Preparation and Water Absorbency of a Novel Poly(acrylate-*co*-acrylamide)/Vermiculite Superabsorbent Composite

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ABSTRACT: A novel poly(acrylate-*co*-acrylamide)/expanded vermiculite (EVMT) superabsorbent composite was synthesized by aqueous solution polymerization method. The water absorbency of the superabsorbent composite still reaches 850 g/g when 50 wt % EVMT is added, which is significant in decreasing the production cost of the superabsorbent composites. By controlling the molar ratio of acrylic acid monomer and acrylamide monomer, and neutralization degree of acrylic acid, the hydrophilic groups on the composite can be adjusted, and it is found that the collaborative absorbent effect of $-CONH_2$, $-COOK$, and $-COOH$ groups is superior to that of single $-CONH_2$, $-COOK$, or $-COOH$ group. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 735–739, 2007

Key words: superabsorbent composite; poly(acrylate-*co*-acrylamide); expanded vermiculite; water absorbency

INTRODUCTION

Superabsorbent polymers have a network structure with a suitable degree of crosslinking.[1,2] Not only are they able to absorb hundreds to thousands times their own mass of water, but also the absorbed water is hardly removed under some pressure. Because of their excellent characteristics, superabsorbents have raised considerable interest and researches, and have been used in health, agriculture, and horticulture[3–7] since the first superabsorbent polymer was reported by the US Department of Agriculture in 1969.[8]

Polyacrylamide and polyacrylate polymers are two kinds of the superabsorbents with higher water absorbency, but the polymers' higher production cost and lower gel strength restrict their application widely. Expanded vermiculite (EVMT) is a layered aluminum 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 superabsorbent composites, are improved by copolymerizing with acrylamide monomer, acrylate monomer, and EVMT micropowder. Consequently, comprehensive absorbent properties of superabsorbents are enhanced and the production cost of superabsorbents is reduced.[1,2,7] In this work, a novel poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite was synthesized by aqueous solution polymerization method. The influence of vermiculite amount, monomer amount, crosslinker, initiator, neutralization degree, and reaction temperature on the absorption properties is discussed.

EXPERIMENTAL

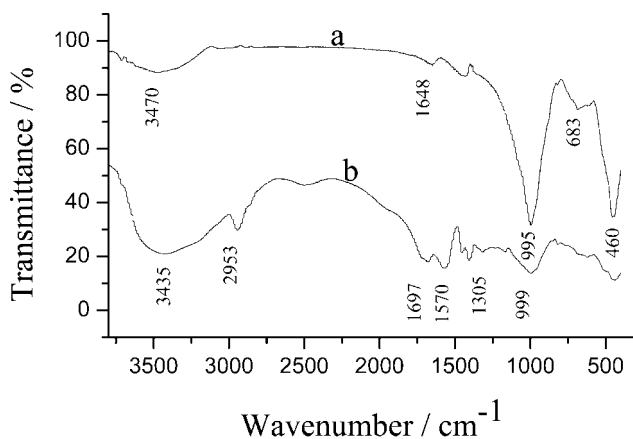### Preparation of poly(acrylate-*co*-acrylamide)/ vermiculite superabsorbent composite

Acrylic acid monomer (36.0 g), distilled under reduced pressure prior to use, was neutralized at room temperature with an aqueous solution containing 21.0 g potassium hydroxide to achieve the desired neutralization degrees (75%) of the sample. Acrylamide monomer (9.0 g) and expanded vermiculite (EVMT; 22.5 g) micropowder with an average particle size smaller than 2×10^{-5} m and specific surface area larger than 20 m^2 g^{-1} were dispersed in the neutralized monomers solution mentioned earlier. Crosslinker N, N'-(dimethylene) acrylamide (0.036 g) was purified by recrystallization from 66 wt % ethanol/ water solution, and dissolved in the monomer/ EVMT mixture. The mixed solution was then degassed under vacuum (∼ 300 Pa) for about 30 min. Radical initiator potassium persulfate (0.54 g) was added to the solution consisting of monomer, EVMT, and crosslinker.

