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Study on starch-*graft*-acrylamide/mineral powder superabsorbent composite

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Abstract

A novel starch-*graft*-acrylamide/mineral powder superabsorbent composite with water absorbency about 4000 times is synthesized by graft-copolymerization reaction among acrylamide, potato starch and mineral ultrafinepowder, followed by hydrolysis with sodium hydroxide. It is found that the composite doped with kaolinite powder possess higher water absorbency than those doped with bentonite or sercite powder, since the kaolinite powder can moderately disperse in the water and cross-link with acrylamide and starch. By controlling the amount of NaOH and reaction time during saponification process, the hydrophilic groups on the composite can be adjusted, it is found that the collaborative absorbent effect of $-\mathrm{CONH_2}$, $-\mathrm{COONa}$ and $-\mathrm{COOH}$ groups is superior to that of single $-\mathrm{CONH_2}$, $-\mathrm{COONa}$ or $-\mathrm{COOH}$ group. By the IR characterization, the polymerization reaction mechanism and structure of the composite is supposed, the mineral ultrafinepowder as a cross-linking point play an important role in the formation of network structure of the superabsorbent composite.

Keywords: Water superabsorbent; Poly-acrylamide multicomponent composite; Graft-copolymerization

1. Introduction

Superabsorbents can absorb a large amount of water compared with general water absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, superabsorbents has raised a considerable interests and researches, and has been used in health, agriculture and horticulture [1–4] since the first superabsorbent polymer was reported by the US Department of Agriculture in 1969 [5].

Starch-*graft*-acrylamide polymer is one of the superabsorbents with the highest water absorbency, but the polymer with higher production cost and lower gel strength restrict its application widely. Minerals are a layered aluminium silicate with exchangeable cations and reactive OH groups on the surface. It is expected that the type and amount of hydrophilic groups, as well as the network structure of the superabsorbents are improved by graft-copolymering reaction among the acrylamide polymer, starch and mineral ultrafine powder. Consequently, comprehensive absorbent properties of superabsorbents are enhanced and the production cost of superabsorbents is reduced [6,7]. In this paper, a novel starch-*graft*-acrylamide/mineral powder superabsorbent composite with water absorbency about 4000 times is synthesized. The influence of mineral powder, cross-linker, initiator, polymerization and saponification process on absorbent properties is discussed in this paper.

2. Experimental part

2.1. Preparation of sample

Mineral bentonite, kaolinite and sercite ultrafinepowder was made by ultrafinecrashing the mineral micropowders which came from Zhejian Ninan Bentonite Factory, Fujian Tongan Kaolinite Factory and Fujian Nanan Sercite Factory, China, respectively. The surface area of the mineral ultrafinepowder was more than $100\ \mathrm{m^2\ g^{-1}}$ and the size of that was less than 1×10^{-6} m.

Starch-*graft*-acrylamide/mineral powder superabsorbent composite was synthesized according to the following steps.

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A mixed solution of acrylamide monomer, cross-linker and mineral ultrafinepowder was made by agitating acrylamide monomer (20 g), cross-linker (*N*,*N*′-methylene-bis-acrylamide) (0.09 g), distilled water (40 ml) and mineral ultrafinepowder (3 g) at ambient temperature. In a four-neck round-bottom flask equipped with a mechanical stirrer, condenser, thermometer and nitrogen line, dried potato starch (6 g) was dispersed in distilled water (70 ml). After purging with nitrogen for 20 min to remove the dissolved oxygen from the solution, the starch solution was heated to 80 °C in a water bath for 10 min under stirring to form starch slurry. The initiator ceric ammonium nitrate was added (0.2 mol l^{-1}, 5 ml) to the starch slurry and allowed to react at 60 °C for 10 min. When the starch slurry changed its color from orange to yellow, the acrylamide-cross-linker-mineral powder mixed solution was added, and the reaction mixture was stirred for 2 h to ensure the completion of graft-copolymerization. A nitrogen atmosphere was maintained throughout the reaction period. The grafted-copolymer was transferred to a sodium hydroxide solution (1 mol l^{-1}) and allowed to saponification react at approximately 90 °C for 2 h.

The saponified product was filtered and washed with distilled water some times to remove any ungrafted molecules, monomer and base until the solution pH = 7. The washed product was dehydrated with methanol and residual methanol was removed with anhydrous ethanol. The dehydrated specimen was vacuum dried at 60 °C until the weight of the specimen was constant. After being ground and then filtered through an 80-mesh screen, a powdered superabsorbent composite was obtained.

