Preparation of a Kaolinite–Poly(acrylic acid acrylamide) Water Superabsorbent by Photopolymerization

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ABSTRACT: A novel kaolinite–poly(acrylic acid acrylamide) water superabsorbent with a water absorbency and salt solution absorbency of 433 and 108 g/g, respectively, was successfully synthesized by the photopolymerization of acrylic acid with acrylamide in the presence of kaolinite powder under 30 min of ultraviolet irradiation at room temperature. The results showed a synergetic effect of the mixed photoinitiators (Michler's ketone and benzophenone) on the water absorbency, and the incorporation of less than 10 wt % kaolinite into the water superabsorbent slightly improved the water absorbency and salt solution absorbency and obviously upgraded the water retention, as demonstrated by retention testing as well as thermogravimetric analysis and differential scanning calorimetry. Fourier transform infrared spectroscopy verified the structure of the kaolinite composite superabsorbent. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2875–2881, 2006

Key words: clay; composites; crosslinking; differential scanning calorimetry (DSC); irradiation

INTRODUCTION

Superabsorbents are loosely crosslinked networks of hydrophilic polymers with a high capacity for water uptake in a short time and high water retention under pressure. Therefore, superabsorbent polymers have great advantages over traditional water-absorbing materials, such as cotton, pulp, and sponges, and they are widely used in many specialized applications, such as hygienic products, horticulture, agriculture, sealing, drug-delivery systems, and coal dehydration. Recently, much attention has been paid to mineral powders for mineral composite superabsorbents, such as kaolinite,[1] montmorillonite,[2–6] mica,[7] bentonite,[8] and sercite,[9] mainly because the incorporation of these mineral powders can not only reduce the cost but also improve the properties (e.g., the swelling ability, gel strength, and mechanical and thermal stability) of superabsorbents.

Ultraviolet (UV) curing can rapidly polymerize functional monomers and oligomers into a solidified polymeric coating at the ambient temperature. Compared with time-consuming thermally induced polymerization, UV curing is extremely fast and time-saving. Besides, the reaction at the ambient temperature makes the process easy to set up, and the energy cost is significantly reduced. Moreover, UV curing is a solvent-free process. A large amount of a toxic solvent is avoided. This brings great advantages over the solvent-based drying of polymer solutions to solidify coatings in terms of environmental protection and material cost.

Kaoline, called porcelain clay, is a well-known natural layered silicate and is mainly composed of kaolinite, whose structural unit consists of one Si—O tetrahedral layer and one Al—O octahedral layer. The intercrystal layers of kaolinite have weak interaction forces, such as hydrogen linkages or van der Waals forces, which result in a structure of stacked and layered silicates of kaolinite and easy penetration for water or other polar molecules into the interlayer galleries. On the other hand, superfine kaolinite powder has many hydroxyl groups and active points, such as the permanent charge, changeable charge, and exchangeable cations, that can react with a high-water-absorption resin and form networks. However, to the best of our knowledge, most of the reported clay composite superabsorbents involve thermally induced polymerization,[1–4,6–8] and there is no publication reporting the preparation of a kaolinite composite superabsorbent by UV-induced polymerization. In this article, the preparation of a kaolinite composite superabsorbent consisting of poly(acrylic acid acrylamide) and kaolinite, synthesized by photopolymerization, with Michler's ketone (MK) and benzophenone (BP) as the photoinitiators and N,N-methylene bisacrylamide (MBA) as the crosslinker, with a water absorbency and salt solution absorbency of 433 and 108 g/g, respectively, is presented, and the

photopolymerization mechanisms are preliminarily discussed.

EXPERIMENTAL

Materials

Acrylic acid (AA; analytical-grade) was purified by distillation *in vacuo*, and acrylamide (AM; analytical-grade) was purified by recrystallization from benzene. MBA (chemical-grade) was used as purchased, MK and BP (chemical-grade) were used without further treatment, and kaolinite (particle size = 50–200 mesh) was used without further purification.

