Molecular Origin of Compressibility and Shear Strength of Swelling Clays

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Abstract. Swelling clays are found all over the world, and the damage caused to the infrastructure in swelling clay areas is estimated to be about 20 billion dollars annually in the United States. Compressibility and shear strength are critical properties of soils that are necessary for the design of infrastructure. Our group has shown that molecular interactions between clay and fluids have a dramatic impact on the macroscale properties of swelling clays. The permeability of the clay increases about 500,000 times when the permeating fluid in the Na-montmorillonite clay is changed from polar fluid water to low polar fluid. This change results from clay–fluid molecular interactions as well as the differences to the microstructure caused by these interactions. In the current work, the compression and shear strength of the clay interlayer is studied by changing the polarity of the fluid in the interlayer and applying compressive and shear stresses using steered molecular dynamics. The results show the strong influence of normal stress as well as fluid polarity on compressibility and shear response of the clay at the molecular scale. The results demonstrate that clay–fluid molecular interactions play a crucial role in the macroscopic compressibility and shear strength of swelling clays.

Keywords: Swelling clay · Compressibility · Shear strength · Molecular dynamics · Fluid polarity

1 Introduction

Swelling clays are extensively found all over the world. The volume of these clays increases in the presence of water, causing an increase in swelling, swelling pressure, and loss of strength. Smectite minerals such as sodium-montmorillonite (Na-MMT) are major constituents of swelling clays. The unit cell of Na-MMT consists of one aluminum octahedral (O) sandwiched between two silica tetrahedral (T) sheets (Mitchell and Soga 2005). The large stresses due to swelling of clays cause severe damage to the buildings, roads, retaining walls, bridges, and embankments (Sebastian et al. 2008; Chen 2012). These clays also have useful applications in engineering due to high swelling capacity, small particle size, large surface area to mass ratio (Van Olphen 1977), and low permeability (Amarasinghe et al. 2012). Thus, these clays have been used as the barrier materials in landfills, as drilling mud and catalyst in petroleum

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engineering, drug delivery systems in pharmaceutical and biomedical applications, enhancing the mechanical properties of polymer-clay-nanocomposites, and modifiers in pavement construction. Shear strength is a critical engineering property that controls the bearing capacity of soils and stability of slopes. Many civil engineering problems are related to the shear strength and compressibility. The failure of the building foundations, landslides, and erosion are some examples of failures that are related to shear properties of clays.

The term clay indicates the particle size as well as mineral type. The clay mineral crystals consist of sheet-like structures that are stacked one upon another and are of colloidal dimension. The lateral dimension of a single clay particle ranges from 10^3 to 10^6 Å and a thickness of about 10 Å. The shape, size, and surface of soil particles and their interactions with various solvents can be evaluated using mineralogy techniques. These characteristics play an important role in various properties of soils such as plasticity, swelling, hydraulic conductivity, compression, and shear strength, and these properties of soils can be further used to mitigate environmental problems like the disposal of hazardous and radioactive wastes (Mitchell and Soga 2005).

To avoid the detrimental effects of swelling clays on infrastructure and effectively use these clays in geoenvironmental applications and geotechnical engineering, understanding of the swelling mechanisms, evaluating the interactions occurring on the molecular scale, the evolution of important engineering properties such as microstructure, swelling pressure, permeability, and consolidation of swelling clay is essential. An attempt has been made to explain the swelling behaviors of clays using the traditional theories, which are based on the electric double layer. The diffuse double layer concept, which is also known as Stern and Guy theory (Stigter 1974), has been used to evaluate the clay–water interactions in the interlayer gallery. However, this theory has various limitations such as evenly distribution of surface charge, an infinite long clay particle, ions in the solution are considered as point charges, and uniform dielectric permittivity throughout double layer (Tan 2010). Furthermore, this theory is unable to precisely describe the expansion of the interlayer as well as swelling behavior (Jo et al. 2001). Additionally, the DLVO theory (Derjaguin, Landau, Verwey, and Overbeek) describes the colloidal suspension stability of clay for the interlayer spacing of more than 20 Å. Thus, the DLVO theory cannot describe the swelling mechanism of the clay interlayer at smaller interlayer spacing. To overcome these limitations, molecular modeling studies are essential to accurately explain the swelling mechanisms and interactions of swelling clays not only with water but also with various organic fluids at the molecular level. The interactions swelling clays with organic fluids with a wide range of dielectric constants: formamide (110), water (80), methanol (33), acetone (20) are chosen. The values in the parentheses represent the dielectric constant values (DEC) of the fluid molecules. According to the United States Environmental Protection Agency (EPA), these organic fluids are commonly found in landfill leachates, which are also identified as toxic and hazardous to health. Furthermore, the classical theory of bearing capacity does not account for clay–fluid interactions, thus reducing its predictive capabilities. Globally, the expenditure of the construction-related properties and services in the civil engineering arena is about $10 trillion a year (Barbosa et al. 2017), and improving the fundamental theory used in the design and construction of the infrastructure will be an important contribution to the field and the society. A better understanding of the shear failure mechanism, accounting for the clay–fluid molecular interactions, is crucial not only for economical design and construction but also for public safety.

