

Journal of Composite Materials

<http://jcm.sagepub.com/>

Synthesis, characterization and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/vermiculite superabsorbent composites

Xiaoning Shi, Wenbo Wang and Aiqin Wang

Journal of Composite Materials 2011 45: 2189 originally published online 6 May 2011

DOI: 10.1177/0021998311401071

The online version of this article can be found at:

<http://jcm.sagepub.com/content/45/21/2189>

Published by:



<http://www.sagepublications.com>

On behalf of:



American Society for Composites

Additional services and information for *Journal of Composite Materials* can be found at:

Email Alerts: <http://jcm.sagepub.com/cgi/alerts>

Subscriptions: <http://jcm.sagepub.com/subscriptions>

Reprints: <http://www.sagepub.com/journalsReprints.nav>

Permissions: <http://www.sagepub.com/journalsPermissions.nav>

Citations: <http://jcm.sagepub.com/content/45/21/2189.refs.html>

>> [Version of Record](#) - Sep 27, 2011

[Proof](#) - May 6, 2011

[What is This?](#)

Synthesis, characterization and swelling behaviors of guar gum-g-poly(sodium acrylate-co-styrene)/vermiculite superabsorbent composites

Xiaoning Shi^{1,2}, Wenbo Wang¹ and Aiqin Wang¹

Abstract

A series of novel superabsorbent composites guar gum-g-poly(sodium acrylate-co-styrene)/vermiculite (GG-g-poly(NaA-co-St)/VMT) were prepared by the simultaneous graft copolymerization of guar gum (GG), partially neutralized acrylic acid (NaA), styrene (St) and vermiculite (VMT) using ammonium persulfate (APS) as the initiator and *N,N'*-methylene-bis-acrylamide (MBA) as the crosslinker. Fourier transform-infrared (FT-IR) and ultraviolet-visible (UV-vis) spectroscopy revealed that NaA and St had been grafted onto GG main-chain, and VMT participated in polymerization reaction. The simultaneous incorporation of St and VMT improved the surface pore structure, and VMT led to a better dispersion in the polymer matrix as shown by field emission scanning electron microscope (FESEM). Swelling results indicated that the inclusion of proper amount of St and VMT in the superabsorbents induced enhanced swelling capability, rate, and salt-resistant performance. Moreover, the composites showed good pH-stability in the solution of various pHs, and exhibited smart swelling-shrinking on-off swelling characteristic in physiological solution, which can be used as promising candidate for its applications in various fields.

Keywords

guar gum, vermiculite, styrene, superabsorbent composite, swelling

Introduction

Superabsorbent polymers (SAPs) are moderately crosslinked hydrophilic network materials that can absorb and retain large quantities of aqueous fluids while preserving their shapes.¹ Because of the unique characteristics, SAPs are extensively applied in various fields, such as agriculture and horticulture,^{2,3} hygienic products as disposable diapers and feminine napkins,⁴ wastewater treatment,^{5–7} bio-medical area as antibacterial materials,⁸ and drug delivery.^{9,10} However, the traditional SAPs are mainly based on fully organic petroleum-based polymers with relatively higher production cost and poor environmental friendly properties.¹¹ Thus, new types of cost-efficient and eco-friendly SAPs derived from naturally available raw materials have long been desired, and the composites of low-cost, renewable, biodegradable, nontoxic, and biocompatible natural polysaccharides with abundant inorganic clays are especially potential^{12–15} because such materials have been honored as the material

families of 'in greening the 21st century materials world'.¹⁶

GG is a hydrophilic, nonionic polysaccharide extracted from the endospermic seed of the plant *Cyamopsis tetragonolobus*. It consists of a linear backbone of β -(1-4)-linked D-mannose units and is solubilized by the presence of randomly attached α -(1-6)-linked galactose units as side chains. GG and its derivatives form valuable ingredients for foods,

¹Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China.

²Graduate University of the Chinese Academy of Sciences, Beijing 100049, P. R. China.

Corresponding author:

Aiqin Wang, Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China
Email: aqwang@licp.cas.cn

cosmetics and pharmaceuticals.¹⁷ GG has better reactivity and can be facilely modified by grafting vinyl monomers onto its backbone to derive new materials with improved structure and performance.¹⁸ Vermiculite (VMT) is a mica-type silicate with a lattice layer structure. Each layer consists of octahedrally coordinated cations (typically Mg, Al, and Fe) sandwiched by tetrahedrally coordinated cations (typically Si and Al). There are reactive –OH groups on the surface of VMT and these groups are accessible to prepare organic–inorganic superabsorbent composites.¹⁹

Recently, it has been observed that introduction of small amount of hydrophobic monomer as co-monomers into hydrophilic superabsorbent network have evidently improved the network structure and swelling properties of the resultant superabsorbent. The proper balance between the hydrophilic and hydrophobic monomers in the copolymer regulates the swelling characteristics of the hydrogel. Many hydrophobic monomers, such as acrylonitrile,²⁰ *N*-butylmethacrylate²¹ and styrene,^{22–25} have been used as co-monomers for the fabrication of hydrogels. Generally, the introduction of tiny amounts of hydrophobic monomer may cause a steric repulsion among hydrophilic network, which decreases the hydrogen bonding interaction between polymeric chains and expands the size of the network pores, and the swelling capacity and swelling rate can be improved.²⁴ It is expected that the superabsorbent composites with improved performance and environmentally friendly properties could be obtained through introducing GG, St, and VMT synchronously.

Based on our previous research on GG-based SAPs,^{14,18,26} in this study, the novel superabsorbent composites guar gum-*g*-poly(sodium acrylate-*co*-styrene)/vermiculite (GG-*g*-poly(NaA-*co*-St)/VMT) were synthesized by introducing St as a hydrophobic comonomer and VMT as an inorganic component. The synchronic effects of St and VMT on the equilibrium swelling capacity and swelling kinetics were mainly investigated. In addition, the swelling behaviors in various media (salt, pH, and hydrophilic solvent) and salt-resistant properties were also evaluated systematically.