Preparation of the kaolinite–poly(acrylic acid acrylamide) water superabsorbent by photopolymerization

Sodium acrylate was prepared by the partial neutralization of a diluted AA solution with a predetermined amount of a 30 wt % aqueous sodium hydroxide solution, which was added dropwise under an ice bath, after which 30 wt % AM, 0.02 wt % MBA, and 10 wt % kaolinite were added to the solution. The obtained suspension was mixed by a magnetic stirrer for 1 h. Finally, mixed photoinitiators MK and BP (2 wt % with respect to the total monomer weight) were added to the obtained suspension. Photopolymerization was achieved by the irradiation of the suspension with a high-pressure mercury lamp (500 W) at room temperature. After about 30 min of irradiation, the kaolinite composite water superabsorbent was obtained, and it was washed with ethanol, desiccated in an oven for several hours, and finally smashed into a fine powder for use.

Determination of the water absorbency with the filtration method

Approximately 20–30 mg of dried superabsorbents was dispersed in 100 mL of deionized water for 60 min to achieve the swelling equilibrium. Then, excess water was allowed to drain through a 200-mesh screen. The weight of the superabsorbent containing absorbed water was measured after it drained for 1 h, and the water absorbency was calculated according to the following equation:

$$\text{Water absorbency (g/g)} = (W_2 - W_1)/W_1 \quad (1)$$

where W_1 and W_2 are the weight of the dry and swollen superabsorbents, respectively.

Determination of the water retention

The water retention was determined by the weighing of the mass of the water-swollen gel before (m_1) and after (m_2) centrifugation at 4000 rpm for 120 min or heating at 60°C for 40 h in an air oven. The water retention

of the sample was calculated as follows:

$$\text{Water retention (\%)} = m_2/m_1 \times 100\%$$

Characterization of the water superabsorbent

Fourier transform infrared (FTIR) spectroscopy was carried out on a PerkinElmer 1750 spectrophotometer (Boston, Massachusetts), equipped with an Epson Endeavour II data station. The samples were prepared as KBr pellets or as liquid films interposed between KBr discs. Differential scanning calorimetry (DSC) of the resins was measured on a PerkinElmer DSC-7 instrument (Norwalk, Connecticut). The temperature program was 10.0 K/min from 0 to 600°C, and the amount of the sample was about 5–15 mg under an atmosphere of N_2. Thermogravimetric analysis (TGA) of the resins was measured on a Dupont 2100 instrument (Wilmington, Delaware). The temperature program was 10.0 K/min from 20 to 600°C, and the amount of the sample was about 48–60 mg under an atmosphere of N_2.

RESULTS AND DISCUSSION

Effect of the photoinitiator type on the swelling equilibrium

Figure 1 shows the variation of the water absorbency of the 10% kaolinite composite superabsorbent with various amounts of photoinitiators MK and BP. The water absorbency increases with increasing irradiation time up to around 30 min, after which the water absorbency levels off. These results indicate that a superabsorbent with a water absorbency of 320–433 g/g can be produced even in the presence of 10% kaolinite powder at the optimum irradiation time of 30 min.

Above all, the mixed photoinitiators MK and BP show a higher water absorbency than a pure MK pho-
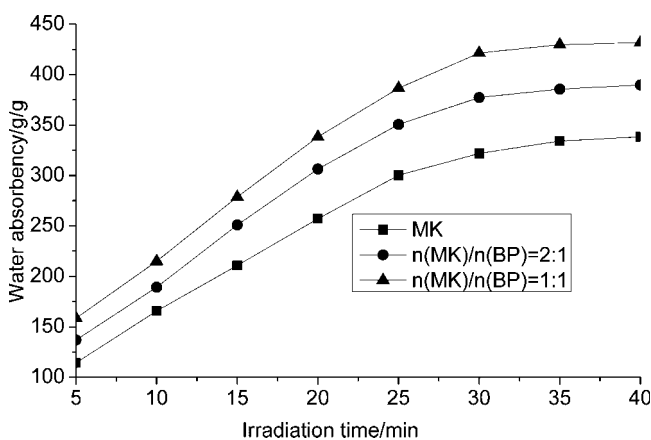

