

# Study on Superabsorbent Composite. VIII. Effects of Acid- and Heat-Activated Attapulgite on Water Absorbency of Polyacrylamide/Attapulgite

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Received 8 December 2005; accepted 6 September 2006

DOI 10.1002/app.25452

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

**ABSTRACT:** A novel superabsorbent composite, polyacrylamide/attapulgite, from acrylamide (AM) and attapulgite (APT), was prepared by free-radical polymerization, using *N,N'*-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator. The effects of hydrochloric acid (HCl) concentration, acidification time, and acidification temperature while acidifying APT and temperature and APT heat-activation on water absorbency of the superabsorbent composite in distilled water and in 0.9 wt % NaCl solution were studied. The water absorbency first decreases with increasing the HCl concentration while acidifying APT, and then increases with further increasing the HCl concentration. Prolongation of acidification time is of benefit to the increase of water absorbency. At a given HCl concentration, water

absorbency for the composite increases with increasing acidification temperature. An important increase in water absorbency was observed after incorporating heat-activated APT into the polymeric network, reaching a maximum of 1964 g g<sup>-1</sup> with the APT heat-activated at 400°C. Acid- and heat-activation can influence chemical composition, crystalline structure, cation exchange capacity (CEC), and specific surface area of APT according to XRF, XRD, FTIR analysis, and physicochemical properties test, and then on water absorbency of corresponding PAM/APT superabsorbent composite. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2419–2424, 2007

**Key words:** attapulgite; polyacrylamide; superabsorbent composites; water absorbency

## INTRODUCTION

Superabsorbents are slightly crosslinked hydrophilic polymers that can absorb, swell, and retain aqueous fluids up to thousands of times their own weight. Because of the excellent properties to traditional water absorbing materials (such as sponge, cotton, pulp, etc.), superabsorbents have raised considerable interests, and are widely used in many fields, such as hygienic products, horticulture, gel actuators, and drug-delivery systems, as well as water-blocking tapes and coal dewatering.<sup>1–5</sup> Since the first superabsorbent was reported by the U.S. Department of agriculture in 1961, many efforts have been made to modify swelling capability, swelling rate, and swollen gel strength of them.<sup>6–8</sup> Recently, much attention has been paid to clays for the preparation of superabsorbents. Various clays, such as montmorillonite,<sup>9,10</sup> kaolin,<sup>11</sup> attapulgite,<sup>12</sup> mica,<sup>13</sup> and sericite,<sup>14</sup> have all

been used to fabricate superabsorbent composites. The incorporation of these mineral powders can not only reduce production cost, but also improve swelling ability, gel strength, mechanical, and thermal stability of corresponding superabsorbent composites. In the clay-based superabsorbent composite field, the kinds of clay on properties of corresponding superabsorbent composite were investigated intensively. On the other hand, the effects of organoclays on improving water absorbency of superabsorbent composites were also focused.<sup>9,15</sup> However, there is little information about the effect of clay's physicochemical properties on the performance of superabsorbent composite. Thus, some efforts need to be done in this field.

APT is a kind of hydrated octahedral layered magnesium aluminum silicate absorbent mineral with reactive —OH groups on its surface and is less sensitive to salts when compared with the other clays (such as smectite).<sup>16</sup> A series of APT-based superabsorbent composites have been synthesized by our research group, such as poly(acrylic acid)/attapulgite,<sup>12</sup> poly(acrylic acid-co-acrylamide)/attapulgite,<sup>17</sup> starch-g-poly(acrylic acid)/attapulgite,<sup>18</sup> and polyacrylamide/attapulgite,<sup>15</sup> and comprehensive properties of these superabsorbents are

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Contract grant sponsor: The Ministry of Science and Technology, People's Republic of China; contract grant number: 2005AA2Z4030.

improved by introducing APT micropowder into the polymeric network. Considering the great impact of APT on properties of corresponding superabsorbent composites, a series acid- and heat-activated APT were incorporated into the polyacrylamide polymeric network to investigate the effects of activated APT on water absorbency of the superabsorbent composites.