Experimental

Materials

GG (food grade, average molecular mass is 220,000) was obtained from Wuhan Tianyuan Biology Corp. (Wuhan, China). Acrylic acid (AA, chemically pure, distilled under reduced pressure before use) and styrene (St, chemically pure, used as received) were supplied by Wulian Chemical Company (Shanghai, China). Ammonium persulfate (APS, analytical pure, used as received) was supplied by Xi'an Chemical Reagent

company (Xi'an, China) and *N,N'*-methylene-*bis*-acrylamide (MBA, chemically pure, used as purchased) was supplied by Shanghai Chemical Reagent Corp. (Shanghai, China). Vermiculite (VMT, Linze, Gansu, China) was milled and passed through a 200-mesh screen prior to use. Other agents used were all of analytical grade and all solution was prepared with distilled water.

Synthesis of GG-*g*-poly(NaA-*co*-St)/VMT superabsorbent composites

The synthesis procedure of GG-*g*-P(NaA-*co*-St)/VMT superabsorbent composites is as following. First, 1.20 g GG powder was dispersed in 34 mL NaOH solution (pH = 12.5) in a 250-mL four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a nitrogen line. Under N₂ purging and continuous stirring, the flask was immersed in an oil bath at 60°C and kept for 1 h to form colloidal slurry. Then, the solution of initiator APS (0.1000 g, 5 mL) was added and the reaction mixture was stirred at 60°C for 10 min to generate radicals. After this, the reactants were cooled to 40°C, and the mixture solution consisting of 7.2 g AA (partially neutralized by 8.5 mL 8 mol/L NaOH solution), 0–0.2000 g St, 0.0216 g MBA and appropriate amount of VMT powder was added. The oil bath was slowly heated to 70°C and kept for 3 h to complete polymerization. Finally, the obtained gel product was washed several times with distilled water and dried in an oven at 70°C for 72 h. The gel product was milled, and passed through a 40–80 mesh (180–380 μm).

Measurements of the equilibrium absorbency and swelling kinetics

Swelling experiments were performed by immersing an accurately weighed sample (m_1) (0.050 ± 0.0001 g, average particle sizes between 180 and 380 μm) of the dry superabsorbent particles into 250 mL distilled water or salt solution for 3 h until the weight of gel reached constant. The swollen gels were filtered by a 100 mesh sieve to remove unabsorbed water, and weighed to obtain the mass of swollen samples as a function of time (m_{2t}).

$$Q_t = (m_{2t} - m_1)/m_1 \quad (1)$$

At equilibrium, $Q_t = Q_{eq}$ (g/g) and $m_{2t} = m_{\infty}$.

Swelling kinetics of the superabsorbents in distilled water was measured as follows: an accurate amount of samples (0.050 ± 0.0001 g) were placed in 500-mL beakers, into which 250 mL of distilled water was then poured. The swollen gels were filtered out using a sieve at given intervals, and the water absorbency of

superabsorbents at a certain moment (Q_t) was measured by weighing the swollen (m_{2t}) and the dry samples (m_1) and was calculated according to Equation (1). In all cases, three parallel samples were used and the averages were reported in this article.

Swelling measurements in various salt solutions and aqueous solution of hydrophilic organic solvents

The swelling behaviors of the superabsorbents in NaCl, CaCl₂, and AlCl₃ solutions of different concentrations and in various solution of ethanol/water and acetone/water was measured by a procedure similar to that in distilled water, and calculated using Equation (1).

Absorbency at various pH solutions

Individual solutions with different pH values were prepared by diluting NaOH (pH=13.0) and HCl (pH=1.0) solutions, respectively. The pH values were precisely checked by a pH-meter (Mettler Toledo, accuracy 6 ± 0.1). Then, 0.050 (± 0.0001) g of the dried samples were used for the swelling measurements and calculated according to Equation (1).

Characterization

FT-IR spectra were recorded on a Nicolet NEXUS FT-IR spectrometer in 4000–400 cm⁻¹ region using KBr pellets. The UV-vis spectra were determined by a UV-vis spectrophotometer (SPECORD 200, Analytik Jera AG), and the samples were fully swollen in distilled water. The surface morphologies of the samples were

examined using a JSM-6701 F Field Emission Scanning Electron Microscope (JEOL) after coating the sample with gold film.

Results and discussion

FT-IR and UV-vis spectra analysis

The FT-IR spectra of (a) GG, (b) VMT, (c) GG-g-PNaA/VMT, (d) GG-g-poly(NaA-co-St), and (e) GG-g-poly(NaA-co-St)/VMT are shown in Figure 1. As can be seen, the characteristic absorption bands of GG (3425 cm⁻¹ for O–H; 1169, 1158, and 1024 cm⁻¹ for C–O) are obviously weakened after reaction. The absorption bands at 1644 and 1431 cm⁻¹ attributed to the O–H bending vibration in the GG, which disappeared after the reaction with NaA. The new bands at 1714, 1726 cm⁻¹ are ascribed to C=O stretching vibration, at 1578–1619 cm⁻¹ and 1409–1455 cm⁻¹ are due to the COO asymmetrical and symmetrical stretching vibration of –COO⁻ groups, respectively (Figure 1(a), (c), (d), (e)). The above information indicates that NaA has been grafted onto the GG chains. It can also be seen from Figure 1 that the (Si) O–H stretching vibration of VMT at 3732 and 3623 cm⁻¹ disappeared after reaction, and the intensity of Si–O absorption bands at 1030 cm⁻¹ also weakened in the spectra of the composites (Figure 1(b), (c), (e)). It confirms that VMT takes part in polymerization reaction by its active silanol groups.^{27,28} In addition, there were no obvious differences for the FT-IR spectra shown in Figure 1(c)–(e) because the characteristic bands of tiny amounts of St was masked by the

