

Synthesis and Properties of a Poly(acrylic acid)/Montmorillonite Superabsorbent Nanocomposite

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ABSTRACT: A novel superabsorbent nanocomposite was synthesized through the intercalation polymerization of partially neutralized acrylic acid and a sodium-type montmorillonite powder with *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate and sodium sulfite as a type of mixed redox initiator. The effects of such factors as the amounts of the sodium-type montmorillonite, crosslinker, and initiator and neutralization degree on the water absorbency of the nanocomposite were investigated. The structure and micrographs of the superabsorbent were characterized with Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. The results showed that

the acrylic acid monomer was successfully intercalated into the montmorillonite layers and banded together with them. The montmorillonite layers were exfoliated and basically dispersed in the composite on a nanoscale after the polymerization. The water absorbency of the nanocomposite was much higher than that of pure poly(acrylic acid). The optimum absorbency of the nanocomposite in distilled water and saline water (NaCl concentration = 0.9%) was 1201 and 83 g/g, respectively. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5725–5730, 2006

Key words: acrylic acid; montmorillonite; superabsorbent; nanocomposite; redox initiator

INTRODUCTION

A superabsorbent is a type of functional polymeric material that can absorb a large amount of water during a short period of time, and the absorbed water is hardly removed even under some pressure. Because of their excellent characteristics, superabsorbents are widely used in many fields, such as agriculture, horticulture, sanitary goods, and medicine.¹⁻³ Tremendous developments have been achieved both in their theoretical study and in their applications^{1,4-6} since the first superabsorbent polymer was reported by the U.S. Department of Agriculture in 1961.⁷

In recent years, many layered, inorganic, mineral micropowders such as mica,⁸ attapulgite,^{9,10} kaolin-

ite,¹¹ and sercite¹¹ have been used in the preparation of polymers to achieve lower production costs and higher properties. Montmorillonite (MMT), a layered aluminum silicate with highly exchangeable cations and reactive groups (—OH) on its surface, also has been widely used to improve the properties of polymers^{12,13} in this field.^{14,15} Lee and Yang¹⁴ reported the synthesis of poly(sodium acrylate)/organic MMT superabsorbents through inverse suspension polymerization. Luo et al.¹⁵ reported the synthesis of starch-grafted poly(acrylamide-co-acrylic acid)/MMT with a γ -ray irradiation technique.

Our main objective has been to find a simple way of preparing superabsorbents with high properties but low production costs. Therefore, we report the synthesis of a superabsorbent nanocomposite via water solution polymerization, which costs less and is simpler than inverse suspension polymerization and radicalization techniques, with a sodium-type montmorillonite (Na-MMT) powder, which is less expensive than organic MMT, and with ammonium persulfate and sodium sulfite as a type of mixed redox initiator, which can lead to a lower reaction temperature for the gel point than a solitary initiator. The effects of such factors as the amounts of the Na-MMT, crosslinker, and initiator and neutralization degree on the water absorbency, as well as the properties of the nanocomposite, have been investigated.

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EXPERIMENTAL

Materials

Acrylic acid (AA; chemically pure) was obtained from Lingfeng Chemical Reagent Corp. (Shanghai, China). *N,N'*-Methylenebisacrylamide (chemically pure) and sodium hydroxide (analytical-grade) were purchased from Chemical Reagent Corp. of the Chinese Medicine Group (Shanghai, China). Ammonium persulfate (analytical-grade) and sodium sulfite (analytical-grade) were supported by the Second Chemical Reagent Factory (Yixing, China). Na-MMT was made from original MMT (Fenghong Chemical Clay Factory, Zhejiang, China) in our laboratory.

Preparation of Na-MMT

In a flask, the original MMT and distilled water, in a mass ratio of 1 : 4, were stirred at room temperature for 30 min initially and then deposited for at least 4 h to remove impurities. The Na-MMT powder was obtained after the upper suspending solution was modified with a sodium carbonate powder under stirring for 30 min, dried at 80°C overnight, and milled through a 300-mesh screen.

