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Influence of physical state of intercalating agents on intercalation process of high speed airflow pretreated montmorillonite in supercritical carbon dioxide

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ABSTRACT

The work aimed at studying the effect of $scCO_2$ processing technology on basal spacing, surface morphology and thermal stability of sodium montmorillonite (MMT) that were pretreated with high speed airflow pulverization method and then modified using myristyltrimethylammonium bromide (MTAB) and tetradecyltrihexylphosphonium chloride (TDTHP) with $scCO_2$ as the medium. X-ray diffraction (XRD) showed that physical state of intercalating agents played an important role on the intercalation process in $scCO_2$. Solid-state MTAB could hardly intercalate into the interlayer of pretreated MMT (PMMT), though addition of co-solvent benefited the intercalation to some extent. However, liquid TDTHP could intercalate into the interlayer of PMMT easily even without co-solvent and the basal spacing of TDTHP-modified PMMT was larger than that of MTAB-modified PMMT. Scanning electron micrographic (SEM) showed the large compact structure for MMT broke into small random structures after airflow processing and some smaller tactoids and more dispersed structures can be observed for both MTAB-modified PMMT and TDTHP-modified PMMT compared to unprocessed MMT. For TDTHP–PMMT, many clay platelets that were separated from the tactoidal structure and more dispersed structure were observed, which may be helpful for MMT exfoliation and dispersion in polymers. Thermogravimetric analysis (TG) demonstrated that TDTHP-modified PMMT was up to 100 °C more stable than MTAB-modified PMMT. These results are very important and relevant to the preparation and application of MMT/polymer nanocomposites.

1. Introduction

Polymer–clay nanocomposites have attracted significant interest from industrial and academic research because numerous properties can be enhanced (barrier properties, thermal properties, flame retardant properties, and mechanical properties) at very small filler content (less than 5 wt%) [1–3]. Nanodispersion of clay sheets is important in improving the polymer properties, and for achieving good clay dispersion, it is usually necessary to render the interlayer spacing of the clay sufficiently organophilic to enhance its affinity with polymer chains [4]. Intercalation of organic surfactants into the interlayer spacing of the clay is a key step for successful exfoliation of clay minerals particles in the polymeric matrix and the procedure is generally performed by traditional solution intercalation [5]. Some technological methods, such as microwave [6] and ultrasound [7], have been employed and are proved to be effective in improving the intercalation process. One major disadvantage of solution intercalation is that the obtained product needs to be dried and milled to form powder, which is tedious and not beneficial for practical applications. Microwave and ultrasonic technologies are limited by the amount of processing every time.

As an effective and simple alternative to modify MMT, intercalation in supercritical carbon dioxide ($scCO_2$) can be adopted. $ScCO_2$ appears to be a very promising medium and has many advantages compared to the organic solvents, such as low toxicity, abundance, low cost and accessible critical parameters (31.1 °C and 73.8 bar). The physicochemical properties of $scCO_2$ can be continuously tuned between vapor-like and liquid-like limits by varying the system pressure and temperature. Besides, the CO_2 can be

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removed entirely from the product without bringing pollution. These unique properties of $scCO_2$ have yet been exploited for intercalating and exfoliating layered silicates [8–10]. Serhatkulu et al. [8] used supercritical CO_2 as the processing medium for intercalating the structure of natural clay and depositing CO_2 – philic sugar acetate. The XRD results showed the gallery spacing of Cloisite Na^+ increased from 0.31 to 0.52 nm and low-energy electron diffraction confirmed the deposition of the sugar acetate in the intercalated structure of the clay after $scCO_2$ processing.

To date, the application of the CO_2-processing technique can be broken down into three categories: (1) dispersion of commercial clays that has been intercalated by different intercalating agents [11]; (2) direct preparation of polymer/MMT nanocomposites with the aid of supercritical CO_2 [12]; (3) intercalating the structure of natural clay with intercalating agents using supercritical CO_2 as the processing medium [13,14]. Generally, the CO_2-processing involves immersing the layered clays or their mixtures with intercalating agents/polymers in supercritical CO_2 for a certain time period at a preset temperature and pressure followed by rapid depressurization. For dispersing commercial clays that have been intercalated, the composition of intercalating agents plays a great role on the final dispersion. The study of Horsch et al. [11] demonstrated that the extent of clay dispersion appears to be dependent on the 'CO_2-philicity', which in turn appears to depend on the surface modifications and inter-gallery spacing. Similarly, the dispersion of MMT in polymer/MMT nanocomposites is dependent on the polymer composition to a great extent, since the solubility of some polymers in CO_2 increases as the molecular weight decreases [15]. Based on these results, it is reasonable to speculate that the composition of intercalating agents, which may influence their solubility in CO_2 [16], will have a great influence on the intercalating process. The result of Naveau et al. [14] verified this speculation and demonstrated that the physical state (solid or molten) of the intercalated surfactant, which was related to the composition, was of critical importance for degrees of exchange and basal spacing change. However, their study focused on the degrees of exchange and basal spacing change, and paid little attention to the surface morphology and the thermal stability of organically modified MMT, which may also have a great effect on their dispersion in polymer and the final application.