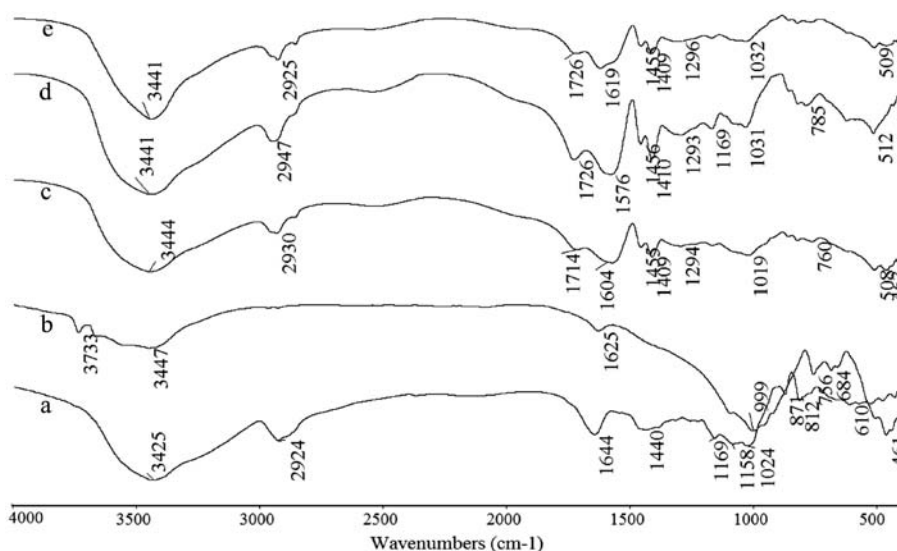


Figure 1. FT-IR spectra of (a) GG, (b) VMT, (c) GG-g-PNaA/VMT, (d) GG-g-poly (NaA-co-St), and (e) GG-g-poly(NaA-co-St)/VMT. The concentration of St in the feed is 24.3 mmol/L, and the VMT content in the feed is 10 wt%.

bulk -COO^- absorption. For proving the existence of St in the synthetic composites, the UV-vis spectra of the swollen superabsorbents can be used. It is obvious that the UV characteristic peak of E band of benzene ring is 263 nm for GG-g-poly (NaA-co-St) and GG-g-poly(NaA-co-St)/VMT ($C_{\text{St}}=24.3$ mmol/L) superabsorbents. However, no UV absorption peaks at 263 nm can be observed in the curves of GG-g-PNaA and GG-g-PNaA/VMT (Figure 2). This gives direct

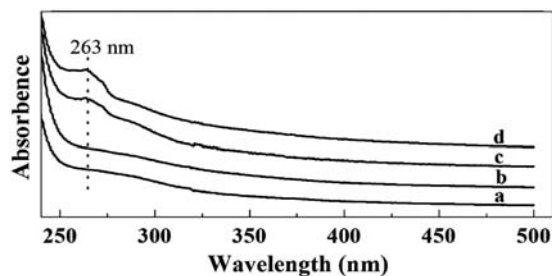


Figure 2. UV-vis spectra of (a) GG-g-PNaA, (b) GG-g-PNaA/VMT, (c, d) GG-g-poly (NaA-co-St)/VMT ($C_{\text{St}}=24.3$ and 38.8 mmol/L, respectively).

evidence that St existed in the polymer network and takes part in graft copolymerization reaction.

Morphological analysis

FESEM micrographs of superabsorbents containing various amounts of St were observed and are shown in Figure 3. It can be observed that GG-g-PNaA/VMT has a leprose and tight surface (Figure 3(a)), but the introduction of St cause a relatively coarse, loose, and pleat surface (Figure 3(b)–(d)). It can also be observed that with increasing the concentration of St, the surface roughness of superabsorbent composites was obviously improved. The composite containing 24.3 mmol/L St showed the best undulant and porous surface (Figure 3(c)). It is supposed that the proper amount of hydrophobic St can improve the surface structure of the hydrophilic polymeric network.²⁵

Effects of St and VMT dosages on equilibrium water absorbency

St and VMT dosages have greater influence on the water absorbency because they participate in

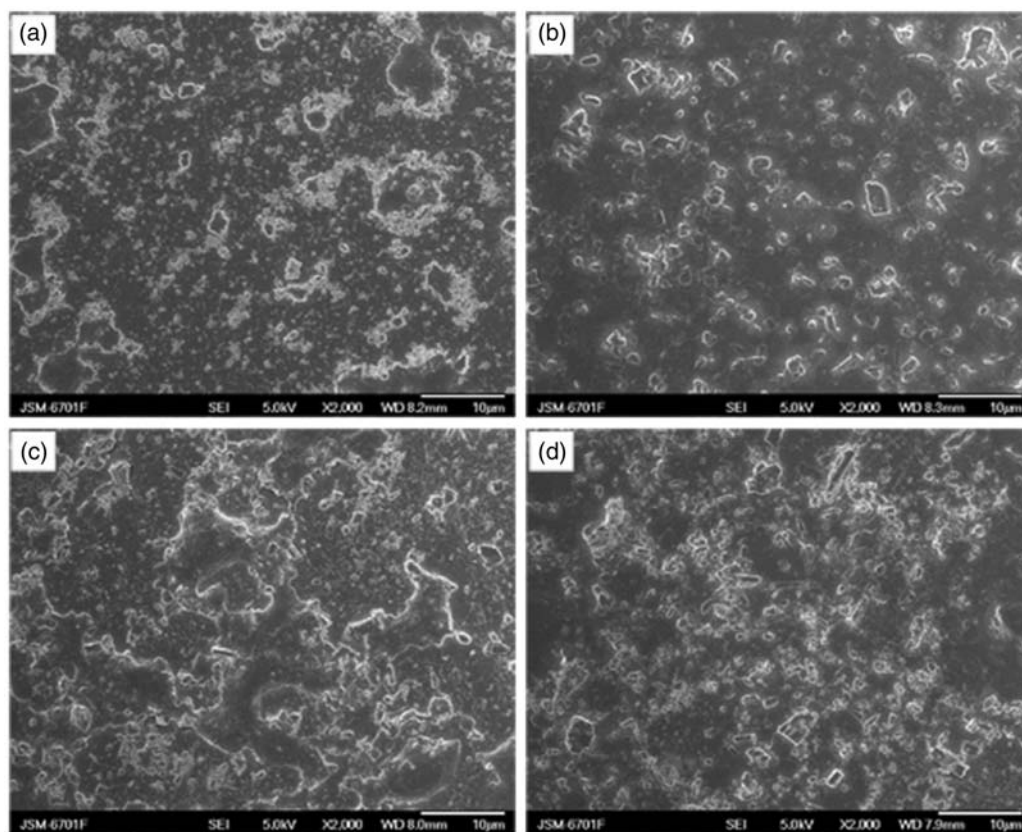


Figure 3. FESEM micrographs of (a) GG-g-PNaA/VMT, (b, c, and d) GG-g-ploy(NaA-co-St)/VMT ($C_{\text{St}}=9.7$, 24.3, and 38.8 mmol/L, respectively).

