Graft Copolymerization of Sodium Acrylate onto Organophilic Montmorillonites Initiated by Potassium Diperiodatonickelate (IV) and Application of Graft Copolymer in Water-Superabsorbent

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ABSTRACT: The graft copolymerization of sodium acrylate (SA) onto organophilic montmorillonites (OMMT) initiated by redox reaction of potassium diperiodatonickelate (IV) [Ni(IV)] with reactive groups on OMMT substrate was studied in alkaline medium. The grafting parameters have been investigated as a function of the ratio of monomer to OMMT, the concentration of initiator, temperature, and pH value. The structure of the graft copolymer (OMMT-*g*-PSA) was systematically characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscope (SEM). It was found that [Ni(IV)] belongs to a highly efficient initiator for graft copolymerization of SA onto OMMT via the redox iniation (grafting efficiency > 95%). Furthermore, the experimental results also showed that the graft copolymer gels synthesized under optimal condition exhibited a maximum water absorbency of 1104 g/g in distilled water and 111 g/g in 0.2 wt % NaCl solution, respectively, and its water retention ability is more than 91% after centrifugal separation for 2 h. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2472–2480, 2008

Key words: graft copolymers; organophilic montmorillonite; potassium diperiodatonickelate (IV); swelling; synthesis

INTRODUCTION

In recent years, the composites containing polymer and layered silicate are one of the most active domains no matter in the basic research or in the development of industry field of the polymeric material.[1–5] Montmorillonite, which has some reactive–OH groups on its surface, and belongs to a class of natural bentonite clay, is often used in the preparation of polymer/clay nanocomposites.[6,7] When compared with virgin polymer or conventional micro and macro-composites, these polymer/layered silicates usually exhibit remarkable improvement in materials properties such as high bioactivity,[8,9] water absorption,[10] thermal stability,[11] electrical performance,[12] mechanical properties,[13] and so on. In the application of these composites, much attention has been concentrated on the preparation of organic–inorganic super absorbent composites because of their relative low production cost, high water absorbency (WA), and their considerable range of applications.[10,14–18] Some inorganic materials such as attapulgite,[14] bentonite,[15] and mica[16] were usually

selected as substrate in order to investigate their swelling behaviors of superabsorbent composites. For example, a series of composite and nanocomposite hydrogels were synthesized by copolymerization reaction of partially neutralized acrylic acid (AA) on bentonite micropowder using N,N'-methylenebisacrylamide as a crosslinker and potassium persulfate as an initiator in aqueous solution.[15] Also, a high water-absorbent polyacrylate/bentonite composite was prepared by the intercalated polymerization and its WA was up to 120 g/g for water, and 30–36 g/g for the saline solution.[17] The starch-*graft*-acrylamide/mineral powder superabsorbent composite with WA about 4000 times was prepared via graft-copolymerization, followed by hydrolysis with sodium hydroxide.[18]

Making mention of modifying polymers, the graft copolymerization of natural and synthetic polymers containing starch, cotton, polyvinyl alcohol, nylon, and so on with common monomers have been successfully performed by our group in the recent years.[19–22] For instance, using potassium diperiodatonickelate(IV) [Ni(IV)] and potassium diperiodatoargentate(III) [Ag(III)] as initiators, the graft copolymerization of methyl acrylate onto poly(vinyl alcohol) was investigated in an alkaline medium and Ni(IV) and Ag(III) were found to be efficient redox initiators for the graft copolymerization.[23,24] The graft copolymerization of butyl acrylate onto casein

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initiated by Ni(IV) was also performed under heterogeneous conditions and a possible initiation mechanism was proposed.[21] The aforementioned studies on graft copolymerization were stemmed from the redox reaction of supernormal valence transition metals including Ag(III), Ni(IV), and Cu(III) with some reductant groups including hydroxyl, amino, and amide on the substrate. Moreover, in order to interpret the formation of radicals and the initiation in the graft copolymerization, a two-step single electron-transfer mechanism has been put forward in our work.[25–27] Till date, however, inorganic materials such as montmorillonites, glass fiber, and kaolin have rarely been used as substrates for graft copolymerization by these transition metal ions. On the basis of high-valence metal ions, the application of these efficient graft initiators is expected to open up one new method to synthesize polymer/inorganic composites.

To get the effective graft copolymerization, the radicals bonded on the substrate must form in the reaction. Ni(IV) ion is an oxidant with high redox potential and often proceeds with a single-electron transition to generate the radicals in its redox reaction. In the graft copolymerization initiated by Ni(IV) ion, the graft chain grows only from the substrate surface or its inside because all the radicals produced were usually bonded to substrate. As a result, higher grafting efficiency ($E\%$) and grafting percentage ($P\%$), as the most important parameters in graft copolymerization, can be easily obtained using Ni(IV) as initiator.[23–27] If the common initiators such as potassium persulfate, benzoyl peroxide, and azobisisobutyronitrile were selected in the graft copolymerization, $E\%$ and $P\%$ were often found to be low because of the obvious homopolymerization of monomers.