2.2. Measurement of water absorbency

A powdered superabsorbent composite (0.1 g) was immersed in distilled water (1000 ml) for at least 8 h at ambient temperature to reach swelling equilibrium, which resulted in the absorption of water inside the network of the composite and the formation of swelled sample. The residual water was removed by filtrating with 80-mesh stainless steel screen and hanging up for 25 min.

The water absorbency (Q_{H_2O}) of superabsorbent composite was determined by weighing the weight of the swelled sample after centrifuging at 4000 rpm for 60 min. The Q_{H_2O} of sample was calculated according to the Eq. (1).

$$Q_{H_2O} = \frac{\text{wt.(swelled sample)} - \text{wt.(dried sample)}}{\text{wt.(dried sample)}} \qquad (1)$$

2.3. Measurement of hydrophilic group

In some extent, R−COONa is a weak alkali, −COONa group amount in the composite can be measured by titrating with stronger acid HCl. A composite sample (0.5 g) was weighed and put into a NaCl saturation solution (to ensure R−COONa ionizes completely [8]), then drips HCl standard solution into the sample solution slowly, and the titration end point was judged by potentiometer. The molar percentage of −COONa in the sample was calculated by following equation.

$$-\text{COONa (mol\%)} = \frac{C_{HCl} \times V_{HCl} \times 71}{W_{sample}} \times 100\% \qquad (2)$$

The −COONa group amount in sample also can be determined with a Perkin Elemer 1100-B atomic absorption spectrophotometer. After equilibrium in water, the swelled sample was dried to constant weight and heated to 700−800 °C. The residue was dissolved in dilute aqueous HCl, and the emission spectrum from Na atom was recorded and converted to the Na weight fraction in the sample. This quantity is used to calculate the molar percentage of −COONa group in the sample.

The −COOH group in the composite can be neutralized by NaOH and its amount can be measured by electrochemistry method. A sample (0.5 g) was immersed in overweight NaOH solution for 24 h to allow −COOH group transfer to −COONa group completely.

The residual NaOH was titrated by using HCl standard solution and the end point of the neutralization reaction was judged by potentiometer. The molar percentage of −COOH in the sample was calculated according to the Eq. (3).

$$-\text{COOH (mol\%)} = \frac{(C_{NaOH} \times V_{NaOH} - C_{HCl} \times V_{HCl}) \times 71}{W_{sample}} \times 100\% \qquad (3)$$

It is difficult to directly measure the percentage of $-CONH_2$ group in the composite, $-CONH_2$ group can be measured by transferring $-CONH_2$ group to −COONa group according to the reaction (4). A sample (0.5 g) was put into an overweight NaOH solution and was heated up to 95 °C for 4 h, then the solution is boiled to ensure the following reaction takes place and the NH_3 was removed completely.

$$R - CONH_2 + NaOH \xrightarrow{95\ ^\circ C,\ 4\ h} R - COONa + NH_3\uparrow \qquad (4)$$

The boiled solution was cooled and titrated with standard HCl solution. Meanwhile, a blank test (without heating 95 °C and boiling) was done. The molar percentage of $-CONH_2$ group in the sample was calculated according to the Eq. (5):

$$-\mathrm{CONH_2}(\mathrm{mol\%}) = \frac{(C_{\mathrm{NaOH}} \times V_{\mathrm{NaOH}} - C_{\mathrm{HCl}} \times V_{\mathrm{HCl}} - C_{\mathrm{blank}} \times V_{\mathrm{blank}}) \times 71}{W_{\mathrm{sample}}} \times 100\% \qquad (5)$$

3. Results and discussion

3.1. The influence of mineral powder on the water absorbency of superabsorbent composites

The type of mineral powder is an important factor affecting absorbent properties of the composite. Superabsorbent composites filled with bentonite, kaolinite and sercite ultrafinepowder were prepared, respectively, under the same conditions and compositions: 10 wt% mineral powder, 20 wt% potato starch, 68 wt% acrylamide monomer, 1.5 wt% initiator and 0.03 wt% cross-linker. The water absorbency ($Q_{\mathrm{H_2O}}$) of the three types of superabsorbant composites was measured and is shown in Fig. 1.

