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The Effect of MMT/Modified MMT on the Structure and Performance of the Superabsorbent Composite

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Summary

A series of superabsorbent composites containing Montmorillonite (MMT), modified-Montmorillonite (OMMT) and sodium acrylate were synthesized by free-radical polymerization in aqueous solution. The structure of composites was characterized by Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and X-ray diffraction (XRD), and the results showed that the polymer chains were grafted onto the edge and the surface of MMT or OMMT. At the same time, the equilibrium swelling ratio of the composites was investigated as a function of the clay content and the results showed that the equilibrium swelling ratio of composites was improved by the introduction of clay. The maximum equilibrium swelling ratio of composite in distilled water and 0.9 wt% sodium chloride solutions were up to 2450 g/g and 118 g/g, respectively. Finally, the result of thermogravimetric analysis (TGA) suggested that the introduction of clay and modified clay could improve the thermal stability of superabsorbent composites.

Keywords

Superabsorbent composite; Exchangeable cationic monomer; Montmorillonite

Introduction

Superabsorbent polymers are loosely crosslinked networks that can absorb a large amount of water in a short time and retain water under pressure. Because of their excellent characteristics, superabsorbents have been used in agriculture and horticulture [1,2], sealing composites [3], artificial snow [4,5], drilling fluid additives [6], medicine for drug delivery system [7-9] since the first superabsorbent polymer was reported by the US Department of Agriculture in 1961 [10]. In few decades, the performance improvement of superabsorbent polymers was always an important domain in progress of functional polymer.

Organic/inorganic composites had been extensively researched in several decades due to their excellent performances. Since there are exchangeable cations and reactive hydroxyl groups on their surface, layer inorganic silicate was employed to prepare various hybrids. [11-13]

In recent years, to enhance the strength of hydrogel and reduce the cost of superabsorbent polymer, [14] the introduction of inorganic layer silicate (such as montmorillonite (MMT), [15] kaolin [16] and hydrotalcite, [17]) was reported in many articles, [18,19] and the improvement of equilibrium swelling ratio of superabsorbent composites was attributed to the formation of nanostructure due to the introduction of layer silicates. Elsewhere, Kourosh et al. [20] suggested that the equilibrium swelling ratio of superabsorbent composites could be reduced due to the phase separation when the inorganic clay particles were added. In our paper, the results demonstrated that the swelling capacity of superabsorbent composites could be great improved due to introduction of MMT and modified MMT. However, the investigation of the composites structure demonstrated that the polymer chains were grafted onto the edge and surface of MMT or modified MMT, and there existed neither intercalation nor exfoliation nanostructure in composites. Thus, the result suggested that the collaborative absorbent effect through the introduction of MMT or OMMT improved improved the swelling capacity of superabsorbent composites.

Experimental

Materials

Acrylic acid (AAc) was obtained from YiLi chemical Co. (Beijing, China), which was neutralized by sodium hydroxide solution. The sodium montmorillonite (Na^+-MMT) with cation exchange capacity (CEC) of 92-mmol/100g, which was obtained from Zhejiang Linan Bentonite Factory (Zhejiang province, China). The size was less than 75×10^{-6} m. Acryloyloxyethyl dimethylbenzyl ammonium chloride (DMABC) was selected as intercalating agent which were obtained from Sanyo Chem. Industries (Sanyo, Japan). N, $N^{'}$-methylenebisacrylamide (NMBA) and ammonium persulfate (APS), which were purchased from sinopharm Chemical Reagent Co., Ltd (Shanghai, China), were used as cross-linking agent and initiator, respectively. All agents were used directly without any further purification.

Preparation of OMMT

Modified- Montmorillonite OMMT was prepared as follows: 10g Na^+-MMT was dispersed in 250ml DMABC (1 M/L) aqueous solution. The mixture was styirred vigorously at 50°C for 24 h, and then OMMT was formed. The separated OMMT was washed with large volume of distilled water and filtered several times until the excessive cationic monomer was completed removed, and then dried in vacuum oven 50°C until the weight was constant.

