Available online at www.sciencedirect.com
ScienceDirect
European Polymer Journal 43 (2007) 1691–1698
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Study on superabsorbent composite XVI. Synthesis, characterization and swelling behaviors of poly(sodium acrylate)/vermiculite superabsorbent composites

Yian Zheng [a], Ping Li [a,b], Junping Zhang [a,b], Aiqin Wang [a,*]

[a] *Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China*
[b] *Graduate University of the Chinese Academy of Sciences, Beijing 100049, PR China*

Received 3 November 2006; received in revised form 2 February 2007; accepted 14 February 2007
Available online 25 February 2007

Abstract

A series of superabsorbent composites were synthesized by copolymerization reaction of partially neutralized acrylic acid on unexpanded vermiculite (UVMT) micropowder using *N*,*N*′-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator in aqueous solution. And the samples were further characterized by means of fourier-transform spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The effects of vermiculite content on water absorbency were studied. Swelling behaviors of the superabsorbent composites in various cationic salt solutions (NaCl, $CaCl_2$ and $FeCl_3$), anionic salt solutions (NaCl, Na_2SO_4 and Na_3PO_4) and pH solutions were also systematically investigated. Results obtained showed that the equilibrium water absorbency increased with increasing UVMT content and the concentration of 20 wt.% clay gave the best absorption (1232 g/g in distilled water and 89 g/g in 0.9 wt.% NaCl). Data achieved also suggested that the water absorbency in various saline solutions decreased with an increase in the ionic strengths of these solutions. And it was found that at a higher ionic strength ($>1 \times 10^{-3}$ M), the water absorbency in monovalent cationic solutions was higher than those in multivalent cationic solutions. However, at the same ionic strength ($>1 \times 10^{-3}$ M), the effect of three anionic salt solutions on the swelling has the following order: $NaCl < Na_2SO_4 < Na_3PO_4$.

Keywords: Superabsorbent composite; Vermiculite; Water absorbency; Swelling behavior

---

1. Introduction

Superabsorbents are loosely crosslinked hydrophilic polymers that can absorb, swell and retain aqueous solutions up to hundreds of times their own weight even under some pressure. Based on their excellent characteristics, superabsorbents have been used widely in agriculture [1], horticulture [2–5], hygienics, foods, cosmetics [6,7] and drug delivery [8,9]. Since the first superabsorbent polymer was reported by the US Department of Agriculture in 1961, lots of researchers attempted to modify

---

[*] Corresponding author. Tel.: +86 931 4968118; fax: +86 931 8277088.
E-mail address: aqwang@lzb.ac.cn (A. Wang).

0014-3057/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2007.02.023

these absorbent polymers to enhance their absorbency, gel strength, and absorption rate [10–13].

In recent years, the preparation of organic–inorganic superabsorbent composites has attracted great attention because of their relatively low production cost, high water absorbency and their considerable range of applications [14–16]. Synthesis and swelling behaviors of superabsorbent composites through polymerization of diluted solution of monomers by using micro-sized inorganic materials such as kaolin [14], attapulgite [17] and mica [18] have been recently investigated. Because of their hydrophilic nature, clays have been more suitable for use in water absorbents as additives.

Vermiculite is a layered aluminium silicate with exchangeable cations and reactive –OH groups on the surface. It is expected that the type and amount of hydrophilic groups, as well as the network structure of the superabsorbent composites are improved by copolymerization of acrylate monomer and vermiculite. Consequently, on the basis of our previous work about superabsorbent composite [17,19–21], a series of novel polyacrylate/vermiculite superabsorbent composites are synthesized in this paper. The effects of vermiculite content on water absorbency were studied. Swelling behaviors of the superabsorbent composites in various cationic salt solutions (NaCl, $CaCl_2$ and $FeCl_3$), anionic salt solutions (NaCl, Na_2SO_4 and Na_3PO_4) and pH solutions were also systematically investigated.

