Effects of organic matter on stiffness of overconsolidated state and anisotropy of engineered organoclays at small strain

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ABSTRACT

Organic rich soils are frequently encountered beneath infrastructure components that are sensitive to dynamic loading, such as bridges in earthquake prone regions. Because the engineering properties of these soils can be significantly impacted by the presence of organic matter, it is important to characterize their small strain dynamic properties. However, natural organic matter, is heterogeneous and highly variable; consequently, this experimental investigation quantified the dynamic behaviors of six organoclays that were synthesized under controlled laboratory conditions using quaternary ammonium cations as organic carbon in the clay interlayer. The small strain properties of these clays were measured with bender element tests to quantify the effects of organic carbon content on the dynamic properties of the soils, particularly on the overconsolidation and stiffness anisotropy. Experimental results demonstrated that the preloading effect of organoclays decreased with increasing total organic content due to the decrease in permanent fabric change and the release of lateral stress locking. Because of relatively limited bound of organoclays (C/Cs: 0.025–0.07) as compared to inorganic soils (C/Cs: 0.1–0.2), the exponent for preloading ratio in the Gmax estimating formula is larger than 0.34, suggesting that tested organoclays showed a significant preloading effect when compared to inorganic soils. Additionally, organoclays tested in this study showed inherent anisotropy (Gmax(HH)/Gmax(VV) when K0 = 1: 0.93–1.42) and cross anisotropy in HV and VH directions ([Gmax(HV)/Gmax(VH): 0.74–1.21), demonstrating behaviors that were comparable to that of inorganic soils.

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1. Introduction

The presence of organic matter in soils and its significant effects on engineering properties of soils have been recognized decades ago (Rashid and Brown, 1975). Because infrastructure is frequently founded on organic soils in seismic activity-prone areas (Boulanger et al., 1998; Bate et al., 2013), the small strain dynamic properties of these organic-rich soils, such as maximum shear modulus (Gmax), shear modulus reduction (G/Gmax vs. γ), shear wave velocity (Vs) and damping ratio of organic soils, are critical in geotechnical earthquake engineering. There have been several attempts to evaluate these dynamic properties of organic soils (Boulanger et al., 1998; Kramer, 2000; Wehling et al., 2003; Kalliolou et al., 2009; Kishida et al., 2009). Those previous studies generally reported that the dynamic properties of organic soils are comparable to those of high plasticity clays. However, the studies on the stiffness of overconsolidated state and stiffness anisotropy of organic soils are very limited. Additionally, the studies on the dependence of maximum shear modulus on total organic content are limited (Bate et al., 2013), and are often on very high-organic-content soils, or peats (Boulanger et al., 1998; Mesri and Ajlouni, 2007; Kalliolou et al., 2009). Because the natural organic carbon content in soils is highly variable, ranging from 0.5% to 5% by weight in the surface horizon soils to as high as 100% in organic soils (Sparks, 2003), it is important to quantify the impact of the organic phase on dynamic properties as a function of total organic carbon content.

Because natural organic matter is composed of a complex structure that interacts with soil particles, it is often difficult, if even possible, to quantify the effects of natural organic matter on geologic materials through a controlled experiment. Therefore, materials with simplified synthetic organic compounds were used instead for the systematic evaluation of the effects of organic content on the behavior of organic soils (Lee et al., 2012; Bate et al., 2014). Bate et al. (2013) synthesized organic soils by coating organic cations with controlled structure and loading density onto montmorillonite particles through an ion exchange reaction. Their results demonstrated that Gmax in the normally consolidated state increased with the size of the organic cations, the length of a single long C-chain, or the amount of organic loading. Increasing the total organic carbon content (TOC) reduced the net surface charge on the particle, which in turn reduced interparticle
repulsion. Consequently, the decreased water content and increased particle contacts resulted in a stiffer soil with a larger value of \( G_{\text{max}} \).

In addition to the organic content, natural fine-grained soils are also impacted by the degree of overconsolidation and anisotropy in their structure. Overconsolidated soils are very common in nature due to multiple mechanisms of preloading, including changes in vertical stress, groundwater fluctuation, desiccation, erosion, glaciation, freeze-thaw, and chemical effects (Jamiolkowski et al., 1985; Chen and Mayne, 1994; Mitchell and Soga, 2005). Because the mechanical properties of soils in the overconsolidated state differ significantly from those of soils in normally consolidated states, a number of studies have been performed to evaluate the effects of preloading ratio on the maximum shear modulus of inorganic soils (Affi and Richart, 1973; Hardin, 1978; Tatsuoka et al., 1979; Hardin and Blandford, 1989; Houlsby and Wroth, 1991; Athanasopoulos, 1994; Jamiolkowski et al., 1995; Viggiani and Atkinson, 1995; Fam and Santamarina, 1997; Choo and Burns, 2014). Additionally, natural soils are often anisotropic because the in-situ stress condition is generally anisotropic or because soil fabric has directivity during deposition (Roesler, 1979; Santamarina et al., 2001; Mitchell and Soga, 2005). A number of studies have been performed to evaluate the stiffness anisotropy of inorganic soils (Wongsaroj et al., 2007; Yimsiri and Soga, 2011; Kang et al., 2014). However, few studies have looked at the effects of preloading and anisotropy on the dynamic behaviors of organic soils.

The goal of this study was to quantify the effects of preloading and anisotropy on the small strain stiffness of organically coated clays, known as organoclays. Organoclays were synthesized in the laboratory in order to control the structure and quantity of the organic phase within the clay soil, and were targeted for total organic content levels ranging from 2.2% to 13.9%. Bender element tests were performed to measure the shear wave velocities of the organoclays in three orthogonal directions during both loading and unloading cycles in order to evaluate the effects of both the preloading and anisotropy on \( G_{\text{max}} \) of organoclays. In addition, results from this study were compared with previous studies on inorganic soils to elucidate the role of organic matter on preloading and anisotropy effects of soils.