Preparation of the superabsorbent composite

In a 50-mL beaker, the AA monomer (10.0 g) was neutralized by sodium hydroxide (11.0M) at a low temperature to a proper neutralization degree. After the neutralization, the proper amount of Na-MMT together with the partly neutralized AA was added to a reactor equipped with a mechanical stirrer and a nitrogen line. Under a nitrogen atmosphere, the solution was stirred at a high speed (2000 rpm) for 20 min. The proper amounts of the crosslinker and initiators (dissolved in 2 mL of distilled water) were added to the solution one by one during this period. Afterwards, the reactor was placed in a thermostated water bath at 45°C for 3 h and then transferred to another thermostated water bath at 80°C for an additional 2 h. The product was dried at 110°C. Thus, being milled and screened through a 100-mesh screen, a particle superabsorbent nanocomposite was obtained.

Measurement of the water absorbency

A proper amount of the superabsorbent nanocomposite (0.1 g) was immersed in distilled water or saline water at the ambient temperature to reach the swelling equilibrium. The residual water was removed by filtration with a 100-mesh screen. The water absorbency (A_1) and saline water absorbency (A_2) of the composite were calculated according to the following equation:

$$A = (m_2 - m_1)/m_1 \quad (1)$$

where A is the water or saline water absorbency and m_1 and m_2 are the weights of the dry and swollen samples, respectively.

Characterization

The infrared spectra of the samples were recorded on a 170SX Fourier transform infrared spectrograph (Thermo-Nicolet, Waltham, USA) in KBr flakes. The dried samples were scanned at a rate of 2°/min by a D/Max-RC X-ray diffractometer (Rigaku, Tokyo, Japan) (40 kV, 100 mA) with a copper target. For each interval of 0.02°, the diffracted X-ray intensity was recorded automatically. The morphologies of the nanocomposites were examined with a JSM-5610LV scanning electron microscope (JEOL, Tokyo, Japan) after the samples were coated with gold.

RESULTS AND DISCUSSION

Infrared spectrum analysis

The infrared spectra of Na-MMT, the poly(acrylic acid) (PAA)/MMT superabsorbent nanocomposite with an 80% neutralization degree, and PAA with an 80% neutralization degree are shown in Figure 1. The characteristic peaks at 3629 and 917 cm^{-1} [Fig. 1(A)], which are ascribed to the stretching vibration and bending vibration of —OH on the surface of layers of MMT, respectively, disappear for the PAA/MMT superabsorbent nanocomposite [Fig. 1(B)]. The absorbance peak at 2515 cm^{-1} [Fig. 1(C)], due to the stretching vibration of the hydroxyl from —CO₂H, becomes weak for the PAA/MMT superabsorbent nanocomposite [Fig. 1(B)]. The absorbance peak at 1636 cm^{-1} , attributed to the intramolecular hydrogen bond of carboxyl, disappears for the PAA/MMT superabsorbent nanocomposite

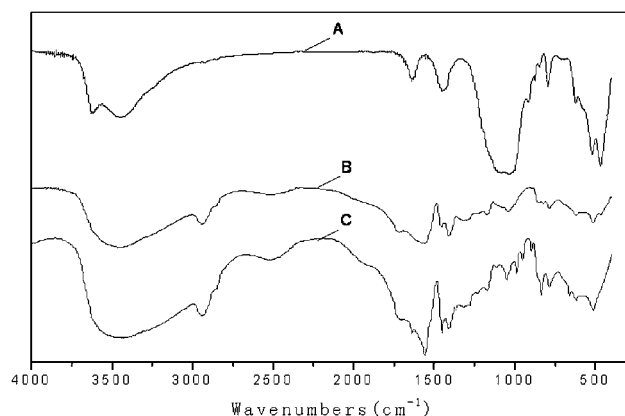


Figure 1 Infrared spectra of (A) Na-MMT, (B) the PAA/MMT nanocomposite, and (C) PAA.

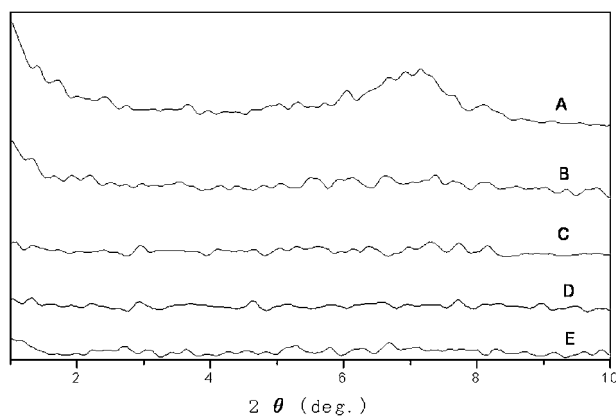


Figure 2 X-ray diffraction patterns of (A) Na-MMT and (B–E) PAA/MMT nanocomposites with various amounts of MMT (3, 5, 7, and 9 wt %, respectively).