According to Fig. 1, the $Q_{\mathrm{H_2O}}$ of the composite doped kaolinite is the highest, that of doped bentonite is lower and that of doped sercite is the lowest in the three types of superabsorbent composites. This is maybe due to the fact that the hydration and distension of bentonite powder is larger than those of kaolinite and sercite. Bentonite powder dissolves more easily and produces much more particulates in water than kaolinite and sercite powder do. The cross-linkage density of the composite doped bentonite powder is larger than that of doped kaolinite and sercite powder. Larger cross-linkage density of a composite means not enough space for water molecules to enter the network, which results in the smaller $Q_{\mathrm{H_2O}}$ of the composite-doped bentonite. On the other hand, the hydration and distension of sercite is the smallest. Here the graft-copolymerization activity of sercite with starch is the lowest, the absorption action of starch and acrylamide groups do not be realized effectively, which leads to the lowest $Q_{\mathrm{H_2O}}$ value for the composites doped sercite powder.

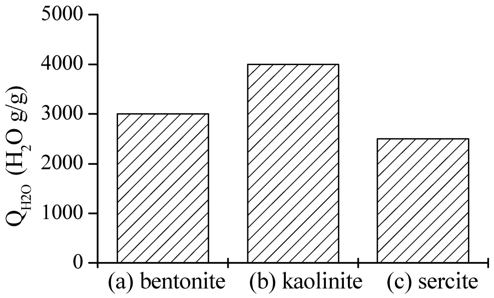


Fig. 1. Variation of $Q_{\mathrm{H_2O}}$ with (a) bentonite, (b) kaonite and (c) sercite for starch-*graft*-acrylamide/clay composites under preparation condition of clay 10%, potato starch 20%.

The amount of mineral powder in the superabsorbent composites is another factor affecting water absorbency. As an example, the influence of the amount of kaolinite powder in the composites on the water absorbency ($Q_{\mathrm{H_2O}}$) is shown in Fig. 2. It can be seen that the $Q_{\mathrm{H_2O}}$ changes the most in the range of 0−20 wt% kaolinite. Beyond a kaolinite concentration of 20 wt%, $Q_{\mathrm{H_2O}}$ decreases.

Supposed kaolinite particle as a cross-linking point exist in the superabsorbent composite, when the amount of kaolinite is suitable, such as amounts of 0−20 wt%, the cross-linkage density and network space of the composite unchanged (or just changes a little), and $Q_{\mathrm{H_2O}}$ of the composite is constant. But with larger amounts of kaolinite (larger than 20 wt%), composite with higher cross-linkage density are formed which lead to a more difficult permeation of water into the composite network. Thereby, $Q_{\mathrm{H_2O}}$ of the composite decreases.

3.2. The influence of cross-linker and initiator on the water absorbency of superabsorbent composites

The influence of the amount of the cross-linker on the water absorbency ($Q_{\mathrm{H_2O}}$) is shown in Fig. 3. It is obvious that $Q_{\mathrm{H_2O}}$ sharply increases with decrease of the cross-linker amount in the range of 0.3−0.02 wt%. Beyond a cross-linker amount of 0.02 wt%, $Q_{\mathrm{H_2O}}$ cannot be measured. Clearly, a higher concentration of cross-linker produces a larger number of growing polymer chains, which are in turn involved in generating an additional network. Thereby, $Q_{\mathrm{H_2O}}$ decreases with an increase in the cross-linker concentration because the network space gets diminished, and less water enters the composite. This tendency is similar to that found for other superabsorbents prepared by ourselves [7] and other groups [8,9].

On the other hand, when the concentration of the cross-linker is lower than 0.02 wt%, the copolymerization reaction between starch molecules and acrylamide monomer

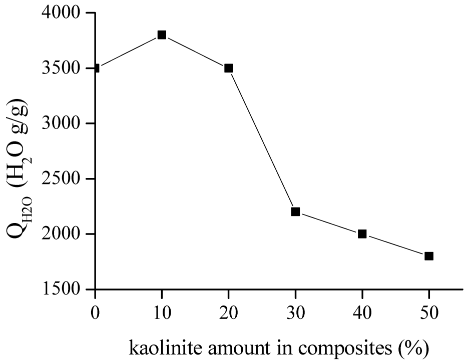


Fig. 2. Variation of $Q_{\mathrm{H_2O}}$ with kaolinite amount for starch-*graft*-acrylamide/kaolinite composites under preparation condition of the amount ratio of acrylamide monomer/potato starch 3:1, initiator 1.5% and cross-linker 0.03%.