Table 1. Equilibrium water absorbency and swelling kinetic parameters of the GG-g-P(NaA-co-St)/VMT superabsorbents with various dosages of St and VMT

Samples	Q_{eq} (g/g)	Q_{∞} (g/g)	K_{is} (g/g/s)	$K_s (\times 10^{-5}, \text{g/g/s})$
St, 0 mmol/L; VMT, 0 wt% (A0)	358	363	3.8174	2.8970
St, 0 mmol/L; VMT, 10 wt% (A1)	387	394	4.0761	2.6298
St, 9.7 mmol/L; VMT, 10 wt% (A2)	487	498	4.4140	1.7833
St, 24.3 mmol/L; VMT, 10 wt% (A3)	562	571	6.2751	1.9218
St, 38.8 mmol/L; VMT, 10 wt% (A4)	444	451	5.3830	2.6530
St, 24.3 mmol/L; VMT, 0 wt% (A5)	199	201	3.8342	9.5090
St, 24.3 mmol/L; VMT, 5 wt% (A6)	311	316	4.3674	4.3887
St, 24.3 mmol/L; VMT, 20 wt% (A7)	356	361	3.6638	2.8112

polymerization reaction and affect the composition of superabsorbent. The effects of St and VMT dosages on equilibrium water absorbency are shown in Table 1. As can be seen, the water absorbency drastically increased with increasing St (VMT dosage was fixed at 10 wt%) or VMT dosage (St concentration was fixed at 24.3 mmol/L) until a maximum absorbency was achieved. The great improvement of water absorbency resulting from the introduction of VMT can be attributed to the fact that, (1) the exfoliated inorganic VMT acts as an effective multifunctional cross-linker and improves the polymeric network; (2) the rigid VMT sheets prevent tangle of graft polymer chains and weaken the hydrogen-bonding interaction among hydrophilic groups;²⁶ (3) the existence of rigid VMT in polymer network may restrain the collapse of network during oven-drying, which is responsible for the improvement of water absorbency. It can also be noticed that the enhancement effect on water absorbency caused by the simultaneous introduction of St and VMT is more obvious than introducing their individual one, and the synergistic effect between the hydrophobic monomer St and inorganic VMT can be observed. Similar to VMT, the introduction of St may weaken the hydrogen-bonding interaction among hydrophilic chains because the phenyl group of St cannot participate in hydrogen bonding and decreased intertwining of polymer chains. As a result, the physical crosslinking was broken and the water absorbency was enhanced. Different from the rigid structure of VMT, the hydrophobic polystyrene chain segments is flexible, and so the introduction of St may remedy the defects resulting from rigid VMT and the synergistic effects on decreasing physical crosslinking occurred. However, the excess VMT only acts as filler, which decreases the amount of hydrophilic groups per unit volume of the composite and reduces the osmotic pressure difference between the polymeric network and the external solution. Likewise, excess hydrophobic monomer decreased the hydrophilicity of polymer network

and restricted the formation of 3D hydrophilic network as a polymerization inhibitor. Thus, the excessive addition of St and VMT leads to the decrease of water absorbency.

Effects of St and VMT dosages on swelling kinetics

The swelling of the superabsorbents containing various amount of St and VMT in the distilled water as a function of contact time were measured and are shown in Figure 4. It is clear that the water absorbency sharply increases with prolonging contact time at initial stage, and then it begins to level off and the swelling kinetic curves became flatter, and the equilibrium swelling was achieved within 900 s. In this section, the swelling kinetics of the superabsorbents in distilled water was expressed by the Schott's second-order swelling kinetic model (Equation (2)):²⁹

$$t/Q_t = 1/K_s Q_{\infty}^2 + t/Q_{\infty} \quad (2)$$

where Q_t is the water absorbency at a given time t ; Q_{∞} the theoretical equilibrium water absorbency; and K_s the swelling rate constant; $K_{is} = K_s Q_{\infty}^2$, is the initial swelling rate. On basis of the experimental data, the plots of t/Q_t vs. t give perfect straight lines with good linear correlation coefficient (>0.99 ; Figure 4(b)), indicating that the swelling of the superabsorbent composite obeys the Schott's theoretical swelling model. By fitting experimental data using Equation (2), the swelling kinetic parameters including K_s , Q_{∞} , and K_{is} can be calculated by the slope and intercept of lines (Table 1). It can be noticed that the initial swelling rate constant (K_{is}) of the superabsorbent composite is drastically influenced by St concentration and VMT content. Compared with the GG-g-PNaA hydrogel without St and VMT, the K_{is} values of the superabsorbents have obviously increased due to the introduction of St (VMT content, 10 wt%), and the fastest swelling rate was achieved when the St concentration is 24.3 mmol/L.

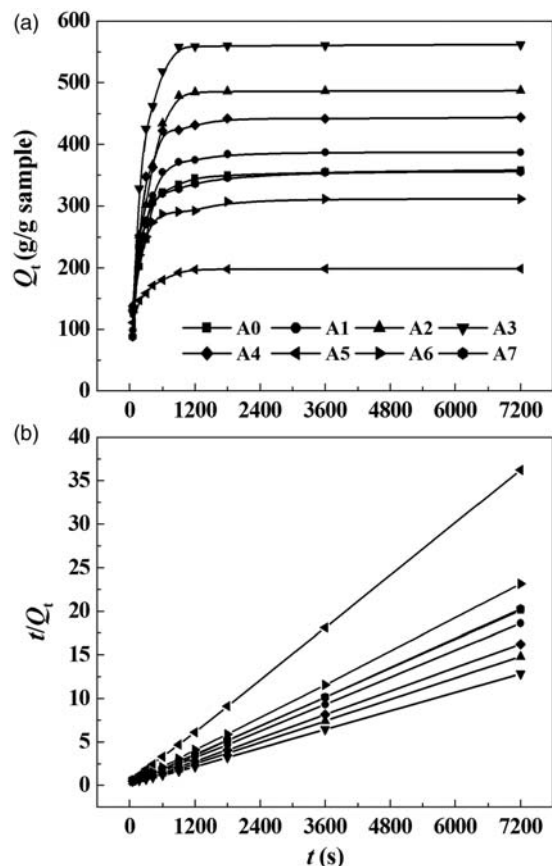


Figure 4. (a) Swelling kinetics curves of GG-g-poly(NaA-co-St)/VMT composites with different St concentration and VMT content in distilled water, and (b) the plots of t/Q_t vs. t .

