Stabilization of Calcareous Subgrade Soils with Polyelectrolytes: Mechanisms and Mechanical Properties

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Organic polyelectrolytes, i.e. anionic poly(sodium 4-styrene sulfonate) (PSS), cationic poly(diallyldimethylammonium chloride) (PDADMAC) and their polyelectrolyte complexes (PECs) were evaluated for stabilization of calcareous sandy subgrade soil. This paper investigated the effects of polymer type, surface charge type of PEC, concentrations of PEC solutions and dosages of polymer solutions added to the soil on improvement of soil mechanical properties. We found that anionic polymers, for both PECs and individual polyelectrolytes, were superior to their cationic counterparts in improving soil strength. Besides, the constituent polyelectrolytes, PSS and PDADMAC, worked better than their PECs for the specific soil investigated. The strength of polymer treated soils was also found to increase with the increase in dosages of the polymer solutions as well as curing periods. Furthermore, polymer-treated soil specimens exhibited significant toughness improvement, which was higher than cement-treated samples. Scanning electron microscopy images revealed the abundance of long palygorskite fibers covering the surfaces of larger calcite and dolomite particles and linking surrounding aggregates after adding polymers. This observation suggests the interconnection of palygorskite fibers and their linking networks between and among coarse aggregates as the likely mechanism of polymer stabilization of the soil studied.

Key Words: subgrade, soil stabilization, polyelectrolytes, unconfined compressive strength, toughness, stabilization mechanism.

Introduction

This paper investigates two organic polymers, poly(sodium 4-styrene sulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC), as well as their polyelectrolyte complexes (PECs), which have not been used previously as stabilizers for improving the performance of the subgrade soil for pavement construction in Qatar. Subgrade stabilization using traditional stabilizers such as cement is a typical method that is used to increase the stiffness of the pavement structure in order to withstand high traffic loads. However, the high stiffness resulting from the use of cement has drawbacks such as susceptibility of the stabilized layer to fracture and fatigue and reduction in the load transfer across cracks (Iyengar *et al.* 2013, Rodriguez *et al.* 2018). In addition, there are concerns with the use of cement as its production is associated with high emission of greenhouse gases (Latifi *et al.* 2017). Consequently, researchers have been investigating polymers over the past two decades as potential soil stabilizers (Yazdandoust and Yasrobi 2010, Lentz 2015, Mirzababaei *et al.* 2017, Georgees *et al.* 2018, Liu *et al.* 2018, Kolay and Dhakal 2019, Soldo *et al.* 2020, Huang *et al.* 2021).

The study of polymer stabilization focuses primarily on the improvement of mechanical properties (e.g. strength, resilient modulus), permeability, and durability. Research by Iyengar et al. (2013) indicated that polymer-treated subgrade soil exhibited higher toughness and less cracking and rutting than their cement-stabilized counterparts. Other researchers reported that polymer-stabilized soils exhibited improvement in resilient moduli (Zhang *et al.* 2017, Georgees *et al.* 2018), shear strength (Liu *et al.* 2019, Soldo and Miletic 2019), permeability (Sujatha and Saisree 2019), shrinking and swelling behaviors (Soltani *et al.* 2017, Cabalar *et al.* 2018). Such benefits continue to attract the interest of researchers in investigating their use as soil stabilizers. Studies have evaluated many types of organic polymers, ranging from synthetic polymers such as polyacrylamide (Georgees *et al.* 2016, Georgees *et al.* 2018), acrylic polymers (Kolay and Dhakal 2019, Kushwaha *et al.* 2019), polyvinyl acetate (Liu *et al.* 2017b, Zumrawi and Mohammed 2019) and urea-formaldehyde resin (Yazdandoust and Yasrobi 2010) to natural biopolymers including xanthan gum (Latifi *et al.* 2016, Lee *et al.* 2017, Joga and Varaprasad 2020), guar gum (Acharya *et al.* 2017, Sujatha and Saisree 2019), lignin (Zhang *et al.* 2017, Liu *et al.* 2020), and chitosan (Hataf *et al.* 2018). However, the search for new organic polymers is still ongoing with the aim of either providing superior mechanical performance or finding new but less-cost polymers.

Research studies have shown that properties of organic polymers such as type of functional groups involved and their charge, molecular weight, and concentration all significantly impact their effectiveness in stabilizing soils (Huang *et al.* 2021). However, the understanding of polymer-soil interactions or mechanisms of polymer stabilization remains incomplete. The general mechanisms of polymer stabilization include electrostatic attractions between opposite charged polymer units and charge sites on soil particles, adsorption of uncharged polymers onto clay mineral surfaces due to entropy gain from release of bound water molecules, pore filling of polymer gel between coarse soil grains, as well as wrapping of polymer films over soil grain surfaces (Huang *et al.* 2021). Unlike the case of well-studied Portland cement, guidelines and standards regarding polymer stabilization are lacking, and sample preparation techniques (such as order of mixing) and curing conditions (temperatures and duration) are still being established (Rezaeimalek *et al.* 2017a, 2017b).

Objectives

The objective of this study is to evaluate two organic polyelectrolytes, PSS and PDADMAC, and their PECs as potential stabilizers to improve the mechanical properties of a calcareous subgrade soil. For this purpose, unconfined compression tests were performed on the treated soil specimens to investigate the following:

1. Effectiveness of PECs with positive and negative excess charges;
2. Effects of PEC dosages and concentration on the strength of the polymer-stabilized soil;
3. Comparisons between PECs and their constituents (PSS and PDADMAC);
4. Effects of curing period on the performance of the polymer-treated soil;
5. Toughness behavior of the polymer-treated soil.

These investigations are necessary because the two polymers have not been evaluated before as soil stabilizers. The PECs formed by mixing these two polymers also have significantly different properties than these polymers individually (Sukhishvili *et al.* 2006).

To better understand the interactions between these polymers and the soils, soil specimens that exhibited significant strength improvement were selected for further analysis using scanning electron microscopy-Energy Dispersive Spectroscopy (SEM-EDS). The SEM images along with the mineralogy information of the soil obtained from X-ray diffraction (XRD) and X-ray fluorescence (XRF) were analyzed to study the morphological, structural changes of the soil after adding polymers. This paper also aims to provide directions for further research on understanding the mechanisms of these two polymers in stabilizing soils.

Materials

Soil

Samples from a typical subgrade soil in Qatar, provided by the Qatar Primary Materials Company (QPMC), were used to investigate the effects of aqueous solutions of organic polymers in improving strength. The obtained subgrade soil was screened first and sizes smaller than 2 mm were further investigated and used to prepare test specimens. Basic characterization tests on the screened soil including particle size distribution, wet sieve analysis, and hydrometer analysis were performed following relevant ASTM standards (ASTM D2487-17 2017, ASTM D7928-21 2021). The particle size distribution of the studied subgrade soil was determined by Beckman Coulter LS13 320 laser diffraction particle size analyzer and hydrometer analysis, and the resulting data are presented in Fig. 1. The soil was classified as silty sand (SM) as per the Unified Soil Classification System (USCS) (ASTM D2487-17 2017). The maximum dry density (MDD) and optimum moisture content (OMC) of the soil were measured using the standard Proctor compactor (ASTM D698-12 2012). The basic physical and mechanical properties of the studied soil are presented in Table 1.

X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to analyze the mineralogy and quantity of common mineral phases in the subgrade soil. This information was utilized to study the interaction mechanisms between the soil minerals and polymers. Soil samples were pulverized in a ball mill to obtain fine powders ((passing sieve #200 (75 μm)) for XRD analysis. XRD was scanned between 3 to 100 deg 2θ. For XRF, samples were analyzed without binder in order to determine the carbonate contents. The XRD analysis showed that the subgrade soil mainly comprises calcite, dolomite, quartz, bassanite, albite and palygorskite. The XRD pattern of the calcareous soil is presented in Fig. 2, and the mineral composition is presented in Table 2. Calcite and dolomite are the dominant minerals (> 75 % in weight) in the soil and palygorskite is the only clay mineral (11%). Other minerals may also exist in the calcareous soil since there are minor peaks unidentified; however, their concentrations in the soil are minimal. The elemental components of the soil based on XRF analysis are shown in Table 3. The XRD and XRF results confirmed that the soil was calcareous and the results agreed with previous research on Qatari soils (Al-Saad 2005, Iyengar *et al.* 2013). It should be noted that the significant difference between the percentage of clay content from XRD analysis (Table 2) and that from the sieve analysis (Table 1) was expected because XRD was conducted on a small, fine portion of the soil sample.