2. Experimental

2.1. Materials

The monomer, acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. The initiator, ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. The crosslinker, *N*,*N*′-methylenebisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. Unexpanded vermiculite micropowder (UVMT, Longyan Colloidal Co., Ltd., Fujian, China), milled through a 320-mesh screen, with a chemical composition of analytical SiO_2 44.23 wt.%, Al_2O_3 15.10 wt.%, Fe_2O_3 14.26 wt.%, MgO 16.69 wt.%, CaO 4.02 wt.%, TiO_2 0.92 wt.%, MnO 0.13 wt.%, K_2O 3.64 wt.%, Na_2O 0.24 wt.%, and $P_2O_5$0.06 wt.%. Other reagents used were all analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of poly(acrylate)/vermiculite (PAA/UVMT) superabsorbent composites

A series of samples with different amounts of UVMT were prepared by the following procedure. 7.2 g AA was dissolved in 20 mL distilled water and then neutralized at 5 °C with 12 mL of sodium hydroxide solution (5 M) in a four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. UVMT powder (0.8 g) was dispersed in the above partially neutralized monomer solution. Under nitrogen atmosphere, the crosslinker MBA (16.0 mg) was added to the AA–UVMT mixture solution and the mixed solution was stirred on a water bath at room temperature for 30 min. The water bath was then heated slowly to 70 °C with vigorous stirring after the radical initiator APS (80.2 mg) was charged to the mixed solution. The polymerization reaction was carried out at 70 °C for 3 h.

2.3. Measurement of water absorbency

After polymerization, the resulting product was washed several times with distilled water, dried at 70 °C to a constant weight, then milled and screened. All samples used for test had a particle size in the range of 40–80 mesh. The powdered composite was immersed in distilled water or salt solutions at room temperature for at least 4 h to reach swelling equilibrium, which resulted in the absorption of water into the network of the composite and the formation of a hydrogel. Swollen samples were then separated from unabsorbed water by filtering with 100-mesh stainless screen and hanging up for 10 min. The equilibrium-swelling ratio (Q_{H_2O}) was calculated according to following equation:

$$Q_{H_2O} = (m_2 - m_1)/m_1$$

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

The determination of water absorbency at various pH solutions was similar to that of above measurement. Fixed at 0.1 M of total ionic strength, pH values of the external solution were adjusted via addition of 0.1 M HCl, 0.1 M NaOH and 0.1 M NaCl solutions. The effects of various pH solutions on water absorbency can then be achieved.

2.4. Characterization

IR spectra of the superabsorbent composite were recorded on a FTIR (Thermo Nicolet, NEXUS, TM) in the range of 4000–400 cm^{-1}, using KBr pellets. SEM studies were carried out in a JSM-5600LV SEM instrument (JEOL, Ltd.) after coating the sample with gold film using an acceleration voltage of 20 kV. TEM was performed on an instrument of JEM1200EX (Japan). The powdered specimen was placed on the copper grids after sonicating its suspension in ethanol dried for 300 s. XRD patterns were obtained from an X'Pert PRO diffractometer (CuKα radiation, 40 kV, 30 mA). Thermal stability studies were performed on a Perkin–Elmer TGA-7 thermogravimetric analyzer, in the temperature range 25–800 °C at a heating rate of 10 °C/min using dry nitrogen purge at a flow rate of 50 mL/min.

3. Results and discussion

3.1. FTIR

The infrared spectra of UVMT, crosslinked PAA and composite containing 10 wt.% UVMT are shown in Fig. 1. Compared with infrared spectra of pure UVMT and crosslinked PAA, the infrared spectrum of composite containing 10 wt.% UVMT showed a broad band in the wave numbers range from 3700 to 3000 cm^{-1}, as well as the band at 1631 cm^{-1}, both characteristic of molecular water, and this spectrum contained all bands characteristic of crosslinked PAA. However, the absorption bands near 1004 cm^{-1} and 685 cm^{-1} that correspond to stretching vibrations of Si–O bond [22] almost disappeared in the spectrum of composite, suggesting the reactions between $-COO^{-}$ groups and –OH groups on the surface of UVMT micropowder.

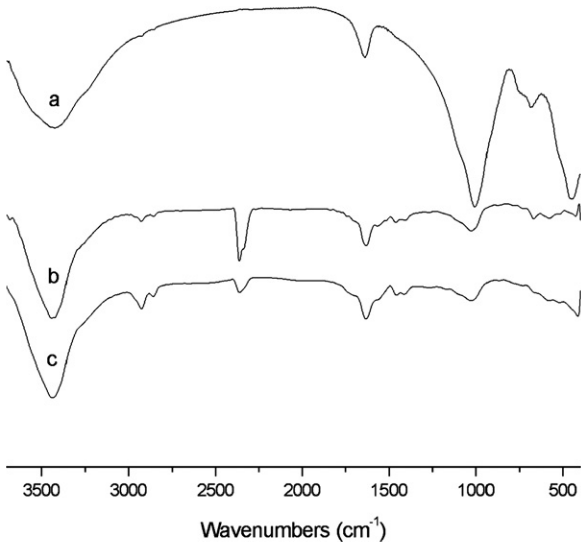

Fig. 1. Infrared spectra of (a) UVMT, (b) crosslinked PAA and (c) composite containing 10 wt.% UVMT.