Preparation of superabsorbent composites

A series of MMT based superabsorbent composites with different amount of MMT were synthesized according to the following procedure. A certain weight AAc (30 g) and 80ml distilled water were introduced into a 250 ml four-neck flask, equipped with a stirrer, a reflux condenser, a thermometer and a nitrogen line. The sodium hydroxyl solution (30 wt %) was added under stirring in cool water bath. The neutralized degree was controlled in range of 80%.The appropriate weight MBA was added and stirred until the MBA was dissolved completely, and then appropriate amount of MMT or OMMT was dispersed in the mixed solution. After the N2 was introduced into the reactor for 1 h, the initiator was added into the system at 60°C under stirring. The reaction was carried out until the gel was obtained. The product were obtained by washed with plentiful distilled water and then precipitated with acetone to remove any unreacted reactants. The depurative product was dried in a vacuum oven at 50°C until the weight of the product was constant.

Swelling measurements

A weighted quantity of the superabsorbent composite (0.1 g) powder(mesh 30~40) was immersed in 400 ml distilled water or 0.9 wt% sodium chloride solution for 24 h to reach swelling equilibrium. Swollen samples were then separated from unabsorbed water by filtering through a 100-mesh screen and the excess water was removed carefully from the retained gel. The equilibrium swelling ratio of composite, Q, was calculated using the following equation:

$$Q= (M - M_0)/M_0 \qquad (\mathbf{1})$$

where M_0 and M are the weights of the dry sample and the swollen sample, respectively. Q is calculated as grams of water per gram of sample.

Characterization

XRD patterns were gotten using a Philips PW1710 BASED X-ray diffractometer (Philips, Netherlands) equipped with an intrinsic germanium detector system. The test was carried out using Cu Kα radiation under a voltage of 40 kv and a current of 30 mA, scanning from 3° to 15° at 3°/min. FTIR spectroscopy was carried out using a Nicolet NEXUS 360 (Nicolet, USA) spectrometer with KBr disk. The analysis was performed in the transmission mode in the 400-4000 cm^{-1} range, with a resolution of 4 cm^{-1} and accumulation of 32 scans. Thermal stability studies of dry samples were performed on a Perkin–Elmer TGA-7 thermogravimetricanalyzer (Perkin–Elmer Cetus Instruments, Norwalk, CT), with a temperature range of 25–600°C at a heating rate of 10°C/min using dry nitrogen purge at a flow rate of 50 mL/min. A JEM-2000EX TEM operated at 200kv was used to study the morphology of the samples. Slices of 50 nm were cut with a Leica Ultracut UCT microtome by a glass knife for the TEM studies. The content of MMT or modified MMT in samples was 11.8 wt% and the modified MMT was cured by 17 wt% DMABC solution as depicted in section of sample preparation.

Results and discussion

The FTIR analysis

The FTIR spectra of MMT, OMMT, PAAc/MMT and PAAc/OMMT composites are shown in Fig. 1.

It is well known that free water molecular exist in the gallery of clay platelets, and there are lots of OH groups on the surface of clay. [21] The two obvious different absorption bands at 3628 and 3450 cm^{-1}(Fig. 1(a) and (b)) ascribed to O–H groups on MMT or modified MMT powder. The appearance of absorption bands (Fig. 1(a) and (b)) at 1040 cm^{-1} attributed to Si–O bends.

After the reaction (Figure. 1(c) and (d)), the stretching vibration absorption bands of C=O belonging to COOH (1720 cm^{-1}) and COO^- (1570 cm^{-1}) for the symmetrical

