

# Study on superabsorbent composite. VI. Preparation, characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgit superabsorbent composite

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## Abstract

A novel starch phosphate-graft-acrylamide/attapulgit superabsorbent composite was prepared by graft-copolymerization among starch phosphate, acrylamide, and attapulgit in aqueous solution. In this paper, factors influencing water absorbency of the superabsorbent composite such as the molar ratio of NaOH to AM and the amount of starch phosphate and attapulgit were investigated. The superabsorbent composite acquired the highest equilibrium water absorbency of  $1268 \text{ g g}^{-1}$  when the molar ratio of  $\text{COO}^-$ ,  $\text{COOH}$ , and  $\text{CONH}_2$  is 10:3:11, the weight ratio of AM to starch phosphate is 5:1, and 10 wt% attapulgit was incorporated. The graft-copolymerization reaction mechanism, morphology, and thermal stability of the composites were also investigated by FTIR, scanning electron microscopy, and thermo-gravimetric analysis, respectively. The introduced starch phosphate and attapulgit endowed the composite a higher thermal stability. In addition, swelling rate, and equilibrium water absorbency in various saline solutions were investigated to study the effect of starch phosphate and attapulgit on swelling behaviors of the composite. The results indicate that the phosphorylation of starch and the introduction of attapulgit could greatly improve equilibrium water absorbency, swelling rate and salt-resistant properties of corresponding superabsorbent composite.

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**Keywords:** Superabsorbent composite; Water absorbency; Phosphorylation; Attapulgit

## 1. Introduction

Superabsorbents are loosely crosslinked network of hydrophilic polymer chains that can absorb and retain a lot of aqueous fluids, and the absorbed water is hardly removable even under some pressure. Due to excellent properties of traditional water absorbing materials (such as sponge, cotton and pulp, etc.), superabsorbents have raised considerable interests, and 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 (Buchholz & Graham, 1998; Shiga, Hirose, Okada, & Kurauchi, 1992; Dorkoosh, Brussee, Verhoef, Borchard, Tehrani, & Junginger, 2000; Raju, Raju, & Mohan, 2003; Ende, Hariharan, & Peppas, 1995). About 90% of superabsorbents are used in disposable

articles and most of them are disposed of landfills or by incineration (Kiatkamjornwong, Mongkolsoawat, & Sonsuk, 2002). Most of them are synthetic polymers, which are poor in degradability, and then there remains an environmental problem with superabsorbent polymers. At present, material's biodegradability has been widely focused because of the renewed attention to environmental protection issues (Lenzi, et al., 2003). In addition, global oil resources run short increasingly. Incorporation of biodegradable and renewable natural high polyols, such as starch (Kiatkamjornwong et al., 2002), cellulose (Farag & Al-Afaleq, 2002) and chitosan (Mahdavinia, Pourjavadi, Hosseinzadeh, & Zohuriaan, 2004), cannot only improve biodegradability of corresponding superabsorbent materials, but also reduce our dependence on petrochemical-derived monomers.

Among the natural high polyols incorporated, starch is mostly used. However, starch needs to be gelatinated first at a high temperature (normally  $95^\circ\text{C}$ ) to facilitate the graft of monomers onto it. The introduction of phosphate groups into starch can increase hydration capacity of starch pastes after gelatinization (Blennow, Engelsen, Nielsen, Baunsgaard

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& Mikkelsen, 2002) and starch phosphate does not need to be gelatinated at a higher temperature. Moreover, phosphate groups are hydrophilic groups and can improve water absorbency of corresponding superabsorbent.

Traditional superabsorbent network from synthetic polymers, such as poly(sodium acrylate) and polyacrylamide, often have some limitations besides poor biodegradability, and these flaws restrict its application widely. Various methods have been tried to improve absorbing properties and to expand application fields of superabsorbents (Lin, Wu, Yang & Pu 2001; Lee & Yang, 2004), since the US Department of Agriculture reported the first superabsorbent polymer (Weaver, Bagley, Fanta, & Doane, 1976). Recently, Clay has become the focus for the preparation of inorganic-organic superabsorbent composite in order to improve swelling properties, enhance gel strength, and reduce production cost of corresponding superabsorbents (Lin et al., 2001; Lee & Yang, 2004; Wu, Lin, Zhou, & Wei, 2000).

Attapulgit, a kind of hydrated octahedral layered magnesium aluminum silicate absorbent mineral with exchangeable cations and reactive OH groups on its surface, is less sensitive to salts compared to other clays (such as smectite) (Neaman & Singer, 2004). It is expected that the type and amount of hydrophilic groups, as well as the network structure of the superabsorbents could be improved by introducing starch phosphate and attapulgit into the polyacrylamide network. Consequently, on the basis of our previous work about superabsorbent composite (Li, Wang & Chen, 2004; Li & Wang, 2005; Li, Liu, & Wang, 2005; Zhang, Chen, & Wang, 2005), a novel starch phosphate-graft-acrylamide/attapulgit superabsorbent composite is synthesized. The influence of saponification process, phosphorylation of starch and attapulgit on water absorbency, and swelling behaviors are discussed in this paper. The results indicate that various properties, including water absorbency, swelling rate, thermal stability, and salt-resistant property of the superabsorbent are improved and the production cost is reduced by introducing starch phosphate and attapulgit into the polyacrylamide network.