Polyelectrolytes

The polymers used in this study were commercial products from Sigma-Aldrich: poly(sodium 4-styrenesulfonate), abbreviated as PSS hereinafter, and poly(diallyldimethylammonium chloride), abbreviated as PDADMAC.

The PSS was a linear anionic polyelectrolyte, structure shown in Fig. 3(a), containing large amounts of negative charges due to the sulfonate groups. Both long-chained and short-chained PSS were used with average molecular weights (MW) of 1,000,000 g/mol and 70,000 g/mol, respectively. A 0.07 g/mL PSS solution was prepared by dissolving PSS solid in distilled water (pH = 6.5) to yield a light-yellow solution, shown in Fig. 3(a). The chemical structure of the cationic polyelectrolyte, PDADMAC, is shown in Fig. 3(b). Opposite to PSS, PDADMAC contains strong cationic radicals and produces abundant positive charges. The PDADMAC used in the experiment had a weight-average of 275,000 g/mol. PDADMAC was obtained directly from the manufacturer as 20 % w/w aqueous solution and was diluted whenever needed in the experiment. The physical properties of the two polyelectrolytes are summarized in Table 4.

Polyelectrolyte Complexes (PECs)

Polyelectrolyte complexes (PECs) were prepared by mixing two opposite-charged polymers, PSS (either long-chained or short-chained) and PDADMAC. PECs formed by mixing PSS and PDADMAC can form hydrophobic segments, making the mixture moisture resistant and can contain various positive or negative charges due to the excess of either component (Sukhishvili *et al.* 2006). The charge type of the PECs, cationic or anionic, was studied in this work and the charge ratio between the components was maintained at 0.4. It should be noted that this ratio was the same for both cationic and anionic PECs, but the excess charge and molecular weights were different, depending on how the PECs were prepared. In general, to prepare an anionic PEC, long-chained PSS (1,000,000 g/mol) and PDADMAC (275,000 g/mol) were mixed; for cationic PEC, short-chained PSS (70,000 g/mol) and PDADMAC (275,000 g/mol) were used instead.

Sample Preparation

Preparations of Polyelectrolyte Complexes (PECs)

Both cationic and anionic PECs were used to stabilize the calcareous soil and these PECs were prepared in the same fashion. Anionic PEC was prepared by adding the solution of the polycation to the long-chained polyanion followed by continuous stirring. Similarly, cationic PEC was prepared by adding the short-chained polyanion to the polycation. The total charges of PECs varied by adjusting the molar ratio of the cationic to anionic polymers or vice versa. Preparations of cationic and anionic PECs were described here in details using two examples. This is necessary since proper preparation techniques guarantee that the final PECs exhibit the desired properties. For example, 100 mL diluted anionic PEC with a cation to anion ratio of 0.4:1 (designated as APEC0.4) was prepared by adding the PDADMAC (275,000 g/mol) to the long-chained PSS (1,000,000 g/mol). The long-chained PSS solution was first prepared by dissolving 5.49 grams of PSS powder in 82.4 mL of distilled water with continuous stirring for at least one hour or until the powder was completely dissolved to form 0.07 g/mL solution. A volume of 8.8 mL of 20% w/w PDADMAC solution was then diluted by adding to 8.8 mL of distilled water, resulting in 17.6 mL diluted PDADMAC solution with a concentration of 0.1 g/mL. The diluted APEC0.4 solution was then formed by adding 17.6 mL PDADMAC to 82.4 mL of PSS solution followed by continuous mixing at 250 rpm for 30 minutes or until small amount of white precipitation was observed. The resulting APEC solution had a concentration of roughly 0.07 g/mL. Therefore, in the 100 mL diluted APEC0.4 solution, 60 % of anionic PSS units remained uncompensated with the polycation charge, resulting in an overall negative charge.

Similarly, to make 100 mL diluted cationic PEC with a cation to anion ratio of 1:0.4, denoted by CPEC0.4, the short-chained PSS (70,000 g/mol) was added to the PDADMAC (275,000 g/mol). The short-chained PSS solution was first prepared by dissolving 2.89 grams of PSS powder in 43.2 mL of distilled water followed by continuous stirring until all the powders were completely dissolved, resulting in a 0.07 g/mL solution. The PDADMAC solution was prepared by diluting 28.4 mL of 20 % w/w PDADMAC solution with 28.4 mL distilled water, forming 56.8 mL of diluted PDADMAC solution with a concentration of 0.1 g/mL. Then the diluted CPEC0.4 solution was prepared by adding 43.2 mL of PSS solution to 56.8 mL of PDADMAC solution followed by continuous stirring at 250 rpm for 30 min or until white opalescence started to occur. Contrary to APEC0.4 solution, there were excessive positive charges in CPEC0.4 solution due to 60 % uncompensated cationic PDADMAC units. The CPEC0.4 solution has a concentration of around 0.08 g/mL.

APECs or CPECs with different concentrations were prepared following the same mixing method and only varying the amount and/or concentrations of PSS and PDADMAC. The stirring time was only 5 min at a low speed of 100 rpm after mixing concentrated PSS and PDADMAC solutions together since the mixture became highly viscous rapidly.

Polymer-Stabilized Soils

The organic polymers were added to the soil matrix in liquid state, that is, as aqueous solutions at different dosages, 2 %, 5 % and 10 % (mass of polymer solution to the mass of soil), respectively. For comparison purposes, ordinary Portland Cement was also used to treat the soils at a dosage of 2 %.

Because of a relatively high viscosity of aqueous polymer solutions, homogeneous distribution of polymers within soil samples was hard to achieve when soil remained in the dry state. To that end, extra water required for compaction, i.e., to achieve the optimum moisture content (OMC), was first added to the soil and mixed uniformly prior to addition of polymer solutions. The OMC for untreated calcareous soil was 16 %, while polymer-treated soils, either anionic or cationic polymers, had an OMC of 18 %. The soil samples were again thoroughly mixed to achieve homogeneous distribution of polymers within the matrix. Soil samples were fabricated within 30 minutes after mixing and were compacted at their individual optimum moisture contents. The soil polymer mixture was placed into a plastic mold and compacted in three layers, twenty-five blows per layer, to achieve the desired maximum dry density, similar to that for traditional stabilizers. The plastic mold had an aspect ratio of two with a diameter of 50 mm and a height of 100 mm. The optimum moisture content and maximum dry density of the untreated and polymer-treated soil specimens are summarized in Table 5.

Soil Curing Conditions

To simulate the hot, dry climate condition in Qatar, the soil specimens were cured in controlled chamber at 40 °C for the required time, following the same curing procedure in previous studies conducted on Qatari soils (Iyengar *et al.* 2013). Plastic wrap was used to cover the sides of the soil cylinders to protect the samples from crumbling during the drying process. Top of the specimens was exposed to air to allow moisture evaporation. The curing durations for the samples were 7 and 28 days, respectively. Cement-treated samples were cured in the same fashion as polymer-treated specimens.

Experimental Measurements of Mechanical Properties

Unconfined compression tests were performed on the polymer-treated soil specimens and untreated specimens after different curing times. The test was conducted using a constant deformation-controlled loading of 1.3 mm/min, following the same testing requirements as cement-treated soils as per ASTM D1633-17 (2017). Data of the compression tests were analyzed to obtain the peak stress the failure point, which is the unconfined compressive strength (UCS). Furthermore, the stress-strain curves were analyzed to evaluate toughness as a measure of improvement of ductility of the stabilized soil layer and the ability to absorb energy (Iyengar *et al.* 2013). Toughness was calculated as the area under the stress-strain curve up to the peak point (Iyengar *et al.* (2013). Toughness is an important parameter in pavement engineering where a higher toughness of the treated subgrade layer can enhance the ability of the subgrade to resist cracking, which, in turn, improves pavement performance (Rodriguez *et al.* 2018).