In the present paper, to better adjust the morphology and improve the dispersion of MMT in polymer matrix, MMT was pretreated with high speed airflow pulverization method (the obtained MMT was denoted as PMMT). Then the PMMT was modified with different intercalating agents with $scCO_2$ as the medium and the influence of $scCO_2$ processing on the surface morphology of PMMT, combined with the change of basal spacing and the thermal stability was systematically investigated.

2. Experiments

2.1. Materials

The unmodified MMT used was provided by Nanocor, Inc., and were purified by immersing in ethanol at 70 °C for 4 h in order to remove any contaminants. The cationic exchange capacity (CEC) of the MMT is 120 meq/100 g. Myristyltrimethylammonium bromide (MTAB) and tetradecyltrihexylphosphonium chloride (TDTHP) were purchased from Sigma–Aldrich Co, and were used as received. Their physical properties were listed in Table 1. The CO_2 (purity: 99.9%) was obtained from Air Liquide, China.

Table 1
The physical properties of MTAB and TDTHP.

Trade	Physical state (40 °C)	Tm (°C)	Molecular formula
MTAB	Solid	245	$C_{17}H_{38}NBr$
TDTHP	Liquid	<20	$C_{32}H_{68}PCl$

2.2. Preparation of pretreated MMT (PMMT)

The pristine MMT was pretreated with a fluidized-bed type airflow crusher (QYF-150, MiYou Group, China). Typically, 25 kg MMT was fed into the pulverizing room by the screw feeder, and then high speed jet of high pressure air to the pulverizing room was accomplished by a special designed supersonic nozzle. The air consumption was 3 m^3/min. The MMT was accelerated in the supersonic jet flow, followed by repeated shocks and crashes at the nozzle, to finally obtain the grinded MMT with size in the range of 1–3 μm.

2.3. Supercritical fluid treatment of clays

20 g of PMMT was dried in an oven at 90 °C for 8 h under vacuum. Then the sample with an excess of surfactant (MTAB or TDTHP, 1.1CEC of MMT) were poured into a 1 L high pressure reactor. The mixture was then processed in $scCO_2$ for 2 h at 40 °C and 20 MPa under constant stirring to obtain the organically modified MMT (OMMT). Then the vessel was depressurized to ambient pressure very quickly. The obtained samples were denoted as MTAB/TDTHP–PMMT. To investigate the effect of post-processing, these samples was further washed with ethanol several times at room temperature to remove the unexchanged surfactants until no chlorine ions were detected with a 0.1 N $AgNO_3$ solution, and followed by drying at 90 °C.

2.4. Characterization

The X-ray diffraction (XRD) patterns of the samples before or after washing were carried out on a Rigaku DMAX 2200 Diffractometer using Cu Kα radiation (40 Kv, 40 mA) at room temperature. The scanning angle was kept between 2° and 10° with a rate of $1°\mathrm{min}^{-1}$ and the basal spacing of the samples was obtained according to Bragg's law. The morphological analysis of the samples was taken on a scanning electron microscope (SEM, KYKY-2800B), after gold coating. The thermal stability and the organic content of the samples were measured on a TA Instruments Q50. It was performed under N_2 flow at a heating rate of 20 °C/min, from room temperature to 800 °C. The surface area of the samples was measured by Brunauer–Emmett–Teller (BET) method on a Quantachrome NEXUS 670 instrument from Nicolet in a N_2 adsorption apparatus.

3. Results and discussion

3.1. Effect of high speed airflow pulverization on the structure of MMT

To better adjust the surface morphology and improve the dispersion of MMT in polymer matrixes, MMT was firstly pretreated with high speed airflow pulverization method (the obtained MMT was denoted as PMMT). As shown in Fig. 1, the diffraction peak at $2\theta = 7.461°$, corresponding to the basal spacing of 1.16 nm, was attributed to the 001 plane of PMMT and was slightly smaller than that of the original MMT (1.31 nm). Additionally, a reduction in the peak intensity for PMMT compared to original MMT was observed. This is probably because the ordered structure of MMT was destroyed to some extent after the processing with high speed airflow pulverization.

From SEM, most of the unprocessed MMT are tightly bound tactoids, composed of a number of highly ordered stacked platelets