



Preparation and Swelling Behaviour of Chitosan-*g*-poly(acrylic acid)/Muscovite Superabsorbent Composites

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ABSTRACT

A series of novel chitosan-*g*-poly(acrylic acid)/muscovite (CTS-*g*-PAA/MVT) granular superabsorbent composites were synthesized by free-radical graft polymerization in aqueous solution. The effects of different ion-exchanged MVT on equilibrium water absorbency, swelling rate and swelling behaviour in various cationic saline solutions and different pH solutions of superabsorbent composites were systematically investigated under the same preparation conditions. The superabsorbents doped with different ion-exchanged MVT were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray fluorescence spectrometry (XRF) and scanning electron microscopy (SEM). FTIR spectroscopy confirmed that AA has been grafted onto CTS and -OH groups of MVT seem to have participated in this reaction, simultaneously. These composites show good dispersion and favourable compatibility of inorganic and organic phases observed in SEM photographs. The introduction of ion-exchanged MVT into chitosan-*g*-poly(acrylic acid) polymeric network could improve water absorbency and swelling rate compared to those of the MVT. It is found that the swelling behaviour of these composites depends on the concentrations of NaCl, CaCl₂, and FeCl₃ solutions; as by increasing the concentration from 0.01 to 10 mM leads to gradual decrease in the swelling rates. All prepared composite samples demonstrate similar swelling behaviour at different pH, while the equilibrium water absorbency of the samples is kept roughly constant in pH range 4-10.

Key Words:

superabsorbent composite;
ion-exchanged muscovite;
graft copolymerization;
swelling behaviour;
water absorbency.

INTRODUCTION

Superabsorbent polymers are weakly cross-link functional polymeric materials with strong hydrophilic groups, which can absorb a large amount of water during a short time and the absorbed water is hardly removable even under pressure [1]. Owing to their excellent properties, superabsorbents have great advantages over traditional water-absorbing materials such as cotton, pulp, and sponge. They have found a variety

of valuable applications, such as healthcare products, agriculture and horticulture, wastewater treatment, as matrixes for drug-delivery systems and other numerous applications [2,3]. Recently, research on the use of superabsorbents as water managing materials for the renewal of arid and desert environment has attracted great attention. Some encouraging results have been observed as they can reduce water

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consumption for irrigation, improve fertilizer retention in soil, lower the mortality rate of plants, and increase plant growth rate [4]. With further development of superabsorbents, material researchers have realized that the swelling ability, gel strength, and thermal stability of superabsorbents could be improved and their production cost would be reduced simultaneously by using some inorganic particles as additives. Thus, many types of inorganic clay, such as kaolin [5], mica [6], attapulgite [7], vermiculite [8], bentonite [9], sepiolite [10], diatomite [11] and rectorite [12] have been introduced into the polymeric networks of poly(acrylic acid) and polyacrylamide, to form organic-inorganic composites.

Muscovite (MVT) belongs to the general family of 2:1 layered silicates. There are reactive -OH groups on the surface of MVT and these groups are accessible to prepare organic-inorganic superabsorbent composites. The structure of MVT consists of the layers of one octahedral sheet sandwiched between two tetrahedral sheets. Due to substitutions in the central positions of the octahedron and tetrahedron sheets, these layers have negative charges around one, which are compensated mostly by large monovalent cations like potassium or sodium [13]. Therefore, the physicochemical properties of MVT could be determined by ion exchange treatment reaction as the changes in the structure and physicochemical properties of MVT play an important role in the performance of corresponding superabsorbent composite.

However, most of the superabsorbents are synthetic polymers, based on acrylic acid and acrylamide which for agricultural and horticultural applications show poor degradability. Thus, the extensive attention has been directed towards superabsorbent polymers being prepared through graft copolymerization of vinyl monomers onto the chain of such natural polymers as starch [14], cellulose [15], chitosan [16], etc. Chitosan (CTS), the most abundant natural aminopolysaccharide with specific structure and properties, has abundant hydroxyl and highly reactive amino groups distributed on its chains which allow it to be easily modified through various chemical modifications. Grafted copolymerization of hydrophilic vinyl monomers onto CTS is considered to be an efficient

approach to prepare superabsorbents [17].

Based on our recent work, in which superabsorbent composites were produced by modified attapulgite [18], montmorillonite [19] and sepiolite [20] doped with poly(acrylic acid), in the present work, however, some novel chitosan-based superabsorbent composites were introduced which were synthesized with different ion-exchanged MVT specimens. The effects of MVTs on equilibrium water absorbency, swelling rate, swelling behaviour in various cationic saline solutions (NaCl, CaCl₂, and FeCl₃) and different pH solutions of superabsorbent composites were systematically investigated and compared with those of non-modified MVT. The results suggested that the introduction of suitable amount of ion-exchanged MVT to CTS-g-PAA improved swelling behaviour of these composites. This work not only provided an approach for granular chitosan-based superabsorbent composite it also helped into study of the influence of clay modification on the swelling performance of superabsorbent composites.

