Dynamic properties of fine-grained soils engineered with a controlled organic phase

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A R T I C L E   I N F O

Article history:
Received 12 July 2012
Received in revised form 29 May 2013
Accepted 12 July 2013
Available online 1 August 2013

Keywords:
Initial tangent shear modulus
Shear wave velocity
Damping ratio
Clay
Organoclays
Bender element
Resonant column
Small strain stiffness
Cyclic loading

A B S T R A C T

Soils with high organic content are frequently encountered beneath earthquake sensitive infrastructure, such as bridges or levees. Historically, the dynamic properties of these organically rich soils have been difficult to predict due to the heterogeneity of the natural organic matter that is found in natural soils, even though their response to dynamic loading remains critical to assessing the ongoing stability of the infrastructure. In this study, an experimental investigation was performed on a montmorillonite soil that was modified with a controlled organic phase. Quaternary ammonium cations were exchanged onto the soil particle surfaces through cation exchange with the clay’s naturally occurring cations (e.g., Na+, Ca2+). Quaternary ammonium cations with a variable structure were chosen, which allowed control on the cation’s size and length of alkyl chain, as well as a control on the density of organic loading on the clay surface. The dynamic properties of organoclays were then quantified experimentally using resonant column and bender element tests. This study demonstrated that the increase in the total organic carbon content of the soil increased the shear wave velocity and stiffness of the soil (Gmax) due to a reduction in the void ratio of the organically rich soil. Cation structure did have a measurable impact on the soil stiffness, with organic cations with carbon concentration primarily in a single tail demonstrating higher stiffness than those soils engineered with a branched cation structure. When compared to inorganic soils, the presence of the organic cations in the soil increased the range of linear elastic behavior of that soil, with the organoclays having a threshold strain of 0.024% or higher. The soil samples with the largest percentage of total organic carbon and the lowest void ratio demonstrated the largest damping ratio (ratio between dissipated and stored energy) during cyclic loading at small strain. Regression analysis of the dynamic test results demonstrated that the total organic content and the void ratio were the most dominant factors in determining Gmax for the high organic content clays.

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1. Introduction

Soils with high organic content are frequently encountered beneath earthquake sensitive infrastructure, such as bridges or levees. Historically, the dynamic properties of these organically rich soils have been difficult to predict due to the heterogeneity of the natural organic matter that is found in natural soils, even though their response to dynamic loading remains critical to assessing the ongoing stability of the infrastructure. In part, the systematic study of soils with high organic content is difficult due to the extreme variability in the nature of the organic matter found in a soil system, which can exist in states that range from low molecular weight dissolved compounds to large fibrous peaty particulates. Additionally, complicating the issue is the fact that organic matter can be geochemically reactive with particle surfaces and pore fluid, and can alter the water retention characteristics of a soil.

While many studies have quantified the dynamic properties of fine grain soils (e.g., [8,10,17,32,47,56]), and either peat or high organic content soils [5,18,19,20,21,23,24,45,50,61], relatively few studies have tested the effect of organic content in soils with low organic carbon contents (total organic carbon content < 15%). Tests on peat sampled beneath a levee in the Sacramento-San Joaquin Delta in California demonstrated that modulus reduction and damping ratio relationships were similar to those observed for high plasticity clays and reported that shear wave velocities were between approximately 20 and 130 m/s [5,61]. Of additional significance for high organic content soil is the fact that previous studies have shown that normalized secant shear modulus values increase and equivalent damping ratios decrease with increasing...
consolidation stress and increasing organic content [21,24,61]. By examining earthquake motions recorded at Union Bay in Seattle, Seed and Idriss [45] estimated that damping ratios of peat were approximately three times larger than those of the clays at the site, and were also more nonlinear than those clays. Resonant column experiments on the peat specimens from the Queensboro Bridge found that, for the tested range of cyclic shear strain (up to approximately 1%, at confining pressures ranging from 7 to 303 kPa), the peat exhibited essentially linear behavior with low damping ratio [50]. Resonant column tests on the Mercer Slough peat presented significant nonlinearity at low consolidation stresses, which decreased as the confining pressure increased [24]. Cyclic triaxial tests on a peat from the Sherman Island levee demonstrated that the normalized secant shear modulus and equivalent damping ratio versus cyclic shear strain amplitude relations were a function of the consolidation stress up to a critical value, exhibiting increasing linearity up to approximately 40 kPa [5,61].