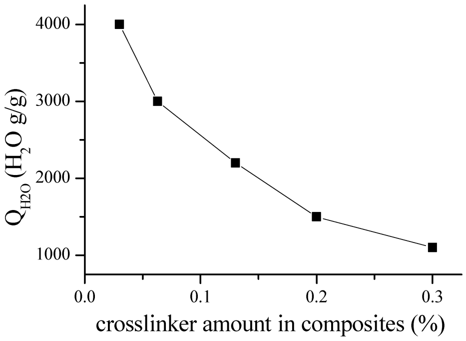


Fig. 3. Variation of Q_{H_2O} with cross-linker amount for starch-*graft*-acrylamide/kaolinite composites under preparation condition of kaolinite 10%, potato starch 20%, acrylamide monomer 68% and initiator 1.5%.

does not occur effectively. In this case, the cross-linkage network cannot form, since starch and acrylamide exist as monomer or low-molecular weight polymers. Such samples represent sol – gel-states in water, and water cannot be tie in the network. In spite of a high absorbency for acrylamide or starch monomer, Q_{H_2O} of the sample cannot be measured. In our experimental conditions, the concentration of the cross-linker should be higher than 0.02 wt%.

The amount of initiator also affects the graft-polymerization reaction course, which results in the change of water absorbency of the composites. From Fig. 4, when the concentration of the initiator is lower than 1.5 wt%, the graft-polymerization reaction is the slower, the polymer network is the fewer and water absorbency is the lower under the same reaction condition. On the other hands, the higher concentration of initiator agent, such as more than 1.5 wt%, means the faster reaction velocity and the smaller polymer network space, which lead to the decrease of the water absorbency of the composites.

3.3. The relation between hydrophilic group and the saponification process

The relation between the molar percentage of $-CONH_2$, $-COONa$ and $-COOH$ group and the amount of NaOH in the saponification reaction is shown in Fig. 5. It can be found that the molar percentage of $-CONH_2$ group decreases and that of $-COOH$ or $-COONa$ group increase with the increase of the amount of NaOH in the saponification reaction, i.e. $-CONH_2$ group is converted to $-COOH$ or $-COONa$ group in the saponification process according to the Eq. (4). Noticeable, owing to the reaction equilibrium and other compounds in the solution, under the condition of preparation, the conversion cannot take place quantificationally. For example, when the molar ratio for NaOH to $CONH_2$ is 1, only 80% of $CONH_2$ is conversed, instead of 100%.

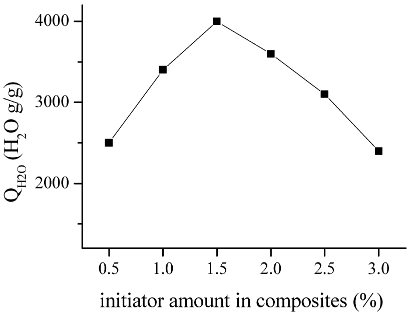


Fig. 4. Variation of Q_{H_2O} with initiator amount for starch-*graft*-acrylamide/kaolinite composites under preparation condition of kaolinite 10%, potato starch 20%, acrylamide monomer 68% and cross-linker 0.03%.

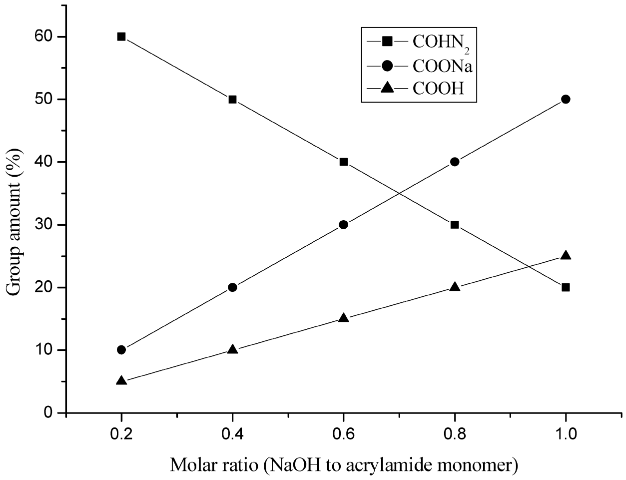


Fig. 5. Variation of the amount of hydrophilic group with the molar ratio for NaOH to acrylamide monomer in saponification reaction for starch-*graft*-acryamide/kaolinite superabsorbent composite under the condition of 60 °C for 4 h, and followed by 4 h wash at room temperature.