EXPERIMENTAL

Materials

Acrylic acid (AA, chemically pure, distilled under reduced pressure before use), ammonium persulphate (APS, analytical grade, recrystallized in distilled water before use) and *N,N'*-methylenebisacrylamide (MBA, chemically pure used as received) were supplied by Shanghai Reagent Corp. (Shanghai, China). Chitosan (CTS, degree of deacetylation of 0.90, with average molecular weight of 300 kDa) was supplied by Zhejiang Yuhuan Ocean Biology Co., China. Muscovite (MVT, Chenxing Industry Co. Ltd., Shijiazhuang, China) was milled through a 320-mesh screen. The cation exchange capacity of muscovite was 40.3 meq/100 g. Other agents used were all of analytical grades and all solutions were prepared with distilled water.

Preparation of Ion-Exchanged MVT

Ion-exchanged MVT (IMVT) samples were obtained according to the following method. An amount of 10.0 g of MVT powder was added to 100 mL of each

salt solution of 1 mol/L of KCl, NaCl, MgCl₂, CaCl₂, AlCl₃, FeCl₃, K₂SO₄, K₂CO₃, K₃PO₄, K₂HPO₄, or KH₂PO₄ at room temperature for 1.0 h under 1250 rpm stirring. The ion-exchanged samples were washed with distilled water until the precipitation was not detected by 0.1 mol/L AgNO₃ or BaCl₂ aqueous solution added to the filtrates, and then dried at 105°C for 8 h and milled through a 320-mesh screen prior to use.

Preparation of CTS-g-PAA/(MVT and IMVT) Superabsorbent Composites

CTS-g-PAA/(MVT and IMVT) superabsorbent composites were synthesized according to the following procedure. An amount of 0.50 g CTS was dissolved in 30 mL acetic acid solution (1% v/v) in a 250 mL four-neck flask, equipped with a mechanical stirrer, a reflux condenser, a funnel and a nitrogen line. After being purged with nitrogen for 30 min to remove the oxygen dissolved in the system, 0.0954 g APS was introduced to initiate CTS to generate radicals. Ten minutes later, a mixed solution of 3.60 g AA, 0.1198 g MBA, 0.4795 g clay (MVT or IMVT) followed by 10 mL water was added. The water bath was kept at 80°C for 3 h to complete the polymerization. The resulting granular product was washed with distilled water to remove residual reactants. It was then transferred into sodium hydroxide aqueous solution (2 mol/L) to be neutralized to pH 7 and swell to equilibrium in distilled water, and finally dehydrated with methanol. The samples were spread on a dish to dry to constant weight at 70°C in an oven after filtration. The product was milled and the particle size of all the samples for test was in the range of 40-80 mesh. Apart from the omission of clay, the preparation method of CTS-g-PAA superabsorbent was similar to that of CTS-g-PAA/MVT superabsorbent composite.

Measurement of Water Absorbency and Swelling Behaviour

A sample (0.05 g) of superabsorbent composite was immersed in excess distilled water (500 mL) at an ambient temperature for 4 h to reach the swelling equilibrium. The swollen sample was then separated from unabsorbed water by filtering through a 100-mesh screen. Water absorbency of the superabsorbent composite, Q_{eq} , is calculated using eqn (1):

$$Q_{eq} = (m_2 - m_1) / m_1 \quad (1)$$

Where, m_1 and m_2 are the weights of dry and swollen samples, respectively. Q_{eq} is calculated as grams of water per gram of sample.

The swelling rate (Q_t) of the samples was measured according to the following process. Samples of 0.05 g of composite were each immersed in a certain amount of distilled water in separate 500-mL beakers. At certain time intervals, the water absorbency of the samples was measured under the same condition as that used for equilibrium water absorbency.

The determination of water absorbency at various pH solutions was similar to that of above measurement. The pH values of the external solutions were adjusted by addition of 0.1 mol/L HCl and/or 0.1 mol/L NaOH solutions. The effects of various pH solutions on water absorbency were then tested. All the tests were carried out three times repeatedly and the average values were reported.

Characterizations

FTIR spectra were recorded on a Nicolet NEXUS FTIR spectrometer (USA) in 4000-400 cm⁻¹ region using KBr platelets. The chemical composition analysis of clay was determined by X-ray fluorescence (XRF) spectrometry (PANalytical minipal4, Finland). SEM studies were carried out by a JSM-5600LV SEM instrument (Jeol, Ltd., Japan) after coating the samples with gold film using an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

FTIR Spectra

The infrared spectra of MVT and ion-exchanged MVT are depicted in Figure 1. The main characteristic bands of MVT at 3625, 3440, 1635, 1028, 827, 529, and 474 cm⁻¹ are ascribed to vibrations of ν (Mg-OH and Al-OH), ν (H₂O), δ (H₂O), ν (Si-O-Si), ν (Si-O-Mg), δ (Si-O-Mg) and δ (Si-O), respectively. The adsorption peaks at 749 and 800 cm⁻¹ are ascribed to the presence of a trace amount of quartz associated in the muscovite [21]. These characteristic adsorption peaks show some changes after