According to Lee's report,³⁰ the initial swelling rate of a superabsorbent is primarily due to the penetration of water into the polymeric network through diffusion and capillarity. So, the reason for the superabsorbent acquiring a higher initial swelling rate is that voluminous phenyl rings of St in the feed mixture could decrease the hydrogen bonding interaction between polymeric chains and cause the expansion of the hydrogel network. Therefore, the capillarity is evident because the segmental mobility was increased, which accelerates the penetration of water molecules into the polymeric network. However, excess of hydrophobic monomer often lead to the decrease of the hydration degree of gel, the hydrophobicity of the gel dominates the expansion effect of the network, which obviously decreases the swelling rate. Similar phenomenon has been observed in the poly(acrylic acid)/organo-attapulgite composite hydrogels.³¹

As shown in Figure 4, the content of VMT also has greater influence on the swelling ratio of the resultant superabsorbent composites. According to the experimental data listed in Table 1, it can also be noticed

that the initial swelling rate of the superabsorbents with various amounts of VMT is in the order: (St, 24.3 mmol/L; VMT, 10 wt%) > (St, 24.3 mmol/L; VMT, 5 wt%) > (St, 24.3 mmol/L; VMT, 0 wt%) > GG-g-PNaA (St, 0 mmol/L; VMT, 0 wt%) > (St, 24.3 mmol/L; VMT, 20 wt%). This indicates that the simultaneous incorporation of moderate amount of St and VMT contributes to improve the swelling rate.

Effects of salt solution on water absorbency

The swelling capacity of superabsorbents in salt solutions is a key factor in the practical applications. Figure 5 represents the swelling behaviors of the composites with different St concentration in NaCl, CaCl₂, and FeCl₃ solutions at different concentration. The absorbency of each sample is almost equal to that of distilled water at lower salt concentration (0.01 mmol/L); however, the swelling capacity of the composites was significantly decreased with increasing the concentration of external salt solutions (Figure 5). It can be explained on the basis of 'charge screening effect' in salt solution; the additional cations cause a nonperfect anion-anion electrostatic repulsion and result in the decrease of osmotic pressure difference between gel network and the external solution, and so the swelling capacity is drastically reduced. It can also be clearly observed that the swelling capacity of the composite ($C_{St} = 24.3$ mmol/L; VMT content, 10 wt%) is very susceptible to the 'type' and 'concentration' of salt. The water absorbency for the composite in the studied solutions is in the order of monovalent > divalent > trivalent cations, and the decreasing tendency of water absorbents with salt concentration are more obvious in multi-valent salt solution than in mono-valent salt solution. The observed results can be explained as follows: in the case of multi-valent cationic solutions, 'ionic crosslinking' in the superabsorbent network derived from the complexation of hydrophilic groups with multi-valent cations often cause an increase in the crosslinking density of the network, and so the swelling capacity consequently decreases. After introducing moderate amount of St and VMT, the water absorbency of the superabsorbent composite in each salt solution greatly enhanced in contrast to the St or VMT-free sample, indicating that the simultaneous introduction of St could enhance the salt-resistant performance of the superabsorbents. The improvement of water absorbency for GG-g-poly(NaA-co-St)/VMT in salt solutions is because that the hydrophobic phenyl groups can interfere the formation of complexation between $-\text{COO}^-$ groups and multi-valent cations, and consequently decreased the physical crosslinking interaction and the screening effect of cations.

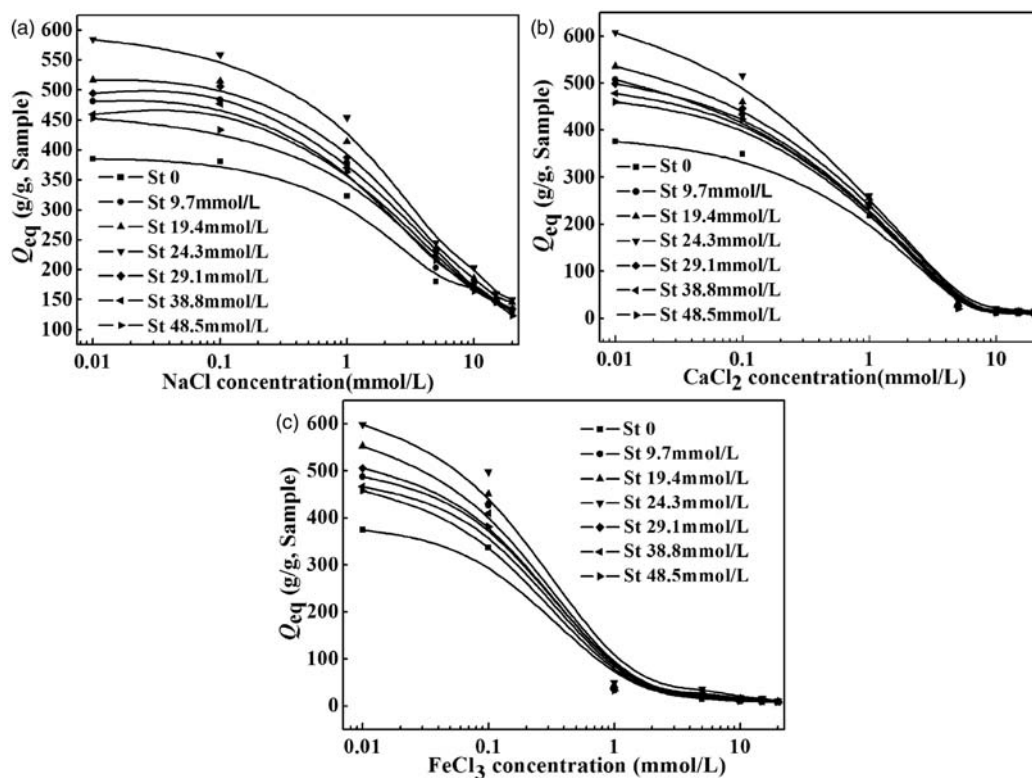


Figure 5. Water absorbency for the composites with different St concentration in NaCl (a), CaCl_2 (b), and FeCl_3 (c) aqueous solutions at various concentration. The VMT content in the feed is 10 wt%.