## 2. Experimental

### 2.1. Materials

Potato starch was supplied by Hua'ou Starch Co., Ltd (Inner Mongoulia, China). Acrylamide was supplied by Shanghai Chemical Factory (Shanghai, China) and purified by recrystallization from benzene. Ammonium persulfate was supplied by Xi'an Chemical Reagent Factory (Xi'an, China) and recrystallized from water before use. *N, N'*-methylenebisacrylamide was supplied by Shanghai Chemical Reagent Corp. (Shanghai, China). Attapulgit micropowder (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 the starch phosphate

Starch phosphate was prepared according to a previously reported method (Zhu, 2003). 9.60 g sodium dihydrogen phosphate and 11.36 g sodium hydrogen phosphate were dissolved in 32.0 ml distilled water, and then 30.0 g starch was added into the phosphate solution. The slurry was heated gradually to 50 °C and stirred vigorously for 30 min. The starch slurry was filtered and the starch cake was oven-dried at 50 °C to a moisture content of about 10%. The starch containing the impregnated orthophosphates was placed in a flask and reacted under stirring at 145 °C for 4 h. The product was ground and washed with 95% v/v ethanol three times to eliminate the residual phosphate. Finally, the product was dried, ground, and sieved to pass through a 200 mesh-sieve. The phosphorus content in the prepared starch phosphate was 0.31 wt% determined by a spectrophotometric method at 825 nm (Fan & Ding, 1997).

### 2.3. Preparation of the starch phosphate-graft-acrylamide/attapulgit (P-st-AM/APT) superabsorbent composites

A series of superabsorbent composites from starch phosphate, AM, and APT micropowder were synthesized according to the following procedure. Appropriate amount of starch phosphate and 20-ml distilled water were introduced into a 250-ml four-neck flask, equipped with a stirrer, a reflux condenser, a thermometer, and a nitrogen line. After being purged with nitrogen for 30 min to remove the oxygen dissolved from the system, the slurry was stirred and heated to 65 °C, and then 96 mg initiator (ammonium persulfate) was introduced to initiate starch phosphate to generate radicals. Ten minutes later, the temperature was reduced to 45 °C, and then the mixture solution of 7.10 g acrylamide, 19.2 mg crosslinker (*N, N'*-methylenebisacrylamide), and certain amount of APT was added. The water bath was heated slowly to 60 °C and kept for 3 h. Then the resulting product was transferred into a sodium hydroxide aqueous solution (4 M) and was saponified at 95 °C for 2 h to transfer a part of CONH<sub>2</sub> to COO<sup>-</sup> and COOH. After saponification, the product was immersed in excess distilled water and then filtered for several times to remove any unreacted reactants until pH = 7 was achieved. The depurative product was dried in an oven at 70 °C until the weight of the product was constant and an ashen composite was obtained. The product was milled and all samples used for test had a particle size in the range of 40–80 mesh.

In order to investigate the effect of phosphorylation of starch on swelling behaviors, the starch-graft-acrylamide/attapulgit (st-AM/APT) superabsorbent composite was synthesized and the synthesis procedure was the same as above. The starch phosphate-graft-acrylamide (P-st-AM) and starch-graft-acrylamide (st-AM) superabsorbents were also prepared according to the above procedure to investigate the effect of APT on swelling properties of the superabsorbent composite.

## 2.4. Measurement of equilibrium water absorbency and swelling rate

0.05 g sample was immersed in excess distilled water (500 ml) at room temperature for 4 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 and no blotting of samples. The equilibrium water absorbency in distilled water of the superabsorbent composite,  $Q_{eq}(\text{H}_2\text{O})$ , was calculated using the following equation:

$$Q_{eq}(\text{H}_2\text{O}) = \frac{m_2 - m_1}{m_1} \quad (1)$$

where  $m_1$  and  $m_2$  are the weights of the dry sample and the swollen sample, respectively.  $Q_{eq}(\text{H}_2\text{O})$  is calculated as grams of water per gram of sample.

Equilibrium water absorbency of the sample in various saline solutions,  $Q'_{eq}$ , with different concentration ( $\text{NaCl}_{(aq)}$ ,  $\text{CaCl}_{2(aq)}$ ,  $\text{FeCl}_{3(aq)}$ ) was tested according to the same procedure. Swelling rate of the superabsorbent composite was measured according to the following process. Sample 0.05 g was poured into 500 ml distilled water at room temperature. At certain time intervals, the water absorbency of the sample was measured according to Eq. (1). The measurement condition is the same as that for equilibrium water absorbency. All the experiments were carried out three times repeatedly and the average values are reported in this paper.

