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Mechanical Properties of Palygorskite Clay Stabilized with Polyelectrolytes

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Declaration of interests

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Revised manuscript (clean version)

Mechanical Properties of Palygorskite Clay Stabilized with Polyelectrolytes

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Abstract

Two polyelectrolytes of opposite charges, sodium polystyrene sulfonate (PSS) and polydiallyldimethylammonium chloride (PDADMAC), were investigated to stabilize palygorskite clay at varying dosages of 0.2, 0.8, 1.6, and 3.2% by the dry weight of the soil. Both PSS and PDADMAC improved the unconfined compressive strength of the palygorskite clay. PSS was effective at all the polymer contents studied after 7 days of dry curing and the strength increased with the dosages of PSS added, ranging from 2 MPa (0.2% PSS) to 3.1 MPa (3.2% PSS), compared with 1.5 MPa of the untreated soil. PDADMAC, on the other hand, showed comparable strength improvements as PSS did at the high polymer contents of 1.6 and 3.2% but did not work at 0.2 and 0.8% dosages. Under wet curing at 100% relative humidity, PSS improved the strength of the clay by 40% (620 kPa at 0.2% PSS) to 77% (764 kPa at 1.6% PSS) compared to the untreated clay (440 kPa). PDADMAC exhibited less improvement than PSS under wet conditions but still worked at dosages of 0.8 and 1.6%. Besides strength, the resilient modulus and fracture toughness of the treated specimens increased by approximately 10% and 66%, respectively, when treated with 1.6% PSS, which was the optimum content based on the strength results. PDADMAC-treated palygorskite, however, exhibited cracking during curing for both tests, showing potential drying crack issues. The adsorption of PSS and PDADMAC on palygorskite clay were also measured using ultraviolet-visible spectroscopy, and binding between these polymers and palygorskite has been confirmed. The measured adsorption capacities of PSS and PDADMAC were comparable (2.9 and 2.7 mg/g, respectively), while the PSS was somewhat more efficient in improving soil mechanical properties.

Keywords: polyelectrolyte, palygorskite, unconfined compressive strength, resilient modulus, fracture toughness.

1 Introduction

Palygorskite clay is a common clay mineral in arid and semi-arid soil and is ubiquitous in Middle Eastern countries such as Qatar, Saudi Arabia, Turkey, and Iran (Elprince et al., 1979; Singer, 1981; Shadfan et al., 1985; Aiban, 2006; Hojati and Khademi, 2011; Yalçin and Bozkaya, 2011; Ryan et al., 2019). This clay mineral has also been found in the United States, France, Spain, China, India, Africa, and Australia (Merkl, 1989; Murray et al., 2011; Zhou and Murray, 2011). Compared to other clay minerals, such as kaolinite and smectite, the occurrence of palygorskite is the least common in nature and therefore its engineering properties are less well understood (Murray et al., 2011). However, in some regions or countries, palygorskite is more common than other clay minerals, and engineers and researchers often have to deal with this type of clay mineral during pavement and highway construction (Iyengar et al., 2013; Rodriguez et al., 2018; Huang et al., 2023). To stabilize subgrade soils, different techniques of mechanical or chemical means have been used successfully in the past including compaction, soil replacement, cement stabilization, lime treatment, electrical stabilization, bituminous stabilization, thermal stabilization and reinforcement of geotextile and fabrics (Sherwood, 1993; Little, 1995; Afrin, 2017; Ayodele et al., 2018). Among these techniques, traditional chemical stabilizers like Portland cement and lime are most often used to improve the strength and durability of the subgrade soil. However, the cement industry accounts for 7 to 8% of emissions of carbon dioxide, the major greenhouse gas that gives rise to global warming (Mahasenan et al., 2003). Due to the growing environmental concerns and the efforts to reduce the carbon footprint of road construction, researchers have been studying other stabilizers such as organic polymers (natural or synthetic) as potential stabilizers over the last decade (Kwon and Ajo-Franklin, 2013; Ringelberg et al., 2014; Arasan et al., 2016; Azhar et al., 2017; Cabalar et al., 2018; Hataf et al., 2018; Golhashem and Uygar, 2019; Cabalar and Demir, 2020; Chang et al., 2020; Ghasemzadeh and Modiri, 2020; Hariharan et al., 2020; Huang et al., 2021; Kumar et al., 2022b).

Stabilization of subgrade soils containing palygorskite using organic polymers has been studied over the past few years. Iyengar et al. (2013) investigated the stabilization of calcareous soil in Qatar using one cationic and one anionic acrylate-based polymer solution and another anionic polymer emulsion. They found that the anionic acrylate-based polymers worked better than their cationic counterparts and significantly improved the strength and toughness of the subgrade soil. Rodriguez et al. (2018) studied polyacrylamide and its three ionic variants (cationic, anionic, and polyampholyte) to stabilize subgrade soils and found that both the anionic variant and the polyampholyte polymers were effective, and the 28-day strength of the stabilized soil was stronger than the soil treated with 9% cement. Huang et al. (2023) used two oppositely charged polyelectrolytes and their complexes to stabilize calcareous soil containing palygorskite, and they found that both the cationic and anionic polymers improved the strength of the calcareous soil, and the strength of the treated soil increased with time. More importantly, they also found that polymers significantly improved soil toughness especially when compared with cement-stabilized soils.

Qatari soil is calcareous due to the dominance of calcite, dolomite, and gypsum; palygorskite accounts for 0 to 20% and is dominant in the clay fraction of the soil (Ryan et al., 2019). Iyengar et al. (2013) believed that the presence of palygorskite (2.8%) in the subgrade soil played an important role due to the interactions between the polymer and the clay mineral. Huang et al. (2023) observed the reorganization and agglomeration of the palygorskite fibers after adding organic polymers due to the adsorption of the polymers on the mineral surfaces. They believe that the “growing” palygorskite fibers contributed to the strength improvement of the calcareous soil by linking and covering the surrounding coarser soil particles due to the abundant charge groups provided by the polymers.

The mechanisms of polymer stabilization have long been studied by researchers; most studies used scanning electron microscopy to compare the morphological and physical changes of the soils before and after treatment (Al-Khanbashi and Abdalla, 2006; Yazdandoust and Yasrobi, 2010; Liu et al., 2011; Qin et al., 2014; Latifi et al., 2016; Rashid et al., 2017; Fatehi et al., 2018; Bu et al., 2019; Kolay and Dhakal, 2019; Almajed et al., 2020; Kumar et al., 2022b; Huang et al., 2023). These studies have contributed tremendously to the understanding of the interactions between the polymers and the soils. However, the quantification of such interactions is very limited, which prevents further understanding of the mechanisms and the significance of the polymer-soil interactions. Therefore, in this study, palygorskite clay was chosen to investigate the interactions between clay minerals and two polyelectrolytes: the anionic sodium polystyrene sulfonate (PSS) and the cationic polydiallyldimethylammonium chloride (PDADMAC). These polyelectrolytes of opposite charge were selected to evaluate their effectiveness in the stabilization of palygorskite clay and to study the effects of polymer contents and curing conditions. Palygorskite contains several charge sites, and the cation-exchange capacities of relatively pure palygorskite samples range from 5 to 30 $cmol_c/kg$ (Singer, 1989). Both PSS and PDADMAC contain large numbers of charged groups; therefore, they are expected to bind with the charge sites on the surfaces and edges of palygorskite due to electrostatic interactions. To avoid sieving large quantities of natural subgrade soils to obtain the palygorskite fractions and to maintain the consistency and the quality of the soil, commercial palygorskite soil was selected instead for this research.

This paper systematically studies the mechanical performance of palygorskite clay treated with two organic polymers that have not been used in soil stabilization. Besides measuring the unconfined compressive strength, this paper also studies the dynamic response of the treated soil by measuring the resilient moduli. Fracture toughness that was rarely studied in polymer-treated soils is also investigated in this paper by examining the mechanical response of the pre-notched soil specimens, which represents the behavior of a subgrade material after the initiation of cracks due to traffic. Furthermore, ultraviolet-visible spectroscopy (UV-Vis) was used in this study to quantify the adsorption of these two polymers on the surface of palygorskite mineral. The objectives of this paper are to: (1) Investigate the mechanical behavior of palygorskite clay treated with PSS and PDADMAC in terms of the unconfined compressive strength, fracture toughness, and fracture energy; (2) Examine the effects of polymer contents and curing conditions on the properties of polymer-stabilized soils; (3) Compare the effectiveness of oppositely charged polyelectrolytes; (4) Study the resilient characteristics of palygorskite after stabilization; (5) Examine the mechanisms of polymer stabilization through adsorption tests. Although the results reported in this paper are based on palygorskite clay related to Qatari soil, the findings also apply to soils in regions with similar climate conditions, and to soils in other countries where palygorskite is present.

2 Materials and Methodology

2.1 Materials

2.1.1 Palygorskite Clay Simulant

Natural palygorskite-rich soil from construction sites usually contains many other soil minerals such as calcite, gypsum, bassanite, quartz, feldspar, and sometimes contaminants (Murray et al., 2011; Iyengar et al., 2013). Therefore, to minimize the effects of other soil minerals and focus on the study of the properties of palygorskite clay, commercially available palygorskite from a natural source, purchased from Jaxon Filtration Company (http://www.jaxonfiltration.com) in the United States, was used in this study. This palygorskite simulant soil contains mainly palygorskite and quartz. The particle sizes of the commercial clay are between 0.25 and 0.6 mm, which accounts for 99% of the bulk soil (provided by the manufacturer). The particle size of the commercial palygorskite is larger than the common clay grain size of 0.002 mm, which is most likely because these soils are crushed from larger quarried palygorskite and then sieved to the selective sizes by the manufacturer. Table 1 shows the chemical compositions of the palygorskite clay (data provided by the manufacturer).