2. Background

2.1. Organoclay

Organically coated clays, or organoclays, are clay minerals that have their naturally occurring charge-balancing cations exchanged with hydrophobic organic phases on the clay surface, as opposed to the hydrophilic organic cations, induces significant changes in the mechanical and chemical properties of the clay when compared to those of uncoated inorganic soils (Xiao et al., 1996; Soule and Burns, 2001; Burns et al., 2006; Zhang and Somasundaran, 2006; de Paiva et al., 2008; Bate and Burns, 2010; Bate, 2011; Gammoudi et al., 2012; Zhao and Burns, 2012; Bate et al., 2013, 2014). Because organoclays have commercial applicability in a variety of engineering applications, including waste containment and sorption applications, extensive studies on the characterization of their physical and chemical properties have been performed (Xu and Boyd, 1995; Redding et al., 2002; Smith et al., 2003; Bartlett-Hunt et al., 2005; Lake and Rowe, 2005; Lorenzetti et al., 2005; de Paiva et al., 2008; Lee et al., 2012). However, many of the mechanical properties of organoclays, in particular their dynamic properties, have not been thoroughly quantified (Soule and Burns, 2001; Bate, 2011; Bate et al., 2013).

2.2. Stiffness in overconsolidated state

The maximum shear modulus \( G_{\text{max}} \) or shear wave velocity \( V_s \) of a soil is a function of both the applied stress and fabric states of the soil. Permanent fabric change and lateral stress locking caused by loading, followed by unloading (overconsolidation), can result in increased values of \( G_{\text{max}} \) (or higher \( V_s \)) (Fam and Santamarina, 1997; Choo and Burns, 2014). Consequently, a number of previous researchers have considered the preloading effect to predict the \( G_{\text{max}} \) of inorganic fine-grained soils (Hardin, 1978; Hardin and Blandford, 1989; Houlsby and Wroth, 1991; Athanasopoulos, 1994; Jamiolkowski et al., 1995; Viggiani and Atkinson, 1995; Fam and Santamarina, 1997). The general expression for the effect of preloading ratio \( \text{PLR} = \sigma'_p / \sigma'_{OC} \) where \( \sigma'_p \) is the maximum preconsolidation stress and \( \sigma'_{OC} \) is the vertical effective stress on maximum shear modulus is:

\[
G_{\text{max}} = A \cdot F(e) \cdot \left( \frac{\sigma'_v}{1 \text{kPa}} \right)^n \cdot \text{PLR}^k
\]

where, \( A \) is a material constant reflecting property of grain; \( F(e) \) void ratio function; \( n \) is experimentally determined stress exponent reflecting stress dependency of soils; and \( k \) is PLR exponent which is primarily determined by the plasticity index \( (P) \) (Hardin and Black, 1968; Seed et al., 1986). Because applied stress controls the change of void ratio (i.e., \( F(e) \propto \sigma'_v \)), a simplified expression, which considers the preloading effect on \( G_{\text{max}} \), is given as follows (Houlsby and Wroth, 1991; Viggiani and Atkinson, 1995; Jovicic and Coop, 1997):

\[
G_{\text{max}} = A' \cdot \left( \frac{\sigma'_v}{1 \text{kPa}} \right)^{n'} \cdot \text{PLR}^k
\]

where, \( A' \) is combination of material constant and void ratio function; \( n' \) is stress exponent reflecting dependency of soils both on stress and on void ratio change.

In this study, Eq. (2) used vertical effective stress as opposed to mean effective stress. Consequently, the function of the \( \text{PLR} \) represented the correction factor for both fabric change and for lateral stress locking during unloading, and the ratio of \( G_{\text{max}} \) during unloading (\( G_{\text{max}}(\text{OC}) \)) to \( G_{\text{max}} \) during loading (\( G_{\text{max}}(\text{NC}) \)) was used to evaluate the preloading effect on the \( G_{\text{max}} \) of the tested organoclays. It follows from Eq. (2), that this ratio was a function of \( \text{PLR} \) as follows (Choo and Burns, 2014):

\[
\frac{G}{G_{\text{max}}} = \frac{G_{\text{max}}(\text{NC})}{G_{\text{max}}(\text{OC})} = \frac{A' \cdot \left( \frac{\sigma'_v}{1 \text{kPa}} \right)^{n}}{A' \cdot \left( \frac{\sigma'_{OC}}{1 \text{kPa}} \right)^{n'}} \approx \text{PLR}^{k}
\]

The effect of preloading on the \( G_{\text{max}} \) of fine-grained soils is an area of disagreement. Some studies suggested that the \( \text{PLR} \) exponent \( (K) \) in Eq. (3) generally ranged from 0.15 to 0.5, depending on the plasticity index, when the void ratio function was not considered (Seed et al., 1986; Houlsby and Wroth, 1991; Viggiani and Atkinson, 1995; Fam and Santamarina, 1997), while other studies noted that preloading had a negligible effect on the \( G_{\text{max}} \) when the void ratio function was considered (Shibuya et al., 1992; Jamiolkowski et al., 1995). For reconstituted clays, the preloading might have less significant effects on the \( G_{\text{max}} \) results when the effect of void ratio change, which reflects fabric change, is considered; however, the effect of \( \text{PLR} \) may not be neglected for natural (undisturbed) clays as noted by Mitchell and Soga (2005).