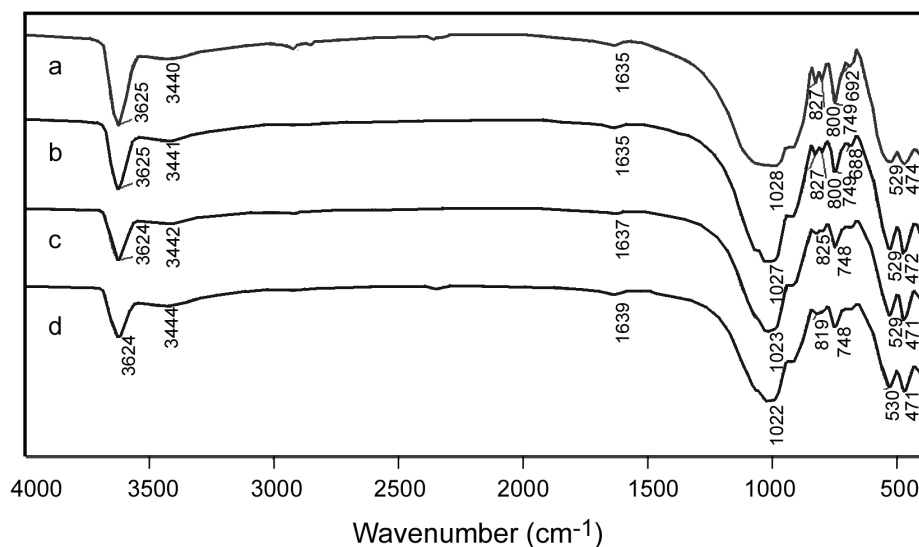


Figure 1. FTIR spectra of (a) MVT, (b) FeCl₃-MVT, (c) K₂CO₃-MVT, and (d) K₂SO₄-MVT.

modification with ion-exchange treatment (spectra b-d in Figure 1). These changes may indicate possible exchange reactions taken place between the ions on the surface and the channels of MVT with ions present in external solutions.

FTIR spectra of CTS-g-PAA, CTS-g-PAA/MVT, CTS-g-PAA/FeCl₃-MVT, CTS-g-PAA/K₂CO₃-MVT and CTS-g-PAA/K₂SO₄-MVT are shown in Figure 2. It can be seen from FTIR spectrum of CTS-g-PAA the characteristic bands at 1562 cm⁻¹ (-COOH stretching

vibration), 1454 cm⁻¹ (asymmetric stretching vibration) and 1408 cm⁻¹ (symmetric stretching vibration of -COO⁻) (spectrum a in Figure 2). There is an absorption peak at 1323 cm⁻¹ (stretching and bending vibrations of the C-N bond of the amide III of CTS). However, the characteristic absorption peaks of the amide I (1658 cm⁻¹), N-H (1594 cm⁻¹) and C₆-OH (1091 cm⁻¹) of CTS could not be found in spectrum a in Figure 2, which confirm that -NH₂, -NHCO, and -OH functional groups of CTS took part

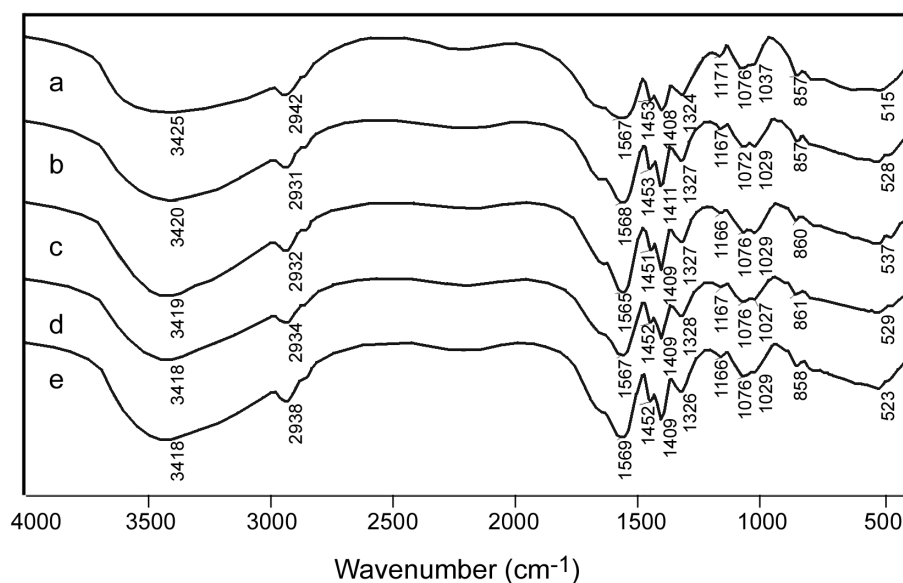


Figure 2. FTIR spectra of (a) CTS-g-PAA, (b) CTS-g-PAA/MVT, (c) CTS-g-PAA/FeCl₃-MVT, (d) CTS-g-PAA/K₂CO₃-MVT, and (e) CTS-g-PAA/K₂SO₄-MVT (Feed clay content: 10 wt%).

in graft reaction with AA [22]. The characteristic peaks of MVT after formation of the composites at 3624 and 1635 cm^{-1} are ascribed to the stretching and bending vibrations of -OH on the surface of layers of MVT, which have disappeared in spectrum b of the composite in Figure 2. The absorption band at 1029 cm^{-1} (assigned to Si-O-Si stretching vibration) which has appeared in the spectrum of these composites has obviously weakened after polymerization reaction (spectra c-e in Figure 2) As a whole, these analyses indicate that MVT and modified MVT have also participated in the grafting copolymerization reaction through active $\equiv\text{Si-OH}$ groups.

