Studies on Poly(acrylic acid)/Attapulgite Superabsorbent Composites. II. Swelling Behaviors of Superabsorbent Composites in Saline Solutions and Hydrophilic Solvent–Water Mixtures

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ABSTRACT: The effect of the attapulgite content on the swelling for a series of poly(acrylic acid)/attapulgite superabsorbent composites in water was studied. The effects of the temperature and pH values on the water absorbency of the superabsorbent composites were investigated. The swelling behavior of the superabsorbent composites in various saline solutions was also investigated. The water absorbency in various salt solutions decreased with an increase in the ionic strength of the solutions. At a high ionic strength ($>1 \times 10^{-3}M$), the water absorbency in monovalent cationic solutions was higher than that in multivalent cation solutions. This dramatic reduction of the water absorbency in multivalent cationic solutions of high ionic strength may have been due to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which resulted in an increased crosslink density of the network. The swelling behavior of the superabsorbent composites in mixtures of water and hydrophilic solvents, including methanol, acetone, ethanol, and dimethyl sulfoxide (DMSO), was also investigated. The water absorbency decreased with an increase in the concentration of any of the four organic solvents, and two transitions were observed in the superabsorbent composite/hydrophilic solvent–water mixture systems. The main transition for the four hydrophilic solvent–water mixtures was a collapse of the swollen gel (at 50–80% methanol, 30–80% acetone, 50–80% ethanol, and 50–80% DMSO). For the methanol–water system, the magnitudes of the first and second transitions for the poly(acrylic acid)/attapulgite superabsorbent composites containing lower proportions of attapulgite were larger than those for the superabsorbent composites with higher attapulgite contents. The effect of the mixture temperature on the water absorbency of the superabsorbent composites in 10 min was also reported. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1869–1876, 2004

Key words: swelling; composites

INTRODUCTION

Since the first superabsorbent polymer was reported by the U.S. Department of Agriculture,[1] there has been considerable interest in water-swellable polymers capable of absorbing and holding large amounts of water. Superabsorbent polymers are used mainly as absorbents in healthcare and agriculture applications and are commonly based on acrylic monomers such as acrylamide, acrylic acid (AA), and the salt of the acid.[2] In such applications, the water absorbency and water retention are essential. The absorption mechanism of water for hydrophilic polymers was explained for nonionic and ionic network structures by Flory.[3] According to his ionic swelling theory, the swelling of a hydrophilic polymer is dependent on the rubbery elasticity, ionic osmotic pressure, and affinity of the polymer toward water. Although superabsorbent polymers have the greatest absorbency in water, the addition of an inorganic salt or organic solvent will reduce the absorbency. Therefore, it is also important to know the swelling behavior of the absorbents in aqueous salt solutions and in mixtures of water and organic solvents.

The swelling behaviors of superabsorbent gels in various salt solutions have been studied by various investigators. The kinetics of the swelling of poly(sodium acrylate) [poly(SA)] were studied by picture analysis with a microscope–VTR (video tape recorder) system, calorimetry, and gravimetry techniques.[4] Castel et al.[5] reported that the calcium ion (Ca^{2+}) could drastically reduce the swelling value for a starch graft polyacrylonitrile because of the complexing ability of the carboxylate groups inducing intramolecular and intermolecular complex formation. The swelling behaviors of a series of crosslinked poly(SA),[6] crosslinked poly(sodium acrylate-co-hydroxyethyl methacrylate) [poly(SA-co-HEMA)],[7] crosslinked poly[sodium acrylate-co-3-dimethyl (methacryloyoxyethyl) ammonium propane sulfonate] [poly(SA-co-

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DMAPS)],[8] crosslinked poly[sodium acrylate-*co*-N,N-dimethyl (acrylamidopropyl) ammonium propane sulfonate],[9] and poly[2-hydroxyethyl methacrylate-*co*-3-dimethyl(methacryloyoxyethyl) ammonium propane sulfonate] hydrogels[10] in aqueous salt solutions were investigated by Lee and coworkers. They found that the swelling behavior of the absorbents depended on the nature of the polymer and the nature of the external solution and could be explained by Flory's theory.