Scanning Electron Microscopy (SEM)

Interactions between soil minerals and organic polymers were examined with an FEI Quanta 400 scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS). Samples for SEM analysis were collected from the soil specimens following the unconfined compression tests. Soil samples were mounted on an aluminum stub using a double-sided carbon tape. The scanning electron microscope's accelerating voltage ranged between 2 and 5 kV. The working distance was set between 9 and 12 mm.

Results and Findings

Compaction Characteristics

The compaction curves of the untreated and polymer-treated subgrade soil are presented in Fig. 4. From Fig. 4, it can be concluded that after treatment with PECs, the optimum moisture content (OMC) of the sandy subgrade soil increased slightly while the maximum dry density (MDD) of the treated soil decreased compared to that of the untreated. The OMC did not vary much with the charge types of the PEC, only 1 to 2 % higher than the untreated, nor with the increase of dosages of PECs used. However, the effects of charge types and PEC dosages on MDD were significant. Overall, the density of the soil treated with anionic PEC was greater than soil treated with the cationic counterpart at the same dosage level; MDD also reduced when 10 % anionic PEC was added to the soil, comparing with 5 % anionic PEC. Same trends were observed when cationic PEC was used.

UCS of Soil Treated with PECs

Anionic PECs and cationic PECs were studied at dosages of 5 % and 10 % of the subgrade soil. As shown in Fig. 5, the soil specimens did not exhibit strength improvement for the first 7 days for either anionic or cationic PECs. However, after 28 days of curing, improvements in strength were observed. Anionic PECs improved the compressive strength at both dosages of 5 % and 10 %; however, the strengths were almost the same at these two dosages, indicating that the strength of anionic PEC-treated soil might have peaked at 5 % dosage. For cationic PECs, the strength of the treated soil specimens increased with the increase of dosages of CPEC. At the dosage of 5 %, CPEC0.4 did not improve the strength, but improvement was observed when the dosage was increased to 10 %. The strength improvement after CPEC0.4 and APEC0.4 treatment was around 30 % at the dosage of 10 %. It should be noted that this improvement might seem insignificant at first, especially when one considers the dosage of 10 % used; however, the concentrations of the polymer solutions here were quite small, 0.07 g/ml for APEC0.4 and 0.08 g/mL for CPEC0.4. This is important, especially when liquid polymers are used, because the component in the polymer solution that is effective is only the polymer, not the solvent, which is water in most cases. Therefore, the effective polymer content of APEC0.4 and CPEC0.4 at dosage of 10% in this work was actually 0.7 % and 0.8 %, respectively, by weight of the dry soil. The authors believe improvement of 30% strength due to using such a small amount of polymer is promising. Consequently, an increase in the content of the effective component polymer, by either increasing the dosage of the PEC solution added to the soil or the concentration of the solution itself, should significantly improve the strength of the soil. Further studies are currently underway to corroborate this position.

The results also showed that APEC0.4-treated soil at a dosage of 5 % achieved the same strength as that of the CPEC0.4-treated at the dosage of 10 % after being cured for 28 days. This indicates that anionic PEC is more effective and thus superior in stabilizing the calcareous sandy subgrade soil in that a lower polymer dosage is required to achieve the same compressive strength. The result is consistent with the previous research carried out by Iyengar *et al.* (2013) where negatively charged polymers performed best in stabilizing calcareous soils with an improvement of compressive strength by 160 % compared to 60 % improvement when treated with cationic polymers. The reason for a higher effectiveness of anionic PEC is likely due to the presence of abundant calcium cations in the calcareous subgrade soil, which could result in a dominant positive charge in these soils (Iyengar *et al.* 2013).

Effects of PEC Concentrations at Constant Effective Polymer Content

The preparation of PEC solutions is usually complex because the concentrations of each component polymer solutions prior to mixing could affect the properties of the final product, which could in turn affect the efficacy of the PECs as soil stabilizers. Therefore, the effects of the concentration of PEC solution while maintaining the total effective polymer content were studied in this paper. APEC0.4 at a dosage of 5% added to the soil was selected. Concentrated APEC0.4 was prepared by mixing PSS and PDADAMC solutions, each at a concentration of 0.2 g/mL in water. The diluted APEC0.4 was prepared by mixing diluted PSS and PDADMAC solution with concentrations of 0.07 g/mL and 0.1 g/mL, respectively. The resulting concentrations of concentrated and diluted solutions of APEC0.4 were 0.2 g/mL and 0.07 g/mL. To maintain the same effective polymer content, dosage at 2 % for the concentrated APEC0.4 and dosage of 5 % for the diluted APEC0.4 were used, respectively. The total effective polymer content was around 0.4 % weight of dry soil in each case.

UCSs of specimens treated with concentrated and diluted APECs are compared in Fig. 6. With similar amount of effective polymer content, the diluted APEC0.4-treated soils showed a higher 28-day UCS than their concentrated counterparts, with an increase of 537 kPa compared to the untreated, while the latter only improved by 230 kPa. This result showed that when the effective polymer content was the same, diluted APEC was preferred. The authors believe this is due to a more uniform distribution of PECs within the soils. We also noticed that when concentrated APEC0.4 was used, the solution was more viscous, which caused difficulty in mixing the soil and polymer uniformly, and may have compromised the effectiveness of stabilization. Further investigation regarding the effects of concentrations of polymers are needed for better understandings of this aspect.

Effects of Constituent Polyelectrolytes

Besides the PECs, the constituent polyelectrolytes, PSS and PDADMAC, were added directly, but separately, to the soil to evaluate their effectiveness. The concentration of PSS and PDADMAC solutions was both 20 % in water and dosage of 2 % was used for each polyelectrolyte, resulting in an effective polymer content of 0.4 %. Portland cement-treated specimens at 2 % dosage were evaluated for comparison, following the same sample preparation procedures and testing protocols.

It can be seen from Fig. 7 that both individual constituent polyelectrolytes, PSS and PDADMAC, were superior to their anionic complex (APEC0.4) in terms of improvement in strength of the subgrade soil. At the same application dosage of 2 %, the anionic PSS worked the best among the three types of polymer solutions. The 28-day UCS increased by 146 %, reaching a value of 4,315 kPa. The cationic PDADMAC improved the strength of the subgrade soil significantly and the strength doubled after 28 days of curing. However, all the polymer-treated specimens provided lower UCS than cement-treated samples, which reached a UCS of 6,446 kPa after 28 days of curing.

Moreover, it should be noted that the effective polymer content for all the polymer-treated soils was only 0.4% while cement used here was 2%. If higher effective polymer content is used, it is reasonable to expect higher strength improvement.

It is noteworthy that contrary to the PECs, which did not show strength improvement at 7 days, PSS- and PDADMAC-treated soil exhibited an early strength improvement after only 7 days of curing, reaching 2,940 kPa and 2,081 kPa, respectively. The anionic PSS performed better than the cationic PDADMAC, indicating anionic polymers are more effective in stabilizing Qatari subgrade soils. This is consistent with previous results where anionic PECs also worked better than cationic PECs. The strength of soils treated with constituent polyelectrolytes also increased over time. The observed improvement of strength over time is intriguing because it indicates the possibility of chemical bonding formations between soil particles and polymer chains, which could contribute to the understanding of the mechanisms of polymer stabilization. Some researchers believe polymer stabilization is more of a physical improvement due to the formation of polymer films “gluing” adjacent soil particles together or the pore filling effect of polymer gels that reduce the pore volume inside the soil-polymer matrix (Mohamed 2004, Chang *et al.* 2016, Liu *et al.* 2017a). Others believe the polymers can chemically adsorb onto the surface of the soil particles through electrostatic attractions, cation bridging, van de Waals forces and hydrogen bonding (Latifi *et al.* 2017, Soltani *et al.* 2019, Huang *et al.* 2021).

