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Shear Wave Velocity (Vs) Anisotropy of Kaolinite and Fly Ash Kaolinite Mixtures Modified with Controlled Organics

by

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16. Abstract

Anisotropy is an inherent property of soils. The anisotropy could either be induced by applied stress or inherent from particle eccentricity and preferential deposition. Other than stress and deposition, the anisotropy was also found resulted from the physicochemical environmental factors, such as pH, bulk fluid type and concentration. The investigations of the anisotropy behavior of clay particles have been carried out by researchers in the literature, however, the effect of organic agents and fly ash on the influence of the anisotropy property of clays still remains not well documented. Shear wave velocity transmitted by bender element was used to quantify the shear wave velocity (Vs) of the soil in three orthogonal directions, i.e., vh, hv, and hh. A floating wall consolidometer type bender element testing system was developed to study the anisotropic behavior of clay particles. The addition of fly ash and organic agents could largely affect the anisotropy property of kaolinite. Particle size analysis, zeta potential, and SEM tests were carried out to understand the micro fabric and Vs anisotropy. Salt treated kaolinite samples with different particle associations were thoroughly investigated. This research found that both salt and organic agents could induce micro fabric change of clay particles by charge neutralization and polymer bridging, thus influencing the anisotropy properties of the soil. Stress could also induce Vs anisotropy by changing the particle alignment. The addition of different amount of fly ash and organic types could induce Vs anisotropy in different directions. This research also supported that the cross-anisotropy was not true for kaolinite samples.

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ABSTRACT: Anisotropy is an inherent property of soils. The anisotropy could either be induced by applied stress or inherent from particle eccentricity and preferential deposition. Other than stress and deposition, the anisotropy was also found resulted from the physicochemical environmental factors, such as pH, bulk fluid type and concentration. The investigations of the anisotropy behavior of clay particles have been carried out by researchers in the literature, however, the effect of organic agents and fly ash on the influence of the anisotropy property of clays still remains not well documented. Shear wave velocity transmitted by bender element was used to quantify the shear wave velocity (Vs) of the soil in three orthogonal directions, i.e., vh, hv, and hh. A floating wall consolidometer type bender element testing system was developed to study the anisotropic behavior of clay particles. The addition of fly ash and organic agents could largely affect the anisotropy property of kaolinite. Particle size analysis, zeta potential, and SEM tests were carried out to understand the micro fabric and Vs anisotropy. Salt treated kaolinite samples with different particle associations were thoroughly investigated. This research found that both salt and organic agents could induce micro fabric change of clay particles by charge neutralization and polymer bridging, thus influencing the anisotropy properties of the soil. Stress could also induce Vs anisotropy by changing the particle alignment. The addition of different amount of fly ash and organic types could induce Vs anisotropy in different directions. This research also supported that the cross-anisotropy was not true for kaolinite samples.

Keywords: kaolinite, fabric, bender element, anisotropy, shear wave velocity, concentration

Introduction

Anisotropy is an inherent property of soils (Santamarina et al., 2001). The anisotropy property of a soil are related to three influencing factors, namely the stress anisotropy, stress-induced fabric anisotropy (consolidation or deformation), and physicochemical conditions (ionic strength and pH). Stress anisotropy is fabric-independent. Isotropic geomaterials, such as round sand, can be anisotropic due to the stress anisotropy. It was found that only stresses on the plane of wave propagation and particle vibration had significant effects on shear wave velocity (Roesler, 1979; Wang and Mok, 2008). This plane is termed polarization plane (Wang and Mok, 2008), which is denoted by two letters, v and h, with the first letter indicates wave propagation direction, and second letter indicates particle vibration direction. In addition to stress anisotropy, for anisotropic geomaterials, such as platy-shaped clay, consolidation under anisotropic stress can also induce fabric anisotropic properties. This is termed stress-induced fabric anisotropy (Santamarina et al., 2001). Anisotropic K_0-consolidation induces preferential alignment of clay fabric in direction normal to the applied loading (Santamarina et al., 2001). The higher the consolidation pressure, the more apparent V_s anisotropy is (Lee et al., 2008).

It is generally believed that the arrangement of particles in soils has a significant effect on the geotechnical properties (Yimsiri and Soga 2000; Santamarina et al., 2001). Most of the researchers (Nagaraj 1959; Seed and Chan 1959; Warkentin and Yong 1960; Olson 1960; Sloane and Kell 1966; McKeys and Yong 1971; Sridharan et al. 1971; Martin and Ladd 1974; McConnachie 1974; Mitchell 1993; and Bai and Smart 1997) focused on the effect of micro fabric on clay’s mechanical behavior and they reported that the shear strength of a cohesive soil were largely dependent on both physical and physicochemical factors. Ionic strength effects was studied on swelling/compressibility (Di Maio, 1996[a], b; Arasan et al. 2010), consolidation (Di

Maio 1996a, b; Gajo and Maines 2007), and strength (Moore and Mitchell 1974; “electromagnetic forces and soil strength” Di Maio and Fenelli 1994; Palomino and Santamarina, 2005; Gojo et al., 2007), while pH effects was studied on strength and Vs (Palomino and Santamarina, 2005; Fabric Map, Gojo et al., 2007). Based on the previous findings, physicochemical properties, such as ionic strength and pH, were found to have significant effects on the micro fabric formation of fine-grained soils (Santamarina et al., 2001). However, the effects of physicochemical properties on the shear wave velocity and its anisotropy have not been extensively studied in the literature.

The objectives of this research are to: (1) using a novel designed bender element system to study the shear wave velocity anisotropy of kaolinite and fly ash kaolinite soil mixtures modified with different organic agents. (2) Investigating the stress-induced fabric anisotropy during K_0 consolidation that affects the anisotropic Vs properties of soils at applied vertical stress up to 800kPa. (3) Studying the effects of fly ash and organic agents on the Vs anisotropy of kaolinite and fly ash kaolinite mixtures. (4) The mechanism of Vs anisotropy and its migration and magnification are explored by the microscopic study (SEM), zeta potential test, and grain size distribution analysis.

Materials and Experimental Methods

Georgia kaolinite (RP-2, Active Minerals International) was used in this study. The grain size distribution curve and the properties of Georgia kaolinite were shown in Table 1. The kaolin was an air-float processed clay, with a specific gravity G_s = 2.65 and an average aggregates diameter (d_{50}) of 0.004 mm. Class F fly ash from Lafarge power plants, Wisconsin, USA was used in this study. This fly ash is classified as Class F (ASTM standard C 618). It is different from class C fly ash, which contains high portion of calcium and exhibits self cementing when mixed with water (Parsa et al. 1996), Class F fly ash has no self cementing and normally used together with lime or other additives in ground improvement and stabilization. Fly ash particles are usually hollowed spheres varied in size under scanning electron microscopy (SEM). Most of the fly ash particles are smooth; however some relatively oversized particles have irregular shape. Also some vitreous unshaped fragments can be seen in the fly ash samples under SEM (Mollah et al 1993; Wang et al 2008). Figure 1 shows the results of SEM images of the fly ash particles. The particles ranged from few micros to a hundred micros. Small particles are attached to large particles, and the contact area varies significantly.

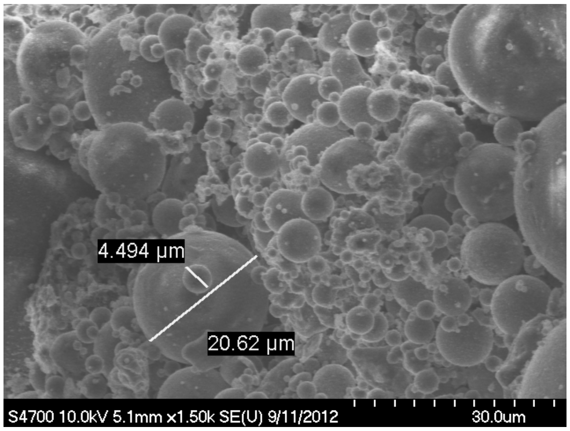


Figure 1 Fly Ash Particle Images under SEM (Lafarge, Wisconsin, Class F)

Table 1. Chemical analysis results and grain size distribution of RP-2 kaolinite (after Active Minerals International)

Chemical analysis results		**Grain Size Distribution**	
SiO2	45.60%	µm	% finer
Al2O3	38.40%	44	99.5

Fe2O3	0.88%	20	99
TiO2	1.69%	10	97
CaO	0.05%	5	95
MgO	0.02%	2	89
K2O	0.15%	1	77
Na2O	0.21%	0.5	60
LOI	13.70%	0.36	50

Nonionic Polyethylene Oxide (PEO), is perceived as a “flexible” polymer, with a structure described as a random coil and can change conformation dynamically in solution. The number and size of these polymer loops and tails will determine the flocculation efficiency and, hence, the settling rates and consolidation of kaolinite dispersions. Mpofu et al. (2004) studied the flocculation and dewatering behavior of kaolinite dispersions induced by PEO under different concentrations and temperature. The PEO was found to increase the settling rate, promote the consolidation process, and induce greater flocculation and dewatering behavior of the kaolinite dispersions.

Chitosan is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (such as crabs and shrimp) and cell walls of fungi. Chitosan is soluble in solutions with pH lower than 6.5 and is a positively charged bio-adhesive. Chitosan can bind particulates and induce flocculation and aggregation to clay particles. Kavazanjian et al (2009) reported that Chitosan could effectively stabilize the soil and increase the wind erosion resistance. Huang and Chen (1996) studied the feasibility of applying Chitosan to coagulate colloidal particles. The test results indicated that the chitosan is a potent coagulant for bentonite suspension. Their test results also indicated that the charge neutralization is not a major mechanism controlling the formation of floc for chitosan coagulation. Divakaran and Pillai (2001) reported that the presence of chitosan could effectively reduce the turbidity due to the flocculation and settling of kaolinite. Flocculation efficiency was found to be sensitive to the pH, and reached the maximum at pH=7.5. The flocculation was faster at higher concentrations of Chitosan and the flocs are larger and settled rapidly.