As an extension of our previous work, graft copolymerization of sodium acrylate (SA) onto organophilic montmorillonites (OMMT) were prepared using potassium diperiodatonickelate Ni(IV) as initiator in this study. To get higher grafting performance, OMMT with more reactive groups, not pure montmorillonites, was selected here as substrate of graft copolymer. We systematically investigated how some reaction conditions in the graft copolymerization affected the grafting parameters. Besides, the WA and the water retention (WR) of the polymer/inorganic composites synthesized were evaluated at different crosslinker content and ratio of SA to OMMT.

EXPERIMENTAL

Materials

Organophilic montmorillonites (OMMT), as a DK$_2$-type product, was provided by Fenghong Chemical Factory (Zhejiang Province, China). Acrylic acid (AA) monomer was purified by vacuum distillation at 63°C/25 mmHg. NN'-methylenebisacrylamide (MBA) as a crosslinking agent, purchased from Huadong Chemical Factory (Tianjin, China) and Sodium hydroxide were used as received. The grafting initiator potassium diperiodatonickelate Ni(IV) was prepared and measured according to the reported procedure.[28] All the other solvents were of analytical grade and were used without any further purification.
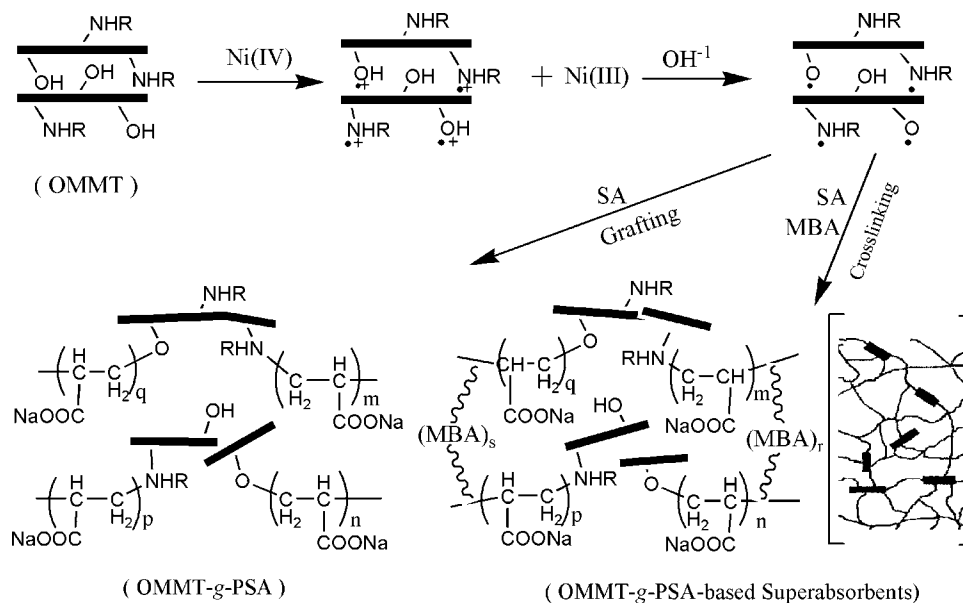
Graft copolymerization procedure

The graft copolymerization of SA onto OMMT was carried out by adding a given amount of OMMT (0.200 g) in a 20 × 200 mm polymerization tube equipped with a magnetic bar. After three standard cycles of evacuation and backfill with dry and pure nitrogen, the glass tube was charged with a required amount of SA monomer solution, which was prepared beforehand by gradually dropping AA into sodium hydroxide solution over an ice bath. The glass tube was kept in a water bath maintained at a proper temperature for about 15 min before adding the initiator. Then the alkaline aqueous Ni(IV) solution was injected by a syringe and the total volume was made up to 8 mL with distilled water. The reaction system was thermostatically controlled at the required temperature and magnetically stirred. The reaction mixture was allowed to react for about 3 h before the reaction was terminated by several drops of HCl solution. A series of graft copolymerizations on the various conditions of different monomer concentration, initiator concentration, temperature, and pH were performed according to the aforementioned procedure.