2 Molecular Model Construction

The chemical formula of the Na-MMT SWy-2 unit cell is $NaSi_{16}(Al_6FeMg)O_{20}(OH)_4$. The initial coordinates were obtained from the model proposed in the literature (Skipper et al. 1995). Also, the atomic charges were obtained from the literature (Teppen et al. 1997). Almost all of the unbalanced charge in the clay sheet comes from isomorphous substitution and is reported as 0.53e. In our models, the charge due to isomorphous substitution in the octahedral sheet is 0.5e per unit cell (Katti et al. 2007). This model has been extensively used for clay–fluid interactions (Katti et al. 2005a, 2007, 2015, Schmidt et al. 2005; Pradhan et al. 2015) using CHARMM force field parameters (Katti et al. 2005a; b; 2007). The Na-MMT clay layers have a T-O-T structure, and each octahedral clay sheet is sandwiched between tetrahedral clay sheets. In our work, the clay model has 6 × 3 unit cells, and the dimensions of the unit cell are 31.68 Å × 27.44 Å × 24.16 Å. Details can be found in our previous work. The Na-MMT and fluids models were developed using Material Studio™ and PSFGen plug-in of visual MD software (VMD 1.9.2) (Humphrey et al. 1996). Inverse calculations were conducted to evaluate the amount of fluid in the interlayer by comparing d-spacing obtained from MD simulations with d-spacing values found from XRD experiments. The molecular models with 10% acetone, 20% methanol, 30% water and 30% formamide matched with the d-spacing results from the XRD experiments. The detailed procedure of the model construction is described in our previous work (Katti et al. 2017).

3 Compressibility of Clay Interlayer with Various Fluid Polarities

The models consist of dry, 10% acetone, methanol, water, and formamide as well as 30% methanol, water, and formamide in the interlayer (Fig. 1). Based on the molecular weight of individual atoms, 10% fluid content has 24 acetone molecules, 40 methanol molecules, 64 water molecules, and 48 formamide molecules. Similarly, 30% fluid content is equivalent to 120 molecules of methanol, 216 molecules of water, and 120 molecules of formamide. Initially, the interlayer fluid molecules in a single layer for 10% fluid and three layers for 30% fluid. The fluid molecules are free to move in all directions. Further, we applied a wide range of compressive loads on each oxygen atom of the top clay sheet. The equivalent stresses were 0, 0.37, 0.74, 1.11, 1.48, 2.22, 2.96, 4.44, 5.92 and 8.88 GPa.

We calculated the interlayer modulus for dry, 10% and 30%, clay–fluid models of the interlayers. The stress–strain plot for clay with all fluids is linear with a relatively shallow slope from 0–1.48 GPa in the region-I with dry clay exhibiting the highest modulus and high polar fluid–filled interlayer having higher modulus than low polar

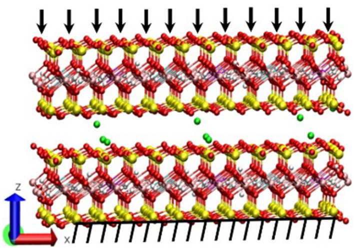
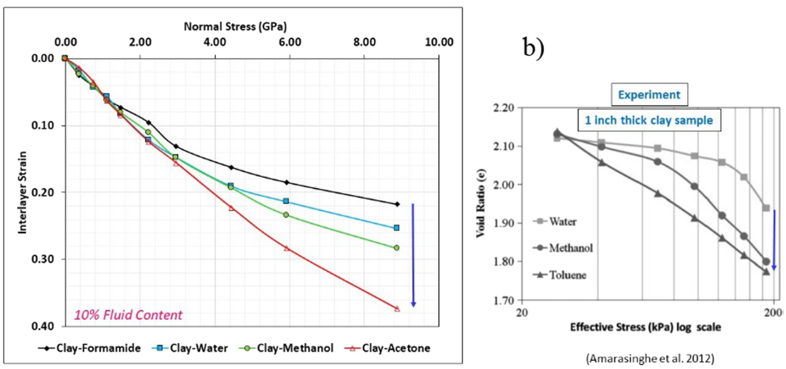


Fig. 1. Molecular model of the sodium montmorillonite clay interlayer showing boundary conditions used to evaluate the compressibility of the clay interlayer.