Figure 1 Effects of the photoinitiator type and irradiation time on the water absorbency of the 10 wt % kaolinite composite superabsorbent.
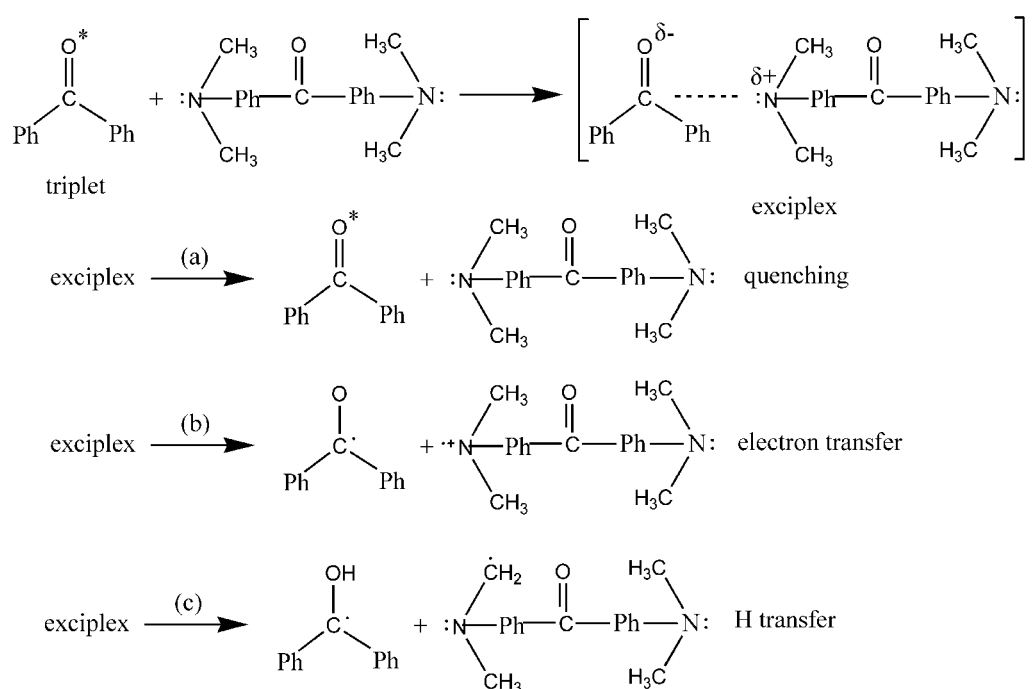
Figure 2 Possible interactions between MK and BP during photopolymerization.

toinitiator system, indicating a synergetic effect of photoinitiators MK and BP on the water absorbency.

Amines are known to participate in redox-initiation and chain-transfer reactions of radical polymerization. Tertiary amines are good synergists in photoinitiation with BP[10–12], and amines are also used as oxygen captors in photocuring formulations to eliminate the oxygen-inhibition effect.

A synergetic effect of the MK–BP complex photoinitiator can be explained by hydrogen transfer through the rapid formation of an excited-state complex (exciplex) between the amine of MK and triplet ketone of BP,[12] leading to the formation of a very active amino alkyl free radical capable of photoinitiating further polymerization processes, as shown in Figure 2. The facility of complex formation between the triplet ketone and amine of MK can be attributed to charge-transfer stabilization, which is due to the relatively low ionization potential of amines.[10]

Effect of the photoinitiator content on the swelling equilibrium

Figure 3 shows the effect of the photoinitiator content on the water absorbency of the superabsorbent composite. The water absorbency increases as the photoinitiator concentration rises from 0.5 to 1.5% but decreases with a further increase in the concentration of the photoinitiator. With an increase in the photoinitiator concentration, the molecular weight of the macromolecules decreases, and the relative concentration of polymer chain ends increases. As mentioned in a previous

study,[13] the polymer chain ends do not contribute to the water absorbency. Therefore, the water absorbency decreases with increasing photoinitiator content. Besides, the use of high concentrations of photoinitiators with strong absorption in a photopolymerization system leads to a screening of the bottom layers of the coating from UV light. Most of the incident radiation is absorbed in the surface region, and insufficient light reaches the deeper lying layers of the film. Therefore, the water absorbency decreases. However, when the concentration of the photoinitiator is below the optimum value of 1.5 wt %, the swelling capacity of the superabsorbent composite also decreases. This may due to a decrease in the number of radicals produced
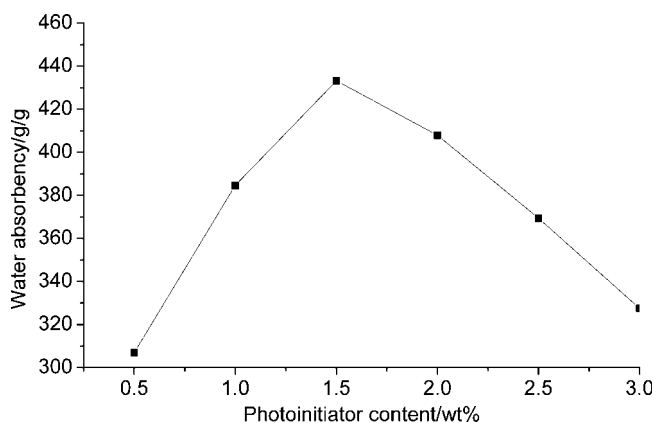