Figure 1 Infrared spectra of (a) EVMT and (b) poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (preparation conditions: 50 wt % vermiculite, 0.08 wt % crosslinker, 1.2 wt % initiator, 75% neutralization degree, 55 wt % monomer concentration, and at 80°C).

The reaction mixture was stirred and heated to 80°C in a water bath for 10 min. After completion of the copolymerization reaction, the mixture was filtered through Whatman filter paper no. 54 and then immersed in excess distilled water to remove any impurities. The product was dried under vacuum (∼300 Pa) at 80°C for more than 3 h to constant weight and milled using a 40-mesh screen. A pure poly(acrylate-*co*-acrylamide) superabsorbent composite with water absorbency of 1400 g/g and a poly(acrylate-*co*-acrylamide) superabsorbent composite containing 50 wt % vermiculite with water absorbency of 850 g/g were thus obtained.

Measurement and characterization

The powdered composite (0.5 g) was immersed in distilled water (1000 mL) at room temperature for at least 3 h to reach swelling equilibrium, which resulted in the absorption of water into the network of the composite and the formation of a hydrogel. The unadsorbed water was removed by filtration over a 40-mesh stainless steel screen and hanging up for 25 min. The water absorbency of the superabsorbent composite was calculated by the following formula:

$$Q_{\mathrm{H_2O}} = \frac{m_2 - m_1}{m_1}$$

where $Q_{\mathrm{H_2O}}$ is water absorbency (in gram per gram), m_1 the mass (in grams) of the dry sample, and m_2 the mass of the swollen sample.

FTIR spectrum of the superabsorbent composite in KBr was obtained using a Nicolet Impact 410 spectrometer. In Figure 1, the absorption peak at 3470 cm^{-1} belonged to the H—O—H stretching, the one at 1648 cm^{-1} is for H—O—H in absorbed water bend-

ing, and the ones at 995 cm^{-1} and 460 cm^{-1} are for Si—O—Si stretching of EVMT. The absorption peaks at 3435 cm^{-1} and 2953 cm^{-1} are ascribed to O—H stretching and —CH$_2$— stretching respectively. Those at 1697 cm^{-1}, 1570 cm^{-1}, and 1305 cm^{-1} belong to C=O bending, —COO$^-$, and the C—H bending respectively. The results indicate the existence of EVMT and formation of polyacrylate and polyacrylamide in the superabsorbent composite.

RESULTS AND DISCUSSION

Effect of crosslinker content

The influence of the amount of the crosslinker on the water absorbency ($Q_{\mathrm{H_2O}}$) is shown in Figure 2. It is obvious that $Q_{\mathrm{H_2O}}$ increases with increase in crosslinker amount from 0.06 to 0.08 wt %. Beyond a crosslinker amount of 0.08 wt %, $Q_{\mathrm{H_2O}}$ of the composite decreases.