fluid–filled interlayers. In region-II, for stress levels greater than 1.48 GPa, the slope of the stress–strain plot is steeper for clay with polar fluid than for low polar fluid. Volumetric analysis of the various components of the interlayer is conducted to identify the key mechanisms for the observed differences in the compressibility of the clay interlayer for fluids with different dielectric constants. The compression of the interlayer under the applied stress is the sum of the volume of the fluid molecules exiting the interlayer, the change in the volume of the clay–fluid interaction zone and the compression of the fluid layer in the interlayer. The largest contribution to the compression is from the compression of the clay–fluid interaction. The volume change of the clay–fluid interaction zone for low polarity fluids (acetone and methanol) is larger than for high polar fluids. Interaction energies between the clay sheets, sodium ions and fluid molecules are calculated that provide an insight into the role of molecular interactions on the compressibility of clay interlayer. The clay interlayer filled with high polar fluids is less compressible than low polar fluids filled interlayers for the same amount of fluid content (Fig. 2).

a)



b)

Fig. 2. a) Compressibility of sodium montmorillonite clay interlayer showing compressibility decreases with increasing fluid polarity, b) similar observations from macroscale experiments.

4 Shear Response of Clay Interlayer with Various Fluid Polarities

The top layer of Na-MMT was pulled in shear for dry Na-MMT and hydrated Na-MMT with 10% and 30% interlayer fluids and under a wide range of normal stresses to evaluate the shear strength parameters of Na-MMT interlayer (Fig. 3).

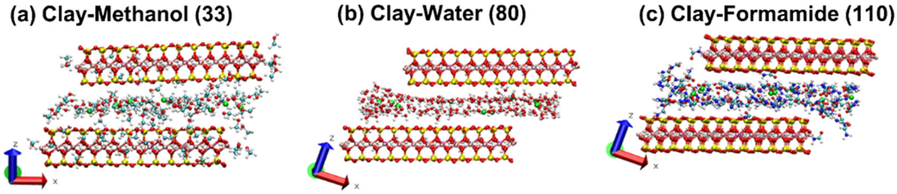


Fig. 3. Shearing of clay interlayers filled with 30% fluids of various polarities represented by dielectric constants in the parenthesis.

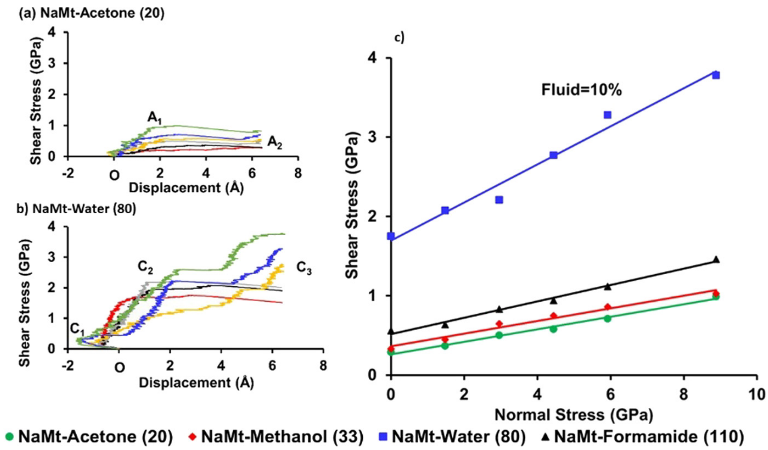


Fig. 4. (a,b) Shear stress-displacement responses of clay interlayers filled with 10% acetone and water up to 20% strain, (c) Shear stress versus normal stress plots based on maximum shear stress values.

The molecular shear strength parameters, angle of internal friction (φ) and cohesion, of dry Na-MMT, as well as Na-MMT hydrated with 10% and 30% fluid, are found (Fig. 4). The friction angle and cohesion, and the value of cohesion was found 769.60 MPa, and the angle of friction was 1.10° for dry Na-MMT. The slope of the Mohr–Coulomb failure envelope and the intercept is influenced by the polarity of the fluids. Increased fluid content showed decreased values of the slopes (friction angle) and intercepts (cohesion).

5 Conclusions

SMD simulations are used to evaluate the compressibility and shear response of the interlayer of dry Na-MMT clay and clay with 10% and 30% fluid content with fluids with a range of polarities. Upon compression, a softer clay interlayer response is observed for clay with fluids than that of dry clay interlayer. Additionally, clay interlayer with polar fluids is less compressible than in the case of clay interlayers with low and medium polar fluids. Shear strength of swelling clay interlayer with polar fluids is significantly higher than that of medium and low polar fluids and is also affected by the fluid content. Thus, the compressibility and shear strength of clay interlayer is influenced by the polarity of the fluid in the interlayer resulting from the molecular interactions between the fluids and the clay constituents.

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