Figure 3 Effect of the photoinitiator content on the water absorbency of the superabsorbent composite in distilled water [kaolinite concentration = 10 wt %, $n(MK)/n(BP) = 1/1$].
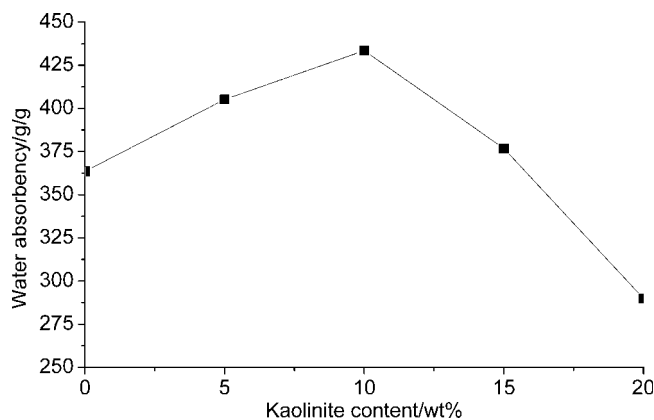
Figure 4 Effect of the kaolinite content on the water absorbency of the superabsorbent composite in distilled water [n(MK)/n(BP) = 1/1].

by the photoinitiator, and a small number of radicals cannot guarantee the rapid crosslinking reaction by photopolymerization. Therefore, the network cannot be formed efficiently during photopolymerization, and the water absorbency decreases.[14]

Effect of the kaolinite content on the water absorbency

Kaolinite powder as network points plays an important role in the formation of the composite superabsorbent. When the concentration of kaoline is suitable (< 10%), the crosslinkage density and network space of the composite are unchanged (or just change a little),[15,16] and the water absorbency slightly increases with an increase in the concentration of kaolinite. However, with larger concentrations of kaolinite (> 15%), a composite superabsorbent with a higher crosslinkage density[17,18] is formed, and this leads to more difficult absorption to water and a reduction of the water absorbency. Besides, with an increase in the
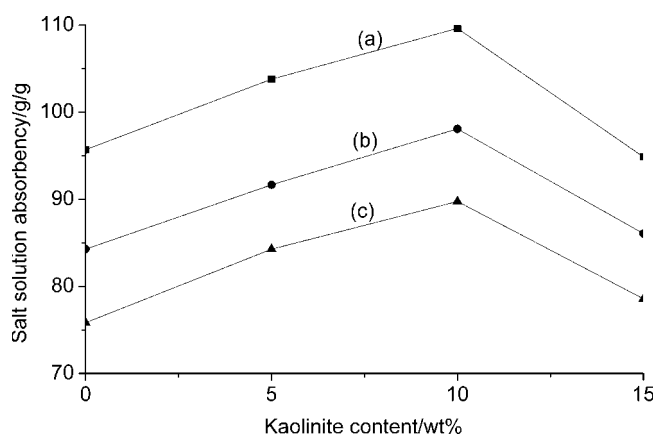
concentration of kaolinite, the degree of reflection and scattering of the incident light is much higher because of kaolinite particles suspended in the reaction systems, so the polymerization rate might decrease on account of the substantial attenuation of the UV light. Therefore, the greater the kaolinite concentration is, the slower the photopolymerization rate is , and the lower the water absorbency is.