Table 1. Chemical analysis of commercial palygorskite

Elements in Soil (Oxides)	Percentage (%)
Silica (SiO_2)	70.85
Aluminum (Al_2O_3)	14.06
Iron (Fe_2O_3)	5.34
Calcium (CaO)	1.62
Magnesium (MgO)	5.71
Potassium (K_2O)	0.84
Sodium (Na_2O)	0.25
Titanium (TiO_2)	0.5
Phosphorous (P_2O_5)	0.84

Basic characterization tests including Atterberg limits, plasticity index, and specific gravity were performed on this palygorskite clay following corresponding ASTM standards (ASTM International, 2014, 2017a, 2017b). A compaction test was performed using a Harvard miniature compactor to obtain the optimum moisture content (OMC) and the maximum dry density (MDD) of the clay (U.S. Department of the Interior, 1984). Table 2 presents the physical and basic geotechnical properties of the palygorskite clay. The soil was classified as high plasticity silt (MH) according to the Unified Soil Classification System (USCS) (ASTM International, 2017b).

Table 2. Physical properties of the palygorskite clay

Property	Value
Liquid limit (%)	95
Plastic limit (%)	77
Plasticity index (%)	18
USCS classification	MH
Specific gravity	2.56
Optimum moisture content (%)	52.5
Maximum dry density (g/cm^3)	0.975

2.1.2 Polyelectrolytes

Polyelectrolytes are a group of organic polymers that, when dissolved in polar solvents like water, possess a number of charged groups in the polymer chains (Stuart et al., 2005). Two polyelectrolytes of opposite charge have been studied comparatively in this work. The anionic polyelectrolyte is PSS, and the cationic polyelectrolyte is PDADMAC. Both PSS and PDADMAC were purchased from Sigma-Aldrich in the United States. Table 3 summarizes the properties of these polymers (provided by the manufacturer). PSS was obtained in a powder form; therefore, when adding PSS to the soil, the powder was dissolved in water first, and the amount of water used was the exact amount required to reach the OMC for compaction. PDADMAC was purchased as an aqueous solution and was further diluted with water prior to adding it to the soil.

Table 3. Physical properties of the studied polyelectrolytes: PSS and PDADMAC

Property	Value	
	PSS	PDADMAC
Physical form	Powder	Clear liquid
Color	White	Light yellow
Relative density at 25 °C (g/mL)	0.801	1.04
Water solubility	Soluble	Soluble
Molecular weight (g/mol)	1,000,000	Average 275,000
Solid content (%)	N/A	20
Liquid content (%)	N/A	80

2.1.3 Pure Palygorskite Powder

Pure palygorskite powder was used in adsorption tests in this work to examine the adsorption of polyelectrolytes on the clay. A soil simulant was not used in this experiment because of the presence of quartz, which could affect the adsorption of the polymers on the clay. Pure palygorskite powder (PFl-1) was purchased from the Source Clays Repository of the Clay Minerals Society. According to the manufacturer, the PFl-1 palygorskite is fairly pure with only a trace amount of quartz.

2.2 Experimental Investigation

2.2.1 Unconfined Compression Test

PSS and PDADMAC were added to the palygorskite clay at contents of 0.2, 0.8, 1.6, and 3.2% (defined as the ratio of dry solid polymer to the mass of dry soil) to study the effectiveness of these polyelectrolytes via an unconfined compression test.

Compaction tests were performed to determine the OMC and MDD at each polymer content, and the samples were compacted at their corresponding OMCs. The polymers were first mixed with water and pre-calculated to reach OMC for compaction until the polymers were completely dissolved, that is, the polymer solutions turned transparent. The polymer solutions were then added to the soil followed by continuous mixing for 5 min until the polymer-soil mixture became homogeneous. A Harvard miniature compactor was used to fabricate the cylindrical samples, and each sample was compacted in five layers and tamped 25 times per layer (U.S. Department of the Interior, 1984). The samples were 60 mm in height and 33 mm in diameter. After compaction, samples were demolded immediately and cured at designed curing conditions for 7 days before testing. Two curing conditions were examined in this study for the unconfined compressive strength (UCS) test: dry curing and wet curing. For the dry-curing method, the samples were put directly in the controlled room at ambient conditions, 23 °C and 50% relative humidity (RH); for the wet-curing method, samples were cured in a humidity chamber at 23 °C and 100% RH.

The UCS test was conducted on the untreated, PSS-treated, and PDADMAC-treated specimens after curing. Triplicate specimens were tested after completion of curing, and all UCS tests were conducted following ASTM D1633 using Instron testing equipment. The loading rate of the compression test was constant strain at 1.3 mm/min (ASTM International, 2017c).

2.2.2 Resilient Modulus Test

For the resilient modulus test, the specimens were statically compacted at a loading rate of 7.5 mm/min into a steel mold with a height of 142 mm and a diameter of 71 mm in three layers at respective OMCs and MDDs using the Instron testing equipment. The content of the polymers added to the soil was 1.6%, which showed the best overall performance in the UCS test. Specimens for the resilient modulus test were cured for 14 days under dry-curing conditions.

The resilient modulus test was conducted following AASHTO T307 (2017). Three different confining pressures (13.8, 27.6, and 41.4 kPa) and five different deviator stresses (13.8, 27.6, 41.4, 55.2, and 68.9 kPa) were applied to each specimen. During the test, the soil specimen was first preconditioned by applying 500 load cycles with cyclic stress of 24.8 kPa at a confining pressure of 41.4 kPa. The purpose of preconditioning is to ensure close contact between the loading plate and the specimen. After preconditioning, 15 testing sequences that had 100 cycles of loads at different combinations of confining pressures and deviator stresses were applied to the test specimen. The cyclic deviator stress was applied as haversine-shaped loading for 0.1 s, followed by 0.9 s of relaxation. Figure 1 shows the configuration of the resilient modulus test.

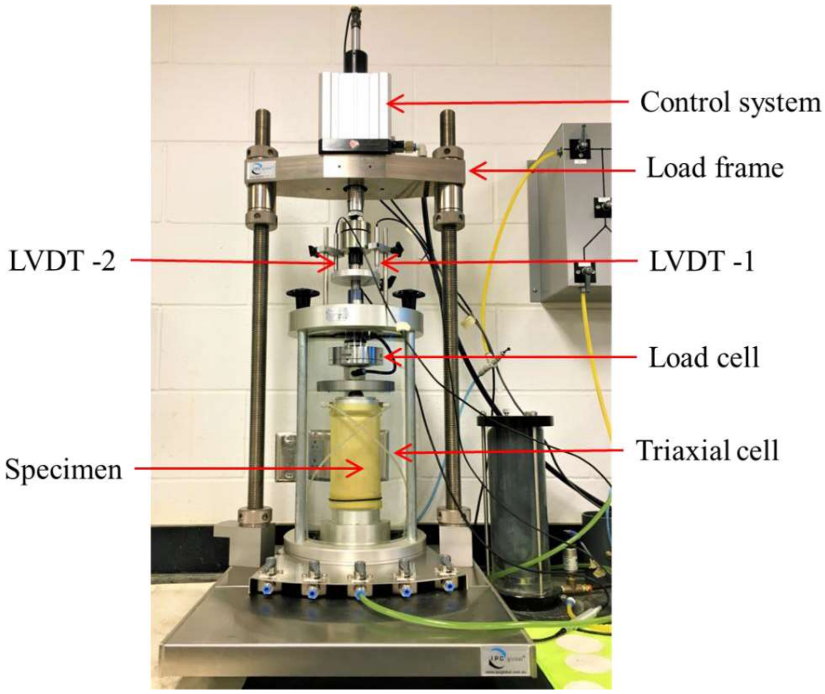

Figure 1. Configuration of the resilient modulus test. Note: LVDT = linear variable differential transducer.

2.2.3 Semicircular Bending Test

The soil specimens for fracture toughness were compacted following the same method as that of the resilient modulus test but with a larger steel mold, which had a diameter of 150 mm and a height of 50 mm. After demolding, the specimens were put in the control room (23 °C and 50% RH) for 14 days. After completion of curing, the cylindrical samples were first cut into two halves and notched with a circular saw along the centerline of each half. The length of the notch was 15 mm. Figure 2 shows the notched samples ready for testing.

Figure 2. Notched soil specimens for the semicircular bending test.

The semicircular bending (SCB) test was conducted on the untreated and treated soil specimens to measure the fracture toughness of these specimens, following the protocols developed by Zhang et al. (2019). During the SCB test, the static compressive load was applied to the specimen at a constant deformation rate of 0.5 mm/min using ElectroForce test equipment from TA instruments (Figure 3). The load-versus-displacement curves were recorded and then replotted to calculate the fracture toughness and fracture energy.

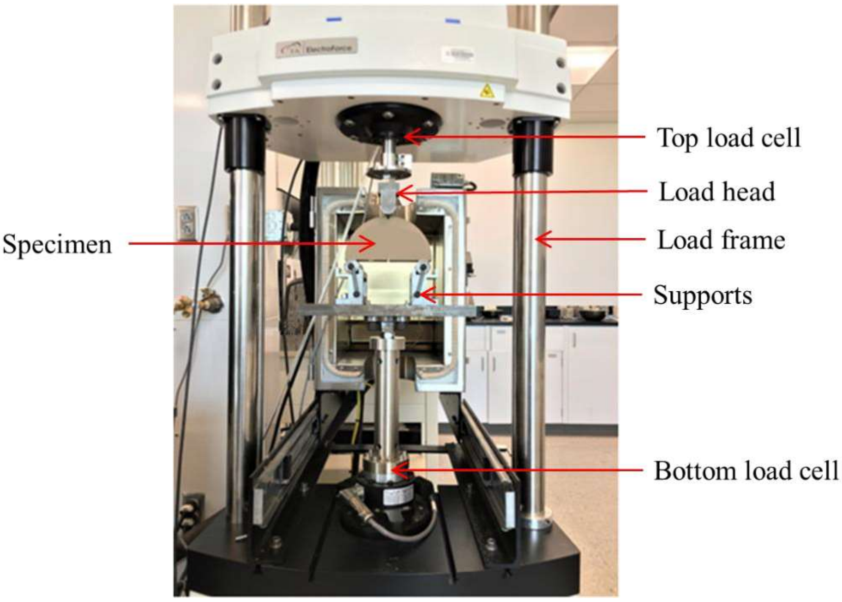

Figure 3. Configuration of the semicircular bending test.

