

### You may also like

### Synthesis, characterization and swelling properties of guar gum-g-poly(sodium acrylate-costyrene)/muscovite superabsorbent composites

To cite this article: Wenbo Wang et al 2010 Sci. Technol. Adv. Mater. 11 025006

View the article online for updates and enhancements.

### - Extreme Variability in a Long-duration Gamma-Ray Burst Associated with a <u>Kilonova</u> P. Veres, P. N. Bhat, E. Burns et al.

- The Minimum Variation Timescales of X-Ray Bursts from SGR J1935+2154 Shuo Xiao, Jiao-Jiao Yang, Xi-Hong Luo et al.
- Single-line multi-voltage threshold method for scintillation detectors Hyeyeun Chu, Minseok Yi, Hyeong Seok Shim et al.

Sci. Technol. Adv. Mater. 11 (2010) 025006 (10pp)

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

### Wenbo Wang<sup>1,2</sup>, Yuru Kang<sup>1</sup> and Aiqin Wang<sup>1</sup>

 <sup>1</sup> Center for Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China
<sup>2</sup> Graduate University of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

E-mail: aqwang@licp.cas.cn

Received 27 December 2009 Accepted for publication 24 February 2010 Published 17 May 2010 Online at stacks.iop.org/STAM/11/025006

#### Abstract

A series of novel guar gum-g-poly(sodium acrylate-co-styrene)/muscovite (GG-g-P(NaA-co-St)/MVT) superabsorbent composites were prepared by free-radical grafting copolymerization of natural guar gum (GG), partially neutralized acrylic acid (NaA), styrene (St) and muscovite (MVT) using ammonium persulfate (APS) as the initiator and N,N-methylene-bis-acrylamide (MBA) as the crosslinker. Optical absorption spectra confirmed that NaA and St had been grafted onto the GG main chain and MVT participated in the polymerization reaction. The simultaneous introduction of St and MVT into the GG-g-PNaA matrix could clearly improve the surface morphologies of the composites, and MVT led to better dispersion in the polymeric matrix without agglomeration, as revealed by electron microscopy. The effects of St and MVT on the water absorption and swelling behavior in various saline solutions, aqueous solutions of hydrophilic organic solvents and surfactant solutions were investigated. Results indicated that the swelling rate and capabilities of the composites were markedly enhanced by the incorporation of the hydrophobic monomer St and inorganic MVT clay mineral. The superabsorbent composite showed a clearer deswelling characteristic in solutions of multivalent saline, acetone and ethanol, and cationic surfactant than that in the solutions of multivalent saline, methanol and anionic surfactant.

Keywords: superabsorbent composite, guar gum, styrene, muscovite, synergistic effects, swelling

#### 1. Introduction

The combination of inorganic clay minerals with organic polymers has attracted unwavering attention in academic and industrial fields because the resultant composites frequently exhibit cost-efficient characteristics and excellent hybrid performance superior to their individual components [1–3]. A superabsorbent is a polymer material that can absorb and conserve large volumes of aqueous fluids owing to its unique 3D hydrophilic network, even under pressure.

Because of the advantages over conventional absorbents (e.g. sponge, cotton, towel and colloidal silica), superabsorbents have attracted unwavering attention and found extensive application in various fields, such as agriculture [4, 5], hygienic products [6], wastewater treatment [7, 8], catalyst supports [9] and drug delivery systems [10]. With the increasing importance of resource and environment issues, new types of natural superabsorbents have attracted considerable attention owing to their renewability, nontoxicity, biocompatibility and biodegradability [11, 12];

the organic–inorganic superabsorbent composites, derived from natural polysaccharide and inorganic clay minerals, are representative families of natural superabsorbents [13]. Many natural superabsorbent composites based on starch [14, 15], cellulose [16], chitosan [17, 18], gelatin [19], dextrin [20] and alginate [21] have been developed, and the resultant materials exhibited satisfactory properties and environmentally friendly characteristics.