Effect of the saline solution and kaolinite content on the water absorbency of the superabsorbent composite

Because of the great impact of external saline solutions on the swelling behaviors of kaolinite superabsorbent composites and the expansion of their applications, especially for oil and gas exploitation and horticulture, the effects of saline solutions [NaCl (aqueous), CaCl$_2$ (aqueous), and FeCl$_3$ (aqueous)] on the water absorbency of superabsorbent composites with different concentrations of kaolinite are shown in Figure 5. The effect of the ionic strength of the external solution on the swelling has been 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. According to eq. (2), the water absorbency of the superabsorbent decreases with an increase in the ionic strength of the external solution. This decrease in the water absorbency with increasing ionic strength can be attributed to the decrease in the osmotic pressure difference between the superabsorbent composite and the external saline solution. As shown in Figure 5, for a given concentration of the salt solution, the water absorbency in the
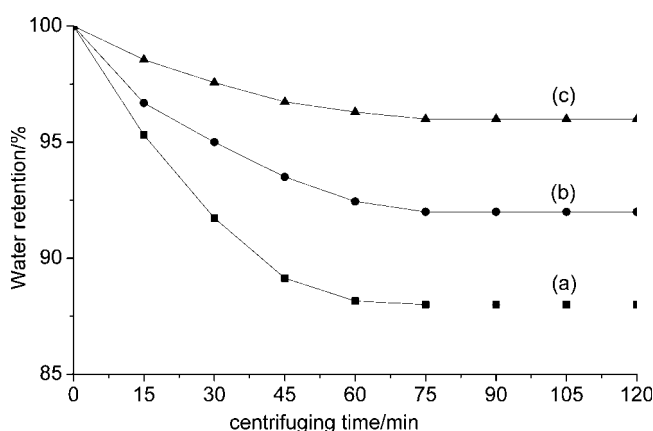

Figure 5 Salt solution absorbency as a function of the kaolinite content: (a) 0.9% NaCl, (b) 0.9%CaCl$_2$, and (c) 0.9% FeCl$_3$.

Figure 6 Water retention as a function of the centrifugation time and kaolinite content at 4000 rpm: (a) 0, (b) 5, and (c) 10% kaolinite.
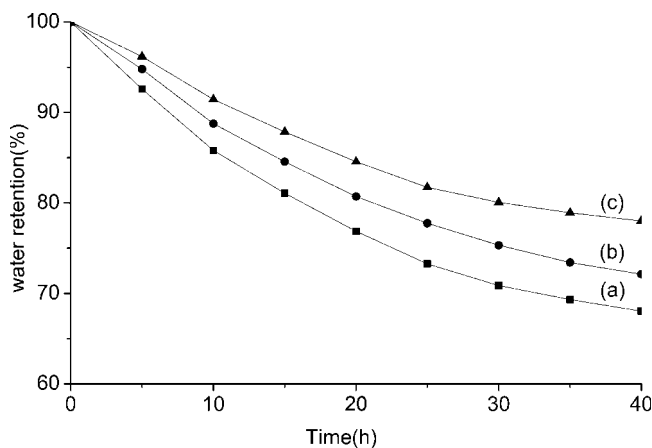
Figure 7 Water-retention capacity of (a) the pure super-absorbent, (b) the 5 wt % kaolinite composite superabsorbent, and (c) the 10 wt % kaolinite composite superabsorbent at 60°C.

NaCl solution is far higher than that in the $CaCl_2$ and $FeCl_3$ solutions. This dramatic decrease in the water absorbency in multivalent cationic solutions may be due to the fact that the complexing ability of the carboxylate groups can induce the formation of intramolecular and intermolecular complexes with divalent and trivalent cations (e.g., Ca^{2+} and Fe^{3+}), which result in an increase in the crosslink density of the network.[20,21] Besides, the complexing ability of carboxylate groups to these three cations is in the order of $Na^+ < Ca^{2+} < Fe^{3+}$. Therefore, the water absorbencies for these three superabsorbents decrease in the order of NaCl (aqueous) > $CaCl_2$ (aqueous) > $FeCl_3$ (aqueous).

