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European Polymer Journal 41 (2005) 1630–1637

EUROPEAN POLYMER JOURNAL

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Synthesis and properties of clay-based superabsorbent composite

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Received 13 August 2004; received in revised form 10 October 2004; accepted 30 January 2005
Available online 8 March 2005

Abstract

A novel superabsorbent composites based on acrylic acid, acrylamide, and inorganic clay mineral-attapulgite were synthesized through a solution polymerization to improve water and saline absorbencies. The superabsorbent composite was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The effects of saline solutions, amount of initiator, crosslinker and attapulgite on the water absorbency of superabsorbent composites were investigated. The water retention test of superabsorbent composites were also carried out. The superabsorbent composite exhibited improved water and saline absorbencies compared with that of crosslinked poly(acrylic acid–co-acrylamide) superabsorbent polymer. The water absorbency of the superabsorbent composite synthesized under optimal synthesis conditions with an attapulgite content of 10% reaches more than 1400 g H_2O/g and 110 g H_2O/g in distilled water and 0.9% NaCl solution, respectively.

Keywords: Acrylic acid; Acrylamide; Attapulgite; Superabsorbent composite; Water absorbency

1. Introduction

Superabsorbent polymers are loosely crosslinked networks that can absorb a large amount of water in a short time and retain water under pressure. Although superabsorbent polymers have been abundantly used in the disposable diaper industry for the past 30 year, their applications are still being expanded to many fields including agriculture and horticulture [1,2], sealing composites [3], artificial snow [4,5], drilling fluid additives [6], medicine for drug delivery system [7–9] and so on.

Recently, the preparation of polymer/clay superabsorbent composites has received great attention because of their relative low production cost and high water absorbency [10,11]. The preparation and the swelling behaviors of poly(acrylic acid)/attapulgite superabsorbent composite have been reported in our previous study [12,13]. In which, we know that the water absorbency of the poly (acrylic acid)/attapulgite superabsorbent composite in distilled water was greatly improved as compared with crosslinked poly (acrylic acid) superabsorbent polymer, but the water absorbing ability of superabsorbent composite in saline solutions only slightly increased. It is well known that the water absorbing ability of a superabsorbent in saline solution is also very important for many applications. Therefore, the synthesis of new superabsorbent composite which has

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0014-3057/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2005.01.028

high water absorbency both in distilled water and saline solution and developing their applications still represent interesting research areas. Acrylamide is a kind of nonionic monomer and has great advantage on its good salt-resistant performance as a raw material for superabsorbent. Attapulgite, as a good substrate for superabsorbent composite materials, is a layered aluminium silicate with reactive groups –OH on the surface. In order to reduce costs and improve the comprehensive water-absorbing properties of the superabsorbent materials, to graft acrylic acid and acrylamide copolymer onto attapulgite and fabricate a composite consisting of polymer and attapulgite micropowder can be a priority. In this paper, we report the synthesis of superabsorbent composites by graft copoly- merization reaction of acylic acid (AA) and acrylamide (AM) on attapulgite micropowder using *N*,*N*-methylene-bisacrylamide (MBA) as a crosslinker and ammonium persulphate (APS) as an initiator in an aqueous solution. Aspects investigated included the optimum synthesizing conditions.

2. Experimental

2.1. Materials

Acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. Acrylamide (AM, chemically pure, Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. Ammonium persulfate (APS, analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. *N*,*N*-methylenebisacrylamide (MBA, chemically pure, Shanghai Chemical Reagent Factory, Shanghai, China) was used as purchased. Attapulgite micropowder, (Xuyi Colloidal Co., Ltd, Jiangsu, China), milled through 320-mesh screen, followed by treatment with 37% hydrochloric acid for 48 h and washed with distilled water until pH 7 to remove any residual hydrochloric acid, was dried at 105 °C for 8 h prior to use. All solutions were prepared with distilled water. The schematic illustration (Fig. 1) of attapulgite is presented as below:

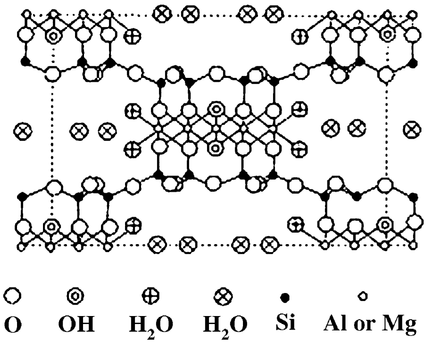

Fig. 1. Schematic structure of attapulgite.