[Fig. 1(B)]. Moreover, another notable characteristic peak at 1720 cm^{-1} in Figure 1(B) belongs to the vibration of $-\text{COOR}$, which indicates that an esterification reaction occurred between MMT and the monomer. All these changes indicate that PAA reacted with MMT during the polymerization. In addition, in Figure 1(A, B), the absorbance peak around 1041 cm^{-1} can be ascribed to the stretching vibration of $\text{Si}-\text{O}$ in MMT, whereas the characteristic absorbance peak around 470 cm^{-1} resulted from its bending vibration.

X-ray diffraction analysis

The X-ray diffraction spectra of PAA/MMT with various amounts of MMT (all the amounts in this article are weight ratios of the relevant reagent to the AA monomer) are shown in Figure 2. There is a notable absorbance peak in curve A, and its corresponding d value is about 1.2 nm according to the Bragg equation.¹⁶ However, there is no obvious peak in the other curves. This means that the layers of MMT mostly exfoliated and dispersed in the composite on a nanoscale after the polymerization.

Scanning electron microscopy

Figure 3 shows scanning electron microscopy photographs of PAA, the nanocomposite with 3% MMT, and the nanocomposite with 7% MMT. A comparison of Figure 3(b,c) and Figure 3(a) shows that the layers of MMT disperse in the superabsorbent composite on a nanoscale, and this is consistent with the results of the X-ray diffraction analysis. The micrograph of the nanocomposite with 7% MMT [Fig. 3(c)], which has the best absorbency in our experiments, shows a denser dispersion of layers of MMT than that of the nanocomposite with 3% MMT in Figure 3(b).

Effect of the Na-MMT amount on the water absorbency

Figure 4 shows the effect of the MMT amount on the distilled water absorbency of the superabsorbent nanocomposite. The water absorbency gradually