The time of saponification reaction also affect the amount and type of hydrophilic groups. From Fig. 6, the molar percentage of $-CONH_2$ group decreases, $-COOH$ and $-COONa$ groups increase with the prolongation of saponification time. The reason is that the reaction will more fully take place with the prolonging of the reaction time, which in turn the higher conversion extent from $-CONH_2$ to COONa or $-COOH$ group.

R – COONa can be considered as a weak alkali, and there

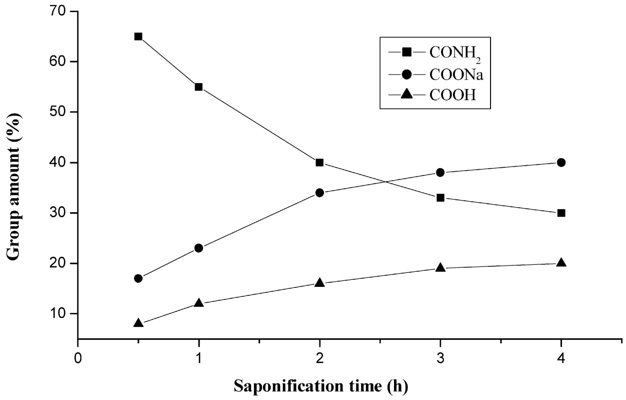


Fig. 6. Variation of the amount of hydrophilic group with the time of saponification reaction for starch-*graft*-acryamide/kaolinite superabsorbent composite under the condition of the ratio for NaOH to acrylamide monomer 0.6 at 60 °C, and followed by 4 h wash at room temperature.

is a hydrolysis equilibrium shown as the Eq. (6) [10], the $-$COONa group will partly transfer to $-$COOH group, especially when sample is immersed in a mass of water and washed many time until to pH = 7. So $-$COONa and $-$COOH will exist in the solution together.

$$\mathrm{R-COONa+H_2O} \overset{K_h=1.8\times10^{-10}}{\leftrightarrow} \mathrm{R-COOH+NaOH} \quad (6)$$

The amount of $-$COOH or $-$COONa group not only depends on the saponification reaction of the grafted-copolymer, but also depends on the wash process in the preparation of superabsorbent composite. From Fig. 7, it is found that the molar percentage of $-CONH_2$ group keep constant, and that of $-$COONa group decreases and $-$COOH group increases with the increase of wash time. This phenomenon may be explained as follow. The diffusible ions, such as OH^-, Na^+ and H^+, have to distribute between the polyelectrolyte network and surrounding water to satisfy the Donnan equilibrium [10]. When a relative small amount of sample is immersed in a large volume of water and the water is replaced repeatedly, the diffusible ions in the water will be removed from the equilibrium system. Therefore, the hydrolysis equilibrium indicated by Eq. (6) should shift to the right-hand side to provide more OH^- and Na^+ ions in the surrounding. Consequently, the molar percentage of $-$COONa group decrease and $-$COOH group increase with the increase of wash time. On the other hand, the reaction (4) do not take place under the condition in wash process, so the molar percentage of $-CONH_2$ is unchangeable.

3.4. The influence of hydrophilic groups on the water absorbency of superaborbent composite

The type and molar percentage of hydrophilic groups $-CONH_2$, $-$COONa and $-$COOH will affect the water absorbency of superabsorbent composites. The influence of the amount of NaOH in the saponification process of the composite preparation on the water absorbency is shown in Fig. 8.

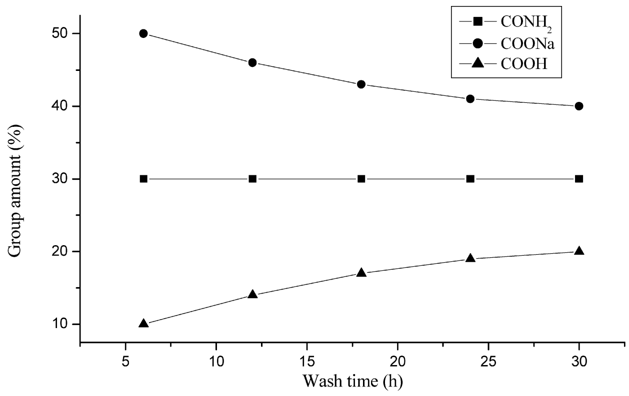


Fig. 7. Variation of the amount of hydrophilic group with the time of wash process for starch-*graft*-acryamide/kaolinite superabsorbent composite under the condition of the ratio for NaOH to acrylamide monomer 0.6 at 60 °C for 4 h, and followed by wash process at room temperature.