Xanthan gum is an anionic polysaccharide, derived from the bacterial coat of Xanthomonas campestris, used as a food additive and rheology modifier, commonly used as a food thickening agent (in salad dressings, for example) and a stabilizer (in cosmetic products, for example, to prevent ingredients from separating). In the oil industry, xanthan gum is used in large quantities, usually to thicken drilling mud (Taylor and Naser-EI-Din 1993). These fluids serve to carry the solids cut by the drilling bit back to the surface. Xanthan gum provides great "low end" rheology. It has also been added to concrete poured underwater, to increase its viscosity and prevent washout (Taylor and Naser-EI-Din 1993). Since the pseudoplastic nature of the xanthan gum solution, it is not suitable to use stoke's law to study the grain size distribution of the particles (Nuggent et al. 2009).

All the samples used in this research were obtained from slurry consolidation. Air-dried kaolinite clay was mixed with de-ionized water/salt solution/organic solution, a solid to water ratio was maintained at approximately 0.2. The mixture was then thoroughly mixed by hand and soaked for 24 hours before translated into the sample preparation cylinder. The dimension of the sample preparation tube is 45.7 x 11.7 cm (18 x 4.5 in) (height x diameter). Care was taken not to entrap air by pouring slowly and contacting slurry to the side of the tube. P5 filter paper (Fisher Scientific) and a nonwoven geotextile were placed on the top and bottom of the sample to secure a double drainage system. After the slurry transferred into the consolidation cylinder, stepped axial consolidation loading was then started, the loading steps were set at 7kPa, 14 kPa, 28 kPa, 62 kPa, 100 kPa, 62 kPa, 30 kPa, 14 kPa, 4 kPa, and 0 kPa respectively. During each loading, the settlement of the loading piston was monitored by an external dial gage; each step of loading was added until the end of primary consolidation was reached (judged by Taylor's method). The bulk solution was drained from the top and bottom. After reaching 100 kPa consolidation pressure, the sample was unloaded to 0 kPa, and then extruded with a small hydraulic jack. After measuring the height, weight, volume, water content of the sample, the sample was wrapped with plastic membrane, then placed into a double locked zip-lock bag, sealed PVC container, and stored in moist curing room. Typical height of the soil samples after slurry consolidation ranged from 12.7 to 17.8 cm (5 – 6 in).

Zeta potential of the kaolinite particles was measured by Malvern Zetasizer Nano ZS90 zeta potential analyzer. The Zetasizer was calibrated prior to measurement by using the standard calibrating solution. A pipette was used to transfer the solution from sedimentation cylinder into the Folded Capillary Cell. The cell was filled slowly with great care so that no air bubbles form being created. The Folded Capillary Cell was rinsed with deionized water 3 times to prevent cross-contamination after each measurement. The test temperature was set at 23.5 ^{o}C during all the experiments.

The grain size distribution of kaolinite particles in the supernatant, suspension and sediments were measured using dynamic light scattering (DLS) technique with the Malvern Zetasizer Nano ZS90 instrument. Samples in supernatant, suspension, and sediments in the sedimentation cylinder were extracted by pipette and transferred into the cuvettes. A 10mm depth of the sample in the cell was maintained for all the measurements. Samples were pipetted carefully into the bottom of the cuvette so that it was filled from the bottom up. After filling the sample, visual inspection was performed to check the trapped air bubbles and any detected air bubbles were cleaned before measurement. The cuvette was rinsed with deionized water 3 times so that to prevent cross-contamination and samples were preconditioned to 25 ^{o}C before each measurement.

Test Results

Particle Associations of Kaolinite

Palomino and Santamarina (2005) summarized from previous studies that at neutral pH, edge-to-face (EF) fabric configuration prevails at NaCl concentration less than 0.02 mol/l, while face-to-face (FF) configuration dominates at NaCl concentration larger than 0.1 mol/l. Edge-to edge (EE) configuration is the typical fabric formation at NaCl conetration between 0.02 and 0.1 mol/l. Scanning electron microscopy (SEM) images of Georgia RP-2 kaolinite under 3 different NaCl concentrations (0.003, 0.02, and 1 mol/l) were presented in Figure 1. The platy shaped kaolinite particle aggregates as indicated by short bold lines, and the fabric configuration of edge-to-face (EF) at 0.003 mol/l, edge-to-edge (EE) at 0.02 mol/l, and face-to-face (FF) at 1 mol/l NaCl concentrations were illustrated in Figure 2. The fabric configurations agree with Palomino and Santamarina (2005).

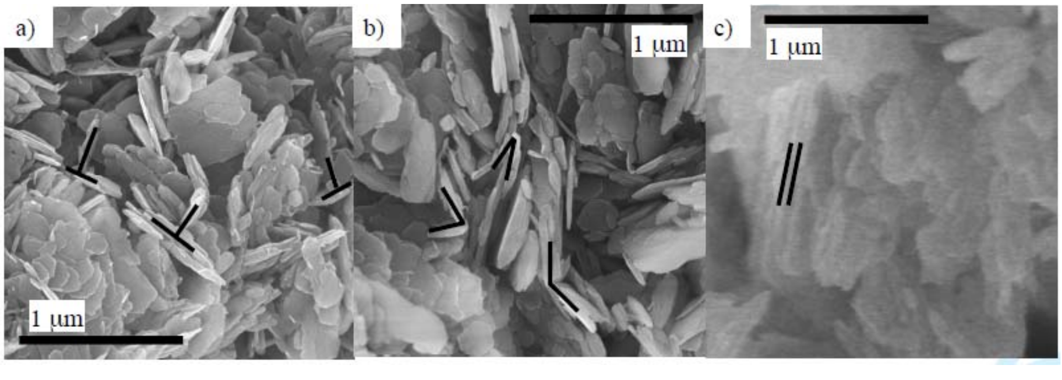


Figure 2. Scanning electron microscopy (SEM) images of Georgia 1 RP-2 kaolinite particles at a) 0.003 mol/l, b) 0.02 mol/l, and c) 1 mol/l of NaCl solutions. The corresponding fabric

configurations are a) edge-to-face (EF), b) edge-to-edge (EE), and c) face-to-face (FF), respectively. Selected fabric configurations were highlighted by short bold lines.

Fabric Anisotropy of Kaolinite and Fly Ash Kaolinite Soil Mixtures

The shear wave velocity change in vh, hv, and hh directions of kaolinite samples at different NaCl concentrations under a nominal consolidation stress of 800kPa were shown in Figure 3. Inherent structure anisotropy could be observed from the plot. In general, the Vs anisotropy decreased as the salt concentration increased (indicated by the two gradual narrowing solid lines), however, the anisotropy reached the smallest point at 0.1mol/L and then increased slightly. Salt concentration has an important impact on the Vs of soils. This was revealed by comparing shear wave velocity of kaolinite samples consolidated from different salt concentrations. Given the same applied vertical stress, Vs of low concentration samples were lower than that of high concentration samples in any of the three orthogonal directions. High salt concentration yielded denser kaolinite aggregations due to the compression of EDL, thus increased the stiffness, and led to an increase in Vs. At 0.1mol/L, the Vs anisotropy was reached the lowest degree, compared with other salt concentrations.

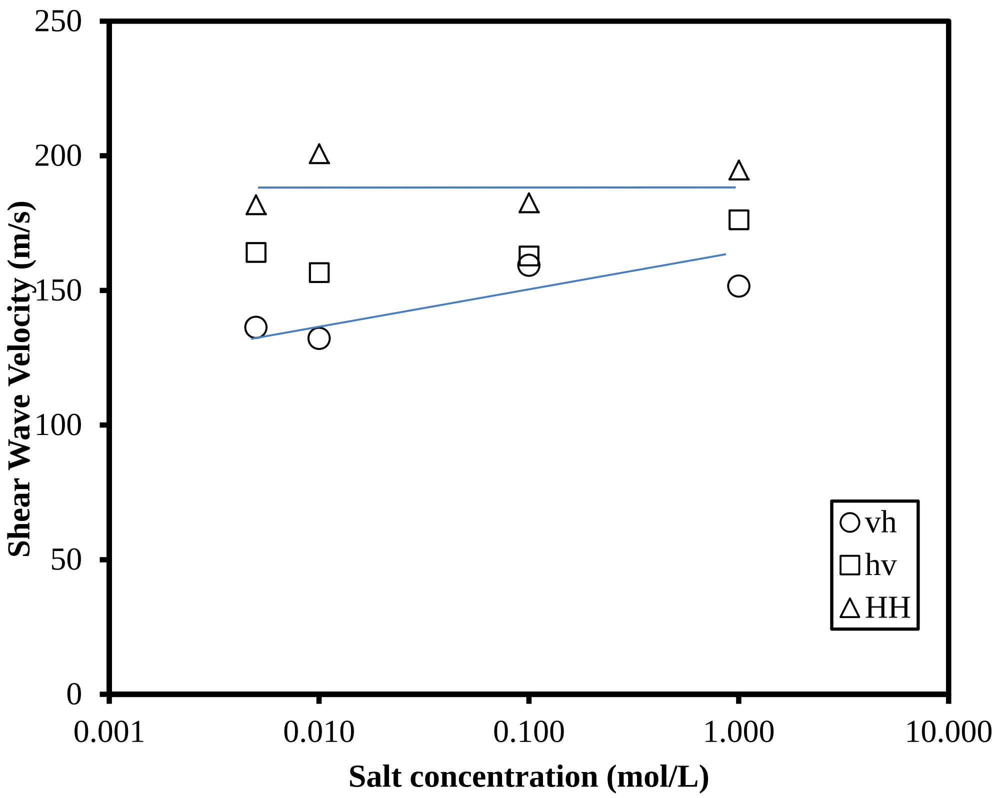


Figure 3 The shear wave velocity change in vh, hv, and hh directions of kaolinite samples at different NaCl concentrations under a nominal consolidation stress of 800kPa

Figure 4 illustrates the shear wave velocity change in vh, hv, and hh directions of fly ash kaolinite mixtures at different mixing ratios under a nominal consolidation stress of 800kPa. At 0% of fly ash, pure kaolinite samples exhibited great Vs anisotropy in vh, hv and hh directions (Figure *). However, as the percentage of fly ash increased, the tendency of Vs anisotropy decreased. When at about 30% fly ash with 70% kaolinite, the Vs values in three directions were almost the same, where the three curves merged to a common point. At 60% Fly ash content, where the fly ash particles were dominant, the Vs anisotropy almost vanished. Since fly ash particles are pretty round compared with platy kaolinite aggregates, the addition of fly ash could largely minimize the mixture's Vs anisotropy. The degree of cross-anisotropy was also enhanced by the addition of fly ash where the Vs difference between hv and hh directions decreased as the fly ash content increased, especially at the fly ash content at 60%.