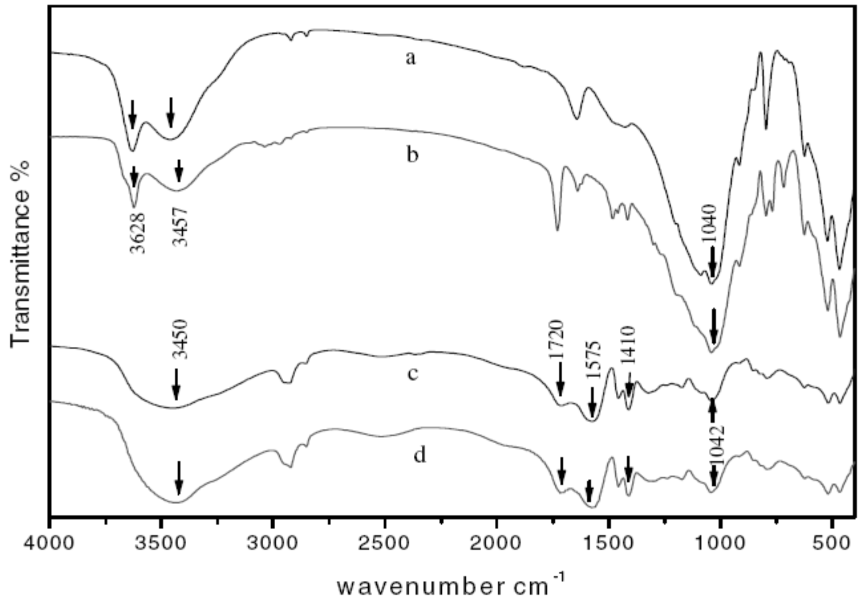

Figure 1 the FT-IR profiles of (a) MMT, (b) OMMT, (c) composite with AAcNa and 11.8 wt% MMT, (d) composite with AAcNa and 11.8 wt% OMMT.

stretching vibration, 1410 cm^{-1} for the asymmetrical stretching vibration) were observed in spectra. [22] The results showed that the chains of poly (sodium acrylate) were grafted onto the MMT or modified MMT. The absorption peak at 3628 cm^{-1} attributing to OH groups on surface of clay diminished after the reaction. Only the absorption peak at 3628 cm^{-1} belonging to OH groups of free water molecular could still be observed in the spectra. The results suggested that the graft polymerization should occur between the OH groups on the surface or edge of MMT/modified MMT and the chains of poly (sodium acrylate). However, a fact must be noted that the absorption peaks at 3450 cm^{-1} belonging to free water molecular could become wider due to the absorption of water, which could hide much valuable information about graft polymerization.

The XRD analysis

It is well known that the change of the d001 of clay platelets is the criterion, by which the intercalated or exfoliated composite can be decided. [23]To investigate the structure of composites, the XRD was employed in this paper. The XRD profiles of MMT, modified MMT and typical composites are shown in Figure 2. A typical XRD pattern of MMT, with a strong peak at 6.610° corresponding to a basal spacing of 13.36 Å, is shown in Figure 2a. After treatment with DMABC, the peak moves to a lower angle ($2\theta = 5.455°$), corresponding to basal spacing of 16.18 Å in Figure 2b. It suggests that DMABC had intercalated into the gallery of MMT during the anion-exchange process.

The XRD profiles of various composites in dry state are showed in Figure 2c and Figure 2d. A fact could be found that the obvious peak still could be observed in the XRD profiles of all composites. The position of peaks was similar to that of MMT and

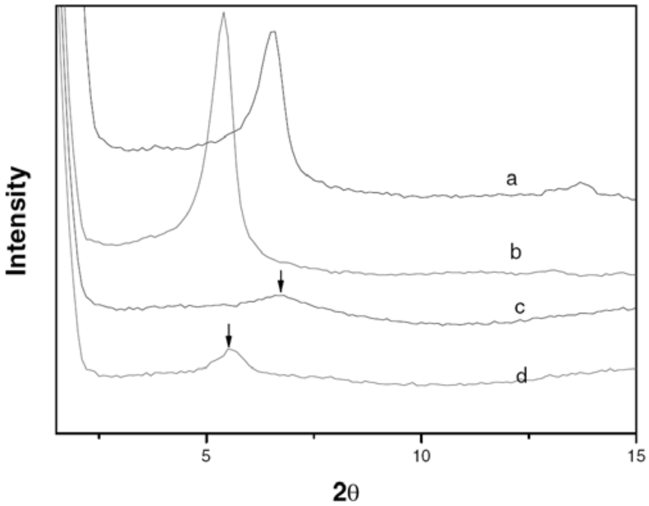

Figure 2 the XRD patterns of (a) MMT, (b) OMMT, (c) composite with AAcNa and 11.8 %MMT, (d) composite with AAcNa and 11.8 wt% OMMT.

modified MMT (the peaks of MMT and modified MMT were at 6.610° and 5.455° respectively, and that of composites containing MMT and modified MMT were 6.775° and 5.555°, respectively). The results showed that d_{001} of MMT or modified MMT platelet was almost not changed during the process of synthesis. It suggested that the platelets of MMT or modified MMT were neither intercalated nor exfoliated during the process of synthesis.