Guar gum (GG) derived from the seeds of the guar plant *Cyanaposis tetragonolobus* (Leguminosae) is a natural, nonionic, branched polysaccharide with  $\beta$ -D-mannopyranosyl units linked (1–4) with single-membered  $\alpha$ -D-galactopyranosyl units occurring as side branches. GG and its derivatives have been used in many fields, including as thickening agent, ion exchange resin and dispersing agent. Muscovite (MVT) is a general family of 2 : 1 layered silicates consisting of layers of one octahedral sheet sandwiched by two tetrahedral sheets. MVT contains numerous reactive –OH groups on its surface and can easily be incorporated into a pure organic matrix to form a composite [22]. It is expected that new types of superabsorbent with improved network structure and performance can be developed by introducing both GG and MVT.

Recently, it has been found that the introduction of a small amount of hydrophobic monomer as comonomers into a hydrophilic network clearly improves the network structure and swelling properties of the resultant superabsorbent [23, 24]. However, little is known about the enhancement effects of the hydrophobic monomer and clay on the swelling properties of natural polymer-based superabsorbent.

In this work, novel guar gum-g-poly(sodium acrylateco-styrene)/muscovite (GG-g-P(NaA-co-St)/MVT) superabsorbent composites were prepared using natural GG as a matrix, partially neutralized acrylic acid (NaA) and styrene (St) as comonomers and MVT as inorganic component. The enhancement effects of St and MVT on the water absorption of the GG-based superabsorbent were investigated, and the swelling behaviors of the developed composites in various saline solutions, aqueous solutions of hydrophilic organic solvents and surfactant solutions were systematically evaluated.

#### 2. Experimental details

#### 2.1. Materials

GG (food grade, average molecular weight 220 000) was received from Wuhan Tianyuan Biology Co., China. Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Styrene (St, chemically pure) was purchased from Sinopharm Chemical Reagent Co., Ltd (China). Muscovite (MVT, Chenxing Industry Co. Ltd, Shijiazhuang, China) was milled and passed through a 320-mesh screen before use. The Brunauer, Emmett and Teller (BET) specific surface area of MVT is 2.993 m<sup>2</sup> g<sup>-1</sup>. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, China), *N,N'*-methylene-*bis*-acrylamide (MBA, chemically

Table 1. Feed compositions of St and MVT for	
GG-g-P(NaA-co-St)/MVT superabsorbent samples (GG, 1.2)	g
APS, 100.8 mg; MBA, 21.6 mg; AA, 7.2 g).	

Code	$C_{\text{St}} (\text{mmol } l^{-1})$	MVT (g)	Code	$C_{\text{St}} (\text{mmol } l^{-1})$	MVT (g)
GSA0	0	0.45	GSA5	45.14	0.45
GSA1	9.37	0.45	GSA6	21.38	0
GSA2	15.33	0.45	GSA7	21.38	0.95
GSA3	21.38	0.45	GSA8	21.38	1.51
GSA4	30.40	0.45	GSA9	21.38	2.08

pure, Shanghai Chemical Reagent Corp., China), dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulfate (SDS, Beijing Chemical Reagents Company, China) were used as purchased. All the other reagents used were of analytical grade and all the solutions were prepared with distilled water.

# 2.2. Preparation of GG-g-P(NaA-co-St)/MVT superabsorbent composites

GG powder (1.20 g) was dispersed in 34 ml of 0.067 M 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. The dispersion was heated to 60°C in an oil bath and kept for 1 h to form a colloidal slurry. Then, 5 ml of an aqueous solution of the initiator APS (0.1008 g) was added under continuous mechanical stirring and kept at 60 °C for 10 min. Acrylic acid (AA, 7.2 g) was neutralized with 8.5 ml of 8 M NaOH to reach a total neutralization degree of 70% (considering the 34 ml of 0.067 M NaOH solution used to disperse GG). Then, 21.6 mg of crosslinker MBA, calculated amounts of St monomer and MVT powder (see table 1) were added to the neutralized AA solution under magnetic stirring until a homogeneous dispersion was formed. After cooling the reactants to 50 °C, the dispersion was added to the reaction flask, and the temperature was gradually increased to  $70 \,^{\circ}$ C and maintained for 3 h to complete the polymerization. A nitrogen atmosphere was purged throughout the reaction period. The obtained gel products were dried to a constant mass at 70 °C and ground and passed through a 40-80-mesh sieve (180–380 µm).