The swelling behaviors of superabsorbent gels in hydrophilic solvent–water mixtures were also investigated by various workers. The swelling behaviors of saponified starch-*g*-polyacrylonitrile polymer gel[11] and a crosslinked poly(acrylic acid-*co*-acrylamide) gel[12] in various organic solvent–water mixtures were reported in a previous study. Murase and Fujita[13] reported on the swelling of a superabsorbent in alcohol (methanol, ethanol, isopropyl alcohol, or glycerol)–water mixtures. To investigate the relationship between the absorbency of a superabsorbent gel and the parameters of the mixing solvents, Chen and Shen[14] selected and used seven organic solvents [methanol, ethanol, glycol, glycerol, acetone, dimethylformamide, and dimethyl sulfoxide (DMSO)] with a wide solubility parameter range and different polarity fractions to study the swelling behaviors of polyacrylate superabsorbents in mixtures of water and hydrophilic solvents. They found that the solubility parameters of the organic solvent–water mixtures had a significant influence on the water absorbency and that the polarity fraction of the solvents could affect the absorbing rate rather than the equilibrium absorbency.

However, the swelling behavior of polymer/clay superabsorbent composites in salt solutions and mixtures of water and organic solvents has rarely been discussed. In the first part of this series, the preparation of novel poly(acrylic acid) (PAA)/attapulgite superabsorbent composite was reported, and our attention was focused on the characterization and synthesis. In this article, the swelling behaviors of superabsorbent composites in various mixtures of water and hydrophilic solvents (including methanol, ethanol, acetone, and DMSO) and various salt solutions are examined. The swelling characteristics of superabsorbent composites in distilled water are studied. The influence of the temperature and pH value on water absorbency in water is also investigated.

EXPERIMENTAL

Materials

AA (chemically pure; Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Ammonium persulfate (APS; analytical-grade; Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. N,N'-Methylene

Scheme 1 Structure of the PAA/attapulgite superabsorbent composite.

bisacrylamide (MBA; chemically pure; Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. Attapulgite micropowder (Xuyi Colloidal Co., Ltd., Jiangsu, China), milled through a 320-mesh screen and then treated with 37% hydrochloric acid for 48 h and washed with distilled water until pH 7 for the removal of any residual hydrochloric acid, was dried at 105°C for 8 h before it was used. All the solutions were prepared with distilled water.

Preparation of the superabsorbent composite

The PAA/attapulgite superabsorbent composite was synthesized through the graft copolymerization of AA on attapulgite micropowder with MBA as a crosslinker and APS as an initiator in an aqueous solution. The inorganic attapulgite particles in the network acted as additional network points. The preparation of the superabsorbent composite is reported in detail in the first part of this series.[15] A schematic illustration of the structure of the superabsorbent composite is shown in Scheme 1.

Water absorbency measurements

A weighed quantity of the superabsorbent composite was immersed in distilled water at the ambient temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water via screening, and the swollen samples were as allowed to drain on the sieve for 10 min. The sieve was then weighed to determine the weight of the swollen samples. The water absorbency of the samples was calculated with the following equation:

$$Q_{\mathrm{H_2O}} = (m_2 - m_1)/m_1 \qquad (1)$$

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

TABLE I
Absorbency and Absorption Rate for the Superabsorbent Composites in Water

| Sample | Attapulgite content (%) | Initial swelling rate (g/min) | | | t_{eq} (min) | Q_{eq} (g/g) |
		3 min	5 min	10 min		
PA$_1$	5	11.23	9.73	4.93	41	1120
PA$_2$	10	5.78	4.88	2.49	67	712
PA$_3$	20	5.75	4.08	2.42	75	641
PA$_4$	35	4.57	3.98	1.98	90	540

Reaction conditions: reaction temperature = 70°C and initial AA concentration = 17.2 wt %; the weight ratios of crosslinker and initiator in the feed were 0.3 and 1.0%, respectively.

Measurement of the swelling rate

Fifty milligrams of the sample was immersed in an excess amount of distilled water at room temperature and was kept for different times until equilibrium was reached. Then, the swollen sample was allowed to drain on a sieve for 10 min. The water absorbency was obtained via the weighing of the swollen sample at various times. The water absorbency was calculated according to eq. (1).

RESULTS AND DISCUSSION

Effect of the attapulgite content on the initial swelling rate and equilibrium water absorbency

The absorption rates for a series of superabsorbent composites are shown in Table I. The sample with a lower attapulgite content had a higher initial swelling rate and a higher water absorbency and required less time to reach absorption equilibrium. The effect of the attapulgite content on the water absorbency is reported in the first part of this series.[15] Lee and Yeh[6] reported that the initial swelling rate was controlled by the diffusion process of water penetrating the interior of gels. The number of hydrophilic groups (COOH and COONa) per unit of volume of the superabsorbent composite increased with decreasing attapulgite content. The diffusion rate of water penetrating the interior of the superabsorbent composite was high when the sample contained more hydrophilic groups. Therefore, superabsorbent composites with lower attapulgite contents (e.g., PA$_1$ and PA$_2$) had higher initial swelling rates.