2.2.4 Adsorption Test

Ultraviolet-visible spectroscopy (UV-Vis) was used to measure the adsorption of the polyelectrolytes onto palygorskite. The adsorption experiments were conducted by mixing palygorskite powder and PSS solutions to obtain 10-g/L aqueous dispersions of palygorskite with a PSS solution at different concentrations (10 to 500 mg/L) upon stirring for 30 min at 300 rpm and room temperature (21 °C). The dispersion was then allowed to settle, and the supernatant solutions were taken and filtered through 0.45-µm filters for UV-Vis measurements. UV-Vis absorption spectroscopy was performed using a Shimadzu UV-2600 spectrophotometer within a wavelength range of 210 to 300 nm. The PSS absorption peaks were found at around 225 nm and 260 nm (Talukdar and Kundu, 2019), and the peak at 225 nm was selected for analysis. Figure 4 illustrates the procedure schematically.

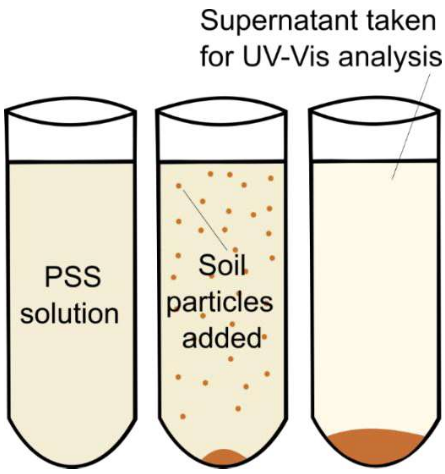

Figure 4. Schematics of the adsorption experiments in an aqueous solution (pH ~7.5).

To correlate the measured UV-Vis absorbances with the amounts of PSS adsorbed on palygorskite, a calibration curve was produced using solutions of PSS of known and varied concentrations (from 5 to 300 mg/L) that did not contain palygorskite minerals. The adsorption capacity of PSS on palygorskite was determined from the dependencies of UV-Vis absorbances detected in a supernatant versus initial concentration of PSS added to palygorskite dispersions.

In the case of PDADMAC, however, this procedure could not be used due to the absence of absorption bands of this polymer in the UV-Vis region (Johna et al., 2002). To address this issue, the amount of polycation remaining in supernatant solutions after binding with the clay mineral was determined by titration of PDADMAC-containing supernatants with a polyanion, poly(methacrylic acid) (PMAA) (with a molecular weight [MW] of 175,000 g/mol), and by measuring the turbidity of these solutions at 400 nm using a UV-Vis spectrometer. The addition of PMAA to the polycation solution results in the formation of polyelectrolyte complexes (PECs) and an increase in solution turbidity. The solution turbidity maximizes at the stochiometric ratio of charges (i.e., charge neutralization) in PECs, allowing indirect determination of the amount of PDADMAC which remains in the supernatant. Prior to measurement of the adsorption of PDADMAC on palygorskite, the turbidity in a series of palygorskite-free solutions was measured. In this control experiment, varied amounts of PMAA solutions (pre-calculated based on the charge ratios) were added to 0.5-g/L PDADMAC solutions to yield different polyanion-to-polycation charge ratios. All solutions in the control experiment were prepared with a 0.01-M phosphate buffer, and pH was maintained at 8.4 ± 0.2 to ensure PMAA was deprotonated (Sukhishvili et al., 2006). The charge ratio, PMAA(-):PDADMAC(+), was calculated as molar charge on the polyelectrolyte units and varied from 0.2 to 1.8. Figure 5 shows the results of the turbidity measurements in PEC solutions performed at 400 nm. PMAA and PDADMAC solutions were directly mixed in a cuvette; the cuvette was flipped ten times and left in a spectrometer for 3 min prior to measurements. As expected, the maximum in turbidity occurred when a PMAA(-):PDADMAC(+) ratio was close to unity (1.2) (see Figure 5[b]). This experimentally confirmed stoichiometry was then used to determine the amounts of PDADMAC in the supernatants.

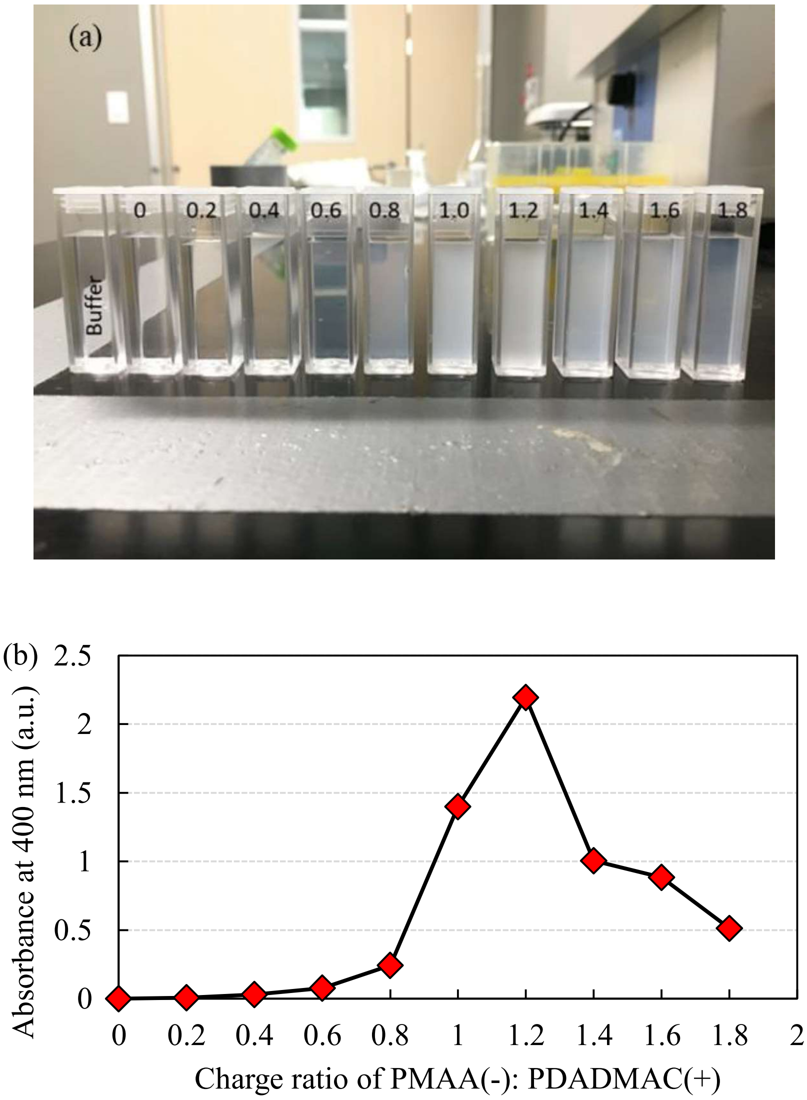

Figure 5. Turbidity measurements in PEC solutions at varied PMAA(-):PDADMAC(+) charge ratios. (a) Pictures of PMAA/PDADMAC complex solutions after turbidity measurements. (b) Turbidity-versus-PMAA/PDADMAC charge ratio.

To determine the amounts of PDADMAC adsorbed on the palygorskite minerals, a 10-g/L palygorskite suspension was prepared by mixing dry palygorskite powder and deionized water. The amount of palygorskite added was maintained constant in these experiments, while different amounts of PDADMAC, 5 to 28 mg/g of palygorskite, were added to the suspension under continuous stirring for 30 min at 300 rpm and room temperature. After allowing the suspension to precipitate, supernatant solutions were collected and filtered through 0.45-μm filters to remove remaining palygorskite particles. Each supernatant solution was diluted by a factor of 2 with 0.01-M phosphate buffer and pH were maintained at 8.4 ± 0.2. The diluted supernatant solution was separated into 10 equal volumes and mixed with 2-g/L PMAA solutions of increasing volumes for turbidity measurements. The titration of the supernatant solutions with PMAA for each supernatant was continued until the occurrence of maxima in turbidity. The concentrations of PDADMAC in the supernatant solutions were then calculated from the amounts of PMAA that corresponded to the occurrence of the maxima in the titration curves and the experimentally determined stoichiometric ratios of 1.2 (see Figure 5). The amount of PDADMAC adsorbed on palygorskite was then determined as a difference between the originally added PDADMAC and the PDADMAC which remained in the supernatant.

3 Results and Discussion

3.1 Optimum Moisture Content and Maximum Dry Density

In the mechanical tests, all the polymer solutions were prepared in aqueous solutions before adding to the soil. Figure 6 shows the compaction curves of the palygorskite clay treated with PSS and PDADMAC. The untreated palygorskite clay has an OMC of 52.5% and an MDD of 0.975 g/cm^3. The high level of OMC was expected since palygorskite has a unique "tunnel" structure, which can absorb a lot of water (Galan, 1996). The addition of the anionic PSS did not change the maximum dry density compared to the untreated soil; however, OMC increased to 60, 58, and 53%, respectively, as the contents of PSS increased to 0.2, 0.8, and 1.6%. When the cationic PDADMAC solution was added to the soil, the reduction of maximum dry density to 0.917 g/cm^3 was recorded and the OMC increased to 56%. Both the OMC and MDD of PDADMAC-treated palygorskite clay did not vary with the contents of PDADMAC.