3.2. Morphology

The micrographs of crosslinked PAA, composites containing 5 wt.% UVMT and 30 wt.% UVMT are depicted in Fig. 2a–c, respectively. It can be observed that crosslinked PAA (Fig. 2a) displays a smooth and tight surface. However, composites containing UVMT (Fig. 2b and c) present an undulant and coarse surface, facilitating the permeation of water into the polymeric network [23]. Moreover, the UVMT micropowders are more finely dispersed in the polymer matrix. Fig. 3 shows a TEM image of composite containing 5 wt.% vermiculite and further proves the characteristic of fine dispersion for UVMT micropowders.

3.3. XRD patterns

Fig. 4 exhibits the XRD patters of pure vermiculite, composites containing 5 wt.% UVMT, 10 wt.% UVMT and 30 wt.% vermiculite, respectively. The XRD pattern of pure UVMT shows a strong peak at $2\theta = 6.17$ which corresponds to a basal spacing of 14.3 Å. After reaction, this peak has almost disappeared, and other diffraction peaks are similar to those of pure UVMT, and 2θ remains unchangeable. Results obtained indicate that UVMT micropowder has been dispersed finely in the polymer matrix [12], and the polymerization reaction is performed on the surface of UVMT micropowder. This is consistent with the results achieved from SEM and TEM.

3.4. TGA analysis

TGA curves of crosslinked PAA (a) and composites containing 5 wt.% UVMT (b) and 30 wt.% UVMT (c) are presented in Fig. 5, respectively. These samples show a similar loss at 25–200 °C, corresponding a loss of water existed in these samples. The major weight loss of crosslinked PAA starts

