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Preparation, Characterization and Swelling Behaviours of a Novel Multifunctional Superabsorbent Composite Based on Ca-Montmorillonite and Sodium Humate

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Abstract: In this work, a novel water-managing superabsorbent composite was prepared by graft copolymerization reaction using acrylic acid (AA) and acrylamide (AM) as the monomers, calcium montmorillonite (Ca-MMT) as an inorganic component and sodium humate (SH) as fertilizer, and well characterized by means of Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The effects of the reaction temperature, neutralization degree of AA, amount of crosslinker, initiator, Ca-MMT and SH on water absorbencies were systematically investigated. The water absorbencies of the superabsorbent composite synthesized under optimal conditions with a Ca-MMT content of 20 wt% and an SH content of 30 wt% are 615 g g^{-1} and 45 g g^{-1} in distilled water and in 0.9 wt% NaCl solution, respectively. The swelling behaviours of the superabsorbent composite in various cationic salt solutions (NaCl, $CaCl_2$ and $FeCl_3$) were also investigated and it was found that at the same saline concentration (> 0.1 mmol L^{-1}), the effect of three cationic salt solutions on the swelling capability has the following order: NaCl < $CaCl_2$ < $FeCl_3$. Here, it is worthy to point out that the water absorbency and swelling behaviours of the developed composite were improved by introducing simultaneously Ca-MMT and SH into PAA-AM network in comparison with that of incorporated single with Ca-MMT or SH.

Introduction

Superabsorbent polymers are loosely crosslinked hydrophilic polymers that have the ability to absorb and retain large volumes of water and aqueous solutions, and the water is hardly removed even under some pressure [1]. As a kind of functional materials, superabsorbent has been widely used in traditional applicable areas, such as hygienic products, horticulture and agriculture, biotechnological devices, and drug-delivery systems [1-5]. In order to further enhance the water absorbency, the gel strength, the thermal stability, and also reduce the production cost, many inorganic components, such as kaolin [6], mica [7], attapulgite [8], vermiculite [9], bentonite [10], sepiolite [11] and diatomite [12] have been introduced into the polymeric network to form organic-inorganic superabsorbent composite.

Montmorillonite (MMT) belongs to smectite group of clay minerals which has a 2:1 type of layer structure. It is comprised of negatively charged silica sheets held together by charge-balancing counterions such as Mg^{2+}, Na^{+}, and Ca^{2+}. MMT has diverse applications in many fields like agriculture, oil industry, ceramic industry, etc. It may be interesting here to mention that MMT can act as additives to amend the soils [13]. Lee et al. prepared some xerogels based on sodium acrylate and montmorillonite and found that the water absorbency increased by adding a small amount of MMT into the copolymeric gels [14]. Santiago et al. synthesized a series of composite by copolymerization reaction of partially neutralized acrylic acid on MMT micropowder and found that the introduction of MMT into the polymer network resulted in an increase in thermal stability [10]. In addition, the interaction between montmorillonite and acryloyloxyethyl trimethyl ammonium chloride can lead to the formation of nanocomposite hydrogel exhibiting excellent gel strength [15].

Humus, as a kind of biomass resource, is consisted of multifunctional aliphatic components and aromatic constituents, and contains a large number of functional groups (such as carboxylates and phenolic hydroxyls) [16]. They are vital for plant growth and for proper soil fertility. They work to balance pH, increase cation exchange capacity (CEC), retain water within the soil profile, increase the quantity and quality of the hair-like feeder roots, and that they do all of this at much lower rates of application than traditional fertilizers. In recent years, we paid our attention on the preparation of this kind of functional superabsorbent composite by introducing sodium humate (SH) into acrylic or acrylamide system [17-19] and discovered that the introduction of SH into superabsorbent composite can not only improve the water absorbency of corresponding superabsorbent, but also endow the developed composite with some exciting slow-release characteristics.

To the best of our knowledge, the superabsorbent, made by combination of Ca-MMT and SH, has not been investigated. Therefore, the present work is aimed at the preparation and characterization of this kind of novel multifunctional superabsorbent composites by introducing simultaneously Ca-MMT and SH into PAA-AM polymeric network. In addition, the swelling behaviours of the composites in various cationic saline solutions are also systematically investigated.

Results and discussion

FTIR analysis

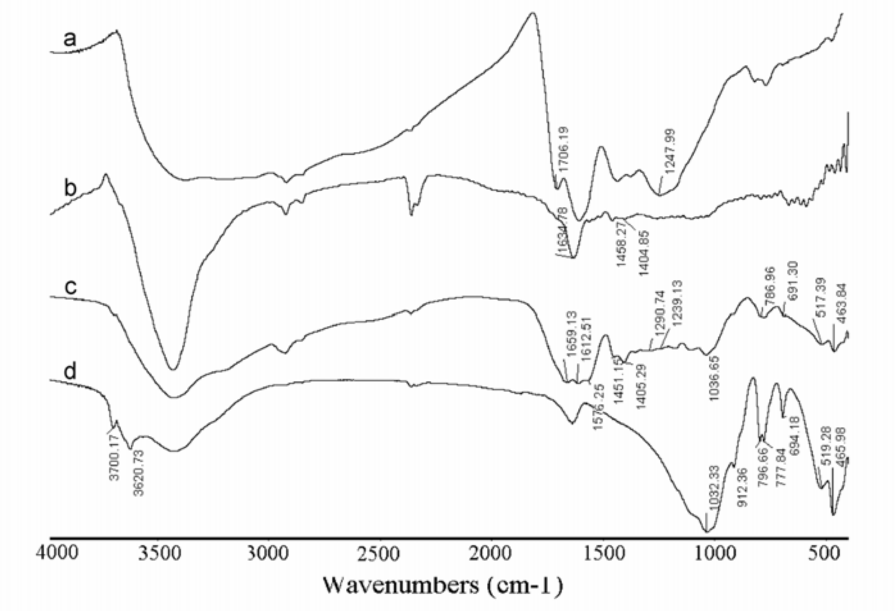

Fig. 1. FTIR spectra of (a) SH, (b) PAA-AM, (c) PAA-AM/MMT/SH, and (d) Ca-MMT.