While significant advances have been made in the understanding of the dynamic behavior of organic/peat soils, mechanistic understanding of their behavior under dynamic load remains complicated by the fact that natural organic matter is composed of such a complex structure. In this study, an experimental investigation was performed on a montmorillonite soil that was modified with a controlled organic phase. Quaternary ammonium cations were exchanged onto the soil particle surfaces through cation exchange with the clay’s naturally occurring cations (e.g., Na+, Ca2+). Quaternary ammonium cations with a variable structure were chosen, which allowed control on the cation’s size and length of alkyl chain, as well as a control on the density of organic loading on the clay surface. The dynamic properties of organoclay specimens were then quantified experimentally using resonant column and bender element tests. The results from this study were evaluated in terms of the effect of shear strain, total organic content, void ratio, plasticity index, and cation structure on the modulus and damping ratio of the organoclays.

2. Materials and methods

Organoclay specimens were prepared using a 1-D slurry consolidation method, as described in Ref. [3]. A brief summary of the preparation method follows. Organoclays were prepared using five quaternary ammonium organic cations: tetracylammonium (TMA, denoted: 4C1) chloride [(CH3)4NCl], tetraethammonium (TEA, denoted: 4C2) bromide [(CH2CH3)4NBr], tetrabutylammonium (TBA, denoted: 4C8) chloride [(CH3)4NCl], decyltrimethylammonium (DTMA, denoted: 1C10) bromide [(CH2)10N(C2H5)3Br], and hexadecyltrimethylammonium (HDTMA, denoted: 1C16) chloride [(CH2)16N(C3H7)3Cl]. All cation salts were obtained from Fisher Scientific, and were used as received. The water used in all experimentation was deionized (Barnstead E-pure).

Cations were chosen that would vary the size and the structure of the organic phase that was exchanged on the clay surface, with the experimental matrix designed to distinguish the effect between uniformly distributing carbon around the molecule center (i.e., TMA→TEA→TBA or 4C1→4C2→4C8) versus distributing the carbon in one long branch (i.e., TMA→DTMA→HDTMA or 4C1→1C10→1C16) (Fig. 1). Additionally, HDTMA-exchanged clays were prepared at 30, 60, and 100% of cation exchange capacity to test the effect of density of surface coverage, while TMA, TEA, TBA, and DTMA-exchanged clays were prepared at 100% of cation exchange capacity, to compare the effects of cation structure and size.

After the organic cations were exchanged onto the clay surfaces through ion exchange, the chosen clay slurry was incrementally loaded in a consolidation cell of 10.2 cm in diameter and 45.7 cm in height. Filter paper (P5, Fisher Scientific) and a geotextile were used to provide drainage from the top and the bottom of the cell, and the vertical load was applied to the slurry using the Load Trac Testing Systems (Geotac). Loading and unloading steps were applied in the following sequence: 3.5, 7, 14, 28, 50, 100, 50, 28, 14, 7, and 3.5 kPa, while deformations were recorded by the accompanying software Sigma-ICON (Geotac). After the end of primary consolidation of each loading step, the next loading step was applied. Six organoclays were prepared for testing with both the resonant column and the bender element: 100TMA, 100TEA, 100TBA, 100DTMA, 60HDTMA, and 100HDTMA. Also, 30HDTMA was tested with the resonant column only. After consolidation was completed, the specimens were extruded, and trimmed to final heights, ranging from 13.2 to 16.5 cm, with a diameter of 7.1 cm for the resonant column test; samples were trimmed to a diameter of 10.3 cm and height of 6.1 cm for the bender element tests.

The total organic carbon content (TOC) was measured for each organoclay using an organic carbon analyzer (TOC-VCPN, Shimadzu) and solid sample module (SSM-5000A, Shimadzu).

Fig. 1. Chemical formulas of organic cations used to synthesize organoclays. (a) TMA (4C1), (b) TEA (4C2), (c) TBA (4C8), (d) DTMA (1C10), (e) HDTMA (1C16).
The sample was combusted at 680 °C in the presence of an oxidation catalyst, and the resulting CO2 was measured using a non-dispersive infrared (NDIR) gas analyzer. A known reference material, anhydrous dextrose powder (Fisher Scientific), was used as the calibration source, and calibrations were performed daily during measurements.