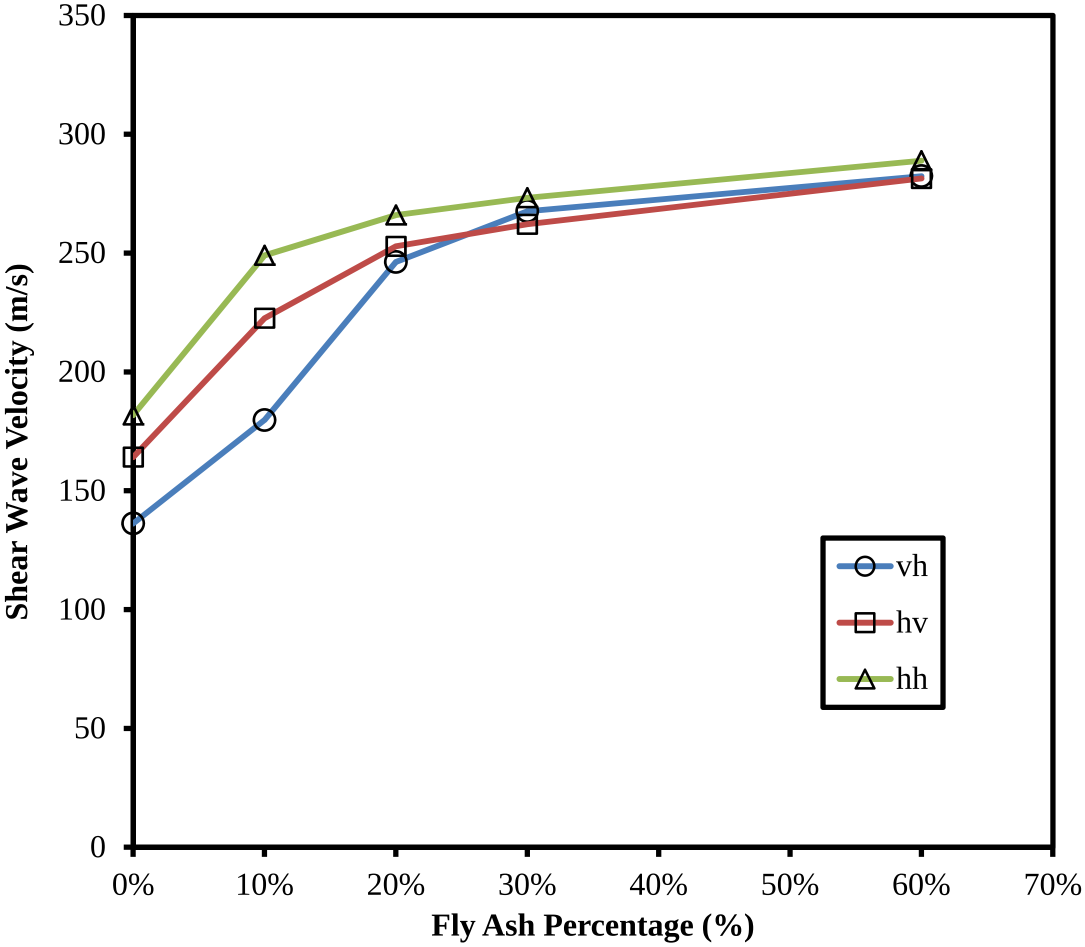


Figure 4 the shear wave velocity changes in vh, hv, and hh directions of fly ash kaolinite mixtures at different mixing ratios under a nominal consolidation stress of 800kPa

Stress Induced Fabric Anisotropy

Shear wave velocity versus applied stress relationship of kaolinite samples consolidated from 1.0 mol/l NaCl 0.01 mol/l NaCl solution in vh, hv, and hh directions were plotted and are shown in Figure 5. Two features were identified that were also true for kaolinite samples at other salt concentrations. 1) During loading, Vs increased as vertical applied stress increased. 2) At a loading less than 100 kPa, Vs in three orthogonal directions almost merged together. At a loading larger than 200 kPa, anisotropy of Vs started to appear. The magnitude of Vs was on the order of hh > hv > vh.

The kaolinite particle was platy-shaped with a thickness of 1 nm and a length of 50 – 2000 nm (Mitchell and Soga 2005). If the applied vertical consolidation pressure was higher than a certain value (50 – 200 kPa), kaolinite plates were suppressed to align more horizontally than vertically. This induced preferential orientation in a horizontal direction for kaolinite plates, and led to fabric anisotropy (Figure 2). Stress-induced fabric anisotropy was manifested by the different magnitudes of Vs values in three orthogonal directions (hh, hv, and vh) (Figure 5). Figure left was 1.0 mol/l NaCl kaolinite sample, which showed slight anisotropy at lower stress condition, however, 0.01 mol/l NaCl kaolinite sample which on the right side had slightly inherent fabric anisotropy and the anisotropy was greater as the loading increased.

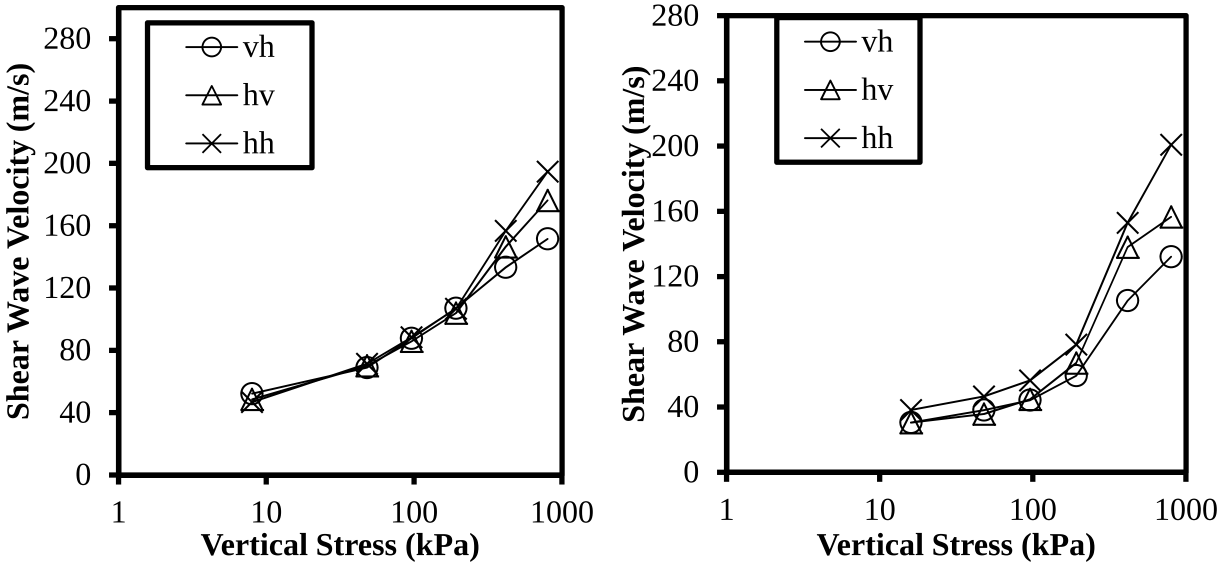


Figure 5 shear wave velocity in vh, hv, and hh directions of kaolinite samples at 1.0 mol/L and 0.01mol/L NaCl salt concentration during loading stage

Organic Effect on the Vs Anisotropy of Kaolinite

Different organic polymers have distinct effects on the Vs anisotropy of kaolinite samples. It is found that PEO, Xanthan Gum, and Chitosan played largely different roles on the Vs anisotropy, either enhancing or decreasing the Vs anisotropy of the kaolinite in different directions and at different degrees. In general, the addition of PEO, Chitosan, and NaCl could all increase the magnitude of Vs in three orthogonal directions. Figure 6 shows the Vs increase in hh direction of kaolinite samples under different polymers and salt concentrations. Among all the polymers used, PEO showed the best performance in enhancing the Vs. Compared with 0.01 mol/L NaCl sample, it can increase Vs up to 100m/s in hh direction at a polymer concentration of 1.0g/l. Initially (at 100kPa), kaolinite samples with PEO exhibited higher Vs which indicated that strong fabric anisotropy was induced during specimen preparation and this fabric anisotropy was then manifested by the further consolidation loading stages as shown in the figure.

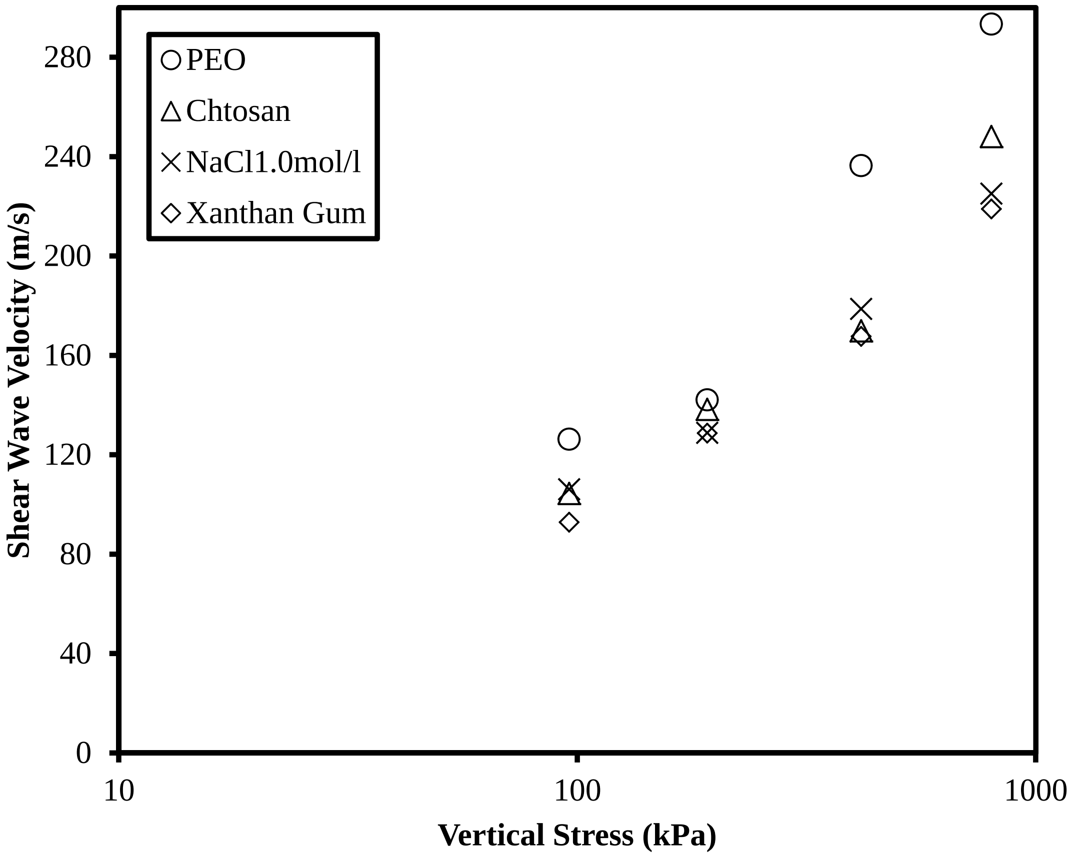


Figure 6 the Vs change in hh direction of kaolinite samples at different polymers and salt concentrations (PEO, Xanthan Gum, and Chitosan at 1.0g/l)