## EXPERIMENTAL

### Materials

Acrylamide (AM) (analytically graded, supplied by Shanghai Chemical Factory, Shanghai, China) was purified by recrystallization from benzene. Ammonium persulfate (APS, analytically graded, 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, Shanghai, China) was used as purchased. APT micropowder (supplied by Linze Colloidal, Gansu, China) was milled through a 320-mesh screen. Other agents used were all of analytical grade and all solutions were prepared with distilled water.

### Acid-activation and heat-activation of APT

Acid-activated APT samples were obtained according to the following three methods. (1) Acid concentration series: Ten grams of APT micropowder was immersed in 100 mL HCl solution of various concentrations (2, 4, 6, 8, and 12M) at 20°C for 1 h. (2) Acidification time series: Ten grams of APT micropowder was immersed in 100 mL 6M HCl solution at 20°C for 1, 2, 4, 8, and 12 h, respectively, (3) Acidification temperature series: Ten grams of APT micropowder was immersed in 100 mL 6M HCl solution for 1 h at 20, 40, 60, 80, and 100°C, respectively. All the above APT samples were washed with distilled water until pH 6 was achieved, and then dried at 105°C for 8 h before use.

Heat-activated APT samples were obtained according to the following recipe. (1) Ten grams of APT micropowder is calcined at 100, 200, 300, 400, and 500°C for 4 h, respectively, and then cooled to room temperature in a desiccator. (2) Ten grams of APT micropowder is calcined at 400°C for 4 h, followed by acid-activation with HCl solution of various concentrations for 1 h. The samples were washed with distilled water until pH 6 was achieved, and then dried at 105°C for 8 h before use.

### Preparation of PAM/APT superabsorbent composites

PAM/APT superabsorbent composites were synthesized according to the following optimized procedure.

Typically, 7.10 g AM was dissolved in 20.0 mL distilled water in a 250-mL four-necked flask, equipped with a stirring rod, a reflux condenser, a thermometer, and a nitrogen line. MBA (15.3 mg) was added to the above-mentioned monomer solution, and then, 3.07 g APT micropowder was dispersed in the mixed solution. After being purged under nitrogen for 30 min to remove the oxygen dissolved in the solution, the mixed solution was heated to 40°C gradually, and then, 40.5 mg APS was introduced into the mixed solution. The solution was stirred vigorously under nitrogen atmosphere for 3 h, and then, 30.0 mL of sodium hydroxide solution (2 mol L<sup>-1</sup>) was added and the primary product was heated to 95°C to be saponified for 2 h. After saponification, the product was washed several times with water and methanol (1 : 9 in volume) 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. The product was milled and all samples used for test had a particle size in the range of 40–80 mesh.

### Measurement of water absorbency

PAM/APT (0.05 g) superabsorbent composite was immersed in excess distilled water (500 mL) or 0.9% NaCl solution (100 mL) at an ambient 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. Water absorbency of the superabsorbent composite,  $Q_{H_2O}$ , is calculated using the following equation:

$$Q_{H_2O} = \frac{m_2 - m_1}{m_1} \quad (1)$$

where  $m_1$  and  $m_2$  are the weights of the dry sample and the swollen sample, respectively.  $Q_{H_2O}$  is calculated as grams of water per gram of sample.