2.2. Preparation of superabsorbent composites

A series of the samples with different amounts of attapulgite, crosslinker, initiator and acrylic acid with different degrees of neutralization were prepared by the following procedure: Typically, acrylic acid (4.2 g) was dissolved in 15 ml distilled water and then neutralized with 4.6 ml of sodium hydroxide solution (5 M) in a four-neck flask equipped with a stirrer, condenser, thermometer, and nitrogen line. attapulgite power (0.72 g) and acrylamide (2.13 g) were added to the above partial neutralized monomer solution. Under a nitrogen atmosphere, the crosslinker MBA (14.3 mg) was added to the AA-AM-attapulgite mixture solution and the mixed solution was stirred at room temperature for 30 min. The water bath was heated slowly to 70 °C with effective stirring after radical initiator APS (71.3 mg) was introduced to the mixed solution. After 3 h of the reaction, the resulting product was washed several times with distilled water, dried at 70 °C to a constant weight, then milled and screened. All samples were used had a particle size in the range of 40–80 mesh.

2.3. Preparation of crosslinked poly(acrylic acid–co-acrylamide) superabsorbent polymer

The procedure of preparation of crosslinked poly (acrylic acid-co-acrylamide) superabsorbent polymer is similar to that of preparation of superabsorbent composite except attapulgite is omitted.

2.4. Water absorbency measurement

A weighted quantity of the superabsorbent composite was immersed in distilled water or saline solutions at room temperature to reach the swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtered over a 100-mesh screen. The water absorbency (Q_{H_2O}) of superabsorbent composite was determined by weighing the swelled samples, and the Q_{H_2O} of the samples was calculated using the following equation:

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

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

2.5. Characterization

The IR spectra of the superabsorbent composite were recorded on a FTIR (Thermo Nicolet, NEXUS, TM) using KBr pellets. Thermal stability studies of dry samples were performed on a Perkin-Elmer TGA-7 thermogravimetric analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT), with a temperature range of 25–700 °C at a heating rate of 10 °C/min using a dry nitrogen purge at a flow rate of 50 ml/min. The morphology of the dried samples was examined using a JSM-5600LV SEM instrument (JEOL, LTD) after coating the sample with gold film.

3. Results and discussion

3.1. Effect of initiator content

Fig. 2 shows the effect of the initiator content on the water absorbency of superabsorbent composite. The water absorbency increases as APS content rises from 0.2% to 1.0% and decreases with further increase in the content of APS. The relation between the average kinetic chain length (V) and concentration of the initiator in free-radical polymerization is given by the following equation [14]:

$$V = 1/2k_p(fk_ik_t)^{-1/2}[I]^{-1/2}[M] \quad (2)$$

where k_p, k_i and k_t are the rate constants for propagation, initiator, and termination, respectively; f, the efficiency of initiation by the initiator; and $[I]$ and $[M]$, the initial concentration of the initiator and monomer, respectively. According to Eq. (2), the molecular weight in free-radical polymerization decreases with increase of the initiator concentration. With decrease of the molecular weight, the relative amount of polymer chain ends increase. As mentioned in previous study [15], the polymer chain ends do not contribute to the water absorbency. Therefore, this is responsible for the decrease in the water absorbency with increase of the initiator content. When the content of APS is below the optimum values, the swelling capacity of superabsorbent composite is also decreased. This may due to a decrease in the number of radicals produced as the content of APS decreases. The network cannot be formed efficiently with a few numbers of radicals in free-radical polymerization reaction, which results in the decrease of the water absorbency [12].