Although the organic agents could enhance the Vs value in three orthogonal directions, their contributions to the Vs anisotropy was largely different. Figure 7 and 8 show the Vs increment of PEO and Chitosan/Xanthan Gum treated Kaolinite samples. The addition of Chitosan/Xanthan increased the magnitude of Vs, however, it mitigated the Vs difference in vh, hv, and hh directions. In other words, the soil treated Chitosan/Xanthan Gum was more isotropic compared with pure kaolinite samples. Only under high consolidation stress (800kPa), slightly stress induced Vs anisotropy was detected. On the other hand, PEO showed distinct behavior in mitigating the Vs anisotropy of kaolinite. The addition of PEO induced strong Vs anisotropy, even at the beginning of the virgin consolidation (>100kPa). As the consolidation stress increased, the Vs difference among vh, hv, and hh directions become even pronounced. At about 800kPa nominal consolidation loading, the Vs anisotropy has reached the maximum where the hh direction had the largest Vs, while the vh had the lowest Vs.

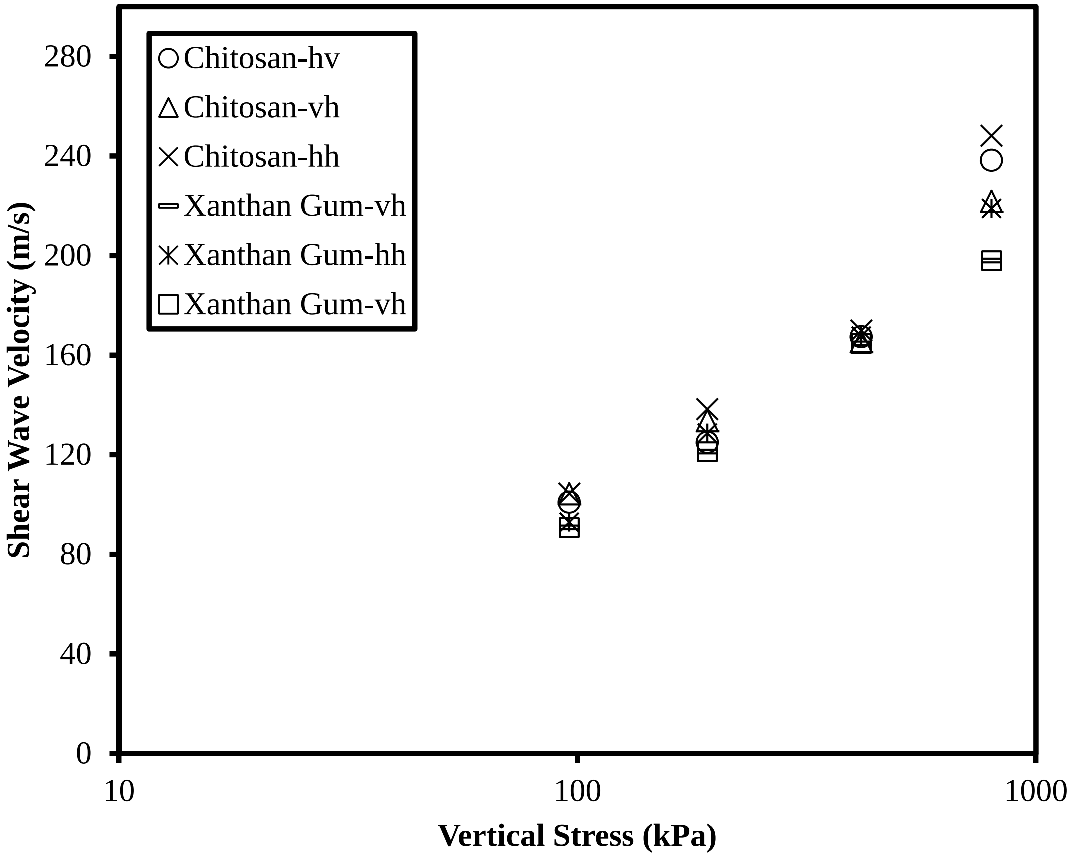


Figure 7 the shear wave velocity of Chitosan and Xanthan Gum treated kaolinite sample in vh, hv, and hh directions during loading stage under virgin consolidation.

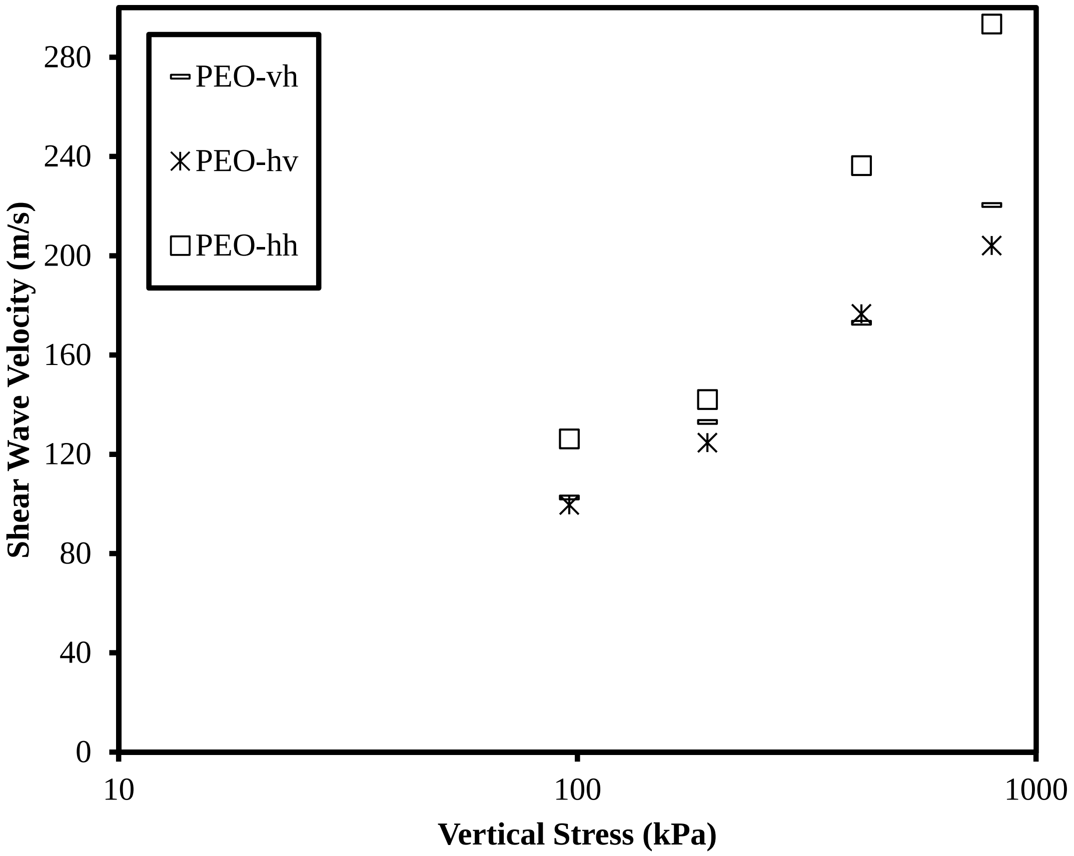


Figure 8 the shear wave velocity of PEO treated kaolinite sample in vh, hv, and hh directions during loading stage under virgin consolidation.

Organic Effect on the Vs Anisotropy of Fly Ash Kaolinite Soil Mixtures

The addition of fly ash could largely modify the Vs anisotropy of fly ash soil mixtures as shown in Figure 9 and 10 where the Vs in vh and hh directions of the fly ash soil mixtures under different nominal consolidation loadings were displaced. In general, the Vs values increased as the fly ash content and loading increased. However, the stress induced Vs anisotropy was largely different which dependent on the fly ash mixing ratios and directions. The Vs differences at different fly ash mixing ratios in vh directions were almost constant as the loading increased, where all the solid lines are parallel to each other (see figure 9). In hh direction, as the loading increased, the fly ash soil mixtures that with less fly ash mixing ratio had greater Vs increment compared with fly ash soil mixtures with higher volume fly ash content. In other words, as the fly ash content increased in the fly ash soil mixture, loading induced fabric anisotropy decreased. Therefore, the addition of fly ash could decrease the degree of stress induced fabric anisotropy in hh directions.