Compared with FTIR spectra of SH, Ca-MMT and PAA-AM, in the FTIR spectrum of PAA-AM/MMT/SH (Fig.1), the appearance of absorption bands at 1659 cm^{-1} and 1451 cm^{-1} (characteristic absorption bands of $-CONH_2$), 1576 cm^{-1} ($-COO^-$ asymmetric stretching), 1239 cm^{-1} (phenolic C-O stretching of SH), 1037 cm^{-1}, 517 cm^{-1}, 464 cm^{-1}(characteristic absorption bands of Si-O-Si and Si-O-R^{3+} in Ca-MMT [20]) provides direct evidence for the presence of Ca-MMT, SH and PAA-AM in the composite. After polymerization, the absorption bands of SH at 1706 cm^{-1} (C=O stretching of carboxylic group), as well as 3621 cm^{-1} (free or weakly hydrogen-bonded water molecule to the surface oxygen of tetrahedral sheet water molecules [21]), 912 cm^{-1} (Al-OH) are absent in the spectrum of PAA-AM/MMT/SH. The new characteristic absorption band at 1290 cm^{-1}, ascribed to alkarylether [22], gives an indication that a graft polymerization reaction between SH, Ca-MMT and PAA-AM occurs during the polymerization.

XRD patterns

XRD patters of Ca-MMT, PAA-AM/MMT and PAA-AM/MMT/SH were studied, as shown in Fig. 2. It can be observed that Ca-MMT shows a characteristic peak at $2\theta=5.92°$ which corresponds to a basal spacing of 1.494 nm. But for PAA-AM/MMT and PAA-AM/MMT/SH, this characteristic diffraction peak has disappeared even when 50 wt% Ca-MMT is incorporated (Fig. 2b). Similar to the system of starch grafted PAA-AM/MMT [23]. This is an indication that the clay platelets of MMT have been exfoliated, and then are thoroughly dispersed in the polymer matrix, forming a composite structure.

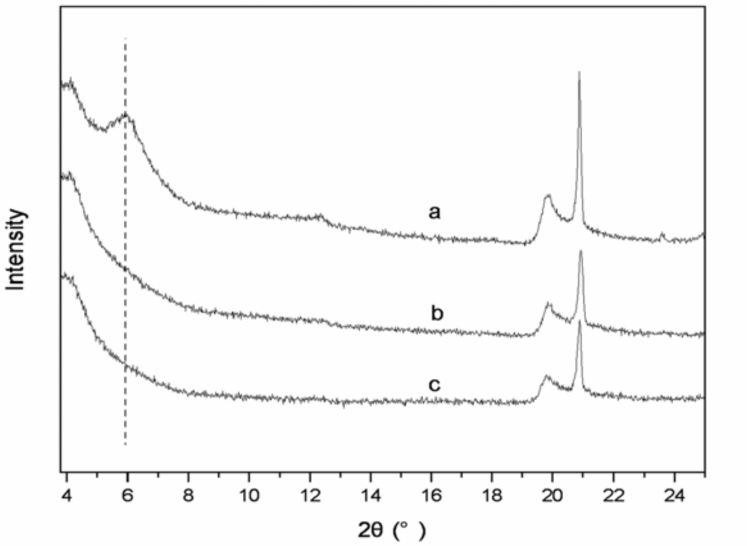

Fig. 2. XRD powder patters of (a) Ca-MMT, (b) PAA-AM/MMT containing 50 wt% Ca-MMT without SH, and (c) PAA-AM/MMT/SH containing 30 wt% SH and 20 wt% Ca-MMT.

Morphology

Fig. 3 shows the micrographs of PAA-AM/MMT/SH superabsorbent composites. It can be observed that single introduction of MMT (3a) displays a coarse surface, and the clay particles are almost embedded within PAA-AM copolymer and more finely dispersed in the polymer matrix, and single introduction of SH (3d) presents an undulant and coarse surface. Compared with Fig. 3a and 3d, simultaneous incorporation of SH and MMT into the composite (3b and 3c) results also in an undulant and coarse surface. As reported, the degree of dispersion of clay particles in the polymer matrix is more important for an organic-inorganic composite [10]. The fine dispersion of clay particles in the polymeric network is helpful for the water absorbency, which prevents the flocculation of clay particles. Then, resulting superabsorbent has a homogeneous composition, which benefits for the final water absorbency. In addition, an undulant and coarse surface can also contribute to the higher water absorbency of the composite [24]. An undulant and coarse surface can increase the surface area for water permeation, making the water easily diffuse into the composite [25]. Then, the interaction of the hydrophilic groups with water affords the final superabsorbent composite with high water absorption [26].