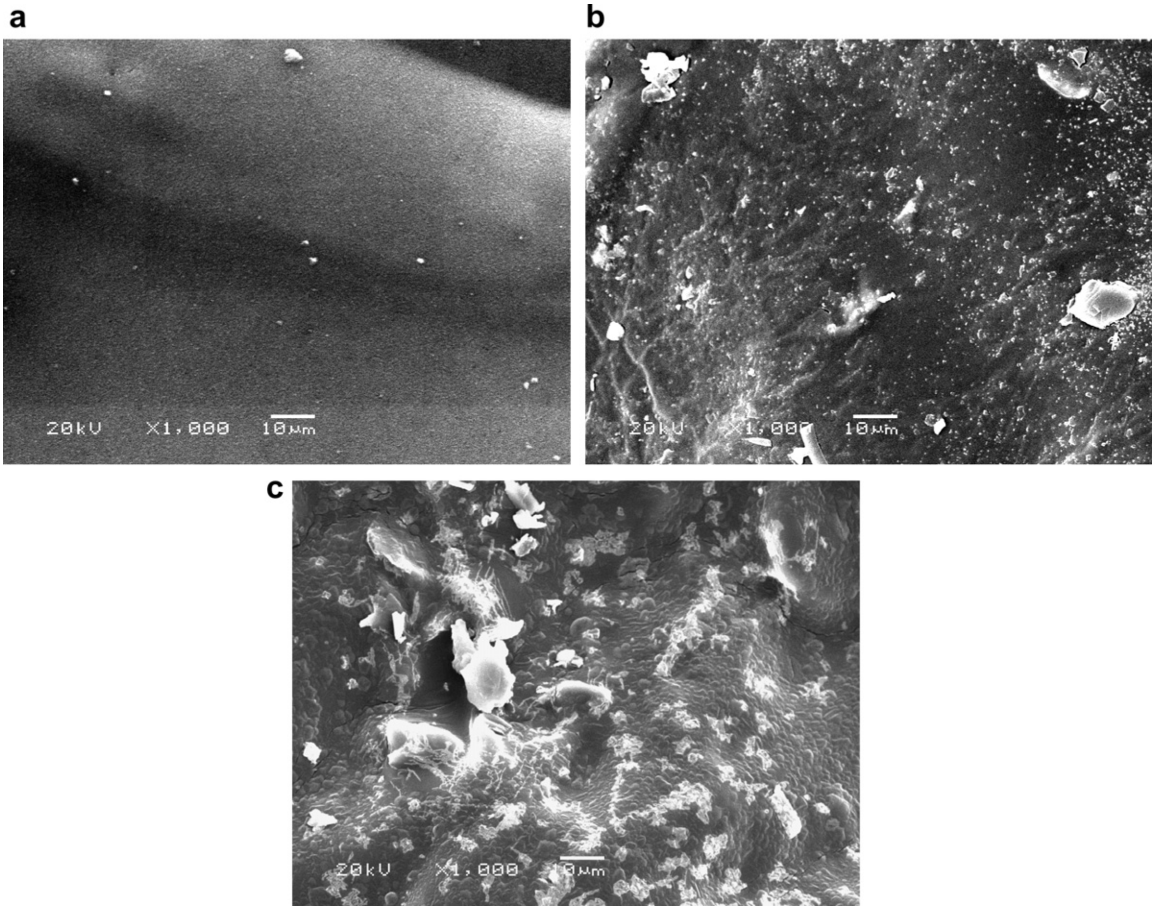

Fig. 2. Scanning electron micrographs for dried superabsorbents: (a) crosslinked PAA, (b) composite containing 5 wt.% UVMT and (c) composite containing 30 wt.% UVMT.

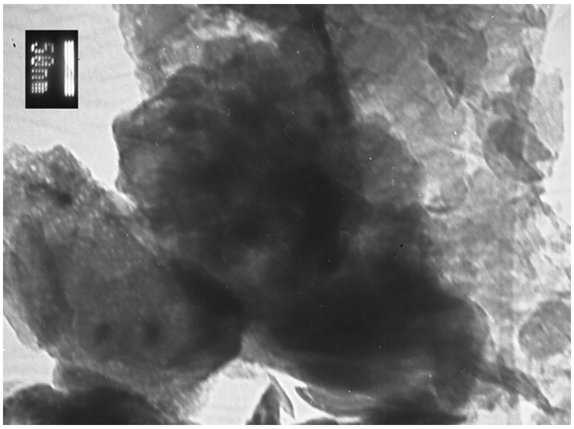

Fig. 3. Transmission electron microscopy for the superabsorbent composite containing 5 wt.% vermiculite.

at 329 °C (22.8%), whereas composite containing 5 wt.% UVMT has a major weight loss starting at 339 °C (31.2%), and composite containing 30 wt.% UVMT exhibits the major weight loss located at 359 °C (48.7%). So, these samples have initial decomposition temperatures of 329 °C, 339 °C and 359 °C, respectively. TGA curves showed a higher onset temperature after the UVMT was incorporated. This may be attributed that the UVMT particles improve the barrier by physically impeding the passage of gases through the matrix, the so-called tortuous path impedance. The enhanced barrier characteristics [24], which benefits from the hindered diffusion pathways through the UVMT particles, will lead to improved thermal stability. In this procedure, UVMT particles can act as the heat barrier. The result is similar to our previous study about attapulgite [19]. Conclusion obtained implies that the incorporation of UVMT is beneficial for the improvement of thermal stability of the composites.