Effect of pH on the water absorbency

Figure 1 shows the effect of the pH values (the pH values of the external solution were adjusted through the addition of HCl and NaOH solutions in water) on the water absorbency of the superabsorbent composite. The absorbency of the superabsorbent composite (PA$_3$) increased sharply as the pH increased from 2 to 4 and drastically decreased in the pH range of 11–14. In addition, the change in the water absorbency was slight from pH 4 to 11. This behavior may be explained by a buffer action of the carboxylate group with an acid or base, as previously reported by Lee and Wu.[7] In an aqueous solution of a low pH, the carboxylate groups on the polymeric chain can turn into carboxylic acid groups. The carboxylic acid groups show neutral electric charge and lead to a reduction of the repulsion between groups on the polymeric chain. Therefore, the electrostatic repulsion of the chains of the polymer decreases, and this leads to a reduction of the water absorbency. At a high pH value, the carboxylic acid groups on the polymeric chain can turn into sodium carboxylate groups. Consequently, the screening effect of the counterion on the polyanion chain leads to a reduction in the expansion of the network. Therefore, the water absorbency is reduced. Similar results were found for crosslinked poly(SA-co-HEMA) gel[7] and crosslinked poly(SA-co-DMAPS) gel[8] systems.

Effect of the temperature on the water absorbency

The effect of the temperature on the water absorbency of the superabsorbent composite in distilled water was
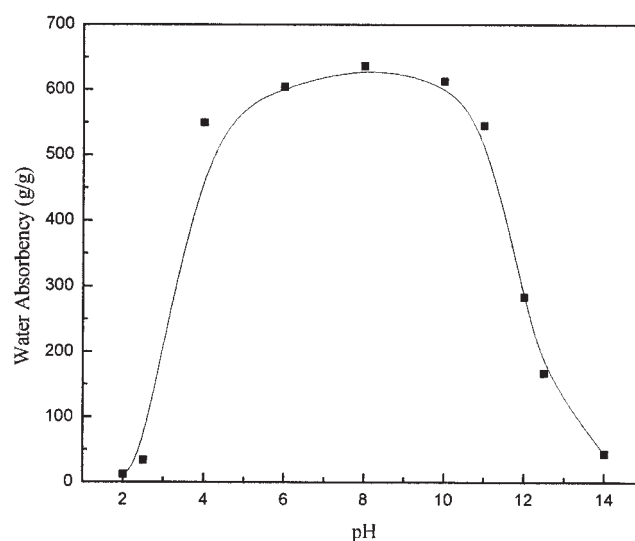

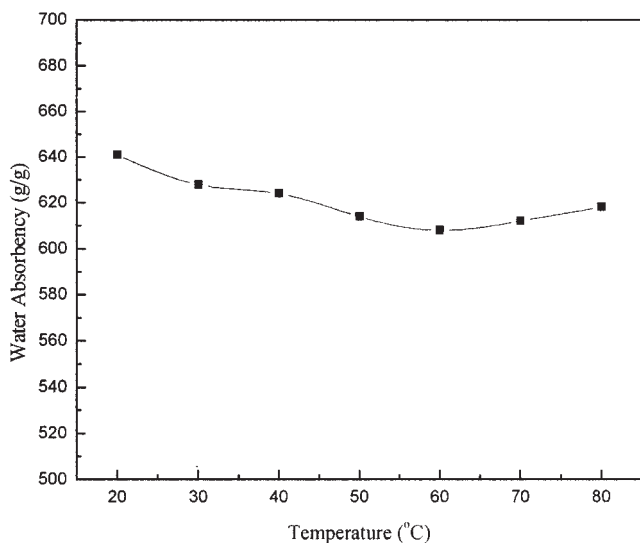**Figure 1** Effect of the pH on the water absorbency of PA$_3$.