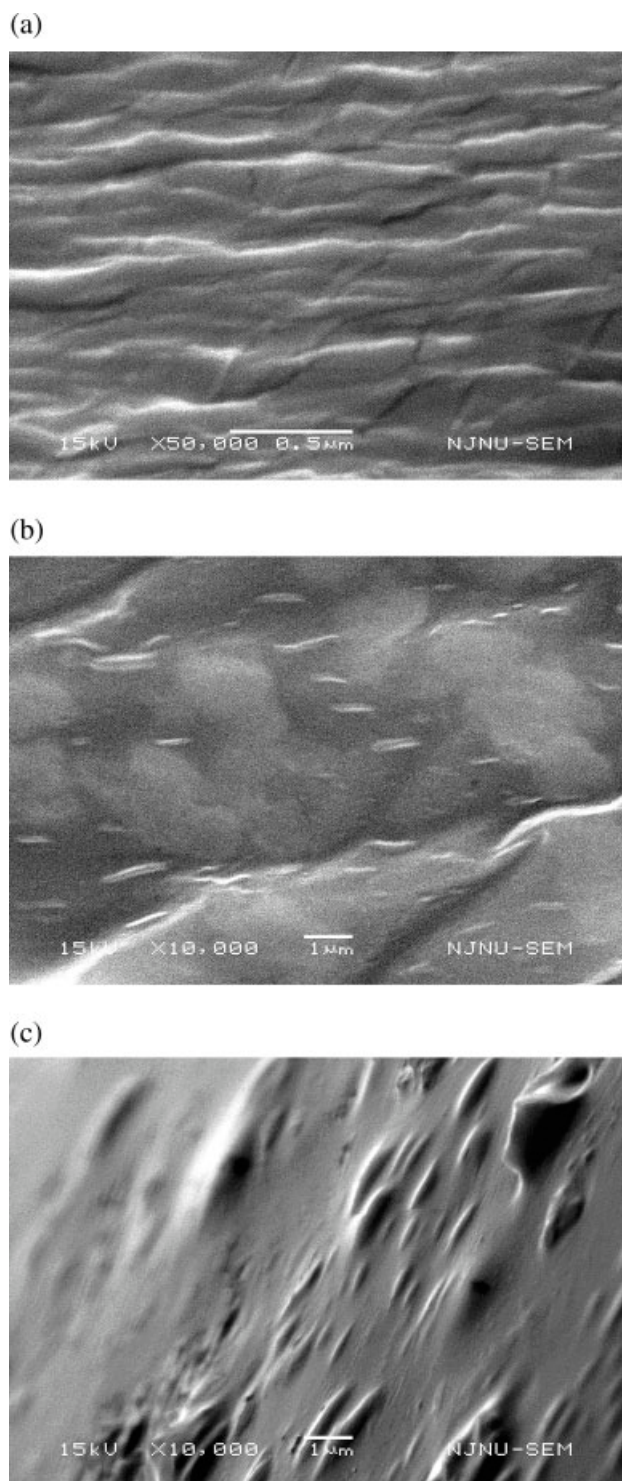


Figure 3 Scanning electron micrographs of (a) PAA, (b) the nanocomposite with 3% MMT, and (c) the nanocomposite with 7% MMT.

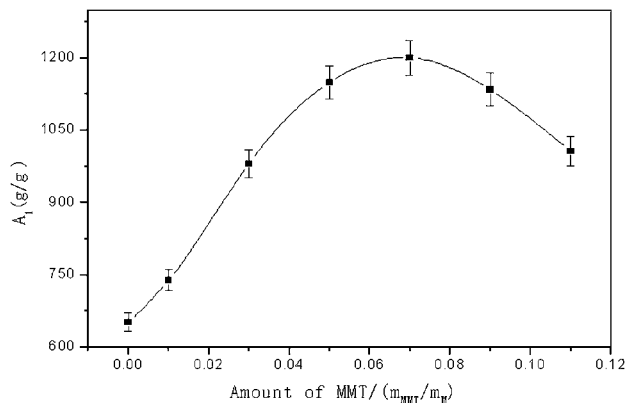
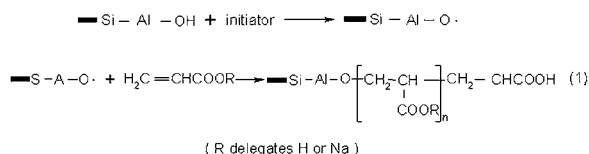


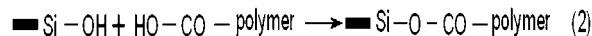
Figure 4 Effect of the MMT amount on the distilled water absorbency of the nanocomposite (0.3% initiator, 0.15% crosslinker, and 80% neutralization degree).

increases as the MMT amount increases from 1 to 7% and decreases as it further increases. The occurrence of this phenomenon can be explained by two reactions between MMT and AA. The first reaction, which is shown in Scheme 1, expresses the fact that MMT acts as an additional network point in the composite after the polymerization.¹⁷ The additional crosslinking points can improve the hydrophilic network because it can increase the length of the polymeric chain. The other reaction, which is described in Scheme 2, means the carboxyl of PAA reacts with $-\text{OH}$ on the surface of layers of MMT.¹⁰ Thus, the carboxyl, as the far end of the polymer chain has been adequately used to form a more efficient water-absorbent network, can chain up more water in it. However, a greater amount of MMT results in the generation of more crosslinker points, which increase the crosslinking density of the superabsorbent nanocomposite and leave less space for water to enter. In addition, MMT itself has lower water absorbency than PAA. Therefore, a superabundant amount of MMT reduces the absorbency of the composite.

The tendency and principle of saline water absorbency of the nanocomposite, depicted in Figure 5, are similar to those of distilled water. However, there is a much lower absorbency in saline water than in pure water. As reported by Zou,¹ the water absorbency of a superabsorbent in saline water is about 1/10 of that in pure water. This is because the ionic intensity in saline water largely reduces the infiltration



Scheme 1 Schematic reaction of MMT and the monomer initiated by the initiator.



Scheme 2 Schematic esterification reaction of MMT and the monomer.

pressure of the polymer network and hence reduces the water absorbency of the superabsorbent.