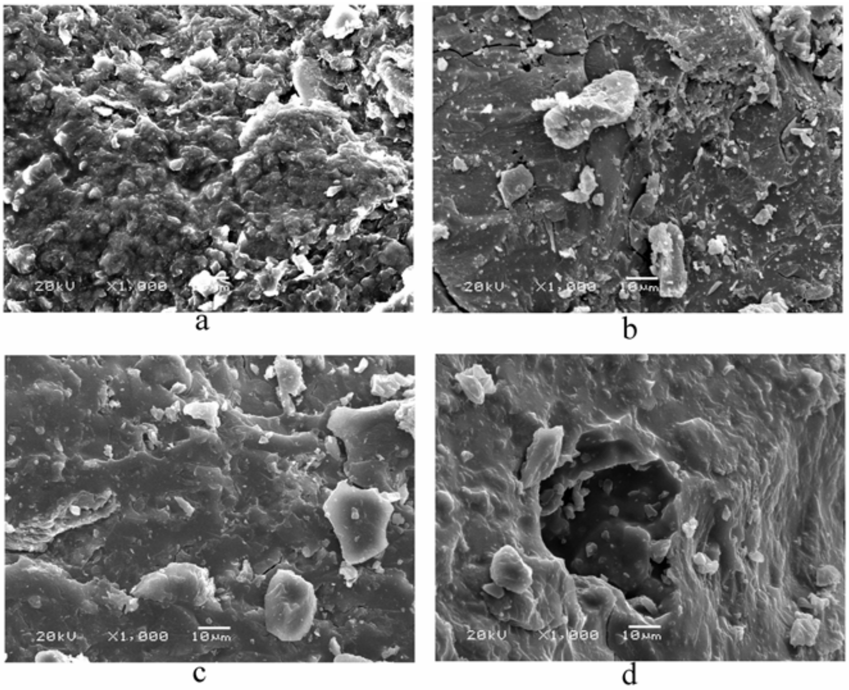

Fig. 3. Scanning electron micrographs for dried superabsorbents: (a) PAA-AM/MMT containing 50 wt% MMT, (b) PAA-AM/MMT/SH containing 30 wt% SH and 20 wt% Ca-MMT, (c) PAA-AM/MMT/SH containing 40 wt% SH and 10 wt% Ca-MMT, and (d) PAA-AM/SH containing 50 wt% SH.

TGA analysis

TGA curves of PAA-AM and PAA-AM/MMT/SH polymeric network show a similar loss at 25-200 °C, corresponding to a loss of moisture existing in these samples (Fig. 4). The major weight losses of PAA-AM polymeric network are located at the temperature of 340, 393 and 423 °C, respectively. However, for PAA-AM/MMT/SH composite, a higher thermal decomposition temperature at 495 °C can be observed. In addition, PAA-AM/MMT/SH can also provide a lower weight loss rate over the temperature investigated. The results indicate that the incorporation of SH and MMT into the PAA-AM polymeric network can enhance the thermal stability of the superabsorbent composite. This may be responsible for two reasons: (i) the generation of chemical bonds between SH and PAA-AM polymeric network as a result of graft copolymerization, making the final thermal stability to be improved; (ii) MMT is a layered structure and small molecules generated during thermal decomposition process cannot permeate, and thus have to bypass MMT layers [27]. This is also called the barrier effect of MMT [10]. Therefore, the introduction of SH and MMT into the composite is proved to be helpful for the improvement of thermal stability of corresponding superabsorbent composite.

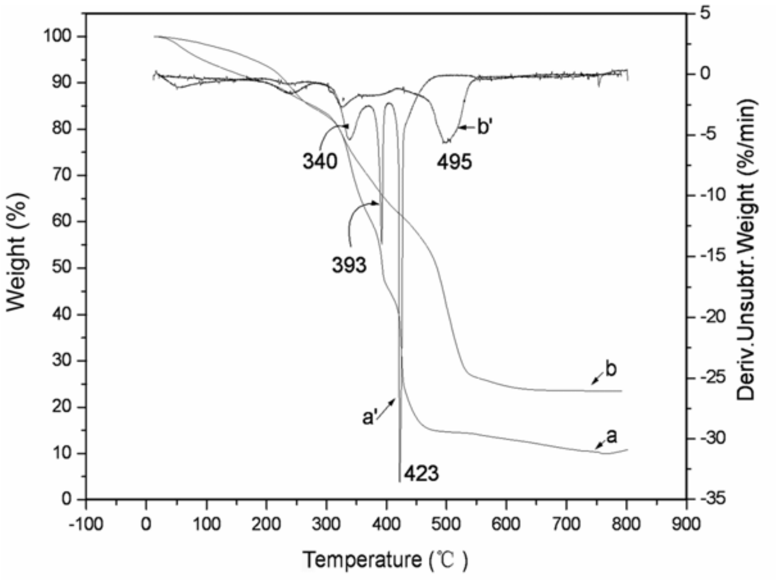

Fig. 4. TGA curves of (a) PAA-AM, and (b) PAA-AM/MMT/SH containing 30 wt% SH and 20 wt% Ca-MMT. Curves a' and b' are the derivative unsubtracted weight of PAA-AM and PAA-AM/MMT/SH, respectively.

Effect of reaction temperature on water absorbency

It is well known that radical polymerization starts by thermal decomposition of an initiator, with an increase in polymerization temperature, the rate of polymerization is strongly enhanced, and meanwhile the termination and transfer reactions are also increased [28]. The effect of polymerization temperature on water absorbency of the superabsorbent composite was investigated, as shown in Fig. 5. With an increase in polymerization temperature from 50 to 90 ^{o}C, the water absorbency increases from 333 to 558 g g^{-1} in distilled water and from 34 to 40 g g^{-1} in 0.9 wt% NaCl solution. Further increase in polymerization temperature would be followed by a decrease in water absorbency, as a result of an increase in the relative amount of the polymer chain ends. Polymer chain ends do not contribute to the absorption capacity. When the polymerization temperature was lower than 50 ^{o}C, the water absorbency of the composite decreased remarkably. This can be ascribed to the formation of more water soluble materials owing to the deficient radicals generated from the thermal decomposition of an initiator. For further study, 80 ^{o}C was selected.