Effects of Ion-Exchanged MVT on Water Absorbency of Superabsorbent Composites

Effects of the ion-exchanged MVT on water absorbency of CTS-g-PAA/MVT superabsorbent composite in distilled water and 0.9 wt% NaCl solution are displayed in Figures 3 and 4, respectively.

It can be seen from Figure 3 that for the series of cation-exchanged MVT, the water absorbency in distilled water increases in the order Ca^{2+} -MVT < MVT < Mg^{2+} -MVT < K^{+} -MVT < Al^{3+} -MVT < Na^{+} -MVT < Fe^{3+} -MVT. The optimal water absorbency of Fe^{3+} -MVT reaches 376.1 and 56.6 $\text{g}\cdot\text{g}^{-1}$ in distilled water and 0.9 wt% NaCl solution,

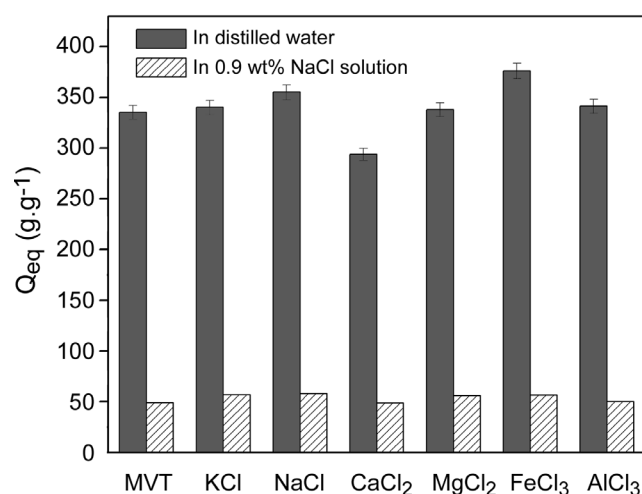


Figure 3. Effects of cation-exchanged MVT on water absorbency of the superabsorbent composites in distilled water and 0.9 wt% NaCl solution (Feed clay content: 10 wt%).

respectively. K^{+} -MVT and Na^{+} -MVT were easily ionized when they were incorporated in composites immersed in water. This enhanced the hydrophilicity of composites and made them swell even more. The inclusion of divalent and trivalent cations like Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+} which entered into intermolecular and intramolecular complexations with hydrophilic groups (such as $-\text{COO}^-$, $-\text{COOH}$ and $-\text{OH}$) of the polymerized matrix, may have probably acted as cross-linking aid to help MBA to form a more regular polymeric network, and have also improved the water absorbency of the corresponding superabsorbent composite. However, due to the intense cross-linking function of Ca^{2+} with these hydrophilic groups, the cross-linking density of polymeric networks increased and resulted in diminished water absorbency.

As it is observed in the series of anion-exchanged MVT of Figure 4, the water absorbency in distilled water increases in the order H_2PO_4^- -MVT < HPO_4^{2-} -MVT < PO_4^{3-} -MVT < MVT < Cl^- -MVT < CO_3^{2-} -MVT < SO_4^{2-} -MVT. The optimal water absorbency of SO_4^{2-} -MVT is 388.0 and 56.9 $\text{g}\cdot\text{g}^{-1}$ in distilled water and 0.9 wt% NaCl solution, respectively. The water absorbency of the majority of the samples shows improvement, no doubt with the introduction of ion-exchanged MVT compared with that of MVT (e.g., 335.2 and 49.0 $\text{g}\cdot\text{g}^{-1}$, respectively). The

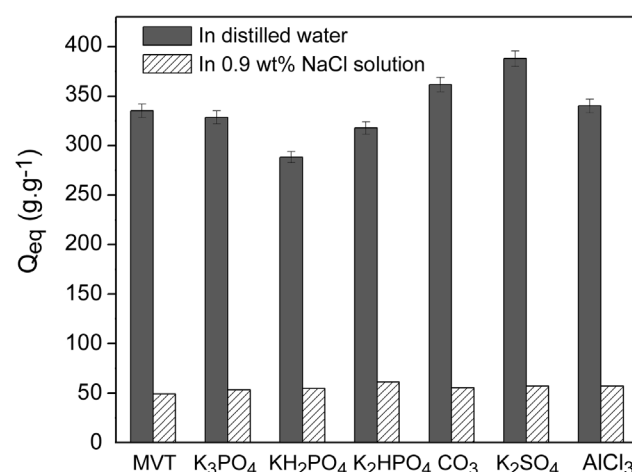


Figure 4. Effects of anion-exchanged MVT on water absorbency of the superabsorbent composites in distilled water and 0.9 wt% NaCl solution (Feed clay content: 10 wt%).

Table 1. Chemical composition of muscovite (MVT) and ion-exchanged muscovite (IMVT) samples.