Salt-responsive behavior of the superabsorbent composite

The swelling–deswelling cycle of the optimized composite was examined by alternately immersing the composite in 0.9 wt% NaCl solution and distilled water at set intervals (Figure 6). In distilled water, the water absorbency of the composite increased with prolonging contact time and the equilibrium swelling was achieved within 30 min. When the swollen composite was transferred in 0.9 wt% NaCl solution, it rapidly deswells and shrinks to a small volume because the incorporation of Na^+ cations decreased the osmotic pressure difference. As the shrunken composite was immersed in fresh distilled water again, some of Na^+ cations come out into the water and the osmotic pressure is increased, and so the gel recovered and the water absorbency is increased subsequently. However, the Na^+ cannot completely transfer from gel network to water, so the swelling capacity gradually decreased in the subsequent several cycles. It can be observed from Figure 6 that the swelling only lost less even after many cycles, and reversible swelling–deswelling behaviors were realized. The evident on–off switching swelling behavior of the composite with altering the external salt solution confirmed the excellent salt-responsive characteristic of the composites.

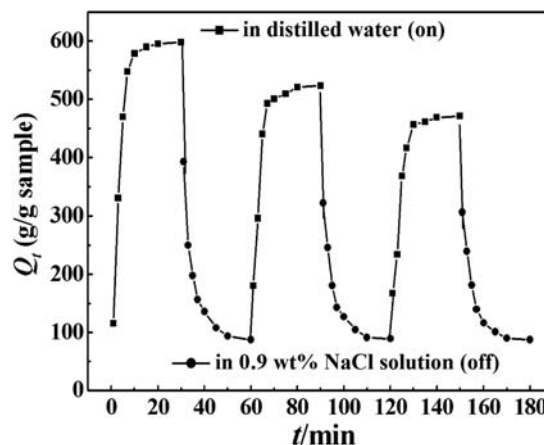


Figure 6. On-off switching swelling behavior as reversible pulsatile swelling (in distilled water) and deswelling (in 0.9 wt% NaCl solution) of the optimized composite.

Effects of various pH solutions on water absorbency

Ionic superabsorbents exhibit swelling changes at a wide range of pH values. In this study, the swelling behavior of the superabsorbents including different St and VMT dosages was studied at various pH solutions ranged from 1.0 to 13.0 (Figure 7). It is clear that the

swelling of all samples increased drastically with the pH value increased from 1 to 4, but decreased when the pH value beyond 10. This can be attributed to the change in the ionic strength of the medium. At low pH (<4), the $-\text{COO}^-$ groups on the polymeric chain turn into $-\text{COOH}$ group (since pKa of AA is 5.4), the main anion-anion electrostatic repulsion are eliminated. Thus, the relaxation of polymer chains was restricted and the expansion of polymer network was reduced, and consequently the water absorbency is lower. When the pH of the solution increased (5–9), some of $-\text{COOH}$ groups are ionized and the electrostatic repulsion among negatively charged $-\text{COO}^-$ groups was increased. This not only increases the osmotic swelling pressure, but also facilitates to the relaxation of polymeric chains. In addition, the hydrogen bonding interactions among the $-\text{COOH}$ groups was partially broken because of the VMT and the hydrophobic St, which widens the mesh size of the network pores and thus enhances the swelling capacity in a wide range of pH values. However, at much higher pH (>10), the ‘charge screening effect’ of excess Na^+ in the swelling medium restricts the net charges of $-\text{COO}^-$ anions and prevents effective anion-anion repulsion. Similar

swelling-pH dependencies could also be observed in other superabsorbent system.¹³

Effects of hydrophilic organic solvents on water absorbency

The influence of the hydrophilic organic solvents on the swelling behavior of the composite was investigated in the mixtures of ethanol, acetone with water and is shown in Figure 8. As can be seen, the water absorbency decreased with increasing the concentration of hydrophilic organic solvents, and two phase transitions could be observed: (1) the minor transition at 10–20 v/v% hydrophilic solvents, resulting from the polymer-polymer affinity; (2) the magnitude transition (the gel collapse), resulting from the interaction between the polar groups in the liquid and the ionic groups in the polymer. Whatever, the decrease of dielectric constant of organic solvents/water mixture is responsible for the lower swelling capacity of the composite, which can be expressed using the Hildebrand Equation (3):³²

$$\Delta H_m / (V\Phi_1\Phi_2) = (\delta_1 - \delta_2)^2 \quad (3)$$

where ΔH_m is the enthalpy change on mixing of a polymer and a solvent, Φ_1 and Φ_2 are the volume fractions for the solvent and the polymer, V is the whole volume of the solution, and δ_1 and δ_2 are the solubility parameters for the solvent and the polymer, respectively. This equation clearly indicates that to dissolve a polymer in a solvent, the δ values must be close to each other. Because the synthesized composite showed maximum absorbency in distilled water, the δ value of distilled water ($23.4 \text{ (cal/cm}^3)^{1/2}$) can be regarded as the solubility parameter of the superabsorbent. So the solubility