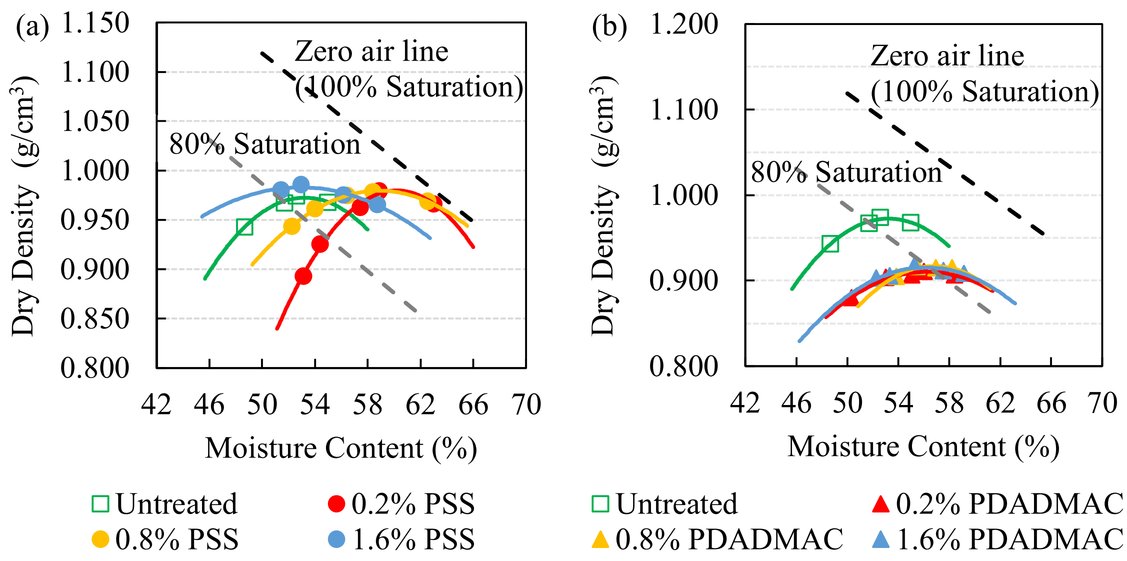

Figure 6. Compaction curves of palygorskite clay treated with (a) PSS (1,000,000 g/mol) and (b) PDADMAC (average 275,000 g/mol).

3.2 Unconfined Compressive Strength

3.2.1 Dry-Curing Conditions

The UCS of the untreated and treated palygorskite clay after 7 days of dry curing was studied. As shown in Figure 7, the anionic PSS improved the UCS of the palygorskite clay at all the contents studied. At a small polymer content of 0.2%, the compressive strength of PSS-treated palygorskite increased by 27%, compared to the untreated soil (1,570 kPa). The strength of the PSS-treated soils kept increasing with the content of PSS. The strength almost doubled when 3.2% of PSS was added to the palygorskite clay. The direct proportional correlation between the strength of the polymer-treated clay soil and the polymer contents added agrees with the literature since much research showed the same trend when using other organic polymers such as polypropylene homopolymer (Azzam, 2014), gellan gum, agar gum (Chang et al., 2015), methylene diphenyl diisocyanate (Gilazghi et al., 2016), xanthan gum (Rashid et al., 2017; Cabalar et al., 2018), styrene-acrylic emulsion (Rezaeimalek et al., 2018), and sodium alginate (Zhao et al., 2020). However, the strength reduction at dosages higher than the optimum polymer contents as reported by Ghasemzadeh and Modiri (2020) and Naeini et al. (2012) was not observed in our study. This could be because the polymer content of 3.2% used in our work is still below the optimum polymer content. It could also be due to the differences between the polymers used. Higher polymer contents can be studied in future to verify this.

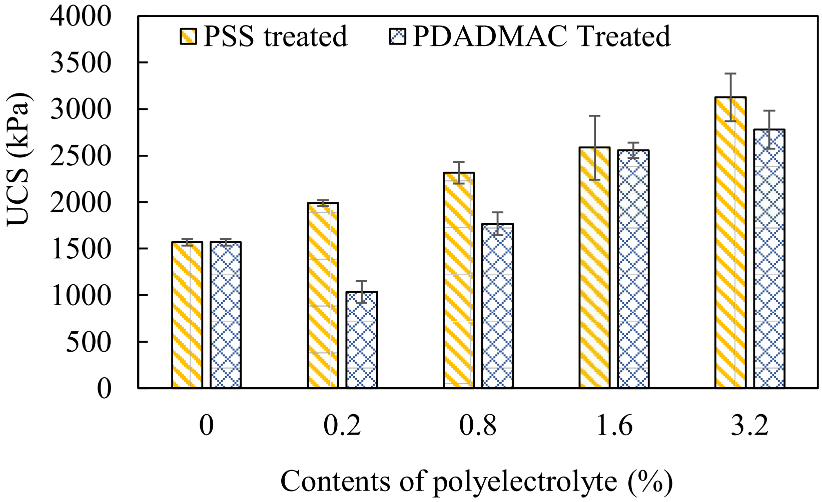

Figure 7. Unconfined compressive strength of palygorskite clay treated with PSS (MW = 1,000,000 g/mol) and PDADMAC (MW = 275,000 g/mol) at varying contents after curing at 23 °C and 50% RH for 7 days.

For the cationic PDADMAC-treated soil samples, no strength improvement was observed at the contents of 0.2 and 0.8%; the treated specimens were weaker than the untreated. However, when the contents of PDADMAC increased to 1.6%, significant strength improvements were observed, and the UCS increased to 2,555 kPa, which was 63% greater than that of the untreated specimens. At the content of 3.2%, PDADMAC-treated palygorskite clay showed the greatest improvement, and the strength reached 2,778 kPa. Compared to PSS-treated samples, it can be concluded that the polycation PDADMAC can obtain comparable strength improvement as the polyanion PSS at a higher polymer content, 1.6% and above; however, when the polymer content is below 0.8%, PSS is superior to PDADMAC. The result that the anionic PSS performs better than the cationic PDADMAC is consistent with previous research by Iyengar et al. (2013) and Huang et al. (2023) when the subgrade soils containing palygorskite clay were treated with polymers with opposite charges. However, the comparable strength improvement of these two polymers at higher dosages is new. The authors believe that the length of polymer chain also contributed to the strength improvement. PSS has much longer polymer chains than PDADMAC due to its high molecular weight (1,000,000 g/mol), compared to 275,000 g/mol of PDADMAC. Therefore, even at a low polymer content of 0.2%, the long PSS chains are able to bind with the soil particles, while for PDADMAC, due to a shorter polymer chain, it is insufficient to bind enough soil particles at such low contents. However, the limitation of a shorter polymer chain became less dominant when enough PDADMAC was used (higher than 0.8%), the presence of abundant PDADMAC polymers could successfully cover and bind enough soil particles, resulting in a strength improvement.

3.2.2 Wet-Curing Conditions

To investigate the effects of moisture on the efficacy, the specimens were cured at 100% humidity in an RH control chamber for 7 days before the UCS tests were conducted. Figure 8 presents the UCS of the PSS- and PDADMAC-treated clay cured under wet-curing conditions. Reductions in strength were observed in all samples studied compared to the dry-curing conditions, indicating the moisture sensitivity of the soil and the polyelectrolytes studied. The same observations were reported by researchers when studying other organic polymers (Tingle and Santoni, 2003; Chang et al., 2015). However, strength improvement was still observed in all PSS-treated samples; the compressive strength of PSS-treated specimens peaked at a content of 1.6% PSS, reaching 764 kPa, which was 74% enhancement compared to the untreated samples. A higher or lower content of PSS added to the soil exhibited strength improvement as well but was inferior to 1.6% PSS. For the PDADMAC-treated clay specimens, a similar trend was observed under wet curing. The compressive strength increased with the content of PDADMAC and peaked at 563 kPa at a content of 0.8%. However, only contents of 0.8 and 1.6% showed improvement; at a low content of 0.2% and a high content of 3.2%, the PDADMAC-treated specimens were weaker than the untreated clay.

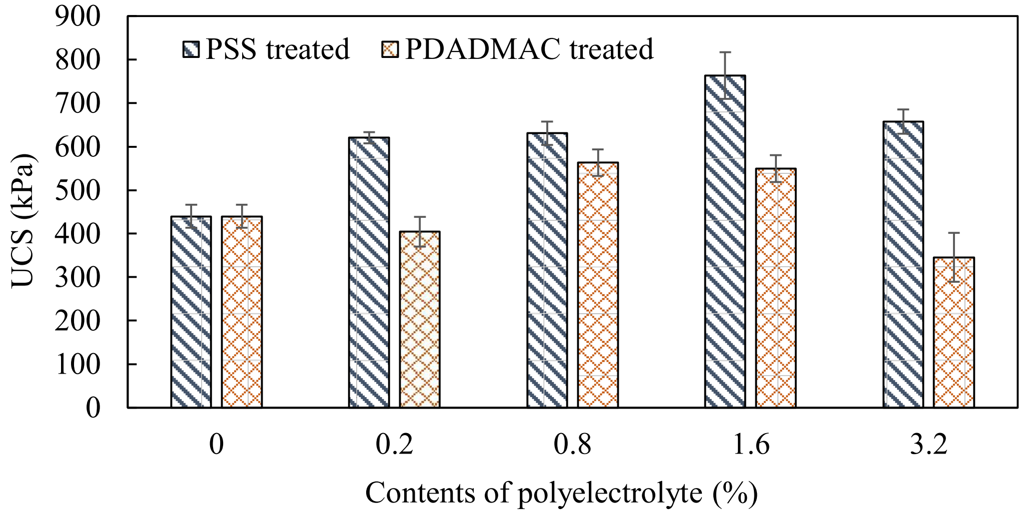

Figure 8. Unconfined compressive strength of palygorskite clay treated with PSS and PDADMAC after curing at 23 °C and 100% RH for 7 days.