Chemical analysis (%)				
Composition	MVT	FeCl ₃ -MVT	K ₂ CO ₃ -MVT	K ₂ SO ₄ -MVT
Al ₂ O ₃	28.250	25.969	26.149	25.645
MgO	1.139	0.730	0.708	0.613
CaO	0.116	0.088	0.089	0.098
SiO ₂	56.083	58.637	58.488	58.993
K ₂ O	9.951	9.983	10.062	10.158
Fe ₂ O ₃	4.461	4.593	4.504	4.493

introduction of SO₄²⁻ could increase the ionic species and the total number of ions in polymeric network, which enhanced the hydrophilicity of the composite and increased the osmotic pressure between the polymeric network and external solution, resulting in water absorbency improvement. In addition, the foaming effect induced by the decomposition reaction between CO₃²⁻ and acidic medium has been helpful for the formation of porous and loose structure of composite, which could make the composite swell even more. Due to the strong cross-linking between different phosphate ions and the positive amino ion and the hydroxyls of protonated chitosan, the cross-linking density of polymeric network has increased and the water absorbency of these composites shows decrease. These results are similar to those of the vermiculite [23].

The chemical compositions of MVT and ion-exchanged MVT determined by XRF are listed in Table 1. After ion-exchanged treatment, the proportions of corresponding cation of samples by different ion-exchanged increased evidently compared with that of MVT from the results of Table 1, the quotients of corresponding cation of FeCl₃-MVT, K₂CO₃-MVT and K₂SO₄-MVT are from 4.461% to 4.593%, 9.951% to 10.062% and 9.951% to 10.158%, respectively. This phenomenon verified that ions enter into the structure and move to the surface of MVT particles through the ion exchange and surface adsorption processes.

Effects of MVT and IMVT Content on Water Absorbency of Superabsorbent Composites

The influence of ion-exchanged MVT content on

water absorbency in distilled water of superabsorbent composites are depicted in Figure 5. It is noticeable that the trends of MVT and ion-exchanged MVT composite samples on water absorbency are similar with increase of clay content. The water absorbency of CTS-g-PAA/MVT and CTS-g-PAA/IMVT increase with increase of clay content from 0 wt% to 10 wt% and decrease with further increase of clay content. By incorporation of ion-exchanged MVT into the composites the water absorbency enhances compared with that of MTV. When the clay content was 10 wt%, the increasing rates of water absorbency of FeCl₃-MVT, K₂CO₃-MVT and K₂SO₄-MVT were 112.2 %, 107.8 % and 115.8%, respectively in contrast to that of MVT. The results could further elucidate the function and significance of modified clay to its

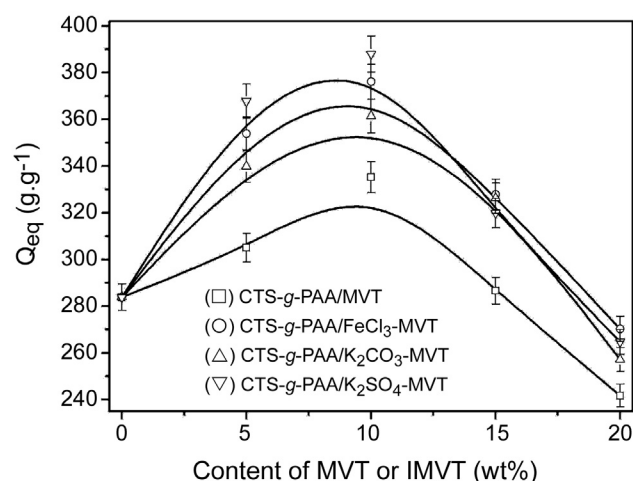


Figure 5. Variation of water absorbency for the superabsorbent composites in distilled water for different clay content.

corresponding superabsorbent composites. This phenomenon is in conformity with our previous study on water absorbency of CTS-g-PAA/ST composites based on acidified sepiolite and cation-exchanged sepiolite [20].

Effects of Modified MVT on Swelling Behaviour of Superabsorbent Composites in Saline Solutions

From the view point of practical applications, it is more important to study the swelling behaviour of the superabsorbent composites in various saline solutions. The swelling behaviours of MVT and ion-exchanged MVT composites in three cationic saline solutions (NaCl, CaCl₂ and FeCl₃) were investigated, as shown in Figures 6-8. From these figures it is evident that the introduction of ion-exchanged MVT to CTS-g-PAA may improve its salt-resistant ability in three saline solutions, and the absorbency of all testing samples is almost equal to those of the same samples at lower saline concentration (0.01 mM for each saline solution). However, with an increase in ionic strength of external solution, i.e., 0.01 to 0.1 mM, a sluggish decrease in these swelling curves can be observed. With further increasing the concentration of external solution, e.g., 0.5 to 10 mM, the absorbencies of all testing samples declined sharply.

This phenomenon can be explained by the fact that when the ionic strength rises, the expansion of the network decreases because of screening effect of the

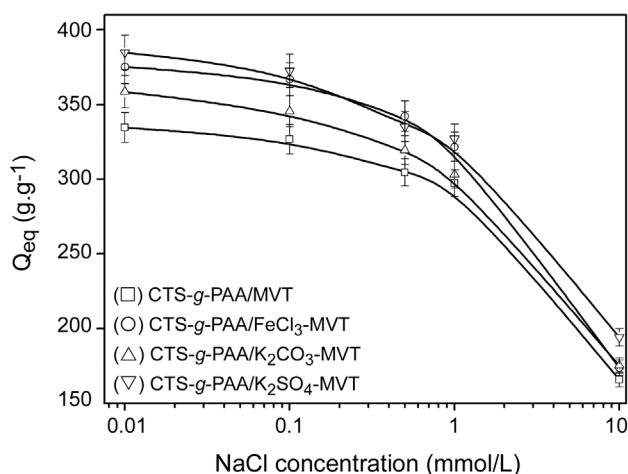


Figure 6. Equilibrium water absorbency of the superabsorbent composites for various NaCl solution concentrations.

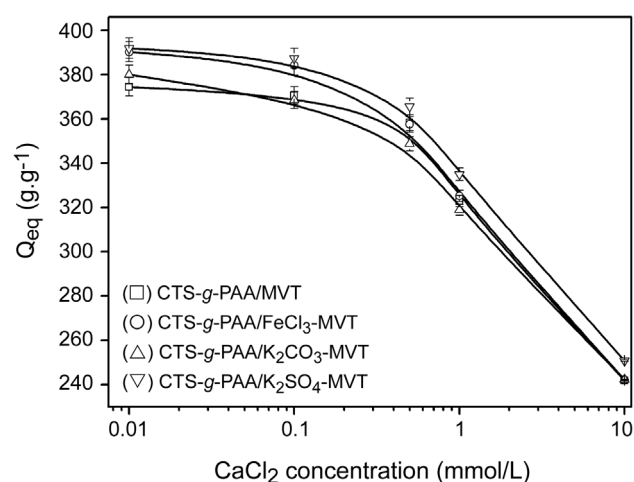


Figure 7. Equilibrium water absorbency of the superabsorbent composites in for various CaCl₂ solution concentrations.

ionic charges bound to the polymeric network and the decrease of osmotic pressure difference between the gel and the external solution [24]. Additionally, we can also understand from Figures 6-8 that the swelling capability of all samples in NaCl solution is higher than theirs in CaCl₂ and FeCl₃ solutions. This is may be due to the coordination of multivalent Ca²⁺ and Fe³⁺ ions with the carboxylic groups on adjacent chains or chain segments of the copolymer which leads to the increased cross-link density and thereupon the polymeric network is sharply shrunk.

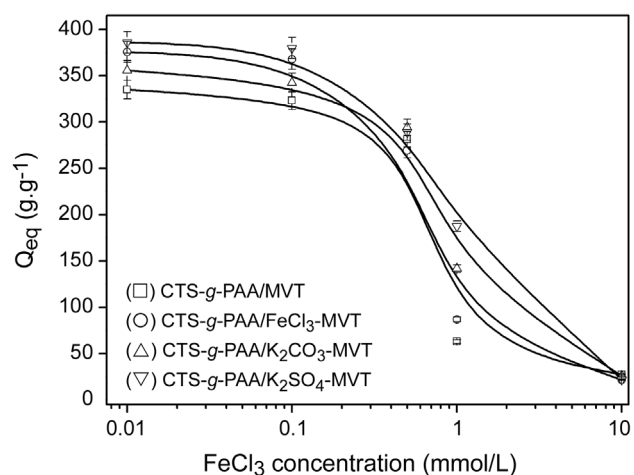


Figure 8. Equilibrium water absorbency of the superabsorbent composites for various FeCl₃ solution concentrations.

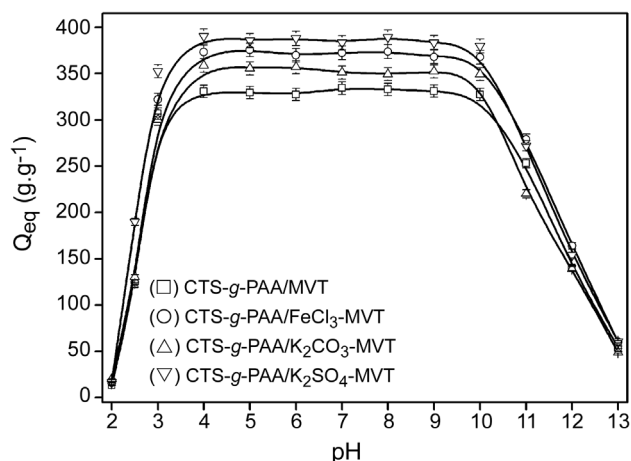


Figure 9. Effect of pH of external solution on water absorbency of the superabsorbent composites.

Effect of Various pH Solutions on Water Absorbency of Superabsorbent Composites

Figure 9 displays the effect of various pH solutions on water absorbency. It is evident from Figure 9 that the water absorbency of all testing samples sharply increases at the pH range 2 - 4 and decreases at the pH range 10 - 13, but almost keeps constant at pH range 4 - 10. This behaviour is attributed to the fact that the $-\text{COOH}$ and $-\text{COO}^-$ groups in these anionic-type superabsorbent polymers have formed a buffer system which has a buffer action on pH changes of the swelling medium. It means that $-\text{COO}^-$ groups can combine with H^+ under an acidic condition, to generate $-\text{COOH}$ groups, which can react with external OH^- to convert to $-\text{COO}^-$ under a basic condition. As a result, the amount of H^+ and OH^- in the external solution may decrease in the pH range 4 to ~ 10 because of the buffer action of $-\text{COOH}$ and $-\text{COO}^-$ groups [25]. However, when the pH is below 4 and beyond 10, the buffer action disappears when a large amount of acid or base is added, and the increased ionic strength of the swelling medium also causes a sharp reduction of osmotic pressure and ultimately decreases the equilibrium water absorbency of the superabsorbent composites.

In order to further illuminate the buffer action of the $-\text{COOH}$ and $-\text{COO}^-$ groups in these superabsorbent composites, the changes of pH of the swelling medium after the swelling of the superabsorbent composites were measured which are shown in Figure 10. It is shown in this figure that the pH of the

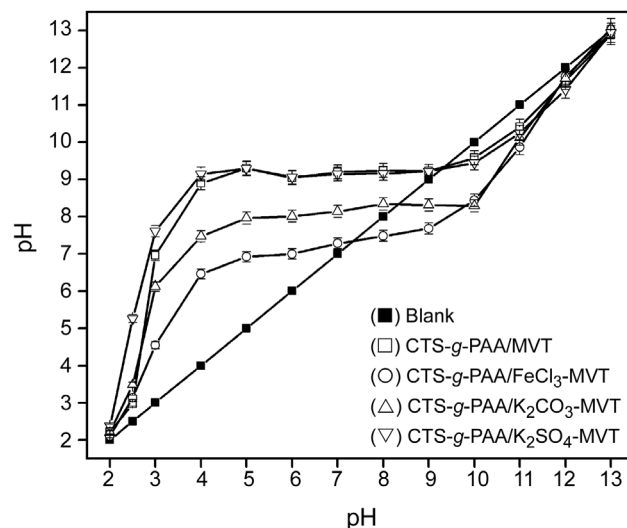


Figure 10. Variation of pH after the swelling of superabsorbent composites.

swelling medium after the swelling of all testing samples shows buffer action on pH of the swelling medium compared with the blank value. For the swelling medium with a pH range 4-10, the pH has been changed in the range 6-9 after the swelling of MVT and IMVT composites, which is responsible for constant water absorbency in this pH range. It is more noticeable that the water absorbency of these superabsorbent composites at a wide range of pH from 4 to 10 is very close and almost equal to its equilibrium water absorbency in distilled water, which is the characteristic of poly(acrylic acid)-based superabsorbent, and this characteristic is helpful to the agricultural and horticultural applications of superabsorbent composites

Swelling Rate and Swelling Dynamics of Superabsorbent Composites

Figure 11 shows the swelling rate of superabsorbent composites in distilled water. It is found that the swelling rate of all testing samples elevated quickly in 0-10 min, and the time of reaching swelling equilibrium is about 2 h. The swelling kinetics was characterized by the Voigt-based viscoelastic model [26,27]:

$$S_t = p(1 - e^{-t/r}) \quad (2)$$

where, S_t is the swelling capability at any moment

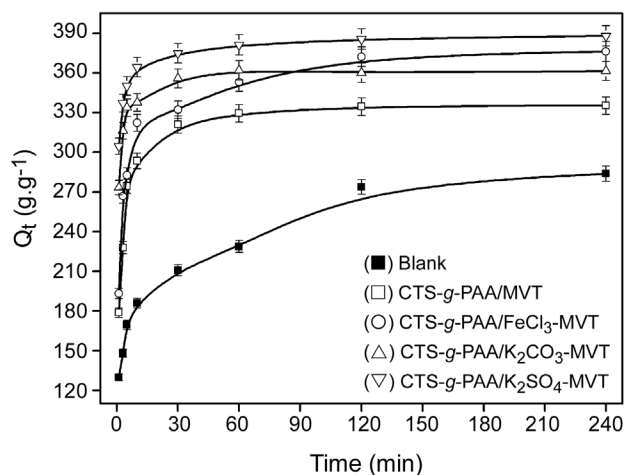


Figure 11. Swelling rate of superabsorbent composites in distilled water.

($\text{g}\cdot\text{g}^{-1}$), p is the power parameter ($\text{g}\cdot\text{g}^{-1}$), t is the time (min), and r is the rate parameter (time in min required to reach 63% of equilibrium swelling). The rate parameter, r , is a measure of the swelling rate of a superabsorbent sample, so that a lower r -value can reflect a quicker swelling rate. The power parameter, p , denotes the water-holding capacity of an individual

Table 2. The parameters of the Voigt-based viscoelastic swelling kinetics model of testing samples.

Samples	Parameters	
	p ($\text{g}\cdot\text{g}^{-1}$)	r (min)
CTS-g-PAA	236.7	2.85
CTS-g-PAA/MVT	317.5	1.81
CTS-g-PAA/ Fe^{3+} -MVT	343.3	1.67
CTS-g-PAA/ K_2CO_3 -MVT	347.8	0.67
CTS-g-PAA/ K_2SO_4 -MVT	369.5	0.59

superabsorbent.

The data obtained from the equilibrium swelling and the swelling rate for each sample were fitted into the above equation to find the values of the rate and power parameters which are displayed in Table 2. These parameters could reflect the quickness or slowness of all samples in certain degree. The swelling rate is in the order CTS-g-PAA/ K_2SO_4 -MVT > CTS-g-PAA/ K_2CO_3 -MVT > CTS-g-PAA/ Fe^{3+} -MVT > CTS-g-PAA/MVT > CTS-g-PAA. From the results of fitting with Voigt-based viscoelastic model

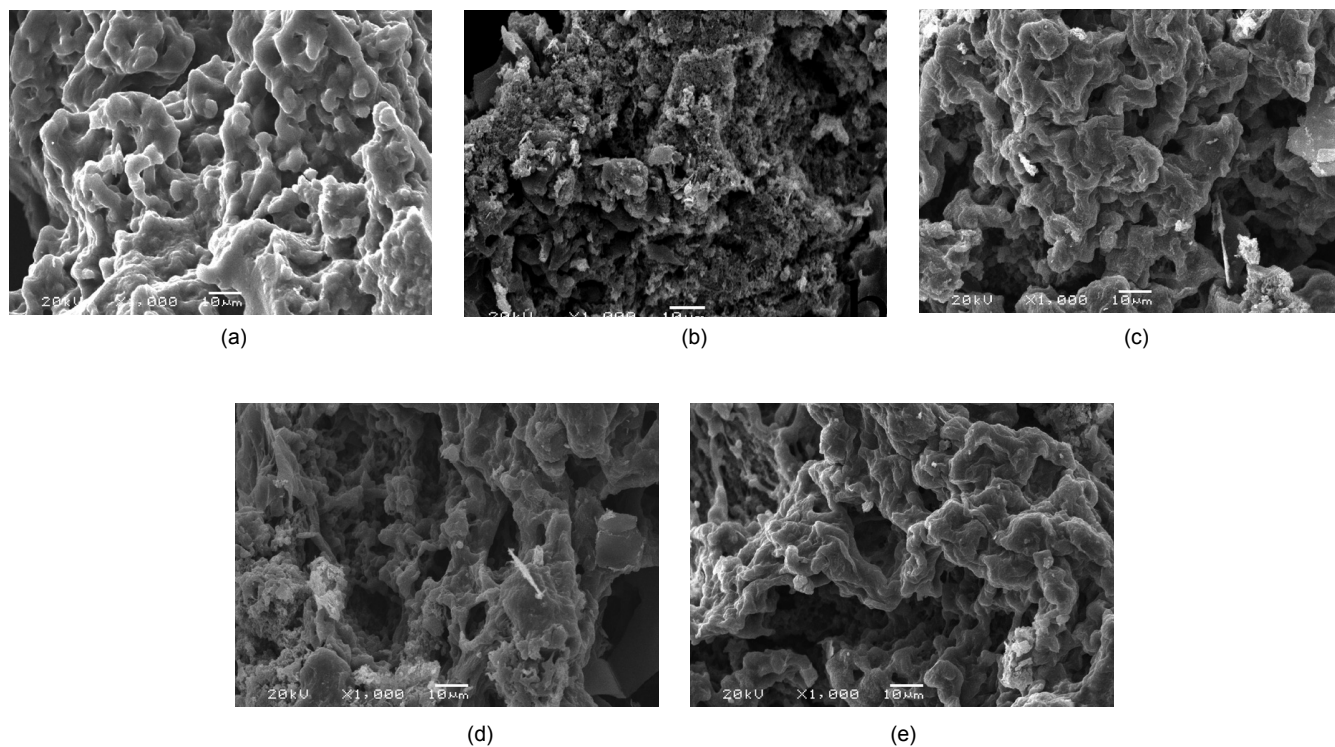


Figure 12. SEM micrographs of (a) CTS-g-PAA, (b) CTS-g-PAA/MVT, (c) CTS-g-PAA/ FeCl_3 -MVT, (d) CTS-g-PAA/ K_2CO_3 -MVT, and (e) CTS-g-PAA/ K_2SO_4 -MVT (Feed clay content: 10 wt%).

about swelling kinetics of these composites, it can be concluded that the incorporation of MVT and ion-exchanged MVT into the composites could enhance the swelling rate. Moreover, introduced ion-exchanged MVT could also improve water-holding capacity. This is because that these composites containing MVT and ion-exchanged MVT have porous structure, which can be confirmed by SEM micrographs in Figure 12. As it is evident in Figure 12, the surface morphology of the CTS-g-PAA/MVT and CTS-g-PAA/IMVT composites is dissimilar from that of CTS-g-PAA. CTS-g-PAA (Figure 12a) shows a smooth and tight surface; however, the surface of MVT and IMVT composite seems to be more loose and spongy (Figures 12b-12e) and the structure can contribute water molecules to penetrate quickly into the polymeric network from the external solution. Additionally, it can be seen from these SEM micrographs that these composites have good dispersion and favourable compatibility of inorganic and organic phases.

CONCLUSION

In this work, a series of MVT and ion-exchanged MVT were incorporated into the CTS-g-PAA polymeric network. The composites obtained after polymerization exhibited a granular and hydrogel product when swelled in distilled water, which were directly formed in aqueous solution by a synthetic process explained in this work. The effects of ion-exchanged MVT on water absorbency and swelling properties of superabsorbent composites in different solutions were investigated, systematically. The results showed that the introduction of suitable amount of ion-exchanged MVT to CTS-g-PAA could not only enhance composites' water absorbency but also improved the swelling rate, water-holding capacity and salt-resistant ability. The -COOH and -COO⁻ groups in the superabsorbent composites form a buffer system which is responsible for the constant water absorbency in the pH range 4-10. Based on this work, it is concluded that the simple and feasible modification of MVT is also an effective approach to improve the performance of organic-inorganic superabsorbent composites. Moreover, the results

obtained from this work could lay a basis for further studies on the correlation between the performance of composites and the structure and physicochemical properties of clays.

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