Resonant column and bender element tests were performed to determine the dynamic properties of organoclays, including maximum shear modulus $G_{\text{max}}$, secant shear modulus $G_s$, and equivalent viscous damping ratio $\lambda$. A typical backbone curve, showing the relationship between the cyclic shear stress $\tau_c$ and cyclic shear strain amplitude $\gamma_c$ is given in Fig. 2. In this plot, the secant shear modulus $G_s$ was defined as $G_s=\tau_c/\gamma_c$ (hereafter the subscript $s$ was omitted for simplicity, and $G$ was used to represent secant shear modulus). The maximum shear modulus (or initial tangent shear modulus, $G_{\text{max}}$) was taken as the maximum value of $G$, which occurred at very small cyclic shear strain amplitude, where secant and tangent shear modulus were the same (Fig. 2). The equivalent viscous damping ratio $\lambda$ (hereafter, referred to as damping ratio) was defined as $\lambda = (1/2\pi)\omega A_{\text{loop}}/G_s\gamma_{\text{loop}}$, where $A_{\text{loop}}$ was the area of the hysteresis loop, and $G_s\gamma_{\text{loop}}$ were the secant shear modulus and cyclic shear strain amplitude at the tip of the backbone curve, respectively. There exists a cyclic threshold shear strain amplitude, defined as the volumetric threshold shear strain, $\gamma_{tv}$, below which soil is nonlinear but remains largely elastic with no, or insignificant, permanent microstructure changes, while above which soil becomes nonlinear and inelastic, with a significant permanent volume change or a permanent pore-water pressure change [57]. Volumetric threshold shear strain varies for different soils [40,46,52]; consequently, the cyclic shear strain magnitude at $G/G_{\text{max}}=0.95$ criterion was used in this study to avoid subjective assessment [15,38].

A Stokoe-type fixed-free resonant column test device was used in this study [34,54]. A coil magnet system was used as the drive mechanism, and torsional excitation was applied to the drive mechanism using sinusoidal voltage. An accelerometer was used to measure displacement at the top of the soil specimen. The loading frequency in the resonant column tests was increased until the response passed a maximum value. The specimen was allowed to vibrate freely throughout the test. All experiments were performed on the Nano-K™ “BISCUIT” vibration isolator platform (Model No. 150BM-1, Minus K technology, Inc.) to minimize the effect of ambient vibration. Current-mode source was used to reduce equipment generated damping ratio to a negligible level in real time [34] to limit counter electromotive force (Counter EMF), induced by the counter reaction of solenoids to the motion of the magnets, which can dissipate energy in the system, resulting in an equipment-generated damping ratio [59]. The specimen was loaded with sinusoidal excitation of a series of frequencies ranging from as low as 10 Hz to up to 300 Hz. The lowest frequency at which the response was locally maximized was the fundamental frequency ($\omega_f$) of the specimen [23], and was a function of the shear wave velocity of the specimen ($V_s$), the mass polar moment of inertia of the specimen ($I$), specimen density ($\rho$) and height ($h$), and the mass polar moment of inertia, $I_o$. The relationship was expressed as

$$I_o = \frac{\rho h^2}{V_s^2} \tan \left( \frac{\rho h^2}{V_s^2} \right)$$

(1)

which was solved by iteration, to obtain the shear wave velocity, $V_s$ ($V/H$), of the organoclays as a function of effective vertical stress. Previous studies have demonstrated the applicability of bender element testing in geotechnical engineering, as well as agreement of bender element test results with those of the resonant column [9,49]. Because the calculated maximum strain level near the bender element in this study was less than 0.0001% [9,26] and was less than the volumetric threshold shear strain in this study, the shear modulus from the bender element tests was taken as the initial tangent shear modulus. A modified oedometer cell (102.5 mm in diameter and 80.3 mm in height) was fitted with bender elements (10 mm in length, 7 mm in width, and 0.6 mm in thickness, with a 4 mm extrusion length from the cell), and was used to record travel time through the modified clay soils [27]. Parallel-type bender elements were employed to minimize electronic coupling between the source and the receiver. Bender elements were directly connected to coaxial cables, coated with polyurethane, electrically shielded with conductive paint, grounded, and anchored into nylon set screws. Shear waves were measured during the consolidation loading stages, and were conducted at no lateral strain condition with vertical stresses ranging from 1.4 to 200 kPa. Control and data acquisition equipment consisted of a function/arbitrary waveform generator (33210A, Agilent), filter/signal conditioner (3364, Krohn-Hite), and an oscilloscope (DSOS014A, Agilent). The transmitter was excited by a square wave of a single frequency $f=20$ Hz, and amplitude $=10$ V, which was generated by a function generator. The receiver was connected to a filter amplifier that, in turn, was connected to the digital oscilloscope with a sampling rate of 2000 data points. The digital oscilloscope also received a direct square wave from the function generator, which was used to determine the time lag between the input and output waves. The waves recorded by the oscilloscope were processed to determine the travel time (t) of the shear wave. The first arrival time (t) of each signal was carefully chosen by considering the near field effect [42], and the tip-to-tip distance between two bender elements was employed as the travel distance (L) [9,11,55]. Qualities of the recorded signals were enhanced through a signal matching process using Mathcad. The maximum shear modulus...
$G_{\text{max}}$ was calculated based on the measured shear wave velocity, $V_s(V_H)$ and mass density ($\rho$) using $G_{\text{max}} = \rho V_s^2$ equation.

