Utilization of Starch and Montmorrilonite for the Preparation of Superabsorbent Nanocomposite

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ABSTRACT: Starch and montmorrilonite (MMT) were used as raw materials for synthesizing starch-*graft*-poly-[acrylamide (AM)–acrylic acid (AA)]/MMT superabsorbent nanocomposite by graft and intercalation copolymerization reaction of starch, AM, and AA in the presence of organic MMT micropowder in aqueous solution. Major factors affecting water absorbency such as weight ratio of monomers to starch, weight ratio of AM to AA, neutralization degree of AA, amount of crosslinker, initiator, and MMT were investigated. The superabsorbent nanocomposite synthesized under optimal synthesis conditions exhibits absorption of 1120 g H_2O/g sample and 128 g H_2O/g sample in deionized water and in 0.9 wt % NaCl solution, respectively. IR spectra showed that the graft copolymerization between ─OH groups on MMT and monomers took place during the reaction, and that crystal interlayer was pulled open in the superabsorbent nanocomposite. X-ray diffraction analysis showed that the crystal interlayer of MMT was pulled open to 2.73 nm, and thus formed nanometer exfoliation composite material. Thermogravimetric analysis showed that starch-*graft*-poly (AM–AA) superabsorbent nanocomposite (8 wt % MMT) has good thermal stability. This superabsorbent nanocomposite with excellent water absorbency and water retention, being biodegradable in nature, economical and environment friendly, could be especially useful in industry, agricultural, and horticultural applications. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2406–2412, 2011

Key words: starch; organic montmorrilonite; intercalation; nanocomposite; characterization; water absorbency; water retention

INTRODUCTION

Superabsorbent polymers are used mainly as absorbents in healthcare, agriculture, and industry applications.[1,2] In such applications, water absorbency and water retention are essential. Although the superabsorbents based on synthetic polymers do have large fluid absorbing capacities, those prepared from saponified starch graft copolymers have a greater demand in industry because of their low cost and large proportion of starch in these gels, which render them biodegradable and thus environmental friendly.[3,4] Recently, the preparation of polymer/clay superabsorbent composites has attracted great attention because of their relative low production cost, high water absorbency, and their considerable applications in agriculture and horticulture.[5–7]

In our previous study, the preparation of superabsorbent resin based on acrylic monomer and starch has been reported.[8] In a continuation of our research in this article, we have directed our attention towards the preparation of the organic–inorganic superabsorbent nanocomposite based on starch and organic montmorrilonite (MMT).

Montmorrilonite (a kind of clay mineral), as a good substrate for superabsorbent composite materials, is a layered aluminium silicate with reactive groups ─OH on the surface. In addition, starch and montmorrilonite are low cost raw materials. So, the chemical blending by means of graft copolymerization reaction of acrylamide (AM), acrylic acid (AA), starch, and MMT and fabricating a superabsorbent composite can significantly reduce the production cost and improve the comprehensive water-absorbing properties of the superabsorbent materials.[9–11]

In this article, we report the synthesis of superabsorbent nanocomposites by in site intercalation and

graft copolymerization reaction of starch, AM, AA, and MMT using N,N-methylene bisacrylamide (MBA) as a crosslinker and ammonium persulphate (APS) as an initiator in the presence of organic MMT micropowder in an aqueous solution. Aspects investigated included the optimum synthesizing conditions.

EXPERIMENTAL

Materials

Corn starch was obtained from Hua'ou Starch Co. (Inner Mongoulia, China). AM (chemically pure, Changzheng Chemical Co., Sichuan, China) was recrystallized. AA (chemically pure, Changzheng Chemical Co., Sichuan, China) was distilled under reduced pressure before use. APS (analytical grade, Xi'an Chemical Reagent Factory, Xi'an, China) was recrystallized from water. N,N-MBA (chemically pure, Suzhou Chemical Reagents Research Institute, Suzhou, China) was used as purchased. MMT micropowder (Weifang Hongyi Bentonite, Shandong, China) was milled and passed through a 320-mesh screen, followed by a treatment with 37% hydrochloric acid for 48 h and washed with deionized water until pH 7 was reached, and then 1 g of hexadecyl trimethyl ammonium bromide (HTMAB) was added per 50 g of MMT; the solution was stirred for 8 h in water bath at 70°C and washed with deionized water until the solution had no NaBr and HTMAB. The separation was dried for 48 h in a vacuum at 35°C, and then deeply brown organic MMT was gained.[12] HTMAB (chemically pure, Yingyuan Chemical factory, Shanghai, China) was used.