Toughness

The stress-strain curves of the untreated and polymer treated subgrade soil are presented in Fig. 8. Fig. 8 (a) and Fig. 8 (b) are for samples cured for 7 days and 28 days, respectively. It is clear from Fig. 8(a) that after curing for 7 days, all polymer treated specimens exhibited higher ductility as strain reached 2.5 % at peak strength. The strain of untreated subgrade soil was around 1.8 % at peak stress. Cement treated soil exhibited higher compressive strength than PDADMAC and APEC0.4;however, it was also much stiffer. The trend was consistent after the samples were cured for 28 days. Soils treated with 2 % PSS (0.2 g/mL) showed the greatest ductility and reached 3 % strain at peak stress. Although cement treated soil was the strongest among all the stabilizers, it was also the most brittle.

Toughness was calculated as the area under the stress-strain curves in Fig. 8 and the results are presented in Fig. 9 for a quantitative comparison. The specimens treated with PSS showed the greatest toughness among all the treated samples after 7 days, reaching 50.8 J/m^3, which was three times that of the untreated soil. Cement treated specimens had the second highest toughness after 7 days, slightly higher than PDADMAC, followed by APEC0.4. After 28 days of curing, the toughness of the PSS-treated specimens increased further and was 60% greater than cement-treated samples. The toughness of PDADMAC-treated soil surpassed that of the cement treated after 28 days, even though the latter exhibited much higher compressive strength (Fig. 7). APEC0.4 also improved toughness of stabilized soil, which was almost double that of the untreated soil; however, it was behind cement due to a much weaker strength.

These results indicate that adding organic polymers to the soil improved toughness significantly. However, for the anionic polyelectrolyte complex (APEC0.4), the improvement in toughness was inferior to both its constituent polymers and Portland cement. This was consistent with the compressive strength results, indicating this PEC mixture was less effective in stabilizing the subgrade soil, at least not at the studied dosages and concentrations.

Scanning Electron Microscopy

The SEM images were used to analyze the interactions between the anionic PSS or cationic PDADMAC and soil particles. A representative portion of the untreated, the PSS- and PDADMAC-treated soil specimens after 28-day unconfined compression test was analyzed under the microscope.

After examinations of SEM images of the untreated calcareous soil, as shown in Fig. 10, presence of calcite, dolomite and palygorskite were confirmed, which is consistent with the XRD results. Since calcite and dolomite are isostructural crystals, the morphology of calcite and dolomite are quite similar under SEM and the differentiation between the two minerals can usually be verified from chemical analysis or from the XRD patterns, see Fig. 2. Calcite and dolomite in the soil have a cubic or prismatic structure

(Area A in Fig. 10) while palygorskite in the soil has a fibrous/needle-shaped structure (Area B in Fig. 10). It is also observed that calcite and dolomite grains were coated by the palygorskite, especially for the smaller calcite and dolomite particles. However, these fibrous palygorskite could not be easily observed under low magnification level, such as 1,000X magnification, see Fig. 11. The angular calcite aggregates could be easily observed while palygorskite could only be spotted sporadically around the edges of large aggregates. This is important as drastic differences were observed when the soils were treated with PSS and PDADMAC. The details will be discussed hereinafter.

Fig. 12 shows the SEM micrographs of the PSS-treated calcareous soil. Abundant fibrous structures were present even under a low magnification level (1,000X), see Fig. 12(a), which was different from the untreated soil (Fig. 11). The same fibrous structures were also observed in the PDADMAC-treated soil, as shown in Fig 13(a), where the calcite aggregates were almost completely covered by the fibers and only a few large aggregates could be identified clearly under SEM with 1,000X magnification.

More detailed images in Fig. 12(b), 12(c), 13(b) and 13(c) reveal these fibers are mostly likely palygorskite, as confirmed by the chemical analysis of these fibers from EDS. As shown in Fig. 14, the fibrous mineral mainly comprised Si, Mg, Al, Fe, Ca, O with a Si: (Mg + Al) ratio of roughly 2:1, determined from the intensities of the peaks from the spectrum. It is known that palygorskite is a magnesium phyllosilicate with the ideal chemical formula of $Mg_5Si_8O_{20}(OH_2)_4 \cdot 4(H_2O)$ (Singer 2002). However, Al usually substitutes Si in the tetrahedra, or replaces Mg in the octahedra. Similarly, Fe and Ca could also replace Mg in the octahedra, but to a lesser extent (Singer 2002). Therefore, based on EDS chemical composition and the fibrous morphology of these minerals, it can be concluded that these fibers abundant in the stabilized soil were largely composed of palygorskite. Although these palygorskite fibers were formed by binding with polymer chains, the small polymer concentration was not detected by EDS. This is likely because the concentration of the elements was too low, below the detection limit of 0.1 wt.% for EDS (Goldstein *et al.* 2017). The dry polymer present in the soil was 0.4 wt.% (mass of dry polymer to mass of dry soil), the concentrations of the elements, such as sulfur (S) in PSS, was much lower, about 0.06 wt.% and nitrogen (N) in PDADMAC was 0.03 %.

The SEM results of the calcareous soil before and after polymer treatment point to the possible mechanism for strength improvement of the Qatari calcareous soil using PSS or PDADMAC. The authors believe that the re-organization and agglomeration of the fine, short fibrous palygorskite clay occurs after addition of polymers and the fibers eventually become abundant and large enough to link and coat the surrounding large calcite or dolomite aggregates.

Before treatment, the fibrous palygorskite clay covers the surface of the calcite and dolomite aggregates. However, these palygorskite fibers are small and usually have a size of a few microns, as shown in Fig. 10; therefore, are sporadically present around or on the edges of the calcite and dolomite. By adding PSS or PDADMAC, the charged units of the polymers adsorbed onto the charge sites on the palygorskite through electrostatic attraction. Since the sizes of palygorskite fibers are on the micron-size levels with average lengths vary between 1 and 2 μm (Singer 2002), they present abundant binding sites for adsorption of smaller individual PSS and PDADMAC coils. At the same time, flexibility of adsorbed polymer chains triggers formation of loops in the adsorbed polymer layers (Pavlukhina and Sukhishvili 2010) and can lead to change of the surface charge properties of palygorskite fibers. Thus, the polymer-palygorskite fibers previously formed can interact with other such fibers due to attractions between the oppositely charged sites available, which results in longer and larger fibers. These fibers intimately intertwine and agglomerate or branch out from the surface of the calcite and link surrounding calcite or dolomite aggregates covered by the same fibers, leading to strength improvement of the stabilized soils. As shown in Fig. 12 and 13, the size of such linked fibers could reach one hundred microns. Therefore, we believe the potential for palygorskite fibers to "grow" is a key to achieve the final mechanical improvement of the stabilized soil. This proposition will be further investigated in future studies.

Discussion

The two polyelectrolytes and their complexes studied in this paper showed improvement in the UCS and toughness of the calcareous sandy subgrade soil. The improvements increased over time and were also related to the dosages of the polymer solutions used as well as the concentrations of the solution itself. These trends agreed with the findings in the literature where other organic polymers were studied (Mohamed 2004, Hataf *et al.* 2018, Soltani-Jigheh *et al.* 2019). For the polyelectrolyte complexes (PECs), anionic PECs outperformed cationic PECs and 5% APEC0.4 achieved the same compressive strength as 10% CPEC0.4. However, the optimum dosages of APEC and CPEC could not be determined from our results since only two dosages, 5% and 10%, were studied. More dosages, especially between 5% and 10%, should be studied to determine the optimum dosage.