Isolation of the grafted and ungrafted polymers

After completion of reaction, the resulting rubbery gel was removed from the reaction tube and cut into small pieces whose length of each piece was about 3 mm by a pair of scissors. The monomer which did-not take part in the reaction was got rid of the crude graft copolymer by exhaustive soxhlet extraction with pure ethanol for 36 h. The crude product contained OMMT-g-PSA and the homopolymer of SA (PSA) was triturated and was dried to a constant weight under vacuum at 100°C. PSA was removed from the crude graft copolymer by exhaustive soxhlet extraction with a mixture of water and methanol (3 : 1 volume) for 36 h. The final titled copolymer, OMMT-g-PSA, was then dried to a constant weight under vacuum at 100°C.

Grafting parameters used in this article were defined and calculated in the following manner:

Scheme 1 The mechanism for graft copolymerization of SA on OMMT.

Monomer conversion ($C\%$) = (Total weight of PSA formed/Weight of SA charged) $\times$ 100%.

Grafting efficiency ($E\%$) = (Weight of PSA grafted/ Total weight of PSA formed) $\times$ 100%.

Grafting ratio ($P\%$) = (Weight of PSA grafted/ Weight of substrate) $\times$ 100%.

Investigation of water absorbency and water retention

In this article, the water absorbency (WA) and the water retention (WR) of the OMMT-g-PSA containing different crosslinker content have been investigated. OMMT-g-PSA (0.1 g) was immersed in an excess distilled water and a 0.2% aqueous solution of NaCl at room temperature for a sufficiently long time. The swollen beads were filtered through a silk sieve (20 mesh) to remove the nonabsorbed liquid and were weighed. The equilibrium absorbency was calculated by the following eq. (1):

$$WA = (W_{wet} - W_{dry})/W_{dry} \qquad (1)$$

where W_{dry} and W_{wet} are the weights of OMMT-g-PSA before and after adsorption, respectively. The WR under an ordinary pressure was determined in terms of the weight change of the swollen beads before and after centrifugal separation at 4000 rpm speed for different time intervals. The WR was calculated by the following eq. (2):

$$WR = (W_2/W_1) \times 100\% \qquad (2)$$

where W_1 and W_2 are defined as the weights of water-adsorbed OMMT-g-PSA before and after centrifugation.

Measurements

All samples were dried in a vacuum oven at 100°C before any test. OMMT-g-PSA and pure PSA were characterized by Fourier transform infrared spectrum with an FTS-40 spectrophotometer (BIORAD, USA) in a potassium bromide pills. Thermogravimetric analysis (TGA) was carried out in a Shimadzu DGC-40 DTATG apparatus (Shimadzu, Japan) over a temperature range of 30–800°C, with a heating rate of 10°C/min, and under a nitrogen flow rate of 10 L/h. A scanning electron microscope (SEM), AMKAY-1000B (Scientific Apparatus Factory of Chinese Academy of Sciences, China), was used to observe the morphologies of PSA, OMMT-g-PSA, and the OMMT.

RESULTS AND DISCUSSION

Mechanism for graft copolymerization

The mechanism for graft copolymerization of SA on OMMT is shown in Scheme 1. First, the higher-oxidizing Ni(IV) ions react with some reductive groups including hydroxyl and amino groups on OMMT to generate the corresponding radical-cation of hydroxyl and amino groups, as well as Ni(III) ions. Second, the OMMT macroradicals used as grafting sites, are generated via further reaction between the radical-cations and hydroxyl ion (OH^{-1}) provided by the alkaline medium. Finally, the grafting monomers SA close to the OMMT macroradicals are initiated, and thereafter PSA chains quickly grow by the continuous radical addition. The intermediate, Ni(III) ions formed during the redox reaction can also oxidize the reactive groups to give radical-cation and Ni(II) ions. The transition from Ni(IV) to Ni(II) ions
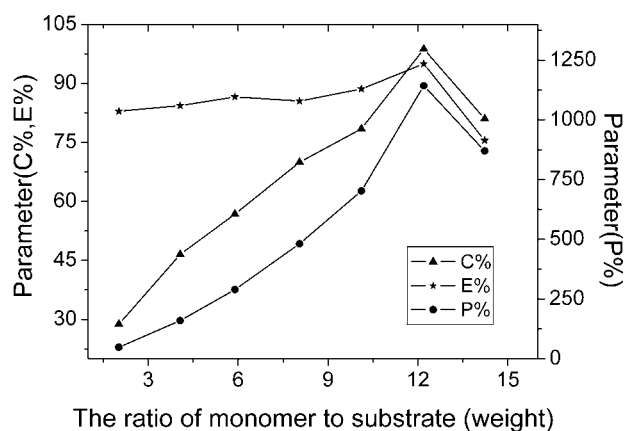
Figure 1 Effect of the monomer to substrate ratio on grafting parameters. Time = 3 h; temperature = 40°C; [Ni] = 1.443 × 10^{-2} mol/L; pH = 12.1.

belongs to a two-step and single-electron process according to the literature.[19,21,23] If MBA, a crosslinker, is added in the graft copolymerization, the PSA chains are crosslinked each other to form vast polymeric network. The large numbers of hydrophilic groups (—COONa) in the graft copolymer also provide many sites for absorbing-water, so as to prepare water-superabsorbent based on polymer/inorganic composites.