## 2.5. Characterization

FTIR spectra of samples were taken as KBr pellets using a Thermo Nicolet NEXUS TM spectrophotometer. The micrographs of st-AM, P-st-AM, st-AM/APT, and P-st-AM/APT were taken using SEM (JSM-5600LV, JEOL, Ltd). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. Thermal stability of st-AM, P-st-AM, st-AM/APT, and P-st-AM/APT 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<sup>-1</sup> using a dry nitrogen purge at a flow rate of 50 ml min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Effect of molar ratio of NaOH to acrylamide on equilibrium water absorbency

According to Flory's network theory, the fixed charges on polymeric network of superabsorbent play an important part in the swelling of the superabsorbents. They are related to electrostatic repulsion between charges on the polymeric backbone and to osmotic pressure difference between polymeric network and external solutions. Therefore, the amount and type of hydrophilic groups on polymeric network play important parts in influencing water-absorbing properties

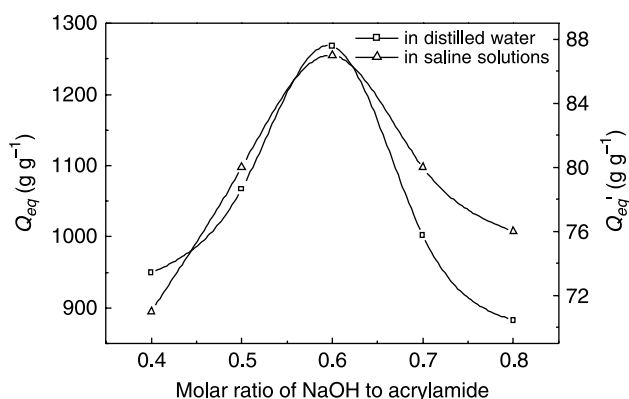


Fig. 1. Equilibrium water absorbency in distilled water and in 0.9 wt% NaCl solution as a function of molar ratio of NaOH to acrylamide for the P-st-AM/APT superabsorbent composite: weight ratio of starch phosphate to acrylamide is 1:5, APT content in the feed is 10 wt%.

of superabsorbent. For the P-st-AM/APT superabsorbent composite, the ratio of different hydrophilic groups can be adjusted by changing the molar ratio of NaOH to AM while saponification. The effect of the molar ratio of NaOH to AM on equilibrium water absorbency of the superabsorbent composite in distilled water and in 0.9 wt% NaCl solution is shown in Fig. 1. As can be seen from Fig. 1, equilibrium water absorbency of the composite increases with increasing the molar ratio of NaOH to AM when the ratio is less than 0.60, and then decreases with further increasing the ratio to 0.80. When AM is saponified with NaOH, the ionic hydrophilic property of the superabsorbent composite and osmotic pressure difference increases, and then electrostatic repulsion of the negatively charged carboxylate groups attached to the polymer chains tends to expand the network. With the molar ratio of NaOH to AM increasing, the electrostatic repulsion, ionic hydrophilic property and osmotic pressure difference increase, which result in an increase of equilibrium water absorbency. However, further increasing the molar ratio to a certain extent results in the generation of more sodium ions in the polymeric network, which reduces the electrostatic repulsion by screening the negative charges of  $-\text{COO}^-$  groups, thus resulting in the decrease of equilibrium water absorbency.

Variation of equilibrium water absorbency with the molar ratio of NaOH to AM while saponification in Fig. 1 means that an appropriate molar ratio is needed to transfer a certain amount of  $-\text{CONH}_2$  to  $-\text{COO}^-$  and  $-\text{COOH}$  in order to obtain excellent superabsorbent composite. The molar ratio of  $-\text{COO}^-$ ,  $-\text{COOH}$ , and  $-\text{CONH}_2$  is 10:3:11 for the composite to obtain the highest water absorbency under our experimental conditions. The content of  $-\text{COO}^-$ ,  $-\text{COOH}$ , and  $-\text{CONH}_2$  groups was quantified by titration (acidometric/alkalimetric) according to a previously reported literature (Wu, Wei, & Lin, 2003). The result from Fig. 1 also indicates that the collaborative effect of  $-\text{COOH}$ ,  $-\text{COO}^-$ , and  $-\text{CONH}_2$  groups is superior to that of single  $-\text{COOH}$ ,  $-\text{COO}^-$ , or  $-\text{CONH}_2$  group, and a similar behavior has been reported for the poly[sodium acrylate-co-3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate] system by Lee and Wu (1997).

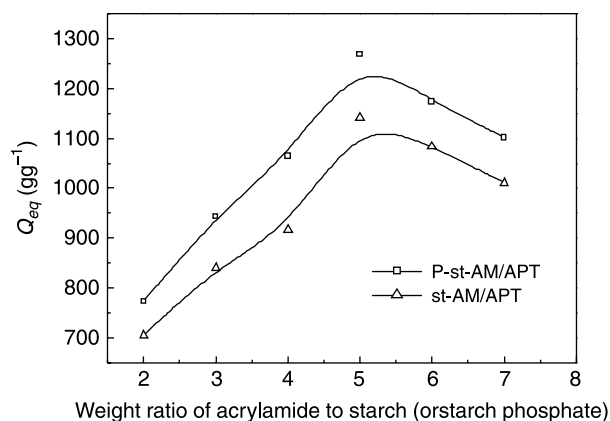


Fig. 2. Equilibrium water absorbency in distilled water as a function of weight ratio of acrylamide to starch phosphate or starch for the st-AM/APT and P-st-AM/APT superabsorbent composite: molar ratio of NaOH to acrylamide is 0.60, APT content in the feed is 10 wt%.