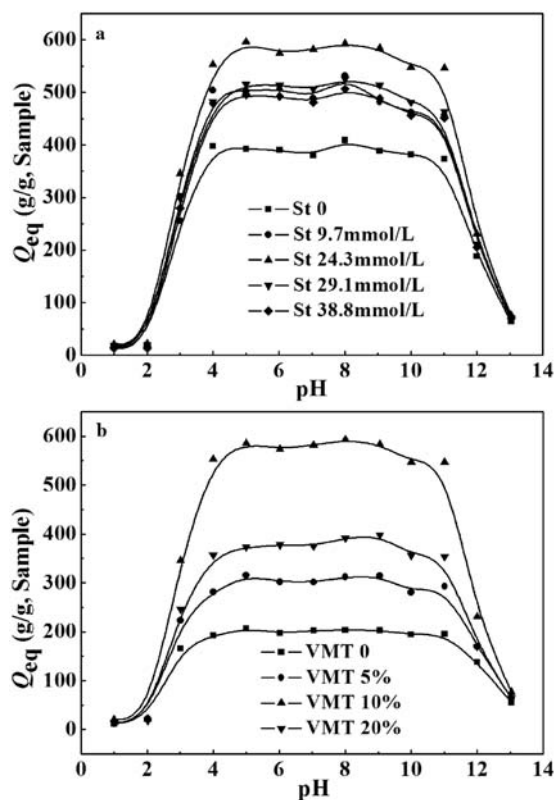


Figure 7. Effect of external pH on water absorbency of the superabsorbents with different St pH concentration (a) and VMT content (b).

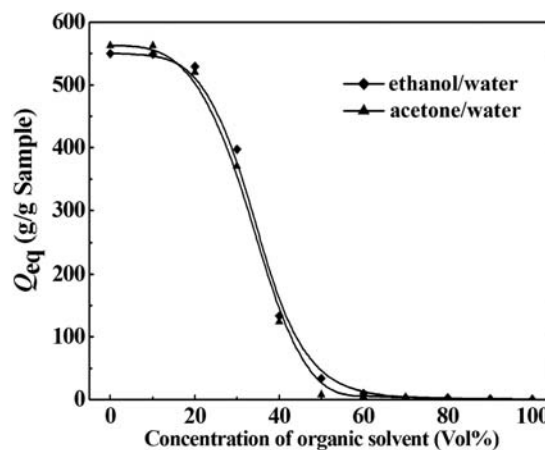


Figure 8. Effect of the concentration of organic solvents on the water absorbency of GG-g-poly(NaA-co-St)/VMT ($C_{St} = 24.3 \text{ mmol/L}$; VMT content = 10 wt%).

Table 2. Solubility parameters for each solution

Solution	δ (or δ_{mix})	Swelling capacity (g/g)
Acetone	9.9	–
Ethanol	12.7	–
Water	23.4	562
Acetone/Water (30/70)	19.35	371
Acetone/Water (70/30)	13.95	3
Ethanol/Water (30/70)	20.19	398
Ethanol/Water (70/30)	15.91	3

Symbols δ and δ_{mix} [(cal/cm³)^{1/2}] are the solubility parameters for the solvent and the solvent–water mixture, respectively.

parameter for solvent–water mixtures (δ_{mix}) may be determined by Equation (4):

$$\delta_{\text{mix}} = \delta_1 \psi_1 + \delta_2 \psi_2 \quad (4)$$

where ψ_1 and ψ_2 are the volume fraction of the two solvents, δ_1 and δ_2 are the solubility parameters. It was noticed that the water absorbency of the composite enhanced with increasing δ_{mix} values to 23.4 (Table 2). This information indicates that the dielectric constant of the solution is main influence factor for the phase transition of the ionic superabsorbents and the collapse of composite network.

Conclusions

As a part of the efforts to reduce the excessive consumption of petroleum resources and the environmental impact resulting from industrial polymers, and to explore the effect of hydrophobic segment in SAPs on the swelling performance of the superabsorbents, the guar gum-*g*-poly(sodium acrylate-*co*-styrene)/vermiculite superabsorbent composites were first synthesized by simultaneously introducing natural GG, VMT clay, and hydrophobic St monomer. FT-IR and UV-vis spectroscopy confirmed that NaA and St had been grafted on to GG mainchain, and VMT participated in polymerization reaction. FESEM observation revealed that the surface structure of the superabsorbent was obviously improved and VMT led to a better dispersion in the polymeric matrix. The St and VMT showed synergistic effects on the water absorbency and swelling rate. The optimum St and VMT dosages in the composite is $C_{\text{St}} = 24.3$ mmol/L and 10 wt%, respectively. The swelling results of the composite with various amounts of St in different salt fluids indicated that the multi-valent salt solution exhibited more remarkable influence on the water absorbency than mono-valent one, and the superabsorbent composite showed excellent on-off switchable swelling characteristic between

distilled water and physiological solution. Swelling measurements of the composites in different pH value solutions and hydrophilic organic solvent solutions indicated that GG-*g*-poly(NaA-*co*-St)/VMT composite had good buffer ability to external pH in the range from 4 to 11, and exhibited clear phase transition in the solution of hydrophilic organic solvent/water. Based on above description, we can conclude that the introduction of suitable amount of hydrophobic St into GG-*g*-PNaA/VMT could not only enhance the swelling capacity of the composites but also improve the swelling rate and salt-resistant ability, which is an effective approach to improve the performance of the superabsorbents.

Acknowledgments

This study was financially supported by '863' Project of the Ministry of Science and Technology, P. R. China [No. 2006AA03Z0454 and 2006AA100215].

References

- Buchholz FL and Peppas NA. *Science and technology: in superabsorbent polymers*. ACS Symposium Series 573, Washington, DC: American Chemical Society, 1994.
- Ni BL, Liu MZ and Lü SY. Multifunctional slow-release urea fertilizer from ethylcellulose and superabsorbent coated formulations. *Chem Eng J* 2009; 155: 892–898.
- Liang R, Yuan HB, Xi GX and Zhou QX. Synthesis of wheat straw-*g*-poly(acrylic acid) superabsorbent composites and release of urea from it. *Carbohydr Polym* 2009; 77: 181–187.
- Kosemund K, Schlatter H, Ochsenhirt JL, Krause EL, Marsman DS and Erasala GN. Safety evaluation of superabsorbent baby diapers. *Regul Toxicol Pharm* 2008; 53: 81–89.
- Chauhan K, Chauhan GS and Ahn J-H. Synthesis and characterization of novel guar gum hydrogels and their use as Cu²⁺ sorbents. *Bioresour Technol* 2009; 100: 3599–3603.
- Kaşgöz H and Durmus A. Dye removal by a novel hydrogel-clay nanocomposite with enhanced swelling properties. *Polym Adv Technol* 2008; 19: 838–845.
- Tang QW, Sun XM, Li QH, Wu JH and Lin JM. Synthesis of polyacrylate/polyethylene glycol interpenetrating network hydrogel and its sorption of heavy-metal ions. *Sci Technol Adv Mater* 2009; 10: 015002 (7p).
- Murthy PSK, Mohan YM, Varaprasad K, Sreedhar B and Raju KM. First successful design of semi-IPN hydrogel–silver nanocomposites: a facile approach for antibacterial application. *J Colloid Interface Sci* 2008; 318: 217–224.
- Sadeghi M and Hosseinzadeh HJ. Synthesis of starch-poly(sodium acrylate-*co*-acrylamide) superabsorbent hydrogel with salt and pH-responsiveness properties as a drug delivery system. *J Bioact Compat Polym* 2008; 23: 381–404.