The concentration of the PECs also played significant roles. When the effective polymer content was the same, concentrated PECs performed worse than their diluted counterparts. The reason could be due to the non-uniform mixing of PECs and soils for concentrated PECs, which were more viscous and difficult to mix. Our results also showed that the constituent polyelectrolyte, PSS and PDADMAC, performed better than their complexes. More studies on each of these two polymers are currently underway to better evaluate their effectiveness. Compared with Portland cement, we found that the PECs, PSS, and PDADMAC did not outperform Portland cement in terms of compressive strength, but still provided decent strength improvement compared to the untreated soil. Moreover, significant toughness improvements were observed after adding polymers, and the toughness of polymer-treated soils were much greater than cement-treated soils.

There is a need for further studies to better evaluate the effectiveness of these polymers and their complexes. First, the results presented in the paper are based on specimens cured at 40°C and the samples were relatively dry. This partly explains why the strength of the untreated soil was high, reaching 1.6 MPa. The high strength of the untreated soil was also because the soils were screened and only sizes smaller than 2 mm were used. Reducing the soil particle sizes often leads to a more uniform structure and therefore becomes stronger than the normal strength values measured in the field. Moisture sensitivity is a concern for using organic polymers in soil stabilization (Huang *et al.* 2021). Investigations on the moisture sensitivity of the studied polymers and PECs are needed and are currently underway.

Degradation of organic polymers might be an issue as it affects the durability of the stabilized soil. In this study, we used small amounts of non-biodegradable polymers that stabilize soils via their binding with different soil minerals. These polymers have a carbon-carbon backbone whose cleavage can occur in the presence of oxygen upon UV radiation (Gewert *et al.* 2015). However, in the conditions of stabilization of subgrade soils, exposure to UV radiation is minimal and thus no significant degradation is expected.

Regarding the mechanism studies of these polymers and soils, SEM of the soil samples was particularly useful in the analysis of changes in soil structure due to polymer treatment. However, SEM often inspects small and localized areas in the soil sample. Therefore, it is recommended that other techniques such as Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-vis), and absorption tests in future studies to better understand the interactions between organic polymers and soil minerals.

Conclusions

This paper investigated two different types of organic polymers - anionic PSS and cationic PDADMAC - as well as their complexes (APEC & CPEC) as potential stabilizers to improve the calcareous sandy subgrade soils. Mechanical properties such as unconfined compressive strength and toughness of the stabilized soil were evaluated, and factors such as polymer charge types, dosages of polymers used, and concentrations of polymer solutions were examined. Comparisons between the effects of polyelectrolytes and their constituent polymers on soil properties were also studied. Besides mechanical properties, SEM-EDS was utilized to examine the mechanisms of polymer stabilization and interactions between these polymers and soils.

Negatively charged polymers performed better than positively charged polymers in strength improvement of the studied calcareous sandy subgrade. For PECs, anionic PECs at a dosage of 5% produced equivalent strength as cationic PEC at dosage of 10%. For individual constituent polyelectrolytes, soils treated with the anionic PSS showed greater strength than the cationic PDADMAC at both 7 days and 28 days. Moreover, the strength of polymer-treated sandy soil increased with an increase in the dosages of the polymer solutions added. However, the increase varied among the different types of polymers. Improvement in strength was recorded when the dosage of cationic PEC (CPEC0.4) increased from 5% to 10%; however, for anionic PEC (APEC0.4), the strengths were almost the same at both dosages of 5% and 10%. Furthermore, differences between PECs and their constituent polymers, PSS and PDADMAC, were also observed. The constituent polymers PSS and PDADMAC performed better in terms of strength improvement than their complexes when the effective polymer content was maintained at the same level. The strength of polymer-treated soil also increased with curing time as all the polymer combinations studied in the paper showed improvement in strength after 28 days of curing. Besides the improvement of strength, significant toughness enhancement of polymer-stabilized soil was recorded, indicating that polymer-treated soil became more ductile. Both PSS- and PDADMAC-treated soils exhibited higher toughness than traditional stabilizer Portland cement, even though the latter had the highest compressive strength.

Based on the SEM results, the mechanism of stabilizing the calcareous subgrade soil using PSS and PDADMAC was identified as a linkage among coarse aggregates through palygorskite fibers. The reorganization and agglomeration of palygorskite fibers occurred due to the adsorption of these polymers onto the soil particles, leading to palygorskite fibers interconnecting with each other through electrostatic attraction and branching out from the surface of the large soil aggregates and eventually covering the surrounding coarse aggregates. This could also indicate that the existence of clay minerals can promote better polymer bonding with soil particles as clay minerals possess more charge sites than sand and silt particles.

The results are promising in terms of the potential use of organic polymers as soil stabilizers. This is especially true when considering that only small amounts of polymers were used in this study. Further studies are currently underway to examine the moisture sensitivity and durability of these polymers and the stabilized soils.

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Declaration of Interest Statement

The authors report there are no competing interests to declare.

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Table 1. Basic physical and mechanical properties of the studied soil

Properties	**Values**
Sand (wt.%)	75
Silt (wt.%)	24.2
Clay (wt.%)	0.8
USCS classification	SM
Optimum moisture content (%)	16
Maximum dry density (g/cm^3)	1.692
Plasticity index (%)	Non-plastic (NP)

Table 2. Semi-quantitative analysis of the calcareous soil using XRD

Mineral	Quantity (wt%)
Calcite	51.1
Dolomite	26.8
Bassanite	6.7
Quartz	3.5
Palygorskite	10.8
Albite	1.1
Weighted Total	100

Table 3. XRF results of the elemental composition of the calcareous soil

Component	Quantity (wt%)	Component	Quantity (wt%)
C	8.01	S	1.03
O	53.8	Cl	0.12
Na	0.23	K	0.08
Mg	3.96	Ca	26.1
Al	1.12	Fe	0.51
Si	5.02	Sr	0.05
P	0.01		

Table 4. Physical properties of polyelectrolytes

Property	Characteristics or Values	
	PSS	PDADMAC
Physical form	Powder	Clear liquid
Appearance	White or light yellow	Light yellow
Melting point	450 °C	-2.8 ~ 0 °C
Relative density at 25 °C (g/mL)	0.801	1.04
Viscosity at 25 °C (cP)	NA	250 ~ 500
pH	NA	5.0 ~ 8.0 at 25 °C
Water solubility	Soluble	Soluble
Hazards	Non-hazardous	Non-hazardous
Molecular weight (g/mol)	1,000,000 & 70,000	Average 275,000
Solid content (%)	NA	20
Water content (%)	NA	80

Table 5. Optimum moisture contents and maximum dry densities of soil specimens

Sample	Charge Type	Dosage (%)	Optimum moisture content (%)	Maximum dry density (g/cm^3)
Untreated	NA	NA	16.0	1.692
APEC0.4	Negative	5	18.7	1.693
		10	17.0	1.680
CPEC0.4	Positive	5	18.0	1.670
		10	17.5	1.650
PSS	Negative	2	18.0	1.711
PDADMAC	Positive	2	17.5	1.685

Note: The concentration of APEC0.4 solution was 0.07 g/mL in water. Concentration of CPEC0.4 solution was 0.08 g/mL in water.