Effect of different factors on grafting parameters

Monomer/OMMT ratio

The effect of ratio of monomer to substrate, OMMT on grafting parameters was shown in Figure 1. The grafting parameters were markedly increased with an increasing Monomer/OMMT ratio when the Monomer/OMMT was less than 12 (w/w). This is mainly because of the following fact that the SA concentration increases relatively with the Monomer/OMMT ratio while OMMT and total volume are kept constant in graft copolymerization. On the other hand, the reaction system becomes gelatinous when the content of copolymer reaches one fixed value, and thereafter the diffusion of monomer is confined greatly. Obviously, the more the unreacted monomers after gelation remained, the higher the Monomer/OMMT ratio. As a result, the grafting parameters of C% is still decreased as Monomer/OMMT ratio is further increased, consequently leading to a decrease in P%. Besides, as more SA is added, the radical transfer to SA related to the homopolymerization, is also heightened, which induces a decrease of P% and E%.
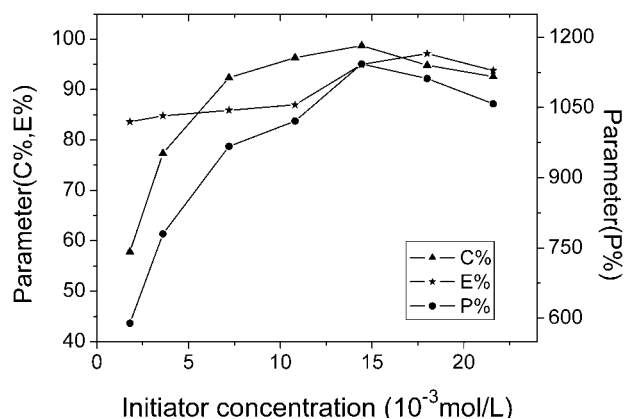
Initiator concentration

Figure 2 has indicated that changing tendency of grafting parameters, i.e., first increasing and then slight decreasing, when Ni(IV) concentration

increased from 2.10 × 10^{-3} mol/L to 21.3 × 10^{-3} mol/L. In graft copolymerization, Ni(IV) ions, strong oxidants, are apt to react with the reductive groups on OMMT such as amine and hydroxyl groups, to create macroradicals directly initiated the graft copolymerization of SA on OMMT. Therefore, higher Ni(IV) concentration affirmatively produces more radicals, leading to higher C%, P% in the same experiment. However, the excessive Ni(IV) ions accelerated another by-reaction, the reaction of radicals with Ni(IV) and Ni(III) ions to form some inert species, terminating the propagation of copolymer chain.[21,29] In addition, the homopolymerization of SA also raised with increasing Ni(IV) concentration. These factors resulted in a decrease of the grafting parameters. It is necessary to point out that the influence of the higher Ni(IV) ion concentration on grafting parameters is slight compared to temperature and pH value.

Temperature

The graft copolymerization of SA onto OMMT was carried out at different temperatures ranging from 20 to 50°C while keeping the other conditions constant. Figure 3 illustrates the effect of temperature on grafting parameters. All the graft parameters boost firs and then level off gradually. As the activation energy involving Ni(IV) redox reaction is commonly a small positive value,[30,31] the rate of radical formation is accelerated with increasing temperature, implying the increase of all graft parameters. In addition, the ascending C% and P% with the increase of temperature is also in agreement with the general principle of radical polymerization. The high temperature, however, quickened up the radical transfer reaction to form monomer and the homopolymerization of SA could not be ignored. Moreover,