## 2.3. Measurements of equilibrium water absorption and swelling kinetics

Aqueous solutions of various saline, hydrophilic organic solvents and surfactants were prepared by dissolving calculated amounts of the corresponding solutes in distilled water. Superabsorbent particles (0.05 g, 180–380  $\mu$ m) were soaked in excess of aqueous solutions (200 ml) at room temperature for 4 h to reach swelling equilibrium. The swollen gels were filtered using a mesh sieve, and then drained on the sieve for 10 min to remove excess water. After weighing the swollen superabsorbents, the equilibrium water absorption ( $Q_{eq}$ , g g<sup>-1</sup>) was calculated using the following equation:

$$Q_{\rm eq} = (w_2 - w_1)/w_1. \tag{1}$$



Scheme 1. Proposed mechanism for the formation of GG-g-P(NaA-co-St)/MVT superabsorbent composite network.

Here,  $Q_{eq}$  is the equilibrium water absorption, defined as grams of water per gram of sample;  $w_1$  and  $w_2$  are the sample masses before and after swelling, respectively.

The swelling kinetics of superabsorbents in distilled water was measured as follows: 0.05 g of superabsorbent samples were immersed in 200 ml of distilled water. The swollen gels were filtered through a sieve after 1, 3, 5, 8, 10, 20, 30 or 60 min. The swollen gels were weighed and the water absorption ( $Q_t$ , g g<sup>-1</sup>) at a given moment was calculated using equation (1). All the results were averaged over three samples.

#### 2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded with a Nicolet NEXUS FTIR spectrometer in the 4000–400 cm<sup>-1</sup> range using KBr pellets. The samples were thoroughly washed with 60 vol.% aqueous solution of ethanol, dehydrated with anhydrous ethanol and dried in an oven. UV-visible spectra were recorded with a UV-vis spectrophotometer (SPECORD 200, Analytik Jera AG) using samples fully swollen in distilled water. The surface morphologies of the samples were examined using a field emission scanning electron microscope (FESEM, JSM-6701F, JEOL) after coating the sample with a gold layer. The transmission electron micrographs (TEM) were obtained using a JEM-2010 high-resolution transmission electron microscope (JEOL, Tokyo, Japan) at an acceleration voltage of 200 kV, the sample was ultrasonically dispersed in ethanol before observation.

#### 3. Results and discussion

A superabsorbent network of GG-g-P(NaA-co-St)/MVT composite can be formed by graft copolymerization of St/NaA comonomers onto GG macromolecular chains, followed by the addition of MVT in the presence of APS and MBA (scheme 1). At the initial step, the initiator APS was decomposed under heating to generate a high concentration of sulfate anion radicals. Subsequently, these radicals stripped down the hydrogen from the –OH groups of GG and formed GG macroradicals. These macroradicals can act as the active sites during reaction and can initiate vinyl groups of monomers to process chain propagation. During the chain



Figure 1. FTIR spectra of (a) MVT, (b) GG, (c) GG-g-PNaA,(d) GSA0 and (e) GSA3.

propagation, the crosslinker MBA with double vinyl groups takes part in the polymerization reaction, whereas MVT combined with a polymeric network through its reactive silanol groups, which makes the copolymer form a crosslinked network structure.

#### 3.1. FTIR and UV-vis spectra

Figure 1 shows FTIR spectra of MVT, GG, GG-g-P(NaAco-St), GG-g-PNaA/MVT and GG-g-P(NaA-co-St)/MVT. They reveal that the C-OH characteristic absorption of GG at 1158, 1082 and  $1017 \,\mathrm{cm}^{-1}$  clearly weakened after the reaction, and the new absorption bands at 1713-1718 cm<sup>-1</sup> (C = O asymmetrical stretching vibration of -COOH groups), at 1570–1575 cm<sup>-1</sup> (COO asymmetrical stretching vibration of  $-COO^{-}$  groups) and at 1410–1455 cm<sup>-1</sup> (COO symmetrical stretching vibration of -COO<sup>-</sup> groups) appeared in the spectra of superabsorbents (figures 1(b)-(e)). This indicates that the NaA monomers have been grafted onto the macromolecular chains of GG. The (Si)O-H stretching vibration of MVT at 3623 cm<sup>-1</sup> disappeared after the reaction, and the Si–O absorption bands of MVT at 1028 cm<sup>-1</sup> emerged in the spectrum of the composite with a weakened intensity (figures 1(a), (d) and (e)). This indicates that MVT also takes part in the polymerization reaction via its active silanol groups [25, 26]. However, the characteristic absorption of St cannot be observed owing to the low concentration of St and the overlap of absorption bands. To prove the existence of St, UV-vis spectra of the swollen superabsorbents were recorded and shown in figure 2. UV absorption peaks are absent in the curves of GG-g-PNaA and GG-g-PNaA/MVT, but the characteristic peak of St at 263 nm (E band of benzene ring)



