Research paper

Effects of dehydration and grinding on the mechanical shear behaviour of Ca-rich montmorillonite

F. Dellisanti[a], A. Calafato[a], G.A. Pini[b], D. Moro[a,c], G. Ulian[a,c], G. Valdrè[a,c,*]

[a] Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna "Alma Mater Studiorum", Piazza di Porta San Donato 1, 40126 Bologna, Italy
[b] Dipartimento di Matematica e Geoscienze, Università degli Studi di Trieste, via Weiss 2, 34128 Trieste, Italy
[c] Centro di Ricerche Interdisciplinari di Biomineralogia, Cristallografia e Biomateriali, Università di Bologna "Alma Mater Studiorum", Piazza di Porta San Donato 1, 40126 Bologna, Italy

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ABSTRACT

In order to investigate in detail the effects of dehydration and grinding on the mechanical shear behaviour of Ca-rich montmorillonite, a cycle of specific experimental shear deformation tests were performed on five typology of samples, preliminary controlled by thermal analysis (TG, DTA) and X-ray diffraction (XRD): (1) a natural Ca-montmorillonite containing about 5% of adsorbed water; (2) the same montmorillonite heated at 80 °C for 2 h to remove only the adsorbed water; (3) up to 250 °C for 2 h to remove also the interlayer water; (4) up to 340 °C for 2 h to complete the removal of interlayer water and start to introduce thermo-structural defects, and (5) the starting natural Ca-rich montmorillonite after hard ball-milling for 20 h to induce mechanical deformation and structural defects in the TOT layers. The five typologies of samples have been tested by a specifically designed and built shear box apparatus, under about 20 MPa condition of normal pressure. All samples, before and after the shear test, have been analysed by Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and XRD. A theoretical mechanical analysis based on the Maxwell model is proposed to explain the $\tau(\varepsilon)$ and $\tau(\dot{\varepsilon})$ shear behaviour of the effects of the different type of dehydration and deformation of the material, that was finally discussed in the context of the microstructural OM, SEM and XRD data.

1. Introduction

Many works have shown that the mechanical behaviour of soils is influenced by the content of clay fraction and the type of clay minerals, and that a change in shearing mechanism can occur based on the arrangement of clay particles (Skinner, 1969; Vaughan et al., 1976; Hight et al., 1979; Lupini et al., 1981). As a general approach, a reduction of residual friction angle was noted in concomitance to the increase of clay content (Skempton, 1964; Chandler, 1984) both in non-cohesive soil without preferential orientation of particles and in pure clay, in which an alignment of clay platelets occurs along the principal failure surface (Morgenstern and Tchalenko, 1967; Yong and McKyes, 1971). Olson (1974) has performed various shear tests on pure minerals (kaolinite, illite and montmorillonite) to delineate the relationship between the mechanical properties and the kind of clay mineral, and thus drawing a dependence of shear strength from interaction of the particles and the different structural arrangement of clay minerals.

However, the fine relationships between clay dehydration and grinding on the mechanical shear behaviour of clay minerals have never been investigated in detail. It was only shown that a decrease of

structural ordering and an increase of lattice defects of smectite can involve changes in the most important physical properties, such as cation exchange capacity (Christidis et al., 2004, 2005; Filipović-Petrović et al., 2002), swelling index (Volzone et al., 1987; Novak et al., 1982; Dellisanti and Valdrè, 2005) and particle size distribution (Christidis et al., 2004, 2005; Dellisanti and Valdrè, 2005). In addition, the possible influence of mechanical grinding and related destabilization of the montmorillonite TOT structure on the mechanical shear behaviour of montmorillonite still need to be investigated.

The scope of the present work is to investigate the details of the relationships between dehydration and grinding on the shear behaviour of montmorillonite. In particular, a cycle of specific experimental shear tests was performed on well-characterized natural Ca-rich montmorillonite samples. To this aim, five typologies of samples were considered and controlled by thermal analysis (TG, DTA) and X-Ray powder Diffraction:

(1) a natural Ca-montmorillonite containing about 5% of adsorbed water;
(2) the same montmorillonite heated at 80 °C for 2 h to remove only the

adsorbed water;

(3) up to 250 °C for 2 h to remove also the interlayer water;
(4) up to 340 °C for 2 h to complete the removal of the interlayer water;
(5) the starting natural Ca-rich montmorillonite after hard ball-milling for 20 h to induce mechanical deformation and structural defects in the TOT layers, but still containing all types of water molecules.

Montmorillonite was used because presents two important types of water molecules: (i) adsorbed water on the surface, and (ii) interlayer water molecules. Furthermore, to investigate and compare the effect of mechanical deformation (defective TOT structure, but still containing water molecules) on the shear behaviour of montmorillonite, some starting natural samples were hard ball milled and successively shear tested without removing any type of water molecules.

Before and after the shear deformation, all the samples have been also analysed from both morphological (optical microscope and SEM observations) and structural points of view (X-ray diffraction).

Finally, a theoretical mechanical analysis, based on the Maxwell's model, is proposed to explain the $\tau(\varepsilon)$ and $\tau(\dot{\varepsilon})$ shear behaviour of the effects of the different type of dehydration and deformation of the montmorillonite, with a related discussion considering the macro- and microstructural OM, SEM and XRD data.