Figure 2 Effect of initiator concentration on grafting parameters. Time = 3 hour; temperature = 35°C; pH = 11.1; SA/OMMT = 12.19.
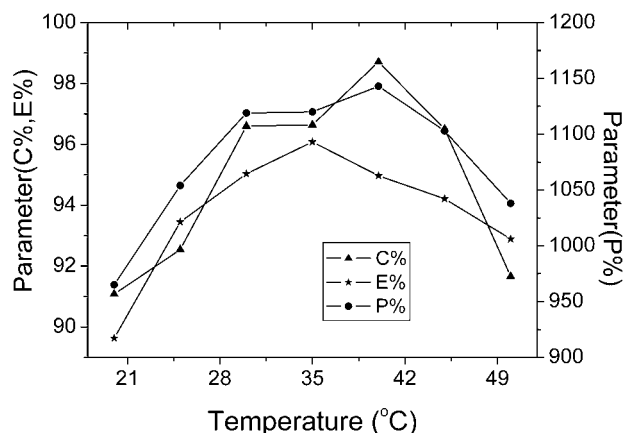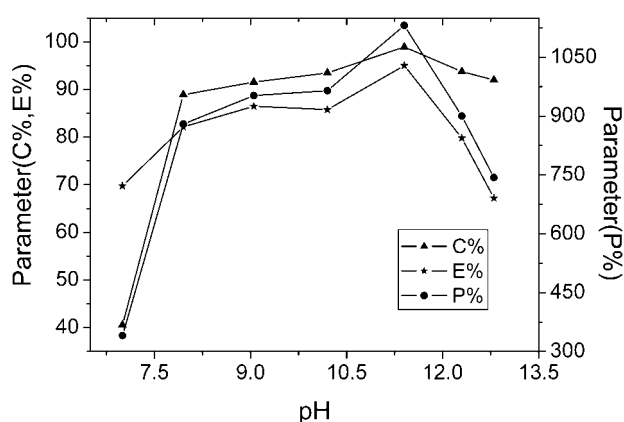
Figure 3 Effect of temperature on grafting parameters. Time = 3 h; [Ni] = 1.443×10^{-2} mol/L; pH = 11.1; SA/OMMT = 12.19.

the radicals were oxidized by Ni(IV) more easily to form some inert species and confined the chain propagation reaction at the higher temperature, resulting in a decrease of $C\%$, $P\%$, and $E\%$.

pH

As shown in Figure 4, the effect of pH value on grafting parameters has been investigated. $C\%$, $P\%$, and $E\%$ initially raised with an increase of pH, and then decreased thereafter. An optimum value of pH was observed in the grafting copolymerization when investigating $C\%$, $P\%$, and $E\%$. This is because, the two main active forms of Ni(IV) complex in alkaline medium, $[Ni(H_3IO_6)_2 \cdot (OH)_2]^{2-}$ and $[Ni(H_2IO_6)(H_3IO_6)(OH)_2]^{3-}$, varies with the change of pH.[30–32] More importantly, different types of Ni(IV) complexes possess different reactivity in the redox reaction. The rate of the Ni(IV) with the reactive groups

on OMMT changes affirmatively with pH value, and further determines the amount of macro-radicals in graft copolymerization. The optimum pH for affording maximum grafting parameters is around 11.4 in this work, which is basically consistent with the previous investigation reported in our work.[33] Furthermore, the optimum pH value 11.4 is approximately close to the one expected for the existence of $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$ ions estimated from the several dissociation constants of periodic acid.[32]
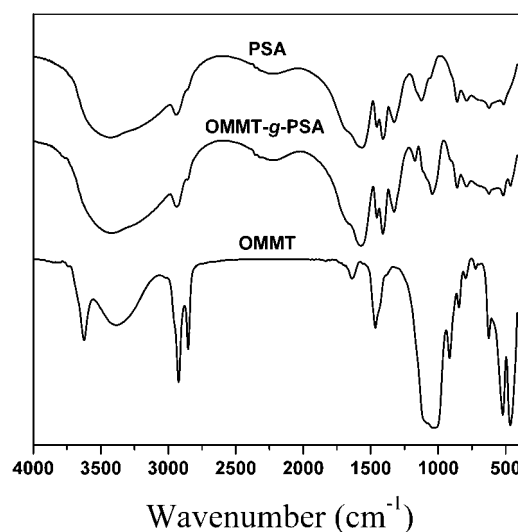
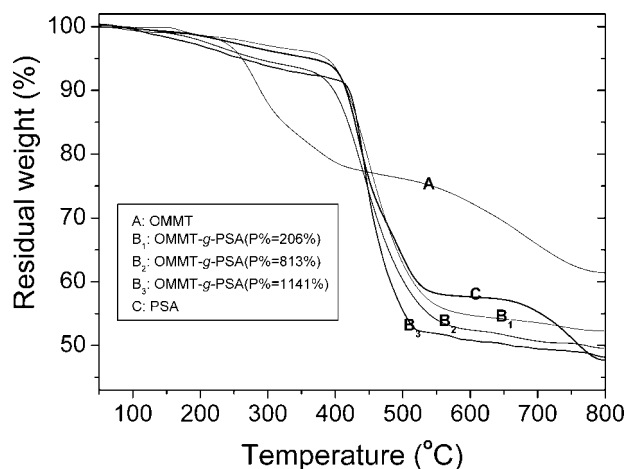## Characterization of graft copolymer

IR spectroscopy

The IR spectra of OMMT, OMMT-g-PSA along with pure PSA are shown in Figure 5. The strong absorption bands observed at 3623 and 3384 cm^{-1} are ascribed to O—H stretching vibrations, and the ones at 1038–1040 cm^{-1}, 2923–2852 cm^{-1} belong to Si—O and —CH$_2$ stretching vibration, respectively, in the IR spectrum of OMMT. When compared with pure OMMT, a strong and new absorption band at 1574 cm^{-1} corresponding to the carboxyl groups in the spectrum of OMMT-g-PSA was also recorded. These data further confirm initiation of the graft polymerization from OMMT and formation of grafted polymer chain. It is necessary to state that the strong adsorption at 3000–3600 cm^{-1} is ascribe to hydroxyl groups on OMMT and bonded water in the PSA chains.

