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Preparation of Organo-Vermiculite by Modification with Hexadecyltrimethylammonium Bromide Under Microwave Irradiation

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Organo-vermiculite (OVMT) was prepared by modification reaction of vermiculite (VMT) with hexadecyltrimethylammonium bromide (CTAB) under microwave irradiation. The structure and properties of organo-vermiculite were investigated by X-ray diffraction (XRD), fourier infrared spectroscopy (FT-IR), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM). The XRD and FT-IR results indicated that CTAB successfully interacted with the vermiculite layer by the microwave irradiation. Scanning electron microscopy showed that the order structure of the vermiculite layer has been destroyed due to intercalation of the CTAB. Simultaneously, the investigation also showed that this intercalation reaction method using microwave irradiation was feasible and has some particular advantages such as simple manipulation, shorter reaction time, *etc*., finally, the intercalation mechanism under microwave irradiation was discussed.

Key Words: Vermiculite, CTAB, Intercalation, Microwave irradiation.

INTRODUCTION

Vermiculite (VMT), which a type silicate and possesses a layered structure, is quite similar to montmorillonite (MMT) on the basis of the analysis of montmorillonite and vermiculite mineralogical origin. Compared with the montmorillonite, vermiculite has many advantages, such as better crystallographic form, stability, cation interchange ability, temperature retention, light weight, frostresisting, antibiosis and abundant resource. Thus, vermiculite had been widely used in polymer[1-4], ions adsorption[5,6], *etc*. and obtained a lot of progress. Zhang *et al*.[4] preparated a new kind of natural rubber (NR)/organo-vermiculite nanocomposites. The tensile strength and the elongation at the breaking point of the NR/organo-vermiculite nanocomposites loading 15 phr of the organo-vermiculite reached 28.4 MPa and 63.2 %, respectively. And the storage modulus and the glass transition temperature of the nanocomposites were increased. However, it is quite difficult to exchange cations with organic molecule because of its high interlayer charges density.

Many studies of synthesis of modified vermiculite with organic molecule have been published earlier. The previous intercalation reaction of vermiculite was achieved by liquid reaction[7], ball milling[8] and melt blending. These methods have limitations such as long time of reaction and high energy. In recent years, microwave irradiation has widely used to simplify and improve organic reactions due to higher yields, cleaner reactions and shorter reaction times compared to conventional heating[9]. In this paper, we use this microwave irradiation technology to prepare organic-vermiculite using CTAB as a modification agent. The structure and properties of organo-vermiculite were investigated by XRD, FT-IR, TGA and SEM.

EXPERIMENTAL

The materials used in this study were of analytical grade (AR) grade. Sodium chloride was procured from Chengdu Kelong Chemical Reagents Company respectively (Sichuan Province, China), CTAB was purchased from Mianyang Rongshen Chemical Reagents Company (Sichuan Province, China). The microwave reaction equipment with stirring equipment and successively adjustable 0-2 KW output power.

Preparation of organo-vermiculite: The vermiculite was first shattered by jet milling, the SEM images of the shattered vermiculite is shown in Fig. 1. Then, vermiculite was pretreated with NaCl according to previous work[10]. The Na-exchanged vermiculite (30 g) and CTAB (10 g) were mixed, the resulting mixture was stirred for 1 h under microwave irradiation condition. The organo-vermiculite was separated by filtration and washed by distilled water for several times until there was no precipitate was observed upon titrating the filtrate with 0.1 mol/L $AgNO_3$. The final organo-vermiculite in the form of fine powder was dried at 160 ºC.

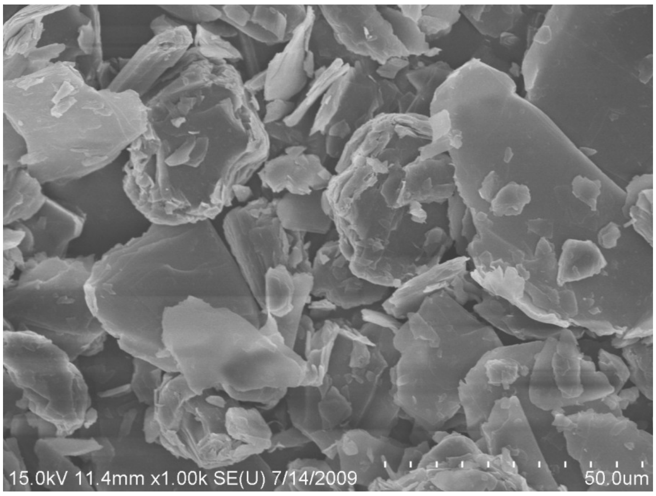

Fig. 1. SEM of shattered vermiculite

RESULTS AND DISCUSSION

XRD analysis of vermiculite and organo-vermiculite: Fig. 2 shows the XRD patterns of the vermiculite (Fig. 2A) and the organo-vermiculite (Fig. 2B). As seen in Fig. 2A, the characteristic peak of $d_{(001)}$ of the vermiculite appears at 5.98, corresponding to a basal spacing of 1.46 nm. In the XRD pattern of the organo-vermiculite sample prepared by intercalation reaction under microwave irradiation, the $d_{(001)}$ of vermiculite disappears at 5.98. The organo-vermiculite exhibits the characteristic peak at about 2.08, corresponding to a basal spacing of 4.88 nm. The disappearance of the $d_{(001)}$ of vermiculite indicates that the order structure of the vermiculite layer has been destroyed. The considerable expansion of height is associated with intercalation of the CTAB and the change of interlayer spacing suggests the successful intercalation of vermiculite.