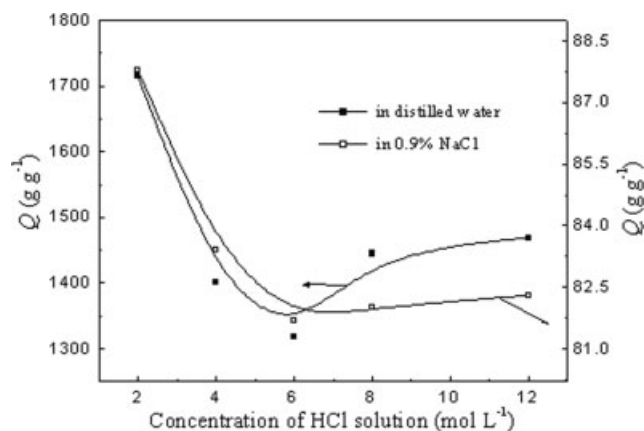
### Characterization

All IR spectra were recorded on a FTIR spectrophotometer (Thermo Nicolet, NEXUS, TM) using KBr pellets. Chemical composition of samples were analyzed using an X-ray Fluorescence Spectrometer (PAN Alytical Magix PW 2403 X). XRD were performed using a diffractometer with Cu anode (PAN alytical X'pert PRO).

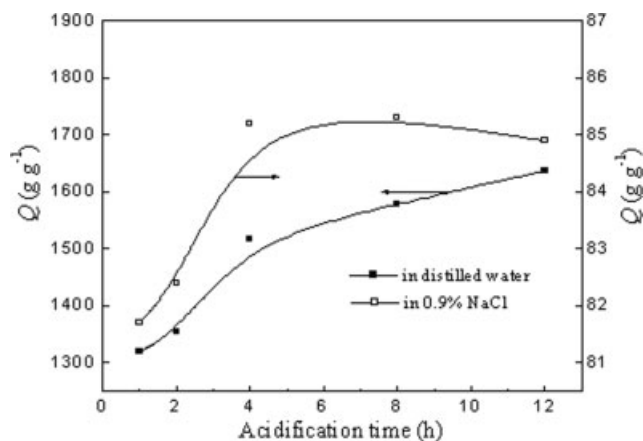
## RESULTS AND DISCUSSION

### Effect of HCl concentration while acidifying APT on water absorbency

The effect of HCl concentration while acidifying APT on water absorbency was shown in Figure 1. It



**Figure 1** Variation of water absorbency for the PAM/APT superabsorbent composite with HCl solution concentration while acidifying APT: acidified for 1 h at 20°C.



**Figure 2** Variation of water absorbency for the PAM/APT superabsorbent composite with acidification time while acidifying APT: 6M HCl solution at 20°C.

can be seen that water absorbency in distilled water of PAM/APT composites decreases from 1715 to 1319  $\text{g g}^{-1}$  with increasing HCl concentration from 2 to 6M, and then increases to 1469  $\text{g g}^{-1}$  with further increasing HCl concentration to 12M. Water absorbency in 0.9 wt % NaCl solution exhibits a similar trend. As dilute HCl solution (2M) was used to acidify APT, carbonate, and cement are decomposed, and then more Si—OH of APT appears, which forms a more intact polymeric network and endows the PAM/APT composite with higher water absorbency when compared with the natural APT (1414  $\text{g g}^{-1}$ ). As HCl concentration increases, more cations on the surface of APT are exchanged by  $\text{H}^+$ , and then the amount of active cation site decreases evidently, which goes against the formation of PAM/APT polymeric network, and then results in the decrease of water absorbency. APT samples activated with 8 and 12M solution show ficelle and off-white color, respectively. This phenomenon means that the exchange degree of cations (especially for ferric ion) in octahedral layer of APT increases evidently when the HCl concentration is higher than 6M, which is of benefit to the improvement of water absorbency for the PAM/APT composite. The variation of water absorbency with HCl solution concentration indicates that a moderate acid concentration is needed to enhance water absorbency of the composite, and the PAM/APT composite incorporated with APT activated with 2M HCl acquires the highest water absorbency under our experimental conditions.