Figure 2 Effect of the temperature on the water absorbency of PA_3 in distilled water.

also investigated, and the results are shown in Figure 2. The water absorbency of the superabsorbent composite (PA_3) decreased as the temperature increased from 20 to 60°C. This was because the bounded water in the composite network became free water or nonbinding water, and then it could be moved rapidly out of the network; this led to a decrease in the water absorbency.[16] However, when the temperature was greater than 60°C, the water absorbency increased slightly. This event may be explained by the fact that the dispersion force of the water molecules was greater than the attraction force of the water and polymeric chain, and so the free water was moved from the surroundings into the composite network, and this led to an increase in the water absorbency.[10]

Effect of the salt solution on the water absorbency

It is important to know the swelling behavior of superabsorbent composites in salt solutions for many applications, especially agricultural and horticultural ones. Figure 3 shows the effect of the ionic strength of NaCl solutions on the water absorbency of the superabsorbent composites. The water absorbency decreased with an increase in the ionic strength of the NaCl solutions. This result may be attributed to the reduction in the osmotic pressure difference between the superabsorbent composite and the external salt solution with increasing ionic strength. In addition, the screening effect of the counterion (Na^+) on the anionic group ($—COO^-$) reduced the water absorbency.[7] Similar results have been reported in previous studies.[12,17,18] Moreover, the water absorbency curves for the superabsorbent composites with high attapulgite contents are flatter than those with low attapulgite

contents; that is, the deswelling of the swollen sample was more evident when a low concentration of attapulgite (high PAA content) was contained in the superabsorbent composite. For sample PA_1, the water absorbency decreased from 1088 to 440 g/g at ionic strengths between 0.0005 and 0.01M, whereas the water absorbency decreased from 660 to 257 g/g, from 457 to 200 g/g, and from 345 to 123 g/g for PA_2, PA_3, and PA_4, respectively. These results may be due to the fact that the screening effect of the counterions (Na^+) on the anionic groups ($—COO^-$) bound to PAA chains was apparent when a high proportion of PAA (a low proportion of attapulgite) was contained in the superabsorbent composite.

The effect of the ionic strength on the swelling was determined with the following relation suggested by Hermans:[19]

$$Q_{eq}^{5/3} = A + Bi^2/I \qquad (2)$$

where Q_{eq} is the water absorbency at equilibrium, i is the concentration of the charges bound to the gel, I is the ionic strength of the external solution, and A and B are empirical parameters. As shown in Figure 4, there is a linear relationship between $Q_{eq}^{5/3}$ and $1/I$ for high ionic strengths. However, a discrepancy was observed for low I values. This corresponded to the fact that the swelling force was counteracted by the crosslinked chain's elastic force.[5,7]

The influence of different cations with a common anion (Cl^-) on the swelling behavior of the superabsorbent composite was also investigated. Figure 5 shows the water absorbency of the superabsorbent composite (PA_3) in various salt solutions [aqueous KCl, $CaCl_2$, and $FeCl_3$] with different ionic strengths.
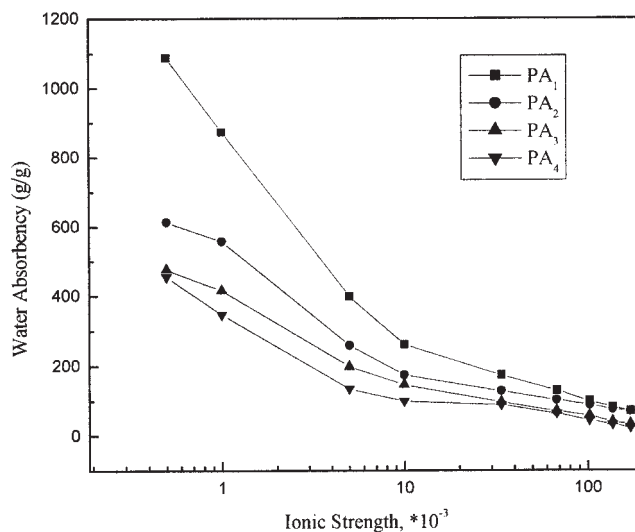

Figure 3 Effect of the ionic strength of the NaCl solution on the water absorbency of PAA/attapulgite.
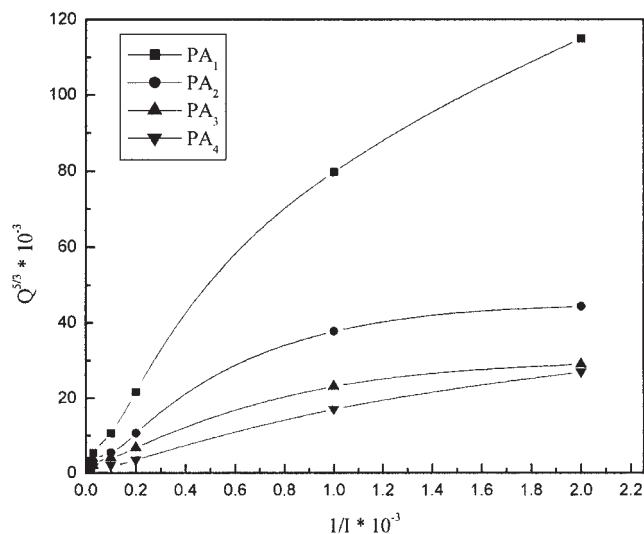
Figure 4 Water absorbency (Q) versus the ionic strength (I) of NaCl solutions.