Above all, the kaolinite composite superabsorbents with less than 10% kaolinite show enhanced salt solution absorbency. This indicates that the incorporation of a suitable amount of kaolinite can upgrade the salt solution absorbency, which may be used for oil and gas exploitation, for which a high degree of ionic strength exists.
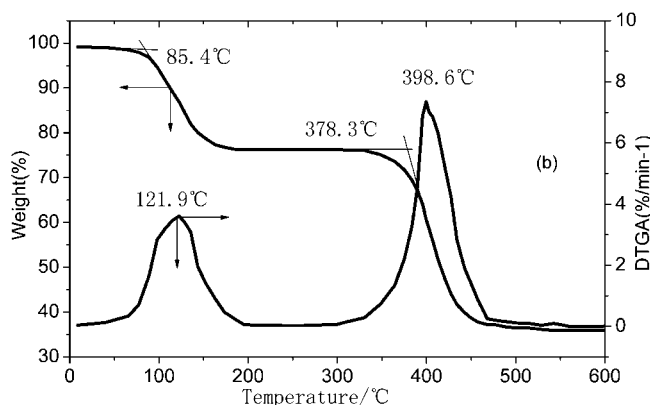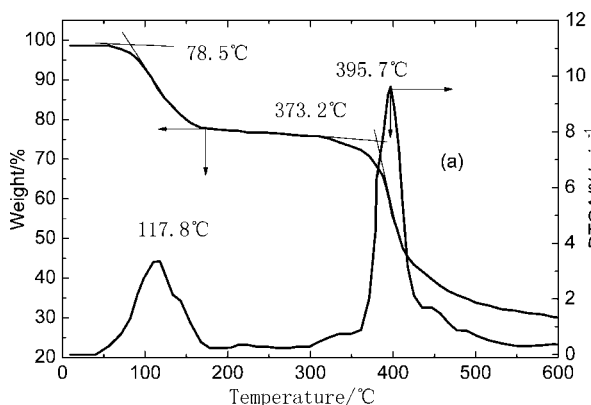
Water-retention test

The water retention of the swollen superabsorbent composite was determined by centrifugation at 4000 rpm for 120 min. Figure 6 shows that the swollen superabsorbent composite samples had enhanced water retention, from 88 to 96%, with an increase in the concentration of kaolinite from 0 to 10%. This indicates that the 10 wt % kaolinite composite superabsorbent exhibits better water retention when applied with an external force, such as centrifugal force. These results show that the composite superabsorbent has excellent comprehensive absorbency properties and may prove useful in oil and gas exploitation.

Some of the most important applications of water superabsorbents are agricultural and horticultural applications, especially the effective utilization of water in dry and desert regions (i.e., to transform dry and desert regions into green, fertile land). The water-retention capacity of the water superabsorbent was determined at 60°C in a hot-air oven. The results are presented in Figure 7. The superabsorbents without and with 10% kaolinite show decreasing trends of water retention with prolonged heating times, with about 68 and 77% distilled water, respectively, maintained at 60°C after 40 h of water-retention testing. However, the kaolinite composite superabsorbent has a better water-retention capacity at higher temperatures than the pure superabsorbent. This can be attributed to kaolinite powders acting as physical crosslinks, thus increasing the network rigidity, making the network difficult to stretch at higher temperatures, and therefore decreasing the dewatering rate.

Thermal stability of the water superabsorbent composite

The water retention of the kaolinite composite water superabsorbent was evaluated with the TGA technique in a programmed heating process (10°C/min). The

Figure 8 TGA and derivative of thermogravimetric analysis (DTGA) curves of (a) the poly(acrylic acid acrylamide) superabsorbent and (b) the superabsorbent containing 10 wt % kaolinite.

results are shown in Figure 8. From the differential curves of TGA, the temperature of the maximum mass loss rate (T_{max}) and the dehydrating onset temperature (T_{onset}) are considered parameters for the estimation of the thermal water retention.

An enhanced thermal water retention of the water superabsorbent can be achieved by the addition of some kaolinite to the superabsorbent. As shown in Figure 8, T_{onset} of the 10 wt % kaolinite composite superabsorbent increases from 78.5 to 85.4°C, and T_{max} increases from 117.8 to 121.9°C, in comparison with those of the pure superabsorbent without kaolinite. The results indicate that the introduction of kaolinite into the polymer network results in an increase in the thermal stability. This phenomenon may be due to the fact that the kaolinite particles increase the network rigidity and restrain the movement of the absorbed water embedded in the network; thus, it needs much more energy to dehydrate at higher temperatures. Besides, the kaolinite particles in the network can act as heat barriers and therefore enhance the overall thermal stability of the composite.