10. Wang Q, Zhang JP and Wang AQ. Preparation and characterization of a novel pH-sensitive chitosan-g-poly (acrylic acid)/attapulgit/sodium alginate composite hydrogel bead for controlled release of diclofenac sodium. *Carbohydr Polym* 2009; 78: 731–737.
11. Kiatkamjornwong S, Mongkolsawat K and Sonsuk M. Synthesis and property characterization of cassava starch grafted poly[acrylamide-co-(maleic acid)] superabsorbent via γ -irradiation. *Polymer* 2002; 43: 3915–3924.
12. Xie YT and Wang AQ. Effects of modified vermiculite on water absorbency and swelling behavior of chitosan-g-poly(acrylic acid)/vermiculite superabsorbent composite. *J Compos Mater* 2009; 43: 2401–2415.
13. Pourjavadi A, Ghasemzadeh H and Soleyman R. Synthesis, characterization, and swelling behavior of alginate-g-poly(sodium acrylate)/kaolin superabsorbent hydrogel composites. *J Appl Polym Sci* 2007; 105: 2631–2639.
14. Wang WB and Wang AQ. Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite. *Carbohydr Polym* 2009; 77: 891–897.
15. Pourjavadi A and Hosseinzadeh H. Synthesis, characterization and swelling behavior of gelatin-g-poly(sodium acrylate)/kaolin superabsorbent hydrogel composites. *J Compos Mater* 2007; 41: 2057–2069.
16. Ray SS and Bousmina M. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. *Prog Mater Sci* 2005; 50: 962–1079.
17. Wan XF, Li YM, Wang XJ, Chen SL and Gu XY. Synthesis of cationic guar gum-graft-polyacrylamide at low temperature and its flocculating properties. *Eur Polym J* 2007; 43: 3655–3661.
18. Wang WB and Wang AQ. Synthesis and swelling properties of guar gum-g-poly(sodium acrylate)/Na-montmorillonite superabsorbent nanocomposite. *J Compos Mater* 2009; 43: 2805–2819.
19. Zhang K, Xu J, Wang KY, Cheng L, Wang J and Liu B. Preparation and characterization of chitosan nanocomposites with vermiculite of different modification. *Polym Degrad Stab* 2009; 94: 2121–2127.
20. Athawale VD and Lele V. Syntheses and characterisation of graft copolymers of maize starch and methacrylonitrile. *Carbohydr Polym* 2000; 41: 407–416.
21. Lee WF and Yeh YC. Studies on preparation and properties of NIPAAm/hydrophobic monomer copolymeric hydrogel. *Eur Polym J* 2005; 41: 2488–2495.
22. Kennedy JE, Lyons JG, Geever LM and Higginbotham CL. Synthesis and characterisation of styrene butadiene styrene-g-acrylic acid for potential use in biomedical applications. *Mater Sci Eng C* 2009; 29: 1655–1661.
23. Tang C, Ye S and Liu H. Electrospinning of poly(styrene-co-maleic anhydride) (SMA) and water swelling behavior of crosslinked/hydrolyzed SMA hydrogel nanofibers. *Polymer* 2007; 48: 4482–4491.
24. Marandi GB, Hariri S and Mahdavinia GR. Effect of hydrophobic monomer on the synthesis and swelling behaviour of a collagen-graft-poly[(acrylic acid)-co-(sodium acrylate)] hydrogel. *Polym Int* 2009; 58: 227–235.
25. Shukla S, Bajpai AK and Kulkarni RA. Preparation, characterization, and water-sorption study of polyvinyl alcohol based hydrogels with grafted hydrophilic and hydrophobic segments. *J Appl Polym Sci* 2005; 95: 1129–1142.
26. Wang WB, Zhang JP and Wang AQ. Preparation and swelling properties of superabsorbent nanocomposites based on natural guar gum and organo-vermiculite. *Appl Clay Sci* 2009; 46: 21–26.
27. Li A, Wang AQ and Chen JM. Studies on poly(acrylic acid)/attapulgit superabsorbent composite I. Synthesis and characterization. *J Appl Polym Sci* 2004; 92: 1596–1603.
28. Wu JH, Lin JM, Li GQ and Wei CR. Influence of the COOH and COONa groups and crosslink density of poly(acrylic acid)/montmorillonite superabsorbent composite on water absorbency. *Polym Int* 2001; 50(9): 1050–1053.
29. Schott H. Swelling kinetics of polymers. *J Macromol Sci Part B Phys* 1992; 31: 1–9.
30. Lee WF and Wum RJ. Superabsorbent polymeric materials I. Swelling behaviors of crosslinked poly(sodium acrylate-co-hydroxyethyl methacrylate) in aqueous salt solution. *J Appl Polym Sci* 1996; 62: 1099–1114.
31. Zhang JP, Chen H, Li P and Wang AQ. (2006). Study on superabsorbent composite, 14. Preparation of poly (acrylic acid)/organo-attapulgit composite hydrogels and swelling behaviors in aqueous electrolyte solution. *Macromol Mater Eng* 1996; 291: 1529–1538.
32. Kabiri K and Zohuriaan-Mehr MJ. Superabsorbent hydrogel composites. *Polym Adv Technol* 2003; 14: 438–444.