TEM observations

TEM is a useful method to detect the dispersion of MMT in matrix, and can supply the direct proof in the study of nanocomposite. In this paper, the morphology of the composites was investigated by TEM and the result is showed at figure 3.

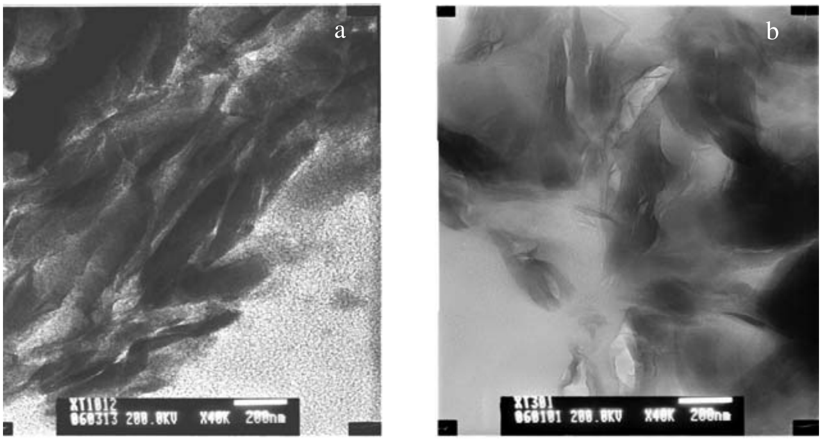

Figure 3 the images of TEM (a) PAAcNa/MMT; (b) PAAcNa/OMMT.

As shown at Figure 3a and 3b, no matter MMT and modified MMT were employed during synthesis, a large number of aggregate of MMT platelets could be found at the image of TEM. It suggested that there existed neither intercalation nor exfoliation structure in the composite.

The effect of the content of MMT/modified-MMT on the equilibrium swelling ratio of superabsorbent composites

MMT or modified MMT played an important role during the process of composite synthesis. In this paper, the content of MMT or modified MMT influences the performance of superabsorbent composites seriously. The results are shown in Figure 4 and Figure 5. When MMT or modified MMT was selected as inorganic

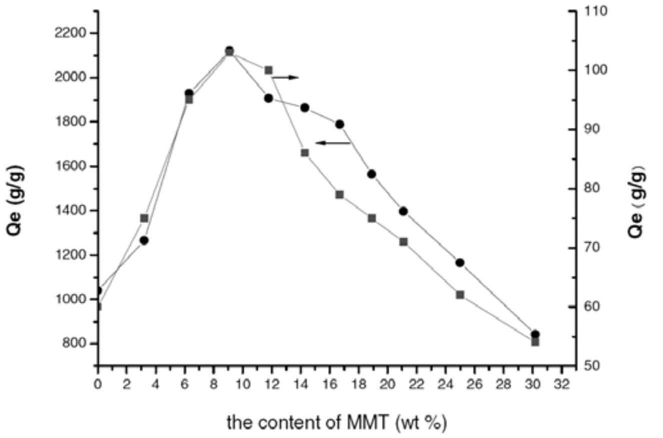

Figure 4 the effect of the MMT content on the equilibrium swelling ratio of superabsorbent composite. (●) the equilibrium swelling ratio in distilled water, (■) the equilibrium swelling ratio in 0.9 wt% NaCl solution