Preparation of starch-*graft*-poly(AM–AA)/MMT superabsorbent nanocomposites

A series of the samples with different amounts of MMT, crosslinker, initiator, starch, AM, and AA with different degrees of neutralization were prepared by the following procedure. A weight quantity of starch and deionized water were put in a 250-mL four-necked flask equipped with a stirrer, a condenser, a thermometer, and a nitrogen line. The slurry was heated to 95°C for 30 min under nitrogen atmosphere. Then the initiator APS was added when the temperature decreased to 60–65°C. After 15 min, the AM and partially neutralized AA, crosslinker (MBA), and organic MMT was added. The water bath was heated slowly to 70°C and kept for 3 h. Then the resulting product was washed several times with deionized water and ethanol and dried at 70°C to a constant weight. The dried product was milled and screened. All samples used had a particle size in the range of 40–80 mesh.

The procedure of preparation of starch-*graft*-poly(AM–AA)/MMT superabsorbent nanocompo-

sites was similar to that of preparation of ordinary superabsorbent resins, except that organic MMT was omitted.

Water absorbency measurement

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

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

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.

Characterization

The IR spectra of the superabsorbent nanocomposite 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 cm^3/min. X-ray powder diffraction patterns were obtained by Rigaku Dmax 2200/PC model instrument with Cu Kα radiation (40 kV, 40 mA). MMT and superabsorbent samples for X-ray diffraction (XRD) measurement were processed to powder form and film form for MMT and superabsorbents, respectively. The space of the layer is calculated by this formula $2d \sin h = n\lambda$. XRD reveals the basal spacing of the MMT before and after in situ incorporation indicating the morphology of the superabsorbent (exfoliated, intercalated, or only dispersed).

RESULTS AND DISCUSSION

Optimization of synthesis process

Effect of weight ratio of AM to AA

Table I shows that the water absorbency of superabsorbent nanocomposite increased with increasing content of AA. The maximum water absorbency was reached when the superabsorbent nanocomposite was synthesized with a weight ratio of AM to AA of 3 : 7. It could be due to the fact that ion groups ─COO$^-$ of the grafted copolymer chain increased with an increase in AA content, and the groups

TABLE I
Effect of Weight Ratio of AM to AA in the Feed on the Water Absorbency of the Superabsorbent Nanocomposite

Weight ratio of AM to AA (g/g)	Water absorbency (g/g)
5 : 5	792
4 : 6	971
3 : 7	1210
2 : 8	826
1 : 9	578

Reaction conditions: reaction temperature, 70°C; starch concentration (CA), 4 wt%; neutralization degree of AA, 75mol%; monomers concentration (CA), 16wt%; weight ratio of initiator, crosslinker and montmorrilonite in the feed is 0.3 wt%, 0.04 wt% and 8 wt%, respectively.

$-COO^-$, $-COOH$, $-CONH_2$ from monomers and $-OH$ from starch arrive optimal synergistic action. With further increase in AA content, the water absorbency decreased. This could be attributed to an increase in line polymer percentages of copolymers, which in turn resulted in an increase in soluble materials.

Effect of weight ratio of monomers to starch

Table II shows that the water absorbency of superabsorbent nanocomposite increased with increasing content of monomers. The maximum water absorbency was reached when the superabsorbent nanocomposite was synthesized with a weight ratio of monomers to starch of 8 : 2. It could be due to the fact that both grafting and the molecular weight of the grafted copolymer chain increased with an increase in content of monomers. With further increase in content of monomers, the water absorbency decreased. This could be attributed to the decrease of crosslinking density between monomers units, which in turn resulted in an increase in soluble materials.