3.2. Effect of crosslinker content

The effect of crosslinker content on water absorbency is shown in Fig. 3. It can be seen from Fig. 3 that the water absorbency decreases with the increase of crosslinker content from 0.2% to 1.0%. The relation between the swelling ratio and network structure parameter for the swelling of ionic network was given by Flory [16], usually used as the following two equivalent equation:

$$Q_m^{5/3} = [(i/2V_uS^{1/2})^2 + (1/2 - X_1)/V_1]/(V_e/V_0) \quad (3)$$

$$Q_m^{5/3} = [(i/2V_uS^{1/2})^2 + (1/2 - X_1)/V_1](M_c/\rho_p) \times (1 - 2M_c/M_n)^{-1} \quad (4)$$

where Q_m is swelling ratio; i/V_u, the concentration of fixed charge referred to the unswollen network; S, the ionic concentration in the external solution; $(1/2 - X_1)/V_1$, the affinity of the hydrogel with water; V_e/V_0, the crosslinked density which refers to the number of effectively crosslinked chains in unit volume; M_c, the average

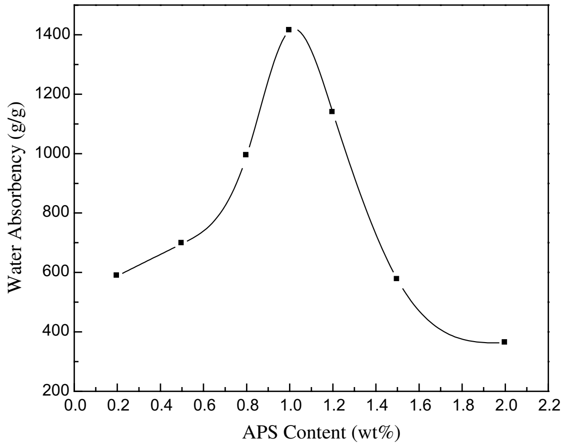

Fig. 2. Effect of initiator content on water absorbency of superabsorbent composite in distilled water: reaction temperature, 70 °C; 40% neutralization degree of AA; molar ratio of AM to AA is 0.51, weight ratio of crosslinker and attapulgite in the feed is 0.2% and 10%, respectively.

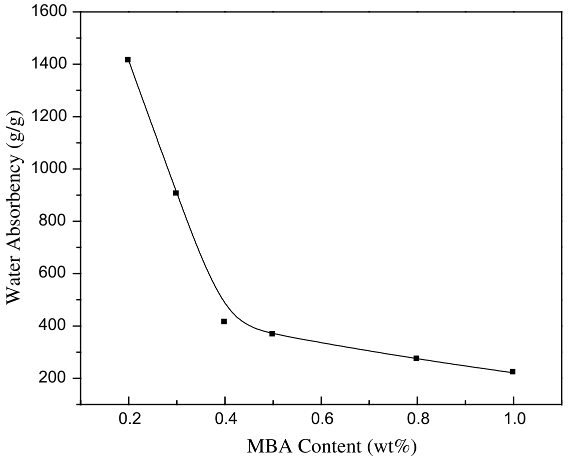

Fig. 3. Effect of crosslinker content on water absorbency of superabsorbent composite in distilled water:reaction temperature, 70 °C; 40% neutralization degree of AA; molar ratio of AM to AA is 0.51, weight ratio of initiator and attapulgite in the feed is 1.0% and 10%, respectively.

molecular weight of the network chains; ρ_p, the density of the polymer, and M_n, the average molecular weight of the polymer before crosslinking. According to Eq. (3), the swelling ratio of the hydrogel has a relation to the ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water. When the crosslinker content increased, the crosslinking density of the superabsorbent composite also increased. This would result in a decrease in the space between the copolymer chain and lead a decrease in water absorbency. When crosslinker content is lower than 0.2%, the absorbency of superabsorbent composite is diminished because of an increase of soluble material. The results are in conformity with Flory's network theory and similar observations have been reported by others [17,18].

3.3. Effect of molar ratio of AM to AA

Fig. 4 shows the effect of the molar ratio of AM to AA on water absorbency of superabsorbent composite. The water absorbency decreases with the increase of the molar ratio of AM to AA in a feed ratio range of 0.51–1.03. However, inverse result was observed when the molar ratio of AM to AA is below 0.51. Similar results were observed in the study of crosslinked acrylic acid and acrylamide copolymers [15]. There are three kinds of hydrophilic groups (–CONH, –COONa and –COOH groups) in the polymer chains of the composite network. As reported in previous study [19], the collaborative absorbent effect of –CONH, –COONa and –COOH groups is superior to that of single –CONH, –COONa or –COOH group. When the –CONH, –COONa and –COOH groups on the composite cooperate in suitable ratio, the repelling action between ions will reduce and the higher water absorbent ability will produce. Under our experimental conditions, the molar ratio of AM to AA in a feed ratio range of 0.51 possesses the highest water absorbency.

