Preparation of Organoclay by a Precipitation–Adsorption Method

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ABSTRACT: Organoclay was prepared by a precipitation–adsorption process in which sodium-montmorillonite (Na-MMT) suspension was fully mixed with an anionic surfactant, sodium dodecylbenzene sulfonate, and then precipitation agent $CaCl_2$ was added to produce a precipitate of organophilic montmorillonite (OMMT). The Na-MMT suspension was obtained by ion-exchange reaction of bentonite with sodium cation resin. Fourier transform infrared spectroscopy spectral analysis confirmed the adsorption of organic groups on the MMT, and the organic groups content was calculated from the results of thermal gravimetric analysis. X-ray diffraction results indicated that the OMMT prepared was exfoliated. In this article, the mechanism of the precipitation–adsorption process was discussed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 971–974, 2009

Key words: adsorption; organoclay; surfactants; TGA

INTRODUCTION

In recent years, polymer/clay nanocomposites have attracted wide attention because of their improved tensile strength and modulus, decreased thermal expansion coefficient, gas permeability, and flammability.[1–4] With the rapid development of polymer/clay nanocomposites, the preparation of organoclay becomes more and more important. A generally used and extensively studied method is intercalation of montmorillonite (MMT) by organic alkylammonium cations.[5–8] However, it has restrictions on the raw material of MMT content, cation exchange capacity (CEC), and layer-charge density. Although intercalation or surface modification of MMT by nonionic surfactants[9] or water-soluble polymers[10,11] has also been researched, little has been reported on the modification of MMT by anionic surfactants.

In this article, a precipitation–adsorption process for the preparation of organic MMT (OMMT) by using anionic surfactant, sodium dodecylbenzene sulfonate (SDBS), as modification agent and $CaCl_2$ as precipitation agent was studied, and the structure of OMMT obtained was characterized by FTIR, thermal gravimetric analysis (TGA), and X-ray diffraction (XRD).

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EXPERIMENTAL

Materials

The bentonate (pristine MMT) used was obtained from Heishan, Liaoning Province, China. This clay has a MMT content of 74.62% and a CEC of 0.6251 mequiv/g. Sodium cation resin was obtained from Dandong Resin Factory, China. The CEC of the sodium cation resin is 4.2 mequiv/g. SDBS and $CaCl_2$ used are of AR grade.

Preparation of OMMT

Pristine MMT (20 g) was immersed in 180 mL of water and stirred. Sodium cation resin (12 g) was added and the mixture was heated under reflux for 120 min. After the cation resin was filtered out, the sample was centrifuged and the precipitate was removed. Thus, the Na-MMT suspension was obtained.

Then, Na-MMT suspension was diluted to a concentration of 2%. A mixture of 200 g of 2% Na-MMT suspension and 2.5 g of SDBS was stirred to a homogeneous dispersion. Then, 200 mL of $0.1M$ $CaCl_2$ solution was added dropwise, and the precipitate was formed. The mixture was agitated for 1 h and separated by centrifugation. The pasty precipitate obtained was freeze-dried and ground to 200 meshes. Thus, the OMMT was obtained.

TABLE I
Properties of Pristine and Treated MMT

Properties	CEC (mequiv/g)	ECa^{2+} (mequiv/g)	EMg^{2+} (mequiv/g)	MMT content (%)
Pristine MMT	0.6251	0.1983	0.2573	74.62
Treated MMT	1.2788	0.0000	0.0000	95.81

Characterization methods

XRD patterns were obtained by using Bruker D8 X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 0.154178 nm). The scanning range was 1.5°–30° with a scanning rate of 4°/min. The TGA was performed using a NETZSCH TG 449 C (Germany) instrument. Samples were heated from 50 to 800°C in air atmosphere at a heating rate of 10°C/min. FTIR spectra were recorded from pressed KBr pellets using Thermo Nicolet NEXUS 470 FTIR spectrometer with the scans being 32 and the resolution being 4000. The measurement of CEC, content of exchangeable calcium ion (ECa$^+$), content of exchangeable magnesium ion (EMg$^+$), and MMT content was carried out according to the method described in Ref. 12.