Clearly, the copolymerization reaction between acrylic acid and acrylamide and the three-dimensional (3D) network of the polymer depend on the crosslinker amount. Under lower crosslinker concentrations, the copolymerization does not occur adequately, and the 3D network of the polymer does not form effectively; the water molecules can not be held, which leads to the decline of the water absorbency. On the other hand, a higher concentration of crosslinker 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 crosslinker concentration because the network space gets diminished, and less water enters the composite. This tendency is similar to that found for other superabsorbents pre-
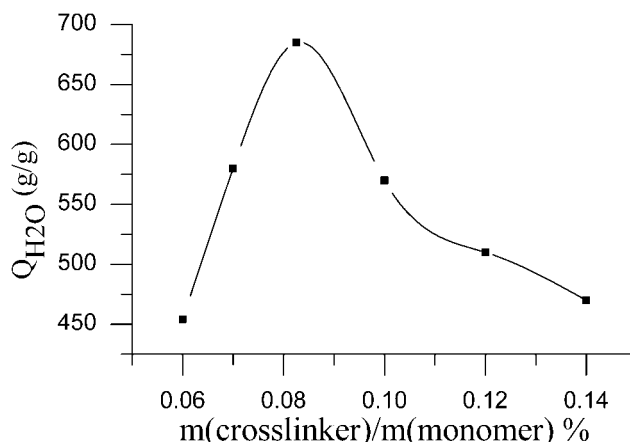
Figure 2 Variation of $Q_{\mathrm{H_2O}}$ with the amount of crosslinker in poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (50 wt % vermiculite, 1.0 wt % initiator, 80% neutralization degree, 50 wt % monomer concentration, and at 80°C).
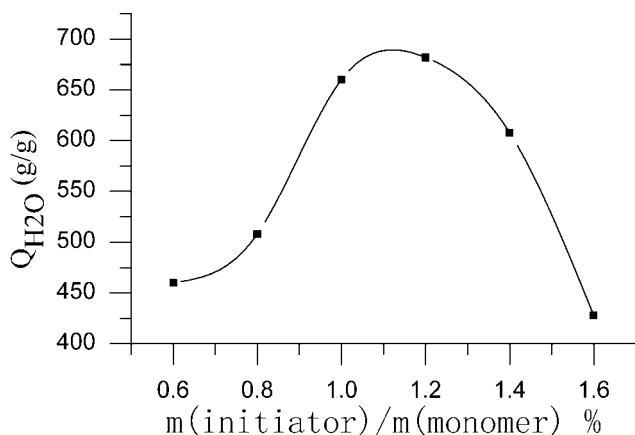
Figure 3 Variation of Q_{H_2O} with the amount of initiator in poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (preparation conditions: 50 wt % vermiculite, 0.08 wt % crosslinker, 80% neutralization degree, 50 wt % monomer concentration, and at 80°C).

pared by us[2,7] and other groups.[9,10] In our experimental conditions, the crosslinker amount of 0.08 wt % is the best.

Effect of initiator content

The amount of initiator also affects the copolymerization reaction course, which results in the change of water absorbency of the composites. When the concentration of the initiator is lower than 1.2 wt %, the copolymerization reaction is slower, the polymer network is fewer, and water absorbency is lower under the same reaction condition (Fig. 3). On the other hand, the higher the concentration of initiator agent, such as more than 1.2 wt %, the faster the reaction velocity and smaller the polymer network space, which lead to the decrease in the water absorbency of the composites. This phenomenon is similar to that found for other superabsorbents prepared by us[7] and other groups.[11]
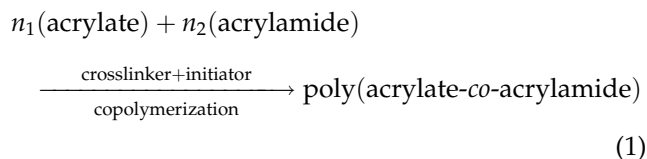
Effect of neutralization degree

When acrylic acid is neutralized with KOH, the carboxylic acid group on acrylic acid turns into a carboxylate group. The influence of the neutralization degree (the molar ratio of KOH to acrylic acid) of samples on the water absorbency is shown in Figure 4. It is apparent that an increase in the neutralization degree from 60 to 75% causes Q_{H_2O} to rise significantly. Beyond a neutralization degree of 75%, Q_{H_2O} decreases. Similar behaviors were found for other superabsorbents prepared by us[12,13] and other groups.[11]