Figure 9 shows the DSC spectra of the 10% kaolinite composite superabsorbent and pure superabsorbent. The 10% kaolinite composite superabsorbent shows an endothermic peak at 122.5°C, whereas the superabsorbent without kaolinite shows an endothermic peak at 117.8°C. This also indicates that the incorporation of kaolinite into the superabsorbent can prominently improve the water-retention capacity.

FTIR spectrum of the kaolinite composite water superabsorbent

The FTIR spectrum in the range of 4000–400 cm^{-1} for the 15 wt % kaolinite composite superabsorbent is shown in Figure 10. The absorption peaks at 3699, 3620, and 915 cm^{-1} contribute to the OH group on kaolinite powders. Besides the characteristic peaks of the
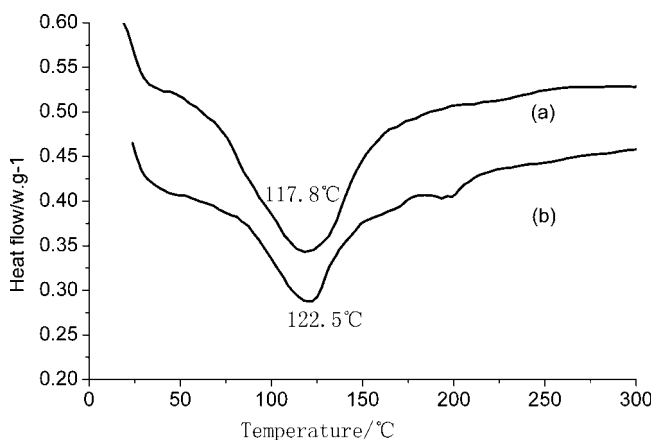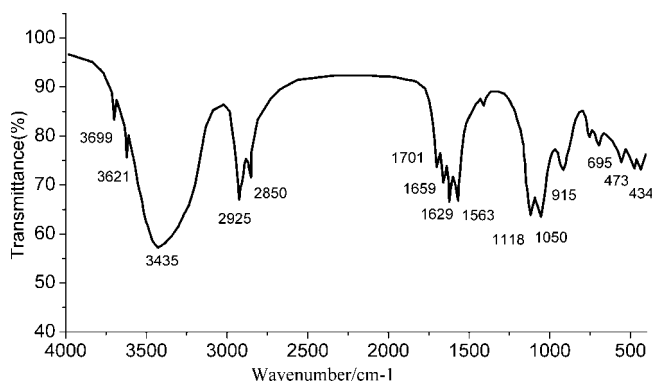

Figure 10 FTIR spectrum of the superabsorbent containing 15 wt % kaolinite.

kaolinite, the bands at 3435 cm^{-1} are the OH and NH stretching frequencies, and the bands at 2850 and 2925 cm^{-1} correspond to the symmetrical and asymmetrical ones for methene, respectively. Furthermore, the spectrum also shows peaks at 1701 and 1659 cm^{-1}, which correspond to the carbonyl group of the acid moiety of the AA unit and the amide moiety of the AM unit, respectively, and the peaks at 1629 and 1563 cm^{-1} are the carboxylates of the sodium acrylate. This FTIR analysis indicates that all the monomeric units—AM, sodium acrylate, and AA—are incorporated into the copolymer backbone.

CONCLUSIONS

Novel superabsorbent composites of crosslinked poly (acrylic acid acrylamide) and kaolinite were prepared in an aqueous solution by the photopolymerization reaction of AA and AM on kaolinite powders with MBA as a crosslinker and MA and BP as mixed photoinitiators. Under our experimental conditions, a crosslinked poly(acrylic acid acrylamide)–kaolinite superabsorbent composite with a water absorbency of 433 g of H_2O/g was synthesized, and it had a composition of 0.02 wt % crosslinker, 1.5 wt % mixed photoinitiators, and 10 wt % kaolinite. The FTIR spectrum indicated that all the monomeric units as well as the kaolinite were incorporated into the composite superabsorbent. Moreover, the kaolinite composite superabsorbent was characterized by improved water retention and enhanced salt water absorbency and might be especially useful in agricultural, horticultural, and oil and gas exploitation applications.

Figure 9 DSC curves of (a) the poly(acrylic acid acrylamide) superabsorbent and (b) the superabsorbent containing 10 wt % kaolinite.

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