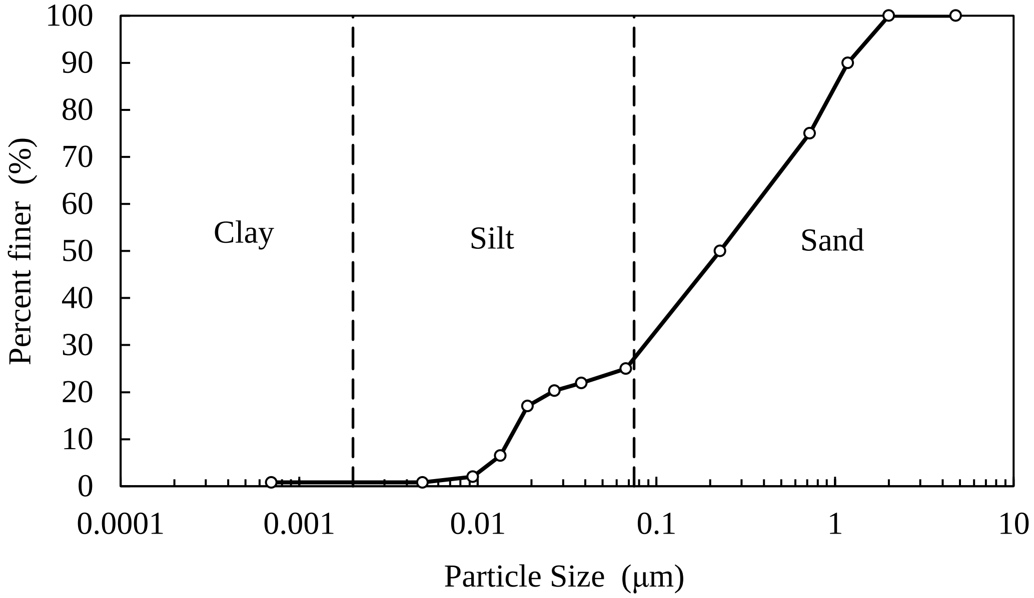
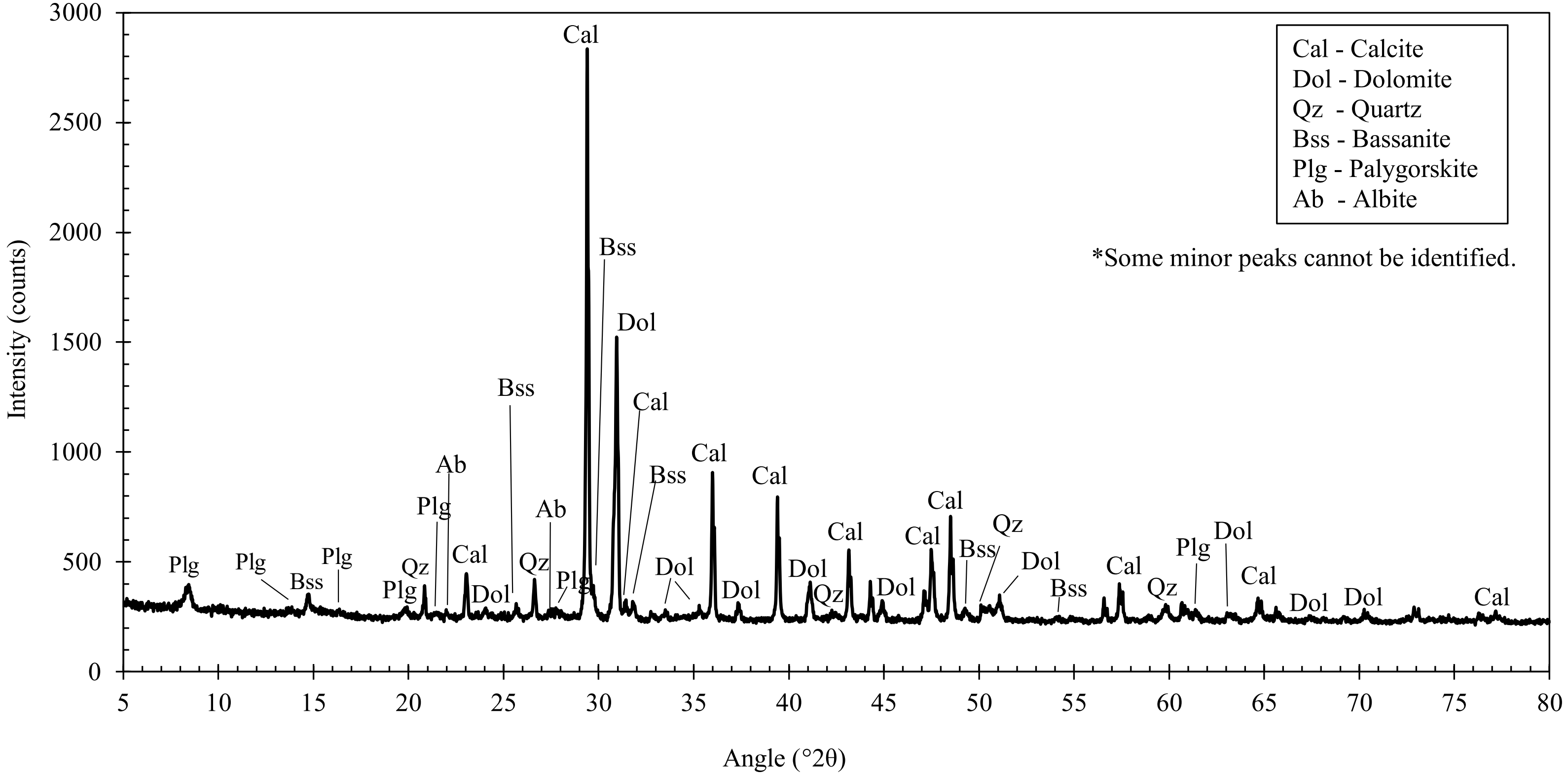

100
90
80
70
60
50
40
30
20
10
0
Percent finer (%)
Clay
Silt
Sand
0.0001
0.001
0.01
0.1
1
10
Particle Size (μm)

Fig. 1



*Some minor peaks cannot be identified.