TABLE II
Effect of Weight Ratio of AA to Starch in the Feed on the Water Absorbency of the Superabsorbent Nanocomposite

Weight ratio of monomers to starch (g/g)	Water absorbency (g/g)
9 : 1	892
8 : 2	1210
7 : 3	921
6 : 4	841
5 : 5	810

Reaction conditions: reaction temperature, 70°C; neutralization degree of AA, 75 mol%; weight ratio of initiator, crosslinker and montmorrilonite in the feed is 0.3 wt%, 0.04 wt% and 8 wt%, respectively; total concentration of starch and monomers is constant (20wt%) and Weight ratio of AM and AA is 3:7.

TABLE III
Effect of Initiator Content on the Water Absorbency of the Superabsorbent Nanocomposite

Initiator content (wt %)	Water absorbency (g/g)
0.1	129
0.3	1210
0.5	1011
0.7	825
0.9	716

Reaction conditions: reaction temperature, 70°C; starch concentration (CA), 4 wt%; neutralization degree of AA, 75mol%; monomers concentration (CA), 16wt%; weight ratio of crosslinker and montmorrilonite in the feed is 0.04 wt% and 8 wt%, respectively; total concentration of starch and monomers is constant (20wt%) and Weight ratio of AM and AA is 3:7. Weight ratio of monomers to starch is 8:2.

Effect of initiator content

The effect of initiator content on water absorbency is shown in Table III. Increase in the content of APS resulted in increase in water absorbency of the superabsorbent nanocomposite, which reached a maximum of 1210 g/g at a APS content of 0.3%. Further increase in APS resulted in the decline of water absorbency of superabsorbent nanocomposite.

This could be due to the fact that the initiator was mostly used in producing a large number of free-radical sites on the starch backbone at which the monomers could be grafted when the initiator content was low. Therefore, the grafting yield, and, in turn, the absorbency of the graft polymer increased with increase in APS content. However, above a critical content of 0.3%, the excess of APS was used, and the number of free radicals increased dramatically, thus brought about the decrease of molecular weight of copolymers, which resulted in the decrease of the water absorbency.

TABLE IV
Effect of Crosslinker Content on the Water Absorbency of the Superabsorbent Nanocomposite

Crosslinker content (wt %)	Water absorbency (g/g)
0.02	842
0.04	1210
0.06	982
0.08	866
0.10	778

Reaction conditions: reaction temperature, 70°C; starch concentration (CA), 4 wt%; neutralization degree of AA, 75mol%; monomers concentration (CA), 16wt%; weight ratio of initiator and montmorrilonite in the feed is 0.3 wt% and 8 wt%, respectively; total concentration of starch and monomers is constant (20wt%) and Weight ratio of AM and AA is 3:7. Weight ratio of monomers to starch is 8:2.

TABLE V
Effect of Neutralization of AA on the Water Absorbency of the Superabsorbent Nanocomposites

Neutralization degree (mol %)	Water absorbency (g/g)
65	679
70	913
75	1210
80	1074
85	859

Reaction conditions: reaction temperature, 70°C; weight ratio of initiator, crosslinker and montmorrilonite in the feed is 0.3 wt%, 0.04 wt% and 8 wt%, respectively; total concentration of starch and monomers is constant (20wt%) and Weight ratio of AM and AA is 3:7. Weight ratio of monomers to starc is 8:2.

Effect of crosslinker content

The effect of crosslinker content on water absorbency is shown in Table IV. As can be seen, the water absorbency decreased with the increase of crosslinker content from 0.04% to 0.10%. Clearly, higher crosslinker content resulted in the generation of more crosslink points, which, in turn, caused the formation of an additional network and decreased the available free volume within the superabsorbent nanocomposite. When the crosslinker content was lower than 0.04%, the absorbency of superabsorbent nanocomposite decreased because of an increase of soluble line polymer molecules. This tendency was similar to poly(AA)/MMT superabsorbent nanocomposite[13] and other superabsorbent hydrogels.[14,15]

Effect of neutralization degree of AA

As shown in Table V, the water absorbency increased with the increase of neutralization degree from 65 to 75 mol % and decreased with further increase in the neutralization degree of AA. When AA was neutralized with sodium hydroxide, the negatively charged carboxyl groups attached to the polymer chains set up an electrostatic repulsion, which tended to expand the network. In a certain range of neutralization degree, the electrostatic repulsion increased with the increase of neutralization degree, resulting in the increase of water absorbency. When the neutralization degree of AA was above the optimum values (75 mol %), the swelling capacity of superabsorbent nanocomposite decreased. This behavior could be ascribed to an increase in chain stiffness and to counterion condensation on the polyion.[16]

They found that the chain could expand to such an extent that the distance between neighboring charges became too high for optimum cooperation effects between the charges.

