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Nanoidentation behavior of clay minerals and clay-based nonstructured multilayers

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NANOINDENTATION BEHAVIOR OF CLAY MINERALS
AND CLAY-BASED NANOSTRUCTURED MULTILAYERS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

In

The Department of Civil and Environmental Engineering

by
Zhongxin Wei
B.S., Tsinghua University, China, 1989
M.S., Tsinghua University, China, 1994
December, 2009
DEDICATION

To my parents

and

my wife
ACKNOWLEDGEMENTS

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ABSTRACT

Clay minerals, ubiquitous in the geosphere, are hydrous layered silicates or phyllosilicates that are made of nanometer-thick 2:1 or 1:1 layers. Understanding their mechanical properties of clay minerals is of vital importance to a variety of disciplines, such as geomechanics, geophysics, mineral physics, and nanocomposites. Owing to their complex crystal structure and size, however, accurate determination of their mechanical properties is a significant challenge. This dissertation presents the first research effort to study systematically the fundamental mechanical properties along the c-axis (e.g., elastic modulus, hardness) of a wide range of phyllosilicates with varying crystal structure and chemical compositions. To explore the applications of clay minerals in nanocomposites and natural geological deposits, research was also extended to study the mechanical behavior of a class of synthesized nanocomposites – clay-oxide nanostructured multilayers possessing a similar layered structure and of the clay aggregates with highly preferred orientation – a layered packing of clay crystals.

The experimental program employed an array of nanocharacterization and nanomechanical testing techniques, including nanoindentation under both static and dynamic loading modes, scanning probe microscopy, and atomic force microscopy (AFM), in order to elucidate the mechanical behavior of the tested materials at the nanoscale and to establish a fundamental understanding of the elastic and plastic deformation mechanisms for these complex layered nanostructured materials. For the nanocomposites and clay aggregates, the characterization was also accompanied by various sample preparation and pre-treatment methods to examine dynamic nature and variability of a material’s properties. Moreover, a simple empirical method was developed of extracting the elastic moduli of both thin films and underlying substrates.

The success of this study proves that nanoindentation is a viable tool to probe the mechanical properties of hydrous phyllosilicates and to study their nanoscale deformation mechanisms. Results reveal that the mechanical properties of clay minerals are significantly dependent upon the characteristics of the crystal structure: layer charge, interlayer complexes, interlayer spacing, and even chemical compositions. In general, higher layer charges result in stronger interlayer cohesion forces and hence higher stiffness and resistance to permanent penetration. A simple empirical model was also proposed to predict the c-axis elasticity of clay minerals.
CHAPTER 1. INTRODUCTION

1.1 Background

The term “clay minerals” refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing as determined by AIPEA (Association Internationale pour l’Etude des Argiles) and CMS (The Clay Minerals Society) Nomenclature Committees (Guggenheim and Martin, 1995). In contrast, the term “clay” refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired (Guggenheim and Martin, 1995). Based on the distinctions between the two terms made here, a clay mineral is a specific mineral which is a naturally occurring homogeneous solid with a definite (but generally not fixed) chemical composition and an ordered atomic arrangement (Hurlbut and Klein, 1977), in which atoms of these elements are organized into crystalline forms. Clay is mainly a size term which corresponds to minerals and nonminerals with a specific grain size range.

Clay minerals are one of the major constituents of natural geomaterials (including soils and rocks) and occur abundantly in geosphere. They account for about 16 % by volume of the earth’s upper 20 km surface. Ubiquitous presence of clay minerals makes their significant importance in multi-disciplinary science including ceramics (main raw material), soils and agronomy (used as nutrients and fertilizer), sedimentary petrology, civil engineering, clay chemistry, and economic geology.

The crystal structures, chemical compositions, particle surface properties, and size distributions of most clay minerals have been considerably revealed with the help of X-ray diffraction, nanoscale imaging (e.g., atomic force microscopy (AFM), transmission electron microscopy (TEM)), and other of modern analytical techniques. Clay minerals are mostly composed of oxygen, silicon, hydrogen, aluminum as well as calcium, sodium, potassium, magnesium, and iron (Mitchell and Soga, 2005). Most clay minerals are composed of two basic planar layers, the 1:1 layer (~ 0.7 nm) and the 2:1 layer (~ 1.0 nm). Clay minerals occur in nature as individual platelet or aggregates with nano/micro dimensions.

The importance of understanding the mechanical properties of clay minerals is well recognized in geophysics, mechanics of geomaterials, fundamental mineral physics, and nanocomposites. In geophysics, subsurface exploration and reservoir characterization using seismic waves require the knowledge of the elastic constants of the reservoir bulk material, which are controlled by the elastic properties of individual solid components and pore-filling fluids (e.g., Smith et al. 2003). The wide range of clay minerals in soils and rocks affects the overall elastic properties of the bulk medium and hence seismic wave propagation in the geosphere (e.g., Klimentos 1991; Marion et al. 1992). An increased understanding of the mechanical properties of clay minerals can enhance seismic resolution and accuracy.

Geomaterials are particulate media whose properties are controlled by the individual particles and interparticle interactions, especially under high stress (Lambe and Whitman 1979). For example, the compressibility of a granular soil is mainly controlled by the particle crushing strength (e.g., Pestena and Whittle 1995). Understanding the macroscopic behavior of geomaterials requires an insight into the micro/nano scale behavior of individual particles.
Therefore, advances in understanding the mechanical properties of individual soil particles, in which clay minerals are abundant, can contribute significantly to micro/nano mechanics and multiscale modeling of geomaterials.

Clay minerals can be treated as nanostructured layered materials or multilayers, thus understanding their nanomechanical behavior will provide insights on the mechanical properties of synthetic nanostructured layered materials. Recently, clays minerals have been widely used to make clay-polymer nanocomposites and clay-based nanostructured multilayers (e.g., Kojima et al., 1993; Beak et al., 2002; Tang et al. 2003; Podsiadlo et al. 2007). Modeling and understanding the behavior of manufactured clay-based nanocomposites require the understanding of the mechanical properties of the filling clay minerals (e.g., Sheng et al. 2004).

To date, however, the mechanical properties of clay minerals have been rarely reported in literature, and the reported values, which are obtained from various testing methods or derived from different theories, are inconsistent. The main reason is that the naturally occurring clay minerals exist in very small particle sizes which are not large enough to be readily handled using conventional mechanical testing instruments (e.g., uniaxial compression/tension test, traditional hardness test).

This research is focused on the determination of mechanical properties of clay minerals and clay-based nanostructured multilayers as well as the influential factors on the properties using a newly developed nanoindentation technique (Oliver and Pharr, 1992) with the help of AFM.

1.2 Objectives

This research will study the mechanical behavior of clay minerals and clay-based nanostructured multilayers using nanoindentation which is a recently developed technique in the characterization of mechanical properties of small scale bulk materials, thin films, coatings, and other nanomaterials assisted with atomic force microscopy (AFM). A rigorous testing scheme, indentation control parameters, and related data analysis methods for such nanomaterials are to be established. Nanoindentation of some typical clay minerals, oriented clay aggregate films, and clay-based nanostructured multilayers are conducted. The influence of layer type, layer spacing, surface charge, interlayer species, and cations in octahedral sheet (dioctahedral or trioctahedral sheet) on the mechanical properties of clay minerals is to be studied. The factors influencing the architecture and processing procedure of clay-based multilayers on their indentation behavior are also investigated. Finally a simple model to interpret the nanoindentation behavior of clay minerals and clay-based nanostructured multilayers is to be established.

1.3 Organization of Dissertation

This dissertation consists of a total of nine chapters. It is based on papers that have been accepted, or published, or are under review, or are to be submitted to peer-reviewed journals or conferences. The technical format approved by the Graduate School of Louisiana State University is applied in the whole dissertation. Each chapter focuses on a specific topic and is relatively independent. However, some essential information may be repeated in some chapters for completeness. The following is a brief summary of each chapter content.
Chapter 2 provides a literature review of clay mineral structures, classification, available mechanical testing methods, the nanoindentation technique as well as the mechanical properties reported in literature.

Chapter 3 first develops an empirical data analysis method to extract the modulus of a thin film from nanoindentation data considering the substrate effects based on the literature data and the nanoindentation tests performed in this dissertation. This method facilitates the data analysis of ultrathin films.

Chapter 4 studies the nanoindentation behavior of muscovite and rectorite whose natural crystal sizes are large enough to be readily handled. This study gives an overall picture on designing the following nanoindentation tests on the nanomaterials with the similar structures including sample preparation method, efficient testing scheme, and nanoindentation control parameters.

Chapter 5 presents nanoindentation tests on large-sized 2:1 layer clay minerals including talc, pyrophyllite, muscovite, phlogopite, and margarite whose ideal layer charges range from zero to two. The mechanical properties of these minerals are determined using Oliver and Pharr’s method and analyzed with respect to crystal structure information available in literature. The influential factors on the mechanical properties are discussed.

Chapter 6 performs nanoindentation on three types of oriented aggregate films whose source minerals include 1:1 layer kaolinite and 2:1 layer minerals, smectite and illite. These minerals have a common feature of small particle sizes which are even difficult to be handled at present with nanoindentation instruments. Making an oriented aggregate clay film is an alternative approach to probe the mechanical properties of them and to make up the deficiency of inability to precisely position the indenter at nanometer scale limited by testing technique and difficulty in directly testing the relatively small particles.

Chapter 7 addresses the application to clay mineral nano-composites. The mechanical properties of clay-based nanostructured multilayers prepared by layer-by-layer (LbL) deposition procedure are studied using nanoindentation technique. The influence of sample preparation (as-deposited or annealed) and cations occupying the interlayer and between successive clay films on the mechanical properties of the multilayers are discussed.

Chapter 8 proposes a simple model to simulate elastic moduli of clay minerals and clay-based nanostructured multilayers based on the nanoindentation tests performed in this dissertation and the analysis of the available data in literature. Moduli of some typical clay minerals with small particle sizes are predicted using the proposed model.

Chapter 9 provides a summary of the conclusions achieved from this dissertation and recommendations for future research in this field.

1.4 References


CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

About 4,000 to 3,000 years B.C., clay was used as one of the basic ingredients to make ceramics in Egypt and Mesopotamia. As reported by Grim (1988), extensive study of clay minerals started from early 1900s when Hadding (1923) in Sweden and Rinne (1924) in Germany started to use X-ray diffraction for the study of clay-sized minerals. Thereafter, more and more clay mineral structures were disclosed by X-ray diffraction and other advanced technologies. For example, Gruner (1932) worked out the crystal structure of kaolinite. Hofmann et al. (1933) studied montmorillonite’s crystal structure and proposed a model that featured an expanding structure. Grim et al. (1937) studied a hydrous mica mineral and introduced a general term illite for micalike clay minerals. To date, most of the clay minerals’ structures have been identified with the aid of X-ray diffraction (Moore and Reynolds, 1997).

This chapter will first review clay mineral structures, the X-ray diffraction method, and classification of clay minerals. Then clay-based nanocomposites’ fabrication methods and properties will be reviewed. This is followed by a summary of the reported experimental results for mechanical properties of clay minerals and clay-based nanostructured multilayers. Nanoindentation testing method, which is mainly used in this dissertation, is the focus of this section.

2.2 Clay Minerals

2.2.1 General Structure Features

Most common clay minerals are hydrous aluminum phyllosilicates, or layer silicates which are constructed from two molecular units: a sheet of corner-linked tetrahedra (Fig. 2-1) and a sheet of edge-linked octahedra (Fig. 2-2) (Bailey, 1980; Brown, 1984; Moore and Reynolds, 1997). Different clay mineral groups are characterized by the stacking arrangements of sheets of these units and the manner in which two successive two- or three-sheet layers are held together (Mitchell and Soga, 2005). This forms two basic layer types: ~0.7 nm thick 1:1 layer (i.e., consisting of 1 tetrahedral sheet and 1 octahedral sheet per layer) and ~1.0 nm thick 2:1 layer (i.e., consisting of 2 tetrahedral sheets and 1 octahedral sheet sandwiched between the tetrahedral sheets). The stacking of either 1:1 or 2:1 layers or a combination of both accounts for major structural difference among these minerals (Fig. 2-3). The layers are held together by different interlayer complexes (e.g., hydrogen bond, non-hydrated cation, or hydrated cation), resulting in different interlayer bonding strength. The interlayer cations also compensate the net negative charges in the layers caused by isomorphous substitution.

Isomorphous substitution occurs when some of the tetrahedral and octahedral spaces are occupied by cations other than those in the ideal structure during initial formation and subsequent alteration of the clay minerals. It usually gives clay layers a permanent negative charge, thus creating the need for cations between the layers in order to preserve electrical neutrality. These cations could be present either in fixed (e.g., K⁺ in mica) or exchangeable positions (e.g., Na⁺, Ca²⁺ in smectite). Another type of charge occurs at the edges of mineral particles where structural patterns terminate with broken bonds. These unsatisfied bonds are
usually satisfied by $\text{H}^+$ and $\text{OH}^-$ which are dependent on the pH value of the environment. The variability of the permanent surface charge and pH dependent edge charge together with the various cations attracted dominates the complicated physicochemical properties of the clay minerals (Moore and Reynolds, 1997; Amonette et al., 2002; Mitchell and Soga, 2005).

Fig. 2-1 Silicon tetrahedron and corner-linked tetrahedral sheet

![Silicon tetrahedron and corner-linked tetrahedral sheet](image)

Fig. 2-2 Octahedron unit and edge-linked octahedral sheet

![Octahedron unit and edge-linked octahedral sheet](image)

2.2.2 X-ray Diffraction (XRD)

X-rays are effective for analysis of crystal structures because their wavelengths of about 1 Å are of the same order as the spacing of atomic planes in crystalline materials. Identification of crystals using X-ray diffraction is based on Bragg’s law:

$$ n \lambda = 2d \sin \theta $$

(2-1)

where $\lambda$ is the wavelength of X ray, $d$ is the distance between parallel atomic planes, $\theta$ is the angle between incident rays and parallel atomic planes, and $n$ is an integer. Constructive interference occurs when the scattered waves satisfy this equation (Fig. 2-4). Since each mineral has its specific spacings of interatomic planes in three dimensions, the angles at which diffraction occurs can be used for identification. Due to the characteristic (001) spacing (shown in Table 2-1.) for each clay mineral, the most intense reflections of these planes can be used for identification of clay minerals.
Fig. 2-3 Schematic illustration of the crystal structures of major clay minerals. $z$ is the negative charge per formula unit layer, $O_5(OH)_4$ for 1:1 layer minerals and $O_{10}(OH)_2$ for 2:1 layer minerals (Bailey, 1980; Brown, 1984; Moore and Reynolds, 1997, Mitchell and Soga, 2005).

Fig. 2-4 Schematic illustration of Bragg’s Law. 1 is one ray of the incident beam; 1’ is one ray of the diffracted beam; KGA is the normal to the planes causing diffraction. (Moore and Reynolds, 1997)
2.2.3 Classifications

Based on the layer types (1:1 or 2:1), layer charge or charge per formula unit, and octahedral types (dioctahedral or trioctahedral), clay minerals can be divided into different groups and subgroups. Each subgroup in turn is divided into mineral species. Such a classification criterion is shown in Table 2-1.

Table 2-1 Classification of clay minerals and related phyllosilicates (Lambe et al., 1979; Brindley, 1981; Bailey, 1980; Brown, 1984; Moore and Reynolds, 1997; Mitchell and Soga, 2005)

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>Interlayer Material</th>
<th>Group</th>
<th>Subgroup</th>
<th>Basal spacing (00l)</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>None or H₂O only (z ~ 0)</td>
<td>Serpentinite-Kaolinite</td>
<td>Serpentine (Tr) Kaolins (Di)</td>
<td>7.2~14.4 Å</td>
<td>Chrysotile, antigorite lizardite, berthierine, odinite Kaolinite, dickite, nacrite, halloysite</td>
</tr>
<tr>
<td></td>
<td>Talc/pyrophyllite</td>
<td>Talc (Tr) Pyrophyllite (Di)</td>
<td>Tr smectite Di smectite</td>
<td>10 Å</td>
<td>Saponite, hectorite Montmorillonite, beidellite, nontronite</td>
</tr>
<tr>
<td></td>
<td>Smectite</td>
<td>Tr smectite Di smectite</td>
<td>9.6 Å~18 Å</td>
<td>Illite, glauconite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vermiculite</td>
<td>Tr vermiculite Di vermiculite</td>
<td>10.5~14Å</td>
<td>Illite, glauconite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Illite</td>
<td>Tri illite ? Di illite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>Hydrated exchangeable cations (z ~ 0.2-0.6)</td>
<td>Smectite</td>
<td>Di smectite</td>
<td>14 Å</td>
<td>Donbassite Sudoite, cookeite (Li)</td>
</tr>
<tr>
<td></td>
<td>Mica</td>
<td>Tr micas Di micas</td>
<td>10 Å</td>
<td>Biotite, phlogopite, lepidolite Muscovite, paragonite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Brittle Mica</td>
<td>Di brittle micas</td>
<td>10 Å</td>
<td>Margarite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydroxide sheet (z ~ variable)</td>
<td>Chlorite</td>
<td>Tr,Tr chlorites Di,Di chlorites Di, Tr chlorites Tr, Di chlorites</td>
<td>14 Å</td>
<td></td>
</tr>
</tbody>
</table>

Note: Tr = trioctahedral; Di = dioctahedral; z = charge per formula unit.

2.3 Clay-based Nanocomposites

Fully exfoliated clay platelets have unique properties such as negative surface charges and high aspect ratio with thickness around ~ 1 nm. This individual nanoscale platelet exhibits strong mechanical properties because it is nearly free of defects. Negative surface charge of the clay platelet enables it to strongly interact with oppositely charged materials. Therefore, exfoliated clay platelets can be used as an ideal nanoscale constituent to fabricate nanocomposites with
other materials which have modified properties or functionalities. Such clay-based nanocomposites include bulk composites and multilayers.

2.3.1 Clay-based Bulk Nanocomposites

Kojima et al. (1993) used exfoliated montmorillonite platelets as a filler to synthesize Nylon 6-clay nanocomposite. The composite constituents were first mixed, and then the mixture was reacted in a reaction vessel at 260 °C for 6 hrs in N₂ under normal pressure. The obtained composite exhibits a high modulus, a high heat distortion temperature, and good barrier properties of gas and water. Beake et al. (2002) made a clay-poly (ethylene oxide) nanocomposite by melting process at 65 °C and found that the creep resistance had been dramatically improved. Tjong et al. (2002) prepared polypropylene-vermiculite nanocomposites by melting the compound at around 200 °C in a blender. His study indicated that the addition of vermiculite could greatly improve the tensile modulus and thermal stability of polypropylene as the clay content in the composite increases. The study of kaolinite-poly nanocomposite prepared by melting process at 262 °C (Ammala et al., 2005) demonstrated that gas-barrier properties could be improved. In all the studies, the exfoliation degree of clay minerals considerably influences the performance gains of the nanocomposites.

2.3.2 Clay-based Nanostructured Multilayers

Fabrication of multilayer nanocomposites is driven by the exceptional mechanical properties (e.g., high strength, hardness) which some biomaterials (e.g., nacre) possess. Investigations of the architectures and compositions of these natural materials exposed their nanoscale layered structures (Aksay et al., 1996; Smith et al., 1999). Based on these observations and in the hope of developing analogous synthetic materials, many man-made nanostructured multilayers were developed in recent decades. Clay-based multilayers, such as clay-polymer multilayers and clay-oxide multilayers, attracted many researchers’ attention because of their remarkable mechanical properties and versatile functionalities. The most common method for making clay-based nanostructured multilayers is the layer-by-layer (LbL) self-assembly method (Decher, 1997; Podsiadlo et al., 2007).

Layer-by-layer technique is a bottom-up process based on sequential adsorption of nanometer-thick monolayers of oppositely charged constituents (e.g. polyelectrolytes, charged nanoparticles, and biological macromolecules) to form a multilayered structure with nanometer-level control over the architecture (Decher 1997, Podsiadlo et al 2007). It is a simple, versatile, low-cost and low-temperature fabrication method to produce nanostructured thin films with desirable properties. The exfoliated clay platelet which has a high aspect ratio with thickness in nanometer scale and bears negative surface charges is used an anionic component during this process. Fig. 2-5 shows a common procedure of making clay-based nanostructured multilayers using LbL method.

The construction of complex film architectures (more than two phases, different cationic and anionic solution involved) can be easily achieved by adding corresponding dipping solution and rinsing procedure in a single deposition cycle as well as adjusting deposition parameters such as solution content, cationic and anionic types, dipping time in each medium. Furthermore, the multilayers can be treated by postdeposition procedure to modify the properties of the multilayers.
In order to enhance the deposition efficiency, Arcot and Luo (2008) modified the deposition procedure by eliminating the rinsing steps to prepare zirconia multilayers. Chen et al. (2008) used the modified method to prepare as-deposited and annealed (400 °C and 600 °C) clay-zirconia multilayers.

Fig. 2-5 Schematic illustration of the clay-based nanostructured multilayer process (two-phase film). Step 1: adsorption of cations; step 2 and step 4: rinsing with water; step 3: adsorption of clay platelets.

To date, many types of synthetic clay-based multilayers have been reported. The clay minerals used include smectite (saponite, montmorillonite, synthetic hectorite, etc.), vermiculite, and kaolinite. The first primary function of clay layers is to enhance the mechanical properties of the multilayers. For example, Podsiadlo et al. (2007) reported ultrastrong and stiff clay (montmorillonite)-polymer nanocomposites with tensile strength of 400 MPa and modulus of 106 GPa which exceeds the stiffness of the strongest carbon-nanotube (CNT)-based fibers (80 GPa) (Dalton et al., 2003). Ou et al. (2007) found that clay (kaolinite)-polymer nanocomposites can largely enhance wet strength of paper. The second primary function of clay layers is to serve as diffusion blocking barriers which are widely used in various fields such as electronic and optical devices. Eckle and Decher (2001) used exfoliated montmorillonite platelets as isolating barrier sheets to tune the performance of LbL assembled organic light emitting diodes. Clay (saponite and montmorillonite)-ployacetylene multilayers exhibited highly enhanced thermal oxidative stability (Kim et al. (2005)). Lutkenhaus et al. (2007) studied clay (synthetic hectorite)-poly (ethylene imine) multilayers and found that in-plane ion transport 100 times faster than cross-plane at 0 % relative humidity. Szabo et al. (2007) reported an ultrathin protein-clay (saponite) multilayer for biosensing and biocatalysis.

Almost all the researches on clay-based nanocomposites concentrate on the fabrication procedure of either bulk composites or multilayers and the overall properties of the composites. The mechanical properties of the nanocomposites, clay aggregates involved, and exfoliated clay-platelets are still rarely identified. However, these mechanical properties are of importance in understanding, designing and modeling clay-based nanocomposites, particularly for high strength clay-based nanocomposites.
2.4 Mechanical Testing Methods for Clay Minerals and Clay-based Nanocomposites

It is difficult to find clay particles large enough to be tested using conventional standard instruments. This leads to rare reports of mechanical properties (e.g., modulus $E$ and hardness $H$) of clay minerals. Since no standard testing method has been established, the reported mechanical properties of clay minerals are largely inconsistent, dependent on the methods being used. These methods include theoretical computation, a combination of theoretical and experimental investigations, and the empirical extrapolation of laboratory measurements. The following section is arranged based on testing methods, and the mechanical properties of clay minerals are reported with the corresponding methods.

2.4.1 Acoustic Method

This method is based on the theory of seismic wave propagation in homogeneous, isotropic, and elastic media. The elastic bulk modulus ($K$) and shear modulus ($G$) of a sample are calculated by

$$K = \rho \left( V_p^2 - \frac{4}{3} V_s^2 \right)$$

and

$$G = \rho V_s^2$$

where $\rho$ is the bulk density of the composite sample, $V_p$ and $V_s$ are the measured compressional and shear velocities through the sample (Mavko et al., 1998). For a two-phase composite, if the elastic properties ($K$ and $G$) of one of the constituents are known, the elastic properties of the other constituent can be inverted using Kroner’s equations (Kroner, 1967). Determination of elastic properties of some minerals using this method has been reported in which the composites were formed by hot-pressing method (Simmon and Chung, 1968; Brace et al., 1969). Wang et al. (2001) selected different clay minerals and prepared different clay-epoxy composites at low temperature ($46 \, ^\circ\text{C}$) to simulate the clay status occurring naturally in reservoir or nonreservoir rocks. By measuring $V_p$ and $V_s$ going through the composites, elastic bulk modulus and shear modulus of sixteen clay minerals including kaolinite, smectite, illite, chlorite, illite-smectite mixed layers, and synthetic mica-montmorillonite were obtained using the weighted Hashin-Shtrikman average (Hashin and Shtrikman, 1963). The Young’s modulus of such randomly distributed clay particles are on the order of 50 - 60 GPa for kaolinite, 65 - 80 GPa for illite, 40 - 50 GPa for montmorillonite, and greater than 100 GPa for chlorite.

Vanorio et al. (2003) designed a cold-pressing apparatus to make clay aggregate samples from pure powders of kaolinite, Na-montmorillonite and Ca-montmorillonite (Fig. 2-6). Ultrasonic P- and S- wave were measured under hydrostatic pressure and uniaxial compaction stresses. Then the relationship of elastic modulus versus porosity was established. The modulus of clay mineral was obtained by the extrapolation of the porosity to zero. The measured elastic modulus values were between 6 and 12 GPa for bulk modulus and between 4 and 6 GPa for
shear modulus. The major uncertainty of this approach lies in the validity of the extrapolation to very low porosity from high porosity.

Mondol et al. (2008) used a similar method to derive the elastic properties of kaolinite and smectite. Both dry and brine-saturated kaolinite and smectite aggregates were mechanically compacted, and the compression ($V_p$) and shear ($V_s$) wave velocities were measured to calculate the elastic parameters. Finally, the elastic parameters of kaolinite and smectite were derived from the extrapolation of porosity-elastic moduli relationships to zero porosity (Fig. 2-7.). The bulk moduli of 7.9 ~ 17.8 GPa for kaolinite and 12.3 ~ 29.0 GPa for smectite were obtained.

### 2.4.2 Molecular Dynamics (MD) Simulation

Molecular dynamic (MD) simulation has been applied to different problems of thermal dynamics and mechanics of clay minerals. Seo et al. (1999) determined the elastic moduli and the strength of bulk quartz, albite, and muscovite under uniaxial compression using MD simulation. Sato et al. (2001) performed the MD simulation of a single clay layer of beidellite under compression and found that clay sheets may bend under compressive strain up to 40% before fractures occur which corresponds to stresses on the order of 0.7 GPa, and the flexibility mainly originates from the change of Si-O-Si angles in the silicate tetrahedral sheets rather than the change of bond lengths. Manevitch and Rutledge (2004) conducted the MD simulation of a single lamella of montmorillonite under compression and obtained values for the in-plane elastic properties $E_i h$ of 250-260 N/m ($E_1, E_2 = 400-420$ GPa assuming $h = 0.615$ nm) and an out-of-plane elastic constant $E_3 h$ of 239 N/m ($E_3 = 390$ GPa assuming $h = 0.615$ nm), where $E_1, E_2$ are Young’s moduli in the in-plane two Cartesian directions, $E_3$ is the Young’s modulus in the direction normal to the in-plane, and $h$ is the thickness of the single lamella. Mazo et al. (2008a) present the results of MD simulation for a single nanoplate of pyrophyllite in the temperature interval from 5 to 750 K and obtained the full elasticity tensor as well as the in-plane elastic properties $E_i h$ ($i = 1, 2$) of 256-284 N/m and out-of-plane elastic constant $E_3 h$ of 163 N/m.
As computational resources increase and efficient classical molecular dynamics algorithms are developed, the large-scale MD simulation of clay minerals which consist of more than 100,000 atoms became possible. Sato et al. (2005) used MD method to determine the elastic constants of kaolinite mineral, and the bulk modulus of 23 GPa was obtained as well as the Young’s modulus of 92 GPa, 170 GPa and 31 GPa for the three crystallographic axes a, b, and c directions, respectively.

After a new force field (CLAYFF), which takes into account the ionic form of metal atoms and oxygen atoms, was developed (Cygan et al., 2004), Suter et al. (2007) simulated montmorillonite containing up to approximately ten million atoms whose dimensions approach those of a realistic clay platelet with an intercalated monolayer of water. Based on the assumption that the clay system is of orthotropic symmetry and Hooke’s law is applicable, an average in-plane Young’s modulus $E_x$ of 172 GPa in the $x$ direction and an average in-plane Young’s modulus $E_y$ of 182 GPa in the $y$ direction ($x$ and $y$ are Cartesian axes) for clay plus
interlayer were obtained. Provided the thickness of clay is 0.9 nm, the Young’s moduli \( E_x \) and \( E_y \) of a single clay sheet were also determined as \( E_x \approx E_y \approx 230-260 \) GPa.

Mazo et al. (2008b) also used the CLAYFF force field to simulate the thermomechanical behavior of sodium montmorillonite (MMT) with monolayer and bilayer of water intercalates (Fig. 2-8). The in-plane moduli of 180 GPa and 150 GPa were calculated for the case of an intercalated monolayer of water and that of an intercalated bilayer of water, respectively. The shear moduli parallel to the lamellae were obtained as 20 GPa for the monolayer case and 2-4 GPa for the bilayer case as well. It is noteworthy that the calculated elasticity tensor possesses orthotropic symmetry and changes are very weakly with temperature in the range 300-350 K.

![Fig. 2-8 Sodium montmorillonite systems with monolayers (a) and bilayers (b) of water between the clay plates. The atoms are colored as follows: Si, yellow; O, red; H, white; Al, green; Na, blue; Mg, magenta. (Mazo et al., 2008b)](image)

Table 2-2 summarizes the elastic moduli and Poisson’s ratios of the single clay lamella and hydrated montmorillonite reported in literature using MD simulation. The clay system is assumed as an orthotropic symmetry, and the Cartesian coordinate system is applied with \( x \), \( y \), and \( z \) axes. The elastic moduli in the three Cartesian axes are denoted by \( E_x \), \( E_y \), and \( E_z \), respectively.

### 2.4.3 Brillouin Scattering Method

Brillouin scattering has been successfully used to measure the elastic moduli of muscovite mica (Vaughan and Guggenheim, 1986; McNeil and Grimsditch, 1993). Very close results for elastic stiffness elements were obtained (\( C_{11} = 181 \) GPa, \( C_{22} = 178.4 \) GPa, and \( C_{33} = 58.6 \) GPa by Vaughan and Guggenheim; \( C_{11} = 176.5 \) GPa, \( C_{22} = 179.5 \) GPa, and \( C_{33} = 60.9 \) GPa by McNeil and Grimsditch). However, this method requires that the specimen must be optically transparent nonluminescent (and highly symmetrical) crystals. Therefore, it is difficult to be applied to all clay minerals because of their small particle size.
Table 2-2 Elastic moduli and Poisson’s ratios of a single clay lamella and hydrated montmorillonite determined by MD in literature

<table>
<thead>
<tr>
<th>References</th>
<th>Minerals</th>
<th>Single Lamella Montmorillonite</th>
<th>Montmorillonite</th>
<th>Hydrated Montmorillonite</th>
<th>Hydrated Montmorillonite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Strain rate =1.5×10^{-3}m/s</td>
<td>Strain rate =2.0×10^{-4}m/s</td>
<td>Montmorillonite</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E_x h(E_x)$</td>
<td>$E_y h(E_y)$</td>
<td>Bilayer H₂O</td>
<td>Monolayer H₂O</td>
</tr>
<tr>
<td>Manevitch &amp; Rutledge (2004)</td>
<td>Single Lamella</td>
<td>229 (N/m)</td>
<td>216 (N/m)</td>
<td>182 GPa</td>
<td>150 GPa</td>
</tr>
<tr>
<td></td>
<td>Montmorillonite</td>
<td>249 (N/m)</td>
<td>256 (N/m)</td>
<td>172 GPa</td>
<td></td>
</tr>
<tr>
<td>Suter et al. (2007)</td>
<td>Montmorillonite</td>
<td>261 (N/m)</td>
<td>230 (N/m)</td>
<td>180 GPa</td>
<td>152 GPa</td>
</tr>
<tr>
<td>Mazo et al. (2008a)</td>
<td>Hydrated</td>
<td>239 (N/m)</td>
<td>163 (N/m)</td>
<td>78.1 GPa</td>
<td>61.7 GPa</td>
</tr>
<tr>
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<td>NA</td>
<td>NA</td>
<td>0.48</td>
<td>0.45</td>
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<tr>
<td>Suter et al. (2007)</td>
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<td>0.41</td>
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<td></td>
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<td>0.14</td>
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<td>0.05</td>
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<td>0.50</td>
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<td>0.45</td>
<td>0.50</td>
<td>0.02</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Note: $h$ denotes layer thickness.

2.4.4 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) has been initially used to characterize the nanomorphology and size distribution of clay particles (kaolinite, and montmorillonite) (Zbik and Smart, 1998; Bickmore et al. 2002; Vaz et al., 2002; Piner et al., 2003; Ploehn and Liu, 2006). In this technique, a sharp tip at the free end of a cantilever (also called probe) is brought into contact with the sample surface, causing the cantilever to bend. A laser spot is reflected from the cantilever onto a position-sensitive photodiode detector. The position of the laser spot changes as the cantilever bends. The topography of the sample surface is measured from deflections of the tip from its equilibrium position (Fig. 2-9).

![Fig. 2-9 Basic AFM principles (Agilent Technologies, 2008)](image-url)
Prasad (2002) used an enhanced AFM technique, named atomic force acoustic microscopy (AFAM) in which ultrasonic transducers are installed to insonify the contact zone between the cantilever and the sample surface, to measure the moduli of clay minerals. The dynamic Young’s modulus is obtained by measuring the difference of the cantilever contact-resonance frequencies relative to its free resonances. The Young’s modulus of dickite was measured as 6.2 GPa. It is noteworthy that many factors are involved in the determination of the contact-resonance frequencies which could affect the accuracy of the test results.

2.4.5 Buckling-based Method

Stafford et al. (2004) introduced a buckling-based method to measure the elastic moduli of polymeric thin films in a thickness regime of 50 -250 nm. This technique exploits a buckling instability that occurs in bilayers consisting of a stiff, thin film coated onto a relatively soft, thick substrate. The film’s elastic modulus was calculated based on the spacing of induced highly periodic wrinkles by applying well-established buckling mechanics. No application of this method on clay minerals has been reported.

2.4.6 X-ray Diffraction with Diamond Anvil Cell (DAC)

This method is typically used to measure unit-cell dimensions of a crystal under high-pressure and/or high temperature. In this method, the crystal is mounted in a miniature diamond-anvil cell (DAC), and the pressure is applied through a hydrostatic pressure medium while X-ray diffraction data are recorded. The bulk modulus K is determined from the relationship of static pressure versus volumetric strain. Table 2-3 summarizes the reported bulk moduli of clay minerals by DAC method.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Bulk Modulus (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Serpentine-kaolinite</td>
<td></td>
<td></td>
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<tr>
<td>Dickite</td>
<td>68.3</td>
<td>Dera et al. (2003)</td>
</tr>
<tr>
<td>2. Talc-pyrophyllite</td>
<td></td>
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</tr>
<tr>
<td>Talc</td>
<td>41.6</td>
<td>Pawley et al. (1995)</td>
</tr>
<tr>
<td>Talc</td>
<td>41.0</td>
<td>Pawley et al. (2002)</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>37.0</td>
<td>Pawley et al. (2002)</td>
</tr>
<tr>
<td>3. Mica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite (K-rich)</td>
<td>49.0</td>
<td>Comodi and Zanazzi (1995)</td>
</tr>
<tr>
<td>Muscovite (Na-rich)</td>
<td>54.0</td>
<td>Comodi and Zanazzi (1995)</td>
</tr>
<tr>
<td>Phengite 2M1</td>
<td>57.0</td>
<td>Smyth et al. (2000)</td>
</tr>
<tr>
<td>Phengite 3T</td>
<td>62.0</td>
<td>Smyth et al. (2000)</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>58.5</td>
<td>Hazen and Finger (1978)</td>
</tr>
<tr>
<td>4. Chlorite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>55.0</td>
<td>Hazen and Finger (1978)</td>
</tr>
<tr>
<td>Clinochlore*</td>
<td>75.4</td>
<td>Welch and Marshall (2001)</td>
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<tr>
<td>Chlorite</td>
<td>86.9</td>
<td>Pawley et al. (2002)</td>
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<tr>
<td>Clinochlore</td>
<td>81.0-83.0</td>
<td>Welch and Crichton (2002)</td>
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<tr>
<td>Clinochlore</td>
<td>71.0</td>
<td>Zanazzi et al. (2007)</td>
</tr>
</tbody>
</table>

Note: * denotes that the data were obtained by using Tungsten carbide anvil cell (WCAC) with neutron diffraction method.
2.4.7 Nanoindentation

Nanoindentation, also named depth-sensing indentation (DSI) testing or instrumented indentation testing (IIT), is based on the theories of contact mechanics. This technique is widely used in the characterization of mechanical properties of small scale bulk materials, thin films, coatings, and other nanomaterials. Due to the micro/nano scale load and the resulting small residual impression left on the surface of the tested material, it can be regarded as a non-destructive testing technique.