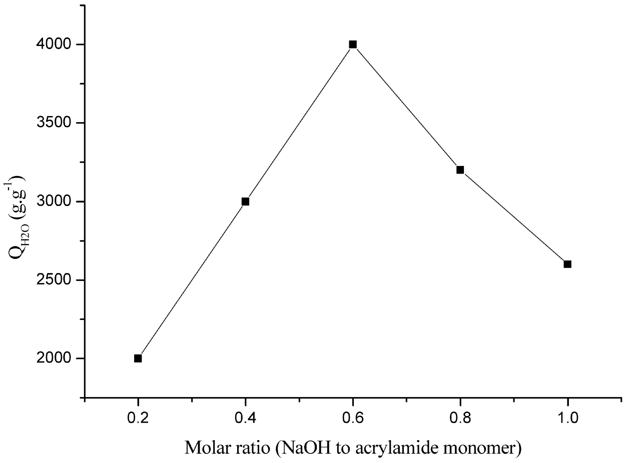
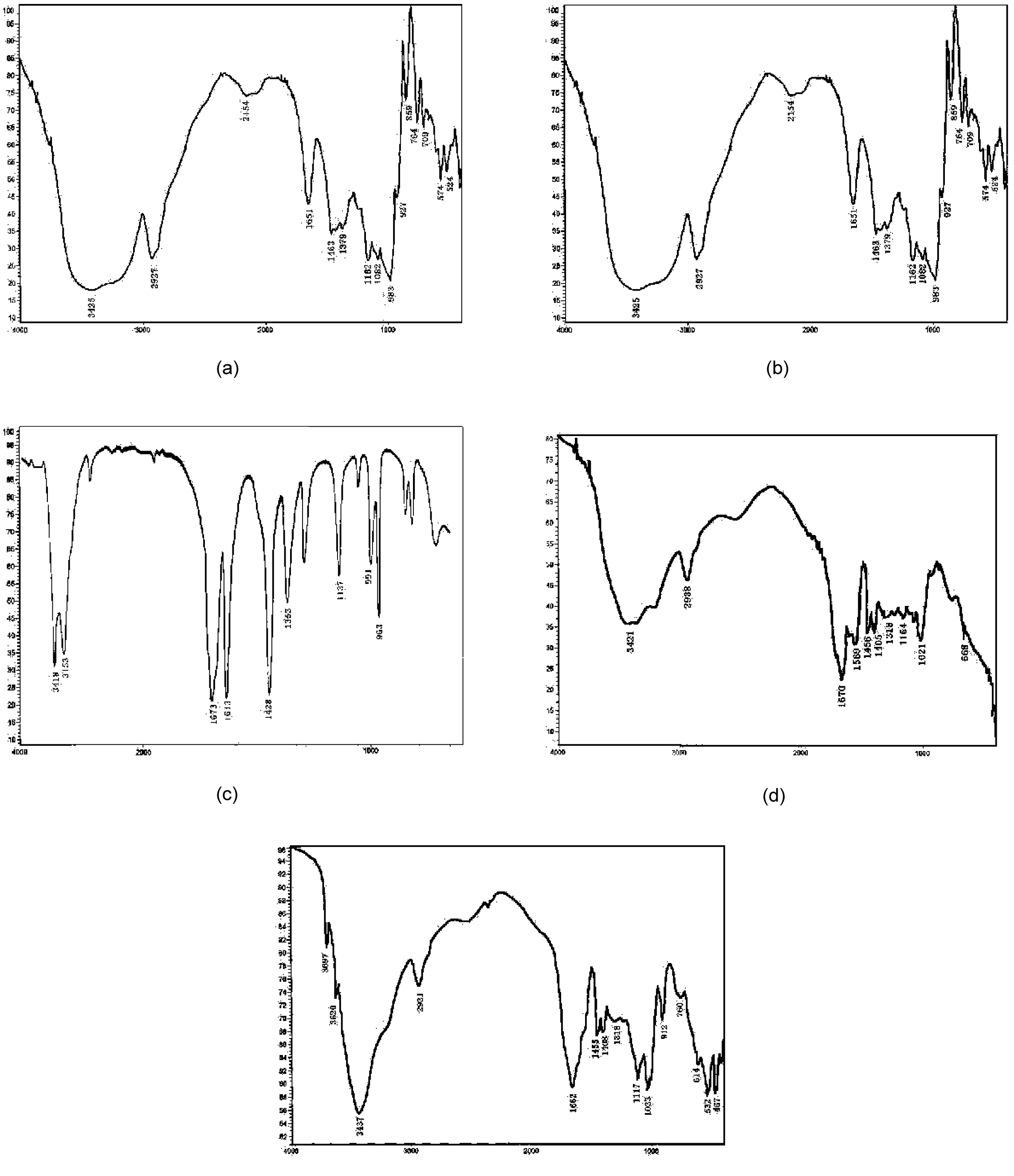


