



Organovermiculite nanofillers in polypropylene

M. Valášková^{a,*}, G. Simha Martynková^a, V. Matějka^a, K. Barabaszová^a, E. Plevová^b, D. Měřínská^c

^a Nanotechnology Centre, VŠB-Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

^b Institute of Geonics AS CR, Studentská 1768, 708 00 Ostrava-Poruba, Czech Republic

^c Faculty of Technology, Tomáš Baťa University in Zlín, Nam. TGM 275, 762 72 Zlín, Czech Republic

ARTICLE INFO

Article history:

Received 13 February 2008

Received in revised form 11 July 2008

Accepted 17 July 2008

Available online 12 August 2008

Keywords:

Organovermiculite

Nanofiller

Exfoliation

X-ray powder diffraction

Jet milling

Thermal stability

ABSTRACT

Vermiculite (VER) was exfoliated to be used as organovermiculite nanofiller (ODA/VER) for polypropylene (PP)/VER nanocomposites. We used three procedures. P1: low-temperature intercalation of melted octadecylamine (ODA) led to the regular bilayer arrangement of organic molecules in the interlayer space. P2: mechanical exfoliation of ODA/VER by jet milling decreased the crystallite size. P3: chemical exfoliation using an oxidizing agent potassium persulfate and subsequent intercalation with ODA created a mixture of monolayer and bilayer arrangements of organic cations in the interlayer. The thermal compounding of the organovermiculites (4 wt.%) with maleated PP at 30 and 50 rpm caused the partial deintercalation of the organovermiculite and organovermiculite pretreated with the oxidizing agent. The jet milled ODA/VER was very well dispersed within PP matrix. Thermal stability of PP and PP/VER nanocomposites with differently exfoliated ODA/VER nanofillers was evaluated by thermogravimetric analysis.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Clay minerals can be used to enhance stiffness, strength, toughness, and thermal stability of polymer/clay mineral nanocomposites. Several reviews have been published on nanocomposites, most of them based on montmorillonite, hectorite and saponite (Giannelis, 1996; Lagaly, 1999; Pinnavaia and Beall, 2002; Lagaly et al., 2006; Ruiz-Hitzky and Van Meerbeek, 2006). A simple mixing of the clay minerals with a polymer may yield an immiscible microcomposite, in which the clay mineral acting as filler is not dispersed in nanometer scale. Therefore, intercalation of long chain quaternary ammonium ions are often used to make clay mineral organophilic (Ray and Okamoto, 2003; D'Souza, 2004). The bilayer arrangement of alkylammonium ions in the interlayer may promote exfoliation of the clay mineral particles during compounding with melted polyvinylchloride (Kalendova et al., 2004). Simha Martynková et al. (2007a) using PXRD analysis and molecular modeling studied an ordering of three different quaternary ammonium surfactant salts in vermiculite (VER). Weiss et al. (2003) performed exfoliation of VER using low-temperature intercalation with octadecylamine (ODA). These authors concluded that a low concentration of ODA resulted in a monolayer arrangement of ODA molecules in the VER interlayer with $d \sim 2.9$ nm, while high concen-

tration led to the bilayer arrangement with $d = 5.8$ nm. The length of the alkyl chain determines the interlayer distance and formation of mono-, bilayers or pseudotrimolecular arrangements (Lagaly et al., 2006). A simple procedure of a nanocomposite, in which the clay mineral intercalated with organic cations was fused together with polymer, was successfully applicable only to polar polymers (Vaia et al., 1993). Therefore, it is rather difficult to achieve a fine dispersion of the clay mineral in non-polar polypropylene (PP) without compatibilizer. Polypropylene-vermiculite nanocomposites can be achieved by simple melt mixing of maleic anhydride-modified vermiculite with polypropylene. Maleic anhydride acts either as a compatibilizer for the polymeric matrix or as a swelling agent for the silicate (Tjong et al., 2002; Tjong and Meng, 2003; Xu et al., 2003). The expansion of the clay mineral in polymeric matrices indicates that an expanded structure should be unstable and collapse when a small quantity of the soft phase in the polymer composite penetrates into the interlayer space (Hasegawa et al., 2000; Nam et al., 2001). Blumstein (1965) first reported the improved thermal stability of a polymer/clay nanocomposites when polymethylmethacrylate was combined with MMT. Recently, Leszczyńska et al. (2007a,b) reported the thermal behavior of PP/MMT composites. The intercalated Cloisite also improved flammability of the PP/Cloisite-composite (Zhang et al., 2006). According to the TG analysis, the degradation temperature increased from 259 °C of pure PP to 309 °C of the PP/Cloisite-composite. Qin et al. (2004) observed the increase of decomposition temperature of PP by TG curves in spite of not dispersed organophilic MMT particles