Although nanoindentation technique has been widely used to determine the hardness and elastic modulus of small-scale materials, applications in clay minerals and related phyllosilicates are only in limited cases. For instance, Broz et al. (2006) reported the mechanical properties of talc mineral as 16.2 GPa for modulus and 0.30 GPa for indentation hardness. Ulm and Abousleiman (2006) obtained the Young’s modulus of 40.3 GPa for kaolinite by indentation testing on kaolinite powder sample. Since nanoindentation is the main method to be used in this research to characterize the mechanical properties of clay minerals and related phyllosilicates, more details about this method are reviewed in next section.

2.5 Principles of Indentation Testing

2.5.1 Conventional Indentation

2.5.1.1 Hardness

Indentation testing is a simple, inexpensive and quick method for mechanically characterizing a material. It consists essentially of touching the material of interest whose mechanical properties such elastic modulus and hardness are unknown with another material whose properties are known (Fischer-Cripps, 2004). The most important parameter determined by indentation testing is hardness. Mohs (1822) first proposed a sufficiently precise and generally accessible method to determine the hardness parameters of minerals. The 10-step, empirical scale of hardness corresponding to 10 index-minerals from diamond (10), corundum (9), topaz (8), quartz (7), feldspar (6), apatite (5), fluorite (4), calcite (3), gypsum (2), and talc (1) is based on the principle that each mineral in the hardness scale scratches its immediate predecessor (Szymanski, 1989). Later, more refined methods were developed including Brinell, Knoop, Vickers, and Rockwell tests in which the term “hardness” is quantified using one of a variety of scales that directly or indirectly indicate the contact pressure involved in deforming the test surface. The indenter used in different methods varies from spherical (Brinell test), pyramidal (Vickers and Knoop test), conical (Rockwell test), or Berkovich indenter as shown in Fig. 2-10.

The indentations with pyramidal, conical, and even Berkovich indenters have geometric similarity (Tabor, 1956). The principle of geometric similarity is of considerable value and widely used in hardness measurements. It implies that the strains and hence stresses are the same for a large indentation and a small indentation. Consequently the mean contact pressure or hardness will be same whatever the size of indentation. It also follows that hardness measurements using one of these types of indenters are expected to yield a value for hardness that is independent of the load if the indentation size effects (ISE) are not considered.
The hardness value is expressed as the load divided by the actual contact surface area (e.g., Brinell hardness number \( BHN \), Vickers hardness \( HV \), and Knoop hardness \( KHN \)) or as the load divided by the projected contact area (e.g., Meyer hardness \( H_M \)). For example, the \( BHN \) is determined as the load generating a fully developed plastic zone divided by the actual area of the surface of the residual impression as follows:

\[
BHN = \frac{P}{A_{\text{actual}}} \tag{2-4}
\]

where \( P \) is the load, and \( A_{\text{actual}} \) is the actual surface area of the residual impression. By contrast, the Meyer hardness is determined as the load divided by the projected area of contact:

\[
H_m = \frac{P}{A_c} \tag{2-5}
\]

where \( A_c \) is the projected contact area. The Meyer hardness is a more physically meaningful concept which is well recognized now.

Since there exists a fairly accurate quantitative relationship between hardness and other mechanical properties of materials such as ultimate tensile strength, yield strength and strain hardening coefficient, fatigue strength, and creep (Tabor, 1956; Atkins and Tabor, 1965; Tabor, 1996), indentation testing is widely used in quality control of materials. For example, experiments show that indentation hardness \( H \) is directly proportional to the material’s yield stress in compression, and can be expressed as:

\[
H \approx C\sigma_y \tag{2-6}
\]

where \( \sigma_y \) is the yield stress of the material, and \( C \) is the constraint factor ranging from 1.5 ~ 3 mainly dependent upon the type of specimen (Fischer-Cripps 2004).
2.5.1.2. Indentation Strain and Indentation Stress

Unlike the conventional uniaxial tension and compression tests in which the stress and strain are related to a specific point or specific cross-section perpendicular to the loading axis, the stress and strain fields within the specimen induced by the indenter are too complicated to be represented by a certain point or plane section. The deformation and pressure distribution on the indenter-specimen contact surface are commonly used to characterize the corresponding strain-stress field of the material. Based on this understanding, the mean contact pressure determined as Eq. (2-4) or Eq. (2-5) is often referred to as the “indentation stress”.

Determination of the “indentation strain” beneath the indenter is not as easy as that of indentation stress. However, for a specific type of an indenter (e.g., a spherical indenter), the contact area radius $a$ divided by the indenter radius $R$ is a dimensionless parameter to reflect the induced shape of the residual impression. Therefore, the ratio $a/R$ is determined as the “indentation strain” (Fischer-Cripps, 2000). For large angles of $\alpha$, the quantity $a/R$ for a spherical indentation is equivalent to $\cot \alpha$ for a conical indenter:

$$\cot \alpha = \frac{a}{R} \quad (2-7)$$

Eq. (2-7) provides a comparable strain level to compare the hardness determined by different indentation testing methods. Considering that the plastic strains are not uniform beneath the indenter, Tabor (1996) found that there exists a representative strain $\varepsilon_r$ in the specimen which is a function of $a/R$:

$$\varepsilon_r = 0.2 \frac{a}{R} \quad (2-8)$$

Therefore, the representative strain for a pyramidal indenter with an equivalent cone angle $\alpha$ can be determined through Eq. (2-7) and Eq. (2-8), and it is constant for a specific indenter. It means that hardness determined by a conical indenter is related to a fixed representative strain.

2.5.2 Nanoindentation

2.5.2.1 Determination of Elastic Modulus and Hardness

Nanoindentation is a relatively a new form of mechanical testing which is developed greatly over the past decades. During nanoindentation, an indenter with a known geometry and properties (e.g., Young’s modulus, Poisson’s ratio) is pressed into the flat surface of a material of unknown properties followed by unloading, while the load and indentation depth are continuously controlled and monitored through high resolution instrumentation. The length scale of the penetration is measured in nanometers (nm) rather than micrometers (\(\mu m\)) or millimeters (mm), the latter being common in conventional indentation tests (Fig. 2-11).

The advantages of nanoindentation include: 1) the contact area between the indenter and the specimen required to calculate the hardness is indirectly determined by measuring the depth of penetration of the indenter with the known geometry into the specimen surface, this overcomes
the difficulties in directly measuring the nanoscale or microscale size of the residual impression which is commonly employed in conventional indentation tests; 2) the continuously recorded load-displacement data provide a wealth of information for characterizing a variety of mechanical properties such as elastic modulus (Doerner and Nix, 1986; Oliver and Pharr, 1992), hardness, strain-hardening (Field and Swain, 1993; Field and Swain, 1995; Swain, 1998), cracking, phase transformations, creep, and energy absorption (Fischer-Cripps, 2004).

![Diagram of nanoindentation process](image)

**Fig. 2-11** Schematic illustration of (a) nanoindentation loading and unloading processes and (b) corresponding load-displacement curve.

Determination of hardness and elastic modulus by nanoindentation is based on the mechanics of elastic contact. An elastic parameter, named reduced modulus ($E_r$) or effective modulus of the indenter-sample contact, can be obtained directly from the load-displacement curves through the following relationship:

$$E_r = \frac{\sqrt{\pi}}{2\beta \sqrt{A_c}} S$$  \hspace{1cm} (2-9)
where $\beta$ is a dimensionless correction factor for the indenter tip shape and $\beta = 1.05$ is commonly recommended (Oliver and Pharr, 2004); $A_c$ is the projected contact area between the indenter and sample; $S$ is the contact stiffness defined as the slope of the initial unloading curve at the maximum indentation depth ($h_{\text{max}}$) (Fig. 2-11) and is usually determined by fitting the beginning portion of the unloading curve using a linear or power law relationship, depending on indenter geometry:

$$S = \frac{dF}{dh}\bigg|_{h=h_{\text{max}}}$$

Eq. (2-9) was initially developed by Sneddon (1965) for the penetration of a flat-surfaced, elastic half space by different probes of particular axisymmetric shapes (e.g., a flat-ended cylindrical punch, a paraboloid of revolution, and a cone) and experimentally verified thereafter suitable for conic and pyramidal indenters (Doerner and Nix, 1986; Oliver and Pharr, 1992).

The reduced modulus can be obtained directly by following the above procedures. $E_r$ actually reflects the elastic contact interaction between the indenter tip and sample and accounts for elastic deformation of both the indenter and the sample. To obtain the elastic modulus of the sample, the following relationship was used (Doerner and Nix, 1986):

$$\frac{1}{E_r} = \frac{1-v_c^2}{E_c} + \frac{1-v_i^2}{E_i}$$

(2-11)

where $v_c$ and $v_i$ are the Poisson’s ratio of the sample and indenter, respectively (for a diamond indenter, $v_i = 0.07$); $E_i$ and $E_c$ are the elastic modulus of the indenter and sample, respectively (for a diamond indenter, $E_i = 1141$ GPa). If the sample can be described as a semi-infinite, elastic half space, $E_c$ is actually the elastic modulus of the sample. If the tested sample is a thin film and the indented zone is affected by the underlying substrate, $E_c$ represents the “mean” response of the film-substrate composite.

Based on the observations that the resulting initial unloading curve is linear for flat punches (Doerner and Nix, 1986) and a power-law function for non-flat punches (Oliver and Pharr, 1992), and the assumption that in both cases the contact area remains constant during unloading, the contact depth $h_c$ can be calculated as:

$$h_c = h_{\text{max}} - \varepsilon \frac{F_{\text{max}}}{S}$$

(2-12)

where $\varepsilon$ is a constant that depends on indenter tip geometry (for Berkovich tip, $\varepsilon = 0.75$), and $F_{\text{max}}$ is the maximum load of an indentation.

The function between the projected contact area $A_c$ and contact depth $h_c$ can be preestablished by performing independent indentation tests on a standard material (e.g., fused silica) with known properties. The indenter area function $A = f(h_c)$ was proposed by Oliver and Pharr (1992) as follows:
\[ A_c = C_0 h_c^2 + \sum_{i=1}^{8} C_i \left( \frac{1}{2} \right)^i \] (2-13)

where \( C_0, C_1, \ldots, C_8 \) are constants for a specific indenter and are determined by curve-fitting procedure of a series of indentation tests with different indentation depth on a standard material.

Indentation hardness (substrate-effect is not considered) is determined as the mean contact pressure at maximum load:

\[ H = \frac{F_{\text{max}}}{A_c} \] (2-14)

It is evident that the indentation hardness here refers to the Meyer hardness.

### 2.5.2.2 Continuous Stiffness Measurement (CSM)

One of the most important improvements in nanoindentation is the continuous stiffness measurement (CSM) technique, in which dynamic contact stiffness is measured continuously during the loading portion of an indentation test by imposing a small dynamic oscillation on the force (or displacement) signal and measuring the amplitude and phase of the corresponding displacement (or force) signal by means of a frequency-specific amplifier (Oliver and Pharr, 1992; Li an Bharat, 2002; Oliver and Pharr; 2004). The most important advantage is that it provides continuous results (modulus, hardness, stiffness, etc.) as a function of indentation depth. In addition, the complicating effects of time-dependent plasticity and thermal drift could be reduced greatly if high frequencies are used.

### 2.5.2.3 Loading Modes

The conventional indentation test is a one point test in which the load is applied, held, and removed following a standard procedure with respect to the used method. The hardness is calculated as the load divided by the actual or projected area of the impression and is not significantly dependent upon the loading modes. Nanoindentation testing, however, provides continuous load-displacement data, and the mechanical properties (e.g., hardness and modulus) are derived from the curves instead of one point data. Therefore, the loading modes, which affect the curves’ features, are more critical in nanoindentation tests. There are two frequently used loading modes for nanoindentation testing: load control mode and displacement control mode. Fig. 2-12(a) shows the load control mode with a constant loading rate:

\[ \frac{dF}{dt} = \frac{F_{\text{max}}}{t_L} = \text{const.} \] (2-15)

where \( t_L \) is the loading time. In this mode, the load is applied from zero to the maximum load \( F_{\text{max}} \) at a constant loading rate determined by Eq. (2-15), and the \( F_{\text{max}} \) is held for a period of \( t_h \). This is followed by unloading to a certain percentage of the \( F_{\text{max}} \) with a defined loading rate, and then the load is kept constant to record the displacement for the correction of thermal drift.
Fig. 2-12 Nanoindentation testing with (a) constant loading rate mode and (b) constant indentation strain rate control mode. \( t_L \) and \( t_h \) denote loading time and holding time with the maximum load \( F_{\text{max}} \), respectively.

Fig.2-12(b) shows the displacement control mode with a constant indentation strain rate which is defined as (Lucas et al., 1997; VanLandingham, 2003):

\[
\dot{\varepsilon} = \frac{\dot{h}}{h} = \frac{1}{\beta} \left( \frac{dF/\text{dt}}{F} - \frac{dH/\text{dt}}{H} \right)
\]  

(2-16)

where \( \beta \) is a constant describing the shape of an idealized indentation tip. The determination of indentation strain rate origins from the assumption that the instantaneous change in contact area \( d(A_c)/\text{dt} \) divided by the instantaneous contact area \( A_c \) may be the most appropriate definition for the indentation strain rate and that the instantaneous displacement rate of the indenter (\( dh/\text{dt} \)) divided by the instantaneous displacement \( h \) is simply related to \( (dA_c/\text{dt})/A_c \) (Lucas and Oliver, 1999).

Eq. (2-16) suggests that an indentation conducted with a indenter with geometrical similarity, during which the loading rate is controlled so that the loading rate divided by the load \( (dF/\text{dt})/F \) is constant, can be controlled with a constant value of the indentation strain rate if a steady-state value of the hardness can be reached. This advantage is widely used together with CSM technique in determination of mechanical properties versus indentation depth.

2.5.2.4 Data Analysis on Thin Films

Nanoindentation is widely recognized as an effective testing method to determine mechanical properties of not only small scale materials, but also thin films on substrates provided that the maximum indentation depth is limited to a certain portion of the film thickness. A commonly used rule is that the penetration depth is less than 10% of the film thickness.
Otherwise the stiffness contribution of the substrate to the indenter-sample contact should be taken into consideration.

Much effort has been devoted to the methods of extracting film modulus and hardness from the measured composite response of tip-film-substrate system. For example, the exponential weighting factors are introduced to divide the contributions of the film and substrate to the composite modulus by Doerner and Nix (1986), King (1987), and Saha and Nix (2002); Gao et al. (1999) derived a closed-form solution for the reduced modulus using a moduli-perturbation method of the film-substrate composite with respect to a rigid cylindrical punch indenting a layered linear elastic half space; Mencik et al. (1997) and Fischer-Cripps (2004) introduced a relatively straightforward procedure to determine film modulus $E_f$ by simply extrapolating the best-fit curve of experimental data to zero $h/t$ in the plot of the measured composite modulus $E_c$ (Mencik et al., 1997) or reduced modulus $E_r$ (Fischer-Cripps, 2004) against the relative indentation depth $h/t$. Jung et al. (2004) extended the solution derived by Hu and Lawn (1998) for indentation with spheres on bilayer structures to the indentation with Berkovich and Vickers indenters to deconvolute the film properties in which the film-substrate composite modulus $E_c$ was expressed as a power-law function. Careful reviews on the above methods indicate that these methods were applied to films with thickness greater than 1 µm, applications on films with thickness less than 1 µm are doubtful because of the indentation size effects (ISE).

In particular, substrate influences will become more important when nanoindentation tests are conducted on clay mineral particles which are often present in thickness less than 1 micrometer scale. Therefore, an effective data analysis method is needed to be developed first in consideration of substrate effects.

### 2.6 Summary of Literature Review

Extensive reviews on the reported methods to determine the mechanical properties of clay minerals and clay-based nanostructured multilayers show that rarely consistent data are reported in the literature (Table 2-4), and it is necessary to find a direct experimental method to determine the relatively accurate mechanical properties of clay minerals and synthesized clay-based multilayers required by the fast developed clay-related material science.

#### Table 2-4 Elastic moduli of clay minerals and related phyllosilicates reported in the literature

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Serpentine-kaolinite</strong></td>
<td></td>
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</tr>
<tr>
<td>Kaolinite</td>
<td>3.4</td>
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<td>1.4</td>
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<td>Mavko et al. (1998)</td>
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<td>Kaolinite</td>
<td></td>
<td>6-12</td>
<td>4-6</td>
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<td>Kaolinite</td>
<td>$E_{11} = 92$</td>
<td>23</td>
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<tr>
<td></td>
<td>$E_{22} = 170$</td>
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<td></td>
<td>$E_{33} = 31$</td>
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<td>Kaolinite (Dickite)</td>
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<td>Dickite</td>
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<td>68.3</td>
<td></td>
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<td>Ulm and Abousleiman (2006)</td>
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<td>Kaolinite, poorly crystallized (KGa-2)</td>
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<td>Kaolinite, well crystallized (KGa-1b)</td>
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<td>19.7</td>
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<td>Wang et al. (2001)</td>
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Table 2-4 continued

2. Talc-pyrophyllite

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3. Smectite

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6. Chlorite

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Note: "*" denotes the value obtained on the assumption that the material is isotropic and linear elastic. \( E_{ij} = E_{ijkl} \) based on the assumption that material is linear elastic, and the stress \( \sigma_{ij} \) is linearly proportional to the strain \( \varepsilon_{ij} \) as expressed by \( \sigma_{ij} = E_{ijkl} \varepsilon_{kl} \), where \( E_{ijkl} \) is a fourth-order tensor.

Nanoindentation provides a promising experimental approach to determine some of the clay minerals and clay-based nanostructured multilayers. Since this is the first time that this method is
applied to a series of clay minerals and clay-based nanostructured multilayers, there is much experimental work and theoretical analysis involved which is impossible to be fully covered by this dissertation. This dissertation focuses on the following parts:

- Develop an empirical nanoindentation data analysis method of extracting mechanical properties of thin films considering substrate effects
- Establish a rigorous nanoindentation testing scheme for thin films (thickness less than a micrometer)
- Investigate the influences of nanoindentation control parameters under load control mode for the future study of viscous behavior of clay minerals
- Study indentation behavior of some clay minerals with large particle sizes
- Study indentation behavior of oriented aggregate films of clay minerals with small particle sizes
- Study indentation behavior of clay-based nanostructured multilayers
- Establish a simple model to simulate elastic modulus of clay minerals and clay-based nanostructured multilayers
- Predict the future work of this research

2.7 References


CHAPTER 3. A SIMPLE METHOD FOR EVALUATING ELASTIC MODULUS OF THIN FILMS BY NANOINDENTATION

3.1 Introduction

Elastic modulus is one of the most important mechanical parameters characterizing a material’s elastic response to loading. It represents the material’s stiffness that correlates with the atomic structure, and is essential for elastoplastic stress-strain analysis of a material subjected to various loading conditions. For macro-scale bulk materials, the elastic modulus is readily determinable using standardized mechanical testing methods such as uniaxial compression or tension tests. On the other hand, determination of elastic modulus of micro- and nano-scale thin films and coatings either on substrate or as free-standing beams and membranes requires some sophisticated micro- and nano-scale characterization techniques. In fact, it has been a longstanding research focus to develop simple mechanical or physical testing techniques to determine the elastic modulus of thin films or other low-dimensional structures and materials. To date, a wide variety of such techniques have been developed. Among these are, for example, rectangular membrane load-deflection (Tabata et al., 1989), microcantilever deflection (Baker and Nix, 1994; Luo et al., 2004), speckle interferometry (Read, 1998), atomic force acoustic microscopy (Prasad et al., 2002), magnetic force modulation microscopy (Pietrement and Troyon, 2000), buckling-based method (Stafford et al., 2004), instrumented indentation or nanoindentation (Oliver and Pharr, 1992; Mencik et al., 1997; Jung et al., 2004; Li and Bhushan, 2002; Li et al. 2005), acoustic surface waves (Schneider and Schultrich, 1998), magnetostrictive sensing (Liang and Prorok, 2007), and combined nanoindentation and acoustic microscopy methods (Bamber et al., 2001; Jennett et al., 2004). Of these techniques, nanoindentation that was initially developed as an effective tool to probe the mechanical properties of small scale bulk materials, has become the most widely used method to determine the elastic modulus of thin films, partly because hardness can be readily determined from the same tests.

Determination of hardness and elastic modulus by nanoindentation is based on the mechanics of elastic contact. During nanoindentation, an indenter with a known geometry and properties (e.g., Young’s modulus, Poisson’s ratio) is pressed into the flat surface of a material of unknown properties followed by unloading, while the load and indentation depth are recorded simultaneously. Compared with the traditional macro- and micro- hardness testing that requires direct measurement or imaging of the residual impressions after load removal in order to determine hardness, nanoindentation testing records continuously the load and depth for both the loading and unloading processes (Fig. 2-11), thus offering an advantage that both hardness and elastic modulus can be determined from the recorded data. An elastic parameter, named reduced modulus \( \bar{E} \) or effective modulus of the indenter-sample contact, can be obtained directly from the load-displacement curves through the following relationship:

\[
\bar{E} = \frac{\sqrt{\pi}}{2\beta \sqrt{A}} S
\]

(3-1)

where \( \beta \) is a dimensionless correction factor for the indenter tip shape and \( \beta = 1.05 \) is commonly used.

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recommended (Oliver and Pharr, 2004); $A_c$ is the projected contact area between the indenter and sample; $S$ is the contact stiffness defined as the slope of the initial unloading curve at the maximum indentation depth ($h_{\text{max}}$) (Fig. 2-11) and is usually determined by fitting the beginning portion of the unloading curve using a linear or power law relationship, depending on indenter geometry. Eq. (3-1) was initially developed by Sneddon (1965) for the penetration of a flat-surfaced, elastic half space by different probes of particular axisymmetric shapes (e.g., a flat-ended cylindrical punch, a paraboloid of revolution, and a cone) and experimentally verified thereafter suitable for conic and pyramidal indenters (Oliver and Pharr, 1992; Doerner and Nix, 1986). The function between the projected contact area $A_c$ and contact depth $h_c$ can be established by performing independent indentation tests on a standard material (e.g., fused silica) with known properties. Based on the observations that the resulting initial unloading curve is linear for flat punches (Doerner and Nix, 1986) and a power-law function for non-flat punches (Oliver and Pharr, 1992), and the assumption that in both cases the contact area remains constant during unloading, the contact depth $h_c$ can be calculated as:

$$h_c = h_{\text{max}} - \varepsilon \frac{F_{\text{max}}}{S}$$  \hfill (3-2)$$

where $\varepsilon$ is a constant that depends on indenter tip geometry (for Berkovich tip, $\varepsilon = 0.75$), and $F_{\text{max}}$ is the maximum load of an indentation.

The reduced modulus can be obtained directly by following the above procedures. $E_r$ actually reflects the elastic contact interaction between the indenter tip and sample and accounts for elastic deformation of both the indenter and the sample. To obtain the elastic modulus of the sample, the following relationship was used (Doerner and Nix, 1986):

$$\frac{1}{E_r} = \frac{1-\nu_c^2}{E_c} + \frac{1-\nu_i^2}{E_i}$$  \hfill (3-3)$$

where $\nu_c$ and $\nu_i$ are the Poisson’s ratio of the sample and indenter, respectively (for a diamond indenter, $\nu_i = 0.07$); $E_i$ and $E_c$ are the elastic modulus of the indenter and sample, respectively (for a diamond indenter, $E_i = 1141$ GPa). If the sample can be described as a semi-infinite, elastic half space, $E_c$ is actually the elastic modulus of the sample. However, as discussed later, if the tested sample is a thin film and the indented zone is affected by the underlying substrate, $E_c$ represents the “mean” response of the film-substrate composite.

The above method used to determine $h_c$ and $S$ is called Oliver and Pharr (1992) method, which has been widely used to determine the hardness and elastic modulus of bulk materials. It also can be used for thin films on substrate provided that the maximum indentation depth is limited to a certain portion of the film thickness. For example, Chen et al. (2008) performed finite element analysis using semi-empirical formulations and found that the deviation of the film modulus by Oliver and Pharr method is acceptable if the penetration depth is less than 10% of the film thickness. However, when this method is applied to thin films on substrate with indentation depth greater than 10% of the film thickness (this situation mostly occurs when the film thickness is less than one micrometer), estimation inaccuracy of modulus will increase or even wrong results may be obtained. One reason is that the stiffness contribution of the substrate to the indenter-sample contact can no longer be neglected (Doerner and Nix, 1986; King, 1987;
Tuck et al., 2001). Moreover, the influence of other factors such as surface roughness (Joslin and Oliver, 1990), crystal grain size (Lilleodden and Nix, 2006; Lian et al., 2007), strain gradient plasticity (Nix and Gao, 1998; Lou et al., 2003), interface bonding strength (Wu et al., 1990), and indenter tip rounding or geometry (Sakai and Nakano, 2004; Bei et al., 2005) on the mechanical properties increases considerably when the film thickness decreases to the submicrometer scale.

In this chapter, a simple empirical method for extracting elastic modulus of thin films on substrates from nanoindentation data is proposed after reviewing some existing methods. New nanoindentation experiments were conducted on very thin films prepared by various techniques, in order to validate this method. In addition, published data obtained from a wide range of thin films and substrates were also used. To obtain the best statistical estimation of the film and substrate properties, this new method requires indentation data covering a wide range of indentation depths. The advantages of this method over others are discussed and recommendations on how to obtain accurate indentation data to estimate thin film properties are also provided.

3.2 Methods of Analysis

3.2.1 Available Analysis Methods

Much effort has been devoted to study the response of film-substrate system under indentation, which is influenced by the properties of both the film and substrate. As an indenter is pressed into the film-substrate composite and the indentation depth increases gradually, the stress and strain fields beneath the indenter propagate through the film, film-substrate interface, and substrate. A transition exists from the film-dominated response to substrate-dominated response. In reality, the indenter tip is not ideally sharp and always has certain roundness, implying that the plastic zone beneath the indenter initiates from a point away from the apex of the indenter, and gradually expands and approaches the contact surface between the indenter and sample. At the same time, the elastic boundary extends outwards from the film and passes the film-substrate interface to the substrate. In contrast to conventional uniaxial compression and tension tests where the stress-strain field is clearly defined at a specific cross-section or point, indentation produces a complex three-dimensional stress-strain field with unclear boundary between the plastic and elastic zones. An analytical solution for indentation on such sandwiched tip-film-substrate system was not available at present.

During nanoindentation, the directly recorded load and displacement actually account for the elastic and plastic response of the whole affected zone under the indenter load. Subsequent unloading only involves the elastic response of the system, which consists of contributions from the indenter, film, and substrate, and the initial unloading contact stiffness can be determined. If the frame compliance has been taken into account, the reduced modulus can be determined by Eq. (3-1). This parameter reflects the overall elastic response of the system and can be defined as:

\[ E_r = f\left(E_i, E_f, E_s, v_i, v_f, v_s, h/t\right) \]  

(3-4)

where subscripts \(i, f,\) and \(s\) denote indenter, film and substrate, respectively. The selection of appropriate functions to apportion the reduced modulus among the indenter, film and substrate
results in different methods to extract the elastic modulus of the thin film. A general assumption made by these methods is that the film property will dominate when the film thickness $t$ approaches infinity, and the substrate property will dominate if $t$ approaches zero. Alternatively, when the relative indentation depth $h/t$ approaches zero, indentation response is dominated by the film; when $h/t$ approaches infinity, indentation response is dominated by the substrate. Several methods have been proposed based on the above general assumption, which are briefly described as follows.

A. Doerner and Nix (1986), King (1987), and Saha and Nix (2002)

The influence of substrate on the elastic modulus of thin films was first taken into account by Doerner and Nix (1986) through the relationship:

$$\frac{1-v_f^2}{E_f} \left(1-e^{-\alpha t/h_c}\right) + \frac{1-v_s^2}{E_s} e^{-\alpha t/h_c} + \frac{1-v_i^2}{E_i}$$

$$E_r = \left(1-v_f^2\right) \left(1-e^{-\alpha t/h_c}\right) + \frac{1-v_s^2}{E_s} e^{-\alpha t/h_c} + \frac{1-v_i^2}{E_i}$$

(3-5)

$$\frac{1-v_s^2}{E_s} = \frac{1-v_f^2}{E_f} \left(1-e^{-\alpha t/h_c}\right) + \frac{1-v_i^2}{E_i}$$

(3-5a)

where $t$ is the film thickness, and $\alpha$ is an empirical constant to be determined from a series of experimental results on films of known properties and thickness. Eq. (3-5a) is obtained by comparing Eqs. (3-5) and (3-3). The weighting factors $1-e^{-\alpha t/h_c}$ and $e^{-\alpha t/h_c}$ account for the separate contributions of the film and substrate to the measured compliance. King (1987) used finite element method to study the problem of flat-ended cylindrical, quadrilateral, and triangular punches indenting on a layered isotropic elastic half-space and modified the above equation by replacing $h_c$ with $a$, the square root of projected contact area $A_e$. Saha and Nix (2002) used the effective film thickness $(t-h)$, where $h$ is the total indentation depth, to replace $t$ in the King’s model to analyze the indentation results obtained by a Berkovich tip. A common feature of these three methods is that the exponential weighting factors are introduced to divide the contributions of the film and substrate to the composite modulus (Eq. (3-5a)), a parameter directly determined from the load-displacement curves.

B. Gao et al. (1992)

Gao et al. (1992) studied the elastic contact problem of a rigid cylindrical punch indenting a layered linear elastic half-space and derived a closed-form solution for the reduced modulus using a moduli-perturbation method of the film-substrate composite:

$$E_r = E_s + \left(E_f - E_s\right) I_0$$

(3-6)

where $I_0$ is a weighting function of $t/b$ (where $b$ is the contact radius) given by:

$$I_0 = \frac{2}{\pi} \tan^{-1} \frac{t}{b} + \frac{1}{2\pi(1-\nu)} \left[\left(1-2\nu\right)\frac{t}{b} \ln \frac{1+\left(t/b\right)^2}{\left(t/b\right)^2} - \frac{t/b}{1+\left(t/b\right)^2}\right]$$

(3-6a)
where \( v \) is the “effective” Poisson’s ratio, which is also a function of \( \nu_s, \nu_f, \) and \( t/b \). It is noteworthy that, by assuming a rigid indenter, the influence of indenter properties on \( E_r \) disappears and \( E_c = (1 - \nu_s^2)E_r \).

Mencik et al. (1997) modified the above equation by proposing an approximate correction for the thickness of film that becomes thinner beneath the indenter due to elastic and plastic deformations and demonstrated that the modified equation fitted better to the experimental data.

C. Mencik et al. (1997) and Fischer-Cripps (2002)

A relatively straightforward procedure was proposed by Mencik et al. (1997) and Fischer-Cripps (2002) in which a series of indentation tests with a conical or pyramidal indenter at different depths are conducted and the measured composite modulus \( E_c \) (Mencik et al., 1997) or reduced modulus \( E_r \) (Fischer-Cripps, 2002) is plotted against the relative indentation depth \( h/t \). The film modulus \( E_f \) is obtained by simply extrapolating the best-fit curve of experimental data to zero \( h/t \), as shown in Fig. 3-1. For example, Jen and Wu (2005) adopted this method to determine elastic modulus of Pd thin films with the following equation to fit the experimental data:

\[
E_r = E_s + (E_f - E_s)e^{-h_0/t^*}
\]

(3-7)

where \( t^* \) is a fitting parameter to be determined from the experimental data.

![Fig. 3-1 Determination of elastic modulus of thin films by curve fitting and extrapolation.](image)

D. Jung et al.(2004)

Jung et al. (2004) extended the solution derived by Hu and Lawn (1998) for indentation with spheres on bilayer structures to the indentation with Berkovich and Vickers indenters. The film-substrate composite modulus \( E_c \) was expressed as a power-law function to enable deconvolution of film properties:
$E_c = E_s \left( \frac{E_f}{E_s} \right)^{\frac{1}{1+A(h/t)^\gamma}}$  \hspace{1cm} (3-8)

where $A$ and $C$ are two adjustable coefficients to be determined by curve-fitting of the experimental data. It is noteworthy that the Poisson’s ratio is not explicitly included in this equation.

3.2.2 Proposed Analysis Method

Due to the complicated stress and strain fields generated beneath the indenter and the influence of the film-substrate interface on the stress-strain fields, analytical solutions for determining the Young’s modulus of the film is difficult to obtain. Energy-based analysis method has been an alternative to probe the mechanical response of the tip-film-substrate system. Korsunsky et al. (1998) and Tuck et al. (2001) proposed a model to estimate the film-substrate composite hardness after analyzing the work of indentation. The composite hardness $H_c$ is defined as:

$$H_c = H_s + \frac{H_f - H_s}{1 + [(h/t)/\beta_0]^X}$$  \hspace{1cm} (3-9)

where $H_s$ and $H_f$ are the intrinsic substrate and film hardness, respectively; and $\beta_0$ and $X$ are two fitted constants. Both $H_f$ and $H_s$ can be obtained by curve fitting the experimental data of $H_c$ plotted against logarithmic $(h/t)$. This model was used to fit macro-, micro-, and nano-indentation data over a wide range of film materials covering hard films on soft substrates and soft films on hard substrates (Tuck et al., 2001).

In this study, it was found that the plots of $Ec$ vs. $\log(h/t)$ have the similar shape as those of $H_c$ vs. $\log(h/t)$. Based on this observation, it is assumed that the type of function used to partition $H_c$ between $H_s$ and $H_f$ is applicable to the elastic modulus. Therefore the following model is proposed:

$$E_c = E_s + \frac{E_f - E_s}{1 + [h/(t\beta_1)]^\gamma}$$  \hspace{1cm} (3-10)

where $\beta_1$ and $Y$ are two constants to be determined through curve-fitting of the experimentally determined $E_c$. $Y$ describes how abruptly the composite response changes from the $E_f$ to $E_s$ on the $\log(h/t)$ scale (2001). $(t\beta_1)$ is a length scale parameter, and $\beta_1$ is a geometry correction factor but also depends on material properties. Actually, this equation has an analogous form of the transformed Eq. (3-8):

$$\log E_c = \log E_s + \frac{\log E_f - \log E_s}{1 + A(h/t)^\gamma}$$  \hspace{1cm} (3-11)
There are several observations to support the use of this new empirical method:

- Eq. (3-10) can be used to fit the sigmoidal shape of the experimentally obtained data $E_c$ plotted against $\log(h/t)$;

- Eqs. (3-10) and (3-6) have nearly the same format (notice that a rigid indenter was assumed for Eq. (3-6)), except that different functions were used to approximate the sigmoidal shape of the reduced or composite modulus. Eq. (3-10) can be treated as an empirical expansion form of Eq. (3-6) with $I_1 = 1 / (1 + ((h/t)/\beta_1)^Y)$. By definition, $I_1$ approaches 1 or 0 when $(h/t)$ approaches 0 or $\infty$. The original $I_0$ has the same asymptotical values (Bei et al., 2005).

- Eq. (3-10) is also a closed-form equation enabling the deconvolution of thin film properties, and thus has the same capability as Eq. (3-8). The influence of $\nu_s$ and $\nu_f$ on $E_c$ is probably implicitly included in the two fitted parameters $\beta_1$ and $Y$.

3.3 Experiments

3.3.1 Film Preparation

Both new and published nanoindentation data were used to validate the newly proposed method. The published data from Saha & Nix (2002) and Jung et al. (2004) were obtained from a wide range of thin films over different substrates, including tungsten, aluminum, silicon oxide, and nitride thin films on silicon, sapphire and glass substrates. New indentation test results were obtained from aluminum, zirconia, and clay-zirconia multilayered thin films prepared by different methods. Table 1 summarizes some basic information of these thin films used for the validation.

Two types of substrates were used to prepare new thin film samples. Undoped single crystal silicon (100) wafers (MTI Corporation, Richmond, CA) with dimensions of $10 \times 10 \times 0.5$ mm were used as substrates for the aluminum films. Epi-polished silicon wafers with thermally oxidized surface layers (SiO$_2$/Si) (Entegris Inc., CA, USA) were used as substrates for zirconia and clay-zirconia multilayered thin films, since a relatively non-reactive SiO$_2$ surface is preferred for the wet chemical synthesis of the two types of thin films.

Magnetron sputtering was used to prepare aluminum films on silicon substrates. Si(100) wafers were cleaned with acetone and dried in air. Explorer 14 (Denton Vacuum, Inc., Moorestown, NJ) equipped with an Angstrom Sciences’ 4-inch diameter magnetron cathode was used to deposit aluminum films under argon gas flow at a constant rate of 25 ml/min. The chamber pressure was set at 10 mTorr. The distance from the aluminum target to silicon substrate was 100 mm and the cathode power supply was kept constant at 200 W. To obtain thin films of different thicknesses, the sputtering time varied from 120 to 240 seconds. Subsequent determination of the film thickness gave an average film growth rate of 3.03 nm per second under these conditions.

Zirconia films were prepared by Hao Chen following a similar procedure described in Arcot and Luo (2008). The Si/SiO$_2$ wafers were ultrasonically cleaned in 0.1 M NaOH solution for 20
minutes, immersed into piranha solution (3 vol. of 95–98 wt.% H₂SO₄ : 1 vol. of 30 wt.% H₂O₂) for 20 minutes, rinsed with deionized water 4 times and dried in air. A NIMA® automatic dip coater (Nima Technology Ltd., Coventry, UK) was used to deposit thin films via a layer-by-layer (LbL) deposition process. The substrates were alternately dipped into 0.06 M Zr⁴⁺ aqueous cationic precursor solution prepared from zirconium (IV) acetate hydroxide (Sigma-Aldrich, Saint Louis, MO, USA) and into 1.0 M aqueous ammonium hydroxide (NH₄OH) anionic precursor solution at a constant advance and withdraw dipping speeds of 20 mm per minute, which finished a deposition cycle. The holding time was 45 s in both anionic and cationic precursor solutions. Repeating the alternate deposition of 30 cycles gave an as-deposited (ZrO₂)₃₀ multilayered film, which was then isothermally annealed at 600°C for 2 hours in a box furnace. The ramped heating and cooling rates were 5 °C per minute.