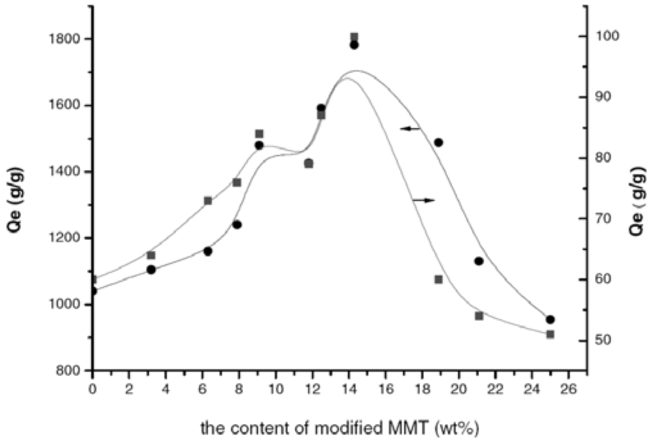

Figure 5 the effect of the modified MMT content on the equilibrium swelling ratio of superabsorbent composite. (●) the equilibrium swelling ratio in distilled water, (■) the equilibrium swelling ratio in 0.9 wt% NaCl solution component, the equilibrium swelling ratio of composite was the highest in the range of 9~14 wt% inorganic component. Outside of the range, the equilibrium swelling ratio of composite decreased. When the content of MMT was 9.0 wt%, the maximum equilibrium swelling ratio of composite containing MMT in distilled water and 0.9 wt% NaCl solution were 2120 g/g and 100 g/g respectively. At the same time, the maximum equilibrium swelling ratio of composite containing modified MMT in distilled water and 0.9 wt% NaCl solution were 1780 g/g and 100 g/g respectively when the content of modified MMT was 14.0 wt%. It could be attributed to the fact that the addition of MMT/modified-MMT particles changed the cross-linking density of composite. Thus, the equilibrium swelling ratio of superabsorbent composites changed with the level of MMT and modified MMT. When the modified MMT was employed during the synthesis of composites, the optimization of modified MMT content was higher than that of MMT. However, the maximum equilibrium swelling ratio of composite with modified MMT was lower than that of composite with MMT. The fact could attribute to the change of disperse stability and hydrophobicity of MMT caused by the introduction of cationic monomer.

The effect of the concentration of exchangeable cationic monomer solution on the equilibrium swelling ratio of superabsorbent composites

To further investigate the influence of the concentration of exchangeable cationic monomer solution on the equilibrium swelling ratio of superabsorbent composites, a series of experiments (content of modified MMT was 11.8 wt%, other conditions were kept constant.) were carried out. From the results shown in Figure 6, an interest tendency could be observed: When the concentration of DMABC solution was 5 wt%, the equilibrium swelling ratio of composite had the highest value of 2450 g/g. However, no matter whether the concentration of DMABC solution increased or decreased, the equilibrium swelling ratio of composites all decreased.

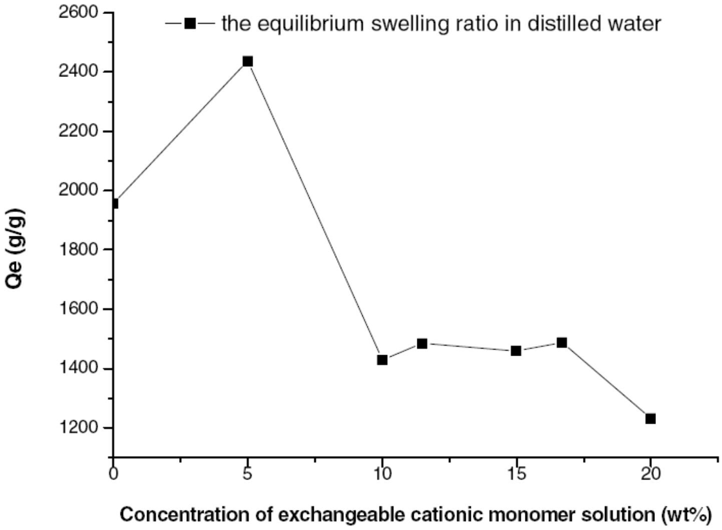

Figure 6 the effect of DMABC solution concentration on the equilibrium swelling ratio of superabsorbent composite.