The presented approach and the related results may find great usefulness not only in soil science and geotechnics, but also in practical and industrial applications of clay minerals, in particular montmorillonites and other swelling, non-swelling and deformed, grinded phyllosilicates. Indeed, montmorillonites are commonly used materials for the production of composites for several applications, such as fuel cells (Wu et al., 2016), polymeric (semi) conductors (Bandara et al., 2005), photocatalysis (Menesi et al., 2008). The results here presented could be helpful, for example, in applications where montmorillonite is employed as lubricant material (Cao et al., 2017; Dong et al., 2015), where the knowledge of the shear mechanical behaviour is of utmost importance.

2. Materials and analytical methods

2.1. Materials and thermal analysis control

The sample used in the present work is a powdered montmorillonite sample, of about 25 μm average grain size, provided by Laviosa SpA (Livorno, Italy). It is mainly composed by Ca-montmorillonite (content > 95%) and opal CT and feldspars as minor phases. The ball-milled grinded sample is represented by this natural commercial Ca-montmorillonite that was mechanically deformed for 20 h *via* a planetary ball mill (Pulverisette 5, Fritsch, Germany), as described by Dellisanti and Valdrè (2005). This mechanical treatment induced a partial destruction of crystalline lattice and an increase of structural disorder in the TOT layers of the montmorillonite, still maintaining all types of water molecules in the sample (adsorbed and interlayer).

In order to plan the thermal treatments to the montmorillonite to specifically remove the different types of water molecules, the thermo-structural behaviour of the natural Ca-montmorillonite – cross checked by X-ray Powder Diffraction (*vide infra*) – was previously studied with a Setaram Labsys double furnace apparatus with simultaneous recording of thermogravimetric (TG) and differential thermal analysis (DTA) data. Thermal analysis was performed in the range 20 to 800 °C with a heating rate of 10 °C/min, using about 60 mg of material/sample, platinum crucibles, calcined Al_2O_3 as reference substance, a flow rate of helium of 0.27 ml/s. The temperature accuracy was about ± 1 °C.

2.2. X-ray diffraction and scanning electron microscopy

All the typology of montmorillonite samples were analysed by powder X-Ray Diffraction (XRD): (i) the starting montmorillonite (not sheared), (ii) the thermal treated not sheared montmorillonites and

finally (iii) the thermal treated sheared montmorillonites. Analyses were performed by using a Philips PW 1710 diffractometer equipped with a graphite monochromator on the diffracted beam, using CuKα radiation, 40 kV/30 mA power supply, 1° divergence and detector slits, 0.02° (2θ step size and a counting time of 10 s/step. XRD patterns were collected from 3° to 65° (2θ). A quasi-random specimen preparation was used as a reference for the natural, heated and ball-milled samples. X-ray diffraction patterns were evaluated using the Winfit computer program (Krumm, 1996), which allows to decompose the spectra and to obtain the crystallographic parameters of (001) and (060) diffraction peaks of montmorillonite. The selected reflections are important mineralogical parameters for Ca-montmorillonite, as the (001) peak can be related to the distance between TOT layers, and consequently on the presence of water molecules in the interlayer, whereas the (060) peak relates to di-trioctahedral character.

Morphology, fabric and alignment of particles of both sheared and not sheared samples were observed by using first an optical microscope, and successively a scanning electron microscope SEM (JSM-5400 JEOL) working at 10 kV of electron accelerating voltage and with a beam current of about 1 nA at the specimen level. Samples were gold-coated with a layer about 10 nm thick with a vacuum of 0.13 Pa metal-coating process.

2.3. Specifically designed shear box apparatus

Direct shear $\tau(\varepsilon)$ tests on soil and mineral specimens are usually carried out in the Casagrande's box (Casagrande, 1932), where samples of $60 \times 60 \times 20$ mm are subjected to a pressure of about 1 MPa. To increase the normal stress up to about 20 MPa, to simulate a pressure behaviour in technological and lithostatic applications, a modified Casagrande's box apparatus was developed and employed, which presents a reduced specimen size surface (from 36 cm^2 to 5 cm^2) (see Fig. 1). The chosen surface area is the result of a compromise between having a higher confining pressure and analysing a specimen not too small with respect to the scale of structures forming during the shear deformation, the latter to make the edge effects negligible.

All the $\tau(\varepsilon)$ tests were performed at room temperature (about 25 °C) and humidity of about 50–60%. The specimens were tested without adding of water. Initially, the powder was pressed in the specimen cell, and loaded with a constant normal stress of about 20 MPa for 140 h. After this time interval, all the samples reached a stable condition under the imposed normal loading, that is there were no significant deformations by compaction. A relatively high rate of shear deformation ($\dot{\varepsilon}$), starting from about $2.16 \times 10^{-4}\,s^{-1}$, was imposed because the absence of water does not involve fluids overpressure, thus the measured stresses are expressed in effective value (Terzaghi, 1936).

The maximum and residual shear strength parameters (angle of inner friction and cohesion) of each group of samples were evaluated performing three shear tests in different normal stress conditions (14.7, 19.6 and 24.5 MPa) and using the well-known Mohr-Coulomb model.

2.4. Mechanical modelling

In order to analytically describe the observed stress (τ) *vs* strain (ε) data, we considered the typical approach of non-linear viscoelasticity, using a Maxwell model in the form of

$$\tau = \eta\dot{\varepsilon}[1 - \exp(t/\lambda)] \tag{1}$$

where η is the viscosity of the material, $\dot{\varepsilon}$ is the strain rate, t is the time and λ is the relaxation time. For $t/\lambda \ll 1$, the exponential term (viscous one) has negligible effects and the system can be depicted as a Hookean spring, $\tau \sim G_0\varepsilon$, with G_0 the maximum shear modulus. It is possible to