A similar LbL deposition technique was used to prepare clay-zirconia multilayered films (Chen et al., 2008). The Si/SiO₂ wafers were cleaned using the same method. A 0.03 wt.% suspension (pH = 7.24) of a sodium montmorillonite (Na-MMT) clay (Cloisite® Na+, Southern Clay Products Inc., Gonzales, TX) was prepared by stirring clays with magnet at 1000 rpm speed in deionized water for 20 minutes and then ultrasonicated for 20 minutes to achieve complete dispersion and exfoliation. The pre-cleaned substrates were dipped using the same dip coater into a 0.1 M zirconium cationic precursor solution (pH = 4.14) prepared from zirconium (IV) acetate hydroxide and into the exfoliated clay suspension alternately without interdipping rinsing. Both the dipping and withdrawing speeds were controlled at 20 mm per minute. The holding time was kept 45 seconds in air, Zr precursor solution, and clay suspension. The deposition cycle was repeated 30 times to prepare a (clay-ZrO₂)₃₀ multilayered film. After completing 30 deposition cycles, the substrate was then air-dried at room temperature to form the as-deposited (clay-ZrO₂)₃₀ films and further annealed isothermally to 600°C for 2 hours to form the annealed (clay-ZrO₂)₃₀ films. A constant heating and cooling rate of 5 °C per minute was used during annealing.

3.3.2 Determination of Film Thickness

Film thickness is an important parameter for all the methods discussed above, as it is explicitly included in the equations and also used to normalize indentation depth. A special setup was used to measure the thickness of aluminum films. Before sputtering, the edges of substrate surface were covered by a piece of 3M® 5413 Kapton Polyimide film tape with an open window inside which the sputtered aluminum film can be kept intact. After sputtering, the tape window was carefully removed from the substrate, creating a step from the bare substrate surface to the deposited aluminum film. The thickness of aluminum films was then determined using NanoVision® attached to an MTS Nano XP indenter (MTS Nano Instruments Inc., Oak Ridge, TN) by scanning the stepped zones covering both bare substrate and sputtered film. Totally 10 cross-sections of 100 m in length were scanned. The scanned profile was then corrected by considering any possible tilting of the substrate introduced by sample mounting (described below) (Fig. 3-2). Although the bare substrate may not be level, it can be easily identified due to its perfectly smooth surface. The average height of all 10 scanned profiles was taken as the nominal thickness of the film. The film growth rate under the above sputtering conditions was calibrated to be 3.03 nm per second based on the measured thickness.

The thickness of the annealed zirconia (ZrO₂)₃₀ films was calculated by a film growth rate of 5.2 nm per cycle (Arcot and Luo, 2008). Similarly, the thickness of as-deposited and annealed
clay-zirconia multilayers was determined based on the film growth rates described in Chen et al (Chen et al., 2008). The thickness of other films was simply taken from the original publications (Table 3-1).

![Graph showing film thickness with and without tilt correction.]

**Fig. 3-2** Determination of the aluminum film thickness using the NanoVision scanned surface profile.

**Table 3-1** Summary of thin film samples used to validate the proposed method.

<table>
<thead>
<tr>
<th>Film</th>
<th>Substrate</th>
<th>Preparation method</th>
<th>Thickness (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Si(100)</td>
<td>Magnetron sputtering</td>
<td>364/728</td>
<td>This paper</td>
</tr>
<tr>
<td>Zirconia</td>
<td>SiO₂/Si (100)</td>
<td>LbL + annealing</td>
<td>156</td>
<td>37</td>
</tr>
<tr>
<td>As-deposited clay-zirconia</td>
<td>SiO₂/Si (100)</td>
<td>LbL</td>
<td>200</td>
<td>38</td>
</tr>
<tr>
<td>Annealed clay-zirconia</td>
<td>SiO₂/Si (100)</td>
<td>LbL + annealing</td>
<td>90</td>
<td>38</td>
</tr>
<tr>
<td>Silicon oxide</td>
<td>Silicon</td>
<td>Thermal oxidation at 1100 °C</td>
<td>120/580/1100</td>
<td>10</td>
</tr>
<tr>
<td>Nitride</td>
<td>Silicon</td>
<td>Low-pressure chemical vapor deposition</td>
<td>50/390/780</td>
<td>10</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Sapphire</td>
<td>Sputtering</td>
<td>640</td>
<td>31</td>
</tr>
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<td></td>
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<td>Sputtering</td>
<td>640</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
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</tr>
</tbody>
</table>

**Table 3-1** Summary of thin film samples used to validate the proposed method.
3.3.3 Sample Mounting

The film together with substrate was mounted onto a cylindrical aluminum puck that fits in the sample tray of the indenter. The puck was heated to 130 °C on a hotplate and then a thin layer of Crystalbond 509 amber resin (Aremco Products Inc., NY, USA), which melts at 130 °C or higher temperatures, was applied to the top surface. This was followed by carefully placing the prepared film with substrate onto the puck surface. Particular attention was paid to prevent from trapping air at the substrate/glue interface and to assure that the sample surface was as level as possible. The aluminum puck was removed immediately from the hotplate to a leveling table in order to prevent from overheating the sample. After the puck cooled down, the sample was ready for installation and testing.

3.3.4 Nanoindentation Testing

Nanoindentation experiments were performed at room temperature on these samples using an MTS Nano XP indenter equipped with two indenter heads: a regular XP head and a dynamic contact module (DCM) head. It also has the continuous stiffness measurement (CSM) capability which can be used with either head. Both heads are installed with a diamond Berkovich indenter tip with a radius of <20 nm. A rigorous testing scheme is adopted to ensure high reliability and accuracy of the test data. This scheme consists of the following 5 sequential steps for both XP and DCM modes:

(i) Tip cleaning: 9 indentations with monotonic loading and unloading were performed on a piece of Scotch double-sided sticky tape that was attached onto the top surface of an aluminum puck to clean the tip;

(ii) Area function calibration: 25 indentations under CSM mode at a constant strain rate (dh/hdt) of 0.05 1/s to a maximum indentation depth of 2000 nm (for XP mode) or 500 nm (for DCM mode) were performed on a standard fused silica sample with known properties (e.g., Young’s modulus is 72 GPa, Poisson’s ratio is 0.18) to calibrate the area function of both the XP and DCM indenter tips. This area function was to be used for subsequent testing on thin films;

(iii) Thin film testing: To obtain reliable data over a wide range of indentation depths, a batch of indentations under both XP and DCM mode were conducted on the thin film sample at locations following a pre-designed pattern, which consists of 15 indenting locations for each mode with a 3 × 5 array uniformly spaced at 150 µm apart (Fig. 3-3). The indentation array of DCM mode has the same pattern as that of XP mode, but with 0.5 spacing shift, which aims to obtain comparable results from the same sample area under these two modes; Details of the XP and DCM indentations are given below.

(iv) Tip checking: 9 indentations under CSM mode using the same testing conditions were made on the standard fused silica again to calibrate the tip area function, which was compared with that obtained before indenting thin films. If the two functions differ significantly, the data obtained in Step 3 were discarded and a new measurement was made starting with Step 1. This step was used to check if the tip was contaminated during indenting films at Step 3. Tip contamination could occur at any indenting locations and thus results of Step 3 were not reliable if tip were contaminated;
(v) Data screening: the 15 load-displacement curves recorded under each mode in Step 3 were plotted together to check their agreement. If large discrepancy exists, then all the data are discarded and indentations were repeated by selecting a new area of the film; if one or two curves shift away from the majority curves, then these curves were discarded and the rest of the data were regarded as acceptable.

The XP and DCM indentations followed the ISO 14577 method (2002) under the load control mode, since no significant creep occurred within the peak load holding period during the preliminary indentation tests. For the 15 indentations under XP mode, the maximum load $F_{\text{max}}$ ranges from 500 mN to 0.39 mN, with each subsequent $F_{\text{max}}$ being 60\% of the previous $F_{\text{max}}$. The same loading scheme was also used for the 15 DCM indentations, except that $F_{\text{max}}$ ranges from 10 mN to 0.008 mN. Each indentation was made on a different location in the array shown in Fig. 3-4. For both modes, a trapezoidal loading profile was used for all indentations, consisting of five steps (Fig. 2-10): (1) increasing load linearly to a specified maximum value ($F_{\text{max}}$) at a constant loading rate with a loading time of 30 seconds; (2) holding $F_{\text{max}}$ constant for 10 seconds; (3) decreasing load linearly to 10\% of $F_{\text{max}}$ at the same rate as loading; (4) holding the load constant for 60 seconds to record the thermal drift of the instrument; and (5) decreasing linearly the load to zero at the same loading rate used in Steps (1) and (3). The typical load-displacement curves of XP and DCM modes were shown in Fig. 3-4.

In addition, the silicon substrate was characterized by the DCM and CSM modes to obtain the substrate properties. Fig. 3-5 shows the elastic modulus of silicon substrate determined by the Oliver and Pharr method. A constant value of 172.4 GPa was obtained over the entire indentation depth.

### 3.3.5 Data Analysis and Curve Fitting

The nanoindenter control program TestWorks Explorer® provided the film-substrate composite elastic modulus ($E_c$) based on the Oliver & Pharr method with an assumed Poisson’s ratio of 0.33 for aluminum and 0.22 for other thin films, which has no significant influence on
the indentation results (Oliver and Pharr, 1992; Saha and Nix, 31). Deconvolution of film properties from composite modulus using Eq. (3-10) was achieved by a statistical analysis program SAS® Version 9.1.3 where nonlinear procedures and Newton iterative method were adopted. Curve fitting was performed on the plots of $E_c$ vs. log($h/t$). The four unknown parameters $E_f$, $E_s$, $\beta_1$, and $Y$ were finely tuned until the best-fit curve was obtained.

Fig. 3-4 Typical load-displacement curves of as-deposited clay-zirconia multilayers recorded by (a) XP mode and (b) DCM mode indentations.
3.4 Analysis of Results

3.4.1 Soft Films on Hard Substrates

Fig. 3-6 shows the composite modulus of sputtered aluminum films with two thickness on silicon substrate obtained by both DCM and XP modes with a normalized indentation depth in a small region (i.e., $1 < h/t < 10$). Fitting the experimental data by Eq. (3-10) gave $E_f = 51.7$ GPa and $E_s = 168.8$ GPa. Compared with the elastic modulus (70 GPa) of bulk aluminum, the $E_f$ is smaller, which may be caused by the different microstructure of the aluminum formed during sputtering or by the film’s surface roughness (Fig. 3-2). The substrate modulus $E_s$ agrees reasonably well with the results shown in Fig. 3-5 ($E_s = 172.4$ GPa) and the value ($E_s = 169.5$ GPa) obtained by Jung et al (2004). It is noteworthy that the large surface roughness (e.g., the largest being ~250 nm for a 364 nm thick film, Fig. 3-2) prevents obtaining accurate data for $h/t < 1$.

Fig. 3-7 shows the data obtained on a 156 nm thick ZrO$_2$ film on Si/SiO$_2$ substrate, together with fitted curve and results, while Figs. 3-8 and 3-9 shows corresponding results for as-deposited and annealed clay-zirconia multilayers. All these three films were prepared on the same kind of substrates, but the estimated $E_s$ (159.8-184.8 GPa) differs from each other slightly, which is probably caused by the different chemicals used in cleaning and LbL deposition and subsequent high-temperature annealing. In addition, the presence of a thin, thermally oxidized SiO$_2$ layer may affect the $E_s$ of silicon substrate. Here, the fitted $E_s$ represents an effective modulus for the Si/SiO$_2$ substrate with a layer of ~100 nm thick native oxide. A good agreement for the $E_s$ values obtained from the three types of films on the same Si/SiO$_2$ substrate indicates the validity of this method. No published data are available to check these films’ elastic modulus, but the annealed clay-zirconia film ($E_f = 119.9$ GPa) shows much higher $E_f$ than the as-deposited
one ($E_f = 67.1$ GPa). The elastic modulus ($E_f = 118.6$ GPa) of the zirconia film is between that of bulk zirconia of 166 GPa and that of zirconia coating (prepared by plasma-sprayed method) of 59 GPa (Ruff, 1996). Table 3-2 summarizes all the fitted parameters for the investigated films.

![Figure 3-6 Composite modulus versus normalized indentation depth for aluminum films together with fitted results.](image)

![Figure 3-7 Composite modulus versus normalized indentation depth for zirconia film together with fitted results.](image)

Table 3-2 summarizes all the fitted parameters for the investigated films.
Some published experimental data were also used to further verify the applicability of the new method. The first data set from Jung et al. (2004) was obtained on amorphous silicon oxide films on silicon substrate. These films of 120 nm, 580 nm and 1100 nm in thickness were prepared by thermal oxidation in moist oxygen atmosphere at 1100 °C. Fig. 3-10 shows the composite modulus of these films plotted against normalized indentation depth. Fitting the data
using Eq. (3-10) yields $E_f = 67.4$ GPa and $E_s = 171.3$ GPa. The obtained $E_f$ and $E_s$ values agrees very well with those fitted by Eq. (3-8) ($E_f = 72.5$ GPa and $E_s = 169.5$ GPa) (Jung et al., 2004).

The second data set taken from Saha and Nix (2002) was obtained under CSM mode with a Berkovich tip on aluminum films of 500 nm in thickness on three substrates (sapphire, silicon, and glass). Fig. 3-11 shows the data and fitted curve, with fitted film and substrate properties shown in Table 3-2. The $E_f$ values for the three films are 60.4, 57.5, and 49.7 GPa, respectively, which are lower than that ($E_f = 73$ GPa) given by Saha and Nix (2002). As discussed in Saha and Nix (2002), aluminum is a soft material, and thus significant pile-up around the indenter tip may affect the determination of indentation depth by the Oliver and Pharr method. However, the $E_s$ values for the three substrates (439.4 GPa for sapphire, 192.9 GPa for silicon, and 96.1 GPa for aluminum) (also) agree reasonably well with those given in the original source (440 GPa for sapphire, 172 GPa for Si, and 73 GPa for glass). It should be pointed out that the original data were obtained by CSM with only one indenter head (it is unclear which head, XP or DCM, was used and the radius of the tip is unknown), which may not provide accurate indentation data over a wide range of depths (e.g., $h = 10$-1000 nm), especially at lower indentation depth. The increased data inaccuracy at lower indentation depth which will be discussed later may be the main reason for the deviation of aluminum moduli among the three samples.
Fig. 3-11 Composite modulus versus normalized indentation depth for 500 nm thick aluminum (Al) films on different substrates (Saha and Nix, 2004). The fitted results are shown in Table 3-2.

Table 3-2 Summary of fitted results for examined thin films.

<table>
<thead>
<tr>
<th>Film/substrate</th>
<th>Film thickness (nm)</th>
<th>$E_s$ (GPa)</th>
<th>$E_f$ (GPa)</th>
<th>$\beta_1$</th>
<th>$Y$</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/Si</td>
<td>364</td>
<td>168.8 ± 17.0</td>
<td>51.7 ± 13.8</td>
<td>3.7 ± 0.5</td>
<td>2.2 ± 0.8</td>
<td>Fig. 7</td>
</tr>
<tr>
<td></td>
<td>728</td>
<td></td>
<td></td>
<td>1.9 ± 0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zirconia/Si</td>
<td>156</td>
<td>173.6 ± 3.4</td>
<td>118.6 ± 9.1</td>
<td>0.6 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited clay-zirconia/Si</td>
<td>200</td>
<td>159.8 ± 7.9</td>
<td>67.1 ± 12.6</td>
<td>0.8 ± 0.2</td>
<td>1.7 ± 0.6</td>
<td>Fig. 9</td>
</tr>
<tr>
<td>Annealed clay-zirconia/Si</td>
<td>90</td>
<td>184.8 ± 4.2</td>
<td>119.9 ± 5.1</td>
<td>1.3 ± 0.2</td>
<td>2.0 ± 0.5</td>
<td>Fig. 10</td>
</tr>
<tr>
<td>Si-oxide/Si</td>
<td>120</td>
<td>171.3 ± 5.9</td>
<td>67.4 ± 8.8</td>
<td>0.6 ± 0.1</td>
<td>1.2 ± 0.2</td>
<td>Fig. 11</td>
</tr>
<tr>
<td></td>
<td>580</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitride/Si</td>
<td>50</td>
<td>165.7 ± 2.2</td>
<td>251.8 ± 6.9</td>
<td>0.4 ± 0.04</td>
<td>2.6 ± 0.4</td>
<td>Fig. 13</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>780</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W/Sapphire</td>
<td>640</td>
<td>459.4 ± 1.7</td>
<td>365.8 ± 16.8</td>
<td>0.1 ± 0.02</td>
<td>2.5 ± 0.6</td>
<td>Fig. 12</td>
</tr>
<tr>
<td>W/ Silicon</td>
<td>640</td>
<td>175.9 ± 8.5</td>
<td>309.0 ± 4.0</td>
<td>0.4 ± 0.04</td>
<td>1.6 ± 0.2</td>
<td>Fig. 12</td>
</tr>
<tr>
<td>W/Glass</td>
<td>780</td>
<td>72.8 ± 3.6</td>
<td>280.5 ± 5.4</td>
<td>0.1 ± 0.01</td>
<td>1.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Al/Sapphire</td>
<td>500</td>
<td>439.4 ± 12.6</td>
<td>60.4 ± 7.8</td>
<td>0.6 ± 0.03</td>
<td>1.7 ± 0.1</td>
<td>Fig. 14</td>
</tr>
<tr>
<td>Al/Silicon</td>
<td>500</td>
<td>192.9 ± 2.9</td>
<td>57.5 ± 4.0</td>
<td>0.4 ± 0.02</td>
<td>1.7 ± 0.2</td>
<td>Fig. 14</td>
</tr>
<tr>
<td>Al/Glass</td>
<td>500</td>
<td>96.1 ± 2.1</td>
<td>49.7 ± 7.0</td>
<td>0.2 ± 0.05</td>
<td>1.5 ± 0.4</td>
<td></td>
</tr>
</tbody>
</table>

Note: The value after “±” is the approximate standard error of the corresponding parameter.

3.4.2 Hard Films on Soft Substrates

Again, two data sets taken from the literature were used to validate the applicability of the new method to hard films on soft substrates. The first data set was the results of amorphous nitride films of 50 nm, 390 nm and 780 nm in thickness on silicon substrates (Jung et al., 2004).
The films were prepared by low-pressure chemical vapor deposition (LPCVD) in SiH$_2$Cl$_2$/NH$_3$ atmosphere at 830 °C. Fig. 3-12 shows the original data together with the fitted results according to Eq. (3-10). Both the $E_s$ ($E_s = 165.7 \text{ GPa}$) and $E_f$ ($E_f = 251.8 \text{ GPa}$) values are consistent with those ($E_s = 169.5 \text{ GPa}$ and $E_f = 266 \text{ GPa}$) obtained by Jung et al. (2004).

![Fig. 3-12 Composite modulus versus normalized indentation depth for nitride films on silicon substrate (Jung et al., 2004) together with fitted results.](image)

The second data set was the CSM indentation results on 640 nm thick tungsten films on three different substrates (sapphire, silicon, and glass) taken from Saha & Nix (2002). Fig. 3-13 shows the original data together with the fitted curves, and the fitted results are shown in Table 3-2. Due to the variations in the original data, the three $E_f$ values are not very consistent. The reason for such deviation may come from the inaccurate data at lower indentation depth as explained above. However, the three $E_s$ values (459.4 GPa for sapphire, 175.9 for silicon, and 72.8 for glass) are consistent with those (440 GPa for sapphire, 170 GPa for Si, and 73 GPa for glass) given in the original source. It should also be pointed out that Eq. (3-10) fitted the original experimental data very well.

### 3.5 Discussion

#### 3.5.1 Advantages of the New Method

This empirical method uses a simple (sigmoidal-delete) function to approximate the experimental data of the composite modulus plotted against the normalized indentation depth at logarithmic scale. Compared with the linear scale, the logarithmic scale emphasizes the importance of the low-depth indentation results (e.g., $h/t < 0.1$), which is critical for the determination of thin film’s properties (Fig. 3-14). It is also convenient to use normalized total indentation depth ($h/t$) instead of contact depth or the radius of projected contact area, since $h$ is a directly recorded experimental data, while the determination of the latter two parameters is
Fig. 3-13 Composite modulus versus normalized indentation depth for tungsten (W) films on different substrates taken from Saha and Nix (2002). The fitted results are shown in Table 3-2.

sometimes not straightforward or involves some assumptions. By using indentation depth, it is also easy to design testing control parameters.

The method can extract both the film and substrate’s elastic modulus from the composite response. If the latter is known (which is usually true for most cases), then the extracted $E_s$ can be used to check the reliability and accuracy of the experimental data, and the indentations with larger depth can be simply reduced or even eliminated. Since the known $E_s$ can be used directly in the curve fitting, there is no need to obtain the composite modulus on larger indentation depth (e.g., $h/t > 2.5$). As an example, Fig. 3-15 compares the fitted results of the clay-zirconia multilayers for two cases: (1) the substrate properties are assumed unknown and a great number of indentations were made for large depths by the XP mode, and (2) the substrate’s $E_s$ is assumed to be 172.4 GPa, and hence no indentations were made under the XP mode. No significant difference in $E_f$ values is observed in Fig. 3-15. Furthermore, to test the sensitivity of the depth (i.e., $h/t$ value) where the $E_s$ value should be added to the plot of $E_c$ vs. log($h/t$), a wide range of $h/t$ values ranging from 5 to 100 were examined, and the results are summarized in Table 3-3, which suggests that there is no influence on the estimated $E_f$ if the known $E_s$ value is placed at a depth of $h/t > 10-15$. This advantage is especially important if the tested film is very hard and stiff, since the total indentation depth is controlled by the maximum load capacity of the indenter head and hence results of indentations made to large depths may not be obtainable. However, if the substrate’s properties are known, there is no need to make indentations to large depths.
Fig. 3-14 The difference in the curve shape with experimental data plotted against linear or logarithmic scale. The data was originally from Saha and Nix (2002) for a 500 nm thick aluminum film on sapphire substrate.

Fig. 3-15 Comparison of the fitted results of clay-zirconia multilayers for two cases: (1) experiment data with large depth indentations obtained by XP mode and $E_s$ is assumed unknown and (2) experimental data without large depth indentations but with an assumed $E_s = 172.4$ GPa.
Table 3-3 Influence of the normalized indentation depth where a known $E_s$ is added to the DCM data on the film and substrate property determination.

<table>
<thead>
<tr>
<th>Extra data in addition to DCM results</th>
<th>$E_s$ (Gpa)</th>
<th>$E_f$ (Gpa)</th>
<th>$\beta_1$</th>
<th>$Y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>XP results</td>
<td>184.8</td>
<td>119.9</td>
<td>1.3098</td>
<td>2.0282</td>
</tr>
<tr>
<td>5</td>
<td>173.7</td>
<td>118.6</td>
<td>1.1176</td>
<td>1.8992</td>
</tr>
<tr>
<td>10</td>
<td>171.3</td>
<td>119.2</td>
<td>1.0779</td>
<td>2.0742</td>
</tr>
<tr>
<td>$h/t$ values where known $E_s$ is added</td>
<td>171.0</td>
<td>119.3</td>
<td>1.0740</td>
<td>2.1043</td>
</tr>
<tr>
<td>15</td>
<td>170.9</td>
<td>119.4</td>
<td>1.0729</td>
<td>2.1146</td>
</tr>
<tr>
<td>20</td>
<td>170.8</td>
<td>119.4</td>
<td>1.0719</td>
<td>2.1256</td>
</tr>
<tr>
<td>50</td>
<td>170.8</td>
<td>119.4</td>
<td>1.0718</td>
<td>2.1272</td>
</tr>
</tbody>
</table>

3.5.2 Comparison among Analysis Methods

The moduli of thin films and substrates obtained from method A (Doerner and Nix (1986; King, 1987; Saha and Nix, 2002), Method C (Mencik et al., 1997; Fischer-Cripps, 2002), Method D (Jung et al., 2004), and the proposed method were summarized in Table 3-4. An assumption of identical Poisson’s ratio $\nu_c = \nu_f = \nu_s$ in Eq. (3-5a) was made for all the samples. Indentation contact depth $h_c$ in Eq. (3-5) and Eq. (3-7) for films of silicon oxide (Jung et al., 2004), nitride (Jung et al., 2004), tungsten (Saha and Nix, 2002), and aluminum (Saha and Nix, 2002) was substituted by total indentation depth $h$ due to unavailability of corresponding data. The linear relationship between $h_c$ and $h$ shown in Eq. (3-2) indicates that this substitute will not introduce large errors to the fitted parameters. It is noteworthy that the proposed method and method D give very close value of $E_f$ and $E_s$ for each sample. Method A gives higher $E_s$ and lower $E_f$ for soft films on hard substrates except Si-oxide/Si compared with the proposed method and method D, while no conclusion can be made for hard films on soft substrates. In addition, unreasonable $E_f$ and $E_s$ were obtained for film systems with high degree of modulus mismatch between film and substrate. For example, $E_f = 12.5$ GPa and $E_s = 254.6$ GPa were obtained for Al/Si and $E_f = 33.8$ GPa and $E_s = 572.4$ GPa for Al/Sapphire. Method C gives a reasonable $E_s$ for each sample as the proposed method and method D, whereas it has the same disadvantage with method A with respect to high modulus mismatch film system. Therefore, the proposed method can be used to fit a large range of experimental data from soft films on hard substrates to hard films on soft substrate and gives reasonable moduli of films and substrates.

3.5.3 Limitations

This simple method has some limitations, just like other methods. First, the Poisson’s ratios of the film and substrate are not explicitly expressed in the proposed model (i.e., Eq. (3-10)). Therefore, $\nu_s$ or $\nu_f$ cannot be determined through the curve fitting, although it might be possible to incorporate these two parameters into the model. Mencik et al. (1997) tried to determine $\nu_s$ or $\nu_f$ by including them in a different model, but the attempts were unfortunately unsuccessful. Second, just like other methods, this simple method requires obtaining indentation results over a wide range of indentation depths (e.g., typically the range of $h/t$ should be ~0.1-10), especially when the substrate properties are unknown. This results in two disadvantages: (1) it is time-consuming to conduct the indentation experiments, and (2) it requires that the indentation facility has the capability to obtain accurate results over a wide range of indentation loads or depths, such as the DCM mode for small loads while XP for large loads. Finally, this method still relies
on the Oliver and Pharr (1992) method to derive the composite modulus. As pointed out by Saha and Nix (2002), the Oliver and Pharr method does not consider the pile-up phenomenon for soft films (e.g., aluminum), which affects the determination of contact depth. Therefore, the limitations of the Oliver and Pharr method are also applicable to this simple method.

Table 3-4 Comparison of fitted moduli using different methods

<table>
<thead>
<tr>
<th>Film/substrate</th>
<th>Film thickness (nm)</th>
<th>Proposed method</th>
<th>Method A</th>
<th>Method C</th>
<th>Method D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E_f$</td>
<td>$E_s$</td>
<td>$E_f$</td>
<td>$E_s$</td>
</tr>
<tr>
<td>Al/Si</td>
<td>364</td>
<td>51.7</td>
<td>168.8</td>
<td>12.5</td>
<td>254.6</td>
</tr>
<tr>
<td></td>
<td>728</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zirconia/Si</td>
<td>156</td>
<td>118.6</td>
<td>173.6</td>
<td>115.0</td>
<td>178.5</td>
</tr>
<tr>
<td>As-deposited clay-zirconia/Si</td>
<td>200</td>
<td>67.1</td>
<td>159.8</td>
<td>62.7</td>
<td>171.8</td>
</tr>
<tr>
<td>Annealed clay-zirconia/Si</td>
<td>90</td>
<td>119.9</td>
<td>184.8</td>
<td>117.0</td>
<td>187.7</td>
</tr>
<tr>
<td>Si-oxide/Si</td>
<td>120</td>
<td>67.4</td>
<td>171.3</td>
<td>74.5</td>
<td>174.2</td>
</tr>
<tr>
<td></td>
<td>580</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitride/Si</td>
<td>390</td>
<td>251.8</td>
<td>165.7</td>
<td>267.8</td>
<td>158.4</td>
</tr>
<tr>
<td></td>
<td>780</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W/Sapphire</td>
<td></td>
<td>365.8</td>
<td>459.4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>W/Silicon</td>
<td>640</td>
<td>309.0</td>
<td>175.9</td>
<td>304.4</td>
<td>171.7</td>
</tr>
<tr>
<td>W/Glass</td>
<td></td>
<td>280.5</td>
<td>72.8</td>
<td>240.8</td>
<td>88.5</td>
</tr>
<tr>
<td>Al/Sapphire</td>
<td></td>
<td>60.4</td>
<td>439.4</td>
<td>33.8</td>
<td>572.4</td>
</tr>
<tr>
<td>Al/Silicon</td>
<td>500</td>
<td>57.5</td>
<td>192.9</td>
<td>50.9</td>
<td>218.3</td>
</tr>
<tr>
<td>Al/Glass</td>
<td></td>
<td>49.7</td>
<td>96.1</td>
<td>47.6</td>
<td>99.4</td>
</tr>
</tbody>
</table>

3.5.4 Sources of Errors

This section discusses all possible sources of errors that affect the accuracy of the determined elastic modulus of thin films. Film thickness is an important parameter for this method as well as for others, as it is explicitly included in the fitting equation and also used to normalize indentation depth. Therefore, film thickness should be determined as accurately as possible. Moreover, as pointed out by Mencik et al. (1997), corrections for film thickness reduction (especially for soft films) induced by both the elastic and plastic compression under the maximum load (as the contact stiffness is always measured at the beginning of unloading) should be made to obtain better results. On the other hand, determination of film thickness is always complicated by the surface roughness that also affects the determination of the sample-tip contact.

Significant errors can also be introduced to the results due to interface debonding, layer delamination (for layered films), and cracking. Usually, giant cracks or interface debonding will cause significant pop-ins or discontinuities in the loading portion of the measured load-displacement curve. The pop-ins are not routinely considered in the calculation of contact
stiffness, and ignorance of such phenomenon usually leads to higher indentation contact depth, and consequently underestimates the contact stiffness. Gao et al. (1992) found the interface bonding condition was a significant factor which affected the reduced modulus.

Finally the pile-up phenomenon that most often occurs in soft films (e.g., aluminum) on hard substrate is not considered by the Oliver and Pharr method to determine the contact depth \( h_c \). As such, the measured reduced modulus was overestimated, giving rise to the underestimate of the film modulus. In contrast, this method can be directly applied to indentation with sink-in cases which are typically observed in most hard metals or other hard films.

3.5.5 Design of Indentation Testing

As discussed above, the proposed method requires obtaining accurate results over a wide spectrum of indentation depth ranging from film-dominated response at small depths to substrate-dominated response at large depth. An indenter with both the DCM and XP modes is most appropriate to meet the requirement. If only DCM mode is used, the data at large depths may not be reliable or simply achievable (limited by the maximum load capacity of the DCM head); if only XP mode is used, the data at small depths are not accurate, especially for very thin films (e.g., thickness < 100 nm). However, as discussed above, if the substrate’s properties are known, indentations at large depths may be eliminated or reduced to simplify the testing process. It is noted that indentation testing using both modes involves a complicated procedure, such as exchanging indenter heads, calibrating two tips, and selecting appropriate loading or depth control parameters.

Although CSM mode has been widely used in nanoindentation due to the advantage of providing continuous results over depth, it is not recommended to be used for thin films with thickness of ~100 nm or less. As the indentation depth decreases, the effects of oscillation displacement on the total indentation displacement increases, and surface roughness and surface contamination will generate a considerable scatter in the indentation data, and indentation size effects will also occur at smaller indentation depths. This indicates that more uncertainties are introduced at smaller indentation depths and the data corresponding to this region are less reliable. For a very thin film, the indentation data at depths as small as possible is required on one hand, and the uncertainties involved in small depth indentation (as stated above) increase significantly on the other hand. A compromise solution is to use the DCM mode with a high load-displacement resolution to increase the accuracy at very small loads and to use one cycle of loading-unloading at each indentation location, instead of using only the loading portion taken by the CSM mode.

3.6 Conclusions

A simple empirical method that extracts the elastic moduli of both the thin films and underlying substrates is proposed and validated by newly designed nanoindentation experiments and published data. Soft and hard thin films of different compositions prepared by various methods were examined, including aluminum, zirconia, clay-zirconia multilayers, silicon oxide, tungsten, and nitride films. Deconvolution of film’s elastic modulus from the measured film-substrate composite response is successfully achieved by statistical estimation through curve-fitting the semi-logarithmic plot of the film-substrate composite elastic modulus against the
indentation depth normalized by film thickness. The estimated elastic moduli of the examined thin films and substrates agree reasonably well with their corresponding standard values or values obtained by other methods, which validates this proposed method. The advantages of this method over others include that, for example, the estimated substrate properties can be used to verify the data accuracy and reliability, and indentations made to large depths can be eliminated or reduced if the substrate’s properties are known. This method relies on the Oliver and Pharr method to derive the composite modulus, so its limitations also apply to this method, such as the influence of pile-up on the contact depth, and no consideration of pop-ins or cracking. To obtain reliable results, the indentation data used for this simple method should be obtained using the high resolution DCM mode and regular XP mode for shallow and deep indentations, respectively.

3.7 References


CHAPTER 4. NANOINDENTATION ON MUSCOVITE
AND RECTORITE†

4.1 Introduction

The elastic constants (e.g., Young’s modulus, shear modulus, and bulk modulus) are among the basic physical or mechanical properties of a material, which control the essential very small strain behavior – a material’s response to force at the elastic regime. On the other hand, hardness ($H$), typically defined as the resistance of a material to permanent penetration by another harder material, is closely related to the plastic yield stress of the material and also provides information on the compressive or tensile strength (McClintock and Argon 1966; Fisher-Cripps 2004). Layered hydrous aluminosilicates including all types of clay minerals and micas are the major constituents of natural geomaterials (including soils and rocks) and occur abundantly in the geosphere. Understanding their elastic modulus ($E$) and hardness is of significance for several scientific and technological issues discussed as follows.

(1) Fundamental mineral physics: Hydrous layered aluminosilicates have two basic layer types: 0.7 nm thick 1:1 layer (i.e., consisting of 1 tetrahedral sheet and 1 octahedral sheet per layer) and ~1.0 nm thick 2:1 layer (i.e., consisting of 2 tetrahedral sheets and 1 octahedral sheet sandwiched between the tetrahedral sheets). The stacking of either 1:1 or 2:1 layers or a combination of both accounts for major structural difference among these minerals. The layers are held together by different interlayer complexes (e.g., hydrogen bond, non-hydrated cation, or hydrated cation), resulting in different interlayer bonding strength. The interlayer cations also compensate the net negative charges in the layers caused by isomorphous substitution. It is of a scientific interest to explore how the thickness and arrangement of nanoscale layers and the interlayer complexes affect the fundamental physical and mechanical properties (e.g., $E$ and $H$) of these layered minerals. In addition, these aluminosilicates can be treated as nanostructured layered materials or multilayers, thus understanding their nanomechanical behavior will provide insights on the mechanical properties of synthetic nanostructured layered materials.

(2) Geophysics: Geophysical subsurface exploration and reservoir characterization using seismic waves require the knowledge of the elastic constants of the reservoir bulk material, which are controlled by the elastic properties of individual solid components and pore-filling fluids (e.g., Smith et al., 2003). Hydrous layered aluminosilicates are ubiquitous in the geosphere, and their presence in soils and rocks affects the overall elastic properties of the bulk medium and hence seismic wave propagation in the geosphere (e.g., Klimentos, 1991; Marion et al., 1992). Therefore, imaging and probing earth properties remotely at increased resolution and accuracy using seismic waves require the elastic properties of the layered hydrous aluminosilicates that are usually present as very fine (i.e., <2 µm) particles.

(3) Multiscale mechanics of geomaterials: Geomaterials are particulate media whose properties are controlled by the individual particles and interparticle interactions, especially under high stress (Lambe and Whitman 1979). For example, the compressibility of a granular soil is

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mainly controlled by the particle crushing strength (e.g., Pestena and Whittle 1995). Understanding the macroscopic behavior of geomaterials requires an insight into the micro/nano scale behavior of individual particles at the particle level. Therefore, advances in understanding the $E$ and $H$ of individual soil particles can contribute significantly to micro/nano mechanics and multiscale modeling of geomaterials.

(4) Nanocomposites: Recently clays or other layered hydrous aluminosilicates have been used to make clay-polymer nanocomposites and clay-based nanostructured multilayers (e.g., Tang et al. 2003; Podsiadlo et al. 2007). Modeling and understanding the behavior of manufactured clay-based nanocomposites require the understanding of the fundamental elastic properties and hardness of the filling clay minerals (e.g., Sheng et al. 2004).