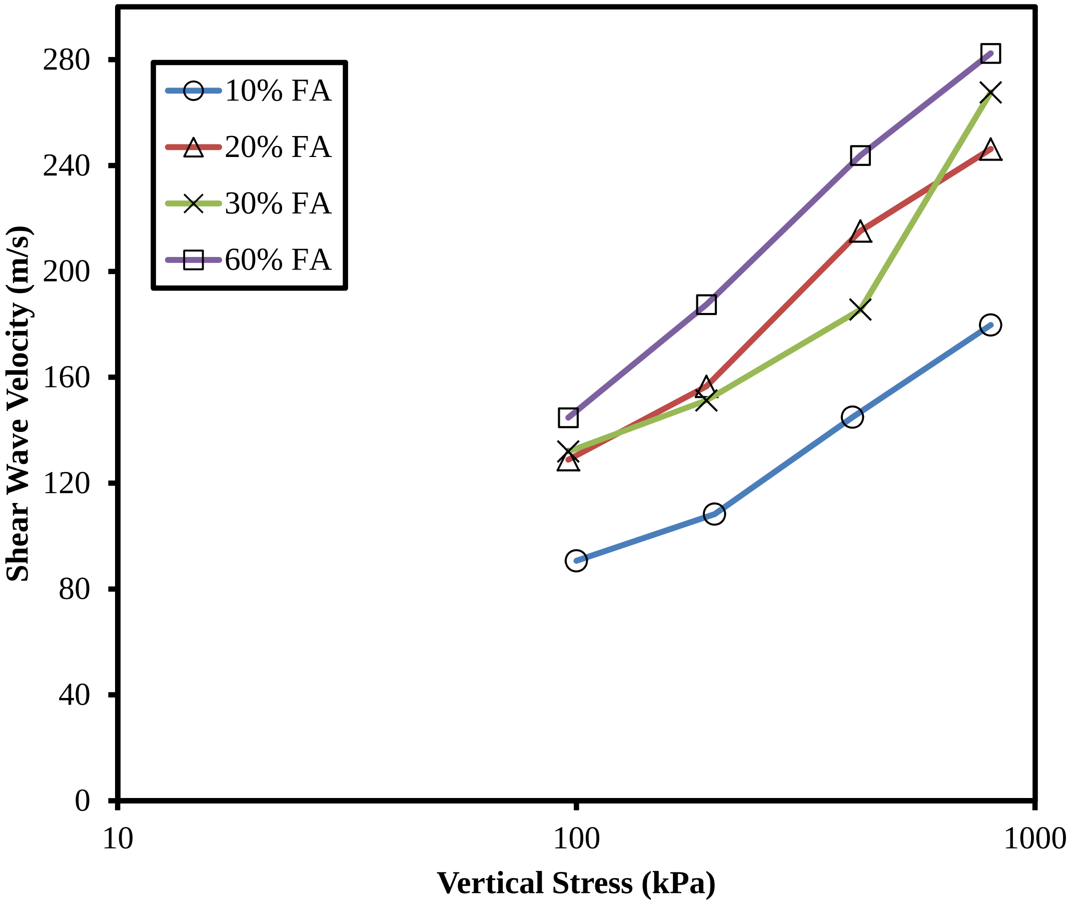


Figure 9 the Vs in vh direction of fly ash soil mixtures at different fly ash content during loading condition

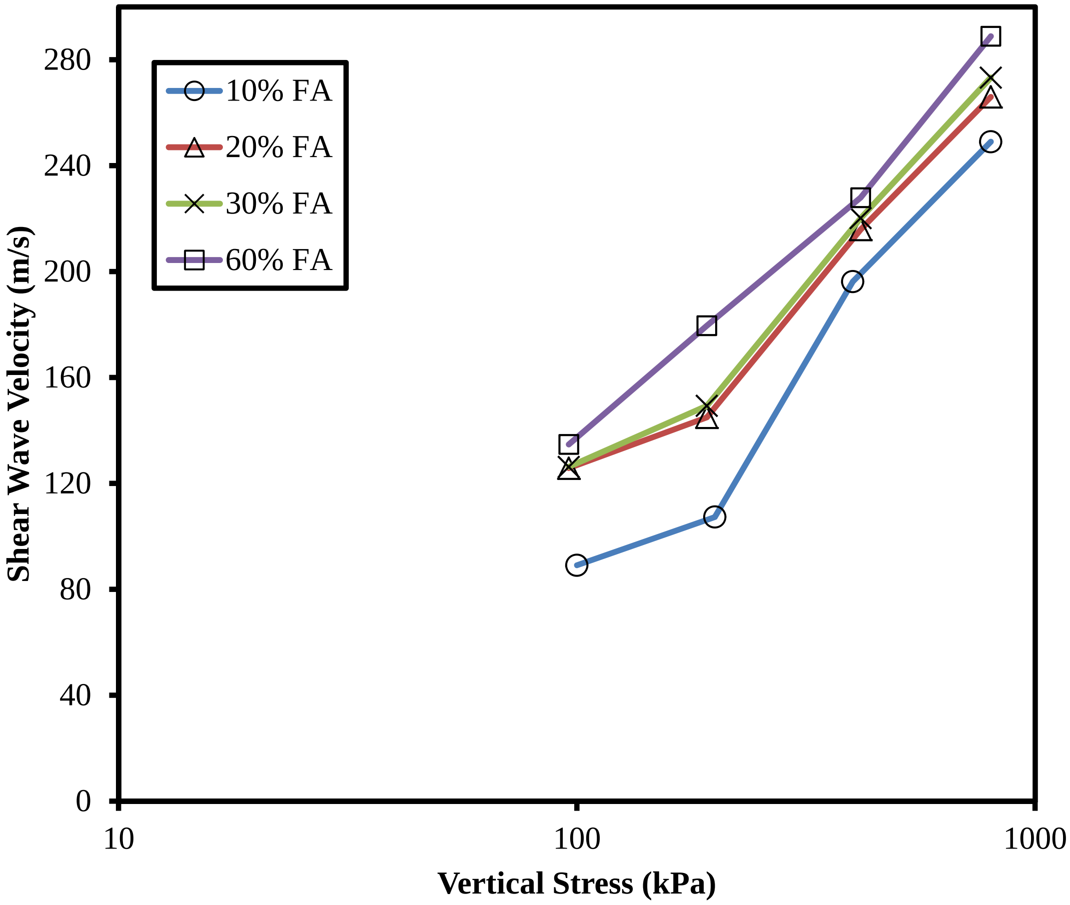


Figure 10 the Vs in hh direction of fly ash soil mixtures at different fly ash content during loading condition

Organic agents were added to the fly ash soil mixtures with a fly ash to kaolinite mixing ration of 30% to 70%. In general, the organic effects could be categorized into two groups, either increase Vs or decrease the Vs as displaced in Figure 11. PEO and Chitosan could increase the Vs of the fly ash soil mixtures as shown in the figure. However, only Vs in vh and hh directions were increased, the vs in hv direction did not change either by PEO or Chitosan treated samples. On the other hand, for xanthan gum, it had distinct effect compared with PEO and Chitosan. The addition of xanthan gum largely decreased the Vs of fly ash soil mixtures. The Vs in all three orthogonal directions was decreased. The decrease of the Vs was attributed to the open void micro structure that the xanthan gum induced in the fly ash soil mixtures. The Vs in hv directions did not change with the addition of the PEO and Chitosan showed great interests to the authors.

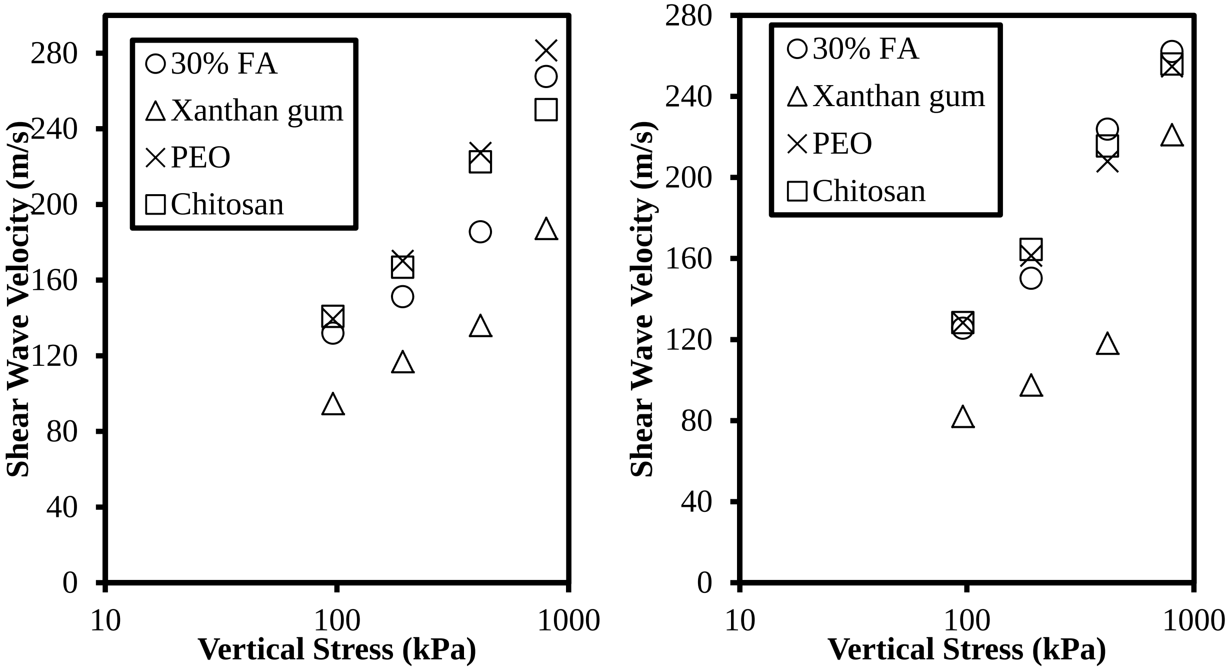


Figure 11 the Vs of organically modified fly ash soil mixtures in vh and hv directions

Apart from the effect of increasing or decreasing the Vs, the degree of anisotropy also has been influenced by the addition of organic agents. Figure 12 shows the Vs of PEO and Chitosan modified fly ash soil mixtures in vh, hv, and hh directions. Although both polymers could increase the Vs compared with the fly ash kaolinite mixtures' Vs, two distinct behaviors were observed. The addition of PEO resulted in higher degree of anisotropy, especially under the maximum nominal consolidation loading. On the other hand, the addition of chitosan did not induce any increase of the Vs anisotropy, or even reduced the degree of Vs anisotropy, as shown in the figure 12. All the Vs values in vh, hv and hh directions were merged together as a straight line as the loading increased. Since fly ash kaolinite mixtures (30%+70%), has very slight degree of Vs anisotropy, compared with PEO modified fly ash soil mixtures at the same mixing ratio, the Vs anisotropy was largely induced by the addition of the PEO polymers. However, Chitosan had less effect compared with PEO on the Vs anisotropy of the fly ash soil mixtures.