**Figure 2.** UV-vis spectra of (a) GG-*g*-PNaA, (b) GSA0, (c) GSA3 and (d) GSA5.

can be observed in the absorption curves of GSA3 and GSA5. This provides direct evidence that St also takes part in the graft copolymerization reaction and existed in the polymer network.

#### 3.2. Morphological FESEM and TEM analyses

Figure 3 shows the FESEM images of GG-g-PNaA, GG-g-P(NaA-co-St), GG-g-PNaA/MVT and GG-g-P(NaA-co-St)/ MVT composites with various St and MVT dosages. The surface of the GG-g-PNaA superabsorbent hydrogel is smooth and dense (figure 3(a)), whereas the superabsorbents that incorporated various amounts of St and MVT all show a relatively coarse, loose and pleat topography (figures 3(b)–(h)). Introduction of St into GG-g-PNaA resulted in wavy pleats and pores in the hydrogel (figure 3(b)). Incorporation of MVT into the GG-g-PNaA matrix also induced surface roughening (figure 3(c)).



Figure 3. SEM images of (a) GG-g-PNaA, (b) GSA6, (c) GSA0, (d) GSA1, (e) GSA3, (f) GSA5, (g) GSA7 and (h) GSA9.



**Figure 4.** TEM image of GG-*g*-P(NaA-co-St)/MVT superabsorbent composite.

With increasing amount of St in GG-g-P(NaA-co-St)/MVT (5 wt%), the number of pleats and degree of roughness of the composite surface were clearly increased, and some pores can be observed in figures 3(d)–(f). Similarly, the degree of the surface roughness of superabsorbent composites increases with increasing MVT content. The composite containing 10 wt% MVT showed the best wavy and porous surface (figure 3(g)), but it become smoother when the MVT content reached 20 wt% (figure 3(h)). This may be explained by void filling with excessive MVT. This observation also reveals that the MVT is almost embedded within GG-g-P(NaA-co-St) and is uniformly dispersed in the polymer matrix. The fine dispersion of MVT in the polymer network prevents the flocculation of clay particles and results in a homogeneous composition.

Figure 4 shows a TEM image of the GG-*g*-P(NaA*co*-St)/MVT superabsorbent composite, MVT platelets can be observed in the composite, which indicates that MVT led to a better dispersion in the polymeric matrix without flocculation. This observation agrees with the SEM results.

#### 3.3. Effect of St concentration on water absorption

Figure 5 shows the effect of St concentration on water absorption. The water absorption of the composite increased with increasing St concentration until reaching a maximum at  $21.38 \text{ mmol }1^{-1}$ . As a comonomer, St may participate in the copolymerization reaction (monitored via UV-vis spectra). On the one hand, the introduction of St led to the formation of a tiny hydrophobic region in the polymeric network during polymerization, which contributed to the formation of the 3D network. On the other hand, the existence of a hydrophobic moiety in the polymer network might weaken the hydrogen-bonding interaction among hydrophilic chains because the phenyl group of St could not participate in the hydrogen bonding and reduced the degree of intertwisting of polymer chains. As a result, the physical crosslinkage was broken and the water absorption was enhanced. As described



Figure 5. Effect of St concentration on water absorption. The MVT content is 5 wt%.



**Figure 6.** Effect of MVT content on water absorption. The St concentration is  $21.38 \text{ mmol } l^{-1}$ .

previously [27], the introduction of clay may also reduce the tangling of polymer chains and the physical crosslinking. However, clay is rigid and is distributed in the polymer network at nanoscale platelets. Different from this, the hydrophobic polystyrene chain segments are flexible. Thus, the introduction of St might decrease the amount of defects resulting from the rigid MVT, and the synergistic effects on decreasing physical crosslinking occurred. It can also be observed that the excessive addition of styrene decreased the water absorption. This is because the introduction of excess hydrophobic monomer decreased the hydrophilicity of the polymer network and restricted the formation of the 3D hydrophilic network as a polymerization inhibitor. As a result, the water absorption decreased.