* Corresponding author. Tel.: +420 596991573; fax: +420 596991640.
E-mail address: marta.valaskova@vsb.cz (M. Valášková).

intercalated with dioctadecylammonium chloride at nanometric scale in the PP matrix.

Generally, different procedures are used for preparation of exfoliated vermiculite. Therefore, we studied the effect of rapid jet milling, especially to evaluate the combination of intercalation and short time jet milling. We used low-temperature intercalation of ODA, mechanical exfoliation by jet milling after intercalation and intercalation after chemical exfoliation with oxidizing agent potassium persulfate.

2. Materials and methods

2.1. Materials

Vermiculite (VER) from weathered ultrabasic zone (Letovice, Czech Republic) was selected as the starting material. The original powder sample was ground in a planetary mill for 20 min, then passed through a 0.045 mm sieve and fraction <40 μm was utilized for experiment. Its formula was $(\text{Si}_{3.13}\text{Al}_{0.86}\text{Ti}_{0.02})^{\text{IV}}(\text{Mg}_{2.53}\text{Fe}_{0.45}^{3+}\text{Al}_{0.02})^{\text{VI}}\text{O}_{10}(\text{OH})_2$ ($\text{Mg}_{0.19}\text{K}_{0.01}\text{Ca}_{0.02}$) per $\text{O}_{10}(\text{OH})_2$ as calculated from the results of the elemental chemical analysis. Octadecylamine (ODA), $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$, (97%, melting point 55–57 °C) and oxidizing agent potassium persulfate, $\text{K}_2\text{S}_2\text{O}_8$ of 99.9% purity were obtained from Sigma-Aldrich, Co.

2.2. Exfoliation vermiculite into organovermiculites

The exfoliated organophilic VER particles were prepared using three different procedures. P1: intercalation of VER (24 h at 80 °C) with ODA (40 wt.%), produced sample 1 (see Weiss et al., 2003). P2: mechanical exfoliation of the intercalated sample 1 by jet milling (10 min at Sturtevant Micronizer 2) yielded sample 2. P3: VER was exfoliated using oxidizing agent potassium persulfate (S) in weight ratio VER:S=1:1 (see Matějka et al., 2006). Dry VER-S was intercalated with octadecylamine following procedure P1, and sample was named sample 3.

2.3. Preparation of polypropylene/vermiculite composites

The mixture of PP balls (Mosten GB 003, Chemopetrol Litvínov) and maleated (MA) polypropylene (EXXELOR PO 1015, KO 1909201 1 3) homogenized at 220 °C and the ODA/VER samples 1, 2 and 3 (4 wt.% related to the amount of PP) were mixed at 220 °C in the kneader Brabender (30 and/or 50 rpm for 30 min), then pressed at 200 °C into the plates and cut into thin sheets. The PP/VER composite samples were named 1-30, 1-50, 2-30, 2-50, 3-30 and 3-50.

2.4. Analytical methods

The X-ray powder diffraction (PXRD) patterns were recorded using the diffractometer INEL equipped with a curved position-sensitive detector CPSD120 (reflection mode, Ge-monochromatized $\text{CuK}\alpha_1$ radiation). The PXRD patterns were measured at five sites on the thin sheets of PP/VER in ambient atmosphere (2000 s, 35 kV, 20 mA).

Morphology was examined using scanning electron microscope (SEM) Philips XL 30. The sample was plated with Au/Pd conducting coats and SEM-images were obtained using a back-scattered electron detector. Light microscopy (LM) images were taken with an Olympus BX microscope, using dark field polarized light at transmission mode.

