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Short communication

Synthesis of nano-layered vermiculite of low density by thermal treatment

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ABSTRACT

The present work consists in the study of the modification of a nano-layered vermiculite by thermal treatment up to 900 °C. Changes in the structure and texture after thermal treatment were used for evaluation of dehydration properties of the studied material. The dehydration properties of the clay are strongly affected by the crystal structure.

The Differential Thermal Analysis (DTA) allows the determination of the specific temperatures at which phase modifications take place, principally the ones attributed to the removal of the interlayer water molecules and the formation of a series of less hydrated phases. Structural and textural studies were carried out using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) analysis. The SEM micrographs reveal structural changes of the sample, such as exfoliation phenomena and contraction of the vermiculite, related to the heating temperature. These observations are confirmed by the XRD patterns, which demonstrate that the d-spacing of the first basal diffraction varies depending on the applied heating temperature, this showing several states of dehydration. As a complementary characterization, porosity analysis by Hg-porosimetry has also been carried out.

1. Introduction

Vermiculite is a mica-type mineral used for insulation, in composite cements, in horticulture and as a substitute for asbestos. It has been exploited widely over the past 50 years or more and because of the low particle size it is used as coating, lightweight additive, etc [1]. This natural silicate mineral is usually formed by the hydrothermal alteration of mica minerals such as biotite and phlogopite [2,3]. Although its dimensions vary from microscopic particles of clay mineral to lustrous brown sheets up to half a meter in size, the particle diameter is usually in the range of 1 mm to 1 cm. Most vermiculites when heated quickly to above 230 °C lose their interlayer water and this results in the flakes exfoliating to form concertina-shaped granules. Being lightweight and resistant to thermal decomposition, this exfoliated vermiculite is valuable as an insulation material and filler, among its many other uses [4–7]. Various methods have been proposed for delaminating and reducing the particle size of vermiculites, such as sonication [8], mechanical treatment and chemical process using hydrogen peroxide [9]. These methods have been used to prepare nanometric vermiculite particles [10,11]. Sonication produces delamination in the [00*l*] direction and breaking of layers in the other crystallographic directions, while the crystalline character is retained [11]. Muromtsev et al. [12] found that in the reaction between the vermiculite and a 30 % hydrogen peroxide solution, the exfoliation is related to the separation of silicate layers with oxygen formed by the decomposition of peroxide and also to the disruption of the equilibrium between the layers and the interlayer cations, due to vigorous release of hydroxide groups from the structure. Upon heating quickly at elevated temperatures, the vermiculite exfoliates and the bulk volume increases 8–12 times [13]. The expansion is related to the separation of the layers due to the sudden release of water; the highest expansion was shown by samples containing mica or mica-vermiculite, which at lower temperatures produced thermal effects compared to pure vermiculites [14,15]. The thickness of a single layer of this silicate material is actually of nanometer size: it is known that the platelets of a vermiculite type layered clay mineral can be exfoliated to single layers that are 1 nm thick [16].

The objective of this work is to study the effect of thermal treatment up to 900 °C on the structure and texture of Palabora vermiculite. Data obtained by DTA, XRD, SEM and mercury porosimetry were used with the aim of revealing the exfoliation mechanism.

1.1. Experimental

The vermiculite samples used in this work were supplied by Palabora Mining Co., South Africa, in particles having an average size of 0.7×0.5 cm and a thickness between 0.1 and 0.3 cm. The chemical composition was determined by X-ray fluorescence analysis on a Philips PW 1480 spectrometer and the results are given in Table 1. The cation exchange

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Table 1
Chemical composition of the starting vermiculite

Oxides	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	P_2O_5	TiO_2	Cr_2O_3	L.O.I
wt.%	47.05	10.73	5.02	26.91	2.5	0.3	0.6	0.01	11.81

capacity of the starting vermiculite was determined as described by Bain and Smith [17] and was found to be 293 meq/100 g. The BET specific surface area and the density were given by the supplier and were 5.3 m^2/g and 0.08 g/cm^3, respectively.

The following structural formula was established from the raw vermiculite chemical analysis:

$$(Si_{3.26}Al_{0.74})^{IV}(Mg_{2.79}Fe(III)_{0.14}K_{0.07})^{VI}Mg_{0.3}O_{10}(OH)_2 \cdot 4.5H_2O$$

Mineralogical composition of the raw sample was determined by XRD analysis on a Rigaku-Geiger Flex diffractometer, using Cu K_α radiation. DTA experiments were performed in air flow on a Setaram M4 thermal microanalyzer, by heating the samples from 25 to 900 °C at a rate of 10 °C/min. SEM observations were carried out on a Philips CM 200 microscope. The mercury porosimetry measurements were performed by a Quantachrome type PoreMaster 60 porosimeter.

1.2. Results and discussion

The DTA curve of starting material is presented in Fig. 1, with four peaks which indicate the thermal changes of the vermiculite.

The first endothermic peak corresponds to a large water loss at about 110 °C, which is attributed to moisture present in the sample. Another endothermic process takes place at 780 °C where dehydroxylation is substantially complete. The exothermic reaction at 740 °C is probably due to the destruction of the silicate structure accompanying the loss of the last hydroxyl water. An exothermic process at about 830 °C could be attributed to a re-crystallization as mullite. This process distinguishes vermiculite from smectite for which the reaction takes place at temperatures higher than 920 °C [18,19].