### 3.2. Effect of starch phosphate content on equilibrium water absorbency

The effect of weight ratio of AM to starch phosphate and starch on equilibrium water absorbency of the superabsorbent composites was investigated and the results are shown in Fig. 2. It can be seen from Fig. 2 that the equilibrium water absorbency increases with increasing the amount of AM, and then decreases with further increasing the ratio. With a weight ratio of AM to starch phosphate and starch of 5:1, the P-st-AM/APT and st-AM/APT superabsorbent composites acquire their maximum equilibrium water absorbency of 1268 g g<sup>-1</sup> and 1142 g g<sup>-1</sup>, respectively. The variation of equilibrium water absorbency with increasing the weight ratio of AM to starch phosphate and starch can be explained as follows. As the amount of AM increases, the fraction of polyacrylamide chains in the composite increases, which enhances hydrophilicity of corresponding composite, and then the equilibrium water absorbency is improved. In addition, more mobile Na<sup>+</sup> ions are generated in the polymeric network while saponification. Consequently, the osmotic pressure difference between the polymeric network and external medium increases. Moreover, both grafting and the molecular weight of the grafted polyacrylamide chains increase, which also contributes to the improvement of equilibrium water absorbency (Reyes, Huggins & Russell, 1968). The decrease of equilibrium water absorbency when the weight ratio is higher than 5:1 may be attributed to an increase in homopolymer percentage of polyacrylamide, which in turn results in an increase of water-soluble materials at a fixed crosslinking density (Reyes, Clark, Comas, Russell & Rist, 1969). Similar observation was also reported by Lu et al. in the starch-g-poly(potassium acrylate-co-acrylamide) polymeric network (Lu, Duan & Lin, 2003).

It also can be seen from Fig. 2 that equilibrium water absorbency of P-st-AM/APT is higher than that of st-AM/APT at a fixed weight ratio of AM to starch phosphate and starch. This result indicates that phosphorylation of starch can benefit the improvement of equilibrium water absorbency for the superabsorbent composite. This phenomenon is attributed to

the fact that hydrophilicity of starch phosphate is higher than that of starch, which results in the higher equilibrium water absorbency of P-st-AM/APT. Furthermore, a new kind of hydrophilic group is introduced into the polymeric network. Wu et al. has reported that the collaborative absorbent effect of different hydrophilic groups is superior to that of a single one in the starch-g-acrylamide/kaolinite polymeric network (Wu et al., 2003).

### 3.3. Effect of attapulgite content on equilibrium water absorbency

Fig. 3 shows the influence of APT content on equilibrium water absorbency for the P-st-AM/APT superabsorbent composite. It is clear that the amount of APT micropowder is an important factor affecting equilibrium water absorbency of the P-st-AM/APT superabsorbent composite. The results showed that equilibrium water absorbency of the composite increases with increasing APT content when the amount of APT was less than 10 wt%. According to our previous study (Li et al., 2004; 2005), OH on the surface of APT could react with acrylic acid and acrylamide, which could improve the polymeric network, and then enhance the equilibrium water absorbency. Further increasing the amount of APT to 30 wt% resulted in a sharp decrease of equilibrium water absorbency and the composite incorporated with 30 wt% APT still acquired a equilibrium water absorbency of as much as 600 g g<sup>-1</sup>. The decreasing tendency of equilibrium water absorbency with increasing APT content may be attributed to the fact that additional APT results in the generation of more crosslink points in the polymeric network, which increases the crosslink density of the composite, and then the elasticity of the polymer chains decreases. Additionally, the content of hydrophilic groups is lower at a higher APT content, and then the osmotic pressure difference decreases, which also results in the shrinkage of the composite. Scheme 1 shows the proposed structure of the P-st-AM/APT superabsorbent composite.

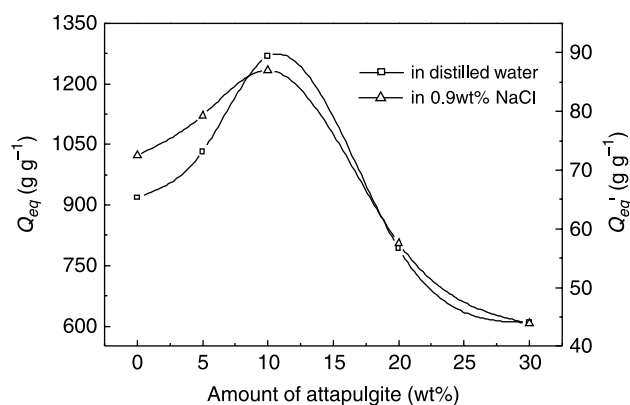
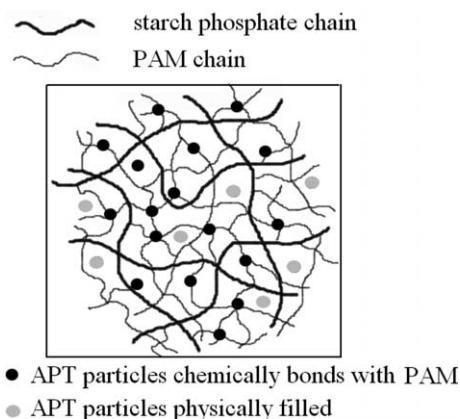


Fig. 3. Variation of equilibrium water absorbency in distilled water and in 0.9 wt% NaCl solution for the P-st-AM/APT superabsorbent composite with attapulgite content: molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate to acrylamide is 1:5.