RESULTS AND DISCUSSION

Preparation of Na-MMT

Pristine MMT was treated with sodium cation resin to convert it into Na-MMT. By this method, the Ca^{2+} and Mg^{2+} ions exchanged out from the MMT could combine with the cation resin, so that they could be exchanged more completely and separated out more easily, without introducing impurities or unwanted anions. Table I lists the properties of pristine MMT and treated MMT. It can be seen that after treating with sodium cation resin, MMT content and CEC of the treated MMT increased from 74.62% and 0.6251 mequiv/g to 95.81% and 1.2788 mequiv/g, respectively, and the exchangeable Ca^{2+} ion and Mg^{2+} ion of the treated MMT was not detected. Figure 1 shows the XRD patterns of pristine MMT and treated MMT. From the peak position of d_{001}-reflection, it was calculated that interlayer distance was 1.546 nm for pristine MMT, corresponding to that of Ca-MMT, and 1.248 nm for the treated MMT, corresponding to that of Na-MMT. This indicated that when treated with sodium cation resin, pristine MMT was effectively purified and simultaneously cations exchanged into Na-MMT.

Mechanism of OMMT preparation

The Na-MMT suspension was then evenly mixed with SDBS. A Tyndall phenomenon was observed in this system, indicating that a colloidal solution was formed. The schematic of this colloidal solution is shown in Figure 2(a). In this system, Na-MMT could be monolayer dispersed, whereas SDBS, as an anion surfactant, formed micelles. When CaCl$_2$ was added, there would be three possible cases to occur as follows:

(1) Ca^{2+} formed chemical bonds with dodecylbenzene sulfonate ion and anion on MMT, respectively.[13] Thus, dodecylbenzene sulfonate group was chemically adsorbed on MMT layers.

$$Ca^{2+} + Na^+\text{-MMT} + C_{12}H_{25}C_6H_4SO_3Na \rightarrow$$
$$(C_{12}H_{25}C_6H_4SO_3)\text{-Ca-MMT} \downarrow + 2Na^+$$
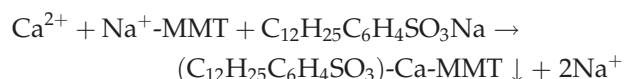
(2) Calcium dodecylbenzene sulfonate (CDBS) was formed. The density of CDBS is smaller than that of the suspension. A small part of CDBS that is insoluble in water would float up to the surface of water, and most parts of CDBS would physically absorb onto the surface MMT layers.

$$Ca^{2+} + 2C_{12}H_{25}C_6H_4SO_3Na \rightarrow$$
$$(C_{12}H_{25}C_6H_4SO_3)_2Ca \downarrow + 2Na^+$$
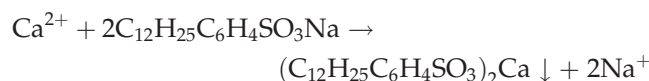
(3) Ca^{2+} replaced the Na$^+$ that existed between the layers of MMT, forming Ca-MMT.
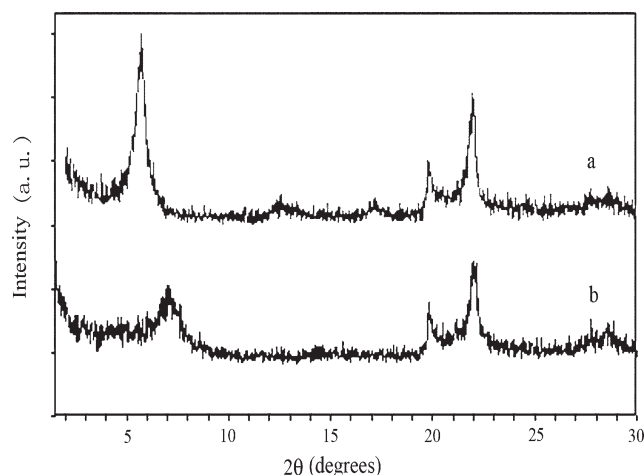

