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Comparative study of ground and sonicated vermiculite

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The aim of this work is to compare the effects of grinding and ultrasonic treatment on vermiculite. Sonication produces a drastic change in particle size (mass median particle diameter 2.4 μm, layer thickness 38 nm), while the resulting material is crystalline as assayed by X-ray diffraction patterns. The TEM study shows that the sonicated vermiculite consists of nanometric flakes. On the other hand, grinding produces particles with medium diameter in the range of about 9 μm and very broad particle size distribution. X-ray and TEM studies of ground sample show an important alteration with grinding time. Prolonged grinding of vermiculite produces the loss of long-range order and eventually an amorphous product is obtained. The results show that grinding treatment produces a decrease of particle size, amorphization and agglomeration of the particles, whereas the ultrasound treatment only produces a decrease of particle size.

1. Introduction

Vermiculite is a clay mineral of significant commercial importance [1]. Natural vermiculites are characterized by high values of aspect ratio. The decrease of particle size of clay minerals is of relevant importance for many industrial applications. When vermiculite is delaminated and its particle thickness and length are decreased and controlled, it has many important applications. Therefore, there is a keen interest in proposing methods for delamination and reducing the particle size of vermiculite.

Wet and dry grinding are common procedures in the processing of minerals. Grinding of phyllosilicates results in particle size reduction (delamination and lateral size reduction), folding and gliding of layers, and aggregation of the newly formed particles into spherical particles [2–5]. Additionally, grinding also produces rearrangement of the coordination polyhedra and diffusion of atoms (mainly protons, "prototropy") within the structure yielding after progressive grinding amorphous materials [6–10]. Grinding also produces surface modification of clays [11, 12]. Short grinding times produce considerable particle size reduction of vermiculite. Increasing grinding time of vermiculite leads to an intense structural degradation with loss of the lamellar shape and a progressive amorphization with formation of hard agglomerates by cold-welding [13]. The resulting heterogeneity of structural defects and chemical contamination may unfavourably change material properties, thus influencing the properties of composites manufactured from submicron-sized phyllosilicates.

A feasible technique recently proposed for particle size reduction is ultrasound. Cavitational collapse sonication on solids leads to microjet and shock-wave impacts on the surface together with interparticle collisions, which can result in particle size reduction [14]. Sonication has been used as a tool for reducing particle-size of vermiculites, caolinites and micas [15–19]. Sonication produces not only a delamination effect in the [001] direction, but also a breaking of layers in the other directions, while the crystalline character is retained [20].

The aim of this work is to compare the effects of grinding and ultrasound treatments on vermiculite.

2. Experimental

Vermiculite from Santa Olalla (Huelva, Spain) was used as starting material having a half-unit cell composition of $(Si_{2.64}Al_{1.36})(Mg_{2.48}Fe^{3+}_{0.324}Fe^{2+}_{0.036}Al_{0.14}Ti_{0.01}Mn_{0.01})O_{10}(OH)_2Mg_{0.439}$ [21]. Before the treatments, the starting material was prepared by cutting the vermiculite flakes to about 2.5 cm in length and 0.5 cm in thickness.

Ultrasonic treatment was performed with a Misonix ultrasonic liquid processor of 600 W output with a 20 KHz converter and a tapped titanium disruptor horn of 12.7 mm in diameter that produces a double (peak-to-peak) amplitude of the radiating face of the tip of 120 μm. The horn tip was dipped into a cylindrical jacketed cooling cell of 5 cm in internal diameter, where 3 g of vermiculite flakes were mixed with 25 ml of

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hydrogen peroxide (30%) solution and 25 ml of freshly deionised water. The dispersions were sonicated for periods ranging between 10 and 100 h. The temperature of the reactor was kept constant at 20°C during the entire treatment by means of a cooling recirculator. Grinding experiments were carried out using a vibratory mill (Herzog HSM-100) which works through friction and impact at 1500 rpm and batches of 10 g of sample.