Scheme 1. Schematic structure of the P-st-AM/APT superabsorbent composite.

### 3.4. FTIR analysis

The FTIR spectra of APT, P-st, PAM, and P-st-AM/APT composite incorporated with 10 wt% APT are shown in Fig. 4. After reaction, the absorption bands at 3616 and 3544  $\text{cm}^{-1}$  ascribed to Si–OH stretching, and absorption band at 989  $\text{cm}^{-1}$  ascribed to Si–OH bending disappeared. This result indicates that Si–OH group on APT micropowder participated in the reaction. The absorption bands at 1170, 1084  $\text{cm}^{-1}$ , and 925  $\text{cm}^{-1}$  ascribed to P=O, C–O–P, and O–P–O confirm the phosphorylation of starch (Fig. 4(b)) (Zhan, Liu, Guo, & Wu, 2004). It can be seen from Fig. 4(b) that the absorption bands at 573 and 525  $\text{cm}^{-1}$  ascribed to OH of P-st are weakened and the absorption bands at 1434 and 1370  $\text{cm}^{-1}$  ascribed to OH bending of P-st disappear after reaction. This means that OH group of P-st also takes part in the reaction. The saponification of PAM is confirmed by the appearance of absorption bands at 1565  $\text{cm}^{-1}$  (asymmetric stretching of  $\text{COO}^-$ ) and 1407  $\text{cm}^{-1}$  (symmetric stretching of  $\text{COO}^-$ ). It can also be seen from Fig. 4(d) that the absorption bands of  $\text{CONH}_2$  at 1673 and 1617  $\text{cm}^{-1}$  changed and new bands at 1153 and 1024  $\text{cm}^{-1}$  appeared. According to the information from FTIR, it can be

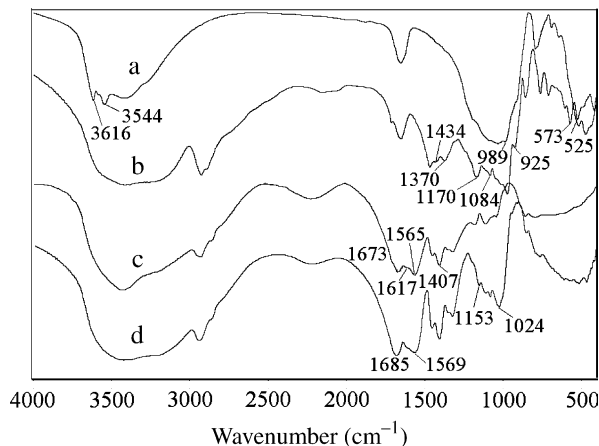


Fig. 4. FTIR spectra of (a) APT, (b) P-st, (c) PAM and (d) P-st-AM/APT composite (10 wt% APT, weight ratio of starch phosphate or starch to acrylamide is 1:5).

concluded that a graft-copolymerization reaction takes place among APT, P-st, and AM and a network structure is formed. This is in conformity with several previous reports on starch-g-AM (Kiatkamjornwong, Mongkolsawal & Sonsuk, 2002; Cao, Qing, Sun, Zhou, & Lin, 2002).

### 3.5. Morphological analysis

The micrographs of st-AM, P-st-AM, st-AM/APT, and P-st-AM/APT superabsorbent composites were observed and are shown in Fig. 5. It can be seen from this figure that st-AM shows a smooth and tight surface, but the phosphorylation of starch lead to an undulant surface (Fig. 5(b)). This undulant surface is convenient for the penetration of water into the polymeric network. Comparing with st-AM and P-st-AM, st-AM/APT and P-st-AM/APT superabsorbent composites show a coarse surface. This surface structure also facilitates the permeation of water. It can be concluded from Fig. 5 that both phosphorylation of starch and incorporation of APT can introduce a coarse surface, which is related to equilibrium water absorbency and swelling behaviors of the corresponding superabsorbent composites.