Thermogravimetric analysis was carried out using multimodular thermal analyzer SETSYS 12-SETARAM equipped with a measurement head TG ATD ROD 1600 °C. The TGA curves were recorded under an air environment from 30 to 900 °C, the heating rate was 20 °C·min⁻¹.

2.5. Determination of crystallite size

The crystallite size L_c is defined as coherently X-ray diffracting domain. The MudMaster program (Eberl et al., 1996) employs Bertaut–

Warren–Averbach-type analysis (Warren and Averbach, 1953) for calculating the mean crystallite size $\langle L_c \rangle$ and the crystallite size distribution for periodic crystals between ~2 and ~100 nm. The program yields area-weighted mean sizes the coherently scattering domains. These domains may or may not equal true particle size (Eberl et al., 1998).

3. Results and discussion

3.1. Organovermiculite

The clay minerals after intercalation can possess ordered or mixed-layer structures. The regularity of basal d_{001} values can be expressed by calculating the coefficient of variability CV (Bailey, 1982), from the sequence of 001 reflections: $\text{CV} = 100 s / \langle x \rangle$, where $\langle x \rangle$ is the mean value of the observed values $l \times d_{001}$ and s is the standard deviation. If CV is <0.75, the structure has a regular alteration of layers.

According to the CV values, the original VER showed a regular alteration of layers (CV=0.21), sample 1 showed slightly randomly layer sequence (CV=0.83).

Sample 2 is characterized by reduced regular stacking along the c axis and the relative intensity of the (001) reflection decreased to 35% in comparison to sample 1 (Fig. 1).

The expansion of the VER particles (Fig. 2a) reduced the particle size (Fig. 2b).

The jet milled original VER flakes have corrugated edges (Fig. 2c), the silicate layers disintegrate and we observe tearing of the tinny layers (Simha Martynková et al., 2007b). The chemical exfoliation by oxidizing agents hydrogen peroxide (Weiss et al., 2006) or potassium persulfate (Matějka et al., 2006) caused intense exfoliation and destruction of the regular VER structure and consequently intercalation of ODA molecules into the interlayer was limited. We assume that the layered structure of sample 3 is preserved only in small nano-domains along the c^* direction, because the relative intensity of the (001) reflection is very low ($I=10\%$) compared to sample 1 (Fig. 1). According to the presence of $d=3.3$ nm and $d=5.5$ nm we consider sample 3 to be a mixture of two types of crystals or consists of larger homogeneous domains of a paraffin-like monolayer and bilayer arrangements of ODA molecules in the VER interlayer (Weiss et al., 2003; Lagaly et al., 2006).

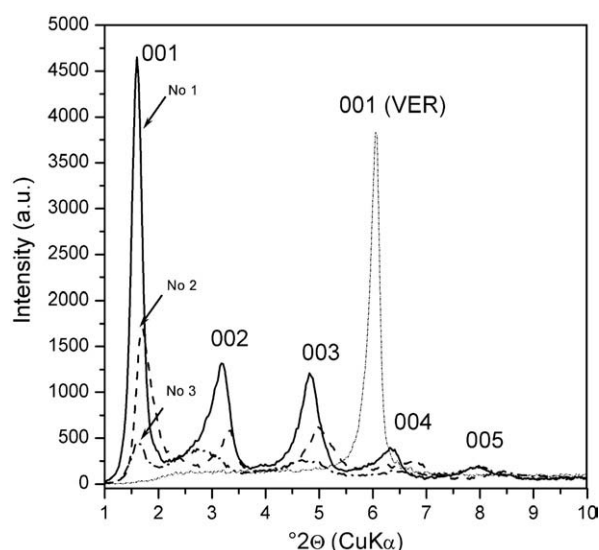


Fig. 1. PXRD patterns with the region of the first basal reflection of natural vermiculite (VER) and ODA/VER samples 1, 2 and 3.

Download English Version:

<https://daneshyari.com/en/article/1696374>

Download Persian Version:

<https://daneshyari.com/article/1696374>

[Daneshyari.com](https://daneshyari.com)