Shear wave velocities for the bender element at vertical normal effective stress of 100 kPa and resonant column tests at isotropic normal effective stress of 50 kPa were compared at similar levels of mean normal effective stress. Experimental studies have demonstrated that the stress normal to the plane of particle movement and shear wave propagation (termed polarization plane) had a negligible effect on the shear modulus [1, 14, 22, 28, 39, 41, 62], so the mean effective normal stress $\sigma_v'$ in the polarization plane was calculated according to:

$$\sigma_v' = \frac{\sigma_v' + K_0 \times \sigma_v'}{2}$$

where $K_0$ is the coefficient of lateral pressure and $\sigma_v'$ is the applied vertical effective stress. Assuming $K_0 = 1 - \sin \phi'$ [16], where the critical state effective friction angle $\phi'$ ranges from 27 to 59° [3], the resulting mean normal stresses were between 57 and 77 kPa for the bender element tests. It was noted that Jaky's equation only provides preliminary estimation [33, 36, 53, 60]. Further validation of the estimated $K_0$ was performed with the $e$-log $\sigma_v'$ curves obtained from the isotropic consolidation results (data not shown) for the same organoclay prepared with the slurry consolidation procedure as described above. The preconsolidation mean normal stresses obtained from the $e$-log $\sigma_v'$ curves range from 50 to 80 kPa, which agreed reasonably well with those obtained from Jaky's equation. Therefore, resonant column tests, performed with a mean effective stress of 50 kPa, were at similar level of mean normal effective stress with bender element tests for the comparison of shear wave velocity test results.

3. Results

3.1. Shear wave velocity

Typical S-wave signals, measured using bender elements, demonstrated significant differences in arrival time as the organic content of the clay increased, as shown by the S-wave signals $V_s(V_H)$ for 100HDTMA (1C$_{16}$) versus 100TMA (4C$_1$) organoclays (Fig. 3). Determination of shear wave velocity, as a function of applied vertical stress for all tested organoclays, clearly showed that by increasing the total organic content bound to the clay particles, the measured shear wave velocity of the soils increased (Fig. 4). Note that the clays tested were slurry consolidated to 100 kPa (nominal) and, up to approximately 50 kPa, demonstrated relatively little sensitivity to applied vertical stress, as was anticipated. The shear wave velocity data also substantiated the observation that the structure of the organic cation influenced the organoclay's dependence on vertical stress. As the vertical stress increased, the measured shear wave velocities increased more rapidly when there was an increase in the size of the cation branch (i.e., TMA compared to TEA and TBA, broken lines in Fig. 4), as compared to the increased length of the long C-chain (i.e., TMA compared to DTMA and HDTMA, solid lines in Fig. 4).

Shear wave velocities and stiffness (in terms of maximum shear modulus $G_{\text{max}}$) were determined by both the resonant column and bender element tests. The frequencies in the resonant column test (22–62 Hz) were significantly different from those in the bender

![Fig. 3](image-url). Typical S-wave signal ($V_s(V_H)$) measured for organoclay specimens: (a) HDTMA clay exchanged at 100% CEC (1C$_{16}$); (b) TMA clay exchanged at 100% CEC (4C$_1$).