The adsorption of N_2 was determined with an automatic system Micromerities 2200 A Model, Morcross GA. The samples were outgassed by heating at 200°C under a flow of He gas for 12 h. The data were recorded at P/Po between 0.05 and 0.95. The specific surface area (s.a.) was determined using the BET method.

A laser method i.e., low angle laser light scattering (LALLS) was used for particle-size analysis (Mastersizer Model, Malvern). The measurements were performed on very diluted dispersions at 20°C. Identical conditions were used for all sample studied here. The standard percentile readings have been calculated for volumes percentages of 10% (D_{v10}), 50% (D_{v50}), and 90% (D_{v90}). X_{v10}, X_{v50}, and X_{v90} can be defined as sizes of particles for which 10, 50 and 90%, respectively, of the sample are below these sizes. D_{v50} is also known as the mass median diameter.

Diffraction patterns were obtained using a diffractometer (Kristalloflex D-500 Siemens at 36 KV and 26 mA with Ni-filtered Cu K_α radiation and a graphite monochromator. The dimensions of the coherently diffracting domains (crystallite size) of vermiculite in the [00l] direction were determined from the full width at half maximum of the X-ray diffraction peaks using the Scherrer equation.

A direct examination of the particles was carried out using a transmission electron microscope (TEM CM 200 model, Philips).

3. Results and discussion

Fig. 1 shows the variation of s.a. for ground and sonicated vermiculite. The s.a. of untreated sample is very small ($<1\ m^2\ g^{-1}$). Initially, it increases with the grinding time, probably due to the decrease in particle size, reaching a maximum value after 2 min grinding ($39\ m^2\ g^{-1}$). Further grinding produces a decrease in the s.a. After 10 min of treatement the s.a. reaches a value of $19.5\ m^2 g^{-1}$. Besides, sonication also increases the s.a. of the vermiculite sample. The s.a. of the original vermiculite increases to $22\ m^2\ g^{-1}$ after 10 h of sonication. For sonication times of 30 h the s.a. increase to $31\ m^2\ g^{-1}$. Beyond 30 h the s.a. increase slightly reaching at 100 h a value of $36\ m^2\ g^{-1}$.

Fig. 2 includes the particle size distribution as calculated by LALLS method for some selected ground and sonicated samples. The sample ground for 2 min, that has the highest s.a., shows a broad particle size distribution with a mass median diameter (D_{v50}) of 9.2 μm; being the values of D_{v10} and D_{v90}, 1.5 and 38.2 μm, respectively. As grinding proceeds, the particle size distribution becomes broader. Thus, Fig. 2b shows as an example the distribution for the sample ground for 10 min. The values of D_{v10}, D_{v50}, and D_{v90} for this distribution are 0.9, 8.1 and 54.1 μm, respectively. In Fig. 2, it has been also included the particle size distribution obtained for the sample sonicated for 40 h (Fig. 2c). It has been previously observed that sonication times longer than 40 h do not produce any further decrease in the particle size of the vermiculite [15]. For the vermiculite sample sonicated for 40 h, the resulting values of D_{v10}, D_{v50}, and D_{v90} are 0.35, 2.4 and 7.7 μm, respectively.

Fig. 2 clearly shows the difference in particle size distribution of vermiculite when subjected to sonication and grinding. Thus, sonication produces a material with a relatively narrow particle size distribution while grinding produces a material with a much broader particle size distribution. Additionally, the median diameter values for the sonicated samples are smaller than those of the ground samples.

Fig. 3 includes the TEM micrographs of the vermiculite sample obtained by treating the original macroscopic vermiculite sample with ultrasound for 40 h.