TGA analysis

The thermogravimetric analysis (TGA) of OMMT, OMMT-g-PSA ($P\%$ = 206% (B$_1$), 813% (B$_2$), 1141% (B$_3$)), and pure PSA illustrated the decomposition

Figure 4 Effect of the value of pH on grafting parameters. Time = 3 h; temperature = 35°C; [Ni(IV)] = 1.443×10^{-2} mol/L; SA/OMMT = 12.19.

**Figure 5** FTIR spectra of PSA, OMMT-g-PSA and OMMT.

Figure 6 Thermal analysis for OMMT (A), OMMT-*g*-PSA (B), and PSA (C).

behaviors under heating in an inert atmosphere. The OMMT-*g*-PSAs studied were prepared under the following experimental conditions: SA/OMMT = 2.07, 8.14, 12.43; [Ni(IV)] = 1.443×10^{-2} mol/L; time = 3 h; temperature = 35°C; pH = 11.4. As shown in Figure 6, all the thermal behaviors of OMMT-*g*-PSAs showed a similar single step degradation that the initial degradation temperature of OMMT-g-PSA started above 390, 391, and 419°C, and the final

decomposition temperature was found to be 559, 538, and 516°C for B_1, B_2, and B_3, respectively. Compared to the pure OMMT, the final degradation temperature of OMMT-*g*-PSA has been found to be increased greatly because of mediation of PSA. Besides, the residual weights of OMMT-*g*-PSA is about 52, 50, and 48% for B_1, B_2, and B_3, respectively, which are approximately consistent with the computation based on grafting percentage and organic-component content in OMMT and the residual weight of pure PSA. The different thermograms of PSA, OMMT, and OMMT-*g*-PSA collaterally revealed that PSA chains have been grafted onto the OMMT substrate.

Scanning electron microscope

As shown in the Figure 7, the SEM micrographs of PSA, OMMT, and OMMT-*g*-PSA-based superabsorbent have indicated structural change before and after graft copolymerization. On one hand, the granule structure of OMMT vanished after graft copolymerization, suggesting that OMMT particles were intercalated by PSA and the compatibility of PSA and OMMT phase is very good. On the other hand, the OMMT-*g*-PSA-based superabsorbent shows an undulant surface rather than the smooth and tight surface of PSA. This undulant surface is very propi-
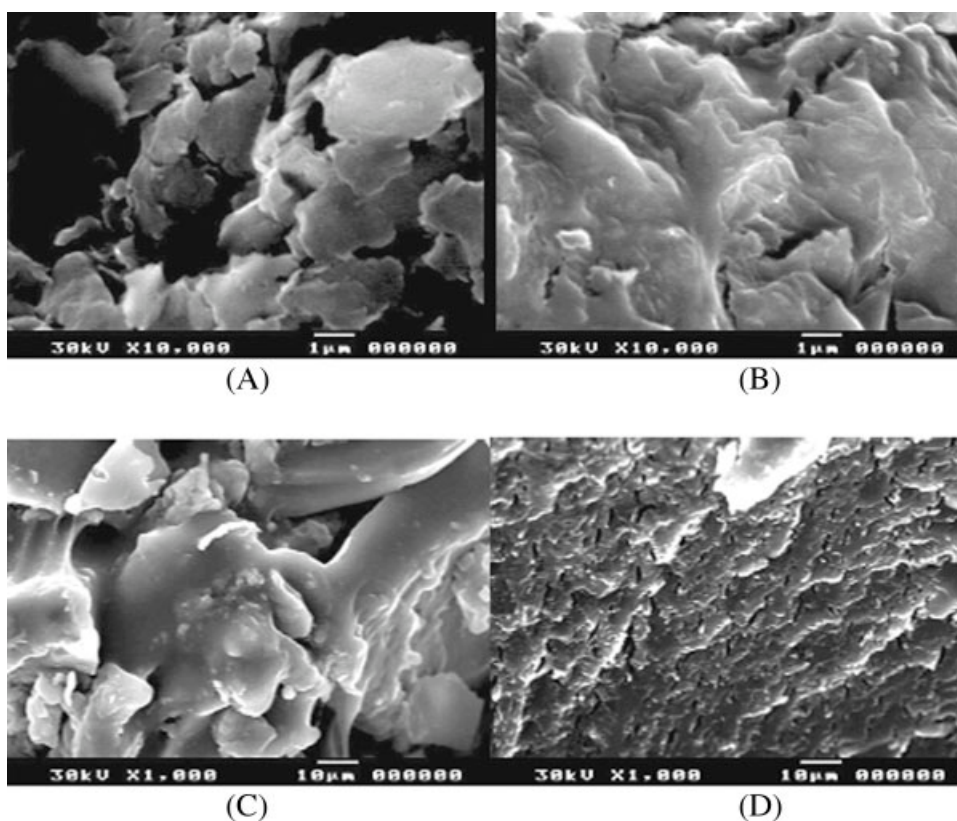
Figure 7 SEM micrographs of OMMT (A), OMMT-*g*-PSA (B), PSA (C), and crosssection of OMMT-*g*-PSA (D).
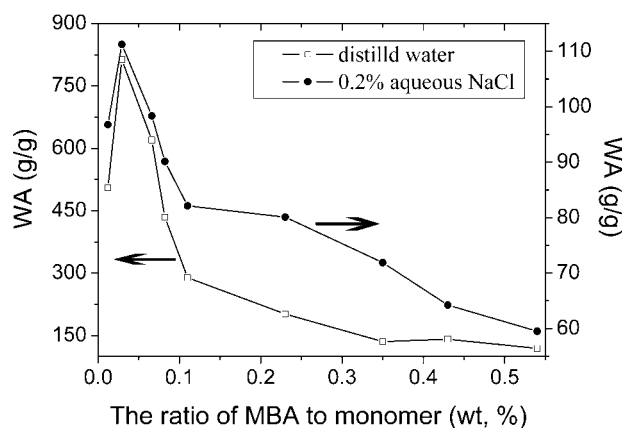
Figure 8 Effect of crosslinker content on water absorbency.