![Fig. 4](image-url). Measured shear wave velocity as a function of vertical effective stress.
element tests (2703–5000 Hz). This difference will affect the maximum shear modulus \[34,48\]. Kramers–Kronig relationship can be used to estimate the frequency influence on maximum shear modulus \[35\]. Due to the difficulty in obtaining the relationship between shear modulus and frequency from zero to infinity, an approximate form of Kramers–Kronig relationship was introduced \[4\] as shown in Eq. (3):

\[
\beta(\omega) = \frac{\pi}{4} \left( \frac{d \ln G_{\max}(x)}{d \ln(x)} \right)_{x = \omega}
\]  

(3)

where \( x \) is the dummy variable used in derivation. With the knowledge of maximum shear modulus, damping ratio, and resonant frequencies of the resonant column test, the maximum shear modulus at the frequencies used in the bender element test can be calculated with Eq. (3). Shear wave velocity and shear modulus at the frequencies used in the bender element test resonant frequencies of the resonant column test, the maximum knowledge of maximum shear modulus, damping ratio, and can be used to estimate the frequency in the resonant column test.

As was anticipated, the measured shear wave velocity of soils was related to the effective stress state. In the absence of capillary forces, the relationship can be described as follows \[41,44\]:

\[
V_s = \alpha \left( \frac{\sigma_0 - \sigma_m}{1 \text{ kPa}} \right)^\beta
\]  

(4)

where \( \sigma_m \) is mean normal effective stress in the polarization plane in kPa, \( \alpha \) = experimentally determined constant = \( f \) (type of packing, e.g., porosity, coordination number, material properties, contact behavior, and fabric changes), and \( \beta \) = experimentally determined constant = \( f \) (contact effects, e.g., particle size, shape, and structure) \[41,44\]. Generally, as the stiffness of soil increases, the \( \alpha \)-factor increases but the \( \beta \)-exponent decreases. Analysis of the shear wave velocity \( V_s \) data measured for organoclays at effective vertical stresses larger than preconsolidation stresses (normally consolidated) showed that as the total organic content increased, the \( \alpha \)-factor increased and the \( \beta \)-exponent decreased, indicating that the stiffness of the organoclays increased with increasing organic carbon content (Fig. 5). Regression analysis of the tested organoclays indicated the following relationship:

\[
\beta = 0.5023 - \frac{\alpha}{217.39}
\]  

(5)

Eq. (5) was plotted along with shear wave velocity trends for inorganic soils \[44\], as well as data collected in a database of field measurements \[25\] in Fig. 6. All data for the organoclays were in the range of soft NC clays and the trend for organoclays was consistent with the results of previous studies.

### 3.2. Initial tangent shear modulus, \( G_{\max} \)

Values of the initial tangent shear modulus \( (G_{\max}) \), determined from resonant column tests, showed that as the total organic carbon content of the organoclays increased, either through an increase at all four branch locations or through an increase in the tail length at one position, the initial tangent shear modulus also increased (Table 1 and Fig. 7a). In addition to the data measured in the resonant column tests, the bender element tests determined that the initial tangent shear modulus was a function of applied vertical stress, and also revealed the same trends as were observed in the resonant column tests (Table 1).

It is important to note that the addition of organic cations to the clay surface induced an increase in the hydrophobicity of the surface, which resulted in the alteration of the water content and the fabric of the clay formed during slurry consolidation. Because the samples were slurry consolidated to constant consolidation stress (100 kPa), the final void ratio for the seven resulting samples varied from a low of 2.5 for 100TMA clay to a high of 8.7 for 100TBA clay. A significant difference in the void ratio of the...
samples contributed to shear modulus values that differed by a factor of as much as six, although clearly the structure of the organic cation also impacted the measured shear modulus value (Fig. 7b).

### 3.3. Secant shear modulus reduction curves

Secant shear modulus reduction curves of organoclays, obtained from resonant column tests, illustrated that $G/G_{\text{max}}$ decreased as strain increased for organoclays with a low organic carbon content ($\text{TOC} \leq 8.5\%$, including 100TMA, 100TEA, 30HDTMA, and 100DTMA); that is, the rate of reduction was lower as the organic carbon content of the organoclay increased (Fig. 8). All four organoclays, with a low organic content, illustrated approximately the same volumetric threshold shear strain at 0.024%. The volumetric threshold shear strain typically measured for clays is approximately 0.01% [31], demonstrating that the exchanged organic cations increased the elastic range of the organoclays. For organoclays with a high organic carbon content ($\text{O.C.} \geq 8.5\%$, including 100TBA, 60HDTMA, and 100HDTMA), reduction of the shear modulus was not observed within the strain limit of the resonant column device. The strain limit was lower for stiffer soils (soils with higher $G_{\text{max}}$), when an equal amount of voltage excitation was applied to the electromagnetic solenoids of the resonant column device.