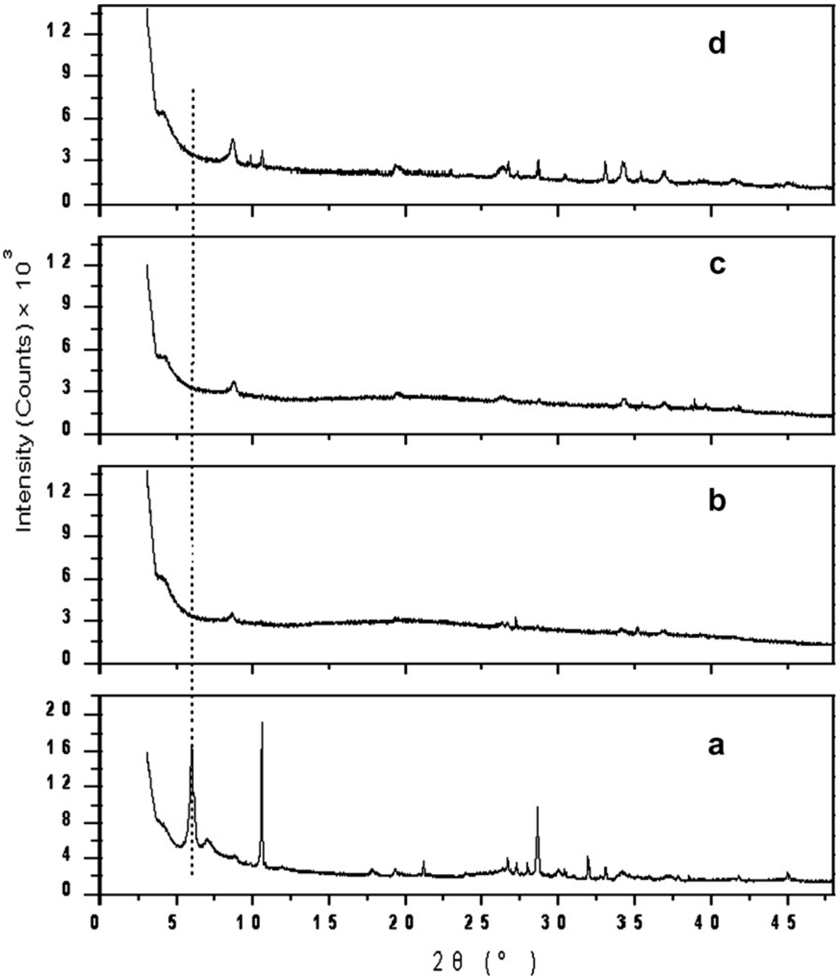

Fig. 4. XRD powder patters for (a) pure UVMT, (b) composite containing 5 wt.% vermiculite, (c) composite containing 10 wt.% vermiculite and (d) composite containing 30 wt.% vermiculite.

3.5. Water absorbency

3.5.1. Effect of UVMT content on equilibrium water absorbency

Water absorbency of the superabsorbent composites incorporated with different amounts of UVMT in distilled water and in 0.9 wt.% NaCl solution is shown in Fig. 6. It is clear that the amount of UVMT micropowder plays an important role in affecting equilibrium water absorbency of the PAA/UVMT superabsorbent composites. The water absorbency increases from 612 g/g to 1232 g/g as the amount of UVMT increases from 0 to 20 wt.%, and further increasing the amount of UVMT decreases the water absorbency. According to a previous study [15], attapulgite can react with AA to improve the polymeric network. In this study, a similar mechanism can be proposed, that is, the reactions between –COO$^-$ groups and –OH groups on the surface of UVMT micropowder can occur, and therefore enhances the water absorbency of the superabsorbent composite as the amount of UVMT increases from 0 to 20 wt.%. In addition, in low UVMT content (<20 wt.%), the cations present in UVMT are easily ionized and dispersed into the polymeric network. This enhances the hydrophilicity of the composites and makes it swell more [25]. The effect of electrostatic interaction on the polymer chains may be also responsible for the increased water absorbency [12]. The decreasing tendency of equilibrium water absorbency with further increasing UVMT content may be attributed to generation of more crosslink points in the polymeric network, inducing an increase in crosslink density of the

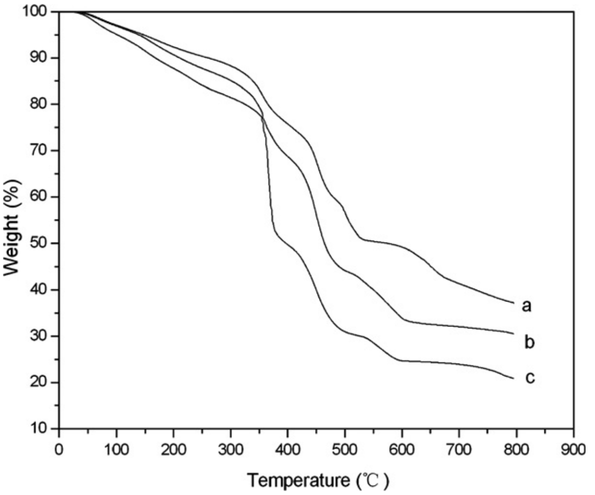

Fig. 5. TGA curves of (a) crosslinked PAA, (b) composite containing 5 wt.% UVMT and (c) composite containing 30 wt.% UVMT.