#### 3.4. Effect of MVT content on water absorption

MVT content has a greater effect on the water absorption because MVT can participate in the polymerization reaction and affect the composition of the superabsorbent [21, 26, 28, 29]. As shown in figure 6, the water absorption of the composite increased by 54%, as compared with the MVT-free sample, when 5 wt% MVT was introduced. This tendency may be ascribed to the



**Figure 7.** (a) Swelling kinetics curves of the superabsorbents with various amounts of St and MVT and (b) plots of  $t/Q_t$  against t for each superabsorbent.

following reasons: MVT contains a large amount of active silanol groups, which can take part in the polymerization reaction. Thus, the incorporation of rigid MVT weakens the hydrogen-bonding interaction among hydrophilic groups and prevents the tangling of polymer chains and collapse of the gel network. This generates a synergistic effect with St in the gel network decreasing the physical crosslinking degree. As a result, the superabsorbent network was improved and the water absorption was enhanced after incorporating MVT. However, the water absorption gradually decreases with the excessive addition of MVT. This tendency results from the fact that the excess MVT may physically stack in network voids, which decreased the hydrophilicity of the composite, and also plugged up some network voids. As a result, the water absorption was decreased. A similar tendency can also be observed in starch phosphate-graft-acrylamide/attapulgite superabsorbent composite [30].

#### 3.5. Effects of St and MVT doses on swelling kinetics

The effects of St and MVT doses on the kinetic swelling behaviors of the superabsorbents were evaluated and are shown in figure 7(a). The swelling rate of the composite is

**Table 2.** Swelling kinetic parameters of GG-g-P(NaA-co-St)/MVT with various dosages of St and MVT.

Samples	$Q_\infty(\mathrm{g}\mathrm{g}^{-1})$	$K_{\rm is} ({\rm g}{\rm g}^{-1}{\rm s}^{-1})$	R
GSA0	422	4.8828	0.9992
GSA1	476	5.6744	0.9998
GSA3	617	6.1966	0.9996
GSA5	461	2.9788	0.9997
GSA6	380	6.0584	0.9996
GSA7	592	4.2887	0.9997
GSA9	446	2.5239	0.9999

initially high (<900 s) and then decreases until a swelling equilibrium is achieved. The kinetic swelling behaviors of the composites can be evaluated using the Schott's second-order swelling kinetic model [31]:

$$t/Q_t = 1/K_{\rm is} + 1/Q_\infty t.$$
 (2)

Here,  $Q_t$  is the water absorption at a given time t;  $K_{is}$ is the initial swelling rate constant  $(gg^{-1}s^{-1}); Q_{\infty}(gg^{-1})$ is the theoretical equilibrium water absorption  $(gg^{-1})$ . The  $t/Q_t$  versus t plots of experimental data showed straight lines with linear correlation coefficient > 0.99 (figure 7(b)), indicating that Schott's swelling theoretical model is suitable for evaluating the kinetic swelling behavior of the composites. By fitting experimental data with equation (2), the swelling kinetic parameters, including the initial swelling rate constant  $(K_{is})$  and the theoretical equilibrium water absorption  $(Q_{\infty})$ , were calculated from the slope and intercept of the lines shown in figure 7(b) and are listed in table 2. It can be seen that the initial swelling rate constant  $(K_{is})$  of the superabsorbents decreased in the order of GSA3 > GSA6 >GSA1 > GSA0 > GSA7 > GSA5 > GSA9. This tendency indicates that the incorporation of moderate amounts of St and MVT contributes to the improvement of swelling rate of the superabsorbent.