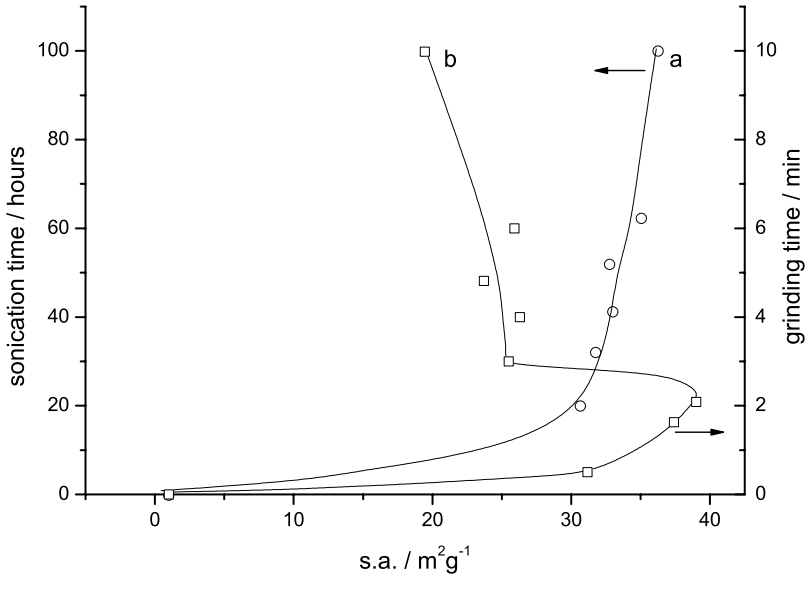

Figure 1 Evolution of the surface area of sonicated (a) and ground (b) vermiculite.

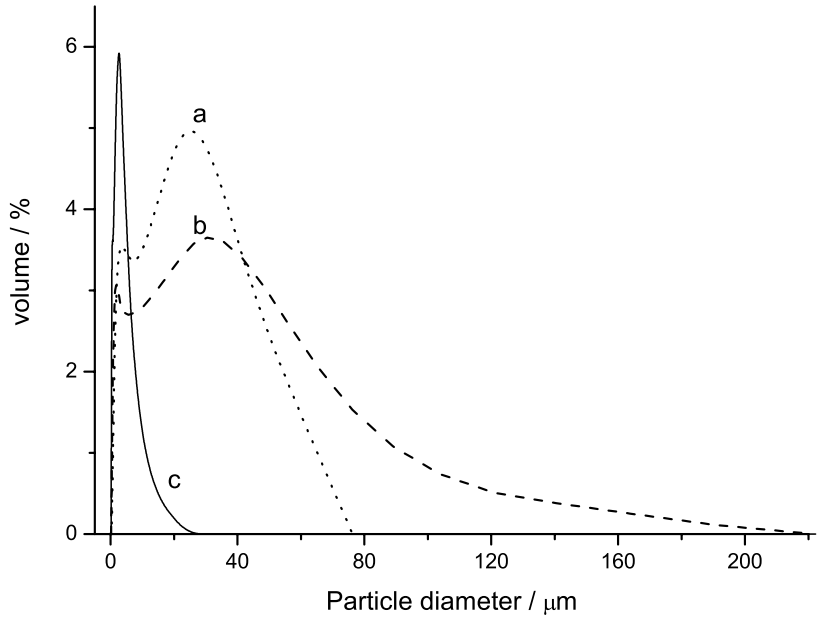

Figure 2 Particle size distribution as determined by LALLS method for the vermiculite sample ground for 2 min (a) and 10 min (b), and for the sample sonicated for 40 h (c).

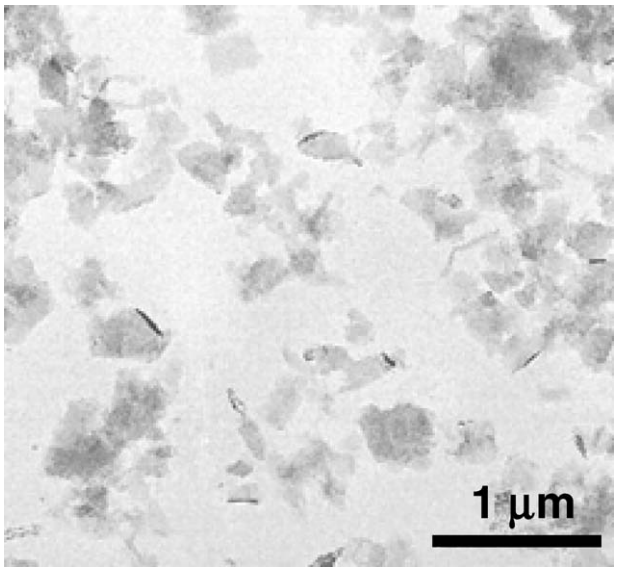

Figure 3 TEM of vermiculite sonicated during 40 h.

