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Reduction of aspect ratio of fluoromica using high-energy milling

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ABSTRACT

In recent decades layered natural and synthetic clay minerals have been used in a multitude of applications including rheology modifiers, functional additives for polymers, coatings, cosmetics and even medical device components. To aid in optimisation of performance and study of biological impacts, it would be most advantageous to have a series of well-defined nano-sized clay particles of the same chemistry with controlled aspect ratio. To date previous studies into milled materials have limited analysis by advanced microscopic techniques, and have also not correlated the impact of processing the materials at laboratory versus pilot/commercial scales. In this study semi-synthetic Na^+ fluoromica was exposed to high-energy milling using lab scale and commercial scale milling systems, using several configurations and separated into size fractions using centrifugation. These fractions were assessed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS) and Fourier transform infrared spectroscopy (FTIR) which were employed to characterise the differences in morphology, particle size and structural changes between the unmilled and milled samples to fully assess the impacts of scale and energy on the process. The effect of a small lab-scale batch mill and a larger semi-commercial scale mill connected to a continuous flow reservoir was compared. The microscopy results showed that the particle size was reduced significantly after high-energy milling using both batch and continuous mill configurations on the lab scale mill, and in addition highly reproducible results were obtained using the larger mill. FTIR spectra revealed that no significant fluoromica crystalline structural changes were detected. Finally, DLS, SEM and TEM techniques were compared in order to identify the most reliable method for determining particle size distribution, and we propose that SEM has more advantages when it comes to characterising clay platelets. Furthermore, according to the SEM results, the larger semi-commercial scale mill resulted in a greater size reduction, which is consistent with existing concepts and theory of horizontal bead mill scale up.

1. Introduction

Over the years, nanoparticles and high performance nanostructured materials have attracted growing interest from both fundamental and applied research communities (Burridge et al., 2011). This is due to nanoparticles having a much higher specific surface area (Zuber et al., 2010) and a higher concentration of atoms in interfacial locations than larger particles of similar composition (Baláž et al., 2004; Jeon and Baek, 2010). Furthermore, small and systematic perturbations in nanoparticle composition, size and/or shape can elicit some novel and significantly improve physical, biological, chemical or mechanical properties. During the past several decades a multitude of nanoparticles, including clay nanoparticles have been explored as fillers to prepare polymer nanocomposites and inorganic–organic hybrid materials to improve thermal, mechanical, and optical properties, or to even introduce new functional properties to these systems (Alexandre and Dubois, 2000; Kojima et al., 1993). However, natural clay minerals have some drawbacks including the presence of contaminants, variable composition and crystallographic defects etc. (Utracki et al., 2007). Thus synthetic clays and organoclays, while being more expensive, are seen to be more attractive than their natural counterparts due to their purity, consistency and tailorability (Daniel et al., 2008; Souza et al., 2011). They are considered to be important nanomaterials finding wide applications in ceramics, absorption and catalysis, environmental remediation or protection, agriculture, cosmetics, health care products, surface coatings and composites (Carretero and Pozo, 2009).

Structural and morphological studies on clay nanoparticles are of significant importance as many applications of clay particles depend on the particle size, or platelet aspect ratio, and surface properties. In order to realize micronisation and achieve particles of controlled size and shape, high-energy milling is a well-established “top-down” process for nanomaterial preparation and dispersion, with the advantages of simplicity, scale and effectiveness (Unifantowicz et al., 2008). A range of metal oxide nanopowders, nanoparticles and nanocomposites have been prepared by high-energy milling (Baláž et al., 2004; Buranasiri et al., 2013; Perrin-Sarazin et al., 2009; Rogachev et al., 2013; Vertuccio et al., 2009). Several kinds of clay minerals have also been subjected to high-energy milling, and the resulting structural changes characterised and reported (Frost et al., 2001; Lee et al.,

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2007). The reported effects on the clay structure from planetary ball milling have been varied and include a reduction of the d_{001} lattice spacing and crystallinity (Dellisanti and Valdre, 2005), increasing structural disorder without deteriorating the primary crystallite structure (Ramadan et al., 2010), as well as increases in the specific surface area, cation exchange capacity and electrophoretic mobility (Sondi et al., 1997; Vdović et al., 2010). Nanoparticles of organo-montmorillonite with narrow particle size distribution have been produced via high-energy ball mill under different conditions in combination with ultrasonication (Mani et al., 2003). Stirred ball/bead mills, which can be operated under wet or dry conditions, utilize the impact between balls or beads, container wall, agitator shaft and impellers to realize powder size reduction. There are several variables which influence the high-energy milling process, such as selection of milling media, ball-to-powder ratio, milling time, temperature of mill and milling speed (Baláž, 2008; Campbell and Kaczmarek, 1996). As expected, better controlled combinations of variables can result in a superior milling effect (Toraman and Katırcıoglu, 2011). Planetary ball mills are widely used for clay powder preparation, however very few studies investigating the use of stirred ball/bead mills under wet conditions to carry out size reduction on clay nanoparticles have been reported, nor have they considered the commercial necessity of scalability. (Ziadeh et al., 2012). Most of the above mentioned studies used microscopy techniques to characterise the size reduction or the morphological changes, but no effective methods are reported to observe the exfoliated layers and thin platelets due to the agglomerates or clumps, which brings limitations to the accurate measurement of the reduced particle size.