Effect of montmorrilonite

Table VI shows the effect of MMT content on the water absorbency. Increase in the MMT content resulted in increase in water absorbency of the superabsorbent nanocomposite, but with the further increase of MMT content the water absorbency decreased. The inorganic clay mineral particle in network acted as an additional network point. The crosslinking density of superabsorbent nanocomposite increased with the increase of MMT content, which resulted in a decrease in water absorbency. Table VI also showed that the superabsorbent nanocomposites had high water absorbing capacity in both deionized water and 0.9% NaCl solution especially when the superabsorbent nanocomposite contained 8 wt % MMT.

The best water absorbency was observed if the material was prepared under the following conditions: neutralization degree of AA is 75 mol %; weight ratio of initiator, crosslinker, and MMT in the feed is 0.3, 0.04, and 8 wt %, respectively; weight ratio of AM and AA is 3 : 7; weight ratio of monomers to starch is 8 : 2 in the condition of reaction temperature 70°C and total concentration of starch and monomers is 20 wt %.

Structure characterizations

IR spectra

When compared with the infrared spectra of MMT and starch-*graft*-poly(AA)/MMT superabsorbent nanocomposite (8 wt % MMT content), the absorption peaks at 3699 cm^{-1} attributed to the —OH groups on the surface of MMT disappeared after reaction and at 3620 and 3448 cm^{-1} attributed to the —OH groups on the interior of MMT disappeared after reaction, showing that the graft copolymerization between —OH groups on MMT and monomers took place during the reaction. Also, when compared with the infrared spectra of

TABLE VI
Effect of Montmorrilonite on the Water Absorbency of the Superabsorbent Nanocomposites

Montmorrilonite content (wt %)	Water absorbency in deionized water (g/g)	Water absorbency in 0.9% NaCl solution (g/g)
4	568	64
6	1018	97
8	1210	128
10	875	83
12	460	51

Reaction conditions: reaction temperature, 70°C; 75% neutralization degree of AA; weight ratio of initiator and crosslinker in the feed is 0.3 wt% and 0.04 wt%, respectively; total concentration of starch and monomers is constant (20wt%) and Weight ratio of AM and AA is 3:7. Weight ratio of monomers to starc is 8:2.
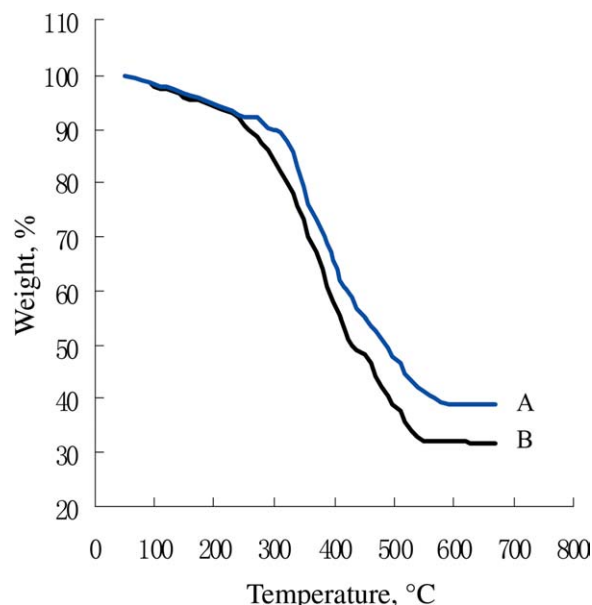
Figure 1 TG curves of starch-*graft*-poly(AA–AM) super-absorbent resin (B curve) and starch-*graft*-poly(AA–AM)/MMT superabsorbent nanocomposite containing 8% MMT (A curve). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