2.3. Stiffness anisotropy

The anisotropy of soil strength was first recognized by Casagrande and Wilson (1951), and is described by two factors: inherent anisotropy due to the directivity when soil fabric is being formed, and stress-induced anisotropy due to anisotropic stress states (Duncan and Seed, 1966; Oda et al., 1985; Bellotti et al., 1996; Pennington et al., 1997; Santamarina et al., 2001; Mitchell and Soga, 2005; Wang and Mok, 2008; da Fonseca et al., 2013). Additionally, Jovicic and Coop (1998) used the term strain-induced anisotropy instead of inherent anisotropy.
for reconstituted clays because the fabric of samples created by compression from slurry is related to the one-dimensional strain history rather than to the mode of deposition. Stiffness anisotropy of soils at small strain can be evaluated by comparing the maximum shear modulus in three different directions, i.e., \( G_{\text{max}}(VH), G_{\text{max}}(HV), \) and \( G_{\text{max}}(HH) \), where the first letter in parentheses denotes the direction of wave propagation and the second letter in parentheses denotes the direction of soil particle vibration \((V = \text{vertical} \quad \text{and} \quad H = \text{horizontal})\). Shear wave velocity can be expressed by dividing the stress terms into two directions: direction of wave propagation and polarization, because in-situ stress states are rarely isotropic, and out-of-plane stress does not affect the \( V_s \) (Eq. (4)) (Roesser, 1979; Yu and Richart, 1984; Bellotti et al., 1996; Santamarina et al., 2001; Fioravante et al., 2013). Consequently, in cases where the direction of wave propagation is parallel to the vertical or horizontal major axis, shear wave velocities can be determined in three different directions \((V_s(VH), V_s(HV), \) and \( V_s(HH) \)) and measured as a function of consolidation loading and unloading in order to yield insight into the stiffness anisotropy of soils. Additionally, the \( G_{\text{max}} \) can be determined from the measured \( V_s \) according to Eq. (5). Therefore, the following relationships (Eqs. (6), (7), (8)) describe the maximum shear modulus as a function of the direction of wave propagation and particle motion by combining Eqs. (4) and (5):

\[
V_s = \alpha \left( \frac{\sigma'_p + \sigma'_m}{2 \text{kPa}} \right)^\xi
\]

\[
G_{\text{max}} = \rho \cdot V_s^2
\]

\[
G_{\text{max}}(VH) = A_1 \left( \frac{\sigma'_p + \sigma'_m}{2 \text{kPa}} \right)^\xi_1 = A_1 \left( \frac{1 + K_0}{2 \text{kPa}} \cdot \sigma'_v \right)^\xi_1
\]

\[
G_{\text{max}}(HV) = A_2 \left( \frac{\sigma'_h + \sigma'_m}{2 \text{kPa}} \right)^\xi_2 = A_2 \left( K_0 + \frac{1}{2 \text{kPa}} \cdot \sigma'_v \right)^\xi_2
\]

\[
G_{\text{max}}(HH) = A_3 \left( \frac{\sigma'_h + \sigma'_m}{2 \text{kPa}} \right)^\xi_3 = A_3 \left( \frac{K_0}{1 \text{kPa}} \cdot \sigma'_v \right)^\xi_3
\]

where, \( \rho \) = saturated soil density (Qiu and Fox, 2008); \( \sigma'_p \) and \( \sigma'_m \) = stresses in the direction of wave propagation and particle motion, respectively; \( \sigma'_v \) and \( \sigma'_h \) = vertical and horizontal effective stresses, respectively; \( \Lambda \) = experimentally determined factor, which is same with the value of \( G_{\text{max}} \) at 1 kPa; \( \xi_1 \) = experimentally determined exponent; and \( K_0 \) = coefficient of lateral earth pressure at rest. Consequently, by combining the above equations, the stiffness anisotropy, in terms of cross anisotropy (the ratio of \( G_{\text{max}}(HV) \) to \( G_{\text{max}}(VH) \)), stress-induced anisotropy (the ratio of \( G_{\text{max}}(HH) \) to \( G_{\text{max}}(HV) \)), and inherent anisotropy (the ratio of \( G_{\text{max}}(HV) \) to \( G_{\text{max}}(VH) \) when \( K_0 = 1 \)), can each be evaluated by Cases 1, 2, and 3 in Table 1, respectively.

Soils with cross anisotropy (or transverse isotropy) have symmetry in the vertical direction (principal axis) due to stratification (Pennington et al., 1997; Agustín, 1999), and this cross anisotropy is the most common type of anisotropy resulting from the mechanism of the deposition of the soil. From the cross anisotropic elasticity, \( G_{\text{max}}(VH) \) should be comparable to \( G_{\text{max}}(HV) \) since shear stiffness in the vertical plane is not affected by shearing mode (Case 1 in Table 1). Under normally consolidated \( K_0 \) condition, vertical stress is typically the major principal stress; consequently, to satisfy the conditions of stress-induced anisotropy, \( G_{\text{max}}(VH) \) or \( G_{\text{max}}(HV) \) will show a larger value than \( G_{\text{max}}(HH) \) (Case 2 in Table 1) (Kawaguchi et al., 2008; Wang and Mok, 2008). In contrast, the inherent anisotropy (or strain-induced anisotropy) can only be separated from the stress-induced anisotropy under an isotropic stress state because isotropic stress conditions excluded the stress state as an influencing factor on the stiffness anisotropy. When the soil deposits satisfy the strain-induced anisotropy, which was caused by preferential orientation of platy particles, \( G_{\text{max}}(HH) \) will show a greater value than \( G_{\text{max}}(VH) \) or \( G_{\text{max}}(HV) \) (Case 3 in Table 1).