### 3.6. Thermal stability

Thermo-gravimetric analysis of st-AM, P-st-AM and representative sample of st-AM/APT and P-st-AM/APT superabsorbent composites incorporated with 10 wt% APT are shown and compared in Fig. 6. The thermogram of these superabsorbent materials exhibits a three-stage thermal decomposition. The first stage is in the range of 80–15  $^{\circ}\text{C}$ , implying a loss of moisture present in the sample. This is followed by weight loss within the temperature of 300–450  $^{\circ}\text{C}$ , which is attributed to the thermal decomposition of starch and starch phosphate, amide side-groups of AM and crosslinker on the network, and similar thermal behavior has been reported by Mathakia et al. and Saeidi et al. for polyacrylamide, respectively (Mathakiya, Vangani & Rakshit 1998; Saeidi, Katbab, Vasheghani-Farahani, & Afshar, 2004). During this period, the onset of st-AM and P-st-AM are almost the same (376.5  $^{\circ}\text{C}$ ); however, the onset shifts to about 404  $^{\circ}\text{C}$  after incorporating APT into the polymeric network. This result indicates that the incorporation of APT is helpful for the improvement of thermal stability of the composite. The role of APT in the polymeric network may be the main reason for the difference in TGA result of this system. APT acts as heat barriers, which delays the diffusion of both the volatile thermo-oxidation products to the gas and oxygen from the gas phase to the polymer, and then enhances the thermal stability of the system. The sharp weight losses of st-AM, P-st-AM, st-AM/APT and P-st-AM/APT composites at 529.8, 549.9, 483.9 and 499.2  $^{\circ}\text{C}$ , respectively, are suggested to be due to the thermal decomposition of the polyacrylamide chains backbone. It can be seen that the composites incorporated with APT show a lower onset temperature, compared to st-AM and P-st-AM. This phenomenon is attributed to the fact that the heat barrier effect of APT would result in a reverse thermal stability.

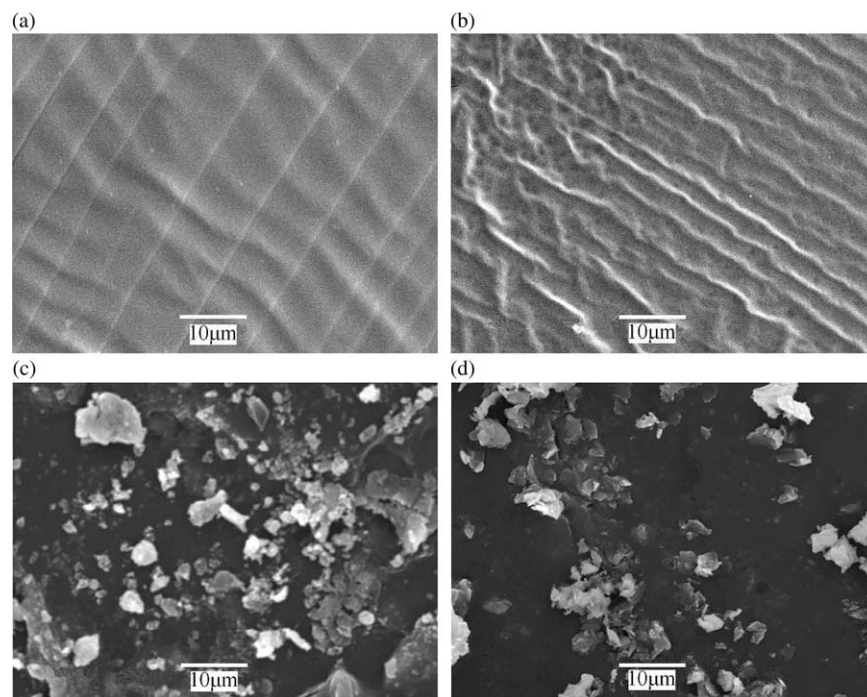


Fig. 5. SEM micrographs of st-AM (a), P-st-AM (b), st-AM/APT (c) and P-st-AM/APT composites (d) molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate or starch to acrylamide is 1:5, APT content in the feed is 10 wt%.

In other words, the stacked silicate layers of APT could hold accumulated heat that could be used as a heat source to accelerate the decomposition process, in conjunction with the heat flow supplied by the outside heat source (Suprakas & Masami, 2003).

### 3.7. Swelling rate

Swelling of superabsorbent composite involves larger scale segmental motion, which ultimately resulted into an increased distance of separation between macromolecular chains (Bajpai & Johnson, 2005). Swelling rate of superabsorbent is mainly determined by swelling ability, surface area, particle size, and density of the polymer (Buchanan, Hird & Letcher 1986). Fig. 7 shows the swelling rate of st-AM, P-st-AM, st-AM/APT, and P-st-AM/APT composites in distilled water. st-AM and P-st-AM have similar swelling tendency and need about 2 h to reach equilibrium water absorbency. This result indicates that phosphorylation of starch has no obvious effect on the superabsorbent to reach equilibrium water absorbency. However, st-AM/APT and P-st-AM/APT composites have higher swelling rate and need about 1.5 h to reach equilibrium water absorbency. This means that introducing APT into the polymeric networks is beneficial for enhancing the swelling rate of corresponding superabsorbents. It also can be seen that the superabsorbents swell faster at the first 30 min, and then the swelling rate decreases. When  $Q_t/Q_{eq} < 0.60$ , osmotic pressure and chain relaxation may be responsible for the higher swelling rate; however, the swelling of the superabsorbents may be only dominated by relaxation of the polymer chains when  $Q_t/Q_{eq} > 0.60$  and then the swelling rate decreases. This result is in

accord with Bajpai's study in the poly(acrylamide-co- sodium acrylate) (Bajpai & Johnson, 2005).

