Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Exfoliation of non-swelling muscovite on dodecylammonium chloride intercalation between layers using wet-jet milling

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ARTICLE INFO

Article history:
Received 1 June 2016
Received in revised form 25 April 2017
Accepted 27 April 2017
Available online xxxx

Keywords:
Muscovite
Exfoliation
Heating process
Intercalation
Wet-jet milling

ABSTRACT

The exfoliation of layered muscovite with non-swelling property has been performed by combining various processes, such as heating, intercalation, and wet-jet milling. The c axis of muscovite was expanded from 2004.0 to 2022.8 pm at 800 °C without the destruction of crystallinity of muscovite. The heating at 800 °C led to the weak attraction force between potassium ions and silicate layers by hydroxylation of muscovite. The muscovite heated at 800 °C progressed the intercalation of dodecylammonium chloride (DDAC) into the layers effectively. Furthermore, the DDAC molecules were inserted to the interlayer of muscovite effectively by suppressing the formation of micelle of DDAC. The sedimentation test of wet-jet milled muscovite slurry showed that the relative packing density of muscovite was decreasing with increasing the amount of the intercalated DDAC. As results, the aspect ratio of muscovite prepared with combining the heating, the intercalation and the wet-jet milling was increased by 253% as compared to the raw muscovite. The aspect ratio was calculated from laser particle size distribution and thickness size distribution which was estimated from field emission-scanning electron microscopic images. The expansion of the interlayer led to the effective exfoliation of muscovite with high aspect ratio.

1. Introduction

Recently, mica is widely used as fillers for polymer material with high performance such as electrical, mechanical, and permeation barrier properties [1–6]. Especially, muscovite, which is one of the most important materials of mica, has been used for the insulating polymer material because of its outstanding electrical insulating properties [7,8]. Generally, it is necessary for development of polymer material with high reliability and functionality, such as insulation and voltage resistance properties, to increase the contents of muscovite as fillers in polymer. However, high filler loading causes various demerits, such as reduction of fluidity and formability, weight increase of material, and decrease of mechanical property, etc. Therefore, it is necessary for the development of polymer material with high performance to prepare muscovite which leads to reliable, functional and mechanical properties. In order to exploit the unique properties of muscovite as layered material, layered material has been exfoliated to thin layers [9,10]. Particularly, in the polymer material field, the nanosheets with high aspect ratio lead to improvement of various performances of polymer material [11–15].

Two-dimensional (2D) layered materials, such as clay minerals, graphene, hexagonal boron nitride (h-BN), and molybdenum disulfide (MoS_2), are stacked in numerous 2D single layers to form a 3D crystal [16]. Among these layered materials, graphene and h-BN can be exfoliated easily by mechanical processes because the interlayers are formed by weak van der Waals interactions [17–20]. On the other hand, in clay minerals, the interlayers are formed by electrostatic interaction and van der Waals interactions because the metal ions, such as sodium, calcium, and potassium ions, are present in the interlayers. In order to reduce the interlayer force of clay minerals, ions and organic molecules as guest are often intercalated between silicate layers [14,21]. It is known that the intercalation process by surface treatment of clay minerals with organic molecules leads to reduction of interlayer force but also improvement of organophilicity of clay minerals [14,22,23]. Among clay minerals, smectite as montmorillonite and vermiculite

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http://dx.doi.org/10.1016/j.apt.2017.04.026
0921-8831/

have been widely used as host materials in order to study the intercalation because of their swelling behavior and ion-exchange properties [24–28]. For example, Usuki's group has expanded the interlayer of montmorillonite by exchanging the sodium ions with ammonium cations of amino acids and caprolactam sequentially [29]. Fornes's group has reported that montmorillonite was exfoliated by extruding the composite with nylon 6 after ion-exchange with alkylammonium chloride [30,31]. Thus, the exfoliation powder with high aspect ratio can be easily achieved by the intercalation of clay minerals with swelling and ion-exchange properties. On the other hand, it is known that muscovite is not swelled in water and the intercalation of ions and organic molecules is not easily caused like smectite. It is known that the layers in muscovite has negative charge by potassium ions in the interlayer. Because the potassium ions are strongly bound to interlayer surfaces, the ion-exchange are not caused easily [32,33]. Therefore, it is difficult to exfoliate the muscovite. Furthermore, the exfoliation of layered materials based on intercalation is often carried out in situ. Lan's group has synthesized monolithic epoxy/exfoliated-clay nanocomposites by polymerizing epoxy and diamine intercalated to layers [34]. Uno's group reported that the exfoliation of sericite, which was intercalated with dodecylammonium salt, was achieved by melt-kneading with nylon 6 [35]. However, in these exfoliation processes, kinds of the guest molecules and polymers are restricted. Therefore, the development of effective methods for fabricating exfoliation powder is of importance rather than exfoliation processes in situ. As an effective exfoliation process, ultrasonication method has been studied to obtain the exfoliated powders [17,36]. Jia's group reported that nano-sheets of muscovite was obtained from muscovite powders by ultrasonication process [33]. However, in case of ultrasonication process, the yield of exfoliated powder is very low. And also, it is known that the particles of exfoliation powder produced by the ultrasonication process method are crushed, resulting that the aspect ratio of exfoliated particles becomes low [37,38]. In our previous study, we demonstrated how the exfoliation powders with high aspect ratio were fabricated effectively by wet-jet milling as mechanical process [20]. By the wet-jet milling process, the exfoliation of laminated h-BN was achieved without breaking the lateral size of h-BN particles.