Water absorbency and Water retention

Effect of crosslinker content on WA

To study the WA and WR of OMMT-*g*-PSA, the graft copolymer-based superabsorbents were obtained under the following experimental conditions: SA/OMMT = 12.19; [Ni(IV)] = 1.443×10^{-2} mol/L; time = 3 h; temperature = 35°C; pH = 11.4.

The WA as a function of MBA concentration was investigated for crosslinked OMMT-*g*-PSA. As shown in the Figure 8, the WA sharply increases with the increase in crosslinker content in the range 0.01–0.029%, and decreases with the further increase of crosslinker in the range 0.029–0.54%. The maximum absorbency is found to be 813.42 g/g when the ratio (wt) of MBA to monomer is 0.029%. If the crosslinker was too little, the graft copolymer failed to form a three-dimensional network structure and it was water-soluble on the macroscopical level. When the graft copolymer formed a three-dimensional network structure completely, the water absorption reached a maximum. However, WA decreases with addition of the excessive crosslinker because the network space gets diminished greatly, and only less water enters inside OMMT-*g*-PSA-based superabsorbent. This tendency is similar to that found for some superabsorbents prepared by other groups[34] and fits in well with P. J. Flory formula.[35] Regarding pure water, a similar tendency was found when investigating WA in 0.2% NaCl aqueous solution with an increasing crosslinker content. The absorb-

ency in 0.2% NaCl aqueous solution reached a maximum of 111 g/g as the ratio of crosslinker MBA to monomer is 0.029%, whereas the absorbency in the saline solution of the polyacrylate/bentonite-based water-absorbent was 30–36 g/g.[17]

In addition, Table I also shows the WR ability of swollen crosslinked OMMT-*g*-PSA superabsorbent after the centrifugal separation at 4000 rpm speed. It can be seen that the weight percentage of the retained water has a decreasing tendency with prolonging the time of centrifugal separation. For example, when the ratio of MBA to monomer is 0.43%, WRs at different centrifugal time including 30, 60, 90, and 120 min are 98.04%, 96.24%, 94.91%, and 93.43%, respectively. On the other hand, the results also indicate that the superabsorbent has different WR ability after centrifugal separation when different crosslinker was added during the superabsorbent synthesis. A smaller free space was formed in the three-dimensional superabsorbent at higher crosslinker content, leading to a remarkable decrease of free water in superabsorbent thrown away during centrifugal separation. Therefore, the WR shows an overall increasing tendency with the crosslinker content.