Nanoindentation, also named depth-sensing indentation or instrumented indentation, is based on the theories of contact mechanics. The test results provide information on elastic modulus, hardness, strain-hardening, cracking, phase transformations, creep, and energy absorption (Fischer-Cripps 2004). This technique is widely used in the characterization of mechanical properties of thin films, coatings, and other nanomaterials. Due to the micro/nano scale load and the resulting small residual impression left on the surface of the tested material, it can be regarded as a non-destructive testing technique. To date, this technique has been used to study geomaterials, but only in limited cases. For instance, nanoindentation has been used to study the mechanical behavior of shales (e.g., Ulman and Abousleiman 2006). No previous research has studied the mechanical behavior of clay minerals by nanoindentation investigation of individual particles.

This chapter presents initial results of a research program that will probe the mechanical properties of individual particles of hydrous aluminosilicate minerals, including clay minerals. Due to the small particle size of clay minerals, it is impractical to use the acoustic method to obtain the elastic properties of individual particles. Similarly, measuring the hardness of clay minerals requires recently developed nanoindentation testing. As the first step, initial research focuses on the well-ordered muscovite and rectorite minerals with cleavage fragments large enough to be handled easily and observable under an optical microscope. This paper only discusses $E$ and $H$ in the direction normal to the basal plane. Properties of layered silicates have been shown to be more variable in this direction rather than directions within the basal plane because of their basic crystal structure.

4.2 Materials and Methods

4.2.1 Sample Preparation

Well-ordered muscovite and rectorite samples were studied. Grade V-4 muscovite samples of $15 \times 15 \times 0.15$ (thickness) mm were supplied by SPI Supplies (Division of Structure Probe, Inc., West Chester, PA). The rectorite was purchased as vermiculite from Phalaborwa, Transvaal, South Africa (Wards Natural Science Establishment, Inc., Rochester, New York). The rectorite samples have a wide range of cleaved flake sizes. The maximum basal planar dimension is about $8 \times 8$ mm, while the thickness ranges from 0.1 to 1 mm.
Circular optical glass slides (25 mm diameter) were used as substrates. The glass slide was heated to 130 °C on a hot plate and then a thin layer of Crystalbond 509 amber resin (Aremco Products, Inc., New York, NY), which melts at 130 °C or higher temperatures, was applied to the slide surface. This was followed by carefully placing sample flakes onto the slide surface. Particular attention was paid to prevent from trapping air at the sample/glue interface and to assure that the sample surface was as level as possible. The glass slide was removed immediately from the hotplate to a leveling table in order to prevent overheating the sample. After the glass slide cooled down, this process was repeated to glue the glass slide with the sample onto an aluminum puck, which fits in the sample tray of the nanoindenter. A very thin layer was cleaved from the surface of muscovite and rectorite with a razor blade to expose a fresh and intact surface to accept indentation.

4.2.2 X-Ray Diffraction (XRD)

XRD patterns of muscovite and air-dried rectorite (an ordered, 50/50 illite (muscovite)/smectite mixed-layer mineral) were collected in a Siemens D-5000 diffractometer using Cu-Kα radiation generated at 40 kV and 30 mA and a scan range of 2-34° 2θ. All scans employed sample spinning and a 0.996° divergence slit, 0.501° scatter slit, 0.1 mm receiving slit, a speed of 1° 2θ/min, and a step size of 0.02° 2θ.

4.2.3 Nanoindentation Testing

Nanoindentation experiments were performed on these two minerals using an MTS Nano XP indenter (MTS Nano Instruments, Inc., Oak Ridge, TN) under load control mode at room temperature. A diamond Berkovich indenter was used, with a tip radius of <20 nm. A trapezoidal loading profile was used for all tests, consists of five steps (Fig. 2-11): (1) increasing load linearly to a specified maximum value ($F_{\text{max}}$) at a constant loading rate; (2) holding $F_{\text{max}}$ constant for a given hold time, $t_h$; (3) decreasing load linearly to 10% of $F_{\text{max}}$ at the same rate as loading; (4) holding the load constant for 60 seconds to record the thermal drift of the instrument; and (5) decreasing linearly the load to zero at the same loading rate used in Steps (1) and (3).

To investigate the influence of each test control parameter on the $E$ and $H$ measurements, three types of tests were conducted: (A) varying $F_{\text{max}}$ from 3.4 mN to 500 mN at a constant loading rate; (B) varying hold time from 0 to 160 seconds for a given loading rate and $F_{\text{max}}$; and (C) varying loading rate from 3.33 μN/s to 33.33 μN/s for a given $F_{\text{max}}$. Each indentation test was performed at different locations on the sample surface separated by a spacing of at least 150 μm. The residual impression of the indents was examined and imaged using an Olympus BX50 optical microscope at a maximum magnification of 800X.

Determination of $E$ and $H$ follows the standard method specified in ISO 14577 (ISO 2002). The elastic modulus $E$ is considered as synonymous with indentation modulus $E_{\text{IT}}$ in this paper, in spite of the anisotropic properties of these layered minerals. The elastic modulus $E$ in the indentation loading direction normal to the basal plane is determined by

$$E = E_{\text{IT}} = \frac{1 - v_s^2}{\frac{1}{E_r} - \frac{1 - v_i^2}{E_i}}$$  

(4-1)
where $\nu_s$ is the Poisson’s ratio of the test sample and $\nu_s = 0.25$ is chosen for both muscovite and rectorite (Mavko et al. (1998) suggested that $\nu = 0.23$-0.28 for muscovite); $\nu_i$ is the Poisson’s ratio of the indenter (for diamond, $\nu = 0.07$); $E_i$ is the elastic modulus of the indenter (for diamond, $E = 1140$ GPa); $E_r$ is the reduced elastic modulus of the indentation contact,

$$E_r = \frac{\sqrt{\pi}}{2 \sqrt{A_p}} S$$

(4-2)

where $A_p$ is the projected (cross-sectional) contact area at $F_{\text{max}}$ and $h_{\text{max}}$. It is a polynomial function of the contact depth $h_c$ at $h_{\text{max}}$, (i.e., $A_p = f(h_c)$), with coefficients determined by indentation tests on a material of known elastic modulus at varying indentation depths. In this study, bulk fused silica with $E = 73$ GPa was used. $S$ is the contact stiffness defined as the slope of the initial unloading curve at the maximum indentation depth $h_{\text{max}}$ (Fig. 2-11(b)),

$$S = \frac{dF}{dh}_{h= h_{\text{max}}}$$

(4-3)

$S$ is estimated by assuming a power law relationship $F = C (h-h_0)m$ of the unloading curve, a method proposed by Oliver and Pharr (1992), where $C$ is a constant and $m$ is an exponent, which depends on indenter geometry; $h_0$ is the residual or plastic indentation depth (Fig. 2-11). $C$, $m$ and $h_0$ are determined using curve fitting the initial 80% unloading curve with the power law relationship.

The contact depth $h_c$ is estimated using

$$h_c = h_{\text{max}} - \epsilon \frac{F_{\text{max}}}{S}$$

(4-4)

where $\epsilon$ is a constant that depends on the indenter geometry (for Berkovich indenter, $\epsilon = 0.75$).

Hardness $H$ is treated the same as the indentation hardness $H_{\text{IT}}$, and is determined as

$$H = \frac{F_{\text{max}}}{A_p}$$

(4-5)

where $A_p$ is again the projected area of contact between the indenter and the sample and is determined using the same method described above.

4.3 Analysis of Results

4.3.1 XRD Patterns

Fig. 4-1 shows the XRD patterns of muscovite and air-dried rectorite. The first strong peak (001) of muscovite proves that its interlayer spacing $d(001)$ is 1.022 nm and its sharpness
indicates that the mineral is composed of well-ordered, large crystallites. Air-dried rectorite has a layer spacing of \(d(001) = 2.580 \text{ nm}\) with an almost rational series of 00l peaks represented by the other peaks in the diffractogram. The variation in peak with \(\theta\) is an indication of ordered interlayering of illite (fixed at 1.0 nm) and air-dried smectite layers (expandable to about 1.5 nm in the presence of atmospheric moisture) as reported in Moore and Reynolds (1989). Some rectorite samples contained peaks indicative of contamination by materials with vermiculite-like layers.

![Fig. 4-1 XRD patterns of muscovite and air-dried rectorite](image)

**4.3.2 Residual Indents**

Fig. 4-2 illustrates selected images of residual indents (or impressions) obtained by optical microscopy. They show different responses of the two minerals to permanent penetration or damage. Both radial cracks emanating from the corners of the indent and discrete chippings around the face surfaces of contact are observed in muscovite, while only the latter features are observed in rectorite. Furthermore, it appears that the three radial cracks occurring in muscovite are deep enough to coalesce at the tip of the indent, while this is not clearly observed in rectorite. The occurrence of the long radial cracks indicates that muscovite behaves more as a brittle material. During indentation on muscovite, cracks initiate most often at the corners where intense stress concentration exists, and the energy unable to be stored in the adjacent regime is dissipated by cracking. For rectorite, due to the weak bonding force between the expandable layers, energy generated by indentation is more easily dissipated via delamination among the 2:1 layers, instead of cracking through many layers. As the indenter penetrates deeper into the material, the delaminated layers are forced to curve up. More penetration eventually results in bending failure.
of the delaminated layers, as manifested by chippings around the contact surfaces. The delamination and bending failure processes also occur in muscovite.

4.3.3 Influence of Maximum Load

Fig. 4-3 shows representative load-displacement curves ($F$-$h$) for both muscovite and rectorite obtained from Type A tests (i.e., varying $F_{\text{max}}$ at constant loading rate and constant hold time of 10 s). Several features are evident: (1) the two layered minerals behave differently. Muscovite exhibits much stiffer response than rectorite and less creep deformation during holding $F_{\text{max}}$ constant (the hold time is 10 s for all tests); (2) the loading part of these curves is not smooth, and steps exist in almost every curve, particularly for higher $F_{\text{max}}$. (3) Either a smaller number of large steps or a larger number of small steps may occur in either mineral. A giant step can be as large as 1000 nm, e.g., rectorite in Fig. 4(c). The size and location of these steps appear to be random, although the steps seem to decrease in size or become less discernable at smaller maximum loads (e.g., Fig. 4(d)).

Fig. 4-2 Residual indent images of (a) rectorite and (b) muscovite obtained by optical microscopy

(a) Rectorite
(b) Muscovite

|$F_{\text{max}}| = 499.5 \text{ mN}$
$|h_{\text{max}}| = 3354 \text{ nm}$

|$F_{\text{max}}| = 500.2 \text{ mN}$
$|h_{\text{max}}| = 3513.1 \text{ nm}$

|$F_{\text{max}}| = 171.3 \text{ mN}$
$|h_{\text{max}}| = 4639.2 \text{ nm}$

|$F_{\text{max}}| = 171.6 \text{ mN}$
$|h_{\text{max}}| = 2145.1 \text{ nm}$
Fig. 4-3 Typical load-displacement curves of muscovite and rectorite under varying maximum indentation load $F_{\text{max}}$ of: (a) 500 mN; (b) 172 mN; (c) 59 mN; and (d) 20 mN.

The step occurring during indentation loading is also called serration or “pop-in”, a phenomenon that has been observed during indentation of bulk metallic glasses (Li et al. 2007; Yang and Nieh 2007), thin films (e.g., TiAlN multilayer films, polymeric films, and GaN films) (Karimi et al. 2002; Geng et al. 2006; Navamathavan et al. 2006), and crystalline germanium (Oliver et al. 2007). Initiation of shear bands in isotropic materials, delamination of thin films from substrates, and formation of nano-, micro-, and macro-scale cracks adjacent to contact surfaces and corners possibly contribute to the formation of steps. For this study, given that the maximum indentation depth $h_{\text{max}}$ for all tests is less than 10% of specimen thickness, delamination between specimen and substrate is not the cause for the steps. Based on the residual
indentations shown in Fig. 4-2, the steps in muscovite are caused by the radial cracks that occur at the corners of the indent and partial delamination among certain layers within the mineral, as observed around the contact surfaces. For rectorite, layer delamination could be the major reason for the steps.

The penetration displacement in most steps usually increases while there is little change in the load. Since $E$ and $H$ are both dependent upon the maximum penetration, $h_{\text{max}}$ (see Eq. 4-1 to Eq. 4-5), the occurrence of these steps affects the resulting $E$ and $H$. Thus, corrections were made to remove these visually discernable steps to obtain a smooth curve for the loading part, thereby reducing $h_{\text{max}}$. After the correction, a relatively smooth curve was obtained and an example is shown in Fig. 4-4.

![Figure 4-4](image_url)

Fig. 4-4 An example showing the correction of the load-displacement curve by removing giant steps

Fig. 4-5 presents the relationship between the accumulative deformation of all steps and $F_{\text{max}}$, showing that the total accumulative deformation of all steps increases non-linearly with $F_{\text{max}}$. In addition, for both muscovite and rectorite, accumulative deformation of the steps account for a fairly large portion of the total displacement. Therefore, a too large $F_{\text{max}}$ may result in underestimating both $E$ and $H$.

Fig. 4-6 plots the $F_{\text{max}}$ and $h_{\text{max}}$ obtained from each indentation test, with and without correction to illustrate a generalized $F$-$h$ curve for both minerals. The following relationship is found to be valid for most homogeneous materials (ISO 2002; Fischer-Cripps 2004):

$$F = ah^3$$  \hspace{1cm} (4-6)
where \( a \) is a constant. Based on the regression results, neither muscovite nor rectorite follows the relationship specified in Eq. (4-6), and a smaller value of the power for the \( h \) exists for both minerals. This is probably due to the fact that the two layered minerals are not isotropic or homogeneous. Moreover, the larger power value indicates that muscovite has a greater capacity to resist permanent penetration than rectorite.

For the case of Berkovich indenter, a completely elastic-plastic contact can be assumed and there should exist the following relationship:

\[
F = E_r \left[ \frac{1}{\sqrt{\pi \tan \alpha}} \sqrt{\frac{E_r}{H}} + \left( \frac{2(\pi - 2)}{\pi} \right) \sqrt{\frac{\pi}{4}} \sqrt{\frac{H}{E_r}} \right] h^2
\]

(4-7)

where \( \alpha \) is the effective cone angle of the indenter. For a Berkovich indenter, \( \alpha = 70.3^\circ \) (Fischer-Cripps 2004). \( E_r \) and \( H \) are chosen as the values corrected by removing steps, as discussed later (Table 1). The simulation of \( F-h \) based on Eq. (4-7) is also plotted in Fig. 4-6. Neither muscovite nor rectorite follows with the \( F-h \) relationship defined in Eq. (4-7), even though the giant steps were removed. The disagreement between the test results and simulations may result from the nanoscale layered structure, which is characteristic for layered hydrous aluminosilicates.

Figs. 4-7 and 4-8 show the influence of the maximum load on \( E \) and \( H \) of muscovite and rectorite, respectively. For muscovite, consistent results were obtained without correction (i.e., removing the discernable giant steps), as both \( E \) and \( H \) decrease with \( F_{max} \), since the total accumulative deformation of the steps increases with \( F_{max} \). After correction, the dependence of \( E \) and \( H \) on \( F_{max} \) tends to disappear, which should be expected for a material homogeneous over...
depth. Moreover, correction significantly increases both $E$ and $H$. For rectorite, the dependence of $E$ and $H$ on $F_{\text{max}}$ is clear, even with correction. This may be caused by the presence of tiny steps that are not visually observable and hence have not been removed from the loading curve. Nevertheless, correction increases both $E$ and $H$. The reason for the irregular relationship between $E/H$ and $F_{\text{max}}$ is unclear and is worth further investigation.

Fig. 4-6 Comparison of load-displacement curves before and after correction
Table 4-1 summarizes the $E$ and $H$ results for both minerals. For muscovite, after correction, average $E$ and $H$ increase from 52.1 to 79.3 GPa and from 2.39 to 5.14 GPa, respectively. Similarly, for rectorite, average $E$ and $H$ increase from 15.7 to 18.3 GPa and from 0.53 to 0.73 GPa, respectively. Moreover, $H$ is more sensitive to $F_{max}$ than $E$, because $H$ is inversely proportional to $h^5$ while $E$ is inversely proportional to $h$. In addition, after correction, the greater percentage of increment in $E$ and $H$ for muscovite than rectorite suggests that the radial cracks observed only in muscovite are an additional source of these giant steps.
### Table 4-1 $E$ and $H$ of muscovite and rectorite

<table>
<thead>
<tr>
<th></th>
<th>Muscovite</th>
<th>Rectorite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$ (GPa)</td>
<td>$H$ (GPa)</td>
</tr>
<tr>
<td>With steps</td>
<td>52.1±6.2</td>
<td>2.39±0.68</td>
</tr>
<tr>
<td>Steps removed</td>
<td>79.3±6.9</td>
<td>5.14±0.82</td>
</tr>
<tr>
<td>Increment</td>
<td>52.2%</td>
<td>115.1%</td>
</tr>
</tbody>
</table>

### 4.3.4 Influence of Creep

Evident creep deformation during holding load was observed in rectorite (Fig. 4-3), and hence it was chosen to study the influence of creep on the determination of $E$ and $H$. A maximum load of 1 mN is applied for indentation test on rectorite, in order to minimize the influence of steps on $E$ and $H$. Fig. 4-9(a) shows a series of load-displacement curves obtained via Type B tests, i.e., varying hold time from 0 to 160 s at the same peak load, $F_{\text{max}} = 1.0$ mN, and at the same constant loading rate of 0.033 mN/s. No discernable steps were observed in the loading part of these curves, and hence there is no need to correct the curves by removing the steps. All loading curves overlap very well with each other, indicating the specimen’s spatial homogeneity. The creep displacement apparently increases with the hold time, indicating that rectorite exhibits highly time-dependent behavior under nanoindentation. The indentation creep CIT is defined as (ISO, 2002)

$$C_{\text{IT}} = \frac{h_2 - h_1}{h_1} \times 100$$

where $h_1$ and $h_2$ are indentation depth at the beginning and the end of the hold period, respectively. As shown in Fig. 4-10(b), indentation creep strain increases nonlinearly with hold time, suggesting that the creep rate decreases with hold time.

The initial slope (i.e., $S$, see Fig. 2-11(b)) of the unloading curves varies significantly with the hold time. Since the determination of both $E$ and $H$ involves the estimate of $S$, the change of $S$ resulting from varying hold time causes the change of $E$ and $H$. In addition, the creep displacement resulting from longer hold times may account for a significant portion of the total penetration, $h_{\text{max}}$, which also affects the contact depth $h_c$. Therefore, both $E$ and $H$ are affected by two creep-related parameters: the initial unloading slope $S$ and the maximum ($h_{\text{max}}$) or contact ($h_c$) depth. Fig. 4-10 shows the effect of creep or hold time on both $E$ and $H$. Clearly, $E$ and $H$ decreases with hold time, if no correction is made to take into account the influence of creep on the initial unloading slope (i.e., $S$). However, no significant changes in both $E$ and $H$ occur when the hold time exceeds 50 s, therefore, a hold time of $>50$ s is required to obtain consistent results.
4.3.5 Influence of Loading Rate

Due to its time-dependent behavior, rectorite was again chosen to study the influence of loading rate on the $E$ & $H$. Two different loading rates of 3.33 $\mu$N/s and 33.33 $\mu$N/s and two maximum loads of 105 $\mu$N and 1005 $\mu$N were used, and hold time again varies from 0 to 160 s. As an example, Fig. 4-11 shows the load-displacement curves with varying loading rate but a

Fig. 4-9 The creep of rectorite under nanoindentation: (a) load-displacement curves and (b) indentation creep strain versus hold time curve.

4.3.5 Influence of Loading Rate

Due to its time-dependent behavior, rectorite was again chosen to study the influence of loading rate on the $E$ & $H$. Two different loading rates of 3.33 $\mu$N/s and 33.33 $\mu$N/s and two maximum loads of 105 $\mu$N and 1005 $\mu$N were used, and hold time again varies from 0 to 160 s. As an example, Fig. 4-11 shows the load-displacement curves with varying loading rate but a
constant hold time of 5 s. Rectorite exhibits a different response to varying load rate. A higher loading rate results in a stiffer response, as expected. The bifurcation of the two load-displacement curves corresponding to two different loading rates occurs at very low load level (e.g., as small as 20 µN), indicating that the plastic deformation caused by delamination between layers and nano/micro cracking develops through the whole loading procedure. Also, the creep deformation depends on loading rate. At a given $F_{\text{max}}$, higher loading rate causes greater creep deformation which occurs within the hold time period. Furthermore, the initial unloading slope ($S$) also varies with loading rate, but its dependence on $F_{\text{max}}$ is greater than that on loading rate (Fig. 4-12).

(a) $F_{\text{max}} = 105$ µN, hold time = 5 s.  
(b) $F_{\text{max}} = 1005$ µN, hold time = 5 s.

Fig. 4-11 Effect of loading rate on load-displacement curves of rectorite
Figs. 4-13 and 4-14 show the dependence of $E$ and $H$ of rectorite on loading rate, respectively. Clearly, at a smaller $F_{\text{max}} = 105 \ \mu N$, both $E$ and $H$ significantly depend on the loading rate. A higher loading rate of 33.33 $\mu N/s$ results in the $E$ and $H$ nearly twice greater than those obtained with a smaller loading rate of 3.33 $\mu N/s$. For a larger $F_{\text{max}}$, the influence of loading rate on $E$ and $H$ tends to disappear. This is probably due to the fact that creep deformation is also dependent on load or stress level, and no correction has been made to take into account the influence of creep.

**Fig. 4-12** Load-displacement curves showing the dependence of $S$ on both loading rate and maximum load (hold time = 5 s)

**Fig. 4-13** Effect of loading rate on the elastic modulus of rectorite

---

(a) $F_{\text{max}} = 105 \ \mu N$

(b) $F_{\text{max}} = 1005 \ \mu N$
4.4 Discussion

4.4.1 Origin of the Different Properties for the Two Minerals

As reported above, muscovite and rectorite possess different elastic modulus and hardness, and exhibit very different responses to permanent penetration. Their different behavior can be related to the difference in their crystal structure.

Both muscovite and rectorite are layered hydrous aluminosilicates formed by the stacking of ~1 nm thick 2:1 layers (i.e., 2 tetrahedral sheets and 1 octahedral sheet). In muscovite, there are single 2:1 layers separated by a non-expandable interlayer, while in rectorite, non-expandable illite (similar to muscovite) layers regularly alternate with smectite-like expandable layers (Fig. 4-15). They possess different negative surface charges, resulting in different bonding mechanisms and bonding strength holding the 2:1 layers together (Table 4-2). In muscovite, the net negative charge is mainly caused by the substitution of Al$^{3+}$ for Si$^{4+}$ in one-fourth of the tetrahedral sheet positions and is balanced by nonhydrated cations (most commonly K$^+$) that are located between the layers and tightly hold the layers together by electrostatic attraction. In rectorite, only about one-seventh to slightly less than one-fourth of the Si$^{4+}$ in tetrahedral sites of the smectite-like layers are substituted by Al$^{3+}$, resulting in a smaller net negative charge in the 2:1 layer, which is balanced by hydrated exchangeable cations (e.g., Na$^+$, Mg$^{2+}$, Ca$^{2+}$) occupying the interlayer space (Amonette et al., 2002). The interlayer spacing in muscovite is occupied by K$^+$ and is non-expandable. In contrast, in the smectite-like layers of rectorite, the equivalent interlayer spacing is expandable and is occupied by hydrated cations. In general, the latter spacing is much greater than that in muscovite. The higher bonding strength between the 2:1
layers and the much smaller interlayer spacing in muscovite cause it to behave as a brittle solid and also provide a greater resistance to layer separation (or delamination) and permanent penetration. For smectitic layers in rectorite, the weak interlayer bonding causes it to be prone to delamination, and the large variable interlayer spacing provides less resistance to permanent penetration (Fig. 4-3). In addition, the weak interlayer bonding may facilitate the relative slippage between layers, which also reduces the resistance to permanent penetration. As a result, muscovite behaves more like a brittle material under nanoindentation, while rectorite is ductile.

![Schematic illustration of the crystal structures of muscovite and rectorite](Fig. 4-15)

**Table 4-2 Basic structural properties of muscovite and rectorite (Mitchell 1993; Amonette et al. 2002; Lambe and Whitman 1979; Brown 1984)**

<table>
<thead>
<tr>
<th></th>
<th>Muscovite</th>
<th>Rectorite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ideal formula</strong></td>
<td>K(Al₂)(Si₃Al)O₁₀(OH)₂</td>
<td>K(Al₂)(Si₃Al)O₁₀(OH)₂</td>
</tr>
<tr>
<td></td>
<td>K⁺</td>
<td>hydrated cations</td>
</tr>
<tr>
<td><strong>Layer type</strong></td>
<td>2:1 non-expandable</td>
<td>2:1 expandable</td>
</tr>
<tr>
<td><strong>Interlayer cation</strong></td>
<td>K⁺</td>
<td>K⁺</td>
</tr>
<tr>
<td><strong>Layer charge (mol per formula unit)</strong></td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td><strong>Cation Exchange Capacity</strong></td>
<td>5-20 meq/100 gm</td>
<td>5-20 meq/100 gm</td>
</tr>
<tr>
<td><strong>Basal spacing d(001)</strong></td>
<td>~1.0 nm</td>
<td>~1.0 nm</td>
</tr>
</tbody>
</table>

**4.4.2 Parameters Affecting the Determination of E & H by Nanoindentation**

As shown in Fig. 2-9, the experimental determination of E & H based on indentation load-displacement curves requires the determination of the initial unloading slope (S) at Fₘₐₓ, which depends on hold time, loading rate, and maximum load. Therefore, for layered hydrous aluminosilicates showing time-dependent behavior, Fₘₐₓ, loading rate, and hold time that are examined in this study all affect the determination of both E and H.
$F_{\text{max}}$ may cause the occurrence of giant steps, which are associated with layer delamination and cracking. An overestimation of overall displacement may be caused by the giant steps, and hence both $E$ and $H$ may be underestimated by applying a too large $F_{\text{max}}$, if no corrections are performed to remove the steps. Disappearance of these giant steps when $F_{\text{max}}$ is reduced to a certain value implies that there exists a critical load which corresponds to the initiation of layer delamination of a specific aluminosilicate. Therefore, selecting a suitable $F_{\text{max}}$ less than this critical load should be done for all samples in order to obtain a smooth load-displacement curve, which eases the calculation of both $E$ and $H$.

The purpose of applying a certain hold time period at the maximum load is mainly to reduce the effect of creep occurring at the loading period on the initial unloading slope $S$. The criterion of selecting hold time is to let the creep rate reach a minimum or steady state before unloading. However, too long a hold time will bring excessive amount of creep deformation in $h_{\text{max}}$, which may also affect the determination of $E$ and $H$. Therefore, an appropriate hold time interval needs to be determined for indentation testing of aluminosilicates.

Loading rate has a profound influence on the determination of $E$ and $H$, especially at low maximum loads. If too fast a loading rate is selected, the time during the loading stage may not be long enough to allow creep to take place, and the creep strain rate before unloading could be still very high. This causes not only an underestimate of displacement but also an overestimate of the initial unloading slope. As a consequence, $E$ will be overestimated. At a lower loading rate, the creep strain rate before unloading could reach a steady state, and hence the $E$ decreases with loading rate.

In summary, selecting a set of appropriate experimental control parameters including maximum load, loading rate, and hold time has a significant influence on the determination of $E$ and $H$ of layered hydrous aluminosilicates using indentation testing. In general, hold time should be long enough to let the material reach a steady state stage of creep. Similarly, loading rate needs to be slow enough to allow creep to reach a steady state before unloading. However, excessive creep deformation should be avoided, as it will contribute undesirably to the total penetration $h_{\text{max}}$. For layered hydrous aluminosilicates prone to layer delamination, $F_{\text{max}}$ should not be too high in order to prevent the occurrence of unwanted giant steps in the loading portion of the load-displacement curves. Although these test control parameters can be determined experimentally or empirically, the process is tedious. Therefore, the development of a theoretical indentation model for such layered aluminosilicates and the understanding of their time-dependent behavior are necessary.

### 4.4.3 Result Accuracy

Table 4-3 compares the $E$ and $H$ values obtained by this study with those reported in the literature. The corrected $E = 79.3$ GPa of muscovite is slightly greater than those values reported in the literature ($E = 54.0-60.9$ GPa), although a higher value $E = 100.8$ has been reported by Mavko et al. (1998). For rectorite, $E = 18.3$ is also slightly higher than the value $E = 14.1$ of vermiculite reported in the literature. In addition, the determination of $E$ by nanoindentation is also influenced by indenter tip geometry and the assumed Poisson’s ratio. For this study, a sharp Berkovich indenter was used, which tends to overestimate the elastic modulus. In general, a blunt tip (such as a cylindrical punch or a spherical tip) might provide a better way to measure
the elastic modulus. The results presented here are not corrected by considering the viscous contribution (i.e., loading rate and hold time) to the total penetration. Nevertheless, the results are close to the values obtained by other methods (e.g., acoustic or seismic).

Table 4-3 Elastic moduli of clay minerals and muscovite reported in the literature

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$E$ (GPa)</th>
<th>$K$ (GPa)</th>
<th>$G$ (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>muscovite</td>
<td>$E_{11}=178$, $E_{33}=54.9$</td>
<td></td>
<td></td>
<td>Aleksandrov and Prodaivoda (1993)</td>
</tr>
<tr>
<td>muscovite</td>
<td>$E_{11}=176.5$, $E_{22}=179.5$, $E_{33}=60.9$</td>
<td></td>
<td></td>
<td>McNeil and Grimsditch (1993)</td>
</tr>
<tr>
<td>muscovite</td>
<td>$E_{11}=181.0$, $E_{22}=178.4$, $E_{33}=58.6$</td>
<td></td>
<td></td>
<td>Vaughan and Guggenheil (1986)</td>
</tr>
<tr>
<td>muscovite</td>
<td>56.8-100.8*</td>
<td>42.9-61.5</td>
<td>22.2-41.1</td>
<td>Mavko et al. (1998)</td>
</tr>
<tr>
<td>vermiculite</td>
<td>14.1</td>
<td></td>
<td></td>
<td>Ballard and Rideal (1983)</td>
</tr>
<tr>
<td>pyrophyllite</td>
<td>55.5*</td>
<td>37.0</td>
<td></td>
<td>Parley et al. (2002)</td>
</tr>
<tr>
<td>talc</td>
<td>61.5*</td>
<td>41.0</td>
<td></td>
<td>Parley et al. (2002)</td>
</tr>
<tr>
<td>muscovite</td>
<td>79.3</td>
<td></td>
<td></td>
<td>This paper</td>
</tr>
<tr>
<td>rectorite</td>
<td>18.3</td>
<td></td>
<td></td>
<td>This paper</td>
</tr>
</tbody>
</table>

Not: The elastic modulus $E$ with “*” is derived from bulk modulus $K$ and shear modulus $G$, the value with “**” is derived from $K$ by assuming a Poisson’s ratio of 0.25.

4.5 Conclusions

This chapter describes the first attempt to determine the elastic modulus and hardness of two layered hydrous aluminosilicates by nanoindentation, consisting of well-ordered muscovite and rectorite. Indentation experiments with varying control parameters were conducted in the micro and nano scale load range to determine $E$ and $H$ and to investigate the influence of loading conditions, including loading rate, maximum load, and hold time. $E$ and $H$ are both affected by these test control parameters.

Numerous steps or “pop-ins” where displacement continuously increases while there is little change in load were observed in the loading part of a typical load-displacement curve, resulting in an underestimate of both $E$ and $H$. The steps were induced by the radial cracks occurring mainly in muscovite and layer delamination occurring in both minerals. However, the steps tend to disappear or become less discernable under smaller loads. Both minerals exhibit time-dependent response to loading under nanoindentation, and rectorite shows more pronounced viscous behavior than muscovite. Based on the indentation tests performed on rectorite, without correction to remove the viscous contribution to penetration, increasing hold time tends to decrease both $E$ and $H$. In addition, both $E$ and $H$ are highly dependent upon the loading rate, and a higher loading rate gives higher values of $E$ and $H$ under the same loading rate condition.

The two minerals behave differently under nanoindentation, which is caused by the difference in their crystal structure, including interlayer bonding strength, types of interlayer complexes, and interlayer space expandability. Muscovite tends to behave more like a brittle material under indentation, while rectorite a soft or viscous material. However, both minerals are nanostructured layered materials possessing anisotropic properties, and delamination tends to occur for both materials under indentation.
The strong dependence of $E$ and $H$ on the test control parameters demonstrates the importance of choosing appropriate test parameters and applying data analysis corrections by removing giant steps and the viscous contribution to the indentation displacement. Furthermore, this study indicates that there is an apparent need to develop contact mechanics and indentation theories for such layered aluminosilicates possessing highly anisotropic and viscous properties.

4.6 References


CHAPTER 5. NANOINDENTATION ON LARGE-SIZED PHYLLOSILICATE MINERALS

5.1 Introduction

Clay minerals, which account for about 16% by volume of the earth’s upper 20 km surface, are one of the major constituents of natural geomaterials (including soils and rocks). Such ubiquitous presence makes them important in many disciplines including ceramics, soils and agronomy, sedimentary petrology, civil engineering, clay chemistry, and economic geology. The crystal structure, chemical composition, particle surface properties, and size characterizations of most clays have been revealed with the help of X-ray diffraction, nanoscale imaging (e.g., atomic force microscopy (AFM), transmission electron microscopy (TEM)), and other newly developed modern analytical techniques. Mechanical properties of clay minerals are of vital importance in many applications, and much effort has been directed toward their accurate determination.

However, mechanical properties of clay minerals are rarely reported in the literature due to the difficulty in finding natural clay minerals with particle sizes large enough to be readily handled by conventional mechanical testing instruments (e.g., uniaxial compression/tension test, macro- or micro-scale hardness test). Although several methods have been used to determine the mechanical properties of clay minerals, such as theoretical computation by molecular dynamics (MD) simulation (Seo et al., 1999; Sato et al., 2001; Manevitch and Rutledge, 2004; Cygan et al., 2004; Suter et al., 2007; Mazo et al., 2008a and 2008b), a combination of theoretical and experimental investigations (Vaughan and Guggenheim, 1986; McNeil and Grimsditch, 1993; Wang et al., 2001; Vanorio et al., 2003), and the empirical extrapolations of laboratory measurements (Mondol et al., 2008), there does not exist a well-recognized standard mechanical testing method for clay minerals. Furthermore, the reported mechanical properties of clay minerals are inconsistent dependent on the methods being used.

This chapter investigates the applications of the nanoindentation technique to determine the elastic modulus and hardness of typical 2:1 phyllosilicate minerals including talc, pyrophyllite, muscovite, phlogopite, and margarite. Nanoindentation is a recently developed technique for the characterization of mechanical properties of small scale bulk materials, thin films, coatings, and other nanomaterials. The selected minerals permit the evaluation of several factors (interlayer composition, layer charge, and types of octahedral sheet) on the mechanical properties measured at the nanoscale.

5.2 Materials and Methods

5.2.1 Sample Preparation

Six highly crystalline minerals were selected for nanoindentation testing. These are talc-17c (Mont Windara, Australia), pyrophyllite-17c (Ibitiara, Bahia, Brazil), muscovite-2M1 (Panasqueira, Portugal), muscovite-2M1 (Diamond Mine, Keystone, South Dakota), margarite-2M1 (Chester County, PA), and Fe-rich phlogopite (Silver Crater Mine, Near Bancroft, Ontario, Canada) which are summarized in Table 5-1. The minimum in-plane dimension is about 1 mm shown in Fig. 5-1.
Table 5-1 Minerals tested by nanoindentation

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Denotation in this chapter</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc-1T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Talc</td>
<td>Mont Windara, Australia</td>
</tr>
<tr>
<td>Pyrophyllite-1T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Pyrophyllite</td>
<td>Ibitiara, Bahia, Brazil</td>
</tr>
<tr>
<td>Muscovite-2M&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Muscovite(P)</td>
<td>Panasqueira, Portugal</td>
</tr>
<tr>
<td>Muscovite-2M&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Muscovite(D)</td>
<td>Diamond Mine, Keystone, South Dakota</td>
</tr>
<tr>
<td>Margarite-2M&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Margarite</td>
<td>Chester County, PA</td>
</tr>
<tr>
<td>Fe-rich phlogopite</td>
<td>Phlogopite</td>
<td>Silver Crater Mine, Near Bancroft, Ontario</td>
</tr>
</tbody>
</table>

Single crystal silicon wafers (100) (MTI Corporation, Richmond, CA) with dimension 10×10×0.6 mm were used as substrates. An aluminum puck was first heated to 130 °C on a hot plate and then a thin layer of Crystalbond 509 amber resin (Aremco Products, Inc., New York, NY), which melts at 130 °C or higher temperatures, was applied to the puck surface with an area of about 10×10 mm<sup>2</sup>. This was followed by carefully placing a Si wafer onto the puck surface. The Si wafer was gently pressed with continuous one-direction rotation in order to displace all the air between the puck/Si wafer interface. Then another thin layer of Crystalbond 509 amber resin was applied on the Si wafer surface and the mineral sample was carefully placed on the wafer keeping the sample surface as parallel as possible to the wafer surface. The whole puck was removed immediately from the hotplate to a leveling table in order to prevent overheating the sample. After the puck cooled down, a very thin layer was cleaved from the surface of sample with a razor blade to expose a fresh and intact surface to accept indentation. Careful attention must be paid during the installation of the puck into the sample tray of the nanoindenter to prevent further contamination of the sample surface.

