Geomechanics for Energy and the Environment 9 (2017) 21–35

Contents lists available at ScienceDirect

Geomechanics for Energy and the Environment

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

Micromechanical characterization of shales through nanoindentation and energy dispersive x-ray spectrometry

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HIGHLIGHTS

- A linked experimental–computational approach is proposed and validated.
- Nanoindentation with Energy and Wavelength Dispersive Spectrometry is performed.
- Experiments are performed at the same spatial locations as the spectroscopy areas.
- Unique phases with distinct nanomechanical morphologies & properties are identified.

ARTICLE INFO

Article history:
Received 28 March 2016
Received in revised form
13 October 2016
Accepted 17 October 2016
Available online 31 October 2016

Keywords:
Micromechanical characterization
Shale
Nanoindentation
Energy and wavelength dispersive x-ray spectrometry
Scanning electron microscopy
Strength homogenization
Cathodoluminescence

ABSTRACT

Shales are heterogeneous sedimentary rocks which typically comprise a variable mineralogy (including compacted clay particles sub-micrometer in size), silt grains, and nanometer sized pores collectively arranged with transversely isotropic symmetry. A detailed understanding of the micro- and sub-microscale geomechanics of these minerals is required to improve models of shale strength and stiffness properties. In this paper, we propose a linked experimental–computational approach and validate a combination of grid nanoindentation and Scanning Electron Microscopy (SEM) with Energy and Wavelength Dispersive X-ray Spectrometry (EDS/WDS) at the same spatial locations to identify both the nano-mechanical morphology and local mineralogy of these nanocomposites. The experimental parameters of each method are chosen to assess a similar volume of material. By considering three different shales of varying mineralogy and mechanical diversity, we show through the EMMIX statistical iterative technique that the constituent phases, including highly compacted plate- or sheet-like clay particles, carbonates, silicates, and sulfides, have distinct nano-mechanical morphologies and associated indentation moduli and hardness. Nanoindentation-based strength homogenization analysis determines an average clay packing density, friction coefficient, and solid cohesion for each tested shale sample. Comparison of bulk to microscale geomechanical properties, through bulk porosimetry measurements, reveals a close correspondence between bulk and microscale clay packing densities. The determination of mechanical microstructure and material properties is useful for predictive microporomechanical models of the stiffness and strength properties of shale. The experimental and computational approaches presented here also apply to other chemically and mechanically complex materials exhibiting nanogranular, composite behavior.

1. Introduction to experimental characterization of shale

Shale, a fine-grained, clastic rock found in sedimentary basins, generally comprises highly compacted clay particles along with

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http://dx.doi.org/10.1016/j.gete.2016.10.004
2352-3808/

a variety of other minerals. The constituent minerals in shale can be granular (e.g. quartz, feldspar), or aggregates of particles (e.g. clays), which together form a granular, porous, anisotropic composite. Due to its multi-scale heterogeneity and anisotropy, shale is a complex material, and determination of its mechanical properties is challenging. Shale, including its pores, can be considered a nanocomposite because it is heterogeneous on multiple length scales, including the nanoscale.[1–3] The clay composite includes the intermixed clay minerals, pores, and any total organic carbon (TOC).

The objective of this research is to link mechanical properties to mineralogical observations using a combination of experimental and numerical techniques and to assess the strength of shale using nanoscale techniques, supported by computational methods. This, in turn, will improve the fundamental understanding of the mechanical properties of shale to be able to better assess and predict bulk and constituent properties. This research is distinguished from prior research as we hypothesize that the tested microstructures can be directly observed, and their compositions are resolved through EDS, allowing us to see differences between fine-grained clays and coarser-grained minerals and draw implications to observed mechanical properties. There is a gap in data at this length scale in existing literature. A motivation for developing and implementing these experimental and computational techniques to evaluate the strength of clay-bearing rocks is to derive reliable input data for multi-scale geomechanical modeling of overburdened reservoir shales, without having to use time-consuming and challenging mechanical experiments on larger scale core plug shales, which are infrequently recovered from the field.

The experimental methods performed must be applicable to the appropriate length scale for reliable results. Hence, nanoindentation was used to measure the modulus and hardness of small, site-dependent material volumes. This type of in-situ testing is not possible with conventional macroscopic experimental methods. Scanning electron microscopy with EDS detection, at the same locations and on similar microvolumes, provides a quantitative measure and spatial map of the local mineralogy of the regions probed by nanoindentation. As part of micromechanical analysis, statistical and image processing analyses are then performed to determine volume fractions of different minerals in each sample and to correlate mineralogy with indentation modulus and hardness of each active mineral phase. This approach clarifies the relationships between mineralogy, microstructures, and physical properties of three different shales.