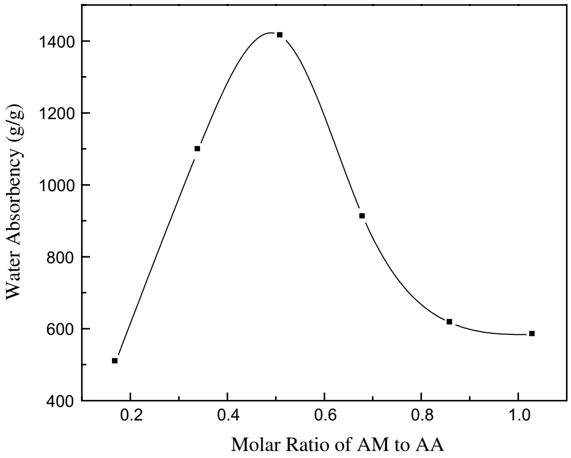

Fig. 4. Effect of molar ratio of AM to AA content on water absorbency of superabsorbent composite in distilled water: reaction temperature, 70 °C; 40% neutralization degree of AA; weight ratio of crosslinker, initiator and attapulgite in the feed is 0.2%, 1.0% and 10%, respectively.

3.4. Effect of attapulgite content

Table 1 shows the effect of attapulgite content on the water absorbency. The water absorbency decreases with the increase of attapulgite content. As described in previous study [10–12], the inorganic clay mineral particle in network acts as an additional network point. The crosslinking density of superabsorbent composite increases with the increase of attapulgite content, which results in a decrease in water absorbency. It also can be seen from Table 1 that the superabsorbent composites show high water–absorbing capacity in both distilled water and 0.9% NaCl solution as compared with PAAM, especially when the superabsorbent composite contains low percentage of attapulgite (for example $PAAM_1$).

The mechanism of PAA grafting onto attapulgite was reported in our previous study [12]. It was presumed by a similar mechanism that the hydroxyl group present in the attapulgite may react with the APS and liberate a free radical on the attapulgite structure and graft polymerization will take place on these free radicals giving poly (acrylic acid-co-acrylamide) (or partial PAA and PAM) branches on the attapulgite backbone. It should be noted that the presence of initiator in the polymerization system leads not only to grafting but also to the initiation of homopolymerization. The homopolymers of PAA and PAM are soluble in the medium of reaction (water) and would be filtered off during filtration. However, in the presence of crosslinker with such a high percentage of 0.2%, the homopolymers can not be extracted completely from the reaction mixture. In addition, These

Table 1
Effect of amount of attapulgite on water absorbency of the superabsorbent composites

Sample no.	Attapulgite percentage (wt.%)	Q_{H_2O} (g/g)	
		Distilled water	0.9 wt.% NaCl
PAAM	0	684	72
$PAAM_1$	10	1414	117
$PAAM_2$	20	960	94
$PAAM_3$	30	800	82
$PAAM_4$	40	691	70

Reaction conditions: reaction temperature, 70 °C; 40% neutralization degree; molar ratio of AM to AA is 0.51, weight ratio of crosslinker and initiator in the feed is 0.2% and 1.0%, respectively.