5.2.2 Nanoindentation Testing

Nanoindentation experiments were performed on the six samples using an MTS Nano XP indenter (MTS Nano Instruments, Inc., Oak Ridge, TN) under strain rate control mode at room temperature. Dynamic contact module (DCM) equipped with a diamond Berkovich indenter (with a tip radius of < 20 nm) and continuous stiffness measurement (CSM) was used. This DCM head has a load resolution of 1 nN and very high displacement resolution < 0.01 nm. For comparison purpose, all the tests were set up with a constant thermal drift rate of 0.03 nm/s and a constant indentation strain rate \((dh/dt)/h = 0.05 \text{ s}^{-1}\), where \(h\) is the indentation depth, and \(t\) is the loading time.

Typical loading profile shown in Fig. 5-2 was used for all tests, consisting of five steps: (1) increasing load to a specified maximum indentation depth \((h_{\text{max}})\) at a constant indentation strain rate 0.05 s<sup>-1</sup>; (2) holding \(F_{\text{max}}\) constant for a given hold time, \(t_h = 10\text{ s}\); (3) decreasing load linearly to 10% of \(F_{\text{max}}\) at the same loading rate as that at \(F_{\text{max}}\); (4) holding the load constant for 100 seconds to record the thermal drift of the instrument; and (5) decreasing linearly the load to zero.

It was discovered that pop-ins or steps occurred on the load-displacement curves of muscovite and rectorite (Zhang et al., 2008) during the nanoindentation tests. This causes the necessity to correct the raw data in order to determine the moduli and hardness of these minerals in accordance with the commonly used Oliver and Pharr’s method (Oliver and Pharr, 1992). To avoid such debatable data correction, relatively smooth load-displacement curves without visible
pop-ins are expected with the constant indentation strain rate approach. Such conditions correspond to low load and require high load resolution as well as high displacement resolution of the nanoindentation system like DCM.

Fig. 5-1 Optical images of the tested minerals
In addition to the utilization of DCM system, a rigorous testing scheme (Fig. 5-3) was applied in order to ensure high reliability and accuracy of the test data. (1) Tip cleaning: 9 indentations with monotonic loading and unloading were performed on a piece of Scotch double-sided sticky tape that was attached onto the top surface of an aluminum puck to clean the tip; (2) Prior-Tip checking: 9 indentations under CSM mode were made on the standard fused silica to check the instrument working condition. (3) Sample testing: a clean area visible under the microscope was selected as a testing area. The position and pattern of the indentation tests was determined case by case according to the surface condition of the selected area. High data acquisition of 20 Hz was set in order to capture small pop-ins on load-displacement curves if present. (4) Post-Tip checking: 9 indentations under CSM mode using the same testing conditions were made on the standard fused silica again to check the instrument working condition. If the measured modulus and hardness value deviate from the standard value more than 5%, the data obtained in Step 3 are discarded and a new measurement will be made starting with Step 1.

The continuously recorded load, displacement, and stiffness versus indentation depth were used to obtain the modulus and hardness in the direction normal to the indentation plane. An elastic parameter, named reduced modulus \( E_r \) or effective modulus of the indenter-sample contact, can be obtained directly through the following relationship:

\[
E_r = \frac{\sqrt{\pi}}{2\beta \sqrt{A_c}} S
\]  

(5-1)

where \( \beta \) is a dimensionless correction factor for the indenter tip shape and \( \beta = 1.05 \) is commonly recommended for a Berkovich indenter (Oliver and Pharr, 2004); \( S \) is the contact stiffness measured during the loading portion using CSM technique (Oliver and Pharr, 1992; Li and

Fig. 5-2 CSM loading profile with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time =10 s.
\[ A_c = C_0 h_c^2 + \sum_{i=1}^{8} C_i h_c^{(1/2)^i} \]  

(5-2)

where the contact depth \( h_c \) can be calculated as:

\[ h_c = h - \varepsilon \frac{F}{S} \]  

(5-3)

where \( \varepsilon \) is a constant that depends on indenter tip geometry (for Berkovich tip, \( \varepsilon = 0.75 \)), and \( F \) is the indentation load; \( C_0 \) through \( C_8 \) are constants. For a perfect Berkovich indenter, the leading term \( C_0 = 24.5 \). The others are most often needed to describe the deviations from the Berkovich geometry due to tip blunting. These constants are determined through nanoindentation tests on a
material with known elastic modulus. In this chapter, a standard fused silica with elastic modulus of 72 GPa was used to calibrate the tip before indentation tests on the samples.

The two mechanical parameters, elastic modulus $E$ and hardness $H$, are the most frequently measured values using nanoindentation. For an isotropic and homogeneous material, the elastic modulus $E$ of the sample can be extracted through the following relationship (Doerner and Nix, 1986):

$$\frac{1}{E_r} = \frac{1 - v_c^2}{E_c} + \frac{1 - v_i^2}{E_i}$$

where $v_c$ and $v_i$ are the Poisson’s ratio of the sample and indenter, respectively (for a diamond indenter, $v_i = 0.07$); $E_i$ and $E_c$ are the elastic modulus of the indenter and sample, respectively (for a diamond indenter, $E_i = 1141$ GPa).

Nanoindentation hardness $H$ is defined as the indentation load divided by the projected contact area (Oliver and Pharr, 1992; ISO, 2002). It is the mean contact pressure that a material can support under load. When CSM method is adopted, hardness versus indentation depth can be obtained during the load portion:

$$H = \frac{F}{A_c}$$

5.2.3 Atomic Force Microscopy (AFM)

After indentation, the indent impressions and surface topography were characterized using a 5500 Scanning Probe Microscope (Agilent Technologies, Inc., Chandler, AZ). The measurement was conducted in ambient temperature in contact mode with a PointProbe®Plus silicon tip (Nanosensors, Neuchatel, Switzerland) with tip height 10-15 µm. The scan resolution is 512 pixels × 512 pixels, set point 1.000V and scan rate 1.0Hz.

5.3 Results

5.3.1 AFM Images of Surface Topography

Fig. 5-4 shows the AFM images of the surface topography of the minerals before indentation tests. Each mineral provides a local area larger than 10µm×10µm with a very flat surface to accept nanoindentation tests with a maximum indentation depth less than 200 nm. Since the width of a Berkovich indenter is approximately 7 times the indentation depth, the available flat surface area of each sample can significantly avoid the influence from neighboring surface features. It is also interesting to note that the talc sample exhibits cleavage steps less than 20 µm apart (Fig. 5-4 (a)).
Fig. 5-4 Atomic Force Microscopy (AFM) images of (a) Talc 1\(T_c\), (b) Margarite 2\(M_1\), (c) Muscovite 2\(M_1\) (Diamond Mine), (d) Muscovite 2\(M_1\) (Panasqueira), (e) Phlogopite 1\(M\), and (f) Pyrophyllite 1\(T_c\).
5.3.2 Load-displacement Features

Fig. 5-5 presents the average load-displacement curves during loading portion for the six samples using DCM head and CSM technique under constant indentation strain rate of 0.05 s\(^{-1}\). Each sample exhibits different resistance to indentation penetration. At indentation depth \(h = 150\) nm, for example, the corresponding indentation load for margarite, muscovite (P & D), phlogopite, talc and pyrophyllite are about 3.4 mN, 2.1 mN, 0.7 mN, 0.36 mN, and 0.16 mN, respectively. Since all the six minerals are 2:1 layer minerals with a nearly common layer spacing of \(\sim 1\) nm, the large variances in penetration resistance could result from their different layer charges and layer composition. It can be qualitatively concluded that the penetration resistance of the minerals decreases as the layer charge \(z\) decreases from margarite \((z = 1.8 – 2.0)\), muscovite and phlogopite \((z = 1.0)\), to talc and pyrophyllite \((z = 0)\). In addition, minerals with the same layer charge but different octahedral sheets have a significant difference in penetration resistance. For example, muscovite with a dioctahedral sheet has a much higher penetration resistance than phlogopite which has a triocahedral sheet.

![Load-displacement curves](image)

Fig. 5-5 Average load-displacement curves with constant indentation loading rate = 0.05 s\(^{-1}\).

Randomly occurring pop-ins have been observed in the loading parts of load-displacement curves of nanoindentation tests on layered minerals (Zhang et al., 2008). These pop-ins induced by radial cracks and delamination will underestimate both elastic modulus \(E\) and hardness \(H\). In particular, the critical load \(F_{\text{cri}}\) or indentation depth \(h_{\text{cri}}\) corresponding to the initiation of visible pop-ins is of importance not only in characterizing the interlayer bonding strength but also in determining \(E\) and \(H\). Fig. 5-6 through Fig. 5-11 show the two typical load-displacement curves of each of the six minerals in order to illustrate \(F_{\text{cri}}\) and \(h_{\text{cri}}\). The insets show that relatively giant steps occurred on the load-displacement curves of margarite and muscovite, but no giant steps for talc and pyrophyllite. The critical indentation depth \(h_{\text{cri}}\) for margarite, muscovite, and phlogopite are about 26 nm, 13 nm, and 17 nm, respectively. The higher layer charges enhance the interlayer bonding strength which renders more layers work integrally to delay the
occurrence of initial delamination or radial cracking as indentation depth increases. For talc and pyrophyllite which have weak interlayer bonding strength, the delamination possibly occurred consecutively layer by layer as the indentation went on, consequently no visible pop-ins appeared on the loading parts of the load-displacement curves. The main reason is that the shear stress in the upper layer induced by the indenter can not be effectively transferred into the lower layer because of the weak bonding strength.

To investigate the reason of giant steps, one residual indent on muscovite (D) was scanned using AFM. Fig. 5-12 shows the load-displacement curve and the corresponding AFM indent image as well as one cross-section profile. This AFM image was taken after one part of the loose material was carefully removed in order to expose the whole delamination/cracking surface. The arc shape layer delamination contributed a lot to the occurrence of the giant pop-ins. It is also noteworthy that the deepest delamination level coincided with almost the same level of the maximum residual indentation depth.

The insets in Fig. 5-6 through Fig. 5-11 show that the creep developed during the hold time is much smaller that the indentation depth at maximum load. This implies that indentation strain rate of 0.05 s\(^{-1}\) and the hold time of 10 s are appropriate for such minerals.

![Fig. 5-6 Typical load-displacement curves of margarite with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time =10 s.](image-url)
Fig. 5-7 Typical load-displacement curves of muscovite (Diamond Mine) with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time = 10 s.

Fig. 5-8 Typical load-displacement curves of muscovite (Panasqueira) with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time = 10 s.
Fig. 5-9 Typical load-displacement curves of phlogopite with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time = 10 s.

Fig. 5-10 Typical load-displacement curves of talc with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time = 10 s.
Fig. 5-11 Typical load-displacement curves of pyrophyllite with constant indentation loading rate = 0.05 s⁻¹ and hold time = 10 s.

Fig. 5-12 Typical load-displacement of muscovite (D) with constant indentation loading rate = 0.05 s⁻¹ and hold time = 10 s.
5.3.3 Elastic Modulus and Hardness

Elastic modulus $E$ and hardness $H$ in the direction normal to the indentation plane of each sample was calculated based on Oliver and Pharr’s method assuming the same Poisson’s ratio of 0.25. Fig. 5-13 and Fig. 5-14 are the average hardness and modulus versus indentation depth of the six samples, respectively. Both $E$ and $H$ decrease with the indentation depth. Except the intrinsic characteristic reason of each mineral, the pop-ins which accumulate as indentation depth increase strengthen the trend of decrease of the $E$ and $H$ value to some degree. To reduce the influence of such pop-ins on $E$ and $H$ as much as possible, it is proposed that $E$ and $H$ values corresponding to indentation depth less than $h_{cri}$ can be the representative values of true modulus and hardness of each sample. Since the tip calibration depth starts from 5 nm, elastic modulus $E$ and hardness $H$ determined before this depth should be ignored.

Fig. 5-13 Typical average hardness with constant indentation loading rate = 0.05 s$^{-1}$ and hold time =10 s.

Fig. 5-15 through Fig. 5-17 are the plots of $E$ and $H$ versus indentation depth of margarite, muscovite, and phlogopite. It is found that $E$ and $H$ of these minerals prior to $h_{cri}$ do not vary a lot and very close to the peak values. Since the indentation hardness $H$ is the measurement of the mean contact pressure and is related to the yield stress of the indented material (Tabor, 1956; Tabor, 1996), it is reasonable to consider that the peak $H$ corresponds to the yield status and may be regarded as the true hardness of the sample. Subsequently, the value $E$ at this yield point is the representative modulus of this sample.
Fig. 5-14 Typical average modulus with constant indentation loading rate = 0.05 s⁻¹ and hold time =10 s.

Fig. 5-15 Typical average modulus and hardness of margarite with constant indentation loading rate = 0.05 s⁻¹ and hold time =10 s.
Fig. 5-16 Typical average modulus of muscovite and phlogopite with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time = 10 s.

Fig. 5-17 Typical average hardness of muscovite and phlogopite with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time = 10 s.
Fig. 5-18 and Fig. 5-19 show the $E$ and $H$ of talc and pyrophyllite. Following the same criterion as above, the representative modulus and hardness were determined even though no visible $h_{cri}$ can be obtained. Table 5-2 is the summary of moduli and hardness of the six samples. The indentation depth at which the peak hardness occurs is constant, equal to ~13 nm. This depth is about 13 layers.

Fig. 5-18 Typical average modulus of talc and pyrophyllite with constant indentation loading rate $=0.05$ s$^{-1}$ and hold time $=10$ s.

Fig. 5-19 Typical average modulus of talc and pyrophyllite with constant indentation loading rate $=0.05$ s$^{-1}$ and hold time $=10$ s.
Table 5-2 \( E \) and \( H \) determined by nanoindentation

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( E ) (GPa)</th>
<th>( H ) (GPa)</th>
<th>( h ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margarite-2( M_1 )</td>
<td>165.5 ± 0.2</td>
<td>16.3 ± 0.1</td>
<td>12.9</td>
</tr>
<tr>
<td>Muscovite-2( M_1 ) (D)</td>
<td>77.4 ± 4.2</td>
<td>8.6 ± 0.8</td>
<td>12.9</td>
</tr>
<tr>
<td>Muscovite-2( M_1 ) (P)</td>
<td>83.5 ± 5.4</td>
<td>10.6 ± 1.3</td>
<td>12.8</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>35.7 ± 1.3</td>
<td>5.1 ± 0.5</td>
<td>13.0</td>
</tr>
<tr>
<td>Talc-1( T_c )</td>
<td>26.8 ± 4.5</td>
<td>3.9 ± 0.9</td>
<td>12.9</td>
</tr>
<tr>
<td>Pyrophyllite-1( T_c )</td>
<td>19.6 ± 0.8</td>
<td>4.6 ± 0.2</td>
<td>12.9</td>
</tr>
</tbody>
</table>

5.4 Discussion

5.4.1 Influence of Net Layer Charge and Octahedral Type

The six samples tested in this paper are 2:1 layer phyllosilicate minerals with identical layer spacing of \( \sim 1 \) nm. The main difference among them is the layer charge \( z \) as well as the octahedral sheet type. The negative layer charge mainly results from the isomorphous substitution of certain number of cation \( \text{Si}^{4+} \) with \( \text{Al}^{3+} \) in the tetrahedral sheet. Adjacent layers are bound together by the cations (most commonly \( \text{Ca}^{2+} \) for margarite, \( \text{K}^- \) for muscovite and phlogopite) located between the basal planes of adjacent layers. For talc and pyrophyllite, there are no cations exist in the interlayer because there is no need to balance the nearly zero layer charge, and Van der Waal’s forces between adjacent basal oxygen planes are considered to bind one layer to another.

Table 5-3 shows the compositions of the samples determined from the literature. For the dioctahedral minerals margarite, muscovite (D), muscovite (P), and pyrophyllite, the negative layer charges per formula with \( \text{O}_{10}(\text{OH})_2 \) are 1.82 (Guggenheim and Bailey, 1975), 1.03 (Guggenheim et al., 1987), 1.05 (Guggenheim et al., 1987), and 0.006 (Lee and Guggenheim, 1981), respectively. Fig. 5-20 and Fig. 5-21 present the modulus \( E \) and hardness \( H \) versus net negative layer charge of the dioctahedral minerals. Both modulus and hardness of a mineral increase with the layer charge through a different second order polynomial function as following:

Table 5-3 Composition of the tested samples

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( \text{Di/Tri} )</th>
<th>Ideal composition</th>
<th>Actual composition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margarite</td>
<td>( \text{Di} ) 2</td>
<td>( \text{Ca}(\text{Al}_2)(\text{Si}_2\text{Al}<em>2)\text{O}</em>{10}(\text{OH})_2 )</td>
<td>( (\text{Ca}<em>{0.81}\text{K}</em>{0.01}\text{Na}<em>{0.19})(\text{Al}</em>{1.99}\text{Fe}<em>{0.01}\text{Mg}</em>{0.03})\text{O}_{10}(\text{OH})_2 )</td>
<td>Guggenheim and Bailey, 1975</td>
</tr>
<tr>
<td>Muscovite</td>
<td>( \text{Di} ) 1</td>
<td>( \text{K}(\text{Al}_2)(\text{Si}<em>3\text{Al})\text{O}</em>{10}(\text{OH})_2 )</td>
<td>( (\text{K}<em>{0.93}\text{Na}</em>{0.08}\text{Ca}<em>{0.01})(\text{Al}</em>{1.83}\text{Fe}<em>{0.16}\text{Mn}</em>{0.01})\text{O}<em>{10}(\text{OH})</em>{1.83}\text{F}_{0.17} ) (for muscovite (D))</td>
<td>Guggenheim et al., 1987</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( (\text{K}<em>{1.00}\text{Na}</em>{0.01}\text{Al}<em>{0.01})(\text{Si}</em>{3.09}\text{Al}<em>{0.78})\text{O}</em>{10}(\text{OH})<em>{1.83}\text{F}</em>{0.12} ) (for muscovite (P))</td>
<td>Guggenheim et al., 1987</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>( \text{Tri} ) 1</td>
<td>( \text{K}(\text{Mg}_3)(\text{Si}<em>3\text{Al})\text{O}</em>{10}(\text{OH})_2 )</td>
<td>( (\text{K}<em>{0.93}\text{Na}</em>{0.08})(\text{Mg}<em>{1.57}\text{Fe}</em>{2.17}\text{Al}<em>{0.11}\text{Ti}</em>{0.01}\text{Mn}<em>{0.06})\text{O}</em>{10}(\text{OH})<em>{1.83}\text{F}</em>{0.12} )</td>
<td>Rancourt et al., 1992</td>
</tr>
<tr>
<td>Talc</td>
<td>( \text{Tri} ) 0</td>
<td>( \text{Mg}_3(\text{Si}<em>4)\text{O}</em>{10}(\text{OH})_2 )</td>
<td>N/A</td>
<td>Lee and Guggenheim, 1981</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>( \text{Di} ) 0</td>
<td>( \text{Al}_2(\text{Si}<em>4)\text{O}</em>{10}(\text{OH})_2 )</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Note: \( \text{Tr} = \text{trioctahedral}; \text{Di} = \text{dioctahedral}; z = \text{negative layer charge per formula unit with O}_{10}(\text{OH})_2 \).
Fig. 5-20 Modulus versus net negative layer charge for 2:1 layer minerals with layer spacing 1 nm.

\[ E = 26.61z^2 + 31.86z + 19.39 \]
\[ R^2 = 0.9991 \]

Fig. 5-21 Hardness versus net negative layer charge for 2:1 layer minerals with layer spacing 1 nm.

\[ H = 1.99z^2 + 2.82z + 4.58 \]
\[ R^2 = 0.9757 \]
\[ E = 26.61z^2 + 31.86z + 19.39 \]  \hspace{1cm} (5-6)

\[ H = 1.99z^2 + 2.82z^2 + 4.58 \]  \hspace{1cm} (5-7)

It is reasonable that higher layer charge results in stronger interlayer bonding strength which consequently enhances the penetration resistance reflected in higher hardness. The good correlation of \( E \) and \( z \) by Eq. (5-6) gives the moduli of margarite, muscovite, and phlogopite with ideal structures (layer charge \( z \) equals to 2.0, 1.0, and 0 respectively) in the direction perpendicular to the layer plane as 157.7GPa, 77.9GPa, and 19.4GPa, respectively (Table 5-4). The hardness obtained by the correlation of Eq. (5-7) is 15.4GPa, 9.4GPa, and 4.6GPa (Table 5-4), respectively.

Table 5-4 Predicted elastic modulus and hardness of dioctahedral 2:1 layer minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>( E ) (GPa)</th>
<th>( H ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margarite</td>
<td>157.7</td>
<td>15.4</td>
</tr>
<tr>
<td>Muscovite</td>
<td>77.9</td>
<td>9.4</td>
</tr>
<tr>
<td>pyrophyllite</td>
<td>19.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

For the trioctahedral minerals phlogopite and talc, the modulus and hardness increase with the layer charge but at a much lower rate than that with the dioctahedral minerals. In addition, the modulus and hardness at layer charge \( z = 0 \) do not vary significantly between the dioctahedral and trioctahedral minerals. However, at \( z = 1.0 \), the modulus and hardness of dioctahedral minerals (\( E = 77.9 \) GPa, \( H = 9.4 \) GPa) are much higher than the trioctahedral mineral (\( E = 35.7 \) GPa, \( H = 5.1 \) GPa). This discovery does not follow the commonly recognized rule that the trioctahedral minerals exhibit the lower compressibility than the dioctahedral minerals due to the greater compressibility of the dioctahedral layer with respect to that of the trioctahedral layer (Comodi and Zanazzi, 1995, Angel et al., 1988). The shortening of some of the interlayer cations to silicone surface oxygen atom distance in the dioctahedral minerals may create a stronger bonding of the layers than in the trioctahedral case when the bond length are essentially the same. Another reason could be that the additional cations Ca occupying in the interlayer region in muscovite (D) and muscovite (P) play a significant role in the increment of modulus and hardness compared with phlogopite without Ca cation within that region (shown in Table 5-2.) This is similar to the discovery by Comodi and Zanazzi (1995) that Na-poor muscovite gave a lower isothermal bulk modulus \( K \) (49 GPa) than Na-rich muscovite (\( K = 54 \) GPa) due to the partial substitution of Na for K in the interlayer region.

If Eq. (5-6) and Eq. (5-7) are valid, the modulus and hardness in the direction perpendicular to the basal plane of illite can be estimated. For example, the modulus and hardness of dioctahedral illite with net negative layer charge \( z = 0.9-1.0 \) can be estimated as 61.6-77.9 GPa and 8.7-9.4 GPa, respectively.

5.4.2 Comparison with Literature Data

The modulus and hardness obtained by nanoindentation are only related to the direction perpendicular to the layers. Clay minerals, however, are highly anisotropic because of the differences in bonding within the 2:1 layers and the bonding between these layers, and almost all
the reported mechanical properties in literature are either individual elastic constants or bulk moduli. Therefore there is a need of conversion between indentation modulus and elastic constants/bulk modulus for comparison purpose.

Given a material is transverse isotropic and linear elastic, the stress and strain are related by the generalized Hooke’s law as follows:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad (5-8)$$

where $\sigma_{ij}$, $\varepsilon_{kl}$, and $C_{ijkl}$ are the elements of the stress tensor, strain tensor, and stiffness tensor, respectively. The indentation modulus obtained by indentation in the $z$ direction relates to the five independent elastic constants $C_{ijkl}$ of the material as follows (Ulm and Abousleiman, 2006):

$$E_z = 2(1 - \nu^2) \sqrt{\frac{C_{31}^2 - C_{13}^2}{C_{11}} + \frac{1}{C_{44}} + \frac{2}{C_{31} + C_{13}}}^{-1} \quad (5-9)$$

where the reduced notations are used as $C_{33} = C_{3333}$, $C_{13} = C_{1133} = C_{3311}$, $C_{31} = \sqrt{C_{11}C_{33}} > C_{13}$, and $C_{44} = C_{2323} = C_{1313}$.

The elastic constants of clay minerals determined by direct experiments are rarely reported because of their small crystal sizes. In literature, the Brillouin scattering method is commonly used (Vaughan and Guggenheim, 1986; McNeil and Grimsditch, 1993; Aleksandrov and Prodaivoda, 1993). Table 5-5 gives the available data for muscovite, phlogopite, and phlogopite in literature and the indentation moduli calculated by Eq. (5-9).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Muscovite</th>
<th>Muscovite</th>
<th>Phlogopite</th>
<th>Phlogopite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>181</td>
<td>176.5</td>
<td>186.0</td>
<td>179.0</td>
</tr>
<tr>
<td>$C_{33}$ (GPa)</td>
<td>58.6</td>
<td>60.9</td>
<td>54.0</td>
<td>51.7</td>
</tr>
<tr>
<td>$C_{44}$ (GPa)</td>
<td>16.5</td>
<td>15.0</td>
<td>5.8</td>
<td>5.6</td>
</tr>
<tr>
<td>$C_{13}$ (GPa)</td>
<td>25.6</td>
<td>20.0</td>
<td>11.6</td>
<td>25.8</td>
</tr>
<tr>
<td>$C_{31}$ (GPa)</td>
<td>103.0</td>
<td>103.7</td>
<td>100.2</td>
<td>96.2</td>
</tr>
<tr>
<td>Cal. $E_z$ (GPa)</td>
<td>52.9</td>
<td>52.3</td>
<td>32.3</td>
<td>30.2</td>
</tr>
</tbody>
</table>

There are no data reported in literature with respect to the elastic constants of margarite, talc, and pyrophyllite. However, one paper by Broz et al. (2006) reported the elastic modulus and hardness of talc by nanoindentation testing method. Since the hardness data are very limited, only the moduli data are compared (Table 5-6).

The indentation modulus of phlogopite agrees well with the estimated value. However, the measured indentation modulus of muscovite is higher than that obtained with Eq. (5-9). This could be caused by the validity of the assumption of taking muscovite as transverse and linear elastic material. The modulus of talc obtained by Broz et al. (2006) is much lower than that
tested in this study. The main reason is that the author used the common Oliver & Pharr’s method, and the modulus was determined based on the unloading from the maximum load. The possible “pop-ins” which occurred before the maximum load gave rise to the increment of the contact depth, subsequently leading to the amplified contact area and underestimated hardness. By contrast, the dynamic contact module (DCM) with high load and displacement resolutions was used in this study. In addition, the continuous stiffness measurement (CSM) was adopted as well as a higher data acquisition frequency aiming to capture “pop-ins” as many as possible. The modulus was determined at the peak hardness and before visible “pop-ins”.

Table 5-6 Comparison of elastic modulus $E$

<table>
<thead>
<tr>
<th>Mineral</th>
<th>This study</th>
<th>Literature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Margarite</td>
<td>157.7 GPa</td>
<td>N/A</td>
<td>Vaughan and Guggenheim (1986)</td>
</tr>
<tr>
<td>Muscovite</td>
<td>77.9 GPa</td>
<td>52.9 GPa</td>
<td>McNeil and Grimsditch (1993)</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>35.7 GPa</td>
<td>30.2-32.3 GPa</td>
<td>Aleksandrov and Prodaivoda (1993)</td>
</tr>
<tr>
<td>Talc-1$T_c$</td>
<td>26.8 GPa</td>
<td>16.2 ± 6.6 GPa</td>
<td>Broz et al. (2006)</td>
</tr>
<tr>
<td>Pyrophyllite-1$T_c$</td>
<td>19.4 GPa</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

5.5 Conclusions

The rigorous nanoindentation testing scheme described above increases the reliability of the test results for macrocrystalline samples of margarite, muscovite, phlogopite, talc, and pyrophyllite. Each mineral exhibits different resistance to indentation penetration. There are relatively giant “pop-ins” for margarite and muscovite corresponding to indentation depths less than 26 nm. No visible ones, however, occurred with talc and pyrophyllite. Higher interlayer bonding strength may suppress the occurrence of initial layer delamination or radial cracking than lower interlayer bonding strength.

The indentation elastic moduli of margarite, muscovite, phlogopite, talc and pyrophyllite were determined to be 157.7 GPa, 77.9 GPa, 35.7 GPa, 26.8 GPa, and 19.4 GPa, respectively, and the indentation hardness as 15.4 GPa, 9.4 GPa, 5.1 GPa, 3.9 GPa, and 4.6 GPa, respectively. Both modulus and hardness of dioctahedral minerals increase with the layer charge through different second order polynomial functions. The cations in octahedral sheet significantly affect the mechanical properties.

The mechanical properties of these six minerals obtained in this study do not agree well with the limited data in literature. This results from not only the differences of the test approaches, but also the data analysis methods. It is important to correlate the indentation parameters to commonly used mechanical parameters. To achieve this object, a good reference material which can be well tested by recognized methods is to be selected. For clay minerals, a mineral with a highly crystalline structures whose structural features are consistent, and with particle sizes large enough which can be easily handled by nanoindentation and at least one conventional testing method maybe be a good choice. Muscovite is a preferable reference material for this purpose. The nanoindentation modulus and hardness in a specific direction have been reported in literature, but the corresponding modulus and hardness determined by conventional testing methods (e.g., uniaxial compression) have not been done. The main obstacles arise from the
difficulties in preparing the sample and the availability of the instrument providing high pressure and high load and deformation resolutions. However, as the instruments are developed, a uniaxial compression test using a flat head indenter on a reference material column, which is carefully prepared with a flat surface and bottom (e.g., focused ion beam (FIB) is used), will greatly contribute to bridging the nanoindentation data with the conventional mechanical data. This will widely broaden the application of nanoindentation techniques.

5.6 References


CHAPTER 6. NANOINDENTATION OF ORIENTED CLAY MINERAL FILMS

6.1 Introduction

Clay minerals in geosphere are formed by physical and chemical processes of weathering (Mitchell and Soga, 2005), and mostly exist as aggregate forms bonded by various materials. Understanding mechanical behavior of aggregated clay particles will contribute to traditional soil mechanics and other areas in which clay minerals are important. Recently, clay minerals have been widely used in fabrication of composites with improved mechanical properties (Kojima et al., 1993; Beake et al., 2002; Podsiadlo et al., 2007; Ou et al., 2007), to enhance thermal stability (Tjong et al., 2002; Kim et al., 2005), and to construct functional barriers (Eckle and Decher, 2001; Ammala et al., 2005; Lutkenhaus et al., 2007; Szabo et al., 2007). The most commonly used clay minerals are small-sized smectite (saponite, montmorillonite, synthetic hectorite, etc.), vermiculite, and kaolinite, and these minerals are usually dispersed into nanoscale clay platelets before incorporating into composites. However, ideal dispersion is difficult, and it is unavoidable that clay particles aggregates are always present. Understanding properties of clay aggregates will facilitate design and fabrication of clay-involved composites.

In addition, since it is difficult to obtain well-crystallized particles of kaolinite, smectite and illite with particle sizes large enough to be readily handled even by advanced experimental techniques like nanoindentation, oriented aggregates films of these minerals provide an alternative way to study their mechanical properties indirectly.

In this chapter, nanoindentation, which is widely used in the characterization of mechanical properties of small scale bulk materials, thin films, coatings, and other nanomaterials, is used to study the mechanical behavior of oriented aggregated clay films (kaolinite, illite, and smectite) prepared by sedimentary deposition. Essential issues with respect to sample preparation, including substrate, clay concentration, and drying speed were studied. The elastic modulus and hardness of each film are determined using Oliver and Pharr’s method (Oliver and Pharr, 1992). The factors which affect the mechanical properties of the oriented aggregated clay films are discussed.

6.2 Materials and Methods

6.2.1 Sample Preparation

Three types of clay minerals (kaolinite, smectite, and illite) were purchased from The Clay Mineral Society’s Source Clays Repository (Purdue University, IN) (Table 6-1), and used for the preparation of oriented aggregated clay mineral films. In order to extract clay-sized (< 2 µm) suspension, 20 g of each clay power were first dispersed in 500 ml distilled deionized (DDI) water. For KGa-1b, 5 ml 0.1N NaOH solution was added as a dispersant. All the beakers were stirred on the Barnstead® Cimarec Stirring Hot Plate SP131325 (BarnsteadInternational, Dubuque, IA) for 10 minutes. Then the beakers were moved to a leveling table for further settling process. After each suspension settled for 205 minutes, the <2 µm equivalent spherical diameter clay fraction which stayed in the top 50 mm of the beaker was collected by Fisherbrand Motorized Pipet Dispenser (Fisher Scientific, Pittsburgh, PA) with Fisherbrand 50 ml serological
pipet (Fisher Scientific, Pittsburgh, PA). Then the residual samples were diluted again using DDI water for further extraction. The extraction procedure was repeated several times until the concentration of the collected suspension significantly reduced.

Table 6-1 Minerals used for preparation of oriented clay aggregate films

<table>
<thead>
<tr>
<th>Source Clay</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGa-1b (Kaolinite)</td>
<td>Washington County, Georgia, USA</td>
</tr>
<tr>
<td>SWy-2 (Na-rich montmorillonite)</td>
<td>Crook County, Wyoming, USA</td>
</tr>
<tr>
<td>STx-1b (Ca-rich montmorillonite)</td>
<td>Gonzales County, Texas, USA</td>
</tr>
<tr>
<td>IMt-1 (Illite-Cambrianshale)</td>
<td>Silver Hill, Montana, USA</td>
</tr>
</tbody>
</table>

It is noteworthy that the particle size determined by the above method is based on the application of Stoke’s law in which the settling velocity of spherical particles is expressed as:

\[
\frac{\gamma_s - \gamma_w}{18\mu} D^2
\]

(6-1)

where \(\gamma_s\) is the unit weight of particles, \(\gamma_w\) is the unit weight of liquid, \(\mu\) is the viscosity of liquid, \(D\) is the diameter of sphere. However, clay particles are actually in planar shape instead of spherical ones. Therefore, the sizes determined according to Stoke’s law are not actual particle diameters, but rather, equivalent spherical diameters (e.s.d.).

For KGa-1b suspension, an additional rinsing step is needed to remove Na\(^+\) ions which were introduced with dispersant. Six 15 ml centrifuge tubes filled with KGa-1b suspension were installed into centrifuge chamber (Centrifuge Model 228, Fisher Scientific, Pittsburgh, PA) and centrifuged for 30 minutes. Then the top clear portion of the tubes was decanted and more DDI water was added. The diluted samples were centrifuged again. This process was repeated three times. The residual portion in the centrifuge tubes was transferred into a flask, and DDI water was used to clean the tubes. The same stirring method as above was used to make a uniform KGa-1b suspension.

Concentration of the clay fraction in each sample suspension was then determined. Eppendorf® Pipette Series 2100 (Eppendorf North America, Inc., Westbury, NY) attached with a 1000 \(\mu\)L pipette tip was used to extract a certain amount of clay suspension, and then the clay suspension was dispensed into a 15×45 mm glass vial (Fisher Scientific, Pittsburgh, PA). A new pipette tip is used for each extraction in order to avoid cross-contamination between minerals. The vials were covered with clean wipers (Kimwipes®, Kimberly-Clark, Dallas, TX) and dried in an oven at 105 °C for 24 hrs. The clay concentration was determined based on the weight measurement on the Voyager® analytical balance (Ohaus Corporation, Pine Brook, NJ) with 0.1 mg readability.

The extracted clay suspension of each mineral was used to prepare clay suspension with a predetermined clay concentration which could avoid film peeling as much as possible. The factors which could cause film peeling mainly include clay concentration, drying speed, substrate surface features (e.g., cleanness, roughness, and chemical properties), film thickness, and particle segregation (Gibbs, 1965; Paterson et al., 1980). In order to exclude as many factors as possible which could affect film structures and subsequent mechanical properties, drying speed for each
film was controlled by placing film in the same desiccator with desiccant for 7 days, and film thickness was controlled by dropping clay suspension as much as possible on the same size of substrate until the substrate could not accommodate any more.

To select an appropriate substrate, Lakeside® glass side (1"×1/16", Hugh & Courtright Co.), VWR precleaned plain micro slide (3"×1", 1.2 mm thick, VWR International, USA), Hydrophilic circle glass slide (HR3-207T, Hampton Research Corp., Aliso Viejo, CA), and Si (100) wafer (10mm×10mm, MTI Corporation, Richmond, CA) were initially used to prepare kaolinite and montmorillonite (SWy-2) films. The results showed that Si (100) wafer was the best one on which film peeling occurred to a minimum degree. Therefore, Si (100) wafer was used for all the following tests in selecting an appropriate clay suspension.

Provided that drying speed, substrate, and dropping method are controlled as described above, a relatively ideal clay concentration with which film peeling could be avoided was obtained. Kaolinite KG1-1b and smectite SWy-2 were chosen as the representatives of 1:1 layer and 2:1 layer minerals in optimizing clay concentration. The clay suspension with clay concentration of 5 mg/ml, 10 mg/ml, 20 mg/ml, and 50 mg/ml of each mineral was first prepared from the extracted clay suspension by adding calculated amount of DDI water. Eppendorf® Pipette Series 2100 attached with 1000 µL pipette tip was used to extract a full tip amount of clay suspension, and then the clay suspension was carefully dropped on Si (100) wafers which were placed on a Scienceware® Leveling table (Bel-Art Products, Pequannock, NJ). The films were first air-dried at ambient temperature until no flowing suspension on the top surface, and then moved to a desiccator for further drying process. The film peeling conditions were checked after 7 days in desiccator as shown in Table 6-2.