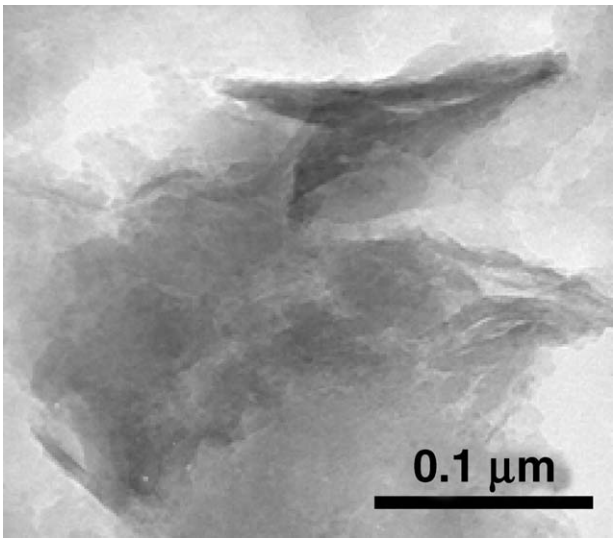

Figure 4 TEM of vermiculite ground during 2 min.

TEM observation indicates that original macroscopic vermiculite flakes are broken up into submicron particles. This sample retains the shape of the macroscopic vermiculite flakes and consists of thin platelet particles free of large aggregates and of a relative narrow particle-size distribution. On the other hand, the study by TEM of the ground vermiculite reveals that the ground material is more heterogeneous in terms of particle size distribution and alteration; as an example, Fig. 4, that shows a detail of the edges of a vermiculite flake ground for 2 min, illustrates that the ground material edges are seriously altered showing folding and gliding of the vermiculite layers.

Fig. 5 shows the X-ray pattern of the vermiculite sample ground for different times. Broadening and decreasing in intensities of the 00*l* X-ray peaks are observed after grinding as a consequence of a loss of periodicity perpendicular to the layer plane and a decrease in the dimension of the crystallites along the [00l] direction. The basal reflections disappear completely after grinding during 15 min (not included in the figure). The surface areas (Fig. 1) of the samples increase with grinding time associated to the decrease in particle size, reaching a maximum value after grinding for 2 min (39 $m^2 g^{-1}$) decreasing at increasing grinding time up to a minimum values in accordance with the progressive formation of amorphous and agglomerated particles. After 2 min grinding the sample shows the highest surface area and also is the limit before important amorphization starts.

Fig. 6 shows the X-ray pattern of the sonicated vermiculite samples. The vermiculite sample after sonication treatment is still crystalline. The X-ray diffraction pattern only shows broadening of the reflections that could be attributed to the decrease in particle size. From the broadening of the 002 reflection, it has been calculated

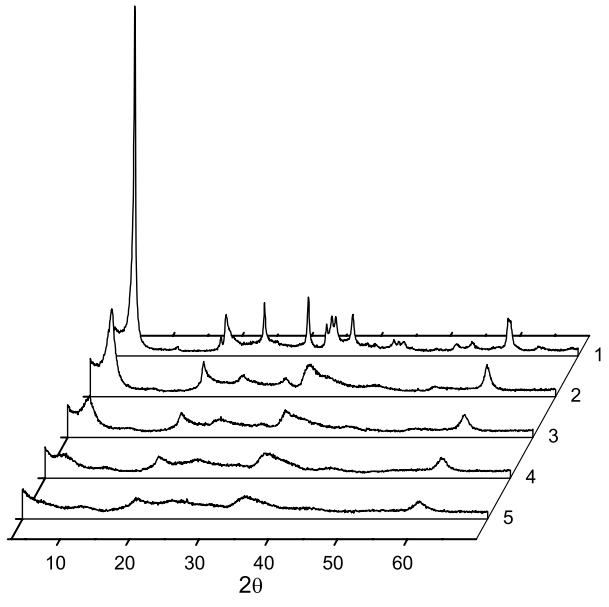

Figure 5 X-ray diffraction patterns of vermiculite sample after grinding during 30 s (Curve 1), 2 min (Curve 2), 4 min (Curve 3), 6 min (Curve 4), and 10 min (Curve 5).