#### 3.6. Effects of saline solution on water absorption

The swelling properties of superabsorbent in saline media are particularly significant to its practical application. In this section, the effects of saline on the water absorption of the superabsorbent composite are evaluated in the solution with different cations (Na<sup>+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup>) and common anion (Cl<sup>-</sup>) (figure 8). The water absorption decreased with increasing concentration of saline solution, and the decreasing trend is clearer in Mg<sup>2+</sup> and Al<sup>3+</sup> solutions than in the Na<sup>+</sup> saline solution. The water absorption is almost zero in 10 mmol l<sup>-1</sup> MgCl<sub>2</sub> and AlCl<sub>3</sub> solutions, but the absorption reached  $159 g g^{-1}$  in the 10 mmol l<sup>-1</sup> NaCl solution. This is because the deswelling of ionic superabsorbents to monovalent saline (e.g. Na<sup>+</sup> and K<sup>+</sup>) is mainly attributed to the reduction of the osmotic pressure difference between the internal gel networks and the external saline-containing medium, as well as the screening effect of cations on the negative charges of polymer chains [32]. In MgCl<sub>2</sub> and AlCl<sub>3</sub> solutions, the complexation interaction between ionic hydrophilic groups and Mg<sup>2+</sup> and Al<sup>3+</sup> occurred, and the



Figure 8. Effect of various saline solutions on water absorption of superabsorbent composite.

additional crosslinking was induced. Besides the decrease in the osmotic pressure difference and the increase in the screening effect, the additional crosslinking leads to a significant deswelling of the superabsorbent composition in the multivalent saline solution, and thus, the water absorption of the superabsorbents was markedly decreased in the MgCl<sub>2</sub> and AlCl<sub>3</sub> solutions.

# 3.7. Effects of hydrophilic organic solvents on water absorption

Phase transitions of hydrogels attracted attention after the collapse of polyacrylamide hydrogels in an aqueous solution of acetone was reported by Tanaka in 1978 [33, 34]. In this section, we describe the effect of hydrophilic organic solvents (methanol, ethanol and acetone) on the swelling behaviors of GG-g-P(NaA-co-St)/MVT superabsorbent composite. Figure 9(a) reveals that the water absorption decreased with increasing concentration of hydrophilic organic solvents until the swelling was close to zero; the decreasing trend was changed in the order of acetone>ethanol> methanol. At low concentrations (<20%, v/v), hydrophilic organic solvents have only a small effect on water absorption, but the clear deswelling was generated with increasing concentration of organic solvents. This tendency is ascribed to the change in the solubility parameter  $(\delta)$  of swelling media resulting from the addition of hydrophilic organic solvents. Water has the largest  $\delta$  value  $(23.2 \,(\text{cal cm}^{-3})^{1/2})$  among the common solvents for polymers, and so the superabsorbent has the highest absorption in water. After adding methanol  $(\delta = 14.5 \text{ (cal cm}^{-3})^{1/2})$ , ethanol  $(\delta = 12.7 \text{ (cal cm}^{-3})^{1/2})$  or acetone  $(\delta = 10.0 \,(\text{cal cm}^{-3})^{1/2})$  to water, the solubility parameter of the mixing solution ( $\delta_{\varphi}$ ) can be expressed as [35, 36]

$$\delta_{\varphi} = 23.2 \left(1 - \varphi\right) + \varphi \delta_{i}. \tag{3}$$

Here,  $\varphi$  is the volume fraction for the hydrophilic organic solvents and  $\delta_i$  is the solubility parameter for hydrophilic organic solvents. It can be calculated using equation (3) that  $\delta_{20}$  for each mixture solution is close to the  $\delta$  value



**Figure 9.** (a) Effect of hydrophilic organic solvents on water absorption of superabsorbent composite. (b) Dependence of solubility parameter ( $\delta$ ) on the concentration of hydrophilic organic solvents.

of water, and so the water absorption decreased slightly at the concentration below 20% (v/v). As shown in figure 9(b), the  $\delta$  values decreased in the order of acetone > ethanol > methanol at each concentration, which is in accordance with the order of water absorption. This indicates that the solubility parameter  $\delta$  is a key factor affecting the water absorption. The phase transition region is in the range of 30-70% (v/v) for methanol and 20-50% (v/v) for ethanol and acetone. The decrease in water absorption at low concentration is attributed to the polymer-polymer affinity, which leads to the extraction of free liquid out of the swollen hydrogel. The decrease in water absorption in the second stage is due to the interaction between the polar groups of the organic solvent and the ionic groups in the polymer and due to the rapid decrease in the solubility parameter of organic solvent/water mixture [37, 38]. The collapse of the hydrogel is a result of the total depletion of water owing to the competitive extraction of water from the solvated polymeric network. The polarities of methanol, ethanol, and acetone are 6.6, 4.3 and 5.4, respectively. Ethanol has lower polarity than methanol, and so the required concentration for the collapse of the composite network in ethanol solution is lower than that in the methanol aqueous solution. However, the composite collapses