starch and superabsorbent nanocomposite, the absorption peak at 574 cm^{-1} attributed to the —OH groups on starch became smaller after reaction, which indicated that the —OH groups on starch changed during the reaction. The IR analysis results indicated that the graft copolymerization of monomer on both MMT and starch took place during polymerization process and the resulting product was a nanocomposite based on poly(AM–AA) incorporating with starch and MMT. The peaks at 538, 470, and 432 cm^{-1} of superabsorbent nanocomposite were very weak and showed that crystal structure of MMT changed and crystal interlayer was pulled open.

Thermal analysis

The TGA of starch-*graft*-poly(AM–AA) superabsorbent resin and starch-*graft*-poly(AM–AA) superabsorbent nanocomposite (8 wt % MMT) were also carried out (Fig. 1). Both starch-*graft*-poly(AM–AA) superabsorbent resin and starch-*graft*-poly(AM–AA) superabsorbent nanocomposite showed a very small weight loss below 100°C, implying a loss of moisture. Starch-*graft*-poly(AM–AA) superabsorbent resin and starch-*graft*-poly(AM–AA) superabsorbent nanocomposite had significant weight loss of 9.3% and 8.1% at 265 and 312°C, respectively. The major weight loss of starch-*graft*-poly(AM–AA) superabsorbent resin started at 542°C (32.7%), whereas for starch-*graft*-poly(AM–AA) superabsorbent nanocom-

posite the major weight loss started at 568°C (39.5%). Therefore, starch-*graft*-poly(AM–AA) superabsorbent resin and starch-*graft*-poly(AM–AA) superabsorbent nanocomposite had a decomposition temperature of 265 and 312°C, respectively. The results indicated that the introduction of MMT to polymer network resulted in an increase in thermal stability.

XRD analysis

XRD patterns of three-structure MMT can be seen in Figure 2. The interlayer distance (d_{001}) of MMT, organic MMT, and poly(AM–AA) superabsorbent nanocomposite was 1.06 nm (a curve, $2\theta = 8.4°$), 1.96 nm (b curve, $2\theta = 4.5°$), and 2.73 nm (c curve, $2\theta = 3.2°$), respectively. In organic MMT, hydrated inorganic cations in clay mineral interlayer could also be replaced by various organic cations through ion exchange reaction, in other words, Na$^+$ was replaced by quaternary ammonium cation in HTMAB. Because after MMT was modified by HTMAB, polymer molecules were connected with clay through hydrophobic hydrocarbon chain. Organic MMT was dispersed and it was packaged in the matrix of superabsorbent resin after in situ intercalation graft copolymerization. Monomers had already inserted into the nanoreactor (interlayer) of MMT, so interlayer distance increased. X-ray diffraction peaks moved toward smaller angle, and interlayer distance (d_{001}) increased to 1.96 nm. Expanding of interlayer distance provided space for monomer going into interlamination in the next step. Interlayer distance (d_{001}) of dry superabsorbent resin samples was up to 2.73 nm, because copolymerization energy expanded interlayer distance of MMT.
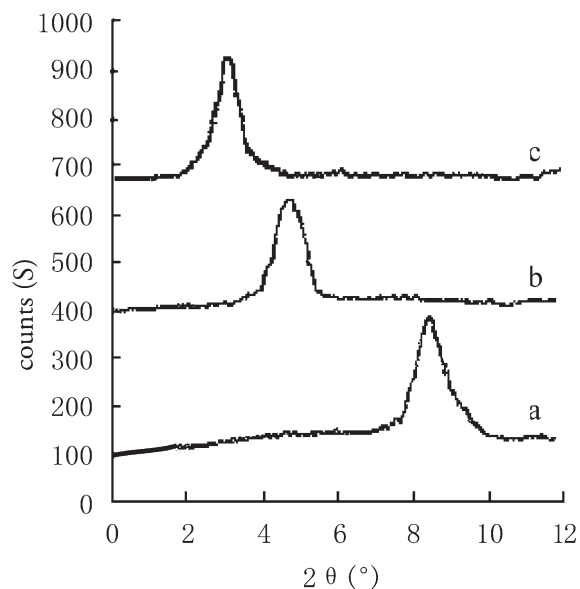