3.2.3 Comparison between Wet- and Dry-Curing Conditions

The percentages of strength improvement under both dry and wet conditions were calculated and plotted, as shown in Figure 9. PSS improved the UCS of the palygorskite clay under both wet and dry conditions. Improvements of 26 to 100% in UCS under dry conditions were observed, and strength increased with PSS contents. Under wet conditions, 40 to 70% of UCS improvement was recorded; unlike under dry conditions, the improvement peaked at a PSS content of 1.6% and started to decrease.

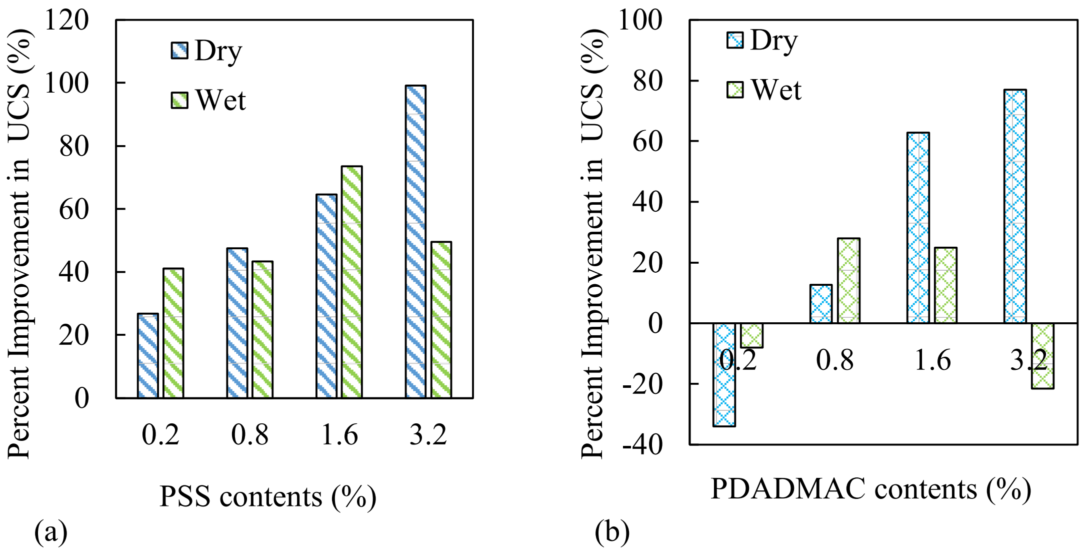

Figure 9. Improvement in unconfined compressive strength of palygorskite clay treated with (a) PSS and (b) PDADMAC after 7 days of dry and wet curing.

For PDADMAC, a 0.2% content did not work under both wet and dry conditions. Improvements occurred at contents higher than 0.8% but followed different trends with or without the presence of moisture. When the samples were cured under dry conditions, the strength improvement increased with PDADMAC contents, and 80% of strength improvement was observed as compared to the untreated samples. However, under wet conditions, the improvements only occurred when 0.8 and 1.6% PDADMAC were used; a higher content of 3.2% resulted in the treated soil being weaker.

In a comparison of PSS and PDADMAC results, both PSS and PDADMAC are sensitive to moisture, but PSS showed more resistance to moisture than PDADMAC. It can also be concluded that both polymers behave very different under dry and wet conditions. Similarly, other polymers such as lignin- and starch-based polymers are also reported to perform differently under such conditions (Yang et al., 2018; Im et al., 2021). Therefore, the selection of each polymer for soil stabilization should consider the actual field conditions and evaluate the feasibility of using these polymers. To further study the resilient behavior and fracture properties of PSS- and PDADMAC-treated palygorskite, a dosage of 1.6% of PSS and PDADMAC was selected since this polymer content had the best performance based on the UCS measurements under both wet and dry conditions.

3.3 Resilient Modulus

Resilient modulus (M_r) tests were conducted for the untreated, 1.6% PSS-treated, and 1.6% PDADMAC-treated palygorskite clay. An extended 14-day dry curing was selected for the M_r test because researchers found that specimens were not dried uniformly after 7 days of dry curing, and the center of the samples was still wet.

Figure 10 presents the M_r test results of both the untreated and PSS-treated palygorskite clay. For the untreated soil, M_r was 144 MPa at 13.8 kPa of confining pressure and 13.8 kPa of deviator stress, and M_r increased with the increasing confining pressures and deviator stresses. The M_r of the untreated clay reached 213.6 MPa at the highest confining pressure (41.4 kPa) and deviator stress (68.9 kPa). After PSS treatment at the content of 1.6%, the M_r increased by 10 to 20% compared to the untreated clay. The M_r of the PSS-treated clay followed the same trend as that of the untreated soil. That is, the M_r increased with both the deviator stress and the confining pressure. The values of the M_r of the PSS-treated soil were greater than that of the untreated soil throughout all stress levels and confining conditions, showing improvements due to the addition of PSS. The improvements in the resilient moduli of soils after polymer treatment were also reported by Georgees et al. (2018). In their study, polyacrylamide was used to stabilize three different types of soils including one clay soil and all three soils showed improvement in resilient moduli after polymer treatment. Arab et al. (2019) used sodium alginate to treat clay and silt soils and both exhibited higher resilient moduli than untreated soils. However, Kumar et al. (2022a) studied the resilient behaviors of silty sand treated with a copolymer emulsion (component unknown) and found that the resilient moduli of the treated soil increased slightly after 3 days but were almost the same as the untreated after 7 days even though significant strength improvement was observed in unconfined compressive strength. Therefore, to fully evaluate the effectiveness of a specific polymer in soil stabilization, more tests are needed other than only using the unconfined compression test.

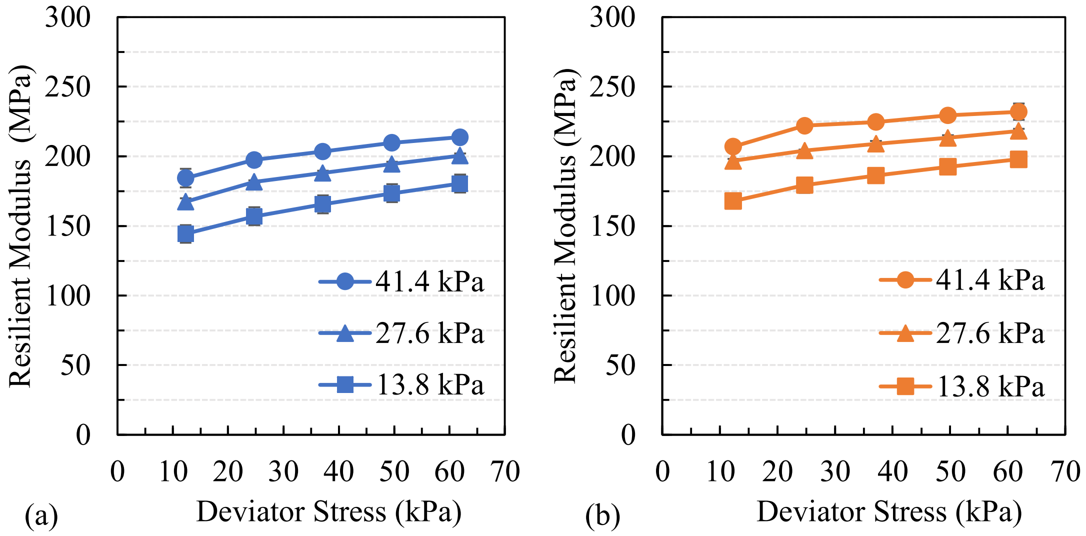

Figure 10. Resilient modulus of palygorskite clay after 14-day curing: (a) untreated versus (b) 1.6% PSS treated.

However, the PDADMAC-treated palygorskite specimens cracked during curing; therefore, the M_r of PDADMAC-treated soil is not included in this paper. This indicates that potential issues such as drying cracking could occur when a high content of PDADMAC is used.

The modified three-parameter universal model suggested by the *Mechanistic-Empirical Pavement Design Guide* was used for characterizing the M_r results of both the untreated and PSS-treated palygorskite clay (National Academies of Sciences Engineering and Medicine, 2008):

$$M_r = k_1 P_a \left(\frac{\theta}{P_a}\right)^{k_2} \left[\left(\frac{\tau_{\text{oct}}}{P_a}\right)+1\right]^{k_3} \quad (1)$$

The logarithmic form of Equation (1) can be expressed as:

$$\log\left(\frac{M_r}{P_a}\right) = \log k_1 + k_2 \log\left(\frac{\theta}{P_a}\right) + k_3 \log\left(\frac{\tau_{\text{oct}}}{P_a}+1\right) \quad (2)$$

where

M_r is the resilient modulus, kPa;

k_1, k_2, and k_3 are model parameters, dimensionless;

P_a is atmospheric pressure = 101.3 kPa;

θ is bulk stress = $\sigma 1 + \sigma 2 + \sigma 3$, kPa; and

τ_{oct} is octahedral shear stress, kPa.