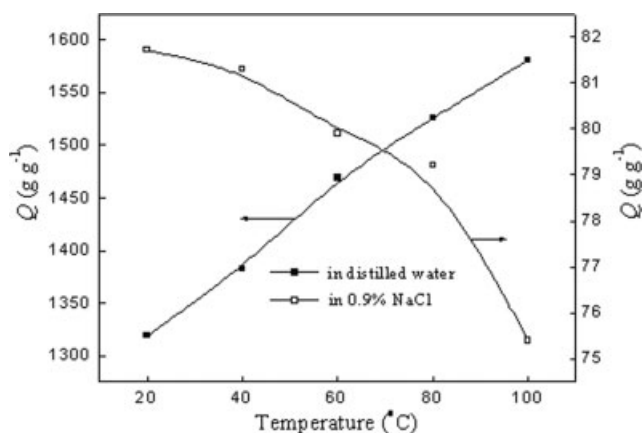
#### Effect of acidification time while acidifying APT on water absorbency

Figure 2 represents the profiles of the effect of acidification time while acidifying APT on water absorbency of the PAM/APT superabsorbent composite. It

can be seen from Figure 2 that water absorbency for the composite in distilled water and in 0.9 wt % NaCl solution increases gradually with the prolongation of acidification time. The water absorbency increases rapidly when the acidification time is less than 4 h. With further increasing the acidification time, the increase degree of water absorbency becomes lower. This phenomenon indicates that a relatively shorter acidification time is enough to enhance water absorbency of the PAM/APT composite to a higher degree and further increasing acidification time is only of little benefit to the improvement of water absorbency. Table I shows the chemical composition changes of APT activated with 6M HCl for different time at 20°C. The contents of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  in the APT sample activated for 1 h decreased evidently when compared with that of the natural APT. The decrease of  $\text{Ca}^{2+}$  content is attributed to the fact that the carbonates in natural APT decomposed in an acidic environment.  $\text{H}^+$  could exchange with the  $\text{Na}^+$  absorbed on the surface of APT, which results in the decrease of  $\text{Na}^+$  content. With the prolongation of acidification time, the amount of  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$  in APT decreases gradually, however, there is no evident change of  $\text{Al}^{3+}$  content. This result indi-

**TABLE I**  
Chemical Composition of APT Acidified with 6M HCl for Different Time (wt %)

Acidification time (h)	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	CaO	$\text{Na}_2\text{O}$
0	57.06	16.59	6.11	8.63	4.55	1.35
1	63.91	17.79	6.50	6.52	0.31	0.53
2	64.12	17.51	6.33	6.33	0.26	0.39
4	64.87	17.46	5.94	5.83	0.29	0.59
8	65.97	17.32	5.44	5.52	0.30	0.59
12	65.77	17.52	5.29	5.96	0.21	0.43



**Figure 3** Variation of water absorbency for the PAM/APT superabsorbent composite with acidification temperature while acidifying APT: 6M HCl solution for 1 h.

cates that  $Mg^{2+}$  and  $Fe^{3+}$  are more easily dissolved or removed by  $H^+$  comparing with  $Al^{3+}$ . This variation of  $Mg^{2+}$  and  $Fe^{3+}$  contents in the APT samples with acidification time is in accordance with the changes of water absorbency of the composite. This result also means that water absorbency of the PAM/APT superabsorbent composite is correlative with the kind and content of cations existed in APT.

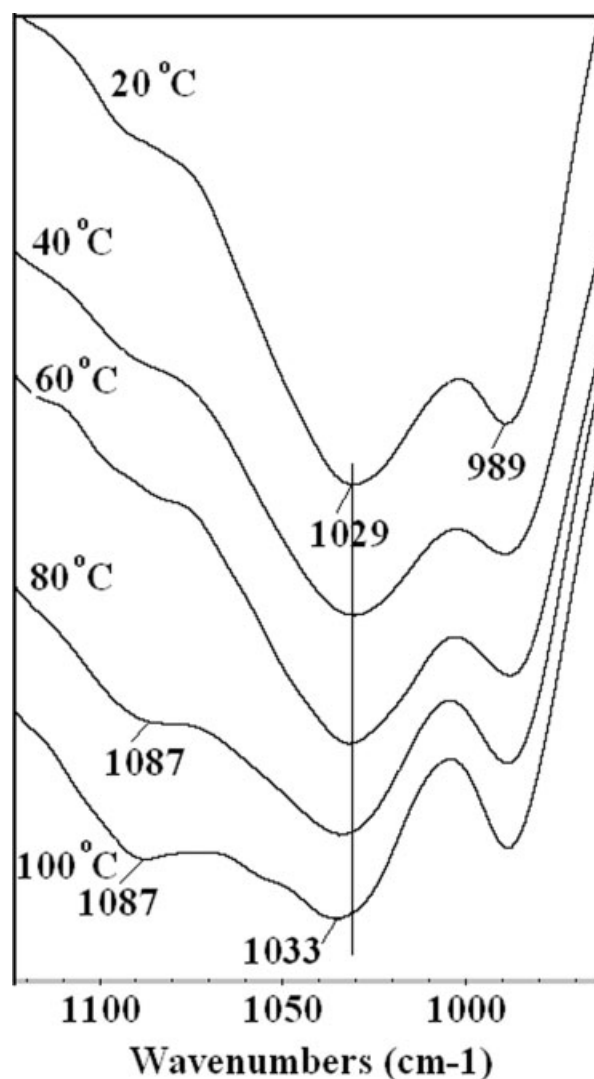
#### Effect of acidification temperature while acidifying APT on water absorbency