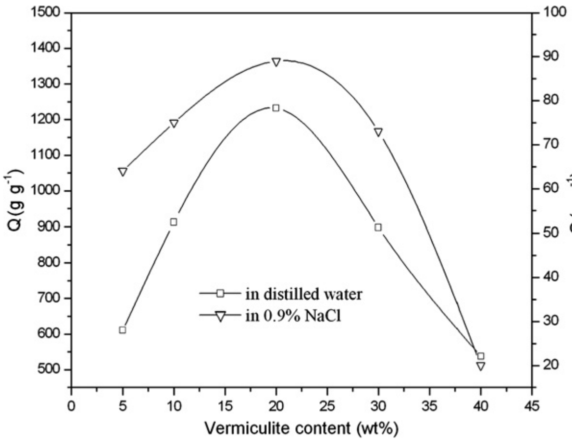

Fig. 6. Effect of UVMT content on water absorbency.

composite, therefore a decrease in the elasticity of the polymer. On the other hand, the water absorbency decreased with increasing UVMT content may be due to the that UVMT particles are partly physically filled in the PAA/UVMT network, the content of hydrophilic groups is lower and the water absorbency thus gradually decreases.

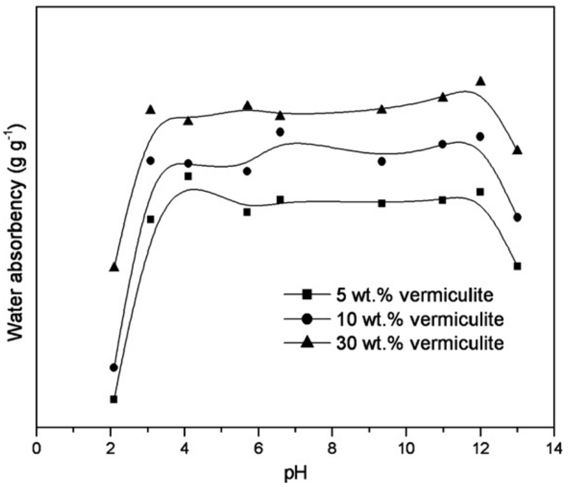

Fig. 7. Effect of various pH solutions on water absorbency.

3.5.2. *Effect of various pH solutions on water absorbency*

Fig. 7 shows the effect of pH values on water absorbency. It can be seen that equilibrium water absorbencies for PAA/UVMT composites keep roughly constant in the pH range from 4 to 12. This behavior was interpreted as a buffer action of –COOH and –COO$^-$ [26]. But when a large amount of acid or base is added, the buffer action of –COOH and –COO$^-$ has disappeared. Fig. 7 also shows that acidic environment has a greater impact on water absorbency than that of basic environment. For the composite containing 10 wt.% UVMT, based on total ionic strength of 0.1 M, water absorbency is lower than 11 g/g when the concentration of H$^+$ is 0.1 M, while it is 65 g/g when the concentration of OH$^-$ is also 0.1 M.

3.5.3. *Effect of various cations on water absorbency*

A typical profile of water absorbency as a function of different ionic strengths for the PAA/UVMT (20 wt.%) in different valence salt solutions [aqueous KCl, $CaCl_2$, and $FeCl_3$] is shown in Fig. 8. The water absorbency decreased as the ionic strength of all three cationic salt solutions increased. The curve of water absorbency for monovalent cationic salt solution was flatter than those for divalent and trivalent cationic salt solution. This is because the divalent calcium ion and trivalent ferric ion would form complexes with the carboxylate group [27]. Hence, the water absorbencies converge to zero for the gels in the divalent and trivalent cationic salt solutions at 0.1 M ionic strength. Moreover, the deswelling of the superabsorbent composite showed different tendencies at various ranges of the ionic strength: $Ca^{2+} < Na^+ < Fe^{3+}$, and $Ca^{2+} < Fe^{3+} < Na^+$ for ionic strengths of lower than 1×10^{-3} M and higher than 1×10^{-3} M, respectively. At a lower ionic strength, the main influence of multivalent cations on the water absorbency was due to the reduc-

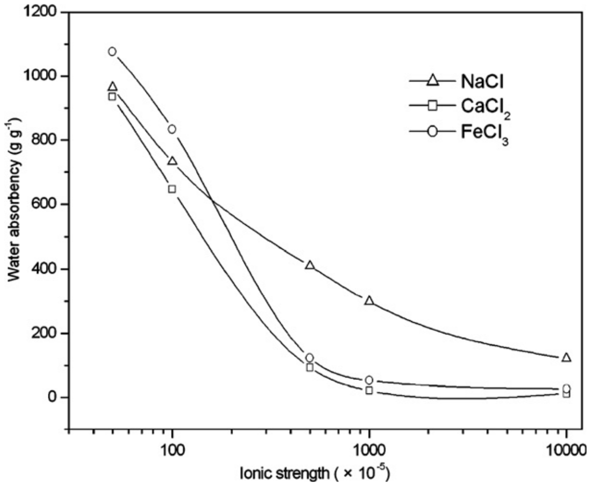

Fig. 8. Water absorbency of composite containing 20 wt.% UVMT in aqueous NaCl, $CaCl_2$ and $FeCl_3$ solutions with various ionic strengths.

tion of osmotic pressure between superabsorbent composite network and external solutions.