This study is focused on a semi-synthetic non-modified Na^+ fluoromica (trade name Somasif ME100). It is a hydrophilic swellable 2:1 fluorinated layered silicate obtained by heating talcum and Na_2SiF_6 at high temperature for several hours, and a supplier reported an aspect ratio of approximately 5000–6000. The interlayer spacing (d_{001}) is 0.95 nm (Peeterbroeck et al., 2005; Utracki and Rapra Technology Limited., 2004). The chemical formulation is $Na_{0.66}Mg_{2.68}(Si_{3.98}Al_{0.02})O_{10.02}F_{1.96}$ (Finnigan et al., 2006). As received ME100 powder was prepared as a slurry in deionized water and subjected to high-energy milling in both a smaller lab scale mill and a larger semi-commercial scale mill (both from Netzsch, Germany), and the finest fractions were then separated using centrifugation. Both of the unmilled and milled samples were characterised by SEM, TEM, DLS and FTIR. The objectives of this study are two-fold. The first is to investigate the influence of stirred bead mills on the size of clay nanoparticles and to explore a direct measurement of clay platelet planar diameter, which has utility for our parallel biomedical research on the relationship between cytotoxicity, biocompatibility, and the clay nanoparticle aspect ratio (Tee et al., 2015). The second objective is to assess the impact of processing scale (eg lab scale versus pilot scale mills) on the resultant particle size distribution.

2. Materials and methods

Somasif ME100 was supplied by CBC Co. Ltd. (Japan). For lab-scale milling, 100 g ME100 powder was mixed with 3 L deionized water. This suspension was milled in the small-volume stirred bead mill (Netzsch laboratory agitator bead mill *LabStar*® = "small mill") with a circulation system. For large-scale milling, 500 g ME100 powder was mixed with 20 L deionized water and milled in the large-volume stirred bead mill (Netzsch Circulation mill system *Zeta*® Type LMZ 10 = "large mill") with a circulation system. The main parameters for the high-energy milling process are shown in Table 1. Milling in the *LabStar* unit was performed at a 3.3% by mass concentration and at 2.5% by mass in the *Zeta* LMZ 10.

The ME100 suspensions produced by both mills were centrifuged at 5250 g_0 (4750 rpm) for 10 min. Both supernatants were collected and centrifuged again at the same speed for 20 min and then again for 30 min in order to remove the large particles and agglomerates. The speed was then increased to 48,400 g_0 (20,000 rpm) and the supernatants were centrifuged for 30 min, twice. Finally, the supernatants representing the finest milled fractions were retained for characterisation.

Table 1
Main parameters of high-energy milling process.

Mill		
Parameter	Netzsch laboratory agitator bead mill *LabStar*	Netzsch circulation mill system *Zeta*®Type LMZ 10
ME100 (g)	100	500
Water (L)	3	20
Mill speed (rpm)	1250	970
Pump speed (rpm)	60	220
ZrO_2 Beads (mm)	0.4	0.4
Beads loading (L)	0.4	7
Temperature (°C)	33	30
Milling time (h)	4	1

A sample of the small-milled and large-milled ME100 suspensions were oven dried at 60 °C and these dry samples were used for FTIR characterisation.

A 1.2 mg sample of as-received ME100 powder was suspended in 50 mL water and the suspension was centrifuged at 931 g_0 (2000 rpm) for 3 min to remove most of the large agglomerates. The supernatant was collected as the "unmilled" ME100 aqueous suspension which would be used for SEM, TEM and DLS analysis for comparison with the milled samples. We acknowledge that the resulting aspect ratio of this unmilled sample will be lower than the supplier's indicative range of 5000–6000 (by also removing the very large platelet fraction), however this pre-treatment avoided problems associated with extensive particle agglomeration and measurement in the sample.

SEM was carried out with a JEOL JSM-6610 microscope operating at 12 kV for the dry powder sample and a JEOL JSM-7001 F field emission microscope operating at 8 kV for the suspension samples. Both of the unmilled and milled ME100 aqueous suspensions were prepared at a concentration of 0.02 mg/mL approximately, dropped onto silicon wafers using small plastic pipette and dried in a vacuum oven operating at 70 °C for a minimum of 7 h. The samples were coated with 5 nm thick Pt layer to increase particle conductivity using a Leica MED-020 Baltec sputter coater.

TEM was carried out with a JEOL JSM-1011 TEM operating at 100 kV. Single droplets of unmilled and milled ME100 aqueous suspension were spotted onto formvar coated Cu TEM grids and dried at room temperature.

Representative microscopy images were selected and 100 individual particles were measured in order to give an adequate data set. Measurements of the average particle size obtained from SEM and TEM were analysed using Image-J image processing software (developed at the National Institute of Health, USA). The particle sizes measured in SEM and TEM images refer to Feret's diameter via Image-J. The measurement details are shown in Table 2.

DLS was performed on Malvern Instrument Nanoziser Nano ZS to analyse the particle size.

The infrared spectra were obtained on a Nicolet 5700 FTIR fitted with a diamond attenuated total reflection (ATR) accessory. The spectra were recorded from a wavenumber range of between 525 and 4000 cm^{-1}, and by running 32 scans at a resolution of 4 cm^{-1}.

Table 2
Measurement details of particle size.

Microscopy	SEM		TEM	
Sample	Num. of images	Num. of particles	Num. of images	Num. of particles
Unmilled ME100	2	100	6	100
Small-milled ME100	3	100	7	100
Large-milled ME100	3	100	7	100