Figure 2 XRD patterns of different samples: (a) MMT; (b) organic MMT; (c) starch-*graft*-poly(AM–AA) superabsorbent nanocomposite (8 wt % MMT).
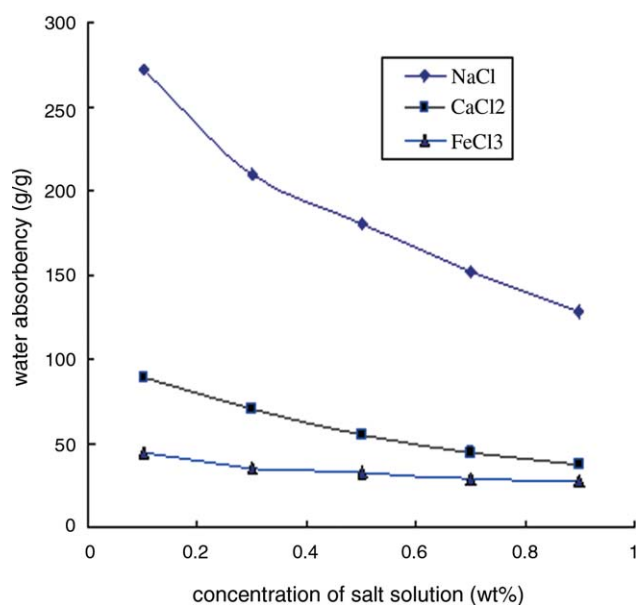
Figure 3 Water absorbency of starch-*graft*-poly(AM–AA)/MMT superabsorbent nanocomposite in NaCl, CaCl₂, and FeCl₃ aqueous solutions with various salt concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Assessment of properties

Effect of saline solutions

Figure 3 shows the effect of the concentration of saline solutions [NaCl (aq), $CaCl_2$(aq), and $FeCl_3$ (aq)] on water absorbency of superabsorbent nanocomposite under optimized synthesis condition. The
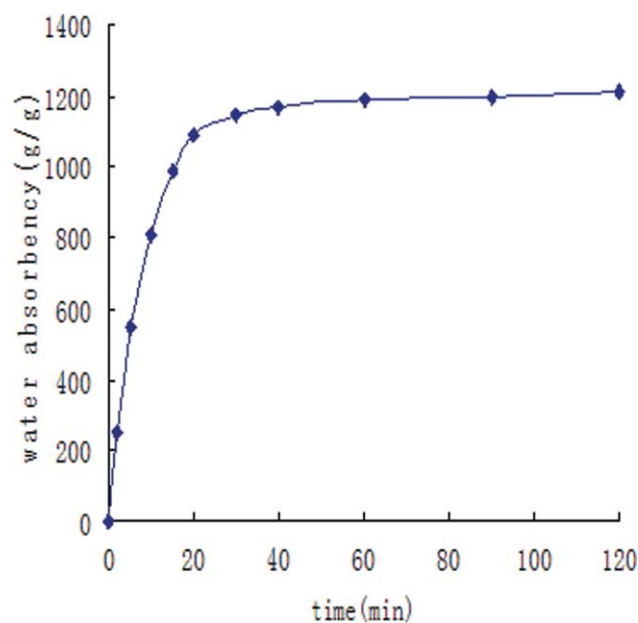