### 3. Materials and methods

#### 3.1. Materials

In this study, five different quaternary ammonium organic cations (QACs): tetramethylammonium (TMA, denoted: 4C\(_1\)) chloride \(((\text{CH}_3)_2\text{NCl})\), tetraethylammonium (TEA, denoted: 4C\(_2\)) bromide \(((\text{CH}_2\text{CH}_3)_4\text{NBr})\), tetrabutylammonium (TBA, denoted: 4C\(_3\)) bromide \(((\text{CH}_3\text{CH}_2)_4\text{NBr})\), decyltrimethylammonium (DTMA, denoted: 1C\(_{10}\)) bromide \(((\text{CH}_3)\text{NCH}_2\text{CH}_2\text{CH}_3\text{Br})\), and hexadecyltrimethylammonium (HDTMA, denoted: 1C\(_{16}\)) bromide \(((\text{CH}_3)\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{Br})\), were used (Figure 1) to prepare six organoclays, at varying cation exchange capacities (CEC) (100TMA, 100TEA, 100TBA, 100DTMA, 60HDTMA, and 100HDTMA bentonite) (Table 2). The salient difference in tested six organoclays can be found in their organic carbon contents, ranging from 2.2% to 13.9% (Table 2). In addition, six organoclays can be categorized into three different structures: 1) variations in cation size (TMA, TEA, and TBA); 2) variations in cation tail length (TMA, DTMA, and HDTMA); and 3) variations in density of coverage (60HDTMA and 100HDTMA) (Figure 1). The physical and chemical properties of the organoclays are summarized in Table 2: specific gravity was measured according to ASTM D854-10; specific surface was determined by the methylene blue method (Santamarina et al., 2002); liquid limit was measured with the fall cone test according to British Standard 1377; plastic limit was determined according to ASTM D4318-05, and TOC was measured using an organic carbon analyzer with a solid module (TOC-NCP-1STP, SSM-5000A, Shimadzu Co., Kyoto, Japan).

#### 3.2. Method

The organoclays were synthesized in the laboratory using the method described in Bate and Burns (2010). A brief summary is given below. The particle surfaces of the bentonite were exposed to an aqueous solution containing a prescribed amount of quaternary ammonium cations. The organic compound was dissolved in 40 l of deionized water, and 2 kg of the bentonite was added to the aqueous solution. The resulting suspension was mechanically stirred for 1 h and left to stand for a minimum of 24 h to allow gravity separation. The supernatant

### Table 1: Evaluation of stiffness anisotropy.

<table>
<thead>
<tr>
<th>Type</th>
<th>Equation</th>
<th>Condition of anisotropy</th>
<th>Test results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cross anisotropy</td>
<td>( \frac{G_{\text{max}}(HV)}{G_{\text{max}}(VH)} = \frac{m'}{m} )</td>
<td>( m' \approx 1 )</td>
<td>0.74–1.21</td>
</tr>
<tr>
<td>2. Stress-induced anisotropy</td>
<td>( \frac{G_{\text{max}}(HH)}{G_{\text{max}}(HV)} = \frac{1}{\pi} \left( \frac{2K_0}{K_0+1} \right)^\xi )</td>
<td>( \frac{1}{\pi} &lt; 1 )</td>
<td>0.85–1.5</td>
</tr>
<tr>
<td>3. Inherent anisotropy</td>
<td>( \frac{G_{\text{max}}(HV)}{G_{\text{max}}(VH)} = \frac{m}{m'} ) (when ( K_0 = 1 ))</td>
<td>( \frac{m'}{m} \approx 1 )</td>
<td>0.93–1.42</td>
</tr>
</tbody>
</table>

Note: \( G_{\text{max}}(VH) = \text{Eq. (6)}; G_{\text{max}}(HV) = \text{Eq. (7)}; G_{\text{max}}(HH) = \text{Eq. (8)}. \)
was then siphoned off, and the sediments were rinsed with deionized water. This process was repeated to remove any salts or loosely bound cations until the conductivity of the supernatant was below 600 μS/cm. Mineralogical impurities were separated by gravity settling. The slurry was then stored in airtight containers until tested.

Specimens were prepared using a one dimensional slurry consolidation method (Sheeran and Krizek, 1971) in a tall cylinder (diameter of 10.29 cm (4.05 in.) and height of 45.72 cm (18 in.)) with a maximum vertical stress of 100 kPa (detailed procedure was elaborated in Bate et al. (2014)). The duration of each load step ranged from 1 to 7 days, depending on the type of organoclay. After consolidation, the specimens were extruded and trimmed to a diameter of 10.25 cm (4 in.) and height of 6.14 cm (2.4 in.) for the bender element tests.

Bender element testing (BET) was introduced as a method of soil testing by Shirley and Hampton (1978), with the results of BET being demonstrated by Dyvik and Madshus (1985). Due to its simplicity and applicability in most soil test devices, BET is a commonly implemented practice to determine the $V_s$ of soils (Lee and Santamarina, 2005). In this study, in order to measure the $V_s$ of the organoclays, three pairs of bender elements were installed in three different configurations, namely $V_{s(H)}$, $V_{s(HV)}$, and $V_{s(HH)}$ directions, inside a modified oedometer cell (Figure 2) (Lee and Santamarina, 2005; Lee et al., 2008). One pair of bender elements was fitted on the top cap and bottom plate to measure $V_{s(VH)}$; while, another two pairs were fitted on the walls of the oedometer cell to measure $V_{s(HV)}$ and $V_{s(HH)}$. Samples were tested in $K_0$ conditions using vertical stresses of 13.5, 25, 50, 100, 200, 100, 50, 25, and 13.5 kPa. Taylor’s square root of time method was used to determine that each stress was applied until the end of primary consolidation. The duration of each load step ranged from 1 to 5 days. Compared to slurry consolidation, shorter durations of each load step were observed due to shorter sample heights and overconsolidation at

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**Figure 1.** Structure of employed quaternary ammonium cations: (a) TMA $(4C_1)$; (b) TEA $(4C_2)$; (c) TBA $(4C_4)$; (d) DTMA $(1C_{10})$; (e) HDTMA $(1C_{16})$.