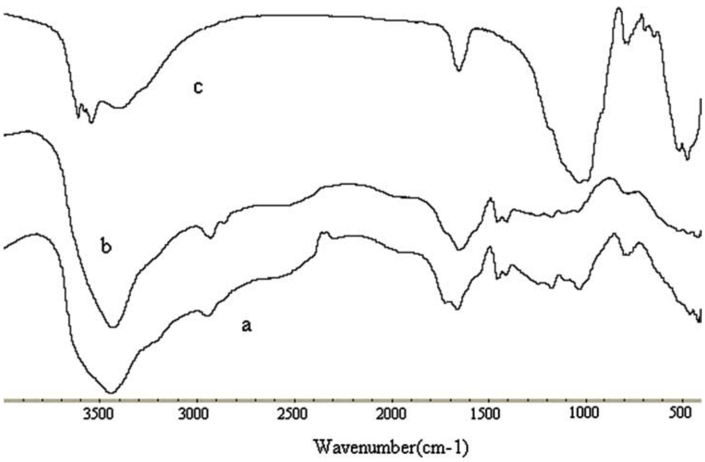

Fig. 5. Infrared spectra of superabsorbent composite (a), PAAM (b) and attapulgite (c).

homopolymers would also be crosslinked and form the network. Since the residual homopolymers in network would help in enhancing the water absorbency of final product, no attempt was made to extract the homopolymers from the superabsorbent composite.

3.5. Infrared spectra

The infrared spectra of superabsorbent composite $PAAM_1$, PAAM and attapulgite are shown in Fig. 5(a)–(c), respectively. According to the IR spectra of $PAAM_1$, The peaks observed were at 3447 cm^{-1}, corresponding to the N–H stretching of acrylamide unit, 2950 cm^{-1}, corresponding to the –C–H stretching of acrylate unite, 1721 cm^{-1}, corresponding to the $\upsilon C{=}O$ of acrylate unit, 1667 cm^{-1}, corresponding to the carbonyl moiety of the acrylamide unit, 1175 cm^{-1}, corresponding to the –CO–O– stretching of acrylate unit, 1031 cm^{-1}, corresponding to the Si–O stretching of attapulgite. The infrared analysis result of superabsorbent composite in Fig. 5(a) shows that all characteristic groups, i.e., –COOH (or –COONa), –CONH–, –CH, and Si–O, exist in product. In addition, by compared with Fig. 5(a) and (c), the absorption peaks at 3621cm^{-1} and 3549cm^{-1} attributed to the OH groups on attapulgite (Fig. 5(c)) disappeared after reaction (Fig. 5(a)), it is suggested that the graft copolymerization between OH groups on attapulgite and monomers take place during the reaction.

3.6. Thermal stability

The thermogravimetic analysis (TGA) of PAAM and $PAAM_1$ are shown in Fig. 6. Both PAAM and $PAAM_1$ show a very small weight loss below 100 °C, implying a loss of moisture. At around 345 °C, PAAM and $PAAM_1$ have similar significant weight losses of 19.3% (342 °C) and 20.1% (348 °C), respectively. The major weight loss of PAAM started at 460 °C (54.4%) whereas $PAAM_1$ has a major weight loss started at 505 °C (62.5%). Therefore, PAAM and $PAAM_1$ has a decomposition temperature of 460 °C and 505 °C, respectively. The results indicated that the introduction of attapulgite to polymer network results in an increase in thermal stability. This phenomenon may be due to the fact that the attapulgite micro-particles in network can act as a heat barrier, which enhances the overall thermal stability of the composite.

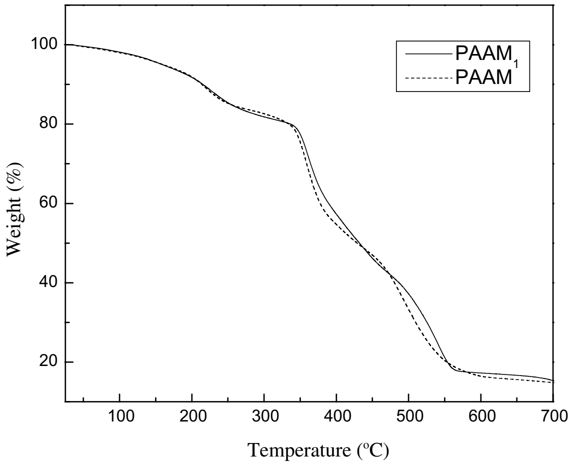

Fig. 6. TGA curves of $PAAM_1$ and PAAM at a heating rate of 10 °C/min.