Effect of crosslinker on water absorbency

The degree of crosslinking has a direct effect on the level of swelling capability of a superabsorbent composite. In this study, the effect of crosslinker on water absorbency was shown in Fig. 6. It is clear that 0.1 wt% crosslinker content gives the best absorbency with 540 g g^{-1} in distilled water and 38 g g^{-1} in 0.9 wt% NaCl solution. Further increase in crosslinker content is followed by a dramatic decrease in water absorbency. According to Flory’s network theory [29], saturated water absorbency of a superabsorbent is inversely proportional to the crosslinking density

[30]. With increasing crosslinker content, the crosslinking density increases, reducing the space in the polymeric network to hold water, thereby a decrease in water absorbency. When the crosslinker content is below 0.1 wt%, water absorbency decreases sharply for that the polymeric network of the composite cannot be formed perfectly and the composite exists as a water soluble material. For further study, 0.1 wt% of crosslinker was recommended.

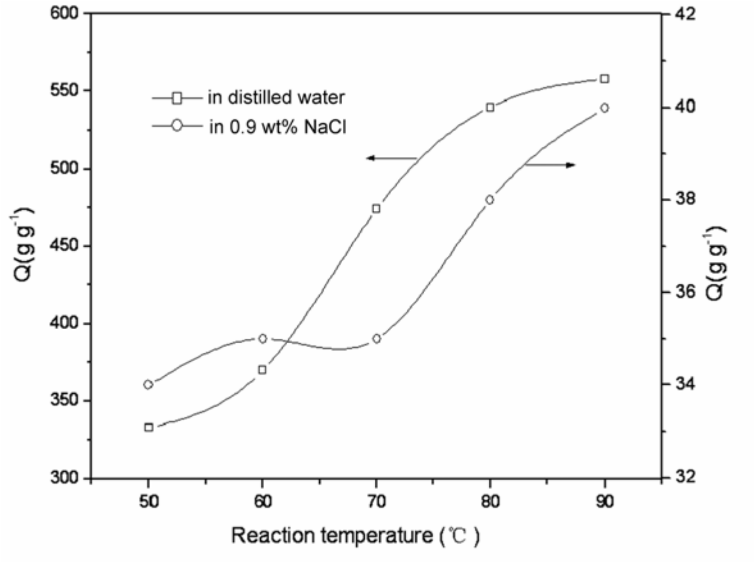

Fig. 5. Reaction temperature dependence of water absorbency for superabsorbent composite: 50% neutralization degree of AA; molar ratio of AA to AM is 1.2; weight ratio of crosslinker, initiator, SH and Ca-MMT in the feed is 0.1, 0.4, 30 and 20 wt%, respectively.

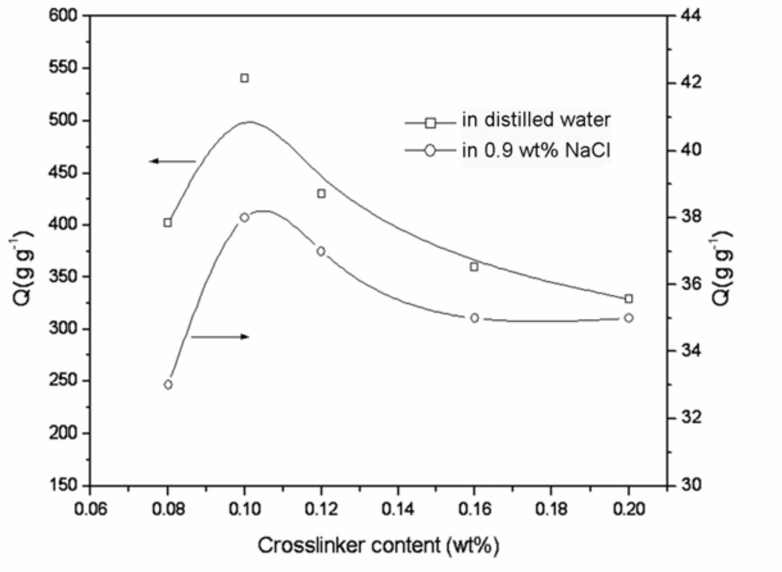

Fig. 6. Dependence of the crosslinker content on the water absorbency for superabsorbent composite: reaction temperature, 80 ^{o}C; 50% neutralization degree of AA; molar ratio of AA to AM is 1.2; weight ratio of initiator, SH and Ca-MMT in the feed is 0.4, 30 and 20 wt%, respectively.

Effect of the initiator on water absorbency

Water absorbency for PAA-AM/MMT/SH superabsorbent composite as a function of initiator content was investigated (Fig. 7). The water absorbencies increased with increasing initiator concentration up to an optimum result of 0.6 wt%, and then decreased slightly with further increase in initiator concentration. It is clear that in free radical chain polymerization using a chemical initiator, the number-average-degree of polymerization is inversely proportional to the square root of the concentration of initiator [31]. At a given monomer concentration, polymerization temperature and crosslinking agent concentration, the higher the initiator concentration, the smaller the molecular weight of the polymer achieved. So, with increasing the initiator concentration, the molecular weight of the polymer backbone decreases and then more polymer chain ends are generated. As discussed above, the polymer ends do not contribute to the water absorbency for a superabsorbent. Thus, further increasing the initiator concentration from 0.6 to 1.6 wt% is responsible for the decrease of water absorbency. However, at a low initiator concentration, a low quantity of free radical is produced and more water soluble materials are then formed. Therefore, the water absorbency decreases remarkably with decreasing the initiator content below the optimum value of 0.6 wt%. Based on these discussions, we selected 0.6 wt% initiator as the optimum amount.