**Table 2** Properties of tested organoclays.

<table>
<thead>
<tr>
<th>Organic cations</th>
<th>CEC (%)</th>
<th>Specific gravityutation</th>
<th>Specific surface $(m^2/g)$</th>
<th>Liquid limit (%)</th>
<th>Plastic limit (%)</th>
<th>TOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA, $4C_1$</td>
<td>100</td>
<td>2.80</td>
<td>149</td>
<td>266</td>
<td>82</td>
<td>2.2</td>
</tr>
<tr>
<td>TEA, $4C_2$</td>
<td>100</td>
<td>2.23</td>
<td>82</td>
<td>140</td>
<td>66</td>
<td>5.3</td>
</tr>
<tr>
<td>TBA, $4C_4$</td>
<td>100</td>
<td>2.20</td>
<td>104</td>
<td>118</td>
<td>73</td>
<td>8.6</td>
</tr>
<tr>
<td>DTMA, $1C_{10}$</td>
<td>100</td>
<td>2.26</td>
<td>65</td>
<td>205</td>
<td>107</td>
<td>8.5</td>
</tr>
<tr>
<td>HDTMA, $1C_{16}$</td>
<td>60</td>
<td>2.07</td>
<td>58</td>
<td>202</td>
<td>112</td>
<td>9.1</td>
</tr>
<tr>
<td>HDTMA, $1C_{16}$</td>
<td>100</td>
<td>1.75</td>
<td>56</td>
<td>219</td>
<td>89</td>
<td>13.9</td>
</tr>
</tbody>
</table>

Note, CEC = cation exchange capacity; TOC = total organic contents. The detailed description of the material properties was reported in Bate (2011).
lower applied vertical stresses (<100 kPa). Shear wave velocity was measured at every loading and unloading step. The transmitter bender element was excited by a function generator (33210A, Agilent) with a square wave of 20 Hz in frequency (0.05 s in period) and 10 V in amplitude because a square wave includes all frequencies and leads to obtaining a clear signal regardless of soil stiffness. A detailed description of electronic peripherals in Fig. 2 can be found from Lee and Santamarina (2005).

Compressibility of tested organoclays was evaluated according to the ASTM D2435 method B. From the measured relation between void ratio ($e$) and applied vertical effective stress ($\log \sigma'$), the compression index ($C_c = \Delta e / \log \Delta \sigma'$, during loading, slope of virgin compression line), and the swelling index ($C_s = \Delta e / \log \Delta \sigma'$, during unloading, slope of swelling line), were calculated.

4. Results

4.1. Shear wave velocity and preloading effect of organoclays

Measured shear wave velocity increased with an increase in applied stress, and a higher $V_s$ was obtained during unloading when compared to loading (Figure 3). This is attributable to the permanent fabric change and lateral stress locking induced during the loading step. The results of replicate experiments demonstrated repeatable data (coefficient of variation <3.5%). Additionally, comparable values of $V_s$ for organoclays were measured using BET and the resonant column test, which was demonstrated previously (Bate et al., 2013). Using the data illustrated in Fig. 3 and the relation between maximum shear modulus and shear wave velocity ($G_{\text{max}} = \rho \cdot V_s^2$, Eq. (5)), the $G_{\text{max}}$ ratio ($G_{\text{max}}$(OC)/$G_{\text{max}}$(NC) – PLR 2, Eq. (3)) was plotted as a function of PLR (Figure 4). Assuming a constant PLR exponent ($k$), the $G_{\text{max}}$ ratio should increase with an increase in PLR. However, the $G_{\text{max}}$ ratio calculated from the bender element tests on organoclays reached a peak at PLR approximately equal to 4, followed by a small decrement or an essentially constant value (Figure 4). This is attributable to the preconsolidation stress of 100 kPa, which was applied during sample preparation with slurry consolidation techniques. As a result, the shear wave velocity (or maximum shear modulus) measured during loading at vertical effective stresses less than 100 kPa were measured in the overconsolidated state, leading to a limited increment in $G_{\text{max}}$ ratio after PLR of 4.

Studies on inorganic soils showed that the PLR exponent ($K$) was a function of plasticity index ($PI$) (Hardin and Black, 1968; Seed et al., 1986): $K$ increased as the plasticity index increased. For the organoclays, the $G_{\text{max}}$ ratio (Eq. (3)) at a PLR = 2 was plotted as a function of the plasticity index; however, no apparent correlation was observed between $G_{\text{max}}$ ratio and PI (Figure 5). Additionally, $G_{\text{max}}$ ratios of tested organoclays were greater than those of inorganic soils, which indicated that the effect of preloading was more significant for these organic soils than for inorganic soils (Wehling et al., 2003). Consequently, in this study, the stress history effect on the tested organoclays was analyzed without consideration of the effects of plasticity index. Prior experimental results also corroborated the fact that plasticity index was not a primary factor influencing the small strain dynamic properties of organoclays (Bate et al., 2013). Instead, the total organic carbon content (TOC) was the primary variable controlling the dynamic properties of organoclays, such as maximum shear modulus, shear modulus reduction, and damping ratio. The $G_{\text{max}}$(OC)/$G_{\text{nc}}$(OC) for organoclays measured at PLR = 2 (unloading vertical effective stress of 100 kPa) revealed an almost linear decrement as total organic carbon content