Fig. 8. Variation of water absorbency Q_{H_2O} with the molar ratio for NaOH to acrylamide monomer in saponification reaction for starch-*graft*-acryamide/kaolinite superabsorbent composite under the condition of 60 °C for 4 h, and followed by 4 h wash at room temperature.

It is seen that the amount of NaOH an increase in from 0.2 to 0.6 (molar ratio of NaOH/acrylamide monomer) causes Q_{H_2O} to increase significantly. Beyond 0.6, Q_{H_2O} decreases. Similar phenomena also were found by others [11,12] and us [13,14]. This behavior may be interpreted that the collaborative absorbent effect of $-CONH_2$, $-$COONa and $-$COOH groups is superior to that of single $-CONH_2$, $-$COONa or $-$COOH group. On the one hand, $-$COONa group will ionize into Na^+ and $-COO^-$ ions in water, higher absorbent ability for $-COO^-$ ions due to ionic hydrophilic and osmotic effect. But $-COO^-$ ions show negative electric charge in water, higher concentration of $-COO^-$ ions will lead in repelling action between groups. On the other hand, in spite of lower water absorbent function, $-$COOH or $-CONH_2$ group shows neutral electric charge in water, the electric repelling action of groups is smaller. Therefore, when the $-$COONa, $-$COOH and $-CONH_2$ groups on the composite cooperate in suitable ratio, the repelling action between ions will reduce and the higher water absorbent ability will produce. In our experimental conditions, when the molar ratio for NaOH to acrylamide monomer is about 0.6, and the composite with the molar ratio of 8:6:3 for $-CONH_2$, $-$COONa and $-$COOH group possesses the highest water absorbent ability.

3.5. The formation mechanism and possible structure of superabsorbent composites

The infrared (IR) spectra of kaolinite powder, starch, acrylamide, starch-*graft*-acrylamide composite and starch-*graft*-acrylamide/kaolinite composite were shown in Fig. 9. The absorption peaks at 3697, 3620 and 913 cm^{-1} contributed to OH group on kaolinite powder (Fig. 9(a)), after the graft-copolymerization, the three peaks become smaller which implies that the OH group on kaolinite participated in the reaction. After the reaction (Fig. 9(d) and



(a) (b)

(c) (d)

(e)

Fig. 9. (a) The infrared spectrum of kaolinite powder; (b) the infrared spectrum of starch; (c) the infrared spectrum of polyacrylamide; (d) the infrared spectrum of starch-*graft*-acrylamide composite; (e) the infrared spectrum of starch-*graft*-acrylamide/kaolinite composite.

(e)) the absorption peak at 574, 524 and 418 cm^{-1} attributed to OH group on starch (Fig. 9(b)) become smaller, which indicated that the OH group on starch change during the reaction. The absorption peaks at 3418, 3153, 1673 and 1613 cm^{-1} attributed to the $-\text{CONH}_2$ group on the acrylamide (Fig. 9(c)) also change during the reaction and a new absorption peak at 1405 cm^{-1} attributed to $-\text{CO}_2$ group appeared (Fig. 9(d) and (e)).

Since the characteristic absorption peak for OH groups on kaolinite and starch, and CONH_2 group has changed after copolymerization reaction, it is suggested that the reaction between OH groups on kaolinite and starch, and CONH_2 group on acrylamide chain take place during the reaction, which lead in the formation of network structure and water absorbed group.

According to Refs. [5,15], the cross-linking mechanism can be speculated as that the circle of starch was opened and formed $-\text{CHO}$ and $^{\cdot}\text{COH}$ groups under initiator, the graft-copolymerization reaction between $^{\cdot}COH$ on starch and the $CH_2{=}CH-CO-NH_2$ take place. A cross-linking reaction between polymer chain and kaolinite particle carry out and a network is formed by cross-linker ($CH_2{=}CH-CO-NH-CH_2-NH-CO-CH{=}CH_2$).

