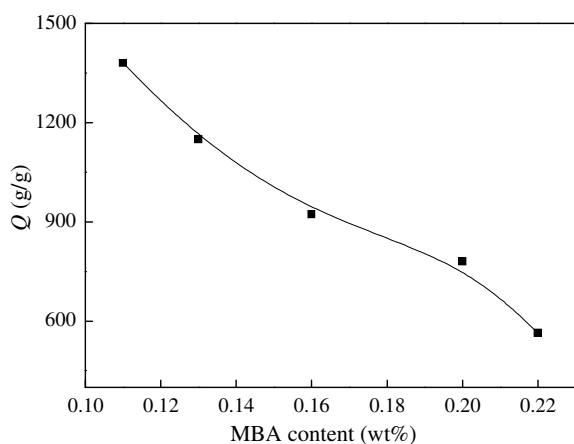


Fig. 5. Effect of MBA content on water absorbency of superabsorbent in distilled water: weight ratio of NaAlg and SH in the feed is 11 and 10 wt%, respectively.

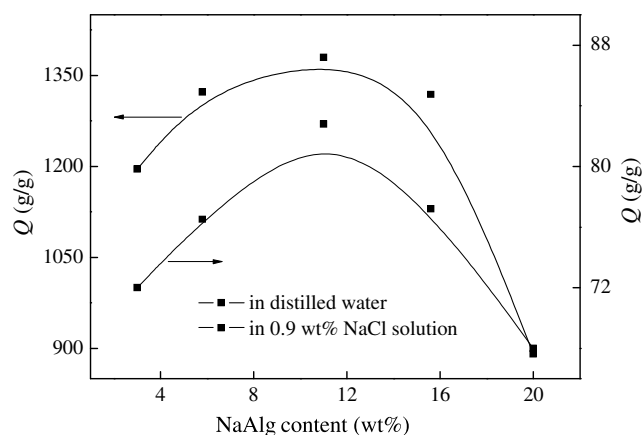


Fig. 6. Effect of NaAlg content on water absorbency: weight ratio of MBA and SH is 0.11, and 10 wt%, respectively.

in Fig. 7. As can be seen, the water absorbency increased with increasing SH content in a weight range of 0–10 wt% in the feed. Water absorbency for NaAlg-g-PAA/SH superabsorbent was greatly enhanced from 840 to 1380 g/g by introducing SH into the NaAlg-g-PAA polymeric network. Further increase in the amount of SH led to a rapid decrease of the water absorbency.

SH contains a large number of hydrophilic functional groups, such as carboxylates, –OH groups (enolic, phenolic and alcoholic) and amino groups (Amir et al., 2006; Chen, Gu, LeBoeuf, Pan, &

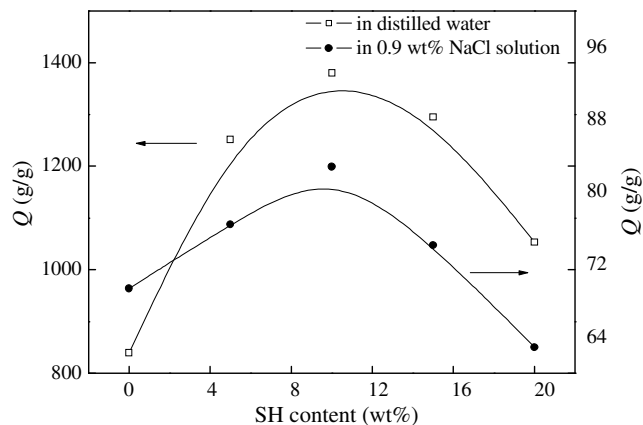


Fig. 7. Effect of SH content on water absorbency: weight ratio of MBA and NaAlg is 0.11 and 11 wt%, respectively.

Dai, 2002). So, SH could react with NaAlg-g-PAA during the polymerization process and improved the polymeric network, and then enhanced the water absorbency. The apparent decrease of water absorbency when the SH content was above 10 wt% may be attributed to the fact that excessive SH only act as a filler and the amount of hydrophilic groups on the polymeric backbone decreased with the increase of SH content, which caused the decrease of osmotic pressure difference between the polymeric network and the external solution.

3.7. Effect of pH on water absorbency

The swelling behavior of NaAlg-g-PAA and NaAlg-g-PAA/SH superabsorbents in solutions of various pH was investigated and shown in Fig. 8. It can be seen that the water absorbency for the NaAlg-g-PAA/SH superabsorbent was always higher than that of pure NaAlg-g-PAA superabsorbent polymer. Both of NaAlg-g-PAA/SH and NaAlg-g-PAA kept roughly constant in a pH value from 5 to 9. This behavior was interpreted as a buffer action of –COOH and –COO[–] (Lee & Wu, 1996), which was very prevalent in the superabsorbent containing –COOH and –COO[–]. But when a large amount of acid or base was added, the buffer action of –COOH and –COO[–] disappeared.