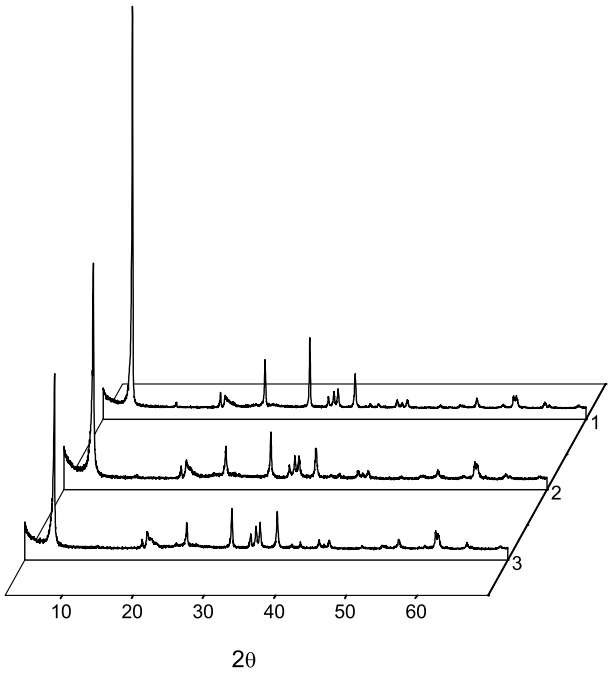

Figure 6 X-ray diffraction patterns of vermiculite sample after sonication during 10 h (Curve 1), 40 h (Curve 2), and 100 h (Curve 3).

the particle thickness. Thus, the particle thickness values show a decrease from 102 nm for 10 h sonication time to 38 nm for 30 h, remaining unchanged for longer treatment times. The crystallite sizes has not been calculated for ground samples because in these samples, there is a contribution of both the small particle size and the random displacement and imperfection in crystal order (mainly produced be edge alteration) to the broadening of the 00*l* diffraction.

Sonication has quite a different effect than grinding on vermiculite. Thus, grinding of vermiculite produces, as in other silicates [6, 22–24], strong delamination and particle degradation accompanied by a high degree of crystal structure breakdown and amorphization. On the other hand, sonication produces particle size reduction without significant structural damages. From the point of view of particle distribution and morphology, the effect of both treatments is also different. The sonicated material retains the plate-like morphology of the precursor, while its particle size is drastically reduced. On the other hand, grinding produces folding and gliding of layers and the resulting material has a much broader particle size distribution and a larger median diameter. The different morphology of these two samples could explain that, although sonication produces a more significant reduction in particle size than grinding, the maximum values of s.a. obtained for both samples are quite similar (39 $m^2 g^{-1}$ for the ground material and 36 $m^2 g^{-1}$ for the sonicated one). Thus, grinding of vermiculite produces scrolled platelet edges, capillaries, cracks and crevices that contribute to nitrogen absorption [25]. This fact produces values of s.a. of ground vermiculite larger than those expected from particle-size considerations under the assumption that only the external surface is measured with nitrogen as adsorbate.

Summarizing, sonication and grinding produce a very different effect on vermiculite. Thus, grinding produces severe structure damage, while the sonicated material remains crystalline to the X-rays. Additionally, sonication produces a more homogeneous material in terms of particle size distribution than grinding and the median diameters are smaller for the sonicated material than for the ground one. It is also significant that the sonicated material retains the plate-like morphology of the original vermiculite, while the ground one is seriously altered, mainly in the edges where N_2 is adsorbed yielding surface areas larger than those expected only from the particle size reduction.

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