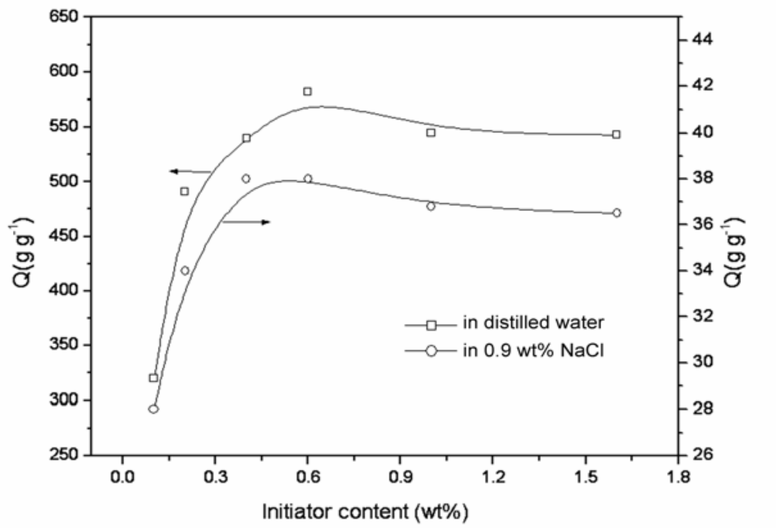

Fig. 7. Variation of water absorbency for superabsorbent composite as a function of an initiator: reaction temperature, 80 °C; 50% neutralization degree of AA; molar ratio of AA to AM is 1.2; weight ratio of crosslinker, SH and Ca-MMT in the feed is 0.1, 30 and 20 wt%, respectively.

Effect of hydrophilic group on water absorbency

Hydrophilic group in the superabsorbent composite plays an important role in swelling capacity, and can be adjusted by changing the neutralization degree of AA and molar ratio of AA to AM. So firstly, the effect of neutralization degree of AA on water absorbency was investigated, as shown in Fig. 8. When AA is neutralized with sodium hydroxide, both the ionic hydrophilic effect of the composite and osmotic pressure difference increase, and the electrostatic repulsion of the negatively charged carboxylate groups attached to the polymer chains tend to expand the network. So, with increasing the neutralization degree from 40 to 70%, the water absorbency increases for corresponding superabsorbent composite. However, further increase in neutralization degree results in the generation of more sodium ions in the polymeric network, which reduces the electrostatic repulsion by screening the negative charges of -COO^- groups, thereby leading to a decrease in water absorbency. Thus, an appropriate neutralization degree, 70% in this work, is required for an excellent superabsorbent composite. Similar observations were also reported by others [32, 33].

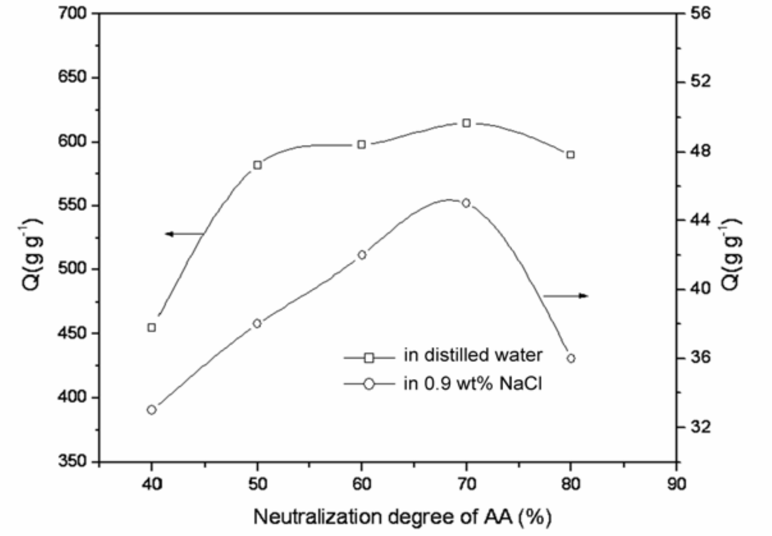

Fig. 8. Water absorbency for superabsorbent composite as a function of neutralization degree: reaction temperature, 80 °C; molar ratio of AA to AM is 1.2; weight ratio of crosslinker, initiator, SH and Ca-MMT in the feed is 0.1, 0.6, 30 and 20 wt%, respectively.