The shear modulus reduction curves for 100TMA, 100TEA, 100DTMA, and 30HDTMA (low organic content organoclays) were compared with the curves proposed by Vucetic and Dobry [58] for soils with plasticity indices between 100 and 200 (corresponding approximately to the plasticity indices measured for the organoclays (74 to 184)) (Fig. 8). The shapes of the shear modulus reduction curves of organoclays were in reasonable agreement with the non-organic soils that were summarized by Vucetic and Dobry [58].

### 3.4. Damping ratio

Data from the resonant column test also allowed analysis of the damping ratio vs. shear strain for the seven organoclays tested in the study (Fig. 9). As was observed for the modulus degradation behavior, the organoclays with a low total organic carbon content ($\text{TOC} \leq 8.5\%$, including 100TMA, 100TEA,
Comparing the organic cation also impacted the measured soil stiffness. The primary mechanism that increased the total organic carbon content of the organoclays controlled organic phase indicated that any mechanism that increased past the volumetric threshold shear strain of approximately 0.024%. Damping ratios of high organic content organoclays were essentially constant at the tested strain range, with much higher values (2.7, 3.9, and 5.5% for 60HDTMA, 100HDTMA, and 100TBA organoclays, respectively) than were observed for the low organic content organoclays at shear strains below threshold strain. Constant damping ratios at tested strain ranges indicated that the elastic range of high organic carbon content organoclays was equal to or higher than 0.024%. However, the damping ratios of high organic content organoclays were much higher than those reported for natural soils by Vucetic and Dobry [58] (reference curves shown in Fig. 9), but were similar to those measured for naturally occurring and artificially prepared organic soils [18].

4. Discussion

4.1. Dynamic properties

The results of the dynamic behavior of soils created with a controlled organic phase indicated that any mechanism that increased the total organic carbon content of the organoclays resulted in increased shear wave velocity, stiffness, and damping ratio of the soil. The primary mechanism that influenced the change in behavior was the reduction in the interlayer water content and, hence, the void ratio, that was due to the presence of organic cations in the clay particle interlayer. Increasing the amount of organic carbon sorbed onto the clay surfaces altered the particle to particle interaction by first decreasing the net surface charge and repulsion forces of the clay particles [2], allowing a closer particle to particle approach. Additionally, the presence of the organic cation in the clay interlayer resulted in a disruption of the sorbed interlayer water, resulting in a dewatering effect.

Given the same small strain, the increased contacts in the denser soils resulted in an increase in shear wave velocity and stiffness of the organoclays and, as would be anticipated, a lower void ratio that led to a higher $G_{\text{max}}$ [8]. However, the structure of the organic cation also impacted the measured soil stiffness. Comparing $G_{\text{max}}$ as a function of cation structure (i.e., cations with branched versus tail structure) and organic carbon content, it was found that adding carbon by increasing the single C-chain length resulted in increased stiffness of organoclays, when compared to distributing the carbon uniformly around the molecule’s center in four branched locations. For example, 100TBA (4C4 branch structure) and 100DTMA (1C16 tail structure) organoclays had similar values of total organic carbon content and maximum shear modulus; however, the void ratio of 100DTMA organoclay was almost twice that of 100TBA organoclay. In contrast, 100TBA (4C4 branch structure) and 100HDTMA (1C16 tail structure) organoclays had similar void ratios, but 100HDTMA organoclay was a much stiffer soil than 100TBA organoclay, indicating that the structure of the organic phase within the clay interlayer was also influencing soil stiffness (Fig. 6). Frequency effects on $G_{\text{max}}$ were secondary as predicted in Eq. (3). Previous studies also support that the frequency in similar range with those in this study (22–62 Hz) did not change $G_{\text{max}}$ significantly [7,19,48,51].