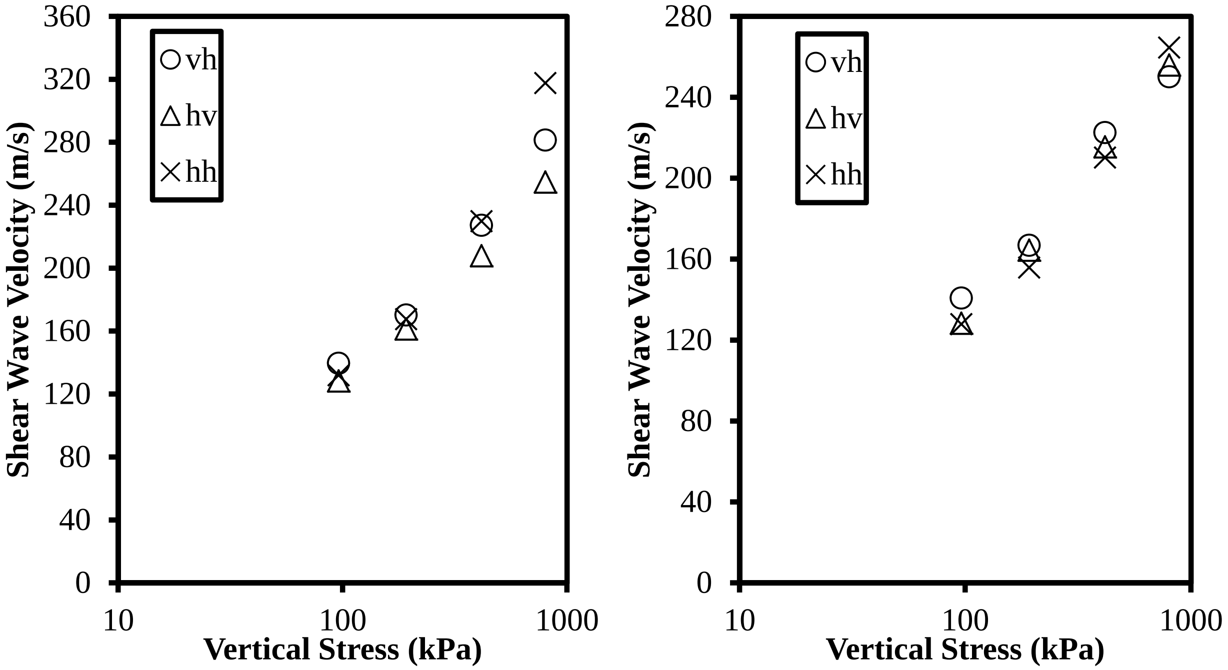


Figure 12 the Vs of PEO and Chitosan where is xanthan? modified fly ash soil mixtures in vh, hv, and hh directions

Discussions

Cross-anisotropy

Cross-anisotropy (or transversely isotropic fabric) materials, where the physical properties in the vh and hv directions were the same, was often assumed in soils in the literature (Bellotti et al. 1996; Chen et al. 2005; Graham et al. 1983; Wang and Mok 2008; Wood 1990; Yimsiri and Soga 2000). This suggested that Vs in the vh and hv directions were the same. While this arguably holds true for coarse-grained particles, such as sand, gravel, and rice, results in this study indicated that it was not the case for fine-grained soils. This hierarchy of Vs anisotropy in hv and vh directions of other fine-grained soils was also reported in the literature. Pennington et al. (1997) also reported that Vs in the hv direction was significantly higher than that in the vh direction for natural Gault clay. In addition, Lee et al. (2008) found Vs, HV > Vs, VH for Incheon marine clay at stresses higher than 100 kPa. The addition of fly ash in kaolinite could gradually decrease the Vs anisotropy (see figure 4), which also resulted in the Vs difference in hv and hh directions decreased, supported that cross-anisotropy may only exist in silt and sandy soils.

Salt induced fabric anisotropy

Salt concentration has an important impact on the stiffness of soils. This was revealed by comparing shear wave velocity of low concentration (0.005 and 0.01 mol/l) and high concentration (0.1 mol/l and 1 mol/l) kaolinite samples. Given the same applied vertical stress, Vs of low concentration samples were lower than that of high concentration samples in any of the three orthogonal directions (Vs in hh and vh directions were shown in Figure 13). High salt concentration yielded denser kaolinite aggregations due to the compression of EDL. This increased the stiffness, and led to an increase in Vs.

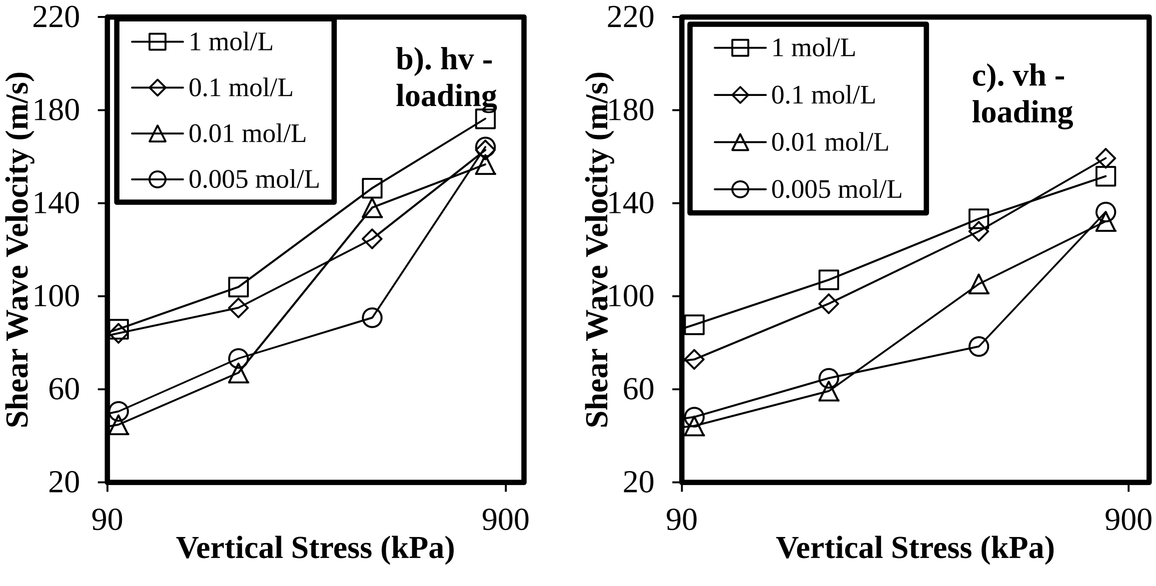


Figure 13 Vs of kaolinite sample consolidated at different salt concentrations in vh, and hv directions

Besides compression of the EDL, an increased concentration of NaCl also changed the fabric of kaolinite (Palomino and Santamarina 2005; Santamarina et al. 2001). Palomino and Santamarina (2005) summarized previous findings of different geotechnical tests on kaolinite in salty condition, and concluded that at a neutral pH ($4 < pH < 7.2$, which held true in this study), there were three different fabric arrangements for kaolinite samples. At a low NaCl concentration (< 0.02 mol/l), kaolinite primarily aligned with an edge-to-face (EF) configuration due to Coulomb's electrical attractive forces between the negative-charged face and positive-charged edge of the fabric. At a high concentration (> 0.1 mol/l), due to dominating Van der Waals force, the kaolinite aligned with a face-to-face (FF) configuration, while in the intermediate NaCl concentration (0.02 – 0.1 mol/l), there was a transition zone, where edge-to-edge (EE) configuration was dominant.

Fly ash effect on the Vs anisotropy

The addition of fly ash into kaolinite largely modified the micro structure and gradation as indicated by the SEM images in Figure 14. Fly ash particles were found surrounded by kaolinite particles/flocs in general. Small kaolinite particles are attached to the large fly ash particle surface. Since the fly ash particles are almost round, they do not have the inherent anisotropy due to the particle shape. On the other hand, the evenly distributed fly ash particles in the fly ash soil mixture replaced the kaolinite particles. Therefore, the higher degree of replacement, the lower degree of the anisotropy, which is supported by the test data in Figure 4, where as the fly ash mixing ratio increased the Vs anisotropy decreased and even vanished.

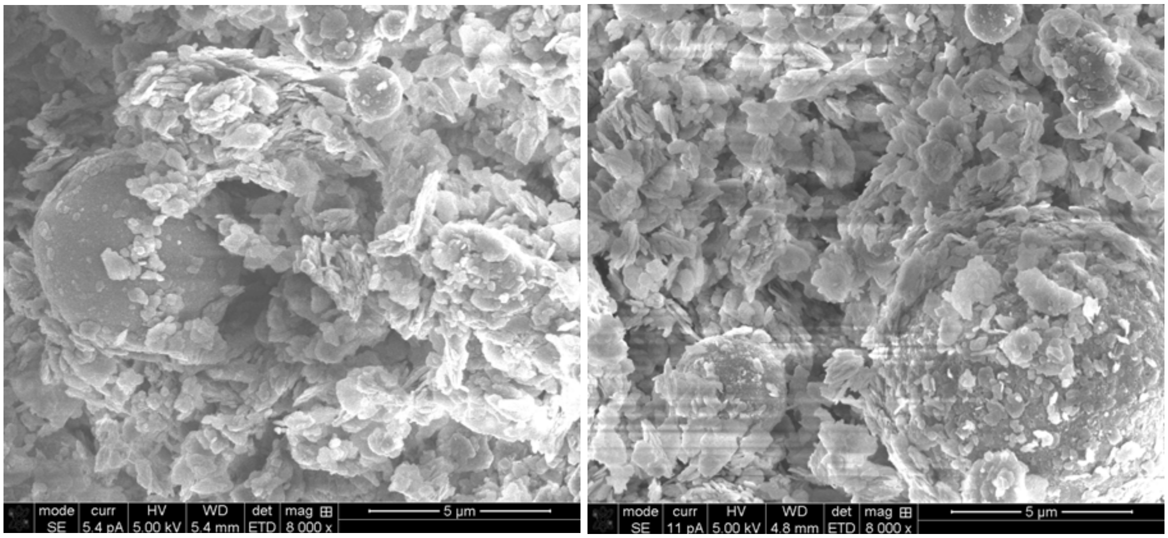


Figure 14 SEM images of fly ash soil mixture with a mixing ratio of 30%FA+70%KA

Organic effect on the anisotropy

The organic agents had two effects on the Vs anisotropy. 1. Organic could induce initial fabric anisotropy in vh, hv, and hh directions. 2. Organic could change the behavior of stress induced fabric anisotropy of the soil. The organic induced initial fabric anisotropy could be found in Figure 6 where the Vs of the kaolinite samples modified by different organics in hh directions were largely different initially. The Vs in hv directions of kaolinite samples treated with different organics were almost the same in the beginning. However, as the consolidation loading increased, the Vs value increased in different degrees which started at about 200 kPa, and then manifested thereafter. Compared with different organics, PEO induced the highest degree of anisotropy, and the NaCl induced the lowest degree of Vs anisotropy.