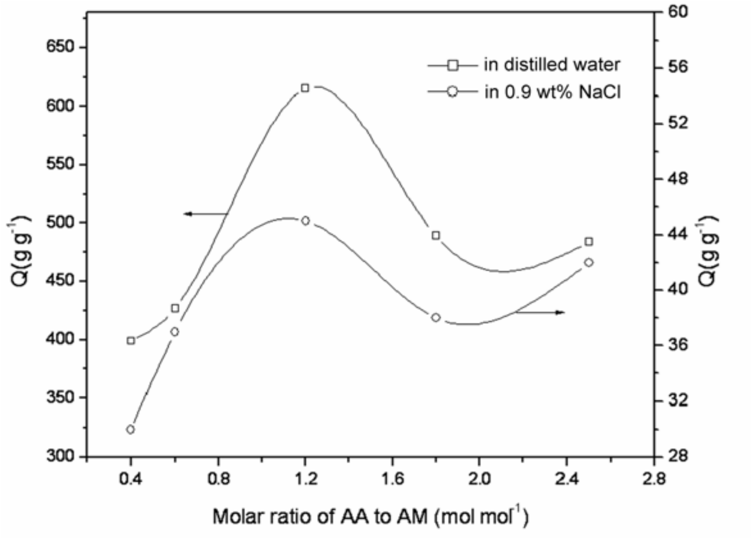

Fig. 9. Effect of molar ratio of AA to AM on water absorbency for superabsorbent composite: reaction temperature, 80 °C; 70% neutralization degree of AA; weight ratio of crosslinker, initiator, SH and Ca-MMT in the feed is 0.1, 0.6, 30 and 20 wt%, respectively.

The effect of molar ratio of AA to AM on water absorbency for PAA-AM/MMT/SH composite was also examined (Fig. 9). It can be seen that the effect of molar ratio of AA to AM on water absorbency is similar to that of neutralization degree of AA. With increasing the molar ratio of AA to AM from 0.4 to 1.2, the water absorbency increases from 399 to 615 g g^{-1}, and then decreases to 484 g g^{-1} with further increase in the molar ratio to 2.5. Results from analysis implied that the synergistic effect of -COOH, -COO^- and -$CONH_2$ groups is superior to that of single -COOH, -COO^- or -$CONH_2$ groups, as studied by our previous study [34].

Effect of SH-to-MMT weight ratio on water absorbency

The total weight ratio of SH and MMT being fixed at 50 wt%, the effect of SH-to-MMT ratio on water absorbency is displayed in Fig. 10. The water absorbency increases to 615 g g^{-1} as SH-to-MMT ratio increases from 0:5 to 3:2. This is ascribed to a large number of hydrophilic functional groups existing in SH. Further increase above this weight ratio of 3:2 is followed by a decrease in water absorbency. That is to say, an appropriate weight ratio of SH to MMT is required to achieve the best water absorbency, similar to that obtained from PAA/SH polymeric network [35]. This behaviour is attributed to the fact that SH is a collection of diverse, relatively low molecular mass components, and described as the supramolecular conformation in which the component molecules are intimately associated with each other, forming a dynamic association [36, 37]. This characteristic prevents it from further absorbency. Thus, a value of 3:2 of SH-to-MMT ratio is selected as the optimum, as a result of synergistic effect of MMT and SH. In addition, it is worthy pointing out that compared with composite when only 50 wt% MMT was introduced, the sample when only 50 wt% SH was introduced possesses higher water absorbency. Though SH was described as a big supramolecular structure, many hydrophilic groups (such as carboxylates and phenolic hydroxyls) were present. These hydrophilic groups can interact with PAA-AM copolymer, forming a perfect three-dimensional structured network, resulting in higher water absorbency. However, excess MMT particles can only act as the filler which would reduce the water absorbency remarkably.

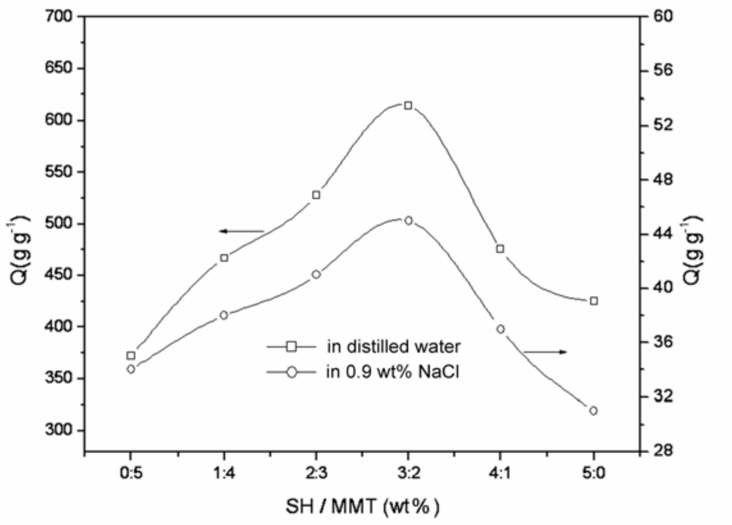

Fig. 10. Effect of relative weight ratio of SH to Ca-MMT on water absorbency for superabsorbent composite: reaction temperature, 80°C; 70% neutralization degree of AA; molar ratio of AA to AM is 1.2; weight ratio of crosslinker, initiator in the feed is 0.1, 0.6 wt%, respectively; the sum of SH and Ca-MMT is 50 wt%.

Swelling behavior in various cationic saline solutions

For practical applications in the fields of agriculture and horticulture, it is more important to know the swelling behaviours of a superabsorbent composite in various saline solutions. The kind of cation is the key factor influencing equilibrium water absorbency of the composite in the saline solutions [38]. Hence, the swelling behaviours of superabsorbent composite in three cationic saline solutions (NaCl, $CaCl_2$ and $FeCl_3$) were investigated and shown in Figs.11-13.