In terms of damping ratio, the soil samples with the largest percentage of total organic carbon and the lowest void ratio demonstrated the largest energy dissipation during cyclic loading at small strain. The three organoclays (60HDTMA, 100HDTMA, and 100TBA) that had organic carbon contents > 8.5% exhibited the highest damping ratios (from ~0.03 to 0.05), while the organoclays with organic carbon contents ≤ 8.5% had damping ratios of ~0.01–0.02. In the one organoclay which had both a low void ratio and low organic carbon content (100TEA 4C2), the carbon content, rather than the void ratio, appeared to dominate the damping ratio response, exhibiting a damping ratio of ~0.02. It is important to note that the damping ratio results in this study were measured at their respective resonant frequencies, and that the damping ratio was a function of measurement frequency [12,34]. reported that the damping ratio of clayey soils increased as the excitation frequency increased from approximately 1 to 30 Hz (measurement frequencies in this study ranged from 22 to 62 Hz). Examination of the damping ratios of organoclays below the volumetric threshold shear strain, plotted as a function of resonant frequency, showed that the damping ratio increased slightly from 22 to 40 Hz, and then significantly from 40 to 60 Hz (Fig. 10). Comparing this to results from other studies [7,19,48,51] demonstrated that the increase in the damping ratio of organoclays could be attributed, in part, to the effects of frequency, but this was not the sole factor in the measured damping ratio.

The measured volumetric threshold shear strain of 0.024% for the low organic content organoclays (high organic content organoclays did not reach threshold) was used to gain insight into the fabric of the organoclays. Using the methods outlined by Santamarina et al. [44], the volumetric threshold shear strain was calculated as a function of clay fabric, assuming that the relative displacement between particles was no more than $10^{-11}$ m in the small-strain regime [44], with the typical length of clay plates of montmorillonite assumed to be 100–300 nm [37]. Four scenarios of fabric were examined: single particles arranged edge-to-edge (EE) or edge-to-face (EF), aggregated face-to-face, aggregated face-to-face with interlayer space, and aggregated edge-to-face formations (Table 3). Electron microscopy results [29,30] have shown that organoclays tend to form aggregates, with face-to-face (FF) aggregation. Assuming that (1) particles aggregate with a face-to-face arrangement, (2) aggregates form edge-to-face contacts with other particle aggregates (Table 3, scenario d), and (3) displacement only occurs at the contacts of aggregates would result in a calculated ratio that ranges from 0.03 to 0.08%. Given such a rough estimation, the assumption of a fabric formed from an edge-to-face assembly of aggregates yielded a volumetric threshold
shear strain range that was very close to the measured value (0.024%).

Overall, the total organic carbon content and void ratio of the soil were the best predictors of the dynamic behavior of the organoclays. Total organic carbon content was an indicator of the interactions within an aggregate (intra-aggregate), while the void ratio contained fabric information about inter-aggregate spaces. In addition, comparison between the two types of structures of organic cations (branch versus tail) indicated that the branched structure led to a less stiff soil and a soil that exhibited a higher dependence on effective vertical stress, when compared to the organic cations that had carbon primarily concentrated in a single tail. As the length of the carbon tail increased (i.e., TMA → DTMA → HDTMA or 4C1 → 1C10 → 1C16), the cations packed into the clay interlayer with the ammonium centered head group attracted to the clay surface, and the carbon-hydrogen tail extending toward the center of the particle’s interlayer [63]. The relatively hydrophobic cation tails interacted through hydrophobic lateral forces, effectively creating a spring-like organic interlayer phase that contributed additional macroscopic stiffness to the soil sample.

4.2. Regression analysis

The interplay of the soil fabric and void ratio, organic carbon content, effective stress, and plasticity index resulted in complex interactions in terms of the dynamic properties of the organoclays. Consequently, a least squares regression analysis was performed to develop relationships to estimate the shear modulus of the organoclays (Mathcad 14). To optimize the best fit between the measured values \( y^{\text{measured}} \) and the estimated \( y^{\text{estimated}} \), the following three error norms were employed in this study [43]:

\[
L_1 = \sum |e_i| \text{ sum of absolute errors}
\]

\[
L_2 = \left( \sum |e_i|^2 \right)^{0.5} \text{ sum of squared errors}
\]

\[
L_\infty = \max(|e_1|, \ldots, |e_2|, \ldots, |e_M|) \text{ maximum error}
\]

where, \( e_i = y^{\text{measured}} - y^{\text{estimated}} \).