This phenomenon may be interpreted in terms that a cooperative absorbing effect between carboxylate and carboxylic acid groups is superior to that of either group. Since in water, the carboxylate group is negatively charged, higher carboxylate concentrations will lead to repulsion among these groups though a better hydrophilic property for carboxylate group, and decrease water absorbency. On the other hand, the carboxylic groups are neutral, in spite of lower hydrophilic capability for carboxylic group than for carboxylate group. Therefore, when carboxylate and carboxylic groups cooperate in a suitable ratio, higher water absorbency will occur. In our experiments, the composite with the neutralization degree of 75% reveals the highest water absorbency.
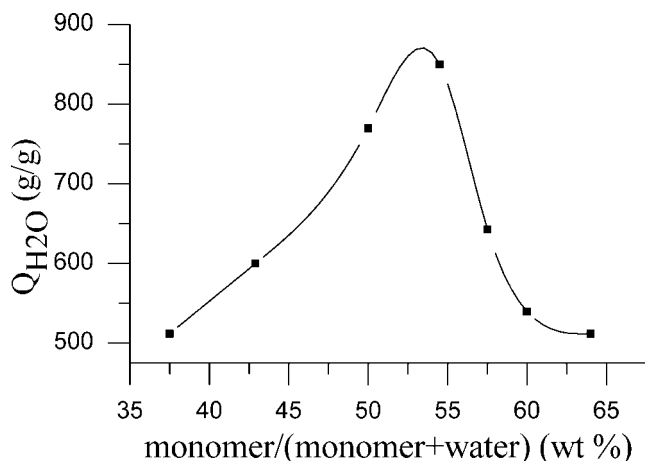
Effect of monomer concentration

The concentration of acrylic acid and acrylamide monomers is another factor affecting the water absorbency of the composite. Figure 5 shows that the water absorbency increases gradually in the range of 38–55 wt % of the monomers concentration, and declines at the concentration of 55–65 wt %. The behavior can be explained according to the polymerization reaction shown as follows:

$$n_1(\text{acrylate}) + n_2(\text{acrylamide})$$

$$\xrightarrow[\text{copolymerization}]{\text{crosslinker+initiator}} \text{poly(acrylate-}co\text{-acrylamide)}$$

(1)

According to the rate law, under a higher concentration of monomers, the reaction takes place faster, which causes an uneven dispersion of the network of polymer; thus lower Q_{H_2O} occurs. On the other hand, under a lower concentration of monomers, the reaction takes place slower (even cannot polymerize effectively), the monomers exist as oligomer rather
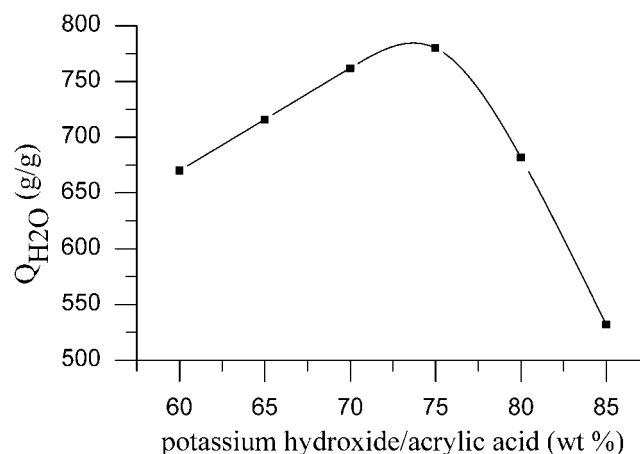
Figure 4 Variation of Q_{H_2O} with neutralization degree in poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (50 wt % vermiculite, 0.08 wt % crosslinker, 1.2 wt % initiator, 50 wt % monomer concentration, and at 80°C).

Figure 5 Variation of Q_{H_2O} with monomer concentration in poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (50 wt % vermiculite, 0.08 wt % crosslinker, 1.2 wt % initiator, 75% neutralization degree, and at 80°C).
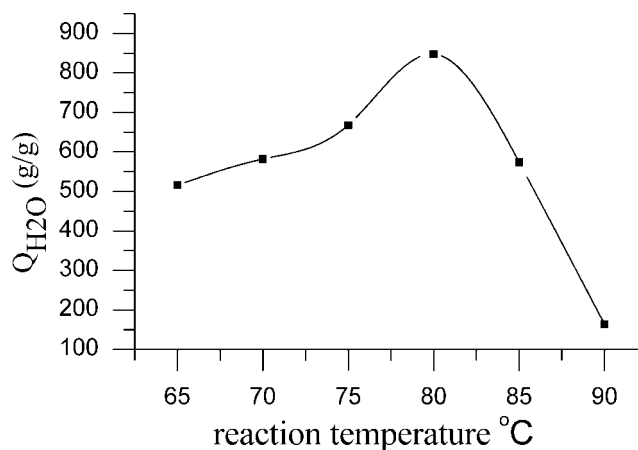