3.7. SEM observations

The micrographs of PAAM and $PAAM_1$ are shown in Fig. 7(a) and (b), respectively. The sample shows a fine network structure and nonporous appears on the

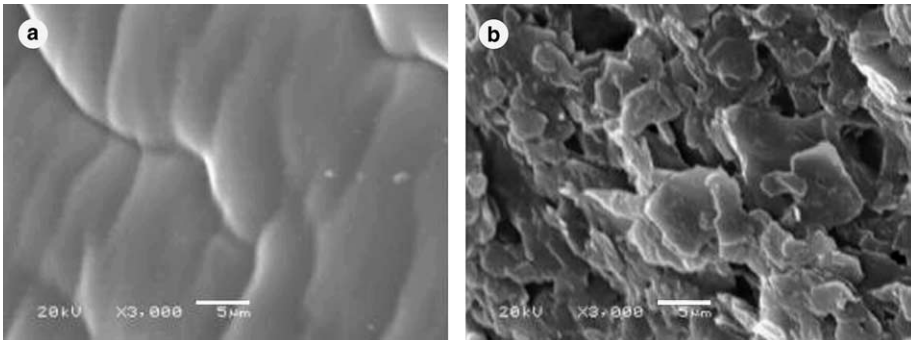

Fig. 7. Scanning electron micrographs of (a) PAAM and (b) $PAAM_1$.

SEM of PAAM, while on the SEM of $PAAM_1$, which has better water absorbency than that of PAAM, the samples is microporous and shows a broad network structure. These observations are in good agreement with our water absorbency observations (see Table 1).

3.8. Effect of saline solution on water absorbency

Fig. 8 shows the effect of saline solutions ($NaCl_{(aq)}$; $MgCl_{2(aq)}$; $CaCl_{2(aq)}$ and $FeCl_{3(aq)}$) on water absorbency of superabsorbent composite. As shown in Fig. 8, the water absorbency decreases with the increase of the concentration of all four salt solutions. The effect of the ionic strength of the external solution on the swelling has been determined using the following relation suggested by Hermans [20]:

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

where Q_{eq} is the water absorbency at equilibrium; i, the concentration of the charges bound to the gel; I, the ionic strength of the external solution, and A and B are empirical parameters. According to the Eq. (5), the water absorbency of superabsorbent decreases with increase of ionic strength of external solution. This decrease in water absorbency with increasing ionic strength may be attributed to the decrease in the osmotic pressure difference between the superabsorbent composite and the external saline solution. This also can be seen from Fig. 8 that for a given concentration of salt solution, the water absorbency in NaCl solution is far higher than that of in $MgCl_2$, $CaCl_2$ and $FeCl_3$ solutions. This dramatic decrease of water absorbency in multivalent cationic solutions may be due to the fact that the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes which result in an increase in the crosslink density of network [13,21].

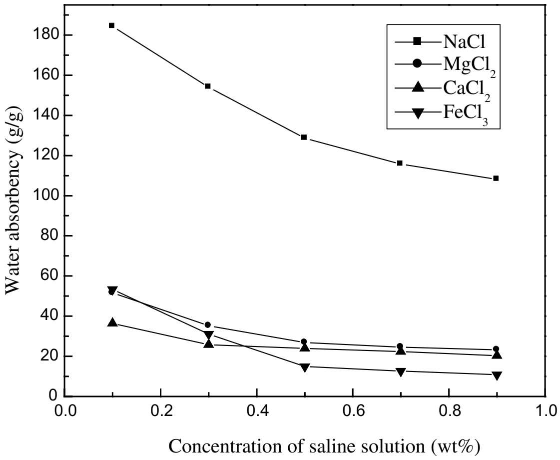

Fig. 8. Water absorbency of $PAAM_1$ in NaCl, $MgCl_2$, $CaCl_2$ and $FeCl_3$ aqueous solutions with various concentrations.

3.9. Swelling rate

The swelling rate of superabsorbent composite was determined and is shown in Fig. 9. It is indicated that the swelling rate of superabsorbent composite is high in 0–30 min and the water absorbency of superabsorbent composite reaches 1135 g/g within 30 min. After 30 min, the swelling rate becomes low and the maximum swelling capacity of superabsorbent composite was reached within 60 min.