3.8. Effect of various cations on swelling kinetics

The change of swelling ability and structure of superabsorbent materials caused by external stimuli such as ionic strength, temperature or solvent composition has been studied extensively (Díez-Peña, Quijada-Garrido, & Barrales-Rienda, 2003; Mohan &

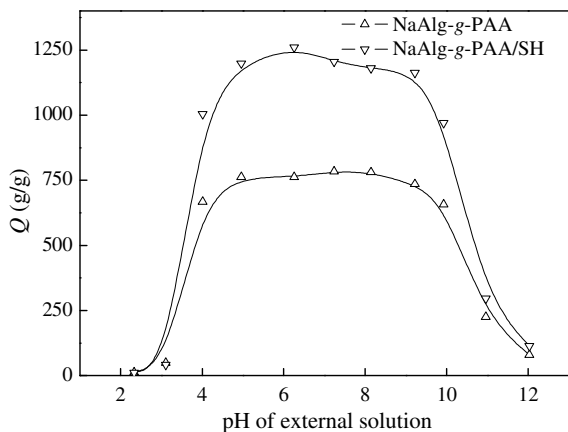


Fig. 8. Effect of pH on water absorbency of NaAlg-g-PAA and NaAlg-g-PAA/SH incorporated with 10 wt% SH superabsorbent.

Geckeler, 2007), but few attention has been paid to the swelling behavior along with the swelling time in saline solutions of different kinds, which is very important for the utilization of the superabsorbent. The swelling kinetics curves of the NaAlg-g-PAA/SH superabsorbent in 5 mmol/L NaCl and CaCl₂ solutions are shown in Fig. 9. In NaCl solution, the water absorbency increased with the prolongation of immersing time and the superabsorbent reached swelling equilibrium within 50 min. Further increase of immersing time had no evident influence on water absorbency of the superabsorbent. However, a distinct swelling behavior was observed in CaCl₂ solution. The water absorbency increased evidently to 100 g/g during the first 10 min, and then decreased with the increase of immersing time. The water absorbency was only 5 g/g when the superabsorbent was immersed in CaCl₂ solution for 120 min. This phenomenon, namely the superabsorbent firstly swelled to a maximum value following by a gradual deswelling until the equilibrium, is actually known as the overshooting effect, which can be interpreted as the consequence of a swelling-deswelling process (Díez-Peña et al., 2003).

In CaCl₂ solutions, with the gradual swelling of superabsorbent, the competition of the following two opposite processes appeared. On the one hand, the water penetration led to the continual spread of polymer network; on the other hand, the complex interaction appeared between carboxyl groups of the superabsorbent and the Ca²⁺ ions in swelling medium, which meant a much more crosslink degree was formed and led to a lower swelling. When the further increased crosslinking points were enough to resist

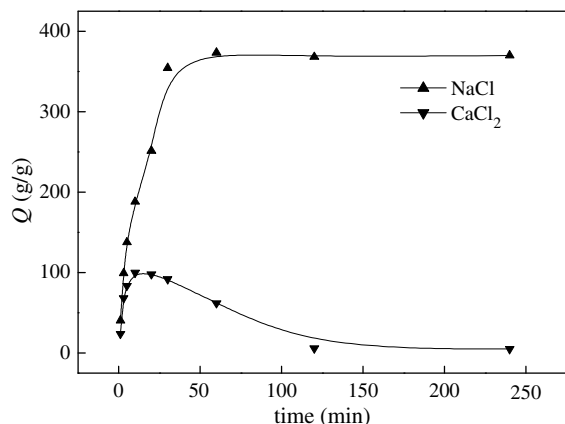


Fig. 9. Dynamic swelling curve of the NaAlg-g-PAA/SH incorporated 10 wt% SH superabsorbent in 5 mmol/L NaCl and CaCl₂ solutions.

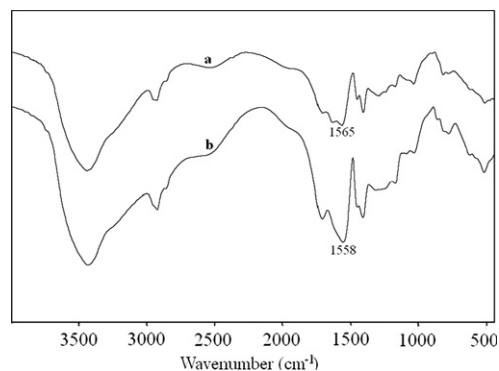


Fig. 10. IR spectra of NaAlg-g-PAA/SH incorporated 10 wt% SH (a) before swelling, (b) after swelling in 5 mmol/L CaCl₂ solution.

the elastic repulsion among the polymer chains, the water absorbency reached a maximum. Subsequently with the continual increase in the complex degree of carboxylate groups and Ca²⁺, the superabsorbent collapsed and the initially absorbed water was squeezed out of the superabsorbent network. The IR spectra (Fig. 10) showed the change of chemical environment of -COO⁻ of the NaAlg-g-PAA/SH superabsorbent in CaCl₂ solution. The absorption band of -COO⁻ at 1565 cm⁻¹ shifted to 1558 cm⁻¹ in the spectrum of superabsorbent after swelling (Fig. 10(b)). The shift of the absorption band of -COO⁻ gave an indication that the complex was formed between -COO⁻ and Ca²⁺.

4. Conclusions

A novel multifunctional NaAlg-g-PAA/SH superabsorbent with biodegradable and slow-release fertilizer properties was prepared by grafted copolymerization reaction through NaAlg and AA in the presence of SH in aqueous solution. Equilibrium water absorbency of NaAlg-g-PAA/SH superabsorbent was significantly affected by the content of SH and the highest water absorbency was obtained when 10 wt% SH is incorporated. SEM investigation revealed that the superabsorbent incorporated with SH micropowers exhibited a coarse surface. TGA implied that introduction of SH into the NaAlg-g-PAA polymeric network was helpful for the improvement of thermal stability of corresponding superabsorbent. A distinct swelling kinetics was observed in CaCl₂ solutions. The result from IR spectra indicated that the complex was formed between -COO⁻ and Ca²⁺ in CaCl₂ solutions.

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