Figure 6 Variation of Q_{H_2O} with reaction temperature in poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (50 wt % vermiculite, 0.08 wt % crosslinker, 1.2 wt % initiator, 75% neutralization degree, and 55 wt % monomer concentration).

than as polymer, and the 3D network of the polymer is incompact, all of which lead to a lower Q_{H_2O}. In our experimental conditions, with the monomer concentration of 55 wt %, the reaction can take place effectively and evenly; the superabsorbent composite possesses the highest Q_{H_2O}.

Effect of reaction temperature

The influence of polymerization reaction temperature on the water absorbency of the composite is shown in Figure 6. The water absorbency increases with the increase of reaction temperature from 65 to 80°C in the copolymerization reaction process, but declines in the range of 80–90°C. As is known, under a lower temperature, the copolymerization reaction takes place slowly (even does not occur at a temperature below 65°C), the polymeric network does not form effectively, and acrylamide, acrylate, and EVMT disperse in the solution as monomer, oligomer, or micropowder, instead of composite, which result in the decrease of the water absorbency of the composite. On the other hand, the copolymerization is an exothermic reaction [shown in eq. (1)], and a higher temperature is unfavorable for the reaction taking place; it even causes a burst-polymerization reaction, which in turn leads to the decline in the water absorbency of the composite.

Effect of vermiculite amount

The relation between water absorbency and the amount of vermiculite present in the superabsorbent nanocomposite is depicted in Figure 7. It can be seen that the linear water absorbency decreases with increasing amounts of vermiculite. When the amount

of vermiculite is 10 wt %, Q_{H_2O} reaches 1360 g/g, and when the vermiculite amount reaches 50 wt %, Q_{H_2O} equals to 850 g/g, which significantly reduces the cost of preparing superabsorbents. Mineral particle fills in the composite in three possible ways:[1,2,7] (a) mineral particle as a crosslink point chemically bonds with polymer; in this case, the dependence relation of the water absorbency on the mineral particle amount shows nonlinear change, such as kaolinite particle in polyacrylaminde and mica particle in polyacrylate[1,2]; (b) mineral particle as terminal point chemically bonds with the polymer; (c) mineral particle physically fills in the network of the polymer. In these two cases, the relationship between the water absorbency and the mineral particle amount
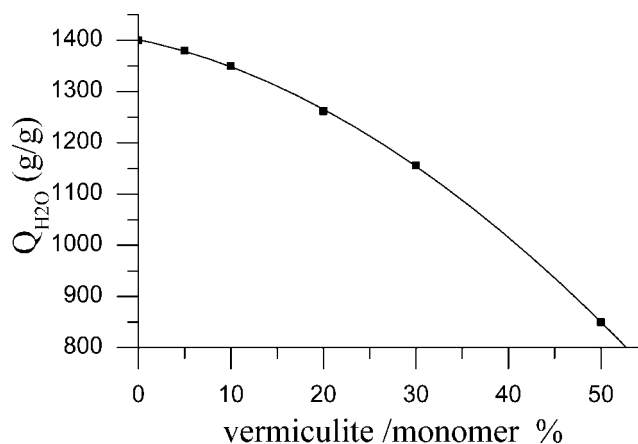
Figure 7 Variation of Q_{H_2O} with mass ratio of vermiculite to monomer in poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (0.08 wt % crosslinker, 1.2 wt % initiator, 75% neutralization degree, 55 wt % monomer concentration, and at 80°C).
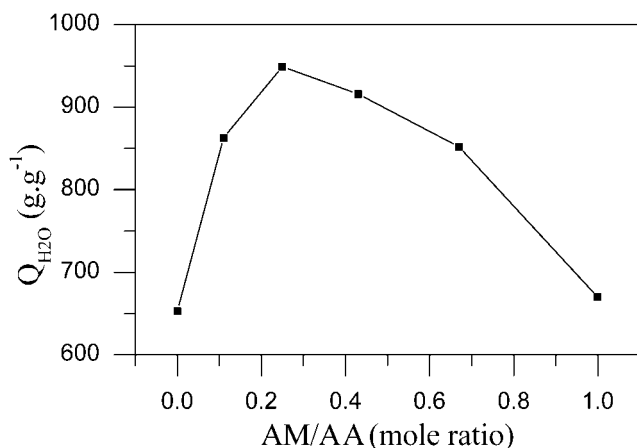
Figure 8 Variation of Q_{H_2O} with the molar ratio of acrylamide to acrylic acid in poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite (preparation conditions: 0.08 wt % crosslinker, 1.2 wt % initiator, 75% neutralization degree, 55 wt % monomer concentration, and at 80°C). AM, acrylamide; AA, acrylic acid.