Effect of the crosslinker amount on the water absorbency

It can be clearly seen in Figure 6 that the absorbency increases with the amount of the crosslinker up to 0.15% and sharply decreases as the crosslinker amount further increases. The swelling behavior of the polymers can be presented by the following equation⁴:

$$Q^{5/3} \approx \left\{ \left[\frac{i}{2 \times V_u} \times S^{1/2} \right]^2 + \frac{1}{2} - X_1 \right\} / V_1 \left\{ (V_e/V_0) \right\} \quad (2)$$

where Q is the absorbency of the superabsorbents, V_e/V_0 is the crosslinking density, $(1/2 - X_1)/V_1$ is the hydrophilic affinity of the polymeric chain, i/V_u is the concentration of the electric charge that is bonded in the polymeric chain, and S is the ionic intensity of the solution outside. The water absorbency of the superabsorbent composite depends on the density of the polymeric space network.^{8,10} According to eq. (2), an increase in the crosslinking density will reduce the water absorbency. The reason that this phenomenon happens is that excessive crosslinking density produces a too dense polymeric network and leaves less space for water to enter. However, a low concentration of the crosslinker cannot form a fine network, and some uncrosslinked polymeric chains will be dissolved in water. Therefore, if the crosslinker amount is too low, the optimal water absorbency of the superabsorbents cannot be obtained.

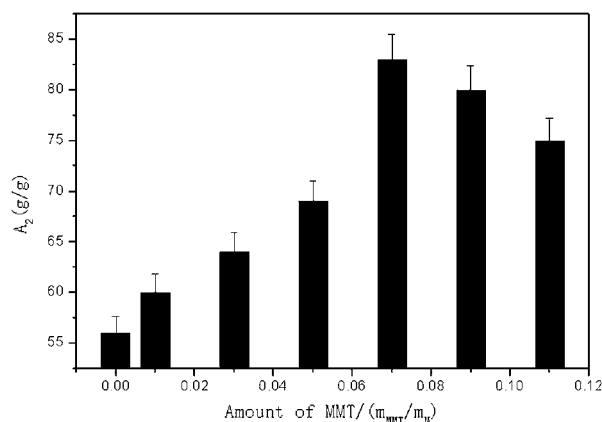


Figure 5 Effect of the MMT amount on the saline water absorbency of the nanocomposite (0.3% initiator, 0.15% crosslinker, and 80% neutralization degree).

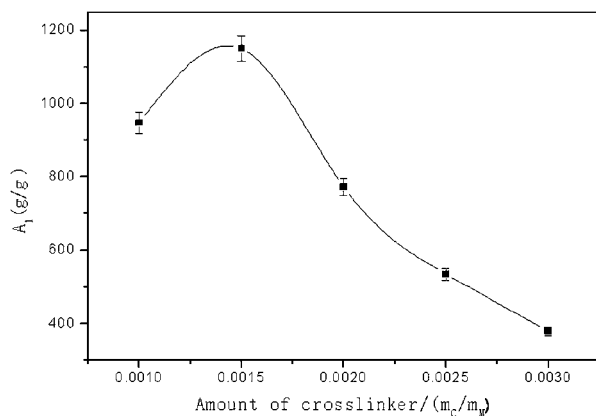


Figure 6 Effect of the crosslinker amount on the water absorbency of the nanocomposite (5% MMT, 0.3% initiator, and 80% neutralization degree).

Effect of the initiator amount on the water absorbency

The effect of another factor, the initiator amount, on the water absorbency of the nanocomposite has also been studied (Fig. 7). The tendency of the initiator amount is similar to the tendency of the crosslinker amount shown in Figure 6. The absorbency of the nanocomposite increases with an increasing initiator amount initially. After reaching a peak, the absorbency sharply decreases. The relationship between the average kinetic chain length (V) and the concentration of the initiator in free-radical polymerization is obtained from the following equation¹⁸:

$$V = 1/2k_p(fk_i k_t)^{-1/2}[I]^{-1/2}[M] \quad (3)$$

where k_p , k_i , and k_t are the rate constants for propagation, initiator, and termination, respectively; f is the initiating efficiency of the initiator; and $[I]$ and $[M]$ are the initial concentrations of the initiator and reactive monomer, respectively. According to the equation, the