The composite is formed by graft-copolymerizing reaction between starch, acrylamide and mineral ultrafine-powder. There are three kinds of ways for kaolinite particle filled in the composite, i.e. (a) kaolinite particle as a cross-link point chemically bond with the polymer (shown in A position in Fig. 10), in this way, the network structure and the water absorbency of the composite would change with the change of kaolinite doped in composite; (b) kaolinite particle as terminal point chemically bond with the polymer (shown in B position in Fig. 10), in this way, the network and water absorbency of the composite hardly changes with the change of the amount of kaolinite doped in the composite; (c) physically filled in the network of the polymer (shown in C position in Fig. 10), in this way, the network and water absorbency of the composite hardly changes with the change of the amount of kaolinite doped in the composite. Since the water absorbency of the composite depends on the amount of kaolinite, it is speculate that kaolinite particle mainly as a cross-link point (a) chemically bonds with the polymer [6].

3.6. The properties of starch-graft-acrylamide/mineral powder superabsorbent composite

The swelling velocity of the composite was determined and is shown in Fig. 11. It is indicated that the water absorbency of the composite reaches 3000 g H_2O/g within 30 min and 4000 g H_2O/g within 120 min. In addition, a test concerning the ability of the composite to keep the water showed that the swollen sample still kept 97 wt% of the distilled water on centrifuging it at 4000 rpm for 60 min. The above results show that the composite reveals excellent comprehensive absorbency properties.

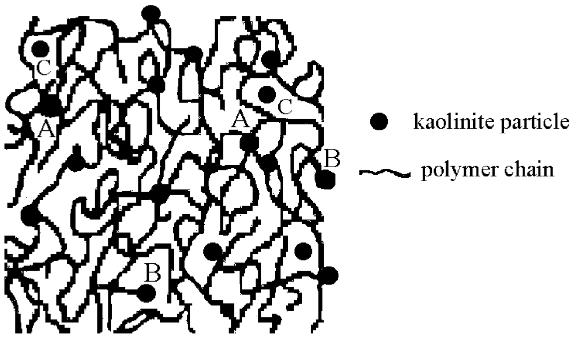


Fig. 10. Sketch for cross-linkage.

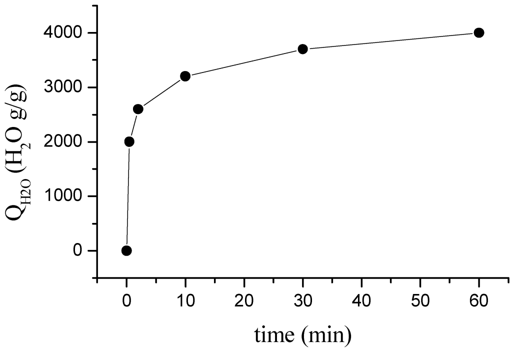


Fig. 11. Variation of Q_{H_2O} with time for starch-*graft*-acrylamide/kaolinite composite under preparation condition of kaolinite 10%, potato starch 20%, acrylamide monomer 68%, initiator 1.5% and cross-linker 0.03%.

4. Conclusions

(1) A novel starch-*graft*-acrylamide/mineral powder superabsorbent composite with water absorbency about 4000 times is synthesized by graft-copolymerization reaction among acrylamide monomer (20 g), potato starch (6 g) and mineral ultrafinepowder (3 g) with initiator (0.45 g), cross-linker (0.09 g) at temperature 60 °C for 120 min, followed by saponification reaction with sodium hydroxide (7 g) at temperature 90 °C for 180 min.

(2) It is found that the composite doped with kaolinite powder possess higher water absorbency than those doped with bentonite or sercite powder, since the kaolinite powder can moderately disperse in the water and cross-link with acrylamide and starch.

(3) By controlling the amount of NaOH and reaction time during saponification process, the hydrophilic groups on the composite can be adjusted, and it is found that the collaborative absorbent effect of $-CONH_2$, $-COONa$ and $-COOH$ groups is superior to that of single $-CONH_2$, $-COONa$ or $-COOH$ group. When the composite with the ratio of 8:6:3 for $-CONH_2$, $-COONa$ and $-COOH$ group possesses the highest water absorbent ability.

(4) By the IR characterization, the polymerization reaction mechanism and structure of the composite is supposed, and the mineral ultrafine powder as a cross-linking point play an important role in the formation of network structure of the superabsorbent composite.

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