3.10. Water retention test

Water retention of the swollen PAAM and superabsorbent composites was determined by centrifuging it at 4000 rpm for 30 min. It can be seen from Table 2 that the swollen superabsorbent composite samples show good ability of water retention and can keep approximately 96% of the distilled water. After the swollen sample thoroughly lost its adsorption water, the resulting dry sample ($PAAM_1$) still retains good water absorbing ability and can keep approximately 84% of initial water absorbency even after repeating 5 times of heating oven

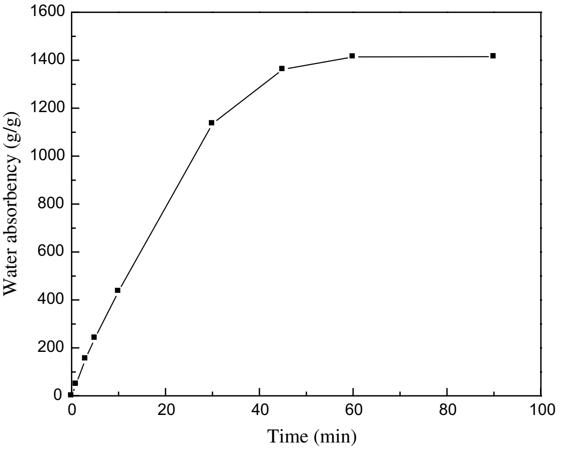

Fig. 9. Water absorbency of $PAAM_1$ as a function of time.

Table 2
Water retention for the swollen samples of superabsorbent composite and crosslinked PAAM

Sample	PAAM	$PAAM_1$	$PAAM_2$	$PAAM_3$	$PAAM_4$
Water retention (%)	95.4	97.2	96.4	96.1	95.8

test at 100 °C (the results are presented in Fig. 10), whereas only approximately 68% initial water absorbency can be kept for the resulting dry sample of PAAM (initial water absorbency of $PAAM_1$ and PAAM see Table 1). Results obtained from this study show that the superabsorbent composites have a good water retention capacity. These superabsorbent composites may prove useful in recyclable superabsorbent materials.

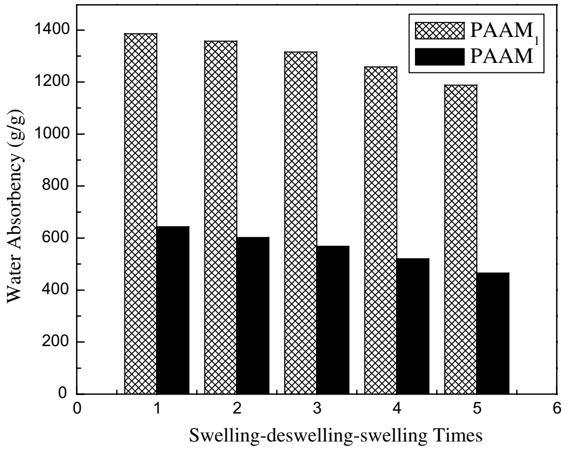

Fig. 10. Water absorbency of $PAAM_1$ as a function of swelling–deswelling–swelling times.

4. Conclusion

Novel poly (acrylic acid-co-acrylamide)/attapulgite superabsorbent composites were synthesized by graft copolymerization reaction of acylic acid and acrylamide on attapulgite micropowder using *N*,*N*-methylene-bis-acrylamide as a crosslinker and ammonium persulphate as an initiator in aqueous solution. Under our experimental conditions, a crosslinked poly(acrylic acid-co-acrylamide)/attapulgite superabsorbent composite with a water absorbency of higher than 1400 g H_2O/g was synthesized having a composition of 0.2% crosslinker, 1.0% initiator and 10% attapulgite. The water retention test of superabsorbent composites were also carried out and results obtained from this study show that the superabsorbent composite have a good water retention capacity. As a novel superabsorbent composite material, the water absorbencies in distilled water and in 0.9% NaCl solution were both improved and the production cost was significant reduced by compared with crosslinked poly (acrylic acid-co-acrylamide) superabsorbent polymer. This excellent water absorbency and water retention under load may prove especially practical in agricultural and horticultural applications.

Acknowledgement

This work was financially supported by the Western Action Project of CAS (No. KGCXZ-SW-502) and the "863" major project of the Ministry of Science and Technology, P. R. China (No. 2002AA6Z0310071).

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