Ni(IV), the initiator used in this article has good activity only in alkaline conditions,[28,29] so, SA was utilized as graft monomer by the complete neutralization of AA before graft copolymerization. To obtain higher WA, the graft copolymer powders (P% = 1050%) was partially acidified at ambient temperature with 1 mol/L HCl solution in the comparative experiment. When the acidification degree (defined as the mole ratio of HCl to SA) reaches 40, 60, 80%, the water absorption of the composite are 671, 911, and 1120 g/g in distilled water, respectively. This means that an appropriate acidification degree is very essential for the superabsorbent composite when only paying respect to higher WA, and this similar behavior has also been reported previously by others.[36,37]

TABLE I
Effect of Various MBA Content (wt) on WR of OMMT-*g*-PSA

Ratio of MBA to SA (wt %)	WR (%) at different centrifugal time			
	30 (min)	60 (min)	90 (min)	120 (min)
0.012	94.65	93.28	92.01	91.33
0.029	94.87	94.36	93.77	92.60
0.066	95.79	95.00	94.45	91.88
0.082	95.93	94.79	93.28	91.63
0.11	96.43	95.68	94.30	92.28
0.23	98.48	96.80	94.90	93.07
0.35	96.26	94.55	93.08	91.49
0.43	98.04	96.24	94.91	93.43
0.54	99.38	98.64	97.41	96.88
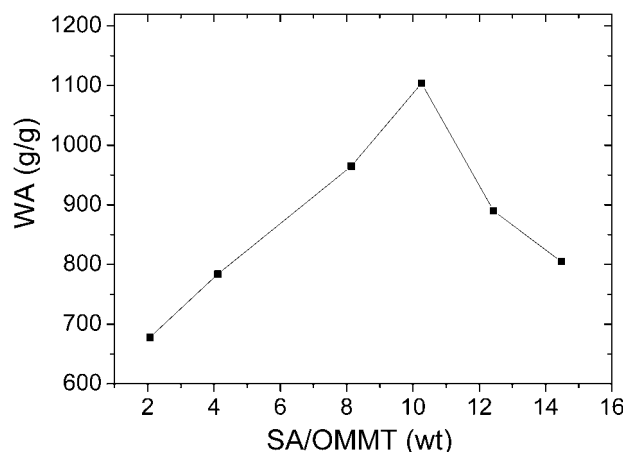
Figure 9 Effect of the ratio of SA to OMMT on water absorbency.

Effect of SA/OMMT on WA

Figure 9 has shown the effect of the ratio of SA to OMMT (SA/OMMT) on WA of the graft copolymer-based suprabsorbents. The suprabsorbents investigated were prepared under the following experimental conditions: SA/OMMT = 2.07, 4.11, 8.14, 10.26, 12.43, 14.47, [Ni(IV)] = 1.443×10^{-2} mol/L; time = 3 h; temperature = 35°C; pH = 11.4, crosslinker content = 0.03%. It is clear that SA/OMMT plays an important role in the synthesis of the suprabsorbent with high WA. The WA increases from 678 to 1104 g/g as the SA/OMMT ratio increase from 2.07 to 10.26 when the crosslinker content was fixed at 0.03%. In fact, the moderate crosslinking and large numbers of hydrophilic groups in the suprabsorbents are the two essential, and indiscerptible conditions for high WA. In this study, both crosslinker MBA and OMMT act as chemical crosslinking in the suprabsorbent. The content of hydrophilic groups, —COO^{-} used as absorbing-water sites, increased with an increasing SA/OMMT, leading to the absorption of more water. According to the study of Makamura et al., most of the water in hydrogel is free water and is restricted by the polymeric network.[38] When SA/OMMT is too high, the overall crosslinking density dramatically decreased because of the lessening of crosslinking from OMMT. Accordingly, when the too high SA/OMMT ratios (12.43, 14.47) were selected in the synthesis, the polymer network with the decreased crosslinking can't district more free water, which resulted in a decrease of WA.

CONCLUSIONS

In this work, the graft polymers with high graft efficiency and grafting percentage have been prepared in alkaline medium by an efficient Ni(IV)—OMMT redox system. The effect of various experimental conditions on the grafting parameters has been evaluated and the Fourier transform infrared spectroscopy (FTIR), TGA, and SEM measurements reveal that PSA macromolecular chain was grafted onto OMMT. The optimum synthesizing conditions were as follows: time = 3 h; temperature = 35°C; [Ni(IV)] = 1.443×10^{-2} mol/L; pH=11.4; weight ratio of SA to OMMT= 12 : 1. The key parameter in the graft copolymerization, grafting efficiency, is as higher as 95% and grafting percentage may be facilely controlled in the range of 100 to 1200%. As superabsorbent composite, the titled OMMT-g-PSA also exhibited excellent WA when a certain crosslinking agent was added in the graft copolymerization. This promising superabsorbent composite with good WA and WR could be especially useful in agricultural and horticultural applications.

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