3.5.4. *Effect of various anions on water absorbency*

Fig. 9 shows the effects of monovalent, divalent, and trivalent anions with a common cation (Na^+) on the water absorbency of the superabsorbent composite. The water absorbency of the superabsorbent composite showed different tendencies at various ranges of the ionic strength: $PO_4^{3-} < Cl^- < SO_4^{2-}$ and $Cl^- < SO_4^{2-} < PO_4^{3-}$ at ionic strengths of lower than 1×10^{-3} M and higher than 1×10^{-3} M, respectively. These results obtained indicated that the water absorbency of the superabsorbent composite in a trivalent anion (PO_4^{3-}) salt solution was higher than that in monovalent anion (Cl^-) and divalent anion (SO_4^{2-}) salt solutions with the same ionic strength, similar to that of PAA/attapulgite [17].

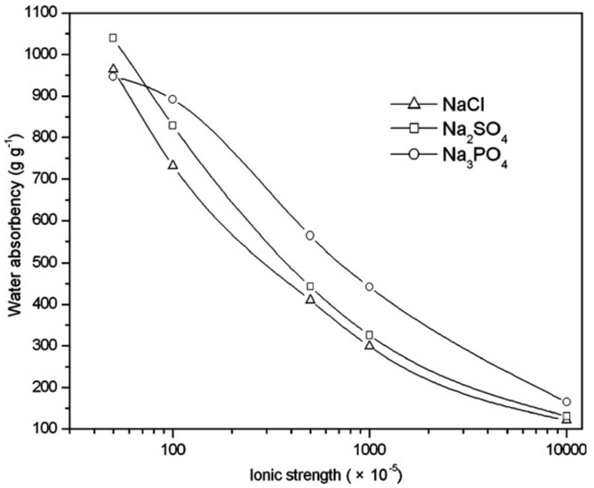

Fig. 9. Water absorbency of composite containing 20 wt.% UVMT in aqueous NaCl, Na_2SO_4 and Na_3PO_4 solutions with various ionic strengths.

4. Conclusions

Equilibrium water absorbency for the PAA/UVMT superabsorbent composite are significantly affected by the content of UVMT and the highest water absorbency is obtained when 20 wt.% UVMT is incorporated. Water absorbency of these composite materials is also significantly dependent on properties of external saline solutions, including valence of ions, ionic strength and pH values. FTIR indicates that the reactions occur between –COO$^-$ groups and –OH groups on the surface of UVMT micropowder. SEM and TEM studies illustrate more finely dispersion of the clay particle in the polymer matrix. In addition, XRD analysis shows that the polymerization reaction is performed on the surface of UVMT and the *d*-space is not changed. TGA implies that introduction of UVMT into the polymer network leads to an increase in thermal stability of the composites.

Acknowledgments

This work was financially supported by the Western Action Project of CAS (No. KGCX2-YW-501) and “863” Project of the Ministry of Science and Technology, PR China (No. 2006AA03Z0454 and 2006AA100215).

References

[1] Buchholz FL, Graham T. Modern superabsorbent polymer technology. New York: Wiley; 1998.
[2] Xu G, Wu GY, Li L. Preparation of water-absorbent resin as synthetic flower-cultivate soil by solution polymerization. Special Petrochem 2002;1:42–4.
[3] Sakiyama T, Chu CH, Fujii T, Yano T. Preparation of a polyelectrolyte complex gel from chitosan and κ-carrageenan and its pH-sensitive swelling. J Appl Polym Sci 1993;50:2021–5.
[4] Shiga T, Hirose Y, Okada A, Kurauchi T. Bending of poly(vinyl alcohol)-poly(sodium acrylate) composite hydrogel in electric fields. J Appl Polym Sci 1992;44:249–53.
[5] Shiga T, Hirose Y, Okada A, Kurauchi T. Bending of ionic polymer gel caused by swelling under sinusoidally varying electric fields. J Appl Polym Sci 1993;47:113–9.

[6] Peppas LB, Harland RS. Absorbent polymer technology. Amsterdam: Elsevier; 1990.

[7] Riccardo P. Water-absorbent polymers: a patent survey. J Macromol Sci Rev Macromol Chem Phys 1994;34:607–62.