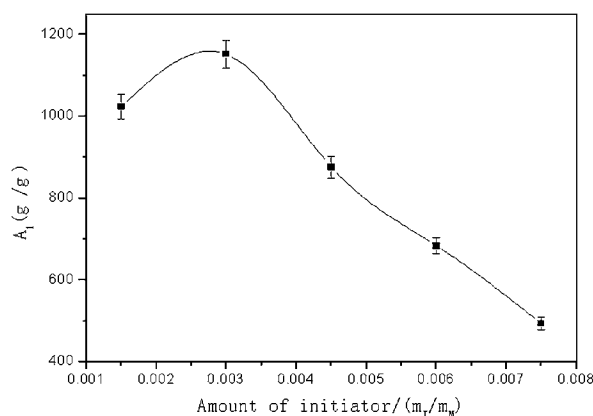


Figure 7 Effect of the initiator amount on the water absorbency of the nanocomposite (5% MMT, 0.15% crosslinker, and 80% neutralization degree).

greater the initiator concentration is, the shorter the average kinetic chain length is. This is because excessive initiator produces superfluous free radicals, which lead to a too dense grafting density between AA and MMT. On the other hand, as reported in another study,¹⁰ the polymeric chain ends do not contribute to the water absorbency. Therefore, increasing the initiator amount reduces the water absorbency. However, when the initiator concentration is below the optimal value, there are not enough free radicals to initiate monomers to form an efficient network, and the superabsorbent cannot reach the optimal water absorbency consequently.

Effect of the neutralization degree on the water absorbency

Figure 8 shows the effect of the neutralization degree on the water absorbency of the superabsorbents. It is obvious that the water absorbency increases as the neutralization degree increases from 45 to 80% and decreases as it further increases. This behavior may be interpreted as a cooperative effect between carboxyl groups and carboxylate groups. Carboxyl groups mainly contribute to the water affinity of the network, whereas carboxylate groups contribute to the infiltration pressure when the superabsorbent is marinated in water surroundings. Additionally, the charge density of the polymer is one of the important factors that affect its water absorbency according to Flory’s network theory.⁴ The extent of neutralization directly determines the charge density: an inadequate neutralization degree leads to less infiltration pressure, whereas an overage neutralization degree results in repulsion among carboxylate groups and decreased water absorbency. Hence, when carboxylate and carboxyl groups cooperate in a suitable ratio, the cooperative effect will reach its maximum. In our experiments, the optimal absorbency of the nanocomposite was obtained at an 80% neutralization degree.

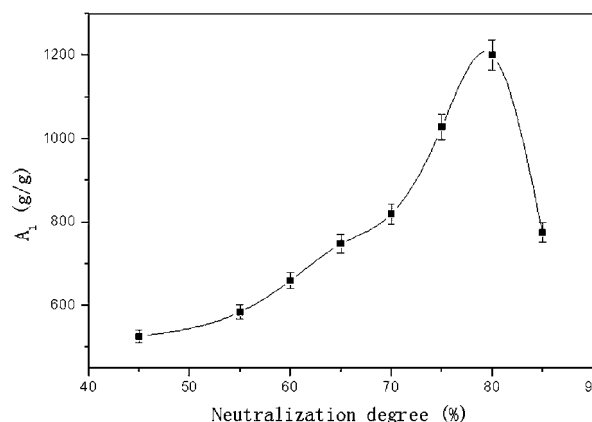


Figure 8 Effect of the neutralization degree on the water absorbency of the nanocomposite (5% MMT, 0.15% crosslinker, and 0.3% initiator).

CONCLUSIONS

A PAA/MMT superabsorbent nanocomposite was synthesized through the solution polymerization of partially neutralized AA and Na-MMT powder with *N,N'*-methylenebisacrylamide as a crosslinker and ammonium persulfate and sodium sulfite as a redox initiator. The optimal parameters were as follows: 7% MMT, 0.15% crosslinker, 0.3% initiator, and 80% neutralization degree. The introduction of MMT into the superabsorbent not only reduced the production cost of the composite but also increased its water absorbency. The infrared analysis indicated that the AA monomer reacted with MMT during the polymerization. The X-ray diffraction analysis and the scanning electron microscopy observation confirmed that the layers of MMT were mostly exfoliated and dispersed in the composite on a nanoscale after polymerization.

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