Table 6-2 Film peeling conditions with different clay concentration

<table>
<thead>
<tr>
<th>Clay Concentration (mg/ml)</th>
<th>Estimated Thickness (µm)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>KGa-1b 5</td>
<td>N/A</td>
<td>Too thin</td>
</tr>
<tr>
<td>10</td>
<td>5-10</td>
<td>good</td>
</tr>
<tr>
<td>20</td>
<td>15-25</td>
<td>better</td>
</tr>
<tr>
<td>50</td>
<td>30-40</td>
<td>worst</td>
</tr>
<tr>
<td>SWy-2 5</td>
<td>N/A</td>
<td>Too thin</td>
</tr>
<tr>
<td>10</td>
<td>5-10</td>
<td>good</td>
</tr>
<tr>
<td>20</td>
<td>15-25</td>
<td>better</td>
</tr>
<tr>
<td>50</td>
<td>30-40</td>
<td>worst</td>
</tr>
</tbody>
</table>

Table 6-2 showed that clay concentration of ~20 mg/ml was a better choice for both minerals to avoid film peeling phenomenon. In considering nanoindentation tests, clay concentration of 30 mg/ml was selected for all of the four minerals in order that thicker clay aggregate films could be prepared aiming to exclude substrate influence on nanoindentation results. The same dropping and drying procedure as described above was applied to prepare oriented aggregated clay mineral films of KGa-1b, IMt-1, STX-1b, and SWy-2. Fig. 6-1 shows the samples on the leveling table after clay suspension was dropped. In order to eliminate the influence of high temperature (~ 130 °C), which is required to glue the substrate to the aluminum puck for subsequent nanoindentation tests, each Si (100) substrate wafer was first glued to the aluminum puck as described in Chapter 4, and then cooled down to room temperature before accepting clay suspension. Two samples for each mineral were prepared.
6.2.2 X-ray Diffraction (XRD)

To verify the source minerals for preparing oriented aggregated clay mineral films, XRD patterns of the above four clay mineral films were collected in a Siemens D-5000 diffractometer using Cu-Kα radiation generated at 40 kV and 30 mA and a scan range of 2-34° 2θ. All scans employed sample spinning and a 0.996° divergence slit, 0.501° scatter slit, 0.1 mm receiving slit, a speed of 1° 2θ/min, and a step size of 0.02° 2θ.

6.2.3 Atomic Force Microscopy (AFM)

Before nanoindentation tests, all the films were first scanned using a 5500 Scanning Probe Microscope (Agilent Technologies, Inc., Chandler, AZ) at ambient temperature in contact mode with a PointProbe® Plus silicon tip (Nanosensors, Neuchatel, Switzerland) with tip height 10-15 μm. The scan resolution is 1024 pixels × 1024 pixels, set point 1.000V, and scan rate 1.0Hz. Surface roughness of each sample was used to choose either XP head (high load and large displacement limit but low resolution) or DCM head (low load and small displacement limit but high resolution). The roughness parameter $R_a$, the arithmetic average of absolute values $y_i$, where $y_i$ is the vertical distance from the mean line to the $i^{th}$ data point, is used to characterize surface topography (ASME, 2002):

$$R_a = \frac{1}{n} \sum_{i=1}^{n} |y_i|$$  \hspace{1cm} (6-2)

where $n$ is the total tracing number within a specific area.
6.2.4 Nanoindentation

Nanoindentation experiments were performed on the four desiccator-dried (~23 °C) and four oven-dried (105 °C for 48 hrs) samples using an MTS Nano XP indenter (MTS Nano Instruments, Inc., Oak Ridge, TN) under strain rate control mode at room temperature. XP mode equipped with a diamond Berkovich indenter (with a tip radius of < 20 nm) and continuous stiffness measurement (CSM) was used. This XP head has a load resolution of 50 nN and displacement resolution < 0.01 nm. Maximum load and maximum indentation depth of XP head are 500 mN and 500 µm, respectively. For comparison purpose, all the tests were set up with a constant allowable thermal drift rate of 0.03 nm/s and a constant indentation strain rate \((dh/dt)/h = 0.05\) 1/s, where \(h\) is the indentation depth, and \(t\) is the loading time.

The loading profile shown in Fig. 6-2 was used for all tests, consisting of five steps: (1) increasing load to a specified maximum indentation depth \(h_{\text{max}}\) at a constant indentation strain rate 0.05 1/s; (2) holding \(F_{\text{max}}\) constant for a given hold time, \(t_h = 10\) s; (3) decreasing load linearly to 10% of \(F_{\text{max}}\) at the same loading rate as that at \(F_{\text{max}}\); (4) holding the load constant for 100 seconds to record the thermal drift of the instrument; and (5) decreasing linearly the load to zero.

![Fig. 6-2 CSM loading profile with constant indentation loading rate = 0.05 s\(^{-1}\) and hold time =10 s.](image)

The rigorous testing scheme described in Chapter 5 was applied in order to ensure high reliability and accuracy of the test data. A total of 16 indentation tests for each film sample formed under each condition were conducted in a 4 ×4 array uniformly spaced at 100 µm apart. Elastic modulus \(E\) and hardness \(H\) of the tested films were calculated following the method proposed by Oliver and Pharr (1992), which were expressed in Eq. (2-11) and Eq. (2-14). An identical Poisson’s ration \(\nu = 0.25\) was used for all samples.
6.3 Results

6.3.1 X-ray Diffraction Patterns

Since all the source minerals were purchased from the Clay Mineral Society and these minerals have been identified using XRD method by many researchers, only XRD patterns of air-dried (AD) and ethylene glycol-solvated (EG) samples were obtained to confirm the identity of the materials. Fig. 6-3 presents the XRD patterns of KGa-1b and IMt-1. The sharp peak at 0.718 nm observed under both AD and EG conditions of KGa-1b indicate that the minerals could be kaolinite or chlorite. But the peak 0.358 nm instead of 0.354 nm excludes the possibility of chlorite (Biscaye, 1965). Therefore KGa-1b is identified as kaolinite. For IMt-1 mineral, the intense 1.0 nm peak of (001) reflection and a 0.33nm peak of (003) reflection that remain unaltered by ethylene glycol salvation indicate that the mineral could be illite or glauconite, but all belong to illite group.

![XRD patterns of IMt-1 and KGa-1b](image)

Fig. 6-3 XRD patterns of IMt-1 and KGa-1b under air-dried (AD) and ethylene glycol (EG) solvated conditions.

Fig. 6-4 shows the XRD patterns of SWy-2 and STx-1 under air-dried and ethylene glycol salvation conditions. For both minerals, when saturated with ethylene glycol, the basal (001) reflection swell to ~ 1.7 nm represented by relatively sharp peaks. Expected high-order peaks under EG were also observed. This indicates that these minerals belong to smectite group whose expandability varies with humidity and exposure to certain organic molecules. Further identifications of these minerals including heat treatment and cation exchange are not conducted in this dissertation, which are not the main objectives herein.
6.3.2 Surface Roughness

Influence of surface roughness of a specimen on the nanoindentation results has been widely reported. In particular, asperity contact with the indenter at shallow indentation depth results in relatively large uncertainties in the determination of the contact area, subsequently affect elastic modulus and hardness. To reduce the uncertainties, a relatively larger indentation depth is required. Fischer-Cripps (2004) shows that the indentation depth should be made at least 20 times $R_a$ in order to obtain an uncertainty of the indentation depth less than 5 % of the indentation depth.

Fig. 6-5 presents the AFM images of the four samples under desiccator-dried condition as well as the surface roughness $R_a$ calculated by software Gwyddion Version 2.9, a modular program for SPM (scanning probe microscopy) data visualization and analysis. The surface topography of KGa-1b film shown in Fig. 6-5 (a) is not clearly presented. This is mainly due to the so weak interaction among clay particles that even the small scanning force applied by the scanning tip could move the surface particles. Fig. 6-5 (b) clearly shows that illite particles are oriented in the horizontal direction, and the particles exhibit flat basal surfaces with maximum dimensions of ~ 900 nm. Particles of STx-1b shown in Fig. 6-5 (c) exhibit the smallest roughness. SWy-2 film in Fig. 6-5 (d) shows that more particles stack together forming larger “blocks” separated by visible “microvalleys’. Based on the obtained surface roughness, the maximum indentation depth was selected as 3000 nm.
Fig. 6-5 AFM images of surface of oriented aggregated clay minerals (a) KGa-1b, (b) IMt-1, (c) STx-1b, and (d) SWy-2. $R_a$ is surface roughness parameter.

The AFM images of the residual indents after nanoindentation tests could not be obtained although much effort was made. The main reason is that it is very difficult to locate the indentation positions after the sample was transferred from Nano Indenter XP stage to the AFM instrument platform.
6.3.3 Nanoindentation Behavior

Fig. 6-6 plots the average load-displacement curves of 16 tests during loading portion of each oriented aggregated clay films under desiccator-dried and oven-dried conditions. In general, 2:1 layer clay minerals offer higher penetration resistance than the 1:1 layer mineral (KGa-1b). No considerable difference of load-displacement behavior was observed between desiccator-dried and oven-dried condition for the three samples, excluding SWy-2.

Average elastic modulus and hardness of each sample (16 tests) are presented in Fig. 6-7 and Fig. 6-8. Under both desiccator-dried and oven-dried conditions, there exists a common tendency that the average modulus and hardness decrease from source mineral SWy-2, STx-1b, IMt-1, to KGa-1b, which is consistent with the load-displacement response. Both elastic modulus and hardness of each film decrease as the indentation depth increases. At initial indentation region, all the films exhibit much higher modulus and hardness which is against the expectation when real topography of film surface is considered. Individual layers or aggregate of corresponding minerals at the uppermost of the film dominates the mechanical response at shallow indentation depth. As the indenter penetrates the film more deeply, the mechanical response mainly results from the movement of particles which give rise to relatively lower modulus and hardness. The modulus and hardness at this stage are almost independent of indentation depth, which is much like the mechanical behavior of isotropic materials. For the comparison purpose, the modulus and hardness of each film were obtained by statistical analysis of the data between indentation depth 1000 nm to 2000 nm. Table 6-3 presents the summary of modulus and hardness obtained.
Fig. 6-7 Average modulus of oriented aggregated clay mineral films with constant indentation strain rate = 0.05 s$^{-1}$. Blue and black denotes desiccator-dried and oven-dried conditions, respectively.

Fig. 6-8 Average hardness of oriented aggregated clay mineral films with constant indentation strain rate = 0.05 s$^{-1}$. Blue and black denotes desiccator-dried and oven-dried conditions, respectively.
Table 6-3 Summary of modulus and hardness of oriented aggregate film

<table>
<thead>
<tr>
<th>Source minerals</th>
<th>Desiccator-dried</th>
<th>Oven-dried</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$ (GPa)</td>
<td>$H$ (MPa)</td>
</tr>
<tr>
<td>KGa-1b</td>
<td>0.46 ± 0.01</td>
<td>7.10 ± 0.30</td>
</tr>
<tr>
<td>IMt-1</td>
<td>0.70 ± 0.02</td>
<td>18.00 ± 2.00</td>
</tr>
<tr>
<td>STx-1b</td>
<td>1.46 ± 0.01</td>
<td>49.00 ± 1.00</td>
</tr>
<tr>
<td>SWy-2</td>
<td>2.61 ± 0.07</td>
<td>91.00 ± 4.00</td>
</tr>
</tbody>
</table>

Note: The modulus and hardness are reported as “mean ± standard deviation”.

6.4 Discussion

6.4.1 Particle Arrangements and Associations

The modulus and hardness of oriented aggregated clay films presented in Table 6-3 demonstrate a large difference among different source minerals. Comparison of modulus and hardness among different source minerals are shown in Fig. 6-9. The different mechanical behavior mainly results from the differences of the clay particle arrangements and interparticle associations for each film. Since the clay suspension, which was used to build oriented aggregated film by deposition method, was prepared by either pure DDI water without addition of any chemicals (for SWy-2, STx-1b, and IMt-1) or pure DDI water with dispersant (0.1 N NaOH) but with postrinsing steps (for KG1-1b), the influence of electrolyte concentration of the clay suspension on the particle arrangements and associations can be assumed as identical for all the samples, and the properties of each source mineral should dominate.

![Fig. 6-9 Comparison of (a) elastic modulus and (b) hardness of oriented aggregated clay mineral films. RT denotes desiccator-dried condition. Error bar denotes standard deviation.](image-url)
KGa-1b is mainly composed of flat and thick pseudohexagonal platy-shaped particles (Pruett and Webb, 1993). Within a particle, the layers are bonded to each other by hydrogen bonding between oxygens of the tetrahedral sheet and the hydroxyls of the next octahedral sheet, the microstructure of the particle is not supposed to be changed at desiccator-dried and oven-dried conditions due to the absence of water in the interlayers. The two outermost planes of each particle, which consist of the plane formed by the oxygens of the basal surfaces of the Si tetrahedral and the plane formed by the hydroxyls of the Al octahedral, are relatively chemically unreactive. Therefore, the interactions between successive platy particles with the preferred orientation in a film mainly result from the physical contacts, and these interactions are weak compared with those with unsatisfied surface charges. Consequently, such intraparticle and interparticle force systems give rise to a relatively loose microstructure of a film, which are demonstrated by the lowest resistance to penetration as well as lowest modulus and hardness.

IMt-1 is a 2:1 layer mineral with a crystal structure similar to muscovite. A net negative layer charge of 0.84 (CMS, 2009) is mainly derived from the charge imbalance caused by substitution of Al$^{3+}$ for Si$^{4+}$ in tetrahedral sheets. This negative layer charge is consequently balanced by the cations (most commonly potassium K) that are located in a plane between the successive layers. No inclusion of water molecules H$_2$O between successive layers leads to the almost identical mechanical response under desiccator-dried and oven-dried conditions. For an individual IMt-1 particle, both of the two outermost planes are formed by the oxygens of the basal surfaces of the Si tetrahedral sheets. However, surface charge of these two planes in certain regions is not satisfied due to cleavage of particles. This unbalanced surface charge as well as the edge charge gives stronger interparticle connections than that of KGa-1b in oriented aggregated films as presented by nanoindentation behavior.

SWy-2 and STx-1b are Na-rich and Ca-rich montmorillonite, respectively, belonging to the dioctahedral smectite group. The layer charge of these two minerals ranging from 0.2 to 0.6 per formula unit (Bailey, 1980; Borchardt, 1989) is mainly generated by the substitution of Mg$^{2+}$ for Al$^{3+}$ in the octahedral sheets, and balanced by interlayer hydrated cations, Na$^+$ or Ca$^{2+}$. The hydration degree of these interlayer cations is very sensitive to moisture condition, which is considered as one of the main reasons for the large discrepancy of mechanical behavior of the films formed under desiccator-dried and oven-dried conditions.

The higher modulus and hardness of SWy-2 than for STx-1b shown in Fig. 6-9 may result from the more surface contacts of particles in SWy-2 film than those of STx-1b film. STx-1b is Ca-rich montmorillonite of which the particles are usually made of several layers, while SWy-2 is Na-rich montmorillonite which exists as particles with much thinner layers (Mitchell and Soga, 2005). Therefore, STx-1b particles exhibit much higher average bending stiffness than that of SWy-2. The lower bending stiffness of SWy-2 particles renders the subsequently deposited particles to adapt themselves to the existing particle surface, and more surface contacts among particles are created than STx-1b. More surface contacts than point contacts of particles will significantly cause the aggregate films to work as an integral unit, and the films will exhibit higher modulus and hardness.
6.4.2 Film Porosity

All the oriented aggregate films in this chapter were prepared under ambient pressure by a sedimentation method. Even though there is not an effective method to determine the porosity of such thin films, it is reasonable to expect that the porosity of each film should approximate to the upper bound compared with that with higher pressure. It is found that elastic modulus of porous solids is dependent on the porosity (Nielsen, 1970) for a specific material. Therefore, the modulus of the films formed in this dissertation should be close to the lower bound due to the higher corresponding porosity. Osipov and Sokolov (1978) reported the sediment porosity of kaolinite, illite, and montmorillonite, which were 96 %, 90 %, and 83 %, respectively, when they sediment in distilled water which is comparable with the condition used in this dissertation. The descending order of moduli of montmorillonite (SWy-2, STx-1), illite (IMt-1), and kaolinite (KGa-1b) under both desiccator-dried and oven-dried conditions shown in Table 6-3 is in agreement with the ascending order of their porosity. Dependence of modulus on porosity of kaolinite and smectite was also reported by Vanorio et al. (2003) and Mondol et al. (2008). Furthermore, if the above film porosities are assumed, the corresponding packing volume fraction will be 4 % for kaolinite, 10 % for illite, and 17 % for montmorillonite. These values are far lower than the maximum packing volume fraction of particles, which is about 82% (Berryman, 1983). This gives rise to much lower modulus and hardness than those of their crystals which have 100 % packing density.

Cementitious materials are not introduced in the aggregate films in this dissertation which is not the case in practice. However, the tests in this chapter provide basic information for further studies on the functions of various cementitious materials in reality.

6.5 Conclusions

Nanoindentation test results on oriented clay films show an increase of modulus and hardness from kaolinite (KGa-1b), illite (IMt-1), to montmorillonite (SWy-2, STx-1b), which is mainly caused by particle arrangements and associations. Much lower modulus and hardness of these oriented aggregated clay films mainly result from the higher film porosities compared with the highest packing density of particles.

Since clay particle arrangements and associations dominate the mechanical properties of oriented aggregated clay films, which are easily determined by nanoindentation testing, nanoindentation technique provides an alternative to deduce details of the depositional and postdepositional history of a deposit which are closely related to structural information.

6.6 References


CHAPTER 7. NANOINDENTATION ON CLAY-BASED NANOSTRUCTURED MULTILAYERS

7.1 Introduction

Clay minerals used as fillers in making composites have been widely reported in which clay minerals are most often exfoliated as nanoscaled clay platelets with thickness around ~ 1 nm. High aspect ratio and nearly free defects of such clay platelets attribute to the enhancement of the composite mechanical properties (Kojima et al., 1993; Beake et al., 2002; Tjong et al., 2002; Ou et al 2007), permeability improvement (Ammala et al., 2005), and ion transport blocking barrier (Lutkenhaus et al 2007). Smectite group minerals, which have intrinsic negative surface charges enabling them to strongly interact with oppositely charged materials, offer greater advantages in clay-based composites. In particular, exfoliated smectite platelets can be used as an ideal nanoscaled constituent to fabricate nanocomposites which have modified properties or functionalities.

Clay-based multilayers with desirable mechanical properties and versatile functionalities, in which smectite minerals are often used, are one of the most important objectives of present-day materials research. The most common method for making clay-based nanostructured multilayers is the layer-by-layer (LbL) self-assembly method (Decher, 1997; Podsiadlo et al., 2007), which is a bottom-up process based on sequential adsorption of nanometer-thick monolayers of oppositely charged constituents (e.g. polyelectrolytes, charged nanoparticles, and biological macromolecules) to form a multilayered structure with nanometer-level control over the architecture. It is a simple, versatile, low-cost and low-temperature fabrication method to produce nanostructured thin films with desirable properties. The exfoliated clay platelet is used an anionic component during this process to make clay-based nanostructured multilayers.

Clay-oxide nanostructured multilayers prepared by a novel LbL deposition technique (Arco and Luo, 2008) have been reported recently by Chen et al. (2008). In their study, nanostructured clay-zirconia multilayers were fabricated by sequentially dipping a substrate in an exfoliated nanoclay (montmorillonite) suspension and a zirconia cationic precursor solution followed by annealing at elevated temperatures. It was found that nanoscale LbL growth is achievable, and the annealed films remain uniform and crack-free. This indicates that a variety of nanostructured clay-oxide multilayers with graded functionalities can be conveniently manufactured by changing the composition or concentration of oxide cationic precursor solutions periodically or continuously.

To facilitate this promising research forward, the mechanical properties, one of the most important aspects for a new material, of the clay-based nanostructured multilayers prepared under as-deposited and annealing conditions need to be investigated. In this chapter, nanoindentation assisted by atomic force microscopy (AFM) and X-ray diffraction (XRD) was used to study the mechanical properties of clay-oxide thin films. The influential factors including postdeposition condition and clay concentration on the mechanical properties are analyzed, and issues with respect to design of desirable clay-oxide nanostructured multilayers are discussed.
All the clay-based multilayer samples used in nanoindentation tests were prepared by Dr. Luo’s group (Clemson University, SC) who is the collaborative partner of this research. Nanoindentation, AFM imaging, and XRD were conducted in Louisiana State University.

7.2 Materials and Methods

7.2.1 Sample Preparation

All the films in this paper, including (ZrO\(_2\))\(_{30}\), (ZrO\(_2\)-MMT)\(_{30}\), (ZrO\(_2\)-MMT)\(_{60}\), (SnO\(_2\)-MMT)\(_{30}\), and (ZrO\(_2\)-MMT-SnO\(_2\)-MMT)\(_{15}\) multilayer films, were prepared via a layer-by-layer (LbL) deposition process. Each kind of film except zirconia film was studied as-deposited and after annealed at 400 ºC and/or 600 ºC. Epi-polished silicon wafer with thermally oxidized surface layers (SiO\(_2\)/Si) (Entegris Inc., CA, USA), which is preferred for the wet chemical synthesis due to its relatively non-reactive SiO\(_2\) surface, was used as substrate for all the films.

Zirconia films were prepared by following a similar procedure described in Arcot and Luo (2008). The Si/SiO\(_2\) wafers were ultrasonically cleaned in 0.1 M NaOH solution for 20 minutes, immersed into piranha solution (3 vol. of 95–98 wt.% H\(_2\)SO\(_4\) : 1 vol. of 30 wt.% H\(_2\)O\(_2\)) for 20 minutes, rinsed with deionized water 4 times and dried in air. A NIMA® automatic dip coater (Nima Technology Ltd., Coventry, UK) was used to deposit thin films via the LbL deposition process. The substrates were alternately dipped into 0.06 M Zr\(^{4+}\) aqueous cationic precursor solution prepared from zirconium (IV) acetate hydroxide (Sigma-Aldrich, Saint Louis, MO, USA) and into 1.0 M aqueous ammonium hydroxide (NH\(_4\)OH) anionic precursor solution at a constant advance and withdrawing dipping speeds of 20 mm per minute, which finished a deposition cycle. The holding time was 45 s in both anionic and cationic precursor solutions. Repeating the alternate deposition of 30 cycles gave an as-deposited (ZrO\(_2\))\(_{30}\) multilayered film, which was then isothermally annealed at 600 ºC for 2 hours in a box furnace. The ramped heating and cooling rates were 5 ºC per minute.

A similar LbL deposition technique was used to prepare clay-zirconia multilayered films (Chen et al., 2008). The Si/SiO\(_2\) wafers were cleaned using the same method described above. Sodium-rich montmorillonite (Na-MMT) clay minerals, Cloisite® Na\(^+\) and SWy-2, which were obtained from Southern Clay Products Inc., Gonzales, TX and The Clay Minerals Society Source Clay Repository (Purdue University, West Lafayette, IN) respectively, were used to prepare 0.03 wt.% and 0.4 wt.% clay suspensions. The clay samples were first stirred with magnet at 1000 rpm speed in deionized water for 20 minutes and then ultrasonicated for 20 minutes to achieve complete dispersion and exfoliation. The pre-cleaned substrates were dipped using the same dip coater into a 0.1 M zirconium cationic precursor solution (pH = 4.14) prepared from zirconium (IV) acetate hydroxide and into the exfoliated clay suspension alternately without interdipping rinsing. Both the dipping and withdrawing speeds were controlled at 20 mm per minute. The holding time was kept 45 seconds in air, Zr precursor solution, and clay suspension. The deposition cycle was repeated 30/60 times to prepare a (clay-ZrO\(_2\))\(_{30/60}\) multilayered film. After completing 30/60 deposition cycles, the substrate was then air-dried at room temperature to form the as-deposited (clay-ZrO\(_2\))\(_{30/60}\) films and further annealed isothermally to 400 or 600 ºC for 2 hours to form the annealed (clay-ZrO\(_2\))\(_{30/60}\) films. A constant heating and cooling rate of 5 ºC per minute were used during annealing.
Clay-Tin oxide films (SnO$_2$)$_{30}$ and (ZrO$_2$-Clay-SnO$_2$-Clay)$_{15}$ multilayer films were prepared with the same method as clay-zirconia films with clay solution of 0.4 wt.%. The cationic precursor solution of 0.05 M SnCl$_2$ was used for corresponding dipping process. The two types of multilayers were obtained as being as-deposited, annealed at 400 ºC and annealed at 600 ºC.

Table 7-1 is the summary of the samples prepared.

<table>
<thead>
<tr>
<th>Film</th>
<th>Clay concentration wt.%</th>
<th>Formed condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{30}$</td>
<td>0.03</td>
<td>As-deposited</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>Annealed at 600 ºC</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{60}$</td>
<td>0.03</td>
<td>As-deposited</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>Annealed at 600 ºC</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{60}$*</td>
<td>0.03</td>
<td>As-deposited</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>Annealed at 600 ºC</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{30}$</td>
<td>0.40</td>
<td>As-deposited</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 400 ºC</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 ºC</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{60}$</td>
<td>0.40</td>
<td>As-deposited</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 ºC</td>
</tr>
<tr>
<td>(ZnO$<em>2$-MMT)$</em>{30}$</td>
<td>0.40</td>
<td>As-deposited</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 400 ºC</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 ºC</td>
</tr>
<tr>
<td>(ZrO$_2$-MMT-SnO$<em>2$-MMT)$</em>{15}$</td>
<td>0.40</td>
<td>Annealed at 400 ºC</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 ºC</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{30}$</td>
<td>0.03</td>
<td>Annealed at 600 ºC</td>
</tr>
</tbody>
</table>

Note: clay suspension is settled 24 hrs before being used.

7.2.2 Nanoindentation Testing

Nanoindentation experiments were performed at room temperature (~24 ºC) on these samples using an MTS Nano XP indenter® equipped with a regular XP head and a dynamic contact module (DCM) head, which has the ability to perform continuous stiffness measurement (CSM) during indentation. The load and displacement resolution are 50 nN and <0.01 nm for XP mode and 1 nN and <0.00002 nm for DCM mode. Each head is installed with a diamond Berkovich indenter tip with a radius of <20 nm whose area function is calibrated prior to testing the samples. During calibration, 25 indentations under CSM mode at a constant strain rate (dh/hdt) of 0.05 1/s to a maximum indentation depth of 2000 nm (for XP mode) or 500 nm (for DCM mode) were performed on a standard fused silica sample with known properties (e.g., Young’s modulus is 72 GPa, Poisson’s ratio is 0.18) to calibrate the area function of both the XP and DCM indenter tips.

Before indentation testing, each film together with its substrate was mounted onto a cylindrical aluminum puck by a thin layer of Crystalbond 509 amber resin (Aremco Products Inc., NY, USA) which melted at 130 ºC on a hotplate. Each sample followed the same rigorous testing scheme in order to ensure high reliability and accuracy of the test data. (1) Tip cleaning: 9 indentations with monotonic loading and unloading were performed on a piece of Scotch double-sided sticky tape that was attached onto the top surface of an aluminum puck to clean the tip; (2) Film testing: a batch of indentations under XP and/or DCM mode were conducted on the film.
sample at locations following a pre-designed pattern, which consists of 15 indenting locations for each mode with a 3 × 5 array uniformly spaced at 150 µm apart. The indentation array of DCM mode has the same pattern as that of XP mode, but with 0.5 spacing shift, which aims to obtain comparable results from the same sample area under these two modes; (3) Tip checking: 9 indentations under CSM mode using the same testing conditions were made on the standard fused silica again to check the instrument working condition. If the measured modulus and hardness value deviate from the standard value significantly, the data obtained in Step 2 were discarded and a new measurement was made starting with Step 1. (4) Data screening: the 15 load-displacement curves recorded under each mode in Step 2 were plotted together to check their agreement. If large discrepancy exists, then all the data are discarded and indentations were repeated by selecting a new area of the film; if one or two curves shift away from the majority curves, then these curves were discarded and the rest of the data were regarded as acceptable.

The XP and DCM indentations followed the ISO 14577 method (ISO, 2002) under the load control mode, since no significant creep occurred within the peak load holding period during the preliminary indentation tests. For the 15 indentations under XP mode, the maximum load $F_{\text{max}}$ ranges from 500 mN to 0.39 mN, with each subsequent $F_{\text{max}}$ being 60% of the previous $F_{\text{max}}$. The same loading scheme was also used for the 15 DCM indentations, except that $F_{\text{max}}$ ranges from 10 mN to 0.008 mN. Each indentation was made on a different location in the array. For both modes, a trapezoidal loading profile was used for all indentations, consisting of five steps (Fig. 7-1): (1) increasing load linearly to a specified maximum value ($F_{\text{max}}$) at a constant loading rate with a loading time of 30 seconds; (2) holding $F_{\text{max}}$ constant for 10 seconds; (3) decreasing load linearly to 10% of $F_{\text{max}}$ at the same rate as loading; (4) holding the load constant for 60 seconds to record the thermal drift of the instrument; and (5) decreasing linearly the load to zero at the same loading rate used in Steps (1) and (3).

![Fig. 7-1 Schematic illustration of nanoindentation loading and unloading processes](image)

In addition, the silicon substrate was characterized by the DCM and CSM modes to obtain the substrate properties. A constant elastic modulus of 172.4 GPa and hardness of 12.28 GPa were obtained over the entire indentation depth by the Oliver and Pharr method.
7.2.3 Data Analysis Method

Determination of hardness and elastic modulus by nanoindentation is based on the mechanics of elastic contact and an assumption that the sample can be described as a semi-infinite, elastic-plastic half space. An elastic parameter, named reduced modulus \( E_r \) or effective modulus of the indenter-sample contact, can be obtained directly from the load-displacement curves through the following relationship (Sneddon, 1965):

\[
E_r = \frac{\sqrt{\pi}}{2\beta \sqrt{A_c}} S \tag{7-1}
\]

where \( \beta \) is a dimensionless correction factor for the indenter tip shape and \( \beta = 1.05 \) is commonly recommended (Oliver and Pharr, 2004); \( A_c \) is the projected contact area between the indenter and sample; \( S \) is the contact stiffness defined as the slope of the initial unloading curve at the maximum indentation depth \( (h_{max}) \) and is usually determined by fitting the beginning portion of the unloading curve using a linear or power law relationship, depending on indenter geometry. The function between the projected contact area \( A_c \) and contact depth \( h_c \) can be established by performing independent indentation tests on a standard material (e.g., fused silica) with known properties. Based on the observations that the resulting initial unloading curve is linear for flat punches (Doerner and Nix, 1986) and a power-law function for non-flat punches (Oliver and Pharr, 1992), and the assumption that in both cases the contact area remains constant during unloading, the contact depth \( h_c \) can be calculated as:

\[
h_c = h_{max} - \varepsilon \frac{F_{max}}{S} \tag{7-2}
\]

where \( \varepsilon \) is a constant that depends on indenter tip geometry (for Berkovich tip, \( \varepsilon = 0.75 \)), and \( F_{max} \) is the maximum load of an indentation.

The reduced modulus \( E_r \) obtained by the above procedures reflects the elastic contact interaction between the indenter tip and the sample. The following equation was proposed to extract the elastic modulus of the sample (Doerner and Nix, 1986):

\[
\frac{1}{E_r} = \frac{1-v_i^2}{E_i} + \frac{1-v_c^2}{E_c} \tag{7-3}
\]

where \( v_c \) and \( v_i \) are the Poisson’s ratio of the sample and indenter, respectively (for a diamond indenter, \( v_i = 0.07 \)); \( E_i \) and \( E_c \) are the elastic modulus of the indenter and sample, respectively (for a diamond indenter, \( E_i = 1141 \text{ GPa} \)). For the case of thin films in which the indented zone is affected by the underlying substrate, \( E_c \) represents the “mean” response of the film-substrate composite.

Indentation hardness (also called composite hardness for substrate-affected films) is determined as:
The above method has been widely used to determine the hardness and elastic modulus of small-scale bulk materials (it is called the Oliver and Pharr method when \( h_c \) is determined according to Eq. (7-2)). It also can be used for thin films on substrate provided that the maximum indentation depth is limited to a certain portion of the film thickness. A common rule is that the penetration depth is less than 10% of the film thickness. Otherwise the stiffness contribution of the substrate to the indenter-sample contact should be taken into consideration. Much effort has been devoted to the methods of extracting film modulus and hardness from the measured composite response of tip-film-substrate system. For example, the exponential weighting factors are introduced to divide the contributions of the film and substrate to the composite modulus by Doerner and Nix (1986), King (1987), and Saha and Nix (2002); Gao et al. (1992) derived a closed-form solution for the reduced modulus using a moduli-perturbation method of the film-substrate composite with respect to a rigid cylindrical punch indenting a layered linear elastic half space; Mencik et al. (1997) and Fischer-Cripps (2004) introduced a relatively straightforward procedure to determine film modulus \( E_f \) by simply extrapolating the best-fit curve of experimental data to zero \( h/t \) in the plot of the measured composite modulus \( E_c \) (Mencik et al., 1997) or reduced modulus \( E_r \) (Fischer-Cripps, 2004) against the relative indentation depth \( h/t \). Jung et al. (2004) extended the solution derived by Hu and Lawn (1998) for indentation with spheres on bilayer structures to the indentation with Berkovich and Vickers indenters to deconvolute the film properties in which the film-substrate composite modulus \( E_c \) was expressed as a power-law function. In this paper, the method proposed by Korsunsky et al. (1998) and Tuck et al. (2001) based on energy-based analysis of indentation testing is used to extract the film hardness \( H_f \):

\[
H_c = H_s + \frac{H_f - H_s}{1 + \left(\frac{h}{t} / \beta_0 \right)^X}
\]  

(7-5)

A similar method proposed by Wei et al. (2008) is used to obtain film modulus \( E_f \):

\[
E_c = E_s + \frac{E_f - E_s}{1 + \left[\frac{h}{t} / \beta_1 \right]^Y}
\]  

(7-6)

where \( \beta_0, \beta_1, X \) and \( Y \) are constants to be determined through curve-fitting of the experimentally determined \( H_c \) and \( E_c \), \( H_s \) and \( E_s \) are the substrate hardness and modulus, respectively. These two methods have been used to fit indentation data over a wide range of film materials covering hard films on soft substrates and soft films on hard substrates (Tuck et al., 2001; Wei et al., 2009). In this study, the film-substrate composite elastic modulus \( E_c \) and composite indentation hardness \( H_c \) were obtained using the nanoindenter control program TestWorks Explorer® based on the Oliver & Pharr (1992) method with an assumed Poisson’s ratio of 0.22 for all the films, which has no significant influence on the indentation results (Mencik et al. 1997; Saha and Nix, 2002). Deconvolution of film properties from composite hardness and modulus using Eq. (7-5) and Eq. (7-6) was achieved by a statistical analysis program SAS® Version 9.1.3 where nonlinear procedures and Newton iterative method were adopted. Inaccuracy of film thickness \( t \) used in normalizing indentation depth only causes the shift of the fitted curve along \( h/t \) axis, but does not
introduce errors to the fitted film hardness $H_f$ and modulus $E_f$ expected. This advantage avoids the time-consuming work on the determination of film thickness. Another advantage is that the fitted substrate $E_s$ and $H_s$ can be used to check the reliability and accuracy of the experiment data since these two parameters of the substrate can be easily obtained from literature or can be accurately determined by nanoindentation. Fig. 7-2 shows an example of experimental data fitting result using statistical analysis program SAS® Version 9.1.3 on the zirconia-MMT multilayers.

Fig. 7-2 Example of film modulus and hardness fitting on experimental data of (ZrO$_2$-MMT)$_{30}$ annealed at 600 °C with clay montmorillonite 0.4 wt.%. Fitted $E_f = 43.75 \pm 4.86$ GPa, $E_s = 169.60 \pm 7.83$ GPa, $H_f = 1.68 \pm 0.36$ GPa and $H_s = 12.50 \pm 0.56$ GPa.

7.2.4. Atomic Force Microscopy (AFM) Images

The surface morphology of the films was characterized using a 5500 Scanning Probe Microscope (Agilent Technologies, Inc., Chandler, AZ). The measurement was conducted in ambient temperature in contact mode with a PointProbe®Plus silicon tip with tip height 10-15 µm. The scan resolution is 512 pixels × 512 pixels, set point 1.000V and scan rate 1.0Hz. The most common used surface roughness parameter $R_a$, the arithmetic average of absolute values $y_i$, where $y_i$ is the vertical distance from the mean line to the $i^{th}$ data point, is used to characterize surface topography:

$$R_a = \frac{1}{n} \sum_{i=1}^{n} |y_i|$$

(7-7)

where $n$ is the total tracing number within a specific area.
The residual indent image scanned by AFM is used to characterize the indent behavior (e.g., pile-up/sink-in, delamination between layers and between film and substrate) in parallel with the corresponding load-displacement curve.

7.2.5 X-ray Diffraction (XRD)

Expandability of the clay-based multilayers formed under as-deposited and annealed conditions was investigated by X-ray diffraction. XRD patterns were collected in a Siemens D-5000 diffractometer using Cu-Kα radiation generated at 40 kV and 30 mA and a scan range of 2-34° 2θ. All scans employed sample spinning and a 0.996° divergence slit, 0.501° scatter slit, 0.1 mm receiving slit, a speed of 1° 2θ/min, and a step size of 0.02° 2θ.