In order to optimize the prediction of shear modulus, three different cases were considered, with the following four parameters: void ratio, plasticity index, total organic carbon content, and effective vertical stress (Table 2). The regression analysis demonstrated that, as was anticipated, void ratio and effective stress were dominant factors in the determination of the maximum shear modulus, with TOC also having a primary impact. Interestingly, the vertical effective stress exponent of 0.51 was similar to that found in previous studies for inorganic soils, indicating that the effect of stress on the maximum shear modulus was similar for both inorganic and organic soils. The void ratio exponent of approximately –0.1 was similar to that found by Kalligolou et al. [18] for organic sands, indicating that \( G_{\text{max}} \) of organic soils was less affected by the void ratio than inorganic soils. Finally, the results of the initial regression analysis indicated that the plasticity index did not have a statistically significant effect on the modulus prediction (\( Pr = 0.966 \)). Consequently, the plasticity index term was removed, and the regression analysis was performed without PI (Case 2). Additionally, to examine the behavior of a further simplified model, a third regression was performed, which also excluded the void ratio, in addition to PI (Case 3). The removal of void ratio from the prediction resulted in a significantly higher variance (Case 3). Most notably, when the void ratio was not considered, the vertical stress exponent increased to 0.73, which was similar to that of Vigliani and Atkinson [55] for inorganic fine grain soils and Wehling et al. [61] for Sherman Island peaty organic soils. Both of these previous studies did not consider the function of the void ratio. Overall, the best prediction was achieved when the parameters of void ratio, TOC, and effective stress were included in the regression. A relatively low variance was produced with these three parameters (Case 2).

Results of the regression analysis (Case 2) were used to develop a relationship for the initial tangent shear modulus that was normalized to account for the total organic content of the soil (Fig. 11, where \( F(\text{TOC}) = \text{TOC}^{0.812} \)). It is well known that increasing void ratio leads to a decrease in the small strain stiffness of a soil ([13,17,32,47,58]). This was also seen in the behavior trend of the organoclays. However, it is interesting to note that the influence of void ratio on \( G_{\text{max}} \) was less significant for organoclays (exponent ~ –1) than it was for inorganic soils (exponent ~ –1.3). This was due to the fact that the decreased void ratio effect was also implicitly included in the function of TOC, as the increasing total organic content resulted in increased mass densities [2].

The measured values of shear wave velocity for the organoclays ranged from approximately 50–200 m/s, which was consistent with values previously determined for peat [5,61]. In contrast with field data, the organoclays tested in this study demonstrated an increase in damping ratio as the organic content increased [21,24,61]. This difference in behavior is attributed to the significant degree of structure that results in the clay interlayer when the interlayer organic phase consists of a single, uniform cation. In natural systems, the structure of the interlayer organic matter is highly heterogeneous.
5. Conclusions

The dynamic response of clay soils engineered with a controlled organic phase was studied using resonant column and bender element tests. The structure of the organic cation, as well as the total organic carbon content, was varied in order to assess the impact of the structure of cation, as well as the distribution of carbon, within the clay’s interlayer space on a soil’s shear wave velocity, stiffness, and damping ratio. This study demonstrated that the increase in the total organic carbon content of the soil increased the shear wave velocity and stiffness of the soil due to a reduction in the void ratio of the organically rich soil. Cation structure did have a measurable impact on the soil stiffness, with organic cations with carbon concentrated primarily in a single tail demonstrating higher stiffness than those soils engineered with a branched cation structure. When compared to
inorganic soils, the presence of the organic cations in the soil increased the range of elastic behavior of that soil, with the organoclays having a volumetric threshold shear strain of 0.024% or higher. The soil samples with the largest percentage of total organic carbon and the lowest void ratio demonstrated the largest damping ratio (ratio between energy dissipation and stored) during cyclic loading at small strain. Regression analysis of the dynamic test results demonstrated that the total organic content and the void ratio were the most dominant factors in determining $G_{\text{max}}$ for the high organic content clays.

Acknowledgement

Dr. Glenn J. Rix provided the resonant column test device and gave valuable suggestions about the resonant column results. Dr. J. Carlos Santamarina offered insightful opinions on the analysis of the results. Their help is greatly appreciated. The authors would also like to gratefully acknowledge The Material Research Center and The Center for Infrastructure Engineering Studies of Missouri University of Science and Technology for their financial support.

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