Fig. 2

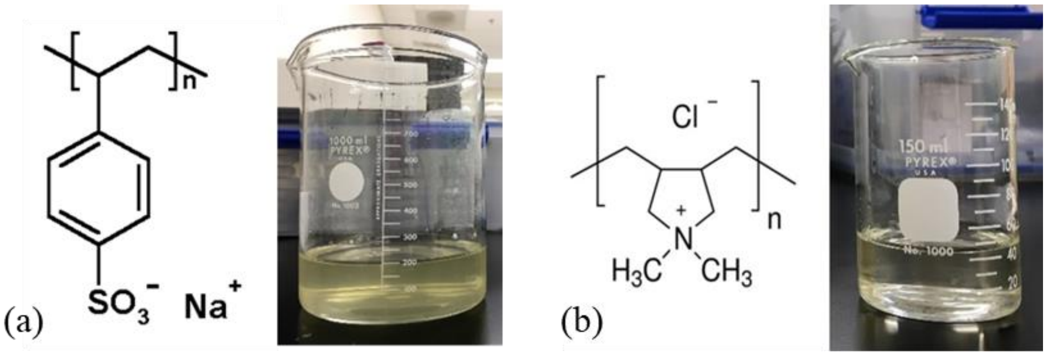


Fig. 3

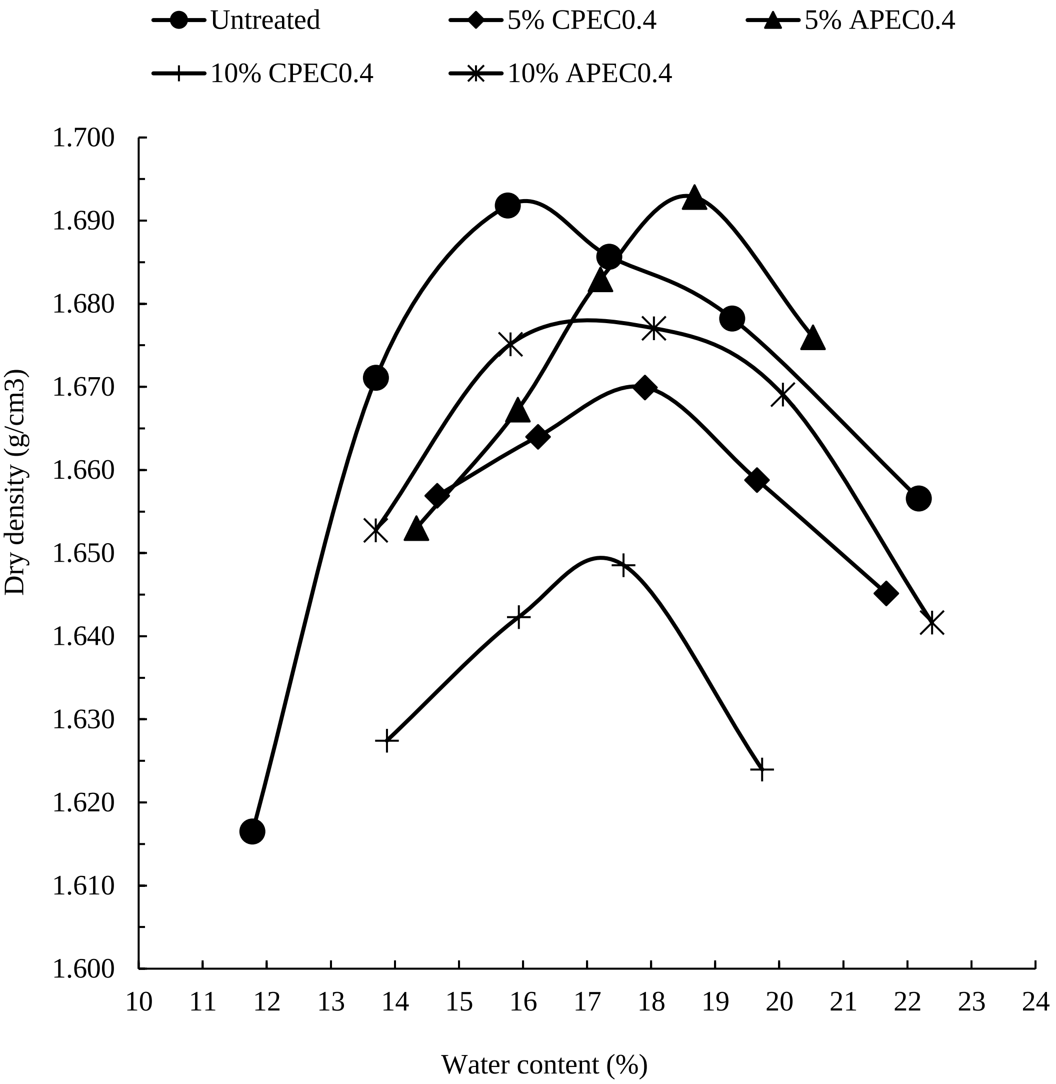

Untreated
5% CPEC0.4
5% APEC0.4
10% CPEC0.4
10% APEC0.4
1.700
1.690
1.680
1.670
1.660
1.650
1.640
1.630
1.620
1.610
1.600
Dry density (g/cm3)
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
Water content (%)

Fig. 4

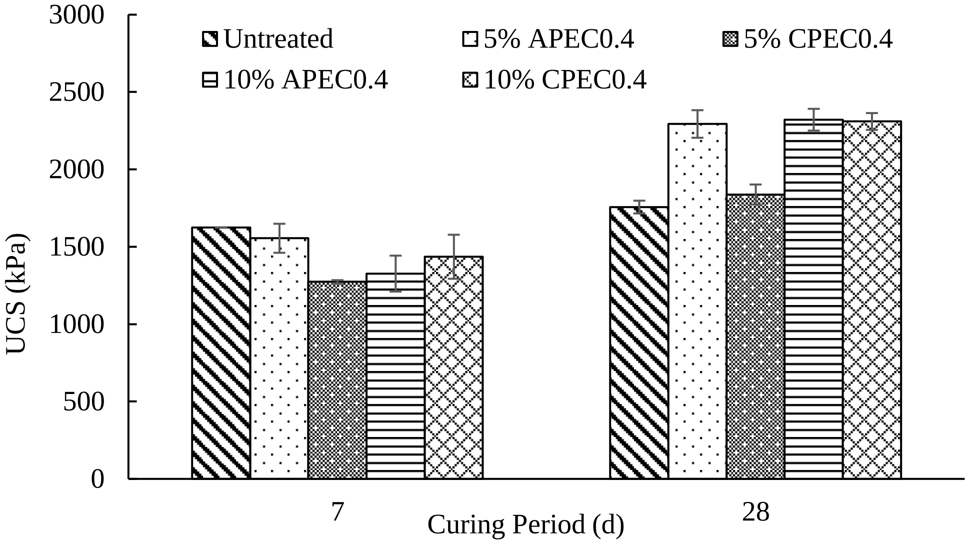

3000
2500
2000
1500
1000
500
0
UCS (kPa)
Untreated
5% APEC0.4
5% CPEC0.4
10% APEC0.4
10% CPEC0.4
7
28
Curing Period (d)

Fig. 5

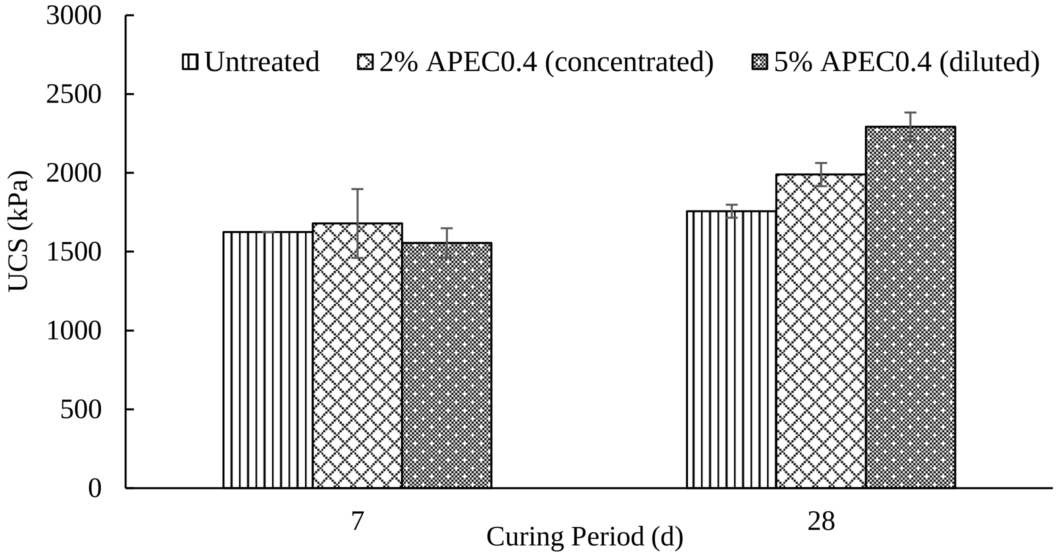

3000
2500
2000
1500
1000
500
0
UCS (kPa)
Untreated
2% APEC0.4 (concentrated)
5% APEC0.4 (diluted)
7
28
Curing Period (d)