The XRD of the raw material shows the peaks characteristic of vermiculite (Fig. 2a). Several peaks at 6.22°, 7.13° and 7.42°, indicate the presence of various hydrated interlayer cations such as $Mg^{2+}$and K^+. A large peak at 3.52° corresponds to some interstratification, while a peak at 18.36° is due to a low amount of octahedral iron in this sample, found by chemical analysis (Table 1). The thermal treatment of vermiculite leads to the removal of the interlayer water molecules and to formation of series of less hydrated phases [19–21]. In a study of the dehydration and the rehydration of a Mg-vermiculite by thermoanalysis and *in situ* XRD, the results confirmed the existence of a number of definite states of hydration [22]. In this work, dehydration started at 25 °C from the 6.22° state and a critical temperature was reached at 300 °C corresponding to a basal spacing of d=14.10 Å (6.27) (Fig. 2b). Further loss of water

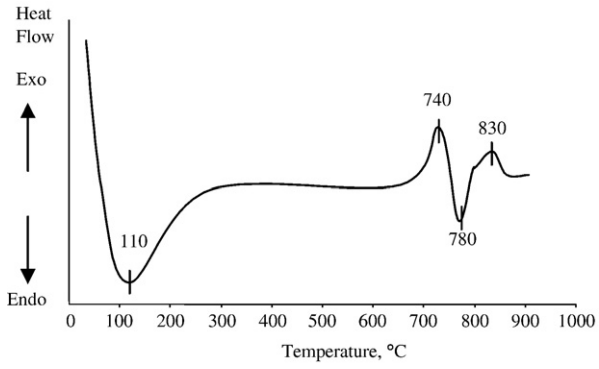

Fig. 1. DTA curve of raw vermiculite.

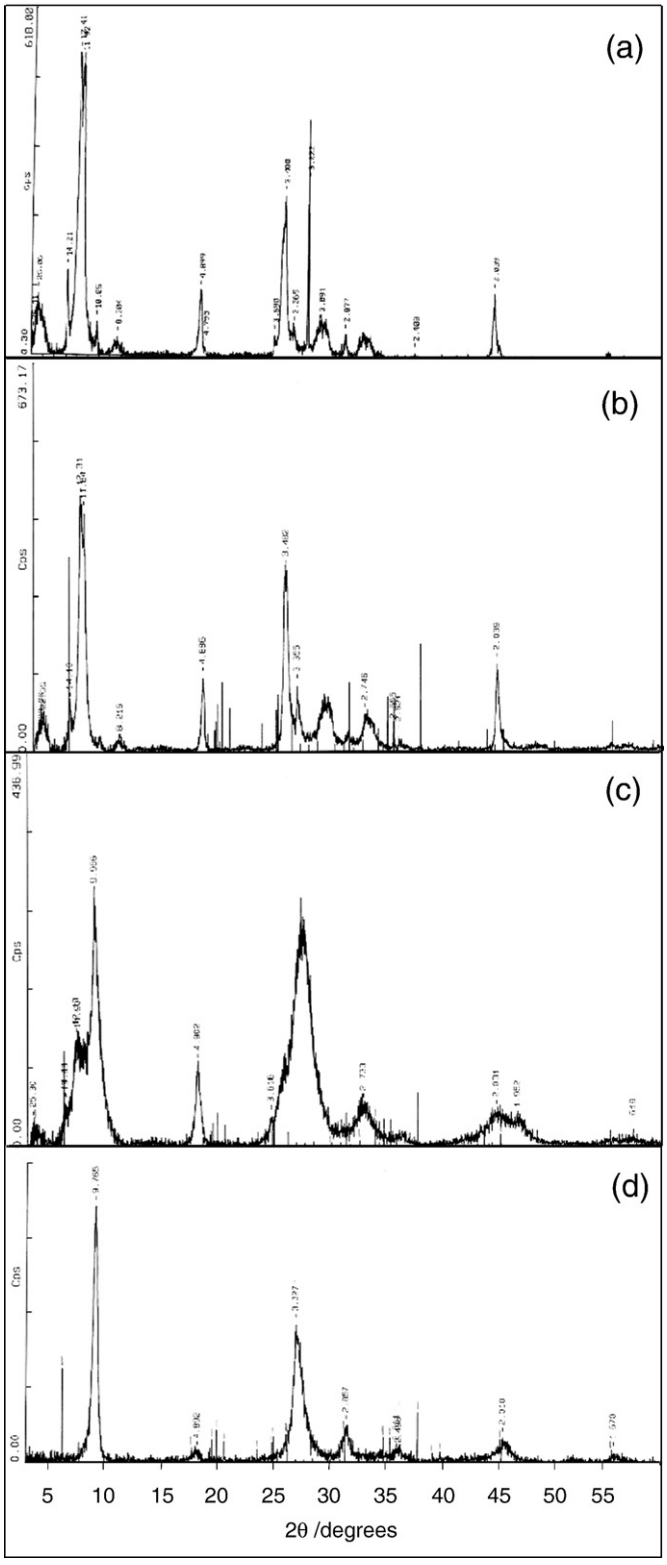

Fig. 2. XRD patterns of vermiculite. a) Raw sample, b) treated at 300 °C, c) treated at 600 °C and d) treated at 900 °C.

molecules leads to the formation of the 8.89° phase at 600 °C. Transformation of the 8.89° phase to the dehydration structure 9.07° has been fully completed at 900 °C. The initial stage of dehydration may be explained by removal of water molecules not in immediate contact with the cation such as Mg in the normally hydrated structure [19]. The end of this stage coincides with the displacement of the 6.22° phase to