Figure 6 Water absorbency of PA_3 in aqueous $NaNO_3$, Na_2SO_4, and Na_3PO_4 solutions with various ionic strengths.

The water absorbency of the superabsorbent composite decreased as the ionic strength of all three cationic salt solutions increased. The curve of the water absorbency for the monovalent cationic salt solutions was far flatter than those for the divalent cationic and trivalent cationic salt solutions. Moreover, the deswelling of the superabsorbent composite showed different tendencies at various ranges of the ionic strength: $K^+ < Ca^{2+} < Fe^{3+}$, $Ca^{2+} < Fe^{3+} < K^+$, and $Fe^{3+} < Ca^{2+} < K^+$ for ionic strengths of less than $1 \times 10^{-3}M$, $1 \times 10^{-3}M$, and $1 \times 10^{-3}M–0.1M$, respectively. For a given high ionic strength ($>1 \times 10^{-3}M$), the water absorbency in the monovalent cationic solutions was higher than that in the multivalent cation
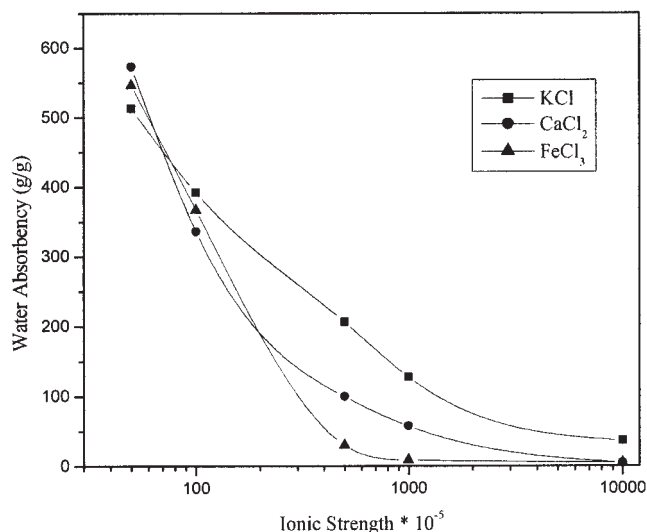

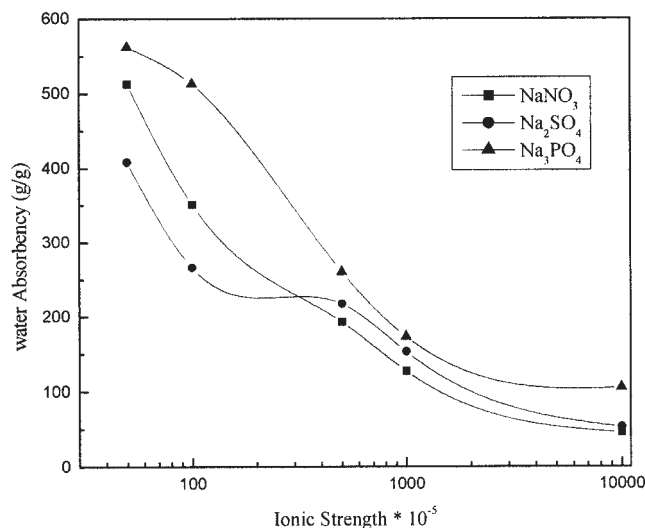**Figure 5** Water absorbency of PA_3 in aqueous KCl, $CaCl_2$, and $FeCl_3$ solutions with various ionic strengths.

solutions. In comparison with monovalent cations, the effect of multivalent cations on the water absorbency of the superabsorbent composite was found at a higher ionic strength range ($>1 \times 10^{-3}M$). This dramatic reduction of the water absorbency in multivalent cationic solutions of high ionic strength may have been due to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which resulted in an increase in the crosslink density of the network.[5] However, the concentration of multivalent cations was low for lower ionic strength salt solutions ($<1 \times 10^{-3}M$), and so the bonding ability of multivalent cations to carboxylate groups was weak. The main influence of multivalent cations on the water absorbency at a lower ionic strength range was due to the reduction of osmotic pressure between the superabsorbent composite network and the external solution. As reported by Lee and Wu[7] while investigating the swelling behaviors of crosslinked poly(SA) and crosslinked poly(SA-co-HEMA) in various multivalent salt solutions with different ionic strengths, the reduction tendencies of the water absorbency of the two gels were in the same order at high ionic strengths: $Fe^{3+} > Ca^{2+} > Zn^{2+} > Cu^{2+}$. They thought that the order, at higher ionic strengths for poly(SA) and poly(SA-co-HEMA) gels with carboxylate groups, could be interpreted with the formation constants of complexation. In this study, the PAA/attapulgite superabsorbent composite showed similar results.