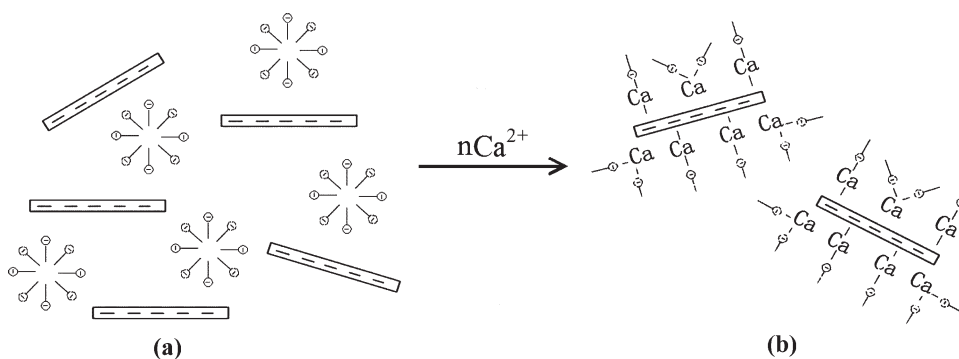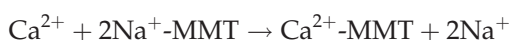**Figure 1** XRD patterns of (a) pristine MMT and (b) treated MMT.

Figure 2 Schematic of precipitation–adsorption process for the preparation of OMMT: (a) colloidal solution of Na-MMT and SDBS and (b) structure of OMMT prepared.

$$Ca^{2+} + 2Na^+\text{-MMT} \rightarrow Ca^{2+}\text{-MMT} + 2Na^+$$

In the first two cases, the surfaces of MMT layers would be decorated with organic dodecylbenzene sulfonate group. The schematic of the structure of this OMMT is shown in Figure 2(b). OMMT is hydrophobic and has a density greater than that of suspension solution, and therefore it can be easily separated from the system by centrifugation.

XRD analysis

Figure 3 shows the XRD patterns of OMMT prepared, Na-MMT, and CDBS. The d_{001}-reflection peak of Na-MMT was found at $2\theta = 7.38°$, whereas the corresponding d_{001}-reflection peak of OMMT turns flat. Similar XRD pattern had been reported by Chang et al.[14] in their research on the PVA/MMT nanocomposites, and their TEM observations showed that the MMT was in an exfoliated state. Thus, we suggest that the OMMT prepared are exfoliated, because the arrangement of the MMT layers

may be prevented by the organic group on the OMMT. However, for alkyl ammonium ion-exchanged clays, because the amount of alkyl ammonium ion that could enter the interlayer of MMT is limited by CEC of MMT, the interlayer distance of MMT could only be increased to some extent. From Figure 3, it can also be found that the XRD diffraction peak of crystalline CDBS was not observed in the XRD patterns of OMMT prepared, suggesting that the aggregation structure of CDBS adsorbed on MMT is different from that of pure CDBS.

FTIR spectral analysis

The FTIR spectra of Na-MMT and OMMT prepared are shown in Figure 4. For OMMT, the IR absorption band at 3441 cm^{-1} is associated with the O—H stretching vibration, and the band at 1642 cm^{-1} is characteristic of the deformation vibration of the interlayer water of MMT. The strong absorption bands at 1039 cm^{-1} could be ascribed to Si—O stretching vibrations of MMT. The absorption bands at 795 and 465 cm^{-1} may result from Al—O
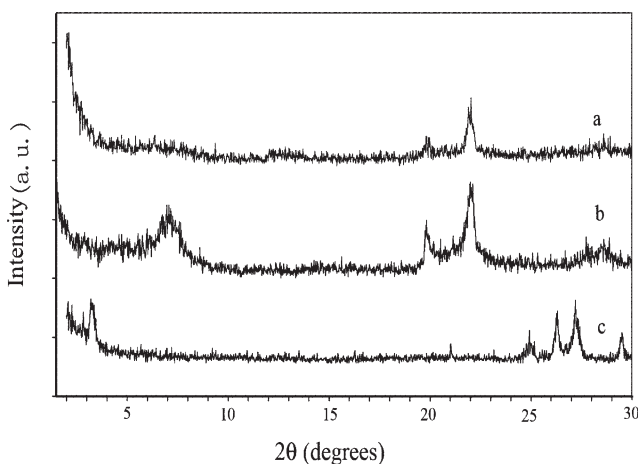