The octahedral shear stress is defined as:

$$\tau_{oct} = \frac{1}{3}\sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2} \quad (3)$$

Under the triaxial condition, $\sigma_2 = \sigma_3$ and equals the confining pressure, and $\sigma_1 - \sigma_3 = \sigma_d$, is the deviator stress which was directly applied to the soil specimens along the longitudinal axis during the test. Therefore, the bulk stress and octahedral stress can be rewritten as Equations (4) and (5), respectively:

$$\theta = \sigma_d + 3\sigma_3 \tag{4}$$

$$\tau_{oct} = \frac{\sqrt{2}}{3}\sigma_d \tag{5}$$

The three-parameter model constants are dimensionless due to stress normalization. Multiple linear regressions were conducted to determine the three model constants. Table 4 summarizes the results of the model constants for both the untreated and PSS-treated clay and the coefficient of determination. Figure 11 shows the goodness of fit between the modeled and laboratory M_r.

Table 4. Model constants for untreated and PSS-treated palygorskite clay

Specimen	Polymer Content (%)	Curing (d)	Model Constants			
			k_1	k_2	k_3	R^2
Untreated	0	14	1681.17	0.290	0.167	0.99
PSS treated	1.6		1952.27	0.264	–0.034	0.98

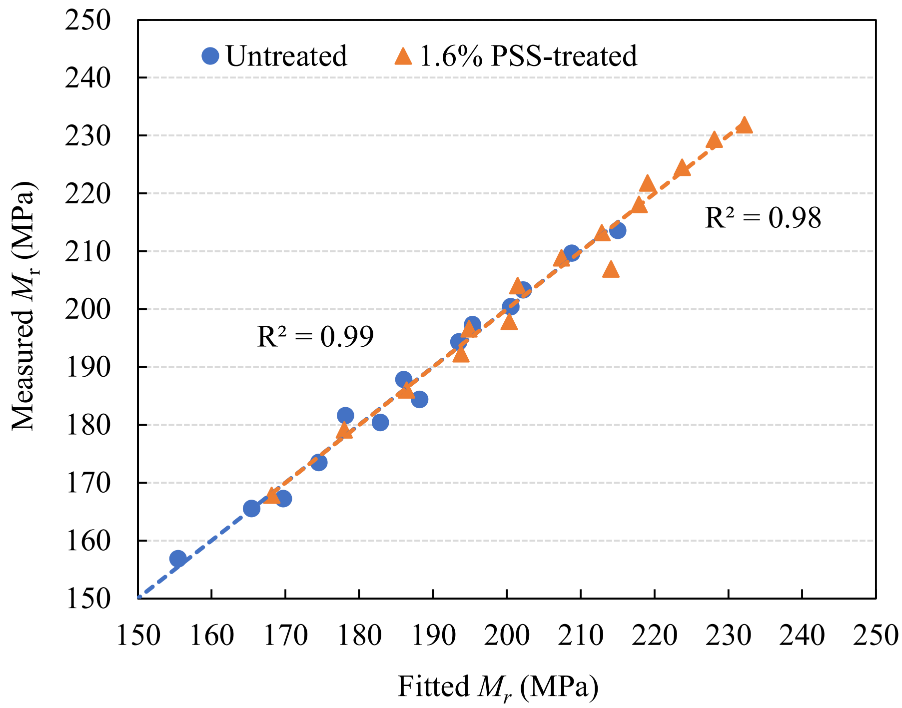

Figure 11. Measured M_r versus fitted M_r for the untreated and PSS-treated palygorskite clay.

The regression analysis obtained R^2 values greater than 0.98, indicating good fitness between the predicted values from the model and experimental results. The model constant k_1 is proportional to the elastic modulus of the soil and is always positive. In this case, k_1 increased after polymer treatment. This means palygorskite clay becomes stiffer after PSS treatment, which agrees with the higher M_r measured. The parameter k_2 is the exponent of the bulk stress term and is positive because an increase in bulk stress results in a higher modulus. Here, k_2 was positive for both the untreated and PSS-treated clay. This means that the M_r of palygorskite clay will increase with an increasing bulk stress. Compared with untreated clay, k_2 was smaller after PSS treatment, indicating that the effects of bulk stress on the M_r of the clay were reduced after the addition of a polymer. The regression parameter k_3 is the exponent for the shear stress term and was positive for the untreated soil and became negative for the polymer-treated specimens. The positive k_3 value for the untreated soil indicates that palygorskite clay, although a clay mineral, shows shear dilation like some sandy soils. Therefore, when shear stress increases, the untreated palygorskite tends to dilate, which results in higher M_r. After PSS treatment, k_3 turns negative, which means an increase in shear stress would likely weaken the soil and result in lower M_r. However, this does not mean the M_r of PSS-treated palygorskite would reduce with increasing deviator stress (proportional to the octahedral shear stress). As Figure 10(b) shows, the M_r of PSS-treated soil increased with the increase in deviator stress. This is because an increase in the deviator stress also increases the bulk stress. Since the exponent of the bulk stress term, k_2, is positive and is greater than the negative k_3 in magnitude, the increase in M_r due to the bulk stress overcomes the decrease in M_r caused by the shear stress, resulting in an overall increasing trend of M_r with the increase of deviator stress.

3.4 Fracture Toughness and Energy

The fracture energy and fracture toughness of the untreated and polymer-treated palygorskite clay were measured using the SCB test. PDADMAC-treated clay specimens cracked again during the curing; therefore, the SCB test results of PDADMAC are omitted from the discussion here due to the significant effects of drying cracks on the test results.

Fracture energy is calculated by dividing the work of fracture by the ligament area of the semicircular disk. The work of fracture is the area under the load-displacement curve, and the ligament area is the area along the centerline after notching. Zhang et al. (2019) provide detailed calculations of fracture energy. Fracture toughness was obtained as the Mode I stress intensity factor K_{IC} at critical load, often defined as plain strain fracture toughness. Equation (6) was used to calculate K_{IC} (Zhang et al., 2019):

$$Y_{\mathrm{I}(0.8)} = \frac{K_{\mathrm{IC}}}{\sigma_0 \sqrt{\pi a}} \tag{6}$$

where

$\sigma_0 = \frac{P}{2rt}$,

P is the applied load, N;

r is the specimen radius, m;

t is the specimen thickness, m;

a is the notch length, m; and

$Y_{\mathrm{I}(0.8)} = 4.782\text{-}1.219(a/r) + 0.063\exp\left[7.045\left(a/r\right)\right]$ is the normalized stress intensity factor, dimensionless (Lim et al., 1993).

Table 5 summarizes the fracture energy and fracture toughness of the untreated and PSS-treated palygorskite clay. Figure 12 shows the load-displacement curves from SCB tests and comparisons of fracture toughness and fracture energy. After PSS treatment, the critical load at failure increased from 136.8 to 224.8 N, resulting in an improvement in fracture toughness and an increment in fracture energy required for crack initiation and propagation. Figure 12 shows that both the untreated and the PSS-treated samples exhibited ductile failure. PSS-treated specimens showed improvements of 65.6 and 85.5% in fracture toughness and fracture energy, respectively. The fracture toughness of soils using the semicircular bending test was also studied by other researchers. Zhang et al. (2019) studied the fracture resistance of limestone and siliceous sand treated separately with a polymer and cement. They found that polymer-treated limestone showed the highest fracture resistance while cement-treated sand exhibited the poorest fracture resistance. Hariharan et al. (2020) treated limestone screens with a polymer and they found that the fracture toughness of the polymer-treated limestone increased by 300% compared to untreated limestone and it increased even further when the polymer content doubled from 2% to 4%.

Table 5. Fracture toughness and fracture energy of palygorskite specimens using SCB tests

Sample	Critical Load P (N)	Specimen Radius r (cm)	Notch Length a (cm)	Specimen Thickness t (cm)	Ligament Area A_{lig} (cm^2)	Geometric Factor $Y_{I(0.8)}$	K_{IC} ($kPa{\cdot}m^{0.5}$)	Fracture Energy (J/m^2)
Untreat-1	127.70	7.51	1.44	5.28	32.05	4.791	16.41	5.01
Untreat-2	145.90	7.46	1.41	5.28	31.94	4.790	18.67	7.20
PSS-1	209.80	7.46	1.47	5.28	31.62	4.794	27.45	9.16
PSS-2	239.70	7.54	1.43	5.27	32.17	4.790	30.65	13.50