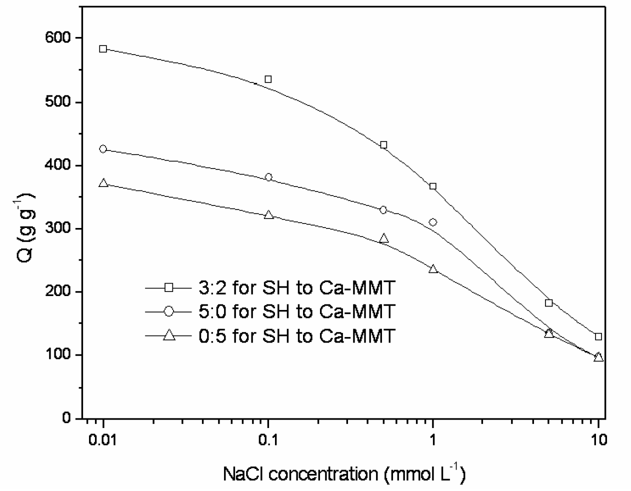

Fig. 11. Equilibrium water absorbency of superabsorbent composites in NaCl solutions with various concentrations.

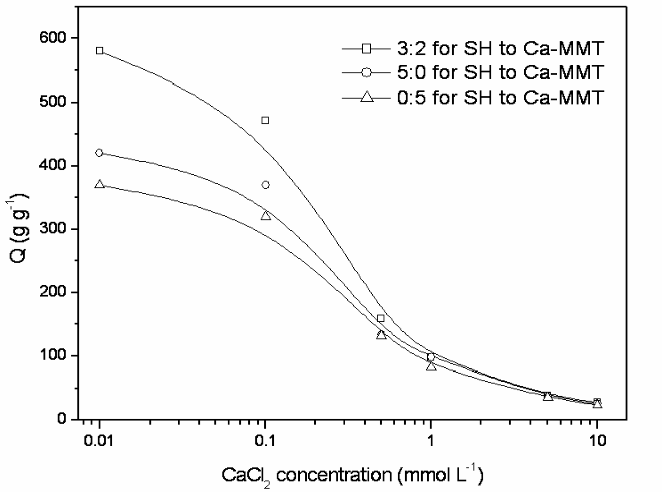

Fig. 12. Equilibrium water absorbency of superabsorbent composite in $CaCl_2$ solutions with various concentrations.

It is clear that at lower saline concentration (0.01 mmol L^{-1} for each saline solution), no obvious difference in water absorbency has been observed for all the superabsorbents. However, increasing the ionic strength of external solution for all the samples tested (>0.1 mmol L^{-1}), a monotonic decrease of the swelling ratio can be observed. This is explained by the fact that at high ionic strength, the expansion of the network decreases because of the screening effect of the ionic charges bound to the network and the decrease of osmotic pressure difference between the gel and the external solutions. This is a typical polyelectrolyte behaviour.

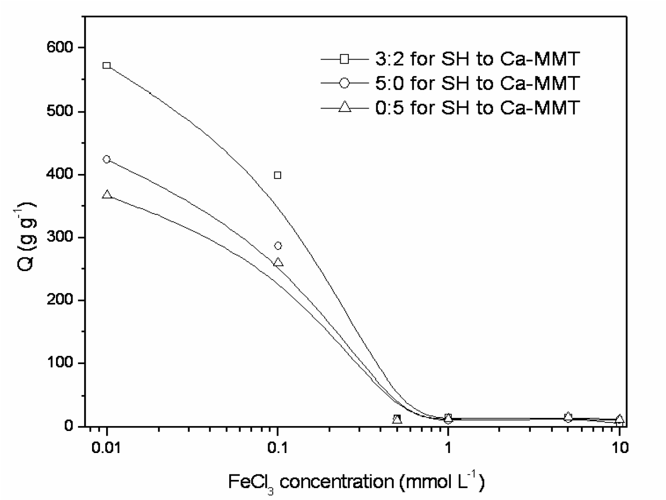

Fig. 13. Equilibrium water absorbency of superabsorbent composite in $FeCl_3$ solutions with various concentrations.

In addition, the swelling data indicate that the swelling capability decreases with higher charge of the cation (multivalent < univalent). That is on account of the coordination of multivalent Ca^{2+} and Fe^{3+} ions to carboxylate groups on the copolymer chains. Consequently, the crosslink density of the network increases, therefore leading to decrease in the water absorbency; similar studies have been performed by Pourjavadi et al [39]. This is further proved by the FTIR analysis, as shown in Fig. 14.

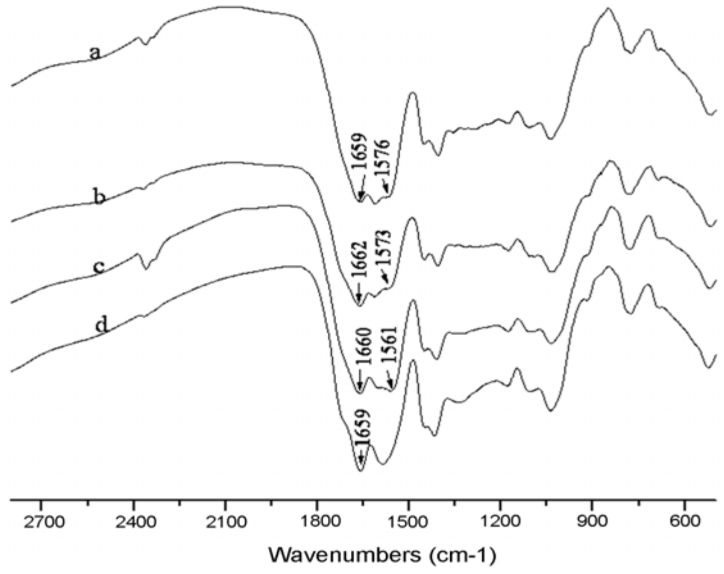

Fig. 14. FTIR spectra of (a) PAA-AM/MMT/SH, (b) PAA-AM/MMT/SH after swelling in 0.01 mmol L^{-1} $CaCl_2$ solution, (c) PAA-AM/MMT/SH after swelling in 10 mmol L^{-1} $CaCl_2$ solution, and (d) PAA-AM/MMT/SH after swelling in 10 mmol L^{-1} $FeCl_3$ solution.