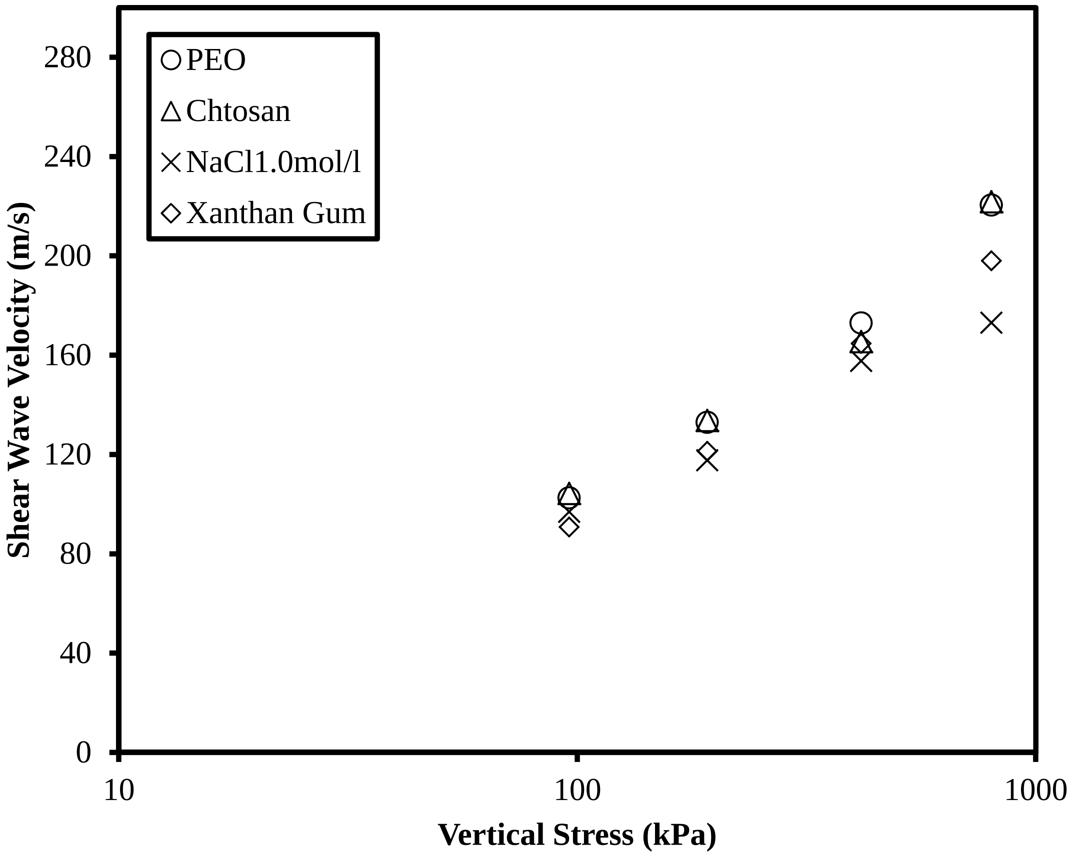


Figure 15 the Vs change in hh direction of kaolinite samples at different polymers and salt concentrations (PEO, Xanthan Gum, and Chitosan at 1.0g/l)

PEO is a nonionic synthetic polymer; it has an extended and flexible long chain structure. When PEO is dissolved in the solution, it could be adsorbed onto the clay surface through polymer bridging so that to produce large flocs (Mpofu et al. 2004). Polymer bridging is resulted from the adsorption of polymer chains on the particle surface, with only a few points of attachments, and with the bulk of the chains projecting into the surround solutions for contact and adherence with other particles (Nasser and James 2007). Therefore, by understanding the PEO adsorption mechanism, it is speculated that the addition of the PEO could induce polymer bridging in the kaolinite suspension, and the polymer bridging could induce large flocs, thus the Vs of the PEO treated kaolinite sample increased. Polymer bridging also induced higher degree of fabric anisotropy (the platy like kaolinite particle alignment tend to lay in horizontally), as the Vs in hh direction increased way too much than the other two directions.

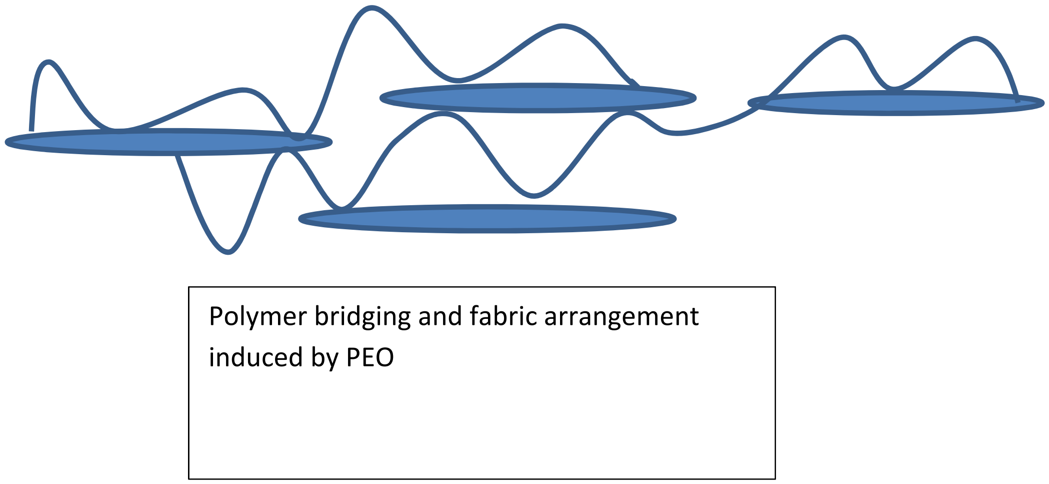
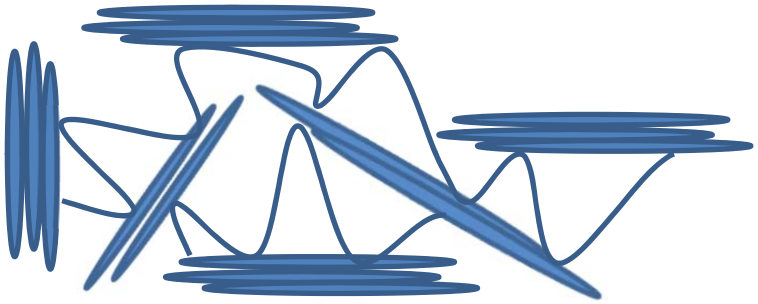


Figure 16 the Vs change in hh direction of kaolinite samples at different polymers and salt concentrations (PEO, Xanthan Gum, and Chitosan at 1.0g/l)

Chitosan is a positively charged polymer with high molecular weight. Li et al. (2013) summarized that the interaction between kaolinite particles and chitosan may be induced by one of the two mechanisms, namely the polymer interparticle bridging and the charge neutralization. When positively charged chitosan is added into clay water colloidal system, the positively charged chitosan will be attracted to the negatively charge sites along kaolinite mineral particle surface. The Colombian attraction is the dominant bonding between the particle and the polymer. Parazak et al (1998) indicated that, other than the polymer bridging and charge neutralization mechanism, the coagulation of kaolinite particles by chitosan could also contributed from the hydrophobic interaction of the polymer molecules with the adjacent particles. This is referred as the hydrophobic flocculation. Therefore, the addition of chitosan could induce coagulation flocculation to the kaolinite particles. Three mechanisms accounted for this phenomenon, namely the cationic behavior of chitosan induced the particle aggregation by charge neutralization, the flocculation of the kaolinite particle induced by the linking and bridging of chitosan, and the hydrophobic flocculation. By reviewing the Vs values in three orthogonal directions of the chitosan treated kaolinite, it is found that the Vs anisotropy was largely minimized. The increase of the Vs in three orthogonal directions was attributed to the induced aggregation of large flocs. The decrease of the Vs anisotropy may attribute to the degree of flocculation by chitosan bridging of large kaolinite flocs. The flocculated kaolinite flocs may reduce the Vs anisotropy as shown in the figure below.

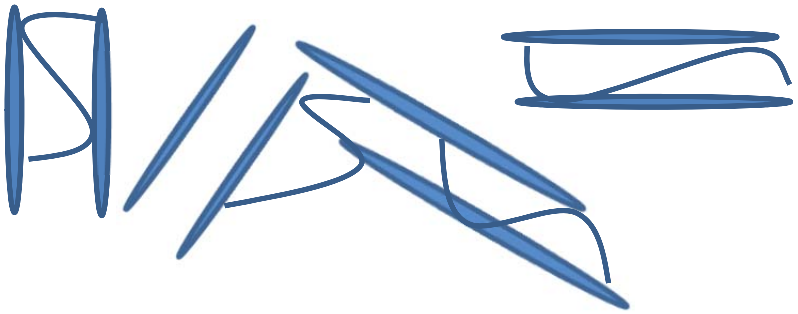


Charge neutralization induced aggregation and polymer bridging induced flocculation by Chitosan

Figure 17 the Vs change in hh direction of kaolinite samples at different polymers and salt concentrations (PEO, Xanthan Gum, and Chitosan at 1.0g/l)

Xanthan gum is an anionic polysaccharide produced by Xanthomonas campestris. When Xanthan gum is dissolved into water, it could increase the viscosity of the aqueous system. (Nuggent, et al 2009). Since the anionic nature of the xanthan gum, the electrostatic repulsion between the kaolinite particle and the xanthan polymer only allows limited polymer adsorption.