Macroscopic measurements of shale strength and/or stiffness in the field and laboratory have typically been conducted using unconfined compression tests,[4] standard triaxial tests,[5–9] polyaxial tests,[10,11] or acoustic techniques.[7,12–17] Such tests are useful indications of bulk behavior at the core plug scale, but the relatively large activated volumes preclude insights into microscale material properties and behavior. Even on the microscale, the stress-dependent anisotropy parameters of shale are defined at least as much by the properties of contacts between the shale phases as by their intrinsic properties.[18] This suggests that particle shape and packing density should be reflected in microporomechanical modeling.[19,20] Clay packing density, expressed in terms of local porosity and the inclusion volume fraction, has become a commonly-used parameter to characterize the background clay matrix of shale.

The diversity of shale types that can be encountered for engineering applications requires that physical properties be measured specifically on representative samples. Recent improvements in force resolution and displacement length scales have allowed researchers to employ techniques for nanomechanical measurements.[1,21,22] Shale nanoindentation has been conducted by Ulm and Abousleiman,[23] who verified that shale is a nanogranular composite whose mechanical properties are governed by particle-to-particle contact and characteristic packing densities. Ortega et al. introduced a theoretical micromechanics method for both strength homogenization of cohesive-frictional porous composites[51] and evaluation of the effects of the clay phase's particle shape and grain-scale properties on shale anisotropy, at multiple length scales[19]. Bobko and Ulm[3] proposed and validated a technique to identify the nanomechanical morphology of shale by means of a series of experimental nanoindentation studies at two different scales. Nanomechanical morphology is the collection of identified mineral phases as well as their distributions and orientations on the nanoscale. The parameters for nanomechanical morphology are the mechanical properties at a specific length scale and the implied shape and mechanical properties at a length scale below.[3,24,25] The shape is based on particle morphologies, which govern the microstructure. Bobko[26] combined nanoindentation with poromechanical analysis in a homogenization model to predict poroelastic properties and strength behavior of shale based on two volume fraction parameters. Bobko et al.[27] used an inverse micromechanics approach to predict the cohesion and friction of the background clay matrix in shale.

Deirieh et al.[28] studied the relationship between mechanical properties of shales and mineralogy using the statistics of indentation data combined with wavelength dispersive spectrometry (WDS) to determine the elemental composition, and thereby the most likely mineralogy at the indentation grid points. The grid locations inferred to contain a porous clay mechanical phase were found to correspond to the clay mineral phase defined on chemical grounds by WDS. In a similar kind of study, Kumar et al.[29] combined nanoindentation with SEM–EDS to investigate the mechanical properties of kerogen. The effects of variable carbonate and quartz content, as well as TOC and clay content, on elastic modulus were also evaluated. Recent work by Eliyahu et al.[30] and Emmanuel et al.[31] estimated elastic properties of minerals and organic matter using a combination of backscattered SEM and atomic force microscopy.

This body of previous research illustrates the utility of and need for coupling chemical microanalysis methods with nanoindentation to study mechanical behavior in highly heterogeneous materials at the sub-micron scale.

2. Materials and methods

2.1. Materials

Three shale samples were used in this study: Mancos Shale from the Western U.S.A. Pierre Shale also from the U.S.A., and Opalinus Clay from Switzerland's Jura Mountains. The Mancos Shale is a sample taken from outcrop. The Pierre Shale was recovered from a drill hole in a clay pit. The Opalinus Clay was taken from a borehole drilled at the Mont Terri underground research laboratory.[32] These samples were selected because preserved material was available for Pierre Shale and Opalinus Clay. Two regions of the same Opalinus Clay sample were found to have significantly different mineralogy (due to the high amount of calcite cement in this particular Opalinus sample, in addition to the clays and quartz) and were investigated as separate data sets. The sample selection was unbiased and focused on characterizing mineralogical variability rather than expectations of probing specific ranges of packing densities or any other parameters.

Sample porosity for the Pierre Shale and Opalinus Clay was determined from the water content and grain density of the preserved and close-to-fully saturated materials through oven drying at 105 °C (Table 1). The porosity for Mancos Shale was determined by nitrogen adsorption. These two methods usually give similar results, although water porosity is usually slightly higher as nitrogen cannot access the smallest pores. The Pierre