In this paper, we demonstrate how the processes of heating, intercalation, and wet-jet milling can act for exfoliation of muscovite. The effect of heating temperature on the expansion of muscovite interlayer and the intercalation of dodecylammonium chloride into the expanded layers were investigated. The heated and intercalated muscovite was evaluated by thermogravimetry analysis (TG) and X-ray diffraction (XRD). We will show how the exfoliation of muscovite intercalated with dodecylammonium chloride is achieved by wet-jet milling process. Furthermore, we will discuss the statements of exfoliated muscovite from viewpoints of lateral size and thickness.

2. Experimental

2.1. Materials and preparation

All chemicals were used as received without further purification. A commercially available muscovite (MU) mica with layered structure (SJ-005, Yamaguchi Mica, Aichi, Japan) was used in this work. Dodecylammonium chloride (DDAC) was obtained from Tokyo Chemical Industry (Tokyo, Japan). Methyl ethyl ketone (MEK) was purchased from Wako Chemicals (Osaka, Japan).

The starting MU powders were prepared by heat temperature of 600, 800, and 1000 °C for 1 h in electrical furnace (SB2025D, Motoyama, Osaka, Japan). In this paper, the MU heated at 600, 800, and 1000 °C were expressed as MU-600, MU-800, and MU-1000, respectively. The MU intercalated with DDAC (DDAC-MU) was fabricated by an ion exchange reaction of MU and DDAC aqueous solution. The concentrations of DDAC solutions and the solid loadings of MU were adjusted to be 0.05–0.50 M and 0.2–2.0 vol.%, respectively. As typical procedures, 11.2 g of the MU (K^+ = 27.4 mmol) were dispersed into 200 mL of 0.5 M DDAC aqueous solution (MU = 2.0 vol.%). The dispersed slurry was stirred with a magnetic stirrer and refluxed at 120 °C for 24 h. After then, the slurry was centrifuged at 3500 rpm for 10 min. The sediment was dispersed in to 200 mL of 0.5 M DDAC aqueous solution once again. After this operation was repeated until the total reflux time was for 96 h to obtain DDAC-MU, the resulting solid was repeatedly washed with distilled water and ethanol to remove excess DDAC. The washed solid was collected by centrifuging at 3500 rpm for 10 min, and was dispersed into 200 mL of MEK. From our previous study, we selected suitable wet-jet milling condition for exfoliation of layered material. The dispersed slurry was collided 3 times at 180 MPa by the wet-jet milling (PRE-03-20-SP; Genus, Saitama, Japan). After the wet-jet milling, the solvent of slurry was replaced with distilled water from MEK by centrifuging. Finally, the wet-jet milled slurry was dried in a freeze-drying oven.

2.2. Measurements and characterization

X-ray diffraction (XRD) of MU was measured using a X-ray diffractometer (RINT2000, Rigaku, Tokyo, Japan) with Cu Kα radiation. The diffraction patterns of MU was measured from 3 to 25° with a step-scanning speed of 2°/min. The diffraction patterns of MU from 2 to 10° was also carried out with a step-scanning speed of 0.5°/min.

Thermogravimetry analysis (TG) was performed at 10 °C/min in the range from 30 to 800 °C in air (TG–8120, Rigaku, Tokyo, Japan). The amount of DDAC intercalated to DDAC-MU was estimated from the total weight loss by TG measurement within the range from 150 to 800 °C.

Infrared diffuse reflectance spectra of samples were measured using a fourier transform infrared spectrometer (FTIR, Spectrum two, Perkin Elmer, USA) with a spectral resolution of 4 cm^{-1}. The sedimentation tests of wet-jet milled MU slurries were carried out in borosilicate glass tubes of 12.3 mm inside diameter and allowed them to stand for two weeks. The initial slurry height was adjusted to be 50 mm. After two weeks, the relative packing density (*RPD*) is calculated from the following (Eq. (1)).

$$RPD(\text{vol.\%}) = C_0(H_0/H_s) \quad (1)$$

where C_0 is initial solid loading of MU in slurry (vol.%), H_0 is height of initial slurry (mm), H_s is height of sedimented MU cake (mm).

The particle size distribution of MU particles was measured by a laser particle analyzer (LA-920, HORIBA, Kyoto, Japan). The thicknesses of MU particles were evaluated by a field emission-scanning electron microscopy (FE-SEM, S-4300, Hitachi, Ibaraki, Japan). The FE-SEM observation was carried out at the accelerating voltage of 10 kV. The thickness of MU particles was estimated from FE-SEM images of 200 samples and the thickness distribution was evaluated.

3. Results

Fig. 1 shows XRD patterns of MU, MU-600, MU-800, and MU-1000. The XRD patterns of heated MU were identical with that of potassium-type mica. The XRD pattern of MU-600 was consistent with that of MU as raw material. On the other hand, the XRD patterns of MU-800 and MU-1000 were slightly shifted to the low angle as compared with MU. Thus, it was found that the extension