Figure 6 shows the effects of monovalent, divalent, and trivalent anions with a common cation (Na^+) on the water absorbency of the superabsorbent composite. The water absorbency of the superabsorbent composite (PA_3) showed different tendencies at various ranges of the ionic strength: $PO_4^{3-} > NO_3^- > SO_4^{2-}$ and
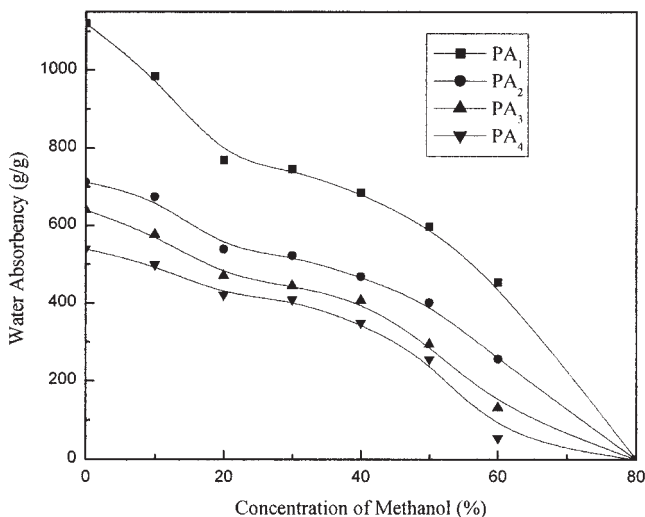
Figure 7 Effect of the concentration of methanol on the water absorbency of PA_3.

$PO_4^{3-} > SO_4^{2-} > NO_3^-$ at ionic strengths of less than 1×10^{-3} and 1×10^{-3}–$0.1M$, respectively. These results indicated the water absorbency of the superabsorbent composite in a trivalent anion (PO_4^{3-}) salt solution was higher than that in monovalent anion (NO_3^-) and divalent anion (SO_4^{2-}) salt solutions with the same ionic strength. At lower ionic strengths ($<1 \times 10^{-3}M$), the water absorbency in the monovalent anion salt solution was higher than that in the divalent anion salt solution. Contrary results were observed at higher ionic strengths (1×10^{-3}–$0.1M$). Similar results were found in a study of the swelling behavior of poly(SA)[6] in various anionic ionic salt solutions [aqueous $NaNO_3$, Na_2SO_4, and Na_3PO_4].

Effect of the hydrophilic solvent

Since Tanaka[20,21] reported the collapse of saponified polyacrylamide gels caused by changes in the temperature and acetone concentration in acetone–water gel fluid mixtures, gel transitions have interested many researchers. In this section, the effect of hydrophilic solvents on the water absorbency of the superabsorbent composite is examined. Figure 7 shows the effect of the methanol concentration on the water absorbency of the superabsorbent composite. The water absorbencies of all four PAA/attapulgite superabsorbent composites with different attapulgite contents decreased as the methanol concentration increased. Also, two phase transitions could be observed: the first (a minor transition) at 10–20 vol % methanol and the second (gel collapse) at 50–80 vol % methanol with a transition point at about 50 vol %. A similar observation was made in a study of gel collapse in a saponified starch-*g*-polyacrylonitrile/water–alcohol system, which was reported by Rodehed and Ranby.[22] As