On the other hand, the polymer molecule may expand into the solution which produces loops and tails due to the repulsion force. Since the repulsion force between kaolinite particles are generated by the anionic xanthan gum and limited polymer adsorption occurred, the micro fabric of the kaolinite suspension is largely dispersed and deflocculated. Under this micro fabric, particle associations are low and loosely ordered. By knowing this nature, correlating the Vs anisotropy of xanthan gum treated kaolinite, it is speculated that the reduction of the Vs anisotropy could be attributed to the dispersed and deflocculated structure that induced from the xanthan gum, and the increase of the Vs could be attributed to the limited aggregation and the consolidation of the diffuse double layers.



Limited polymer bridging, and aggregation induced by Xanthan Gum, dispersed and deflocculated structure.

Figure 18 the Vs change in hh direction of kaolinite samples at different polymers and salt concentrations (PEO, Xanthan Gum, and Chitosan at 1.0g/l)

Zeta potential and particle size analysis of the organically modified fly ash soil mixtures

Zeta potential, or electrokinetic potential, is the electrical potential generated at the shear plane of a particle in the colloid system (Hunter 1981). Shear plane is an imaginary plane, which separates the moving portion of the particles and the bulk fluid during electrophoretic movement. Changes in pH, ionic strength, type of ions in bulk fluid, and temperature will lead to the change of the net surface charge which can be measured by the corresponding changes in zeta potential. Zeta potential can be used to evaluate the net surface charge of colloid systems, thus it is a good indicator of the net surface charge of fine grain particles.

Figure 15 show the test results of zeta potentials on kaolinite at varied NaCl concentrations. The general trend is that as the salt concentration decreased, the zeta potential of the kaolinite became more negative. The adsorption of Na^+ on kaolinite particles would compress the DDL layer, thus resulting in a lower zeta potential (less negative). The zeta potential indicated the repulsive force among kaolinite particles. the lower the zeta potential (less negative), the smaller the repulsion force, which means that kaolinite particles tend to attract by each other through Van der Waals attraction force and flocculate. On the other hand, if the zeta potential is high (more negative), which means the repulsive force among particles is large so that the particles are dispersed to each other by the thick DDL repulsive force. Similarly, by adding organic agents into the kaolinite, the zeta potential of the kaolinite is largely affected by the polymer type. PEO and Chitosan could largely reduce the zeta potential of kaolinite by adsorption and charge neutralization, thus polymer mediated aggregation and flocculation micro structures are favored. On the other hand, the addition of xanthan gum in the kaolinite caused the zeta potential to decrease (more negative), so an open and dispersed micro fabric is formed, only limited polymer bridging were occurred due to the polymer adsorption. Since the xanthan gum solution is highly pseudoplastic, the xanthan gum treated kaolinite had very low permeability and high compressibility.

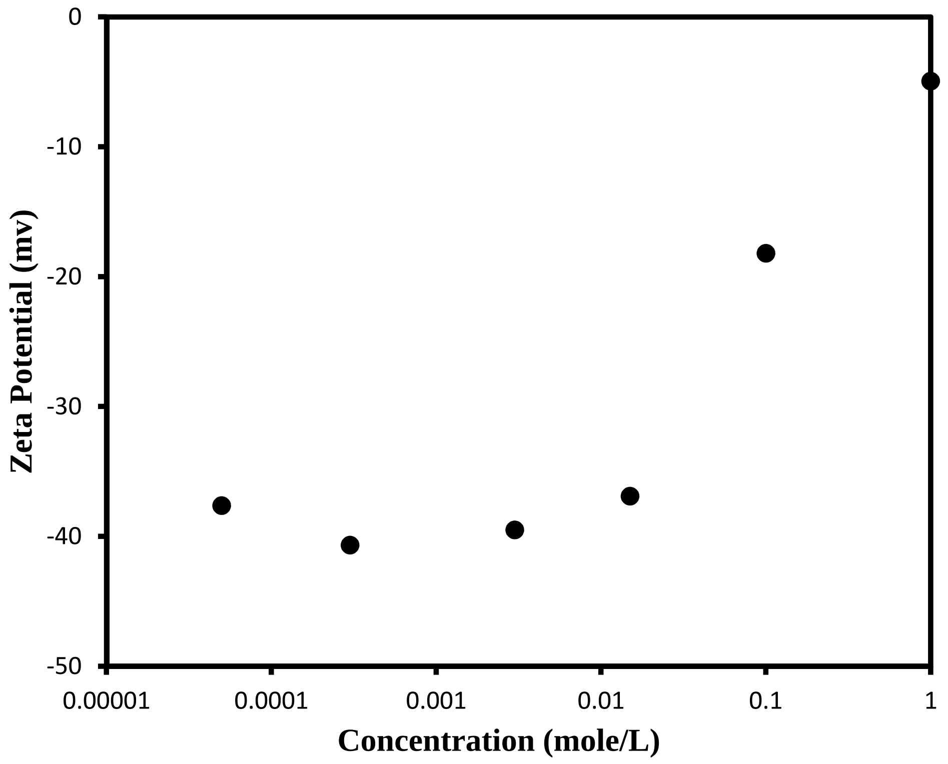


Figure 15 the zeta potential of Kaolinite at different Salt Concentrations

The grain size of the kaolinite flocs depends on the thickness of the DDL, and polymer adsorption and bridging, thus the ionic concentration in the system could largely influence the grain size distribution of the kaolinite. The grain size distribution of kaolinite flocs treated with salt in a colloidal system is measured and displaced in Figure 16. Samples from supernatant, suspension, and sediment were taken to measure the average size. As the salt concentration increased, the measured particle size increased gradually. This could be understood by the changing of the zeta potential. At high salt concentration, the Van der Waals attraction force is dominant, thus aggregated kaolinite flocs are favored and the average size was large. However, at lower salt concentration, DDL repulsion force is dominant. The DDL repulsion force could prohibit the particles aggregate to each other thus the measured flocs size was small. By adding organic agents, such as PEO and Chitosan, the measured flocs size were larger than kaolinite flocs without any additives, which indicated that the polymer induced aggregation and flocculation increased the flocs size in the treated soils.

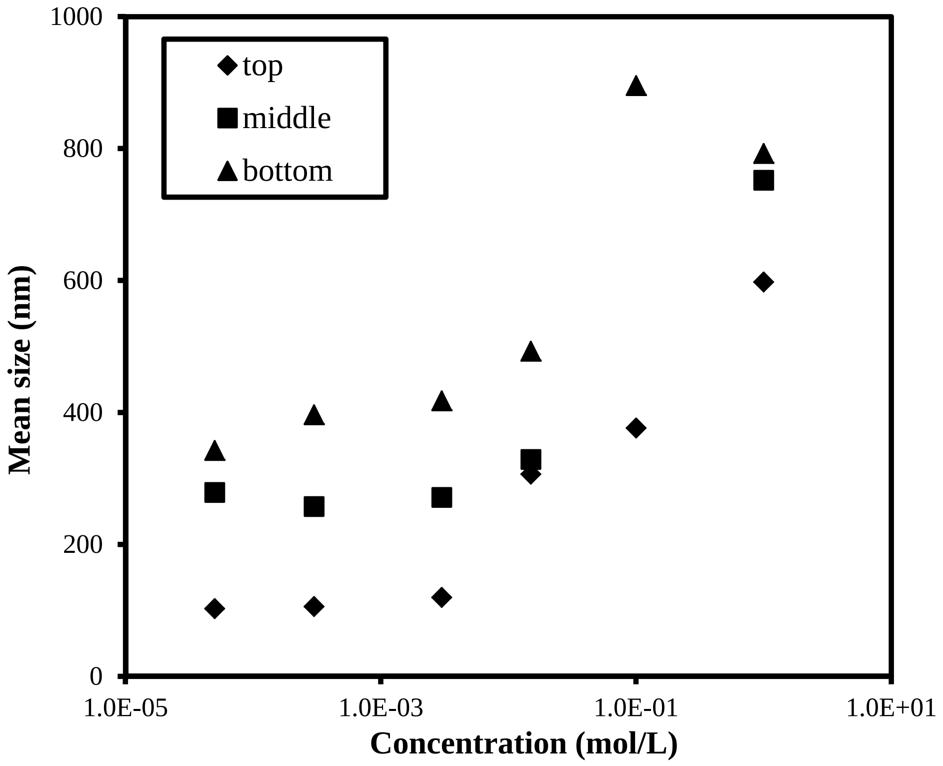


Figure 16 Grain Size Distribution of Kaolinite Flocs at different Salt Concentrations

Conclusions

Shear wave velocity (V_s) anisotropy of kaolinite and fly ash kaolinite mixtures modified with controlled organic agents was studied by using a novel designed floating wall consolidometer type bender element (BE) testing system. Shear wave velocity transmitted by bender element was obtained in three orthogonal directions, i.e., vh, hv, and hh, to study the anisotropic behavior of clay particles. Zeta potential test, grain size distribution test and Scanning Electron Microscopic technique were adopted to understand the micro fabric and particle interactions of the organically treated soils. This study demonstrated that the addition of fly ash and organic agents could largely affect the V_s anisotropy of kaolinite. Salt treated kaolinite with different inherent micro fabrics were studied to verify the inherent fabric anisotropy and stress induced anisotropy behaviors of controlled salt samples. The organic polymers could coagulate and flocculate clay particles through charge neutralization, polymer bridging, and hydrophobic bonding, which in turn induced larger flocs of kaolinite and different micro fabrics. The increase of Vs in three orthogonal directions of the organically treated soil is attributed to the larger flocs that induced by polymer aggregation which was also supported by the grain size analysis results. The Vs anisotropy in three orthogonal directions was attributed to the polymer bridging effect which resulted in different flocculated micro fabrics. This research also supported that the cross-anisotropy was not true for kaolinite samples. However, by adding non-platy particles, such as fly ash, could largely minimize the Vs anisotropy, at least, could induce a true cross-anisotropy of the modified soil.

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