FTIR analysis of vermiculite and organo-vermiculite: The FT-IR spectra of vermiculite and organo-vermiculite was shown in Fig. 3. In the spectra, the peaks at 3435 cm^{-1} and 1632 cm^{-1} contibute to of O-H the stretching vibration and deformation vibration, respectively. The absorption peak at 994 cm^{-1} is attributed to the Si-O stretching vibration of vermiculite. Compared to the vermiculite, four new absorption peaks appear in the pattern of organo-vermiculite, the absorption peak at 2850 cm^{-1} and 2919 cm^{-1} belongs to C-H symmetrical and asymmetric stretching vibration, respectively and the absorption peak at 1472 cm^{-1} contribute to C-N stretching vibration. FTIR analysis further confirmed that CTAB successfully interacted with the vermiculite layer.

SEM analysis of vermiculite and organo-vermiculite: Fig. 4 shows the SEM images of the vermiculite (Fig. 4A) and the organo-vermiculite (Fig. 4B). As observed by the SEM, Fig. 4A, the vermiculite is typical layer structure. The particles of shattered vermiculite were not completely regular and the average size of the vermiculite particles was 30 μm. After intercalation of vermiculite with CTAB, the interface of vermiculite between layer and layer become vague, which indicate that vermiculite was successfully modified with CTAB, the molecule chain of CTAB has entered into layer space of vermiculite and the order structure of the vermiculite layer has been destroyed. However, the average size of the particle of vermiculite and organo-vermiculite do not change, this result indicates that microwave irradiation do not affect the size of product.

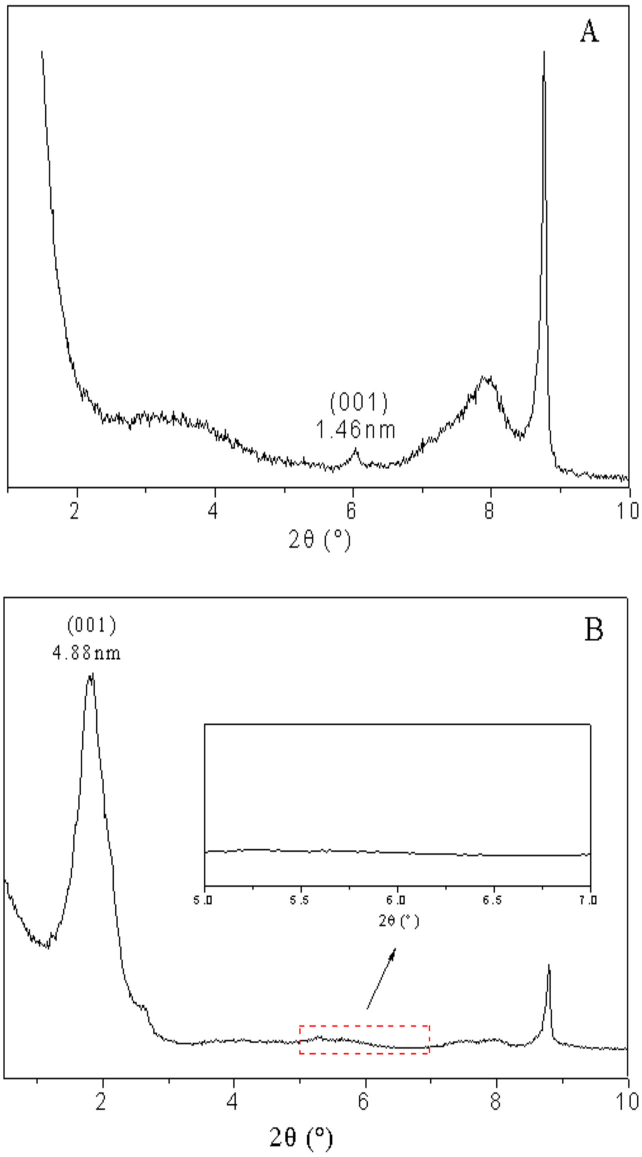

Fig. 2. XRD of vermiculite (A) and organo-vermiculite (B)

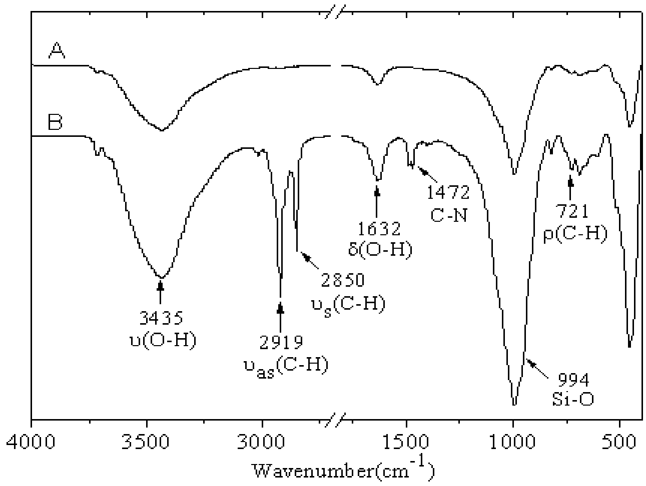

Fig. 3. FT-IR of vermiculite (A) and organo-vermiculite (B)