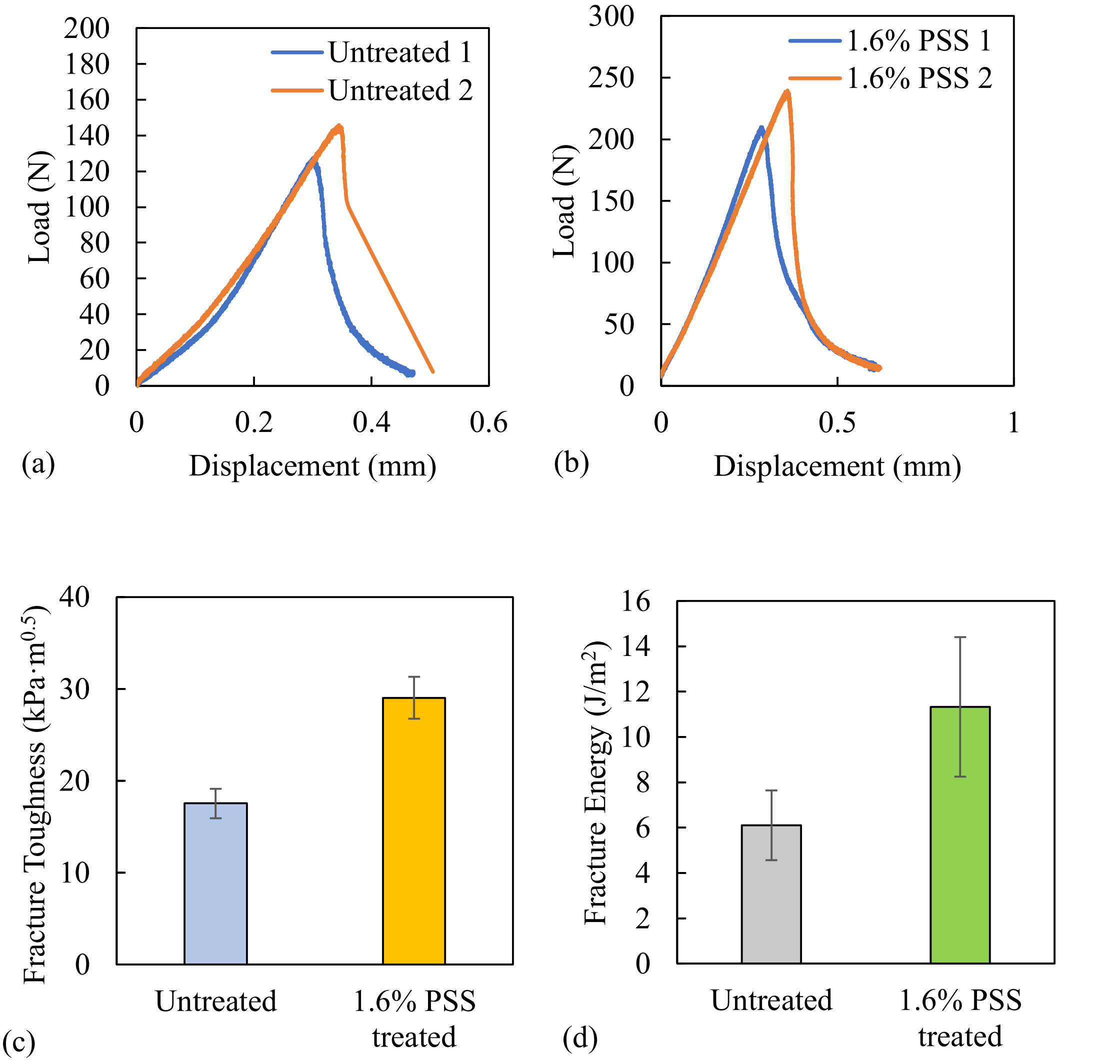

Figure 12. Load-displacement curves of (a) untreated and (b) 1.6% PSS-treated clay after SCB tests, and (c) fracture toughness and (d) fracture energy of the specimens.

3.5 Adsorption Tests

3.5.1 Adsorption of PSS

Prior to the study of the adsorption capacity of palygorskite toward PSS, a calibration graph of PSS concentration versus absorbance (Figure 13) was constructed by recording the UV-Vis spectra of PSS solutions at known varied concentrations (5 to 300 mg/L) in palygorskite-free solutions.

The extinction coefficient of PSS determined from this plot using Beer's law (ε = 6992 $M^{-1}cm^{-1}$) allowed correlation of the measured absorbances with PSS solution concentration.

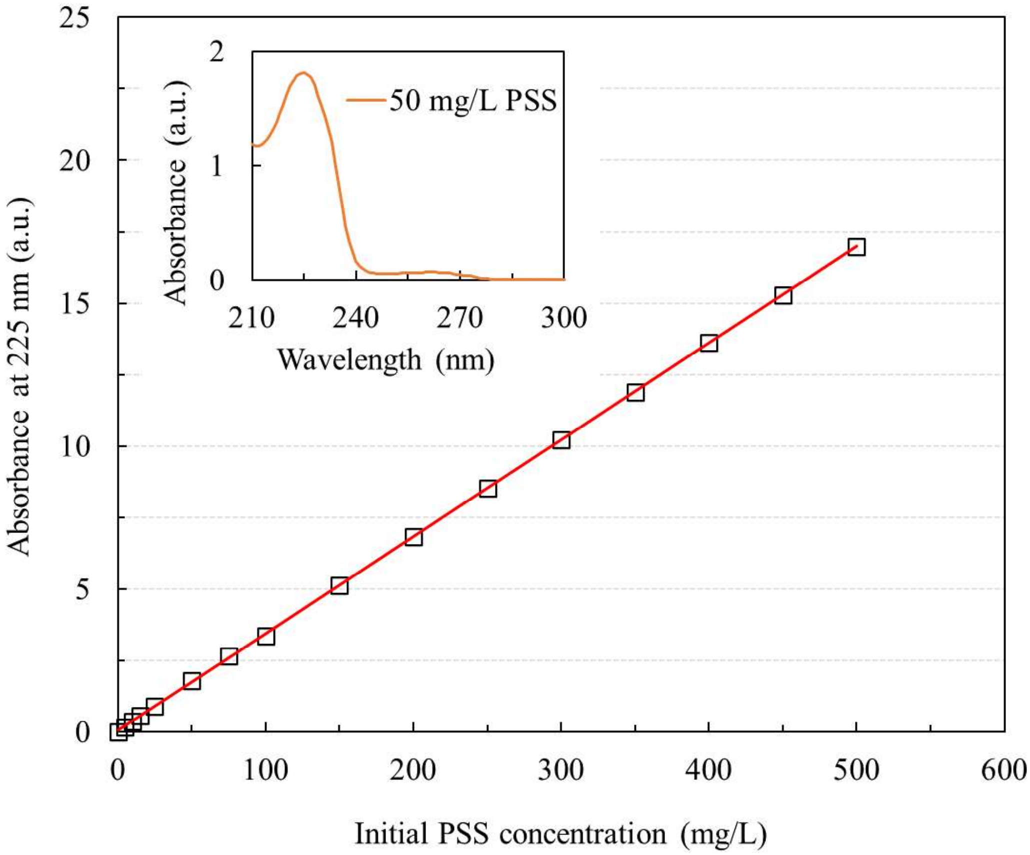

Figure 13. Calibration plot of PSS absorbances plotted as absorbance at 225 nm versus PSS concentration. Inset: UV-Vis absorption spectra of a PSS solution without palygorskite.

The amount of PSS adsorbed polymer was calculated using Equation (7):

$$q = \frac{(C_0 - C)V}{m} \quad (7)$$

where

q is the amount of PSS adsorbed on palygorskite, mg/g;

C_0 is the initial PSS concentration, mg/L;

C is the final PSS concentration in the supernatants, mg/L;

V is the volume of solution, L; and

m is the mass of palygorskite, g.

Figure 14 presents the amounts of PSS in control, palygorskite-free solutions and in PSS supernatants after the addition of 10-g/L palygorskite. The amount of PSS adsorbed on palygorskite determined from Equation (7) increased with an increase in PSS concentration (see the inset in Figure 14) but leveled off when all adsorption sites available on the mineral became occupied with polymer chains, yielding an adsorption capacity of 2.9 mg/g, which is equivalent to 14.1 μmol of PSS repeating units per gram of palygorskite.

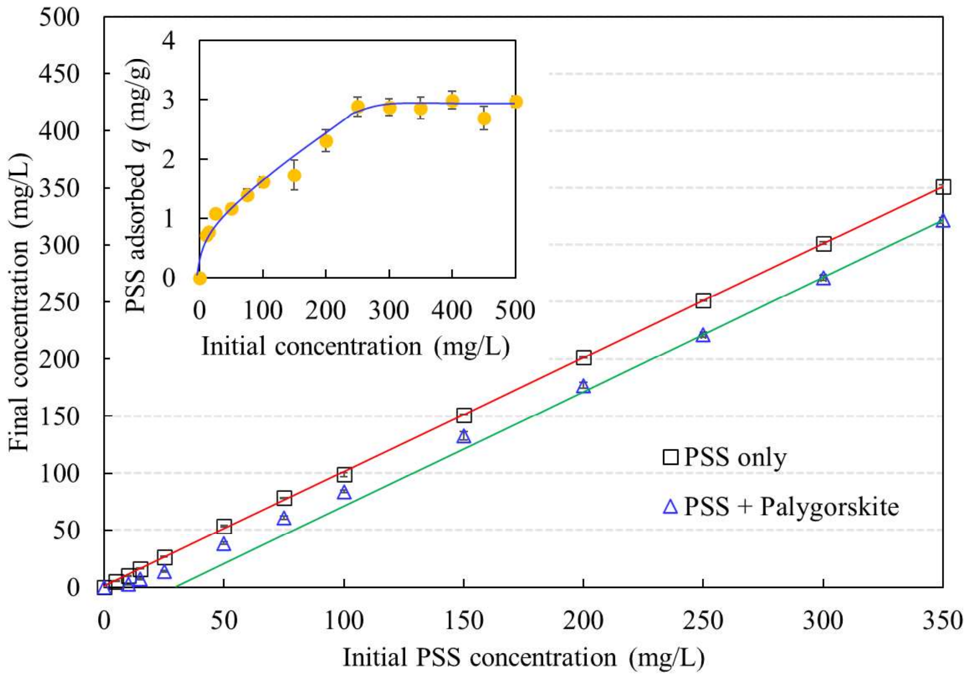

Figure 14. Adsorption of PSS on palygorskite. Inset: Amount of PSS adsorbed (q) on palygorskite as a function of PSS concentration added to 10-g/L palygorskite.

3.5.2 Adsorption of PDADMAC

Unlike PSS, PDADMAC lacks distinct absorption bands in the UV-Vis region, and thus its concentration was determined via detecting the maximum turbidity of PECs formed after the addition of PMAA (see the "Experimental Investigation" section). Figure 15 shows the titration results.