Figure 4 Variation of the water absorbency with time for starch-*graft*-poly(AM–AA)/MMT superabsorbent nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
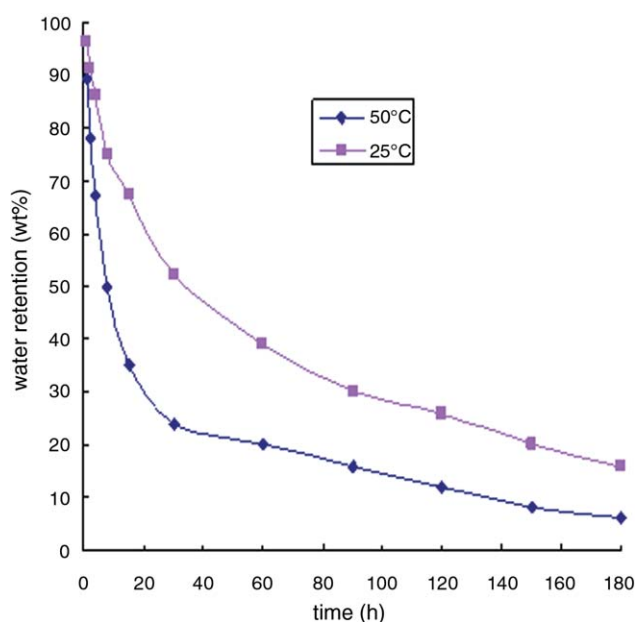

Figure 5 Water retention of swollen samples starch-*graft*-poly(AM–AA)/MMT superabsorbent nanocomposite (20 g, 40 mesh) as a function of time at 25 and 50°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water absorbency decreased with the increase in the concentration of all three saline solutions. The water absorbency of superabsorbent decreased with increase in ionic strength of external solution. This decrease in water absorbency with increasing ionic strength could be attributed to the decrease in the osmotic pressure difference between the superabsorbent nanocomposite and the external saline solutions. Figure 3 also showed that for a given concentration of saline solution, the water absorbency in NaCl solution was far higher than that in $CaCl_2$ and $FeCl_3$ solutions. This dramatic decrease of water absorbency in multivalent cationic solutions could be because of the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which resulted in an increase in the crosslinking density of network.

Swelling rate

Figure 4 indicates that the swelling rate of superabsorbent nanocomposite was high in 0–20 min and the water absorbency of superabsorbent nanocomposite reached 1090 g/g within 20 min. After 20 min, the swelling rate became low, and the maximum swelling capacity of superabsorbent nanocomposite was reached within 120 min.

Water retention test

Water retention of the swollen superabsorbent nanocomposites was determined at 25°C and by a heating

oven at 50°C. Figure 5 shows the water retention capacity of swollen superabsorbent nanocomposite (20 g, 40 mesh) as a function of time at 25 and 50°C. The swollen sample had a decreasing tendency of water retention with prolonging time. About 16% of deionized water could be held at 25°C after 180 h of water retention test. In the case of 50°C water retention test, the water loss almost reached 94% after 180 h. Water retention of the swollen superabsorbent nanocomposite was also determined by centrifuging it at 4000 rpm. The result showed that the starch-*graft*-poly(AA)/MMT superabsorbent nanocomposite had a good water retention ability and could keep more than 90% of the deionized water after centrifugation at 4000 rpm for 10 min.

CONCLUSIONS

A novel starch-*graft*-poly(AM–AA)/MMT superabsorbent nanocomposite was synthesized by graft copolymerization reaction of starch, AM, and AA in the presence of MMT powder in aqueous solution. The optimum synthesizing conditions were as follows: neutralization degree of AA, 75 mol %; initiator content, 0.3 wt %; crosslinker content, 0.04 wt %; organic MMT content, 8 wt %; weight ratio of AM and AA, 3 : 7; weight ratio of monomers to starch, 8 : 2. The superabsorbent nanocomposite synthesized under optimal synthesis conditions exhibited absorption of 1210 and 128 g H_2O/g sample in deionized water and in 0.9% NaCl solution, respectively. IR spectra showed that the graft copolymerization between ─OH groups on MMT and monomers took place during the reaction, and that crystal structure of MMT change and crystal interlayer was pulled open in this superabsorbent nanocomposite. XRD analysis showed that the crystal interlayer of MMT was pulled open to 2.73 nm, and thus nanometer intercalation composite material was prepared. TGA showed that starch-*graft*-poly(AM–AA) superabsorbent nanocomposite (8 wt % MMT) has good thermal stability.

This new approach is promising in using natural resource such as starch and MMT in the production of superabsorbent material, which could significantly reduce the production cost and make the technique quite environmental friendly. Also, this novel superabsorbent nanocomposite with excellent water absorbency and water retention could be especially useful in industry, agricultural, and horticultural applications.

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