It is well known that the adsorption of organic cations on MMT can be assigned two steps of ion-exchange adsorption and partition adsorption [24]. When the concentration of organic cations is less than the CEC of MMT, the adsorption is assigned to ion-exchange adsorption. However, the organic cations can flow into the gallery of MMT after the total metal ions in MMT gallery were exchanged. It can be explained as follow: the organic cations exchanged via ion-exchange can form partition phase in the gallery of MMT, and there exists non-Coulombic interaction among the organic components. The partition adsorption of organic cations on the MMT makes the cation level in the gallery of MMT surpass the CEC of MMT. Boyd et al [25]suggested that few organic cations in the gallery of MMT could promote the adsorption between other organic components and MMT. Thus, when modified MMT containing few DMABC is employed, the interaction between organic monomers (AAc) and MMT is more distinct than pristine MMT. Meanwhile, because the volume of DMABC molecular is bigger than that of sodium acrylate molecular, the hydrogen bonds between hydrophilic groups in polymer networks can be weakened and the ionic interaction between charges in networks can be obstructed by DMABC molecular, which improves the swelling capacity of superabsorbent composites. Additionally, the long alkyl chains acting as obstructers for the reaction between propagation radicals and monomeric double bonds increases the opportunity for cyclization reaction of MBA, and then the crosslink degree of network is also less [26]. However, with increasing of the DMABC solution concentration, the stability of modified MMT obviously decreases and the hydrophobicity of modified MMT increases, which impairs the swelling capacity of composites.

The thermal stability of superabsorbent composite

The thermogravimetric analysis (TGA) of poly (sodium acrylate) and the superabsorbent composites containing 11.8 wt% MMT and modified MMT was carried out. As shown in Figure 7, all samples showed a very small weight loss below 100°C, corresponding to a loss of moisture. As for poly (sodium acrylate), the major weight loss started at 368°C (19.13%), whereas the major loss weight of composites

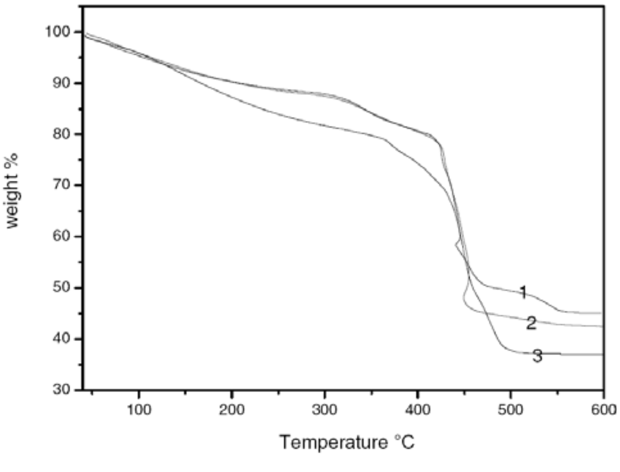

Figure 7 TGA curves of (1) poly (sodium acrylate), (2) composite with MMT and AAcNa, (3) composite with modified MMT and AAcNa.

containing MMT and modified MMT started at 424°C (20.84%) and 425°C (20.80%), respectively. Thus, the decomposition temperatures of composites containing MMT and modified MMT were higher than the polymer matrix. The result indicated that the introduction of MMT and modified MMT could improve the thermal stability.

Conclusions

In this paper, a series of superabsorbent composites, containing sodium acrylate and MMT or modified MMT, were synthesized by solution polymerization in aqueous. The FTIR and XRD were employed to investigate the structure and possible formation mechanism of composites. It suggested that the polymer chains were grafted onto the surface and edge of clay particles during graft polymerization and the superabsorbent composites were considered as conventional composites. At the same time, the equilibrium swelling ratio of the composites was investigated as a function of the content of inorganic clay particles. The results showed that the performances of composites were improved by the introduction of inorganic clay particles. The maximum equilibrium swelling ratios of composite in distilled water and 0.9-wt% sodium chloride solutions were up to 2450 g/g and 118 g/g, respectively. It confirmed that the dependence of equilibrium swelling ratio on disperse stability of clay was insignificant during graft polymerization. The disperse stability of clay and the graft polymerization between of MMT and monomer should be considered as the most important factors, which could seriously influence the equilibrium swelling ratio of composites. Finally, the result of TGA suggested that the introduction of MMT and modified MMT could improve the thermal stability.

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