The absorption band at 1659 cm^{-1} of $-CONH_2$ in the superabsorbent composite is almost unchangeable with an increase in Ca^{2+} concentration, while the absorption band of asymmetric vibration absorbency (v_{asCOO}) of $-COO^-$ in the superabsorbent composite has shifted from 1576 cm^{-1} to 1561 cm^{-1} with 10 mmol L^{-1} $CaCl_2$ solution and disappears with 10 mmol L^{-1} $FeCl_3$ solution, an indication of the formation of coordination bond of carboxylate with metals present in the cationic saline solutions [40]. Because the formation of coordination bond between carboxylate and metals will diminish the charge density on the carboxylate oxygen and thus decrease the force constant of it, which is responsible for the lower wave number shift of v_{asCOO}. It is worthy pointing out that the simultaneous introduction of Ca-MMT and SH can provide better salt-resistance property compared to that when only Ca-MMT or SH is involved.

Conclusions

In this study, a series of PAA-AM/MMT/SH superabsorbent composites were synthesized and the results suggested that the water absorbency was closely dependent on these variables: reaction temperature, amounts of MBA and APS, neutralization degree of AA, the molar ratio of AA to AM, and SH-to-MMT weight ratio. The final optimum conditions was composed of 0.1 wt% crosslinker, 0.6 wt% initiator, 70% neutralization degree, AA:AM=1.2 (molar ratio), SH:MMT=3:2 (weight ratio) at 80 ^{o}C. FTIR indicated that a graft reaction between SH, Ca-MMT and PAA-AM had taken place during the polymerization. XRD analysis showed that even when 50 wt% Ca-MMT was introduced into PAA-AM polymeric network, the characteristic peak at ca. $2\theta=5.92°$ which corresponds to a basal spacing of 1.494 nm could not be observed, suggesting that the clay platelets of Ca-MMT had been exfoliated during the polymerization and then were thoroughly dispersed in the polymer matrix, forming a composite structure. SEM showed that the simultaneous incorporation of SH and MMT into the composite resulted in an undulant and coarse surface, which was helpful for the water absorbency. In addition, the clay particles were more finely dispersed in the polymer matrix, consistent with the XRD analysis. TGA curves implied that the simultaneous introduction of SH and Ca-MMT into the polymeric network led to an increase in thermal stability of corresponding composite. Apart from an improved water absorbency in distilled water, simultaneous introduction of SH and MMT into the polymeric network was also helpful for the swelling capabilities in saline solutions. This developed superabsorbent material can be used as the water-managing materials with the multifunctional properties.

Experimental part

Materials

Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Acrylamide (AM, analytical grade, Beijing Chemical Factory, Beijing, China) was purified by recrystallization from benzene. The initiator, ammonium persulfate (APS, analytical grade, Tianjin Chemical Reagent Factory, Tianjin, China) was recrystallized from water. The crosslinker, N,N′-methylene-bisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. Sodium humate (SH, Shuanglong Ltd., Xinjiang, China) and calcium montmorillonite (Ca-MMT, Longfeng Montmorillonite Co., Shandong, China) were milled through a 320-

mesh screen prior to use. Other reagents used were all analytical grade and all solutions were prepared with distilled water.

Preparation of PAA-AM/ MMT/SH superabsorbent composite

A series of superabsorbent composites with different amounts of AA, AM, MMT and SH were prepared as follows. Typically, 3.55 g AM and 4.32 g AA with a partial neutralization degree (neutralized with 4 M sodium hydroxide solution in an ice bath) were introduced into 36 mL distilled water in a 250 mL four-neck flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. Under nitrogen atmosphere, the crosslinker MBA (15.9 mg) was added to above mixed solution and then the appropriate amounts of SH and MMT were dispersed. After stirring for 30 min, the mixture was heated to 50 ^{o}C gradually, and then the initiator APS (95.6 mg) was put into the flask. The solution was stirred vigorously at 80 ^{o}C for 3 h to complete the polymerization reaction. After polymerization, the resulting product was dried at 70 ^{o}C to a constant weight. The products were milled and all samples used for test had a particle size in the range of 40-80 mesh.

Measurement of water absorbency

A series of weighted dried samples (m_1) were immersed in excess distilled water or in different saline solutions at room temperature until swelling equilibrium was achieved. Swollen samples (m_2) were then separated from unabsorbed water by filtering with 100-mesh stainless screen and hanging up for 10 min. The equilibrium swelling ratio (Q) was then calculated from the following equation:

$$Q = (m_2 - m_1) / m_1 \qquad (1)$$

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

Characterization of the superabsorbent composite

FTIR spectra were recorded on a FT-IR (Thermo Nicolet NEXUS TM, KBr pellets) in the range of 4000 cm^{-1}-400 cm^{-1}. XRD patterns were obtained from an X′Pert PRO diffractometer (CuKα radiation, 40 kV, 30 mA). SEM studies were carried out in a JSM-5600LV SEM instrument (JEOL, Ltd.) after coating the sample with gold film. Thermal stability studies were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer, in the temperature range of 25-800 ^{o}C at a heating rate of 10 ^{o}C/min using dry nitrogen purge at a flow rate of 50 mL/min.

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