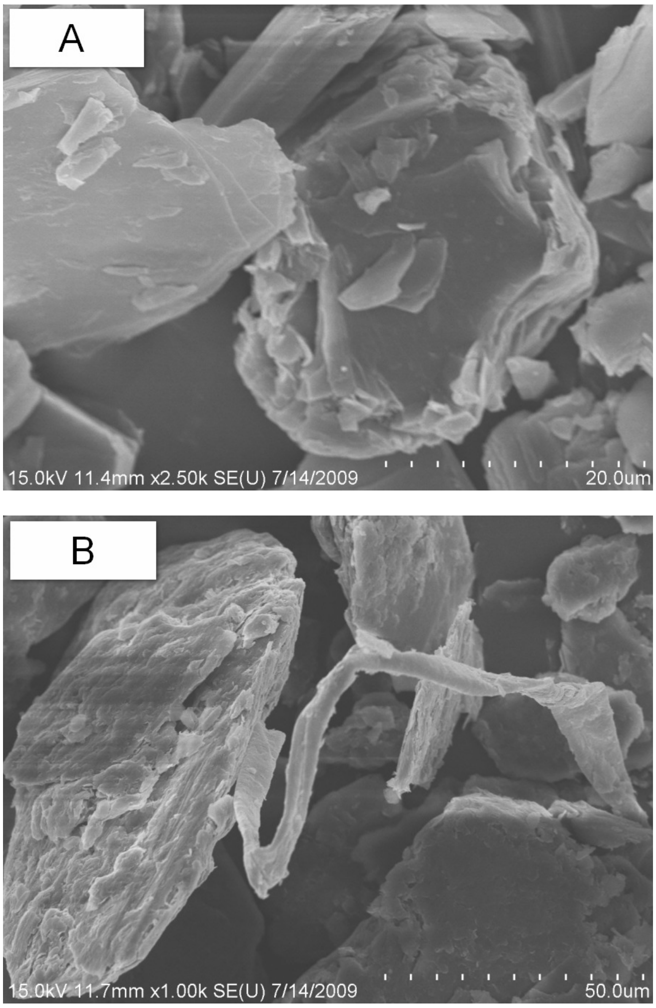

Fig. 4. SEM of vermiculite (A) and organo-vermiculite (B)

Intercalation mechanism of vermiculite with CTAB under microwave irradiation: It is well-known that there existed molecular water between Na-exchanged vermiculite layer and the binding force between vermiculite layer and molecular water is very weak. When Na-exchanged vermiculite is irradiated under microwave irradiation, because microwave can provide so enough energy that the binding force between water molecular and Na-exchanged vermiculite layer is destroyed, the molecular water will be evaporated. At the same time, when water is evaporated, the CTAB molecules will enter into vermiculite layer and the CTAB molecules and the vermiculite layer can interact with each other under microwave irradiation. Because of the interaction of CTAB and the vermiculite layer, the order structure of the vermiculite layer is destroyed. The vermiculite layer is exfoliated and dispersed by CTAB.

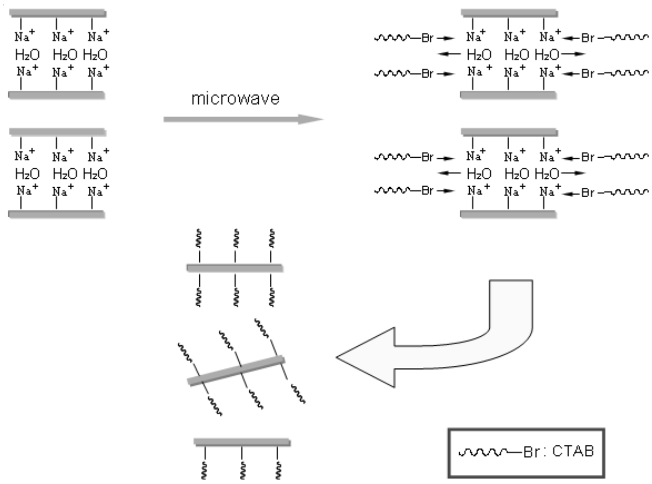

Fig. 5. Intercalation mechanism of vermiculite with CTAB under microwave irradiation

Conclusion

Organo-vermiculite was prepared by modification reaction of vermiculite with CTAB under microwave irradiation. The XRD and FT-IR results indicated that CTAB successfully interacted with the vermiculite layer by the microwave irradiation. SEM showed that the order structure of the vermiculite layer has been destroyed, however, microwave irradiation do not affect the size of organo-vermiculite.

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