The effect of acidification temperature while acidifying APT on water absorbency of the PAM/APT superabsorbent composite in distilled water and in 0.9 wt % NaCl solution are shown in Figure 3. The water absorbency in distilled water increases rapidly with increasing acidification temperature from 20 to 100 °C. In general, a higher acidification temperature is of benefit to the exchange of  $H^+$  with cations on the octahedral sheet of APT.<sup>19</sup> The  $H^+$  ions could easily penetrate into the inside of APT from the edge of octahedral sheet at a higher temperature and the cations on the octahedral sheet are exchanged by  $H^+$  gradually. At the same time, lots of reactive Si—OH groups are generated. The exchanged cations inside APT are remained in tunnels of APT in a dissociative state, which may chemically bond to the PAM polymeric network, and then the network is more intact and thus has additional space to hold more water. It should be noted that water absorbency in 0.9 wt % NaCl for the PAM/APT composite decreases with increasing acidification temperature and this is contrary to the variation of water absorbency in distilled water. This is attributed to the fact that the cations existed in APT endowed it an excellent salt-resistant property.<sup>20</sup> Figure 4 shows the FTIR spectra of APT acid-activated with 6M HCl for 1 h at different temperature. As shown in Figure 4,

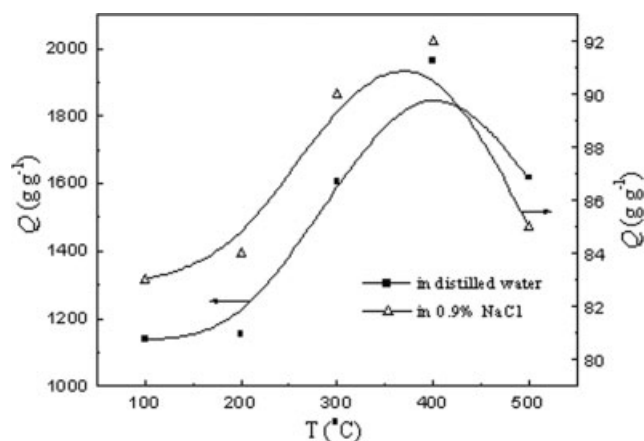
some changes have happened with the increase of acidification time. A new absorption band at  $1087\text{ cm}^{-1}$  appeared when the temperature is above 80 °C, and the absorption band is more evident when APT was acid-activated at 100 °C. The absorption band at  $1029\text{ cm}^{-1}$  ascribed to Si—O—Si bending shifted to  $1033\text{ cm}^{-1}$  with increasing temperature from 20 to 100 °C. The changes in the FTIR spectra of APT acid-activated in the different temperature indicate that the crystalline structure of APT has been changed in some extent, which results in the increase and decrease of water absorbency for the superabsorbent composite in distilled water and in 0.9 wt % NaCl solution, respectively.