shows linear change. Since the water absorbency of poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite linearly depends on the amount of EVMT, it is speculated that EVMT particles are physically filled in the poly(acrylate-*co*-acrylamide) network, the space network for water molecules to enter becomes smaller, and the water absorbency thus linearly decreases. Further experiments to clarify whether the interaction between EVMT and polymer host is a chemical combination, or a physical fill, or both are necessary.

Effect of the molar ratio of acrylamide to acrylic acid

Figure 8 shows the influence of the molar ratio of acrylamide to acrylic acid on water absorbency of superabsorbent composite. The water absorbency decreases with the increase in the molar ratio of acrylamide to acrylic acid in a feed ratio range of 0.0–0.25. However, inverse result is observed when the molar ratio of acrylamide to acrylic acid is higher than 0.25. Similar results were observed in the study of crosslinked acrylic acid and acrylamide copolymers.[11,14] There are three kinds of hydrophilic groups (—CONH$_2$, —COO$^-$, and —COOH groups) in the polymer chains of the composite network. As reported in previous studies,[8,13] the collaborative absorbent effect of —CONH$_2$, —COO$^-$, and —COOH groups is superior to that of single —CONH$_2$, —COO$^-$, or —COOH group. When the —CONH$_2$, —COO$^-$, and —COOH groups on the composite cooperate in a suitable ratio, the repelling action between

ions will reduce, thereby producing a higher water absorbent ability. Under our experimental conditions, the molar ratio of acrylamide to acrylic acid of 0.25 possesses the highest water absorbency.

CONCLUSIONS

1. A novel poly(acrylate-*co*-acrylamide)/EVMT superabsorbent composite was synthesized by aqueous solution polymerization method. The preparation conditions were optimized as follows: crosslinker, 0.08 wt %; initiator, 1.2 wt %; neutralization degree, 75%; the monomer molar ratio of acrylamide to acrylic acid, 1 : 4; monomer concentration, 55 wt %; and reaction temperature, 80°C.
2. The water absorbency of the poly(acrylate-*co*-acrylamide)/vermiculite superabsorbent composite with EVMT amount of 10 wt % is 1360 g/g, and the water absorbency still reaches 850 g/g when 50 wt % EVMT is added, which is significant in decreasing the production cost of the superabsorbent composites.
3. By controlling the molar ratio of acrylic acid monomer and acrylamide monomer, and neutralization degree of acrylic acid, the hydrophilic groups on the composite can be adjusted, and it is found that the collaborative absorbent effect of —CONH$_2$, —COOK, and —COOH groups is superior to that of single —CONH$_2$, —COOK, or —COOH group. When the molar ratio of acrylamide monomer to acrylic acid monomer is 1 : 4, and the neutralization degree is 75%, the composite possesses the highest water absorbent ability.

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