7.3 Results

7.3.1 Typical Indentation Load-displacement Curves and Residual Images

The typical load-displacement curves and indent impressions of (SnO$_2$-MMT)$_{30}$ and (ZrO$_2$-MMT-SnO$_2$-MMT)$_{15}$ multilayers are shown in Fig. 7-3 and Fig. 7-4. The total indentation depth and residual depth under the same maximum load were greatly reduced as the annealing temperature increases for both multilayers. The indent images show that the apparent pile-up occurred around the contact impressions for the as-deposited films. A tendency of sink-in

![AFM images of typical indent impressions](image-url)

Fig. 7-3 AFM images of typical indent impressions of (a) as-deposited, (b) annealed at 400 °C, and (c) annealed at 600 °C for 2 hrs (SnO$_2$-MMT)$_{30}$ multilayers with MMT 0.4 wt.% and corresponding load-displacement curves.
impressions increases with the increment of the annealing temperature which makes the film become stiffer. No visible radial cracks developed for all the samples as had happened in muscovite which is a naturally formed nanostructured multilayer (Zhang et al., 2008). A partial lateral crack and a few particles were observed in the AFM image shown in insert (b) of Fig. 7-4. These particles with dimensions of 300 to 600 nm are possibly unexfoliated clay particles.

Fig. 7-4 AFM images of typical indent impressions of (a) as-deposited, (b) amplified part of (a), (c) annealed at 400 °C, and (d) annealed at 600 °C for 2 hrs \((\text{ZrO}_2\text{-MMT-SnO}_2\text{-MMT})_{15}\) multilayers with MMT 0.4 wt.% and corresponding load-displacement curves.
Smooth loading curves and non-visible cracks in Fig. 7-3 and Fig. 7-4 demonstrated that the bonding strength either between clay platelets and cation layers or at the interface between films and substrate is strong enough to resist the complicated stress and strain fields generated by the sharp indenter. The film thickness of annealed films at 600 ºC considerably shrinks by ~ 50% compared with that of as-deposited condition (Chen et al., 2008). Such structural integrity may be attributed to high lateral bond strength of clay platelets as well as high bonding strength. Clay-oxide multilayers prepared by the above method have a great advantage of superior tolerance to mechanical strain.

An AFM image of one indent impression of as-deposited (ZrO₂-MMT)₃₀ multilayers with MMT 0.03 wt.% was taken after 4 months of indentation testing and is shown in insert (a) in Fig. 7-5. The corresponding load-displacement curve indicates that small cracks occurred during both loading and unloading. However the jumped displacement under relatively constant loading rate shown by the load-displacement curve was far smaller than that measured by AFM images shown in the cross-section profile. This is mainly due to the continuous recovery of the strain.

Fig. 7-5 AFM images of typical indent impression of as-deposited (ZrO₂-MMT)₃₀ multilayers with MMT 0.03 wt.% and corresponding cross-section profiles.
within the indentation-affected volume during the long unloading time which makes the cracked part rise upwards. Further investigation of the indent impression was done by carefully removing the cracked part and taking the AFM image shown in insert (b). The cross-section profile shows that the deepest cracking surface occurred far below the residual apex level. This indicated that the crack had passed the interface between the film and substrate and propagated into the substrate. Smoothness of the exposed crack surface further manifested that the delamination either between the multilayers or at the interface between the multilayers and the substrate did not appear.

**7.3.2 Effect of As-deposited and Annealing Procedure**

Table 7-2 is the summary of the fitted film hardness and moduli of all the testing samples. Fig. 7-6 shows the fitted hardness and moduli of the as-deposited and annealed (at 600 °C) (ZrO$_2$-MMT)$_{30}$ and (ZrO$_2$-MMT)$_{60}$ multilayers with 0.03 wt.% of clay suspension. It is evident that the annealing process considerably enhances the film hardness $H_f$ (from 1.82 GPa to 6.29 GPa for (ZrO$_2$-MMT)$_{30}$, and from 1.67 GPa to 2.89 GPa for (ZrO$_2$-MMT)$_{60}$). Meanwhile, significant increment of moduli $E_f$ of the annealed multilayers (from 67.06 GPa to 119.9 GPa for (ZrO$_2$-MMT)$_{30}$, and from 63.78 GPa to 120.1 GPa for (ZrO$_2$-MMT)$_{60}$) were observed compared with the as-deposited ones.

**Table 7-2 Summary of fitted film hardness and modulus**

<table>
<thead>
<tr>
<th>Film</th>
<th>Clay wt.%</th>
<th>Formed condition</th>
<th>Film hardness $H_f$ (GPa)</th>
<th>Film modulus $E_f$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{30}$</td>
<td>0.03</td>
<td>As-deposited</td>
<td>1.82</td>
<td>67.06</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>Annealed at 600 °C</td>
<td>6.29</td>
<td>119.90</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{60}$</td>
<td>0.03</td>
<td>As-deposited</td>
<td>1.67</td>
<td>63.78</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>Annealed at 600 °C</td>
<td>2.89</td>
<td>120.10</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{60}$*</td>
<td>0.03</td>
<td>As-deposited</td>
<td>1.26</td>
<td>32.35</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>Annealed at 600 °C</td>
<td>7.19</td>
<td>113.10</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{30}$</td>
<td>0.40</td>
<td>As-deposited</td>
<td>0.33</td>
<td>9.94</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 400 °C</td>
<td>0.49</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 °C</td>
<td>1.68</td>
<td>43.75</td>
</tr>
<tr>
<td>(ZrO$<em>2$-MMT)$</em>{60}$</td>
<td>0.40</td>
<td>As-deposited</td>
<td>0.39</td>
<td>9.36</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 °C</td>
<td>1.86</td>
<td>40.69</td>
</tr>
<tr>
<td>(SnO$<em>2$-MMT)$</em>{30}$</td>
<td>0.40</td>
<td>As-deposited</td>
<td>0.38</td>
<td>8.80</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 400 °C</td>
<td>1.67</td>
<td>77.20</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 °C</td>
<td>0.77</td>
<td>9.09</td>
</tr>
<tr>
<td>(ZrO$_2$-MMT-SnO$<em>2$-MMT)$</em>{15}$</td>
<td>0.40</td>
<td>As-deposited</td>
<td>0.43</td>
<td>6.20</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 400 °C</td>
<td>1.32</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>Annealed at 600 °C</td>
<td>1.50</td>
<td>30.72</td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{30}$</td>
<td>0.03</td>
<td>Annealed at 600 °C</td>
<td>10.30</td>
<td>118.60</td>
</tr>
</tbody>
</table>

*Note: clay suspension is settled 24 hrs before being used.

Fig. 7-7 presents the fitting results of clay-zirconia multilayers with a higher clay suspension concentration of 0.4 wt. %. The same trend of hardness and moduli as that of with lower clay concentration was observed in which $H_f$ was increased from 0.33 GPa to 1.68 GPa for (ZrO$_2$-MMT)$_{30}$, from 0.39 GPa to 1.86 GPa for (ZrO$_2$-MMT)$_{60}$, and $E_f$ was increased from 9.94 GPa to 43.75 GPa for r (ZrO$_2$-MMT)$_{30}$, from 9.36 GPa to 40.69 GPa. One reason for such enhancement of hardness and moduli is that the annealing process strengthens the bonding interaction between clay layers and Zr$^{4+}$ cationic layers in which excess water was expelled by physical and chemical reaction. Consequently the interlayer spacing of clay layers occupied by Zr$^{4+}$ cationic layers was
reduced which results in a much thinner thickness of annealed multilayers than the as-deposited one. This was manifested by the average film growth rates of as-deposited and annealed multilayers of ~6.8 nm and 3.2 nm, respectively (Chen et al., 2008).

Fig. 7-6 Hardness and modulus of Zirconia-clay multilayers under as-deposited and annealed at 600 ºC condition with clay montmorillonite 0.03 wt.%.

![Graph](image)

Doted line and solid line denote hardness and modulus respectively.

Fig. 7-7 Hardness and modulus of Zirconia-clay multilayers under as-deposited and annealed at 400 ºC/600 ºC condition with clay montmorillonite 0.4 wt.%.

Doted line and solid line denote hardness and modulus respectively.
7.3.3 Effect of Clay Concentration

Hardness and moduli of clay-Zirconia multilayers (30 and 60 deposition cycles) formed by LbL procedure with two different clay suspension concentration of 0.03 wt.% and 0.4 wt.% were presented in Fig. 7-8 and Fig. 7-9. The films with lower clay concentration exhibit much higher hardness and moduli than those with higher clay concentration for both as-deposited and annealed (at 600 ºC) multilayers. It indicates that high clay concentration does not facilitate the

![Fig. 7-8 Effect on clay suspension concentration on hardness of Zirconia-clay multilayers under as-deposited and annealed at 600 ºC condition.](image)

![Fig. 7-9 Effect on clay suspension concentration on hardness of Zirconia-clay multilayers under as-deposited and annealed at 600 ºC condition.](image)
increment of hardness and modulus of multilayers. One reason is that the higher clay concentration generates higher film growth rate of 37 nm/cycle (personal communication with Chen et al., 2008) which is much higher than 5.7 nm/cycle corresponding to clay concentration of 0.03 wt.%, subsequently creating higher porosity within the multilayers. In addition, each thicker individual clay layer constructs a strong thermal barrier which inhibits the effectiveness of annealing process across the whole film thickness.

### 7.3.4 Effect of Annealing Temperature

Annealing was applied at 400 ºC and 600 ºC on the three different multilayers (ZrO$_2$-MMT)$_{30}$, (ZrO$_2$-MMT-SnO$_2$-MMT)$_{15}$, and (SnO$_2$-MMT)$_{30}$. Fig. 7-10 and Fig. 7-11 show the fitted hardness and moduli of the films formed under as-deposited, annealed at 400 ºC, and annealed at 600 ºC conditions. At as-deposited deposition condition, all three multilayers have almost the same hardness (0.33GPa, 0.43 GPa, and 0.43 GPa) and slightly different moduli (9.94 GPa, 6.2 GPa, and 8.8 GPa). However, significant difference of hardness and moduli was observed as annealing temperature varies. (ZrO$_2$-MMT)$_{30}$ film exhibits highest hardness and modulus at annealing temperature 600 ºC among these three formed conditions, whereas (SnO$_2$-MMT)$_{30}$ film reaches highest hardness and modulus at temperature 400 ºC, then drops down sharply at 600 ºC which are much lower that those of (ZrO$_2$-MMT)$_{30}$ multilayers. The hardness and modulus of (ZrO$_2$-MMT-SnO$_2$-MMT)$_{15}$ reasonably resides between those of (ZrO$_2$-MMT)$_{30}$ and (SnO$_2$-MMT)$_{30}$. This implies that there does exist a relationship between an annealing temperature and a corresponding hardness and modulus for a specific clay-oxide multilayer.

![Fig. 7-10 Hardness of Zirconia-clay multilayers under as-deposited and annealed at 400 and 600 ºC condition with clay montmorillonite 0.4 wt.%](image-url)
7.3.5 Expandability versus Forming Conditions

XRD patterns of as-deposited and annealed multilayers $(\text{ZrO}_2\text{-MMT})_{30}$, $(\text{ZrO}_2\text{-MMT})_{60}$, $(\text{ZrO}_2\text{-MMT-SnO}_2)_{15}$, and $(\text{SnO}_2\text{-MMT})_{30}$ under air-dried (AD) and ethylene glycol-solvated (EG) preparation were obtained to study their expandability versus forming conditions as shown in Fig. 7-12 to Fig. 7-15.

The similar as-deposited and annealed at 600 °C XRD patterns of $(\text{ZrO}_2\text{-MMT})_{30}$ and $(\text{ZrO}_2\text{-MMT})_{60}$ shown in Fig. 7-12 and Fig. 7-13 indicates that preparation of multilayers with consistent structures is achievable. Both as-deposited films have a broad peak region with the basal spacing from $\sim 1.16 \text{ nm}$ to $\sim 1.54 \text{ nm}$. These peaks should result from montmorillonite with hydrated interlayer cation $\text{Zr}^{4+}$ at different degree of hydration, which agree well with commonly recognized $d(001)$ spacing around 1.0-2.0 nm. The presence of these multiple layers of montmorillonite demonstrates that some clay particles were undesirably adsorbed during the process of dipping in clay suspension. In particular, no visible peak related to the periodic thickness formed by each deposition cycle for multilayers was observed, which had been successfully observed in clay-zirconia multilayers prepared with clay concentration 0.03 wt. % (Chen et al., 2008). Since the clay concentration used to prepare the above samples is 0.4 wt. %, it manifests that it is necessary to determine a proper clay concentration in order to fabricate a clay-based multilayer with consistent periodic layered structures. Highly amorphous structures were observed from the XRD patterns of both annealed samples, which is not as expected as that with clay concentration of 0.03 wt. % reported by Chen et al. (2008). This further proves the importance of clay concentration in preparation of clay-based nanostructured multilayers.
Fig. 7-12 XRD patterns of clay-oxide multilayers (ZrO$_2$-MMT)$_{30}$ with clay concentration wt. 0.40 % in which Na-HMP (5g/L) was added to exfoliate the clay particles.

Fig. 7-13 XRD patterns of clay-oxide multilayers (ZrO$_2$-MMT)$_{60}$ with clay concentration wt. 0.40 % in which Na-HMP (5g/L) was added to exfoliate the clay particles.
Fig. 7-14 XRD patterns of clay-oxide multilayers (ZrO$_2$-MMT-SnO$_2$)$_{15}$ with clay concentration wt. 0.40 %.

Fig. 7-15 XRD patterns of clay-oxide multilayers (SnO$_2$-MMT)$_{30}$ with clay concentration wt. 0.40 %.
Fig. 7-14 shows the XRD patterns of \((\text{ZrO}_2-\text{MMT-SnO}_2)_{15}\) under as-deposited and annealed at 400/600 °C conditions. Air-dried and Ethylene glycol-solvated as-deposited samples exhibit two relatively sharp peaks 1.26 nm and 1.71 nm, respectively. This observation again verified the existence of clay particles adsorbed in clay-based multilayers. This finding can also be obtained from the XRD patterns of the annealed samples (at 400 °C) which have weak peaks but with almost the same values as those of as-deposited samples less than 10° (2θ). It is further inferred that the expandability of montmorillonite with hydrated interlayer cations \(\text{Zr}^{4+}\) and \(\text{Sn}^{4+}\) is reversible even after being annealed at 400 °C. However, the corresponding peaks were not observed from the XRD patterns of the annealed (at 600 °C) samples, probably due to the growth of \(\text{ZrO}_2\) and \(\text{SnO}_2\) nanocrystals which disordered the multilayer structures (Chen et al., 2008).

The XRD patterns of \((\text{SnO}_2-\text{MMT})_{30}\) shown in Fig. 7-15 have almost the same features as those of \((\text{ZrO}_2-\text{MMT-SnO}_2)_{15}\) except that two nearly identical peaks 0.96 nm (AD) and 0.98 nm (EG) were observed. It could result from the consistent periodic deposition layers rather than montmorillonite particles because montmorillonite particles should be expandable under ethylene glycol-solvated preparation. If these peaks are assumed due to montmorillonite particles, the only interpretation is that \(\text{SnO}_2\) nanocrystals formed under annealing temperature 600 °C contribute to the unexpandibility of the formed clay-oxide multilayers. If this true, the multilayers \((\text{SnO}_2-\text{MMT})_{30}\) after being annealed at 600 °C should have better periodic layers than \((\text{ZrO}_2-\text{MMT})_{30}\). Since this chapter focuses on the mechanical properties of clay-multilayers, further study was not conducted.

### 7.4 Discussion

#### 7.4.1 Analytical Method

The multilayers formed by LbL procedure have intrinsic anisotropic properties. Since there is not a theory applicable to the determination of mechanical properties such micro- to nano-meter thick film presently, an analytical method used in this paper is just an approach to approximately estimate the true film hardness and modulus in the direction perpendicular to the indentation surface, in which the main purpose is to use these mechanical parameters as references to check multilayer design variables and compare different film-forming conditions. The hardness defined by the applied load divided by the corresponding projected area is the mean contact pressure and is found to be proportional to the film’s yield or flow stress in compression for isotropic materials (Fischer-Cripps, 2004). The hardness of multilayers has a similar physical meaning if the same concept is assumed valid. The difficulty is the interpretation of the modulus of the multilayer determined by nanoindentation test. This is mainly due to the complex stress and strain spaces generated beneath the indenter and the continuously changed boundary conditions as the indenter penetrates into the sample. However, the modulus determined by the above method could be a good comprehensive parameter to characterize the elastic properties because it is obtained based on the elastic response of the film during unloading. The true modulus normal to the loading surface is believed to be related to the measured modulus with some extent degree dependent on the anisotropy of the film. This correlation is unclear and to be studied further.

Another concern is the error due to pile-up mainly observed in soft films on hard substrates (e.g., as-deposited multilayers in this paper). The main reason is that the contact depth \(h_c\) in Eq.
(7-2) is determined based on elastic contact analysis without consideration of plastic deformation which occurs for elastic-plastic materials. The consequence of ignorance of pile-up results in an underestimation of the contact area, which subsequently gives rise to overestimated hardness and modulus. For example, the hardness and modulus obtained for as-deposited multilayers in this paper, which exhibit pile-up around the contact impressions, should be the upper bound value.

7.4.2 Multilayer Design

This paper focuses on the mechanical behavior of multilayers formed by LbL deposition process at different conditions. The factors affecting on the mechanical properties mainly include cationic precursor, anionic precursor, dipping control parameters, and post-deposition treatment measures, which are the primary design parameters to achieve the expected requirements. Among these factors, the anionic precursor, exfoliated clay platelets (montmorillonite) in this paper, is the most difficult control parameter because of the inability to effectively characterize the exfoliation status. The unexfoliated clay aggregates could coexist with exfoliated clay platelets in the suspension, and the exfoliated clay platelets are also possible to reaggregate as the dipping deposition cycle proceeds. Therefore, it is difficult to ensure the identical clay layer for each deposition cycle. Even in the same deposition cycle, the in-plane distribution of clay platelets and particles is not uniform which results in uneven surface of the deposited clay layer. The annealing process can significantly reduce the porosity of the multilayers by the shrinkage normal to the deposition surface but can not reduce the sizes of clay aggregates. The growth of the oxide crystals during the annealing process also could deform the clay layers by displacement (Chen et al., 2008). The surface roughness presents the degree of such accumulative evenness of a certain number of depositing cycles as shown in Fig. 7-16. The surface roughness in both cases is not at the same order of the individual clay platelet thickness (~ 1 nm). This implies that an effective dispersing and exfoliating method of clay particles is needed to prepare clay suspension in which an uniform clay layer in thickness and in in-plane distribution for each dipping cycle could generate.

![Surface roughness comparison](image)

Fig. 7-16 Surface roughness of (a) as-deposited and (b) annealed (at 600 °C) (ZrO$_2$-MMT)$_{30}$ with clay montmorillonite 0.4 wt.\%.
7.5 Conclusions

The load-displacement curves and residual AFM images show that all the multilayers exhibit a superior tolerance to mechanical strain because of the high lateral bond strength of clay platelets and strong bonding strength between interlayers. In addition, annealing significantly enhances the resistance against penetration into multilayers.

A common tendency was found that the modulus and hardness of all clay-based multilayers with lower clay concentration have much higher values than those with higher clay concentration. This is probably due to higher porosity of the films generated by higher clay concentration, and subsequent higher periodicity of multilayers also diminished the annealing effects for annealed samples.

Analysis of the results with two annealing temperatures indicates that there is a relationship between an annealing temperature and a corresponding hardness and modulus for a specific clay-oxide multilayer, and optimization of annealing temperature are expected to be determined with respect to each type of clay-oxide multilayer.

Clay-oxide multilayers prepared by LbL method have a promising future with the improvement in accurate control of clay exfoliation, clay concentration, and optimization of annealing temperatures. Elastic modulus by nanoindentation is a suitable quantity for characterization of multilayers even though there still exist some theoretical issues unsolved with respect to nanoindentation tests on anisotropic materials.

7.6 References


8.1 Modulus Model of Phyllosilicate Minerals

Clay minerals are phyllosilicate minerals composed of 1:1 and 2:1 nanoscaled layers as well as a variety of interlayer species. Generally, the architecture of a phyllosilicate mineral in the direction perpendicular to the layers can be divided into two constituent layer components: a single 1:1 or 2:1 layer and an interlayer between successive 1:1 or 2:1 layers. The interlayer can be further subdivided into several sublayers according to the species within it, such as non-hydrated cations (brittle mica, mica, and illite), hydrated cations (smectite, vermiculite), hydroxide (chlorite), and no interlayer species (kaolin-serpentine, talc-pyrophyllite). For each layer type mineral, the variations of the interlayer complexes dominate the mechanical properties of the phyllosilicate minerals. Ignoring the influence of the in-plane structures, the modulus of a phyllosilicate mineral in the direction perpendicular to the layers which consist of different sublayers can be modeled using the principle of springs in series. For example, a 2:1 layer mineral with a sublayer of hydrated cations can be modeled as in Fig. 8-1.

![Fig. 8-1 Schematic illustration of (a) the crystal structure and (b) simple series model of a 2:1 layer clay mineral](image)

If the material is assumed to follow Hooke’s law, there is:

\[ \sigma_i = \varepsilon_i E_i = \frac{\Delta h_i}{h_i} E_i \]  \hspace{1cm} (8-1)

where \( i \) is the layer/sublayer number, \( \varepsilon_i \) is the uniaxial strain in the direction perpendicular to the layers, \( E_i \) is the Young’s modulus in the same direction as \( \varepsilon_i \), \( \Delta h_i \) is the deformation of the layer/sublayer \( i \) under stress \( \sigma_i \), and \( h_i \) is the initial thickness of the layer/sublayer. It is evident that \( \sigma_i \) is identical for each layer/sublayer if the influence of Poisson’s ratios is ignored. Let \( \sigma_i = \sigma \), there is:

\[ \Delta h_i = \frac{h_i}{E_i} \sigma \]  \hspace{1cm} (8-2)
The total deformation can be obtained from Eq. (8-2):

$$\sum \Delta h_i = \sigma \sum \frac{h_i}{E_i} \quad (8-3)$$

The equivalent strain of the composed material is calculated as:

$$\varepsilon_c = \frac{\sum \Delta h_i}{\sum h_i} \quad (8-4)$$

The equivalent modulus is derived by Eq. (8-1), Eq. (8-2), and Eq. (8-3):

$$E_c = \frac{\sigma}{\varepsilon_c} = \frac{\sum h_i}{\sum \frac{h_i}{E_i}} \quad (8-5)$$

Eq. (8-5) can be reformed as follows:

$$\sum \frac{h_i}{E_c} = \sum \frac{h_i}{E_i} \quad (8-6)$$

Young’s modulus of a specific phyllosilicate mineral can be easily determined if the mineral’s structural information and the modulus of each constituent component is known (Eq. (8-6)). Therefore, the main task is to determine the modulus of each layer/sublayer.

Determination of the modulus of a single 2:1 layer, or 1:1 layer, or hydroxide sublayer by direct experiment is impossible to date. One possible way is to use theoretical or semi-experimental methods such as molecular dynamics (MD) simulation technique. Therefore, the objective of the following sections is to determine the modulus of a single 2:1 layer, 1:1 layer, and hydroxide sublayer based on source data from MD and Brillouin scattering in literature.

Another objective is to determine the modulus of a mineral, which is composed of several constituent components, highly crystalline, and almost defect-free, based on experimental data. The available experimental methods reported in literature and in this report are briefly summarized as follows:

1) Brillouin scattering method (Vaughan and Guggenheim, 1986; McNeil and Grimsditch, 1993; Aleksandrov and Prodaivoda, 1993) is effectively used to determine the elastic constants of a crystal, and the modulus in a specific direction can be derived from Eq. (5-9) (Ulm and Abousleiman, 2006);

2) X-ray diffraction or neutron diffraction with a diamond anvil cell (DAC) or tungsten carbide anvil cell (WCAC) is frequently used to directly measure the unit cell dimensions of a crystal under certain pressure and thermal conditions (Hazen and Finger, 1978; Comodi and Zanazzi, 1995; Pawley et al., 1995; Smyth et al., 2000; Welch and
Marshall, 2001; Pawley et al., 2002; Welch and Crichton, 2002; Dera et al., 2003; Zanazzi et al., 2007). The axial Young’s moduli can be derived based on these original data and some assumptions. This is one of main objectives in the following sections;

3) Nanoindentation test on a specific mineral gives the modulus of the mineral in the direction parallel to the loading direction (Broz et al., 2006; Zhang et al., 2009).

The moduli of layers/sublayers which can not be determined from the available data or methods will be derived from previously determined moduli.

The calculated modulus of individual layer/sublayer offers a great advantage to estimate the moduli of clay minerals with small particle sizes, which are difficult to handle with conventional mechanical testing methods.

### 8.2 Modulus of a Single 2:1 Layer

Molecular dynamics (MD) simulation of a single 2:1 layer clay platelet is only available for dioctahedral minerals in literature. Fig. 8-2 shows the schematic structures of the simulated clay platelets. The MD simulation results are summarized in Table 8-1.

![Fig. 8-2 Structures of a simulated 2:1 layer nanoplate with the chemical formula (a) Al₂Si₄O₁₀(OH)₂ (Manevitch & Rutledge (2004); Mazo et al., 2008a) and (b) (Al₃.₇₅Mgₐ₀.₂₅)(Si₃.₈₇₅Al₀.₁₂₅)O₁₀(OH)₂ (Cygan et al., 2004; Suter et al., 2007)](image)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Elastic constants</th>
<th>Reference for source data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂Si₄O₁₀(OH)₂</td>
<td>$E_x$, $h$ ($E_x$)</td>
<td>Manevitch and Rutledge (2004)</td>
</tr>
<tr>
<td></td>
<td>229 N/m (349 GPa)</td>
<td>261 N/m (398 GPa)</td>
</tr>
<tr>
<td></td>
<td>256 N/m (390 GPa)</td>
<td>284 N/m (433 GPa)</td>
</tr>
<tr>
<td>(Al₃.₇₅Mgₐ₀.₂₅)(Si₃.₈₇₅Al₀.₁₂₅)O₁₀(OH)₂</td>
<td>$E_x$, $h$ ($E_x$)</td>
<td>Cygan et al. (2004); Suter et al. (2007)</td>
</tr>
<tr>
<td></td>
<td>216 N/m (329 GPa)</td>
<td>230 N/m (351 GPa)</td>
</tr>
</tbody>
</table>

Note: $h$ denotes the thickness of the platelet. The value in parentheses are calculate assuming $h = 0.656$ nm.

The accurate thickness of the platelet significantly affects the axial moduli $E_x$, $E_y$, and $E_z$. For example, Manevitch and Rutledge (2004) assumed $h = 0.615$ nm and obtained in-plane moduli of the platelet as about 400 GPa. Suter et al. (2007) used $h = 0.937$ nm to obtain the in-plane moduli
as about 240 GPa, and used \( h = 0.669 \) nm as about 335 GPa. Therefore, it is necessary to
determine an appropriate value of the 2:1 thickness for further analysis.

The unit cell dimensions of some layered minerals are summarized in Table 8-2. It is found
that the 2:1 layer thickness does not deviate in a large range. Therefore it is reasonable to take
the average of all the values as the thickness of a typical 2:1 layer, which is equal to 0.656 nm.
The axial moduli are subsequently determined based on this value as shown in Table 8-1 as the
value in the parentheses. The in-plane moduli range from 329 GPa to 433 GPa, while the
modulus in the loading direction ranges from 249 to 364 GPa.

Table 8-2 Structural details of some 2:1 layer minerals in literature

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral</td>
<td>Muscovite (Portugal)</td>
<td>Muscovite (South Dakota)</td>
<td>Pyrophyllite</td>
<td>Phlogopite (Silver Crator)</td>
<td>Margarite</td>
</tr>
<tr>
<td>Tet. Thickness (nm)</td>
<td>0.2234</td>
<td>0.2248</td>
<td>0.2153</td>
<td>0.2249</td>
<td>0.2263</td>
</tr>
<tr>
<td>Oct. thickness (nm)</td>
<td>0.2081</td>
<td>0.2097</td>
<td>0.2079</td>
<td>0.2174</td>
<td>0.2074</td>
</tr>
<tr>
<td>2:1 layer thickness (nm)</td>
<td>0.6549</td>
<td>0.6593</td>
<td>0.6385</td>
<td>0.6672</td>
<td>0.6600</td>
</tr>
<tr>
<td>Interlayer thickness (nm)</td>
<td>0.3436</td>
<td>0.3386</td>
<td>0.2759</td>
<td>0.3344</td>
<td>0.2868</td>
</tr>
<tr>
<td>d (001) spacing (nm)</td>
<td>0.9985</td>
<td>0.9979</td>
<td>0.9144</td>
<td>1.0016</td>
<td>0.9468</td>
</tr>
</tbody>
</table>

8.3 Moduli of Clay Minerals by Experimental Method

The moduli of clay minerals determined by direct experimental methods are very limited in
literature. The available methods include: Brillouin scattering method, diamond anvil cell (DAC)
or tungsten carbide anvil cell (WCAC) method, and nanoindentation.

8.3.1 Moduli of Clay Minerals by Brillouin Scattering Method

This method is only applicable to a crystal, and the elastic constants of the crystal can be
determined. Chapter 5 summarized the results of some clay minerals by this method. For
convenience, the results are presented in Table 8-3 again.

Table 8-3 Elastic moduli of some clay minerals by Brillouin method

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>References</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{11} ) (GPa)</td>
<td>181</td>
<td>176.5</td>
<td>186.0</td>
<td>179.0</td>
</tr>
<tr>
<td>( C_{33} ) (GPa)</td>
<td>58.6</td>
<td>60.9</td>
<td>54.0</td>
<td>51.7</td>
</tr>
<tr>
<td>( C_{44} ) (GPa)</td>
<td>16.5</td>
<td>15.0</td>
<td>5.8</td>
<td>5.6</td>
</tr>
<tr>
<td>( C_{13} ) (GPa)</td>
<td>25.6</td>
<td>20.0</td>
<td>11.6</td>
<td>25.8</td>
</tr>
<tr>
<td>( C_{44} ) (GPa)</td>
<td>103.0</td>
<td>103.7</td>
<td>100.2</td>
<td>96.2</td>
</tr>
<tr>
<td>Cal. ( E_z ) (GPa)</td>
<td>52.9</td>
<td>52.3</td>
<td>32.3</td>
<td>30.2</td>
</tr>
</tbody>
</table>

Note: \( E_z \) is the indentation modulus calculated by Eq. (5-9).
8.3.2 Moduli of Clay Minerals by DAC/WCAC Method

In DAC/WCAC tests, the unit cell dimensions of a sample, a crystal of a specific clay mineral, are measured as the hydrostatic pressure increases within the cell. The mechanical parameter, which is measured directly by this kind of experiment, is the bulk modulus. The bulk modulus of the mineral is directly obtained from the data of the hydrostatic pressure versus the volumetric strain.

In order to extract the axial moduli from the experiment data, some assumptions have to be made. The most important assumption is that each of the layered mineral is assumed as an orthotropic material that has at least 2 orthogonal planes of symmetry, where material properties are independent of direction within each plane. There are 9 independent variables required in their constitutive matrices, including the 3 Young’s moduli $E_x, E_y, E_z$, the 3 Poisson’s ratio $\nu_{yz}, \nu_{zx}, \nu_{xy}$, and the 3 shear moduli $G_{yz}, G_{zx}, G_{xy}$. These parameters are related through Hook’s Law:

\[
\begin{bmatrix}
  \varepsilon_{xx} \\
  \varepsilon_{yy} \\
  \varepsilon_{zz} \\
  \varepsilon_{xy} \\
  \varepsilon_{yz} \\
  \varepsilon_{zx}
\end{bmatrix} =
\begin{bmatrix}
  \frac{1}{E_x} & -\frac{\nu_{yx}}{E_y} & -\frac{\nu_{zx}}{E_z} & 0 & 0 & 0 \\
  -\frac{\nu_{yx}}{E_x} & \frac{1}{E_y} & -\frac{\nu_{zy}}{E_z} & 0 & 0 & 0 \\
  -\frac{\nu_{zx}}{E_x} & -\frac{\nu_{zy}}{E_y} & \frac{1}{E_z} & 0 & 0 & 0 \\
  0 & 0 & 0 & \frac{1}{2G_{yz}} & 0 & 0 \\
  0 & 0 & 0 & 0 & \frac{1}{2G_{zx}} & 0 \\
  0 & 0 & 0 & 0 & 0 & \frac{1}{2G_{xy}}
\end{bmatrix}\begin{bmatrix}
  \sigma_{xx} \\
  \sigma_{yy} \\
  \sigma_{zz} \\
  \sigma_{xy} \\
  \sigma_{yz} \\
  \sigma_{zx}
\end{bmatrix}
\]

\( (8-7) \)

Under hydrostatic pressure $\sigma_0$, there exists a relationship $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma_0$. The three elastic moduli can be successively obtained by reforming the first three equations:

\[
E_z = \frac{\left(1-\nu_{xy}\nu_{yx}\right)\left(1-\nu_{yz}\nu_{zy}\right)\left(\nu_{zx} + \nu_{zy}\nu_{yx}\right)}{\left(1-\nu_{xy}\nu_{yx}\right)\frac{\varepsilon_{xz}}{\sigma_0} + \frac{\varepsilon_{xy}}{\sigma_0}\nu_{yz} + \left(\frac{\varepsilon_{yx}}{\sigma_0} + \frac{\varepsilon_{yy}}{\sigma_0}\nu_{yx}\right)\left(\nu_{xz} + \nu_{zy}\nu_{yx}\right)}
\]

\( (8-8) \)

\[
E_x = \frac{1-\nu_{xy}\nu_{yx}}{\left(\frac{\varepsilon_{xx}}{\sigma_0} + \frac{\varepsilon_{yy}}{\sigma_0}\nu_{yx}\right) + \frac{\varepsilon_{yx}}{\sigma_0} + \frac{\varepsilon_{yy}}{\sigma_0}\nu_{yx}}
\]

\( (8-9) \)

\[
E_y = \left[\frac{\varepsilon_{yx}}{\sigma_0} + \frac{\nu_{yx}}{E_x} + \frac{\nu_{zy}}{E_z}\right]^{-1}
\]

\( (8-10) \)
Eq. (8-9) and Eq. (8-10) indicate that the axial elastic moduli can be determined from DAC/WCAC data if a set of Poisson’s ratios are assumed because the axial strains can be directly calculated from the experiment data. However, determination of the Poisson’s ratios of a nanoscaled layered clay mineral by direct experiment is almost impossible. The only method present in literature is molecular dynamics simulation. Table 8-4 gives the Poisson’s ratios reported in literature by MD simulations for some minerals.

Table 8-4 Poisson’s ratios of a single 2:1 layer and layers with interlayer species in literature

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Single Lamella</th>
<th>Hydrated Montmorillonite</th>
<th>Hydrated Pyrophyllite</th>
<th>Hydrated Montmorillonite</th>
<th>Hydrated Monolayer H₂O</th>
<th>Bilayer H₂O</th>
<th>Monolayer H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manevitch &amp; Rutledge (2004)</td>
<td>0.45</td>
<td>0.48</td>
<td>0.45</td>
<td>0.44</td>
<td>0.44</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Mazo et al. (2008a)</td>
<td>0.41</td>
<td>0.44</td>
<td>0.50</td>
<td>0.44</td>
<td>0.46</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Mazo et al. (2008b)</td>
<td>0.14</td>
<td>NA</td>
<td>0.12</td>
<td>0.12</td>
<td>0.06</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Suter et al. (2007)</td>
<td>0.27</td>
<td>0.18</td>
<td>0.05</td>
<td>0.02</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>NA</td>
<td>0.1</td>
<td>0.23</td>
<td>0.04</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.17</td>
<td>0.14</td>
<td>0.32</td>
<td>0.02</td>
<td>0.17</td>
<td></td>
</tr>
</tbody>
</table>

The Poisson’s ratios of layered minerals (Table 8-4) scatter greatly even for the same mineral. Therefore, the influence of the Poisson’s ratios on the axial moduli is to be studied first. For this purpose, axial moduli $E_x$, $E_y$, and $E_z$ of K-rich muscovite (Comodi and Zanazzi, 1995) were calculated by Eq. (8-8) to Eq. (8-10) using the Poisson’s ratios for monolayer water montmorillonite by Mazo et al. (2008b), those by Suter et al. (2007), and identical Poisson’s ratio equal to 0.25 (Mavko et al. (1998)), respectively. The axial moduli versus hydrostatic pressure are presented in Fig. 8-3. The Poisson’s ratios do not considerably influence the axial moduli. Based on this observation and for the comparison purpose, the identical Poisson’s ratio of 0.25 was used for the following calculations of axial moduli based on the DAC or WCAC data.