#### Effect of heat-activation of APT on water absorbency

Figure 5 shows typical water absorbency of PAM/APT superabsorbent composite incorporated with



**Figure 4** FTIR spectra of APT acidified at different temperature: 6M HCl solution for 1 h.



**Figure 5** Variation of water absorbency for the PAM/APT superabsorbent composite with heat-activation temperature.

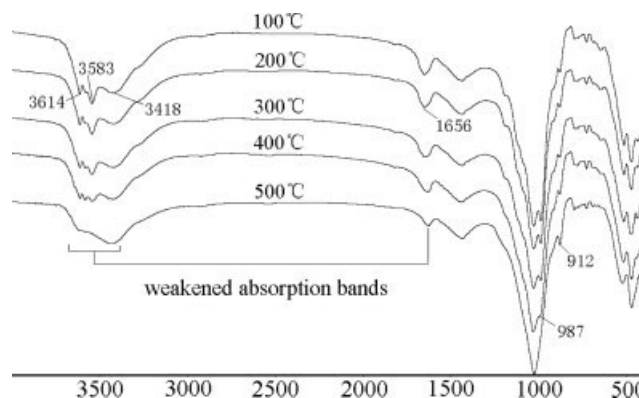
APT activated at different temperature. As shown in Figure 5, the water absorbency in distilled water and in 0.9 wt % NaCl solution increases from 1138 and 83  $\text{g g}^{-1}$  to 1964 and 92  $\text{g g}^{-1}$  with increasing heat-activation temperature from 100 to 400°C, and then decreased to 1617 and 85  $\text{g g}^{-1}$  with further increasing temperature to 500°C. This variation of water absorbency is consistent with cationic exchange capacity (CEC) and specific surface area of APT activated at different temperature (Table II). With increasing temperature from 100 to 300°C, specific surface area of APT increased from 134.5 to 150.1  $\text{m}^2 \text{g}^{-1}$ , and then decreased to 115.9  $\text{m}^2 \text{g}^{-1}$  at 500°C. The CEC increased from 20.1 to 44.6 mmol per 100 g with increasing the temperature from 100 to 500°C. This is attributed to the change of crystalline structure of APT while heat-activation. According to the results of powder XRD, the typical diffraction peak (110) of APT at 8.45° shifted to 8.49° after being heat-activated at 400°C. As the temperature increased to 500°C, all the characteristic diffraction peaks become weaker. The heat-activation of APT is also characterized by FTIR and the spectra of APT activated at different temperature are shown in Figure 6. It can be seen from this figure that heat-activation has

**TABLE II**  
CEC and Specific Surface Area of APT Treated at Different Temperatures

Temperature (°C)	CEC (mmol per 100 g) <sup>a</sup>	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ ) <sup>b</sup>
100	20.1	134.5
200	24.3	146.9
300	26.5	150.1
400	28.4	147.5
500	44.6	115.9

<sup>a</sup> Determined by the ammonium acetate method.<sup>21</sup>

<sup>b</sup> Measured by the glycol aether ( $\text{C}_4\text{H}_{10}\text{O}_2$ ) method.<sup>22</sup>