Figure 10. Effect of surfactant solutions on water absorption of superabsorbent composite.

more rapidly in the acetone solution than in the ethanol and methanol solutions even if acetone has a higher polarity than ethanol. This is because ethanol interacts more easily with the ionizable groups (-COOH or  $-COO^-$ ) in the superabsorbents. This information indicates that the dielectric constant, polarity and structure of organic solvents are the main factors affecting the phase transition of superabsorbents.

#### 3.8. Effects of surfactant solutions on water absorption

Besides the saline solution, ionic surfactants have a considerable effect on the swelling behavior of superabsorbents. To evaluate this, the equilibrium water absorption of the composite in SDS and DTAB solutions was determined and is shown in figure 10. It reveals that the water absorption of the composite decreased with increasing surfactant concentration, but the decreasing trend is more clear in the DTAB solution than in the SDS solution. The water absorption is almost equal to zero in the DTAB solution but reaches  $191 \text{ g g}^{-1}$  in the SDS solution at  $10 \text{ mmol l}^{-1}$ , which indicates that the water absorption is mainly dependent on the charge and concentration of the surfactant. As an anionic superabsorbent composite, the negatively charged -COO<sup>-</sup> groups form a strong association, binding or interaction with positively charged DTAB molecules, and the -COOH groups may also form a strong hydrogen bond with the quaternary ammonium cations of DTAB. In addition, the surfactant molecules may aggregate within or over the networks of composites, which can markedly decrease the hydrophilicity of the polymer network and reduce the water absorption [39]. These factors are responsible for the rapidly decreasing rate and lower swelling capacity of the composite in the DTAB solution. In the anionic surfactant SDS, the negatively charged -COO<sup>-</sup> groups strongly repulse the anions of the polymeric chains, and thus, the SDS molecules barely enter the network of the superabsorbent composite. As a result, the composite showed a comparatively higher water absorption in the anionic surfactant solution than in the cationic surfactant solution.

#### 4. Conclusions

In efforts to reduce the consumption of petroleum products and the environmental impact resulting from industrial polymers and to extend the application of superabsorbents, new types of superabsorbent composite with enhanced water absorption by the simultaneous introduction of St and MVT were prepared using natural GG, NaA, St and MVT as raw materials. FTIR and SEM revealed that the St and NaA comonomers have been grafted onto the GG backbone, and the surface morphologies of the composite were clearly improved owing to the incorporation of St and MVT. The anticipated enhancement effects of St and MVT on the water absorption were observed. The composite containing  $21.38 \text{ mmol } 1^{-1}$  St and 5 wt% MVT shows the best absorption of 598 g g<sup>-1</sup> in distilled water and 59 g g<sup>-1</sup> in 0.9 wt% NaCl solution. Moreover, the swelling rate of the composites was markedly improved after incorporating St and MVT. The superabsorbent composite exhibited interesting deswelling behaviors in various saline solutions, aqueous solutions of hydrophilic organic solvents and surfactants, and the deswelling trend is more clear in multivalent cationic saline solution, acetone and cationic surfactant DTAB solutions than in other solutions. Therefore, the superabsorbent composites based on renewable and biodegradable GG and abundant MVT showed enhanced swelling capability, swelling rate and excellent swelling properties in various saline, organic solvent and surfactant solutions, which can be used as potential water-manageable materials and as a candidate for petroleum-based synthetic absorbents.

#### Acknowledgments

The authors are grateful to the National Natural Science Foundation of China (No. 20877077) and '863' Project of the Ministry of Science and Technology, P. R. China (Nos 2006AA03Z0454 and 2006AA100215) for financial support.