The unit-cell dimensions of $a$, $b$, and $c$ under different hydrostatic pressure of mica (including muscovite, phlogopite), talc, pyrophyllite, and chlorite obtained by DAC or WCAC method, were collected from literature (Comodi et al., 1995; Smyth et al., 2000; Hazen and Finger, 1978; Pawley et al., 1995; Pawley et al., 2002). In the general triclinic system, the crystal is described by vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ with unequal lengths, and these vectors are not mutually orthogonal as shown in Fig. 8-4 with the corresponding Cartesian coordinate system, in which the vectors $\mathbf{a}$ and $\mathbf{b}$ are in the x-y plane. The volume and $d$-spacing of the unit cell can be determined as:

$$V = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$  \hspace{1cm} (8-11)

$$d = \frac{c}{\sin \gamma} \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$  \hspace{1cm} (8-12)
Therefore, either the volumetric strain $\varepsilon_v$ or the uniaxial strain $\varepsilon_z$ can be directly obtained from the DAC/WCAC data. Provided the uniaxial strains $\varepsilon_x$ and $\varepsilon_y$ are identical, they can be subsequently determined from the volumetric strain and uniaxial strain $\varepsilon_z$. The axial moduli $E_x$, $E_y$, and $E_z$ are then calculated using Eq. (8-8) to Eq. (8-10). Fig. 8-5, Fig. 8-6, and Fig. 8-7 present the calculated axial moduli of three groups of phyllosilicate minerals: mica (muscovite and phlogopite), talc-pyrophyllite, and chlorite with identical Poisson’s ratio of 0.25. It is noteworthy that the data collected here are only from a temperature at 298K-300K. The data out of this range are excluded during the analysis.
Hydrostatic pressure $\sigma$ [GPa]

<table>
<thead>
<tr>
<th>Modulus, $E_x$ &amp; $E_y$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>90</td>
</tr>
<tr>
<td>120</td>
</tr>
<tr>
<td>150</td>
</tr>
</tbody>
</table>

Fig. 8-5 Axial moduli determined from DAC data of muscovite (Comodi et al., 1995) and phlogopite (Hazen and Finger, 1978). The statistical value for $E_{x/y}$ and $E_z$ are $113.2 \pm 11.2$ GPa, $64.2 \pm 8.7$ GPa, respectively.

Hydrostatic pressure $\sigma_m$ [GPa]

$E_{x/y} = 0.28 \sigma_m + 109.89$

$E_z = 2.10 \sigma_m + 58.11$

Fig. 8-6 Axial moduli determined from DAC data of talc [1] (Pawley et al., 1995), talc [2] (Pawley et al., 2002), and pyrophyllite (Pawley et al., 2002). The statistical value for $E_{x/y}$ and $E_z$ are $102.7 \pm 11.2$ GPa, $62.5 \pm 12.8$ GPa, respectively.
Fig. 8-5 to Fig. 8-7 show that the axial moduli of minerals from mica group and chlorite group are approximately independent of the hydrostatic pressure. However, the axial moduli of talc-pyrophyllite minerals increase with the hydrostatic pressure. Since the main focus of this study is the mechanical properties in the direction perpendicular to the layers, the axial modulus $E_z$ obtained in the above section is the most interesting part, which could be used to be linked to the indentation modulus. Therefore, Table 8-5 only summarizes the axial modulus $E_z$ of the three mineral groups determined from DAC and WCAC data by assuming identical Poisson’s ratio of 0.25.

Table 8-5 Axial modulus $E_z$ determined from DAC or WCAC data

<table>
<thead>
<tr>
<th>Mineral Group</th>
<th>Mineral</th>
<th>References for source data</th>
<th>Modulus $E_z$ (GPa)</th>
<th>$E_z \sim \sigma_m \pm$ $\sigma_m$</th>
<th>$\mu \pm s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc-pyrophyllite</td>
<td>Talc</td>
<td>Pawley et al. (1995)</td>
<td>$E_z = 6.34 \sigma_m + 41.07$</td>
<td>$62.5 \pm 12.8$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Talc</td>
<td>Pawley et al. (2002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrophyllite</td>
<td>Pawley et al. (2002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica</td>
<td>Muscovite (Na)</td>
<td>Comodi et al. (1995)</td>
<td>$E_z = 2.10 \sigma_m + 58.11$</td>
<td>$64.2 \pm 8.7$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Muscovite (K)</td>
<td>Comodi et al. (1995)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phlogopite</td>
<td>Hazen and Finger (1978)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>Chlorite</td>
<td>Hazen and Finger (1978)</td>
<td>$E_z = 0.18 \sigma_m + 115.24$</td>
<td>$111.7 \pm 25.7$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clinochlore</td>
<td>Welch and Marshall (2001)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clinochlore</td>
<td>Welch and Crichton (2002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe-chlorite</td>
<td>Pawley et al. (2002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg-chlorite</td>
<td>Pawley et al. (1995)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: $\sigma_m$ denotes hydrostatic pressure, $\mu$ denotes mean value, and $s$ denotes standard deviation.
8.3.3 Moduli of Clay Minerals by Nanoindentation

Moduli of phyllosilicate minerals determined by nanoindentation tests are rarely reported. Table 8-6 presents the moduli of some phyllosilicate minerals in literature as well as in this dissertation.

Table 8-6 Moduli of some phyllosilicate minerals determined by nanoindentation

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Modulus (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1 Minerals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Margarite</td>
<td>157.7</td>
<td>This dissertation</td>
</tr>
<tr>
<td>Muscovite</td>
<td>77.9</td>
<td>This dissertation</td>
</tr>
<tr>
<td>Muscovite</td>
<td>79.3</td>
<td>Zhang et al. (2009)</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>35.7</td>
<td>This dissertation</td>
</tr>
<tr>
<td>Talc</td>
<td>26.8</td>
<td>This dissertation</td>
</tr>
<tr>
<td>Talc</td>
<td>16.2</td>
<td>Broz et al. (2006)</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>19.4</td>
<td>This dissertation</td>
</tr>
<tr>
<td>Rectorite</td>
<td>18.3</td>
<td>Zhang et al. (2009)</td>
</tr>
<tr>
<td>1:1 Minerals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>40.3</td>
<td>Ulm and Abousleiman (2006)</td>
</tr>
</tbody>
</table>

8.4 Moduli of Interlayer Species

In phyllosilicate minerals, the interlayer species vary from non-hydrated cations, hydrated cations, and octahedral hydroxides. The mechanical properties of a same layer type phyllosilicate mineral depend largely on the interlayer species. Eq. (8-2) indicates that the modulus of an interlayer species in a typical mineral can be estimated provided that all other components are available. The following section will estimate the modulus of different interlayer species using available data from the literature and in this dissertation. This analysis will lay the basic foundation for the future modeling of mechanical properties of phyllosilicate minerals.

8.4.1 Moduli of Non-hydrated cation Sublayers

Non-hydrated cations exist in 2:1 layer phyllosilicate minerals such as micas, illite, and brittle micas. These non-hydrated cations in the interlayers tightly hold successive layers and balance high layer charges. The crystal structures of these minerals are presented in Fig. 2-3 in Chapter 2. The structural information of mica and brittle mica with ideal structures is shown in Table 8-7.

Table 8-7 Ideal formulas and layer charges for micas and brittle micas (Dixon and Weed, 1989)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Layer charge</th>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Interlayer</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Muscovite</td>
<td>1</td>
<td>K</td>
<td>Al_2</td>
</tr>
<tr>
<td>Paragonite</td>
<td>1</td>
<td>Na</td>
<td>Al_2</td>
</tr>
<tr>
<td>Margarite*</td>
<td>2</td>
<td>Ca</td>
<td>Al_2</td>
</tr>
<tr>
<td>Biotite</td>
<td>1</td>
<td>K</td>
<td>(Mg, Fe^{2+})_3</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>1</td>
<td>K</td>
<td>Mg_3</td>
</tr>
<tr>
<td>Clintonite*</td>
<td>2</td>
<td>Ca</td>
<td>Mg_2Al</td>
</tr>
</tbody>
</table>

Note: * denotes brittle micas.
Provided that the single 2:1 layer in mica and brittle mica has the same modulus in the direction perpendicular to the layers as that of talc regardless of the differences in the isomorphous substitutions and octahedral types, the modulus of a single 2:1 layer determined by MD method (Manevitch and Rutledge, 2004; Mazo et al., 2008a) shown in Table 8-1 can be used as the modulus of a generalized single 2:1 layer. Here an average value of about 300 GPa from MD analysis is used as the modulus of a single 2:1 layer $E_{2:1}$.

The thickness of a single 2:1 layer $h_{2:1}$ and that of the interlayer $h_{\text{Int}}$ are taken as the average value of the same mineral from Table 8-2. Eq. (8-6) is expressed as:

$$
\frac{h_c}{E_c} = \frac{h_{2:1}}{E_{2:1}} + \frac{h_{\text{Int}}}{E_{\text{Int}}}
$$

(8-13)

where $E_{\text{Int}}$ is the modulus of the interlayer with non-hydrated cation $K^+$ or $Ca^{2+}$. The modulus of the 2:1 layer mineral $E_c$ can be chosen as the average value of the modulus determined from DAC and WCAC data presented in Table 8-5 or the value determined from Brillouin scattering data shown in Table 5-6, or the value determined by nanoindentation in this dissertation. Table 8-8 presents the obtained modulus $E_{\text{Int}}$ of non-hydrated cation sublayer in each mineral.

Table 8-8 Modulus of the interlayer with non-hydrated cations

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Interlayer Cation</th>
<th>Layer thickness [nm]</th>
<th>Modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$h_{2:1}$</td>
<td>$h_{\text{Int}}$</td>
<td>$E_c$</td>
</tr>
<tr>
<td>Margarite</td>
<td>Ca</td>
<td>0.6600</td>
<td>0.2868</td>
</tr>
<tr>
<td>Muscovite</td>
<td>K</td>
<td>0.6571</td>
<td>0.3411</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.6571</td>
<td>0.3411</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.6571</td>
<td>0.3411</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>K</td>
<td>0.6672</td>
<td>0.3344</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>0.6672</td>
<td>0.3344</td>
</tr>
</tbody>
</table>

Note: $^{[1]}$, $^{[2]}$, and $^{[3]}$ denote values determined from nanoindentation tests, Brillouin scattering method, and DAC or WCAC method, respectively.

The modulus $E_{\text{Int}}$ mainly reflects the mechanical behavior of the K-O bond or Ca-O bond between successive 2:1 layers. The higher value $E_{\text{Int}}$ of margarite than that of muscovite indicates that the interlayer with divalent cation is more incompressible than that of monovalent cation, and the enhancement is approximately proportional to the cation valence. Comparison of $E_{\text{Int}}$ between muscovite and phlogopite implies that the cations in the octahedral sheets of 2:1 layers significantly affect the mechanical behavior of the interlayer.

8.4.2 Moduli of Hydrated Cation Sublayers

Hydrated cations are present in the interlayers of smectite and vermiculite groups of phyllosilicate minerals. The diverse cations and large range of net negative layer charges hamper the selection of a well recognized reference mineral for each group. Furthermore, naturally occurred particles of these minerals are too small to be directly tested by available experiment techniques. Even though several papers reported the moduli of 2:1 layer minerals with hydrated cations as shown in Table 2-3, none of them, on the strict interpretation, is for crystals but rather for aggregated particles. The only available data are from the reference by Zhang et al. (2009) in which the axial modulus of rectorite with hydrated divalent cations occupying the interlayer.
gall
ery was determined as 18.3 GPa by nanoindentation. The structure information is presented in Fig. 8-8. The modulus of the single 2:1 layer is taken as 300 GPa which is obtained by MD method. The modulus of the interlayer with one potassium cation per unit cell is taken as the average value of 26.0 GPa obtained from the above section. Thus the modulus of the hydrated cation sublayer can be obtained from the following equation:

\[
\sum \frac{h_i}{E_c} = \frac{h_{2:1}}{E_{2:1}} + \frac{h_{\text{hyd}}}{E_{\text{hyd}}} + \frac{h_{2:1}}{E_{2:1}} + \frac{h_{K}}{E_{K}}
\]  

(8-14)

where subscript \(h_{\text{hyd}}\) denotes the sublayer with hydrayed cations. The modulus \(E_{\text{hyd}}\) is obtained as 12.3 GPa.

**8.4.3 Moduli of Unoccupied Sublayers of 2:1 Layer Minerals**

Non-occupancy in the interlayer gallery occurs in 1:1 layer serpentine-kaolin group and 2:1 talc-pyrophyllite group. Ideally, these minerals have no tetrahedral or octahedral substitution, no layer charge, and no interlayer material. Even though natural minerals have a small amount of substitution which gives a small amount of ionic attraction between layers, the main force that holds adjacent layers of talc-pyrophyllite minerals is van der Waals bonding. The reported experimental methods to determine the moduli of these minerals are only limited to DAC/WCAC and nanoindentation. The following section is based on 2:1 layer talc-pyrophyllite minerals only. The modulus of non-occupancy sublayer of 1:1 layer minerals will be discussed in a latter section.

Since the moduli of talc-pyrophyllite minerals derived from DAC/WCAC data depend on the hydrostatic pressure, the value corresponding to ambient pressure is taken as the representative modulus. The individual layer thickness of pyrophyllite is taken from Table 8-2. The structural information of talc is chosen from a personal communication with Guggenheim (2009). The modulus of 2:1 layer is kept the same as previous calculation, \(E_{2:1}=300\) GPa. Table 8-9 gives the modulus of unoccupied sublayer of talc-pyrophyllite minerals.
Table 8-9 Modulus of non-occupancy sublayer of talc-pyrophyllite minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Interlayer Cation</th>
<th>Layer thickness [nm]</th>
<th>Modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$h_{2:1}$</td>
<td>$h_{int}$</td>
</tr>
<tr>
<td>Talc</td>
<td>Non</td>
<td>0.6520</td>
<td>0.2832</td>
</tr>
<tr>
<td></td>
<td>Non</td>
<td>0.6520</td>
<td>0.2832</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>Non</td>
<td>0.6385</td>
<td>0.2759</td>
</tr>
<tr>
<td>Talc-pyrophyllite</td>
<td>Non</td>
<td>0.6453</td>
<td>0.2796</td>
</tr>
</tbody>
</table>

Note: $^{[1]}$, $^{[2]}$, and $^{[3]}$ denotes values determined from nanoindentation in this dissertation, nanoindentation by Broz et al. (2006), and DAC or WCAC method, respectively.

8.4.4 Moduli of Hydroxide Sublayers

The crystal structure of chlorite group minerals is composed of a 2:1 layer that is structurally similar to mica, and an interlayer hydroxide sheet which is frequently dominated by either Al(OH)$_3$ (gibbsite) or Mg(OH)$_2$ (brucite). This interlayer hydroxide sheet is different from the octahedral sheet in layer silicates in that it does not share atoms with an adjacent tetrahedral sheet or sheets.

The modulus of the interlayer hydroxide sheet is determined from the literature data of elastic constants using Eq. (5-9) proposed by Ulm and Abousleiman (2006). The elastic constants of gibbsite were determined using solid state ab initio quantum mechanical methods (Gale et al., 2001), while the elastic constants of brucite were obtained using Brillouin scattering method. Table 8-10 presents the elastic constants and calculated modulus in the direction perpendicular to the layer.

Table 8-10 Elastic constants and calculated $E_z$ of brucite and gibbsite

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Brucite</th>
<th>Gibbsite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>156.7</td>
<td>154.0</td>
</tr>
<tr>
<td>$C_{33}$ (GPa)</td>
<td>46.3</td>
<td>49.7</td>
</tr>
<tr>
<td>$C_{44}$ (GPa)</td>
<td>21.7</td>
<td>21.3</td>
</tr>
<tr>
<td>$C_{13}$ (GPa)</td>
<td>12.0</td>
<td>7.8</td>
</tr>
<tr>
<td>$C_{31}$ (GPa)</td>
<td>85.2</td>
<td>87.5</td>
</tr>
<tr>
<td>Cal. $E_z$ (GPa)</td>
<td>51.8</td>
<td>53.5</td>
</tr>
</tbody>
</table>

Note: * and ** denote that the data were analyzed using ab initio and ionic force field methods, respectively.

8.4.5 Moduli of Unoccupied Sublayers with Hydrogen Bonds

The schematic crystal structure of chlorite is shown in Fig. 8-9. The d(001) spacing of chlorite ranges from 1.40 ~ 1.44 nm, depending on the substitution of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral sites and Fe$^{2+}$ for Mg$^{2+}$ or Al$^{3+}$ in octahedral sites. The modulus of chlorite calculated from DAC/WCAC data shown in Table 8-5 is used as the representative modulus. The individual layer thickness is taken from the ideal structure of chlorite (clinochlore) with the formula Mg$_5$AlSi$_3$AlO$_{10}$(OH)$_8$ (Welch and Marshall, 2001). In this ideal structure, the van der Waals force and hydrogen bonds are involved in the bonding between the interlayer hydroxide sheet and both tetrahedral sheets.
The modulus of each component in a unit cell is related by the following equation:

\[
\sum h_i \cdot \frac{E_c}{E_i} = \frac{h_{2:1}}{E_{2:1}} + \frac{h_{\text{Int}}}{E_{\text{Int}}} + \frac{h_{\text{Oct}}}{E_{\text{Oct}}} + \frac{h_{\text{Int}}}{E_{\text{Int}}} \quad (8-15)
\]

where \(\text{Int}\) and \(\text{Oct}\) denote the hydrogen bond sublayer and hydroxide sublayer, respectively. The modulus \(E_{\text{Oct}}\) of either brucite or gibbsite is taken as the average of the literature value even though there is a large discrepancy for gibbsite. Similar to the above calculations, \(E_{2:1} = 300\) GPa is applied. Thus, when \(E_{\text{Oct}} = 52.7\) GPa for brucite is used, the modulus of the hydrogen bond sublayer is determined as \(E_{\text{Int}} = 83.1\) GPa. When \(E_{\text{Oct}} = 71.8\) GPa for gibbsite is used, the modulus of the hydrogen bond sublayer is determined as \(E_{\text{Int}} = 72.4\) GPa.

### 8.5 Modulus of a Single 1:1 layer

Kaolin-serpentine group minerals are composed of 1:1 layers stacked in the \(c\) direction. Hydrogen bonds and van der Waals forces connect the tetrahedral sheet in one layer to the octahedral sheet in the neighboring layer as shown in Fig. 8-10. The theoretical thickness of a single 1:1 layer is about 0.426 nm (Meunier, 2005). The d(001) spacing is about 0.72 nm (Brown, 1984).
\[
\sum \frac{h_i}{E_c} = \frac{h_{1:1}}{E_{1:1}} + \frac{h_{\text{int}}}{E_{\text{int}}}
\]  

(8-16)

where \( E_c \) is the modulus of a 1:1 layer mineral, and \( E_c = 40.3 \) GPa which is the only experimental data in literature (Ulm and Abousleiman, 2006) is used. The modulus \( E_{1:1} \) is obtained as 30.9 GPa for kaolinite.

### 8.6 Summary of Moduli of Constituent Layers/Sublayers

The modulus of each constituent layer component of phyllosilicate minerals obtained by the proposed simple series model is summarized in Table 8-11. Even though these component moduli are based on limited experimental data in this dissertation and literature, they are the first systematic report with respect to phyllosilicate minerals, and give an overall picture of mechanical properties of each constituent component. These moduli are supposed to be verified in future research as advanced experimental techniques develop.

<table>
<thead>
<tr>
<th>Layer component</th>
<th>Thickness (nm)</th>
<th>Modulus ( E_z ) (GPa)</th>
<th>Dioctahedral</th>
<th>Triocahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1 layer</td>
<td>0.4260</td>
<td>30.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:1 layer</td>
<td>0.6571 – 0.6650</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brucite [Mg(OH)(_2)]</td>
<td>0.1990</td>
<td>51.8 ~ 53.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gibbsite [Al(OH)(_3)]</td>
<td>0.1990</td>
<td>50.9 ~ 92.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-hydrated cation: Ca</td>
<td>0.2826</td>
<td>75.4</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>0.3344 ~ 0.3411</td>
<td>20.3 ~ 32.1</td>
<td></td>
<td>11.2 ~ 13.0</td>
</tr>
<tr>
<td>Hydrated cation</td>
<td>0.6929</td>
<td>12.3</td>
<td></td>
<td>12.3</td>
</tr>
<tr>
<td>Hydrogen bond [OH-O, brucite]</td>
<td>0.2830 ~ 0.2940</td>
<td>83.1</td>
<td>83.1</td>
<td></td>
</tr>
<tr>
<td>Hydrogen bond [OH-O, gibbsite]</td>
<td>0.2830 ~ 0.2940</td>
<td>72.4</td>
<td>72.4</td>
<td></td>
</tr>
<tr>
<td>Van der Waals force [Tet-Tet]</td>
<td>0.2759 ~ 0.2832</td>
<td>5.1 ~ 13.7</td>
<td>6.1 ~ 13.7</td>
<td></td>
</tr>
</tbody>
</table>

Note: “Tet” denotes tetrahedral sheet.

### 8.7 Prediction of Moduli of Typical Clay Minerals

Application of the proposed simple series model combining the fundamental data of each constituent component in Table 8-11 offers a great advantage to estimate the modulus of a layered mineral provided the structural information is available. The structural information can be obtained by widely used X-ray diffraction method as well as chemical composition analysis. The following section gives some examples to estimate the moduli of some clay minerals, and each estimate is compared with that obtained by other methods.

#### Example 1: Kaolinite

Kaolinite is a 1:1 layer dioctahedral mineral composed of one tetrahedral sheet linked to one octahedral sheet. The bonding between successive layers is by both van der Waals forces and hydrogen bonds (Mitchell and Soga, 2005). The input information as well as the estimated modulus of kaolinite is as follows:

Typical component layer thickness: \( h = 0.7200 \) nm

\[ h_{1:1} = 0.4260 \text{ nm} \]
 Constituent modulus: \( E_{1:1} = 30.9 \) GPa
\( E_{\text{Int}} = 83.1 \) GPa
Estimated modulus of Kaolinite: \( E_c = 41.6 \) GPa

Sato et al. (2005) calculated the elastic constants of kaolinite from first principles within density functional theory (DFT) as \( C_{11} = 178.5 \) GPa, \( C_{33} = 32.1 \) GPa, \( C_{44} = 11.2 \) GPa, \( C_{13} = 2.0 \) GPa. Given the mineral is assumed as orthotropic and the method proposed by Ulm and Abousleiman (2006) is used, the elastic modulus of kaolinite in the direction perpendicular to the layers can be determined as \( E_z = 32.3 \) GPa which is 78% of the estimated value.

Lonardelli et al. (2007) applied a methodology based on the crystallographic Rietveld method to analyze complicated diffraction images of shale obtained by hard monochromatic X-ray synchrotron diffraction, and the elastic constants of kaolinite were determined as \( C_{11} = 79.3 \) GPa, \( C_{33} = 72.5 \) GPa, \( C_{44} = 25.6 \) GPa, \( C_{13} = 24.1 \) GPa. Following the same method as above, the elastic modulus of kaolinite \( E_z \) can be obtained as 66.1 GPa. The reason for the higher value which is 159% of the estimated value arises from the fact that the investigated sample is shale instead of kaolinite crystal.

The elastic constants of kaolinite crystal were also reported by Brillouin scattering method (Alexandrov and Ryzhova, 1961; Bayuk et al., 2007) as \( C_{11} = 171.5 \) GPa, \( C_{33} = 52.6 \) GPa, \( C_{44} = 14.8 \) GPa, \( C_{13} = 27.1 \) GPa. Based on these data, the elastic modulus \( E_z \) is calculated as 46.9 GPa, which is 113% of the estimated value. This value is in close agreement with the estimated value by the proposed series model.

**Example 2: Illite**

Illite is often dioctahedral with a structure quite similar to that of muscovite, and it is sometimes referred to as hydrous mica. It has less interlayer cation K than muscovite. The net negative layer charge \( z \) is between muscovite and smectite, but close to muscovite. Herein the modulus of the interlayer with cation K is assumed as:

\[
E_{\text{Int}} = z E_{\text{Int}}^* \tag{8-17}
\]

where \( z \) is the net negative layer charge per unit; \( E_{\text{Int}}^* \) is the standard layer modulus with non-hydrated cation K in muscovite shown in Table 8-11. If the net negative layer large is assumed as the lower boundary value of 0.6 and upper boundary value of 0.9, the interlayer modulus \( E_{\text{Int}} \) is obtained as 15.7 GPa and 23.6 GPa, respectively. The other information and the calculated modulus are as follows:

Typical component layer thickness: \( h = 1.0000 \) nm
\( h_{2:1} = 0.6650 \) nm
\( h_{\text{Int}} = 0.3350 \) nm

Constituent modulus: \( E_{2:1} = 300.0 \) GPa
Estimated modulus of illite: \( E_c = 42.5 \) GPa (lower boundary)
\( E_c = 60.9 \) GPa (upper boundary)
Wenk et al. (2007) used the same method as Lonardelli et al. (2007) to obtain elastic constants of illite during the study of illite-rich shale. The obtained elastic constants of illite are $C_{11} = 161.2$ GPa, $C_{33} = 72.1$ GPa, $C_{44} = 30.9$ GPa, $C_{13} = 33.3$ GPa. The calculated modulus of illite is $E_c = 75.1$ GPa.

Alexandrov and Ryzhova (1961) reported the elastic constants of illite as $C_{11} = 179.0$ GPa, $C_{33} = 55.0$ GPa, $C_{44} = 11.7$ GPa, $C_{13} = 14.5$ GPa using Brillouin scattering method. The modulus of illite is obtained as $E_c = 44.6$ GPa following the method by Ulm and Abousleiman (2006).

The estimated modulus of illite by the proposed model is within the ranges of literature value.

**Example 3: Smectite**

Smectite minerals are 2:1 layer minerals consisting of an octahedral sheet sandwiched between two tetrahedral sheets. The net negative layer charge is in the range of 0.2 - 0.6. Van der Waals forces and hydrated cations bond successive layers together. These weak bonds are easily modified by water or other polar liquids which give rise to swelling or expansion properties of the minerals of this group. Due to the large range of layer charges and diversity of interlayer cations, the mechanical properties of these minerals may vary considerably. The modulus $E_{\text{Int}}$ of the hydrated cation sublayer shown in Table 8-11 is derived from the nanindentation tests on rectorite only, it may not exactly represent the actual hydrated cations in smectite group. Therefore, the following estimation of modulus of smectite is only related to a mineral with the same cations as those of rectorite.

The input information and calculated modulus of smectite are as follow:

Typical component layer thickness: $h = 1.2300$ nm; $1.4745$ nm

\[
\begin{align*}
    h_{2:1} &= 0.6650 \text{ nm} \\
    h_{\text{Int}} &= 0.5650 \text{ nm}; 0.8095 \text{ nm}
\end{align*}
\]

Constituent modulus: $E_{2:1} = 300.0$ GPa  
\[E_{\text{Int}} = 12.3 \text{ GPa}\]

Estimated modulus of smectite: $E_c = 25.5$ GPa ($h = 1.2300$ nm)  
\[E_c = 21.7 \text{ GPa ($h = 1.4745$ nm)}\]

The layer thickness $h$ is chosen as the same value as that used in literature for comparison purpose as shown in Table 8-12 in which the axial moduli of Wyoming type sodium montmorillonite (MMT) using MD method are presented.

The estimated modulus of smectite by the proposed model in this dissertation is much lower than that by MD method. The main reason may be attributed to the large range of net negative layer charges and variety of the hydrated cations as interpreted above. However, it is noteworthy that there exists a common trend of the modulus obtained by both methods: increasing interlayer cation hydration will decrease the modulus of the mineral.
### Table 8-12 Elastic properties of 2:1 layer minerals determined by MD in literature

<table>
<thead>
<tr>
<th>Formula</th>
<th>d (001) spacing (nm)</th>
<th>Axial moduli (GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$<em>{0.375}$($\text{Al}</em>{1.75}\text{Mg}<em>{0.25}$)($\text{Si}</em>{3.875}\text{Al}<em>{0.125}$)$\text{O}</em>{10}$(OH)$_2$$\cdot$H$_2$O</td>
<td>1.2300</td>
<td>182</td>
<td>172</td>
</tr>
<tr>
<td>Na$<em>{0.375}$($\text{Al}</em>{1.75}\text{Mg}<em>{0.25}$)($\text{Si}</em>{3.875}\text{Al}<em>{0.125}$)$\text{O}</em>{10}$(OH)$_2$$\cdot$H$_2$O</td>
<td>1.2300</td>
<td>182</td>
<td>180</td>
</tr>
<tr>
<td>Na$<em>{0.375}$($\text{Al}</em>{1.75}\text{Mg}<em>{0.25}$)($\text{Si}</em>{3.875}\text{Al}<em>{0.125}$)$\text{O}</em>{10}$(OH)$_2$$\cdot$2H$_2$O</td>
<td>1.4745</td>
<td>150</td>
<td>152</td>
</tr>
</tbody>
</table>

### 8.8 Conclusions

The proposed model and the obtained modulus of each constituent layer/sublayer were used to estimate the moduli of clay minerals with small particle sizes. The estimated moduli of kaolinite and illite agree quite well with those by other methods, but the estimate modulus of smectite and that by MD have a large discrepancy which may result from the large range of net negative layer charges and various types of hydrated cations for smectite group minerals. There is a need to refine the modulus of the sublayer with hydrated cations.

### 8.9 References


CHAPTER 9. CONCLUSIONS AND DIRECTIONS FOR FUTURE RESEARCH

9.1 Conclusions

9.1.1 Extraction of Elastic Modulus of Thin Film

A new simple empirical method that extracts the elastic moduli of both the thin films and underlying substrates is proposed and validated by newly designed nanoindentation experiments and published data. A wide range of soft and hard thin films, including aluminum, zirconia, clay-zirconia multilayers, silicon oxide, tungsten, and nitride films, were successfully examined by the proposed method. Elastic modulus of the thin film was deconvolved from the measured film-substrate composite response by statistical estimation through curve-fitting the semi-logarithmic plot of the film-substrate composite elastic modulus against the indentation depth normalized by film thickness. The estimated elastic moduli of the examined thin films and substrates agree reasonably well with their corresponding standard values or values obtained by other methods, which validates this proposed method. The advantages of this method over others include that, for example, the estimated substrate properties can be used to verify the data accuracy and reliability, and indentations made to large depths can be eliminated or reduced if the substrate’s properties are known.

This method offers an effective method to determine elastic modulus of ultrathin (<100 nm) film, which has been a main obstacle in material research for a long time, provided that the surface roughness is much lower than film thickness and the area function of the indenter is carefully calibrated. It should be aware that the limitations of Oliver and Pharr method also apply to this method, such as the influence of pile-up on the contact depth, and no consideration of pop-ins or cracking. To obtain reliable results, the indentation data used for this simple method should be obtained using the high resolution DCM mode and regular XP mode for shallow and deep indentations, respectively.

9.1.2 Nanoindentation Behavior of Large-sized Phyllosilicate Minerals

This dissertation presents the first effort to determine the elastic modulus and hardness of a large range of phyllosilicate minerals including margarite, muscovite, rectorite, talc, pyrophyllite, and phlogopite using a newly developed nanoindentation technique.

A rigorous nanoindentation testing scheme was established for such nanoscaled layered materials in order to ensure that the obtained data are reliable. The indentation results following this rigorous scheme show that each mineral exhibits different resistant capacity to indentation penetration. Occurrence of “pop-ins” resulting from layer delamination or radial cracking were observed to be dependent on the crystal structure, including layer composition, types of interlayer complexes, and interlayer space expandability. Nanoindentation control parameters under load control mode including loading rate, maximum load, and hold time, were studied. The results demonstrate the strong dependence of modulus and hardness on the test control parameters, indicating that it is of importance to choose appropriate test parameters.

The indentation elastic moduli and hardness of the above minerals were determined. It is discovered that both modulus and hardness of dioctahedral minerals increase with the layer charge through a different second order polynomial function, and the cations in octahedral play a
significant role in the mechanical properties. The mechanical parameters of some of the minerals obtained in this dissertation agree well with the limited data in literature, but not for all the minerals. It is necessary to correlate mechanical properties determined by nanoindentation with those by others. This could be achieved by selecting an appropriate layered reference material which can be handled by nanoindentation and a well recognized method.

The mechanical properties of phyllosilicate minerals determined by nanoindentation will contribute greatly to development in geophysics, mechanics of geomaterials, fundamental mineral physics, and clay-based nanocomposites.

9.1.3 Nanoindentation Behavior of Oriented Aggregated Clay Mineral Films

Nanoindentation tests using continuous stiffness measurement (CSM) were performed on the oriented aggregated clay mineral films (kaolinite, illite, and montmorillonite) prepared by sedimentary method. The mechanical properties of the films under desiccator-dried and oven-dried conditions were examined. The results show the ascending tendency of modulus and hardness from montmorillonite, illite, to kaolinite, which is mainly due to different particle arrangements and associations. In addition, much lower modulus and hardness of these oriented aggregated clay mineral films were obtained than those of corresponding crystals.

Important issues related to preparation of oriented aggregated clay mineral films by sedimentation method, including appropriate clay concentration, film substrate, and drying speed, were also investigated aiming to eliminate film peeling phenomenon.

Although the results of oriented aggregated clay mineral films are only preliminary, they indicate that nanoindentation testing method is an alternative approach to deduce details of the depositional and postdepositional history of a deposit which are closely related to structural information manifested by mechanical properties.

9.1.4 Nanoindentation Behavior of Clay-based Nanostructured Multilayers

Nanoindentation tests were performed on as-deposited and annealed at 400 °C/600 °C clay-based multilayers, which were prepared using layer-by-layer (LbL) method with different precursor cations and multilayer architecture. The modulus and hardness of each sample were extracted from the measured composite response using the method proposed in Chapter 3 of this dissertation. The load-displacement curves and residual AFM images show that all the multilayers exhibit a superior tolerance to mechanical strain because of the high lateral bond strength of clay platelets and strong bonding strength between interalyers. In addition, annealing procedure significantly enhance the resistance against penetration into multilayers.

The results show that the clay-based multilayers with lower clay concentration exhibit much higher modulus and hardness than those with higher clay concentration. This is probably due to higher porosity of the films generated by higher clay concentration, and subsequent higher periodicity of multilayers also diminished the annealing effects for annealed samples. It is also found that does exist a relationship between an annealing temperature and a corresponding hardness and modulus for a specific clay-oxide multilayer.
Nanoindentation tests on clay-based nanostructured multilayers indicate some improvements with respect to LbL method are to be made, including enhancement of exfoliation degree of clay particles, selection of clay concentration, precise control of clay platelet stacking mode, and optimization of annealing temperature for a specific clay-oxide multilayer. However, it demonstrates that fabrication of clay-based multilayers with desirable mechanical properties, graded functionalities, enhanced thermal stability, and blocking barriers can be controlled at nanometer scale. This will most likely open up a promising filed in material science.

9.1.5 Elastic Modulus Modeling of Phyllosilicate Minerals

A simple model was proposed to simulate elastic modulus in the direction perpendicular to the layers of phyllosilicate minerals. Elastic modulus of individual component, including a single 1:1 layer, 2:1 layer, non-hydrated cation sublayer, hydrated cation sublayer, hydroxide sublayer, hydrogen bond sublayer, and non-occupancy (van der Waals bonding) sublayer was determined based on nanoindentation test results in this dissertation and the analysis of experimental data available in literature. Predicted moduli of kaolinite and illite agree well those reported, while predicted modulus of smectite is much lower than that by MD due the large range of layer charge and diversity of interlayer species of smectite group minerals.

The proposed model will offer a great advantage to estimate elastic modulus of a phyllosilicate mineral if further refinement of modulus of individual component is made. In particular, moduli of clay minerals which naturally occur as small particle sizes can be determined. This will facilitate the development of clay-related multiscience.

9.2 Recommendations for Future Research

This dissertation presents the first effort to determine mechanical properties of a series of clay minerals and clay-based nanostructured multilayers using recently developed nanoindentation technique. Experiments and analysis in this dissertation reveal a promising prospect in clay-related science. The following recommendations are made for future research in this area:

- Uniaxial compression test on nano- or micro- mineral column of a well-crystallized phyllosilicate mineral is needed to determine its intrinsic elastic modulus. Large discrepancy of elastic modulus of clay minerals exists depending on the testing and analysis methods among different researchers. This requires that a well-recognized method and a referential mineral with relatively consistent chemical composition and structure are to be determined. The most commonly used method to determine elastic modulus of a material is uniaxial compression or extension test. For phyllosilicate minerals, uniaxial compression test has more advantages than uniaxial extension test. If uniaxial compression test is determined, the most difficult issue is sample preparation. Since the thickness of well-crystallized phyllosilicate mineral particles is normally in the nano- or micro- meter scale, the diameter of the testing sample should be in the same range. Preparation of such nano- or micro- meter high column is challenging in which many difficulties will be involved. However, once the nano- or micro-meter scale column is prepared, uniaxial compression can be conducted by nanoindentation instrument with a flat head indenter in which continuous load can be
applied and corresponding displacement can be recorded. The intrinsic modulus of the test material can be determined from the load-displacement data using conventional method. Furthermore, correlation between indentation elastic modulus and uniaxial elastic modulus can be established.

- Nanomechanics of nanoscaled layered materials is to be established. Provided the uniaxial compression testing of phyllosilicate minerals is realized, mechanical behavior of their constituent layers/sublayers can be probed, and nanomechanics of nanoscaled layered materials.

- Computational simulation including molecular dynamics (MD) simulation and finite element (FE) analysis of phyllosilicate minerals under pressure are to be improved based on the uniaxial compression data. This will greatly contribute to design of clay-based nanocomposites and clay-related science.

- An effective method to exfoliate clay particles into individual clay platelets and to remain suspension stability is to be studied first. This is followed by establishment of stacking mechanism of clay platelets in LbL procedure. Solving these problems will substantially facilitate the development of clay-based composites, particularly clay-based nanostructured multilayers.

- Anisotropic mechanical properties of clay minerals resulting from naturally occurred structures are to be investigated. The relationship between indentation modulus and bulk modulus of anisotropic material is expected to be established.
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The degree of Doctor of Philosophy will be awarded to Zhongxin Wei at the December 2009 commencement.