4. Results

4.1. Shear wave velocity and preloading effect of organoclays

Measured shear wave velocity increased with an increase in applied stress, and a higher $V_s$ was obtained during unloading when compared to loading (Figure 3). This is attributable to the permanent fabric change and lateral stress locking induced during the loading step. The results of replicate experiments demonstrated repeatable data (coefficient of variation <3.5%). Additionally, comparable values of $V_s$ for organoclays were measured using BET and the resonant column test, which was demonstrated previously (Bate et al., 2013). Using the data illustrated in Fig. 3 and the relation between maximum shear modulus and shear wave velocity ($G_{\text{max}} = \rho \cdot V_s^2$, Eq. (5)), the $G_{\text{max}}$ ratio ($G_{\text{max}}$(OC)/$G_{\text{max}}$(NC) – PLR 2, Eq. (3)) was plotted as a function of PLR (Figure 4). Assuming a constant PLR exponent ($k$), the $G_{\text{max}}$ ratio should increase with an increase in PLR. However, the $G_{\text{max}}$ ratio calculated from the bender element tests on organoclays reached a peak at PLR approximately equal to 4, followed by a small decrement or an essentially constant value (Figure 4). This is attributable to the preconsolidation stress of 100 kPa, which was applied during sample preparation with slurry consolidation techniques. As a result, the shear wave velocity (or maximum shear modulus) measured during loading at vertical effective stresses less than 100 kPa were measured in the overconsolidated state, leading to a limited increment in $G_{\text{max}}$ ratio after PLR of 4.

Studies on inorganic soils showed that the PLR exponent ($K$) was a function of plasticity index ($PI$) (Hardin and Black, 1968; Seed et al., 1986): $K$ increased as the plasticity index increased. For the organoclays, the $G_{\text{max}}$ ratio (Eq. (3)) at a PLR = 2 was plotted as a function of the plasticity index; however, no apparent correlation was observed between $G_{\text{max}}$ ratio and PI (Figure 5). Additionally, $G_{\text{max}}$ ratios of tested organoclays were greater than those of inorganic soils, which indicated that the effect of preloading was more significant for these organic soils than for inorganic soils (Wehling et al., 2003). Consequently, in this study, the stress history effect on the tested organoclays was analyzed without consideration of the effects of plasticity index. Prior experimental results also corroborated the fact that plasticity index was not a primary factor influencing the small strain dynamic properties of organoclays (Bate et al., 2013). Instead, the total organic carbon content (TOC) was the primary variable controlling the dynamic properties of organoclays, such as maximum shear modulus, shear modulus reduction, and damping ratio. The $G_{\text{max}}$(OC)/$G_{\text{nc}}$(OC) for organoclays measured at PLR = 2 (unloading vertical effective stress of 100 kPa) revealed an almost linear decrement as total organic carbon content
increased (Figure 6). This trend suggested that the effect of stress history was less significant at higher levels of total organic carbon content. In contrast, the effect of cation structure (i.e., cation’s size, length of alkyl chain, and density of organic loading) on the preloading effect of organoclays was not significant.

4.2. Stiffness anisotropy of organoclays

The ratio of $G_{\text{max}}(HV)$ to $G_{\text{max}}(VH)$ ($G_{\text{max}}(HV)/G_{\text{max}}(VH) = \Lambda_2 / \Lambda_1$, Case 1 in Table 1) was compared under the vertical effective stress of 100 kPa (loading) to quantify the cross anisotropy of organoclays (Figure 7). The measured $G_{\text{max}}(HV)/G_{\text{max}}(VH)$ values of the tested organoclays ranged between 0.74 and 1.21 at applied vertical stresses of 50, 100, and 200 kPa during both loading and unloading (Table 1), which was taken as evidence that the lab-prepared engineered organoclays showed cross anisotropy at the applied stress level (up to 200 kPa vertically), as was anticipated because of the sample preparation method (i.e., one-dimensional compression from slurry) (Jovicic and Coop, 1998).

The ratio of $G_{\text{max}}(HH)$ to $G_{\text{max}}(VH)$ for the tested organoclays located between 0.85 and 1.5, indicating that the effect of stress-induced anisotropy was small (Case 2 in Table 1 and Figure 8). Additionally, the ratio of $G_{\text{max}}(HH)/G_{\text{max}}(VH)$ increased with loading ($\sigma_v' = 100 \rightarrow 200$ kPa) and unloading ($\sigma_v' = 200 \rightarrow 100$ kPa) processes, reflecting a gradual increase in the orientation of soil particles to the horizontal direction (Kawaguchi et al., 2008) and an increase in horizontal stress.
due to lateral stress locking, respectively (Figure 8a). In addition, the ratio of $G_{\text{max}}(HH)/G_{\text{max}}(VH)$ decreased with an increase in total organic content (Figure 8b). Therefore, it may be notable that with an increase in TOC, organoclays will have greater stiffness and strength (Bate et al., 2013, 2014) leading to a decrease both in horizontal stress (Jaky, 1944) and the ratio of $G_{\text{max}}(HH)/G_{\text{max}}(VH)$. In contrast, similar to the result of the preloading effect, the effect of cation structure (i.e., cation's size, length of alkyl chain, and density of organic loading) on stiffness anisotropy of organoclays was not significant.