The initial swelling rates of these four superabsorbents are shown in Table 1. The values in Table 1 indicate that the initial swelling rate is in the order st-AM < P-st-AM < st-AM/APT < P-st-AM/APT. Mathakiya et al. reported that the initial swelling rate is primarily due to the penetration of water into the polymeric network through diffusion and capillarity (Mathakiya et al., 1998). A higher initial swelling rate in distilled water is obtained when starch is phosphated and APT is introduced to the polymeric network. This behavior is because starch phosphate and OH on the surface of APT

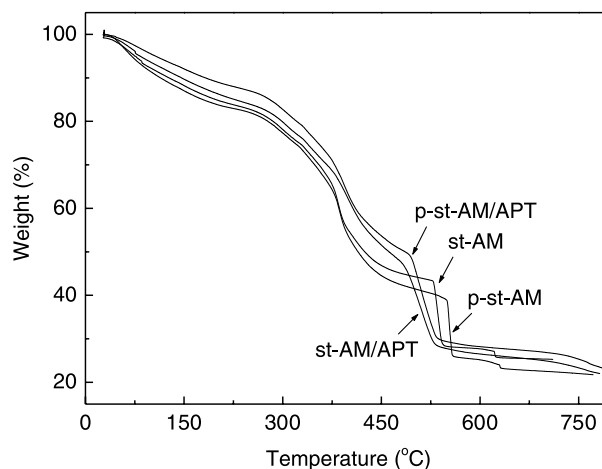


Fig. 6. TGA curves of st-AM, P-st-AM, st-AM/APT and P-st-AM/APT composites at a heating rate of 10 °C/min: molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate or starch to acrylamide is 1:5, APT content in the feed is 10 wt%.

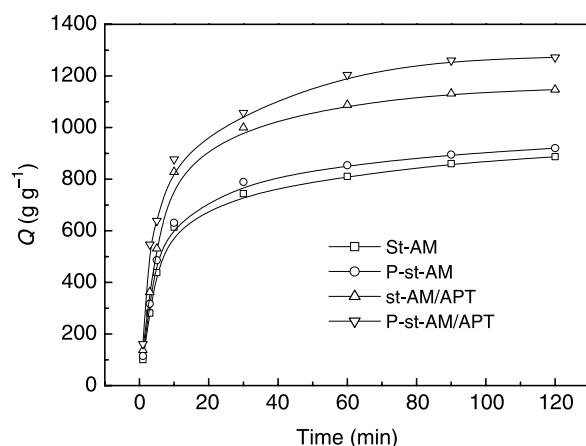


Fig. 7. Swelling rate of the st-AM, P-st-AM, st-AM/APT and P-st-AM/APT composites in distilled water: molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate or starch to acrylamide is 1:5, APT content in the feed is 10 wt%.

increase affinity of the polymeric network to water molecules. Another reason for the composites introduced starch phosphate and APT acquiring higher initial swelling rate may be that they have coarse surface (see Fig. 5) and the capillarity is more evident, which accelerate the penetration of water molecules into the polymeric network.

### 3.8. Equilibrium water absorbency in various saline solutions

Considering the great impact of external saline solutions on water absorbency of superabsorbents and the expanding of their applications, especially for agriculture and hygienic products, the interaction of various saline solutions and the superabsorbent composite was investigated in this section. Equilibrium water absorbencies of st-AM, P-st-AM, st-AM/APT and P-st-AM/APT, composites in NaCl(aq), CaCl<sub>2</sub>(aq), and FeCl<sub>3</sub>(aq) solution of various concentration are shown in Figs. 8–10, respectively. It can be seen from Figs. 8–10 that equilibrium water absorbencies of these four superabsorbents in various saline solutions of the same concentration are all in the order st-AM < P-st-AM < st-AM/APT < P-st-AM/APT. This phenomenon may be attributed to the facts that APT is insensitive to saline solution and the phosphorylation of starch enhanced osmotic pressure difference between the polymeric network and external saline

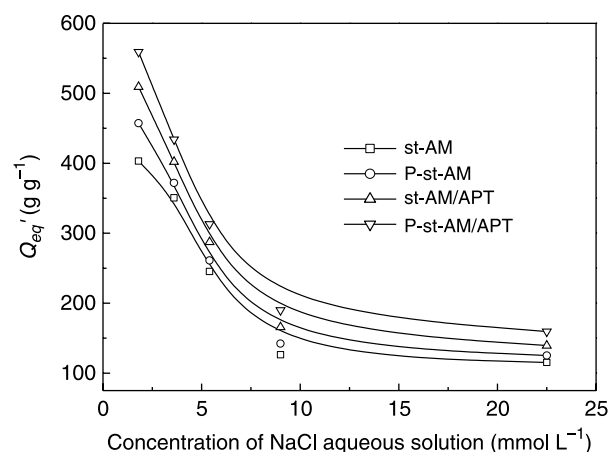


Fig. 8. Variation of equilibrium water absorbency for st-AM, P-st-AM, st-AM/APT and P-st-AM/APT composites with concentration of NaCl aqueous solution: molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate or starch to acrylamide is 1:5, APT content in the feed is 10 wt%.