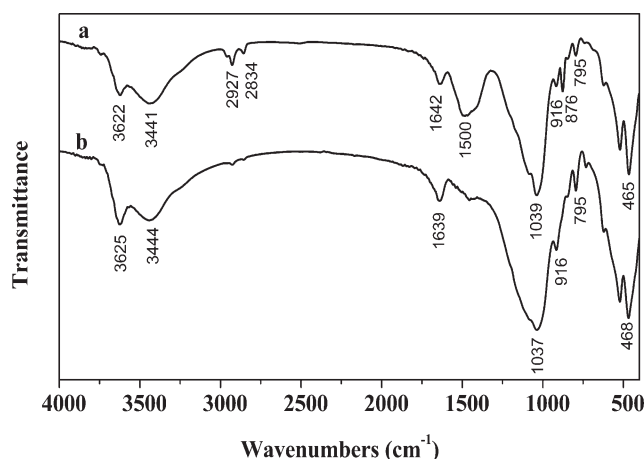**Figure 3** XRD patterns of (a) OMMT prepared, (b) Na-MMT, and (c) CDBS.

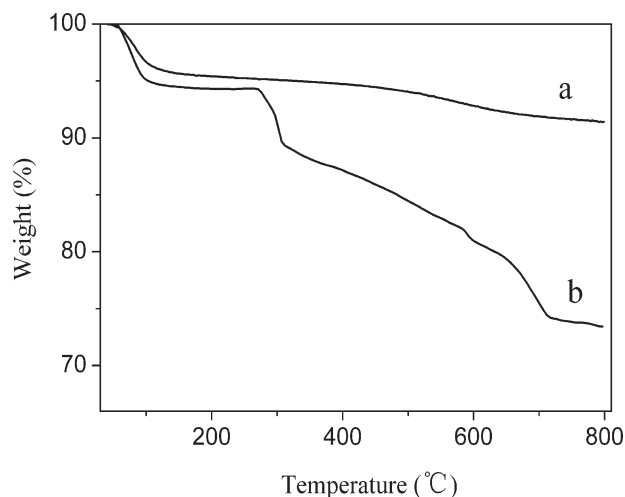**Figure 4** IR spectra of (a) OMMT prepared and (b) Na-MMT.

Figure 5 TGA thermograms of (a) Na-MMT and (b) OMMT prepared.

stretching and O—Si—O bending vibrations of MMT. Compared with that of Na-MMT, the IR spectrum of OMMT prepared show new characteristic bands at 2927 – and 2834 cm^{-1}, which are associated with the C—H stretching vibration of the methylene; characteristic bands at 1500 and 876 cm^{-1} are associated with the C—C stretching and the C—H deformation vibration of the benzene ring, respectively. This indicates the existence of dodecylbenzene group on the OMMT prepared.

Thermal gravimetric analysis

The TGA thermograms of Na-MMT and OMMT are presented in Figure 5. The mass loss at about 100°C is attributed to the removal of absorbed water. The mass loss for Na-MMT and OMMT is 4.6% and 5.7%, respectively. For Na-MMT, the second mass loss at temperature 500–800°C is due to the dehydroxylation of the alumino-silicate lattice.[15] For OMMT, the mass loss at temperature 260–800°C can be attributed mainly to the decomposition of the organic group[16] and partly to dehydroxylation of the alumino-silicate lattice. The content of the organic substance in OMMT is characterized by the difference in mass losses between the organic MMT and Na-MMT. In the temperature range of 260–800°C, the overall mass loss of Na-MMT is about 4.3%, whereas that of OMMT is about 20.9%. The mass loss of OMMT is 16.6% higher than that of Na-

MMT, which is resulting from the degradation of organic material on the surface of MMT. So, the content of organic material on the MMT was determined to be about 16.6 wt %.

CONCLUSIONS

By treating with sodium cation resin, pristine MMT was effectively purified and simultaneously cations exchanged into Na-MMT suspension. The Na-MMT suspension was then turned into OMMT by a precipitation–adsorption process, using SDBS as modification agent and CaCl$_2$ as precipitation agent. The mechanism of this process is supposed to be the chemical absorption resulting from the formation of (C$_{12}$H$_{25}$C$_6$H$_4$SO$_3$)-Ca-MMT and the physical absorption of CDBS precipitate on the surface MMT layers. FTIR spectral analysis confirms that there exist organic groups on the OMMT prepared. XRD results indicate that the OMMT prepared is exfoliated. From TGA results, it was calculated that organic material content on MMT was up to 16.6 wt %.

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