The measured ratios of $G_{\text{max}}(HH)$ to $G_{\text{max}}(VH)$ of organoclays in Fig. 8 were similar to that of previous studies on inorganic fine grained soils (Jamiolkowski et al., 1995; Pennington et al., 1997; Jovicic and Coop, 1998) indicating that the presence of organic matter on soils may not alter the stiffness anisotropy of soils at small strain. Conversely, this high ratio of $G_{\text{max}}(HH)$ to $G_{\text{max}}(VH)$ may reflect that the strain-induced anisotropy (or inherent anisotropy) was more significant in the stiffness anisotropy of organoclays, indicating that organoclays are stiffer horizontally rather than vertically. This significant strain-induced anisotropy effect, which was caused by preferential orientation of platy particles, can be qualitatively demonstrated by the comparison of the ratio of $G_{\text{max}}(HH)$ to $G_{\text{max}}(VH)$ at unloading vertical stress ranging from 12.5 kPa to 50 kPa ($G_{\text{max}}(HH)/G_{\text{max}}(VH) = \Lambda_3 / \Lambda_1$, condition of Case 3 in Table 1), because it could be assumed that $\sigma'_{\text{fl}} \approx \sigma'_{\text{fi}}$ due to the lateral stress locking around this stress level (Figure 9). The obtained inherent anisotropy factors ($\Lambda_3/\Lambda_1$) ranged from 0.93 for 100TMA to 1.42 for 100 TEA, meaning that organoclays showed significant strain-induced anisotropy (or inherent anisotropy).

5. Discussion

5.1. Stiffness of organoclays in overconsolidated state as a function of TOC

The stress history effect is observed in cases where soils have higher shear wave velocity (or maximum shear modulus) during unloading when compared to loading, which reflects both permanent deformation (fabric change) and horizontal stress locking. Using this framework for analyzing the effect of stress history for the organoclays, a simple phase relationship calculation illustrated that the parameter $(1 - C_s/C_c)$, where $C_s$ is the swelling index and $C_c$ is the compression index, is the ratio between the permanent void ratio change and the total void ratio change. Subsequently, the parameter $(1 - C_s/C_c)$ was employed as a surrogate to represent the relative permanent fabric change of organoclays. The parameter $(1 - C_s/C_c)$ is close to zero for the soils with purely elastic deformation ($C_s \approx C_c$), but will increase with permanent fabric change (i.e., plastic deformation) of soils. From the test results: $(1 - C_s/C_c)$ of organoclays was a function of TOC as shown in Fig. 10. The data demonstrate that, with the exception of 100TMA, the relative permanent fabric change decreased with increasing total organic carbon content. This suggested that organoclays with high organic carbon content experienced smaller stress history effects than those with low organic carbon content, due to the smaller permanent fabric change (Figures 6 and 10).

The measured compression index ($C_c$) was inconsistent with previous settlement test results on highly organic soils (Kishida et al., 2006; Kallioglou et al., 2009), as $C_c$ of engineered organoclays decreased with increasing TOC (Figure 11). This behavior can be attributed to the hydrophobicity of organoclays; as the percentage of organic carbon sorbed to the clay surface was increased, a hydrophobic interlayer was created, resulting in a reduction in the amount of sorbed water in the clay interlayer and a smaller compression index at higher organic contents (Burns et al., 2006). In contrast, swelling indices of organoclays initially decreased with increasing TOC, reached the minimum values at approximately 8% TOC, and then increased as TOC continued to increase (Figure 11). The reason for this complex behavior in swelling indices was not clear; however, it can be postulated that there were competing mechanisms between hydrophobicity and the interlayer arrangement of cations in the organoclays. Organoclays with high organic contents would have more complex interlayer structure than those with low organic contents because, as total organic content increased, the arrangement of the organic cations on the particle surface changed from a monolayer structure to a bilayer or a paraffin (pseudo-trilayers) structure (Zhao and Burns, 2012; Bate et al., 2014). Consequently, organoclays with high TOC may recover greater strain than those with low TOC due to the structured arrangement of the cations in the interlayer. On the other hand, organoclays with high TOC also have higher hydrophobicity and are likely to experience limited swelling due to lack of hydration by water. These two interacting mechanisms may be the reason for both the complex behavior of swelling indices of organoclays and $(1 - C_s/C_c)$ of 100TMA, which showed a smaller value when compared to other organoclays (Figures 10 and 11). Consequently, the maximum $G/G_{\text{max}}$ was obtained at approximately TOC = 5% (Figure 6), but due to the higher lateral stress locking of 100TMA when compared to other organoclays, the stress history effect appeared to decrease with increasing TOC.

Mayne and Kulhawy (1982) proposed a relationship between the coefficient of lateral earth pressure at rest ($K_0$) and the critical state
friction angle ($\varphi_{cs}$) for overconsolidated soils during loading and unloading:

$$K_0 = (1 - \sin \varphi_{cs}) \cdot \text{OCR}^{0.45}. \quad (9)$$

It is worth noting that Eq. (9) only provides a preliminary estimation (Terzaghi et al., 1943; Watabe et al., 2003); therefore, additional validation of $K_0$ was performed by rearranging the equation of Case 2 in Table 1, which is the estimation of $K_0$ stress states by employing paired $G_{\text{max}}$ modes (Sully and Campanella, 1995; Zeng and Ni, 1998; Cai et al., 2011; Ku and Mayne, 2013). Good agreement between $K_0$ estimated by Mayne and Kulhawy’s equation and the equation of Case 2 in Table 1 was found (data not shown). Therefore, $K_0$ of tested organoclays was estimated with Eq. (9). Previous studies found that the critical state friction angle of organoclays increased with total organic content and with the critical state friction angles for the five organoclays in this study, i.e., 100TMA, 100TEA, 100TBA, 100DTMA, and 100HDTMA bentonites, which measured as 41.1°, 46.7°, 48.4°, 52.6°, and 60.8°, respectively (Bate et al., 2014). The critical state friction angle of 60HDTMA was not determined in Bate et al. (2014). A result, the horizontal stress of organoclays with low total organic content experienced high lateral stress during unloading (Figure 12), which resulted from the fabric interlocking due to stress overconsolidation. The increase in friction resulted in a lower coefficient of lateral earth pressure at rest ($K_0$) during unloading, and a larger impact of overconsolidation as the total organic content was decreased. That is, the stress history effect of organoclays decreased with increasing TOC (Figure 6).