solutions, and then the P-st-AM/APT composite acquired the highest equilibrium water absorbency in saline solutions. It also can be seen that equilibrium water absorbencies for the four superabsorbents in various saline solutions decrease evidently with increasing concentration. The shrink of the polymeric hydrogels is mainly caused by the following facts. With the increase of external saline solution concentration, the osmotic pressure difference decreases, and the screening effect of penetrated counterions (Na<sup>+</sup>, Ca<sup>2+</sup>, and Fe<sup>3+</sup>) on anionic hydrophilic groups, which restricts the expanding of polymeric network, is more evident. Furthermore, equilibrium water absorbencies in saline solutions for these four superabsorbents decrease in the order NaCl(aq) > CaCl<sub>2</sub>(aq) > FeCl<sub>3</sub>(aq). This is because of the complexing ability difference of anionic hydrophilic groups on superabsorbent network to cations. The complexing ability of anionic hydrophilic groups to these three cations are in the order Na<sup>+</sup> < Ca<sup>2+</sup> < Fe<sup>3+</sup> according to their formation constants with ethylenediamine tetraacetic acid (EDTA); the logarithm of formation constants of EDTA with

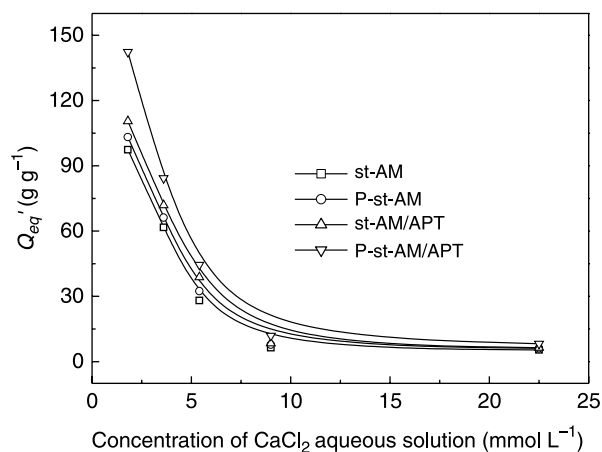


Fig. 9. Variation of equilibrium water absorbency for st-AM, P-st-AM, st-AM/APT and P-st-AM/APT composites with concentration of CaCl<sub>2</sub> aqueous solution: molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate or starch to acrylamide is 1:5, APT content in the feed is 10 wt%.

Table 1

Initial swelling rates for st-AM, P-st-AM, st-AM/APT and P-st-AM/APT composites in distilled water: molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate and starch to acrylamide is 1:5, APT content in the feed is 10 wt%

Samples	st-AM	P-st-AM	st-AM/APT	P-st-AM/APT
Initial swelling rate ( $Q/\text{min}$ )				
1 min	101	115	138	161
1–3 min	90	101	112	140
3–5 min	78	84	92	99

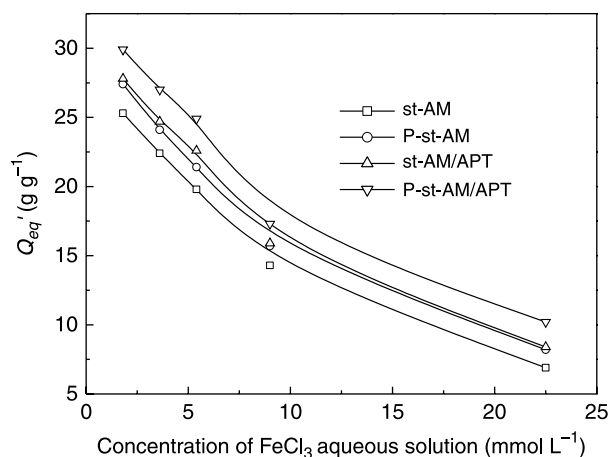


Fig. 10. Variation of equilibrium water absorbency for st-AM, P-st-AM, st-AM/APT and P-st-AM/APT composites with concentration of FeCl<sub>3</sub> aqueous solution: molar ratio of NaOH to acrylamide is 0.60, weight ratio of starch phosphate or starch to acrylamide is 1:5, APT content in the feed is 10 wt%.

cations is 0, 10.69, and 25.10 for Na<sup>+</sup>, Ca<sup>2+</sup>, and Fe<sup>3+</sup>, respectively (Lee & Wu, 1996).

#### 4. Conclusions

A novel starch phosphate-graft-acrylamide/attapulgit superabsorbent composite was prepared by graft-copolymerization reaction among starch phosphate, acrylamide and attapulgit in aqueous solution. Equilibrium water absorbency of the superabsorbent composite is greatly enhanced to 1268 g g<sup>-1</sup> in distilled water by introducing starch phosphate and attapulgit into the polymeric system. The investigation of surface morphology and swelling rate of the superabsorbent composite reveals that the composite incorporated with starch phosphate and attapulgit exhibits a coarse surface and a higher swelling rate. The impact of external saline solutions on water absorbency of the composite is correlated with the kind, valence of cations, and the complexing ability of anionic hydrophilic groups with them, and the trivalent cation (Fe<sup>3+</sup>) has the greatest effect on decreasing equilibrium water absorbency of the superabsorbent composite.

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