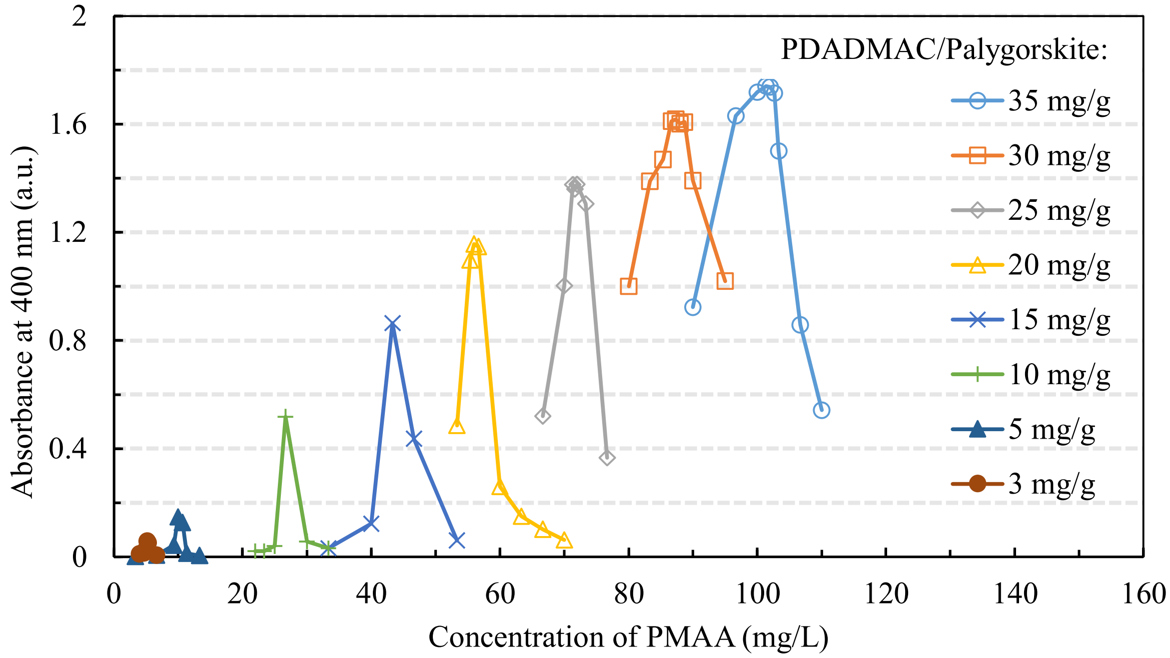

Figure 15. Turbidity emerging in PDADMAC supernatant solutions after the addition of different amounts of 2-g/L PMAA. The turbidity curves were collected with a series of supernatants formed after the addition of varied amounts of PDADMAC (indicated in the labels) to 10-g/L palygorskite dispersions.

Using the calibration turbidity curve for the stoichiometry of PDADMAC/PMAA complexes (see the “Experimental Investigation” section), the amounts of PMAA in Figure 15 that correspond to the maxima in turbidity could be converted to the amounts of PDADMAC remaining in the supernatant. Figure 16 shows the amounts of PDADMAC in control, palygorskite-free solutions (upper curve), as well as in PDADMAC supernatants after the addition of 10-g/L palygorskite. Similar to the case of PSS, the adsorption capacity could be determined using Equation (6). The calculated adsorption capacity of PDADMAC on palygorskite of 2.7 mg/g (see the inset in Figure

16), equivalent to 16.7 µmol of PDADMAC repeating units per gram of clay, was slightly higher than that of PSS (14.1 µmol).

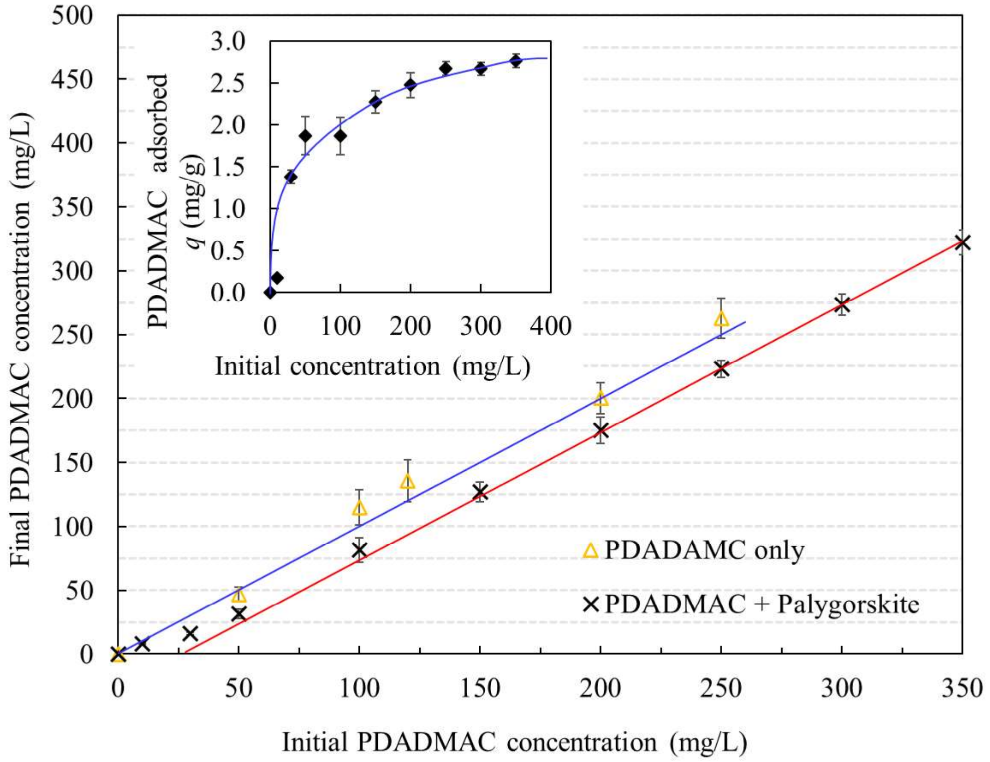

Figure 16. Adsorption of PDADMAC on palygorskite clay. Inset: Amount of PDADMAC adsorbed (*q*) on palygorskite as a function of PDADMAC concentration added to 10 g/L of palygorskite.

These measurements of the adsorption capacity of PSS and PDADMAC polymers with palygorskite minerals provide a fundamental mechanism for improvement of the mechanical properties of soils stabilized with these polymers. Despite similar adsorption capacities of PSS and PDADMAC, PSS-treated palygorskite exhibited higher unconfined compressive strength than PDADMAC at the same polymer content. This observation is consistent with a weaker ionic pairing between PDADMAC and the mineral surfaces due to the presence of significant steric bulk hindrance (Xu et al., 2011) at the amino group of this polymer as compared to PSS.

4 Conclusions

This paper investigates two polyelectrolytes, PSS and PDADMAC, as soil stabilizers by examining the mechanical properties of the palygorskite clay after polymer treatment: unconfined compressive strength (UCS), resilient modulus, and fracture toughness. The effects of dosages of these polymers (0.2 to 3.2%) and the curing conditions (wet and dry curing) on the mechanical properties were studied. The study also included conducting adsorption tests to investigate the mechanism of polymer stabilization. Consequently, the results confirmed binding of polymers and the studied soils, and were used to quantify the adsorption capacity of these polymers on the palygorskite clay.

Following the addition of polymers, the compaction characteristics of the palygorskite clay changed and varied between PSS- and PDADMAC-treated soils. For PSS, the anionic polyelectrolyte, the optimum moisture content (OMC) of the soil increased to 53% - 60%, depending on the contents added, compared to the 52.5% OMC of untreated soil. However, the maximum dry densities (MDDs) of PSS-treated soil did not vary and were almost the same as those of the untreated soil, which was 0.975 g/cm^3. For soil treated with the cationic PDADMAC, the OMCs increased to 56%, but did not change with the dosages of PDADMAC added. Contrary to PSS, the MDDs of PDADMAC-treated clay were around 0.917 g/cm^3, smaller than those of untreated clay.

In terms of UCS, PSS improved the strength of the soil at all contents studied after 7 days of dry curing at 23 °C and 50% relative humidity (RH), and the strength increased with the increasing contents from 0.2 to 3.2%, reaching 2 to 3 MPa (untreated soil had a UCS of 1.5 MPa). PDADMAC did not work at low polymer contents of 0.2 and 0.8% under the same curing conditions; however, significant strength improvements were recorded when high contents of 1.6 and 3.2% were used, and the strength of the treated specimens (2.5 to 2.8 MPa) was comparable to that of the PSS-treated clay. The strength results show that PSS is more effective in stabilizing the palygorskite clay than PDADMAC is. Both polymers showed moisture sensitivity, and the strength dropped when a wet-curing (100% RH) method was used. However, specimens treated with PSS and PDADMAC still exhibited greater strength than the untreated specimens. With the presence of moisture, the UCS of PSS-treated soil improved by 60 and 80% at polymer contents of 1.6 and 3.2%, respectively, while PDADMAC-treated soil improved by around 25% at dosages of 0.8 and 1.6%. These results show reasonable moisture resistance for these two polymers.

The resilient modulus and fracture toughness of the palygorskite clay treated with PSS and PDADMAC at a polymer content of 1.6% were also analyzed. The authors found that PSS improved the resilient modulus by 20% and increased the fracture toughness by 66% compared to untreated soils. However, PDADMAC-treated specimens cracked during the curing period; therefore, the resilient modulus and fracture energy were not measured. This indicates potential cracking issues in applying PDADMAC to the palygorskite clay.

The binding of both PSS and PDADMAC with palygorskite was experimentally confirmed, and the adsorption capacity of the two polyelectrolytes was found to be similar, i.e., 2.9 and 2.7 mg/g of palygorskite, respectively. When converting to charges, 1 g of palygorskite adsorbs 14.1 μmol of PSS repeating units or 16.7 μmol of PDADMAC repeating units. Despite the similar adsorbed amount, PDADMAC was slightly less efficient in the overall improvement of the mechanical properties of palygorskite due to its larger steric bulk at the polyelectrolyte charge.

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