5.2. Comparison with inorganic fine grained soil by regression analysis

To compare the results of the tested organoclays with those of inorganic soils, regression analysis was performed using the regression software (R) (Team, 2010). All possible factors impacting the maximum shear modulus of inorganic or organic soils were considered in order to get the functional relationship of each parameter with maximum shear modulus of organoclays (Table 3). Cases 1 and 2 in Table 3 were obtained by employing vertical effective stress and mean effective stress, respectively. It can be observed from the above two equations that void ratio, organic carbon content, preloading ratio, and applied stress are the primary variables determining the stiffness of organoclays. From the regression analysis of the experimental results, plasticity index ($PI$) did not identify a statistically significant effect ($P_r = 0.59$); therefore, the $PI$ term was not included. Additionally, the effect of TOC on $G_{\text{max}}$ was discussed by Bate et al. (2013), and will not be reported in this study.

By employing mean effective stress instead of vertical effective stress, the impact of stress history on the maximum shear modulus can be reduced because the mean effective stress reflects the increased horizontal stress due to lateral stress locking. However, deviating from the behavior observed for inorganic fine grains (Shibuya et al., 1992; Jamiolkowski et al., 1995), the PLR exponents of Cases 1 and 2 in Table 3 were greater than 0.3, even though the void ratio function was employed. The relatively high PLR exponent, when compared to inorganic soils, may be attributed to the unique settlement characteristics of organoclays. That is, for inorganic fine grains, the ratio of swelling index to compression index generally ranged from 0.1 to 0.2 (Das, 2001); however, for the tested organoclays, it ranged from 0.025 to 0.07 as a result of the limited rebound of the organoclays. This results in greater permanent fabric change for organoclays compared to inorganic soils.

In addition, by comparing the above equations with those used to estimate $G_{\text{max}}$ for inorganic soils, it is clear that the stress exponent was very similar to that of inorganic soils, while the void ratio exponent was smaller than that of inorganic soils (Bate et al., 2013). Further comparison with the behavior of inorganic fine grained soils was performed by excluding the void ratio function as shown in Cases 3 and 4 (Table 3). By excluding the void ratio function, a decrease in $r^2$ can be observed, reflecting the importance of the void ratio function to the proper estimation of $G_{\text{max}}$. In addition, two pronounced changes, reflected by an increase in the PLR and stress exponents, were also observed. It is notable that this increased PLR exponent of 0.71 in Case 3 is similar to that of Wehling et al. (2003) for the Sherman Island peaty organic soils, which indicated that the effect of preloading was more significant for organic soils than for inorganic soils. The stress exponent of 0.77 was similar to previously reported values on both inorganic soils (Viggiani and Atkinson, 1995) and organic soils.

Table 3

<table>
<thead>
<tr>
<th>Regression equation</th>
<th>$r^2$</th>
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<tr>
<td>$G_{\text{max}}(\text{VH}) = 104.3 \times e^{-1} \times \text{TOC}^{0.825} \times P_a^{0.885} \times \sigma_{m}^{0.885}$</td>
<td>0.957</td>
</tr>
<tr>
<td>$G_{\text{max}}(\text{VH}) = 115.6 \times e^{-1} \times \text{TOC}^{0.881} \times P_a^{0.882} \times \sigma_{m}^{0.885}$</td>
<td>0.957</td>
</tr>
<tr>
<td>$G_{\text{max}}(\text{VH}) = 24.1 \times \text{TOC}^{0.775} \times \sigma_{m}^{0.775} \times P_a^{0.825}$</td>
<td>0.859</td>
</tr>
<tr>
<td>$G_{\text{max}}(\text{VH}) = 28.2 \times \text{TOC}^{0.885} \times \sigma_{m}^{0.775} \times P_a^{0.825}$</td>
<td>0.859</td>
</tr>
</tbody>
</table>

Note, $e =$ void ratio; $\text{TOC} =$ organic carbon content in %; $\text{PLR} =$ preloading ratio; $\sigma_{m} =$ vertical and mean effective stress, respectively, in kPa; $P_a =$ atmosphere pressure (100 kPa); $r^2 =$ coefficient of determination.
2. The preloading effect of organoclays decreased with increasing total
1. In contrast to the behavior observed for inorganic organoclays, the following key observations were drawn:

References
3. Tested organoclays showed cross anisotropy; while, stress-induced with variable properties, this experimental investigation examined
6. Conclusions

Because natural organic matter has a highly heterogeneous structure with variable properties, this experimental investigation examined the effects of preloading and anisotropy at small strain on dynamic properties of organoclays synthesized using five different quaternary ammonium cations. By performing bender element tests on those organoclays, the following key observations were drawn:

1. In contrast to the behavior observed for inorganic fine grained soils, the preloading effect (or PLR exponent) for organoclays was not a function of the plasticity index.

2. The preloading effect of organoclays decreased with increasing total organic content due to a decrease in permanent fabric change and lateral stress locking. The PLR exponent in the maximum shear modulus estimating formulas was larger than that observed for inorganic fine grained soils due to the limited rebound of organoclays.

3. Tested organoclays showed cross anisotropy; while, stress-induced anisotropy was not significant. In contrast, organoclays indicated significant strain-induced anisotropy (or inherent anisotropy), indicating that the structure of organoclays was stiffer in the horizontal direction than in the vertical direction.

4. Stiffness anisotropy of engineered organoclays was comparable to that of inorganic fine grained soils.

5. Although the natural organic matter has a much more complex structure than the quaternary ammonium cations used in this study, the effects of preloading and anisotropy on the stiffness of the organoclays in this study is consistent with the results from previous studies on natural organic soils.

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