Fig. 6

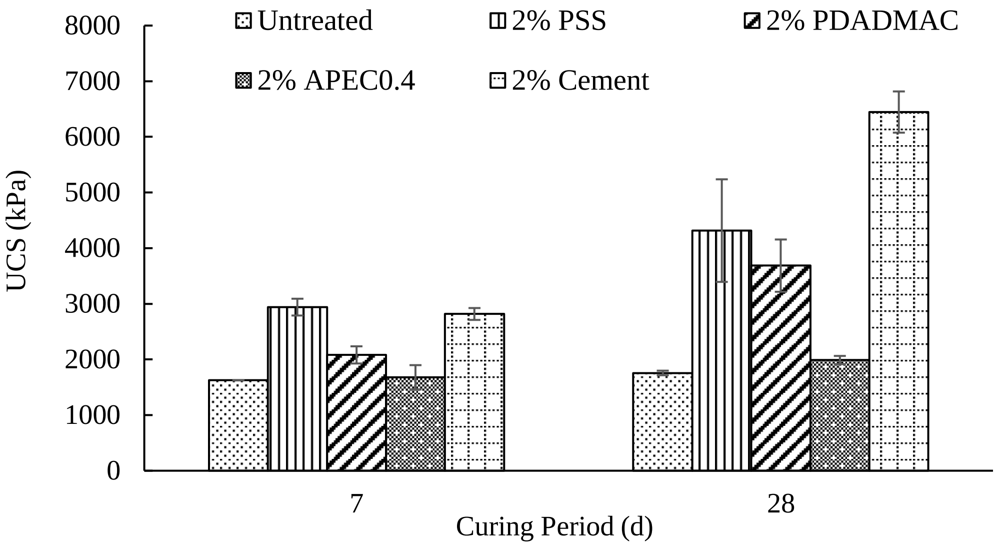
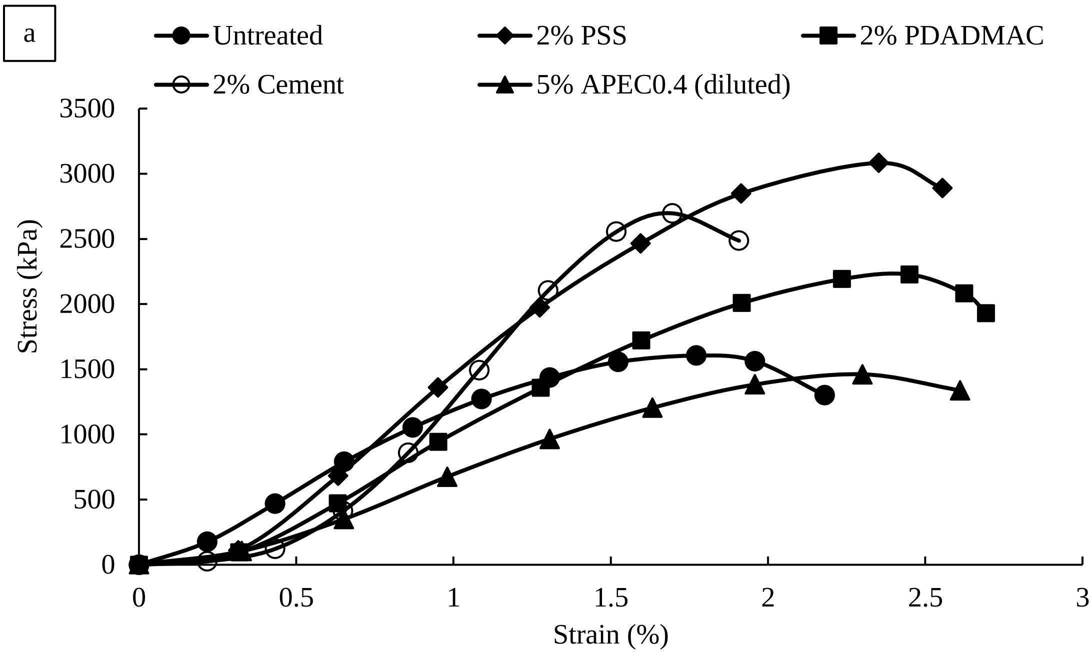
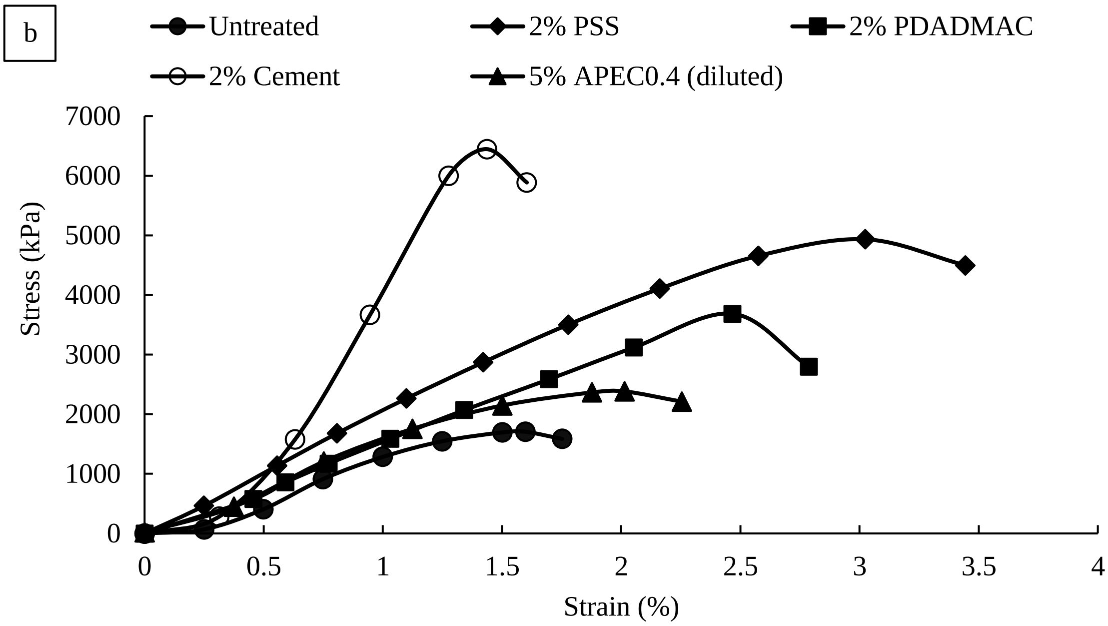

Untreated
2% PSS
2% PDADMAC
2% APEC0.4
2% Cement
8000
7000
6000
5000
4000
3000
2000
1000
0
UCS (kPa)
7
28
Curing Period (d)

Fig. 7


a
Untreated
2% PSS
2% PDADMAC
2% Cement
5% APEC0.4 (diluted)
Stress (kPa)
3500
3000
2500
2000
1500
1000
500
0
0
0.5
1
1.5
2
2.5
3
Strain (%)

1


b
Untreated
2% PSS
2% PDADMAC
2% Cement
5% APEC0.4 (diluted)
Stress (kPa)
7000
6000
5000
4000
3000
2000
1000
0
0
0.5
1
1.5
2
2.5
3
3.5
4
Strain (%)

2

3 Fig. 8

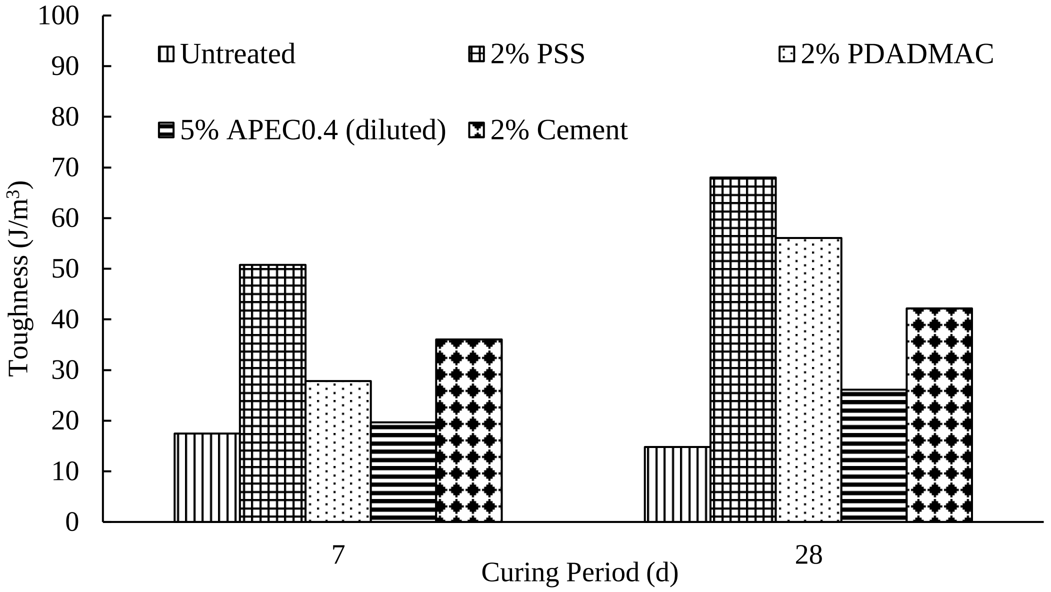

Untreated
2% PSS
2% PDADMAC