#### References

- [1] Ray S S and Okamoto M 2003 Prog. Polym. Sci. 28 1539
- [2] Utracki L A, Sepehr M and Boccaleri E 2007 Polym. Adv. Technol. 18 1
- [3] Liu P 2007 Appl. Clay Sci. 38 64
- [4] Teodorescu M, Lungu A, Stanescu P O and Neamtu C 2009 Ind. Eng. Chem. Res. 48 6527
- [5] Karadağ E, Saraydin D, Çaldiran Y and Güven O 2000 Polym. Adv. Technol. 11 59
- [6] Kosemund K, Schlatter H, Ochsenhirt J L, Krause E L, Marsman D S and Erasala G N 2008 *Regul. Toxicol. Pharm.* 53 81
- [7] Kaşgöz H, Durmus A and Kaşgöz A 2008 Polym. Adv. Technol. 19 213
- [8] Tang Q W, Sun X M, Li Q H, Wu J H and Lin J M 2009 Sci. Technol. Adv. Mater. 10 015002
- [9] Tang Q W, Lin J M, Wu J H and Huang M L 2007 Eur. Polym. J. 43 2214
- [10] Wang Q, Zhang J P and Wang A Q 2009 Carbohydr. Polym. 78 731
- [11] Kiatkamjornwong S, Mongkolsawat K and Sonsuk M 2002 Polymer 43 3915

- [12] Pourjavadi A, Barzegar Sh and Mahdavinia G R 2006 Carbohydr. Polym. 66 386
- [13] Wang A Q and Zhang J P 2006 Organic–Inorganic Superabsorbent Composites (Beijing: Science Press)
- [14] Li A, Zhang J P and Wang A Q 2007 Bioresour. Technol. 98 327
- [15] Luo W, Zhang W A, Chen P and Fang Y E 2005 J. Appl. Polym. Sci. 96 1341
- [16] Pourjavadi A and Mahdavinia G R 2006 Polym. Polym. Compos. 14 701
- [17] Xie Y T and Wang A Q 2009 J. Compos. Mater. 43 2401
- [18] Zhang J P, Wang Q and Wang A Q 2007 Carbohydr. Polym. 68 367
- [19] Pourjavadi A, Hosseinzadeh H and Sadeghi M 2007 J. Compos. Mater. 41 2057
- [20] Ding X, Li L, Liu P S, Zhang J, Zhou N L, Lu S, Wei S H and Shen J 2009 Polym. Compos. 30 976
- [21] Pourjavadi A, Ghasemzadeh H and Soleyman R 2007 J. Appl. Polym. Sci. 105 2631
- [22] Gridi-Bennadji F, Beneu B, Laval J P and Blanchart P 2008 Appl. Clay Sci. 38 259
- [23] Bajpai A K and Shrivastava M 2002 J. Appl. Polym. Sci. 85 1419
- [24] Marandi G B, Hariria S and Mahdaviniac G R 2009 Polym. Int. 58 227

- [25] Li A, Wang A Q and Chen J M 2004 J. Appl. Polym. Sci. 92 1596
- [26] Wu J H, Lin J M, Li G Q and Wei C R 2001 *Polym. Int.* 50 1050
- [27] Wang W B, Zhang J P and Wang A Q 2009 Appl. Clay Sci. 46 21
- [28] Xie Y T and Wang A Q 2010 Iran . Polym. J. 19 131
- [29] Foungfung D, Phattanarudee S, Seetapan N and Kiatkamjornwong S 2010 Polym. Adv. Technol. at press, doi: 10.1002/pat.1559
- [30] Zhang J P, Li A and Wang A Q 2006 Carbohydr. Polym. 65 150
- [31] Schott H 1992 J. Macromol. Sci. B 31 1
- [32] Lee W F and Wu R J 1996 J. Appl. Polym. Sci. 62 1099
- [33] Tanaka T 1978 Phys. Rev. Lett. 40 820
- [34] Tanaka T 1979 Polymer 20 1404
- [35] Chen J W and Shen J R 2000 J. Appl. Polym. Sci. 75 1331
- [36] Kabiri K, Zohuriaan-Mehr M J, Mirzadeh H and Kheirabadi M 2010 J. Polym. Res. 17 203
- [37] Rodehed C and Ranby B 1986 Polymer 27 313
- [38] Liu Y, Xie J J, Zhu M F and Zhang X Y 2004 Macromol. Mater. Eng. 289 1074
- [39] Mohan Y M, Premkumar T, Joseph D K and Geckeler K E 2007 React. Funct. Polym. 67 844