[8] Kikuchi A, Okano T. Pulsatile drug release control using hydrogels. Adv Drug Deliver Rev 2002;54:53–77.

[9] Pourjavadi A, Sadeghi M, Hashemi MM, Hosseinzadeh H. Synthesis and absorbency of gelatin-graft-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel with saltand pH-responsiveness properties. E-Polymers 2006;57:1–15.

[10] Yoshinobu M, Morita M, Sakata I. Porous structure and rheological properties of hydrogels of highly water-absorptive cellulose graft copolymers. J Appl Polym Sci 1992; 45: 805–12.

[11] Lokhande HT, Varadarjan PV, Iyer V. Water-superabsorbent polymers through gamma radiation-induced graft-copolymerization of acrylonitrile on guargum. J Appl Polym Sci 1992;45:2031–6.

[12] Santiago F, Mucientes AE, Osorio M, Rivera C. Preparation of composites and nanocomposites based on bentonite and poly(sodium acrylate). Effect of amount of bentonite on the swelling behaviour. Eur Polym J 2007;43:1–9.

[13] Lee WF, Yang LG. Superabsorbent polymeric materials. XIII. Effect of oxyethylene chain length on water absorbency for the sodium acrylate and poly(ethylene glycol) methyl ether acrylate ($PEGMEA_n$) copolymeric gels. J Appl Polym Sci 2006;102:927–34.

[14] Kabiri K, Zohuriaan-Mehr MJ. Superabsorbent hydrogel composites. Polym Adv Technol 2003;14:438–44.

[15] Li A, Wang AQ, Chen JM. Studies on poly(acrylic acid)/attapulgite superabsorbent composite. I. Synthesis and characterization. J Appl Polym Sci 2004;92:1596–603.

[16] Lee WF, Chen YC. Superabsorbent polymeric materials. XIV. Preparation and water absorbency of nanocomposite superabsorbents containing intercalated hydrotalcite. J Appl Polym Sci 2004;94:2417–24.

[17] Li A, Wang AQ, Chen JM. Studies on poly(acrylic acid)/attapulgite superabsorbent composites. II. Swelling behaviors of superabsorbent composites in saline solutions and hydrophilic solvent–water mixtures. J Appl Polym Sci 2004; 94:1869–76.

[18] Lin J, Wu J, Yang Z, Pu M. Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. Macromol Rapid Commun 2001;22:422–4.

[19] Li A, Wang AQ. Synthesis and properties of clay based superabsorbent composite. Eur Polym J 2005;41(7):1630–7.

[20] Li A, Liu RF, Wang AQ. Preparation of starch-graft-poly(acrylamide)/attapulgite superabsorbent composite. Polym Adv Technol 2005;98(3):1351–7.

[21] Zhang JP, Chen H, Wang AQ. Study on superabsorbent composite. III. Swelling behaviors of polyacrylamide/attapulgite composite based on acidified attapulgite and organo-attapulgite. Eur Polym J 2005;41:2434–42.

[22] Tomanec R, Popov S, Vučinič D, Lazič P. Vermiculite from Kopaonik (Yugoslavia) characterization and processing. Fizykochem Problemy Mineral 1997;31:247–54.

[23] Zhang J, Li A, Wang AQ. Study on superabsorbent composite. VI. Preparation, characterization and swelling behaviors of starch phosphate-graft-acrylamide/attapulgite superabsorbent composite. Carbohyd polym 2006;65:150–8.

[24] Tong X, Zhao H, Tang T, Feng Z, Huang B. Preparation and characterization of poly(ethyl acrylate)/bentonite nanocomposites by *in situ* emulsion polymerization. J Polym Sci Part A: Polym Chem 2002;40:1706–11.

[25] Lee WF, Yang LG. Superabsorbent polymeric materials. XII. Effect of montmorillonite on water absorbency for poly(sodium acrylate) and montmorillonite nanocomposite superabsorbents. J Appl Polym Sci 2004;92:3422–9.

[26] Lee WF, Wum RJ. Superabsorbent polymeric materials. 1. Swelling behaviors of crosslinked poly(sodium acrylateco-hydroxyethyl methacrylate) in aqueous salt solution. J Appl Polym Sci 1996;62:1099–114.

[27] Zhang JP, Chen H, Wang AQ. Study on superabsorbent composite. IV. Effects of organification degree of attapulgite on swelling behaviors of polyacrylamide/organo-attapulgite composite. Eur Polym J 2006;42:101–8.