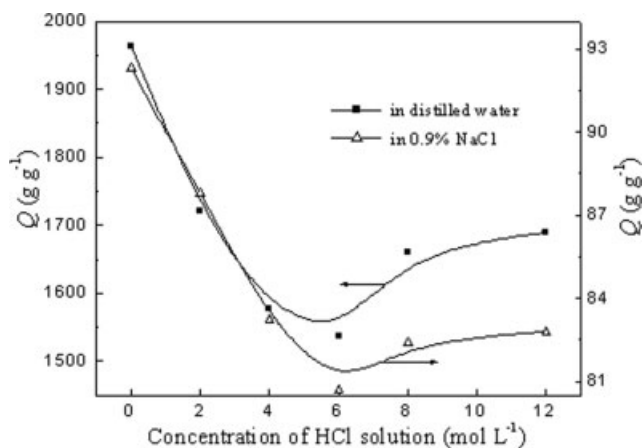


**Figure 6** FTIR spectra of APT heat activated at different temperature.

no obvious influence on the structure of APT when the temperature is below 300°C. As the temperature increased to 400°C, the intensity of most of the APT-absorption bands (•••) becomes weaker evidently when compared with those activated at a lower temperature. The typical absorption band at 987  $\text{cm}^{-1}$  almost disappeared. This information indicates that a higher temperature results in the loss of a part of crystalline water, which could cause the collapse of APT tunnels. With further increasing temperature to 500°C, most of APT absorption bands disappeared absolutely. In addition, the absorption band at 912  $\text{cm}^{-1}$  increases observably, which indicates that the crystalline structure of APT is destroyed in some degree. Table III summarized the characteristic absorption bands of APT. The results from XRD and FTIR revealed that a higher heat-activation temperature could affect the crystalline structure of APT, and then influence CEC and specific surface area. According to Flory's network theory, water absorbency of a hydrogel is dependent on ionic osmotic pressure, crosslinking density, and the affinity for water.<sup>23</sup> After incorporating APT with a higher CEC, hydrophilicity of the PAM/APT superabsorbent composite was enhanced, which makes the compos-

**TABLE III**  
Characteristic Absorption Bands of APT in Figures 4 and 6

Wave numbers ( $\text{cm}^{-1}$ )	Groups
3614	$\nu(\text{Al}^{3+}-\text{OH})$
3583	$\nu(\text{Fe}^{3+}, \text{Fe}^{2+}-\text{OH})$
3418	$\text{Si}-\text{O}(\text{H})-\text{Si}$
3270–3260	$\text{Si}-\text{O}(\text{H})-\text{Al}$
1656	$\delta(\text{OH}_2)$
1087	$\nu_{\text{as}}(\text{Si}-\text{O})$
1029	$\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$
987	$\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$
912	$\nu_{\text{s}}(\text{Si}-\text{O})$
798	$\nu_{\text{s}}(\text{Si}-\text{O}-\text{Si})$



**Figure 7** Variation of water absorbency for the PAM/APT superabsorbent composite incorporated with APT first heat-activated at 400°C, followed by acid-activation with HCl solution of various concentrations for 1 h.

ite swell more. A higher specific surface area of APT could enhance the interaction between APT and PAM polymeric network, which is helpful for the formation of a more intact polymeric network just like acid-activation, which also contributes to the improvement of water absorbency for the PAM/APT composite.

Considering acid-activation and heat-activation have so great influence on water absorbency of the PAM/APT superabsorbent composite, synergistic effect of them was investigated in this section. It has been shown in Figure 5 that the composite acquires higher water absorbency as APT heat-activated at 400°C was introduced into the polymeric network. On this basis, the APT samples first heat-activated at 400°C followed by acid-activation with HCl solution of various concentrations for 1 h were charged into the PAM system. Figure 7 shows water absorbency for the PAM/APT superabsorbent composite as a function of HCl solution concentration. It can be seen that the water absorbency decreases with increasing HCl solution concentration from 0 to 6M, and then increases with further increasing the concentration. This variation trend is similar to that observed in Figure 1, but relatively higher water absorbency was obtained. This result indicates that the collaborative effect of acid- and heat-activation is superior to that of single acid-activation or heat-activation.

## CONCLUSIONS

Acid- and heat-activation of attapulgite have great influences on physicochemical properties of APT

and on water absorbency of the corresponding PAM/APT superabsorbent composite. Most of the PAM/APT superabsorbent composites incorporated with acid-activated or heat-activated APT have higher water absorbency when compared with that incorporated with natural APT. Dilute HCl solution and relatively long time while acid-activation of APT are of great benefit to water absorbency. A higher temperature is needed during heat-activation of APT for the composite to acquire higher water absorbency. The collaborative effect of acid- and heat-activation is superior to that of single acid-activation or heat-activation. The relation between physicochemical properties of APT and water absorbency of the PAM/APT superabsorbent composite is revealed in this article and may provide some references for the preparation of clay-based superabsorbent composites.

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