interpreted by Rodehed and Ranby, the first transition was due to polymer–polymer affinity causing the free liquid in the gel to be forced out and was an effect of increased alcohol content. The second transition (the gel collapse) was due to an interaction between the polar groups in the liquid and the ionic groups in the polymer. The magnitude of this transition was larger and more pronounced when the starch backbone was removed by acid hydrolysis and left a more expanded polymer network. In this study, the magnitude of the first and second transitions for the PAA/attapulgite superabsorbent composites containing lower proportions of attapulgite (PA_1 and PA_2) was larger than that of the superabsorbent composites with higher attapulgite contents (PA_3 and PA_4). A lower proportion of attapulgite meant more PAA was contained in the superabsorbent composite and a more expanded superabsorbent composite network. Therefore, for the first transition, the effect of the polymer–polymer affinity at low methanol concentrations on the transition was more evident; it induced the expulsion of more free water from the network. For the second transition, at the same concentration of methanol, the effects of interactions between the polar molecules of the solvent and ionic groups of the superabsorbent composite on the transition became stronger when the superabsorbent composite contained more ionic groups (more PAA content), which resulted in a more obvious gel collapse. More attapulgite resulted in the generation of more crosslink points, which increased the crosslinking density of the superabsorbent composite and reduced the swelling ability of the composite. It could also reduce the magnitude of the transition of the superabsorbent composite. These results agreed with previous studies finding that the phase transition was enhanced by an increasing concentration of charged groups[23] and decreasing network density.[24]

To investigate the relationship between the polarity of the organic solvent and the water absorbency of the superabsorbent composite, we selected three organic solvents (ethanol, acetone, and DMSO) with different polarities. Figure 8 shows the water absorbency of the superabsorbent composite (PA_3) in three solvent–water mixtures. The water absorbency in all three solvent–water mixtures decreased with an increase in the organic solvent concentration. The water absorbency decreased slowly from 10 to 30% acetone, from 10 to 50% ethanol, and from 10 to 50% DMSO. The main transition for the acetone–water, ethanol–water, and DMSO–water systems was a sharp reduction of the absorbency at 30–80% acetone, 50–80% ethanol, and 50–80% DMSO, respectively. When the concentration was greater than 80%, the water absorbency dropped almost to zero. This phenomenon revealed that there was a continuous transition for the superabsorbent composite in all three organic solvent–water mixtures. For the acetone–water and DMSO–water systems, the
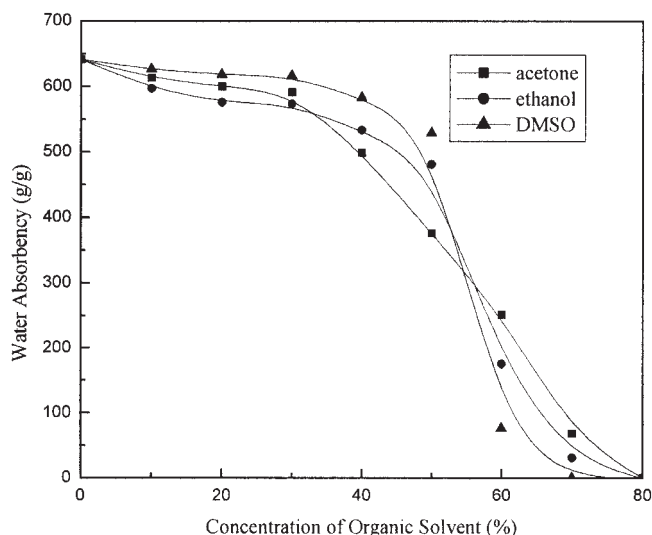
Figure 8 Effect of the concentration of organic solvents on the water absorbency of PA$_3$.

first transition was not as obvious as that of the ethanol–water system. In a study of gel collapse in a saponified starch-g-polyacrylonitrile/water–alcohol system, Rodehed and Ranby[22] attributed the second transition (the gel collapse) to an interaction between the polar groups in the liquid and the ionic groups in the polymer, and the collapse of the gel was a result of the total depletion of water due to the competitive extraction of water from the solvated polymer network. In their study, this could explain why the ethanol–water system collapsed at a lower alcohol content than the methanol–water system because methanol has a higher polarity than ethanol. However, in this study, even though acetone and DMSO have higher polarities than ethanol, the acetone–water system collapsed at a lower concentration than the ethanol–water system, and the DMSO–water system collapse almost at the same concentration as the ethanol–water system. This result may be due to the fact that ethanol, although it has a lower polarity than acetone, more easily interacted with the ionizable groups (—COOH or —COO$^-$) on the PAA branches in the superabsorbent composite network. Therefore, in the acetone/water mixture, the free water of the swollen samples could be more easily extracted from the network than that in the ethanol/water mixture, and this resulted in a collapse of the gel at a lower concentration of acetone than for ethanol. This result also indicated that the polarity of the organic solvent was not clearly related to the transition of the superabsorbent composite, even if the gel collapse in the saponified starch-g-polyacrylonitrile/water–alcohol system could be well explained by the polarity of the organic solvent in the alcohol/water system. Similar observations were also made during the study of the swelling behaviors of polyacrylate superabsorbents in various hydrophilic solvent–water mixtures.[14]

Figure 9 shows the effect of the mixture temperature on the water absorbency of the superabsorbent composite (PA$_3$) in 10 min. Raising the mixture temperature slightly increased the water absorbency for all three mixtures. This may have occurred because the diffusion rate of water penetrating the interior of the superabsorbent composite was high when the temperature rose. Therefore, the absorbency in 10 min increased. Also, at a given concentration of the organic solvent, the absorbency in 10 min increased with an increase in the polarity of the organic solvent. This result agreed with a previous study, which found that the polarity of the organic solvent could affect the absorbing rate rather than the equilibrium absorbency.[14]

CONCLUSIONS

The swelling characteristics of a series of PAA/attapulgite superabsorbent composites in water were studied. The superabsorbent composite with a lower attapulgite content had a higher initial swelling rate and a higher water absorbency and required less time to reach absorption equilibrium. The effects of the temperature and pH on the water absorbency of the superabsorbent composites were investigated. The effect of NaCl solutions of various ionic strengths on the water absorbency of the superabsorbent composites was also investigated, and the deswelling of the swollen samples was quite evident when a low proportion of attapulgite (a high PAA content) was contained in the superabsorbent composites. This may have occurred because the screening effect of the counterions (Na$^+$) on the anionic groups (—COO$^-$) bound to PAA chains was apparent when the high proportion of
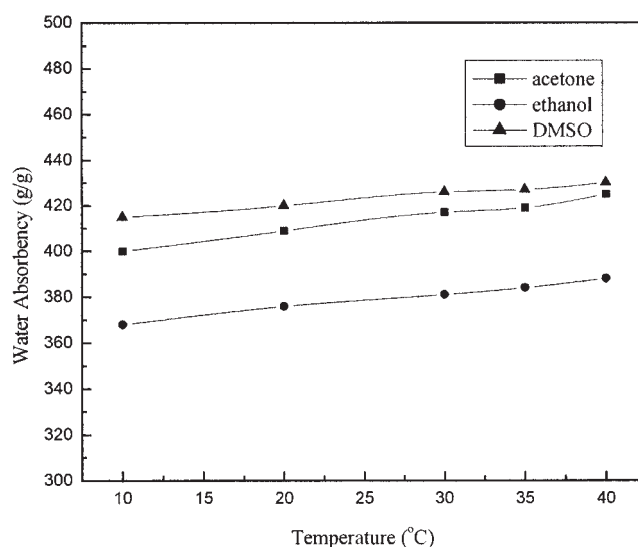

Figure 9 Effect of the mixture (20% organic solvent concentration) temperature on the water absorbency of PA$_3$.

PAA (a low proportion of attapulgite) was contained in the superabsorbent composites. The water absorbency in the monovalent and multivalent cationic salt solutions decreased with an increase in the ionic strength of the salt solutions. For a given high ionic strength ($>1 \times 10^{-3}M$), the water absorbency in the monovalent cationic solutions was higher than that in the multivalent cation solutions. This dramatic decrease in the water absorbency in multivalent cationic solutions with high ionic strengths may be due to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which resulted in an increase in the crosslink density of the network. In the cases of various anion solutions with a common cation (Na^+), the water absorbencies for the superabsorbent composite showed different tendencies at various ranges of the ionic strength: $PO_4^{3-} > NO_3^- > SO_4^{2-}$ and $PO_4^{3-} > SO_4^{2-} > NO_3^-$ at ionic strengths of less than $1 \times 10^{-3}M$ and 1×10^{-3}–$0.1M$, respectively. The investigation of the swelling behaviors for the superabsorbent composites in mixtures of water and organic solvents, including methanol, acetone, ethanol, and DMSO, showed that the water absorbency decreased with an increase in the concentration of all four organic solvent–water mixtures, and two transitions were observed in the superabsorbent composite/organic solvent–water mixture systems. The main transition for the four hydrophilic solvent–water mixtures was a collapse of the swollen gel at 50–80% methanol, 30–80% acetone, 50–80% ethanol, and 50–80% DMSO, respectively. In the case of the methanol–water system, the magnitude of both the first and second transitions for the PAA/attapulgite superabsorbent composites containing lower proportions of attapulgite was larger than that of the superabsorbent composites with higher attapulgite contents. The effect of the mixture temperature on the water absorbency of the superabsorbent composite in 10 min was also investigated. Raising the mixture temperature slightly increased the water absorbency for all three mixtures. This observation may be due to the fact that the diffusion rate of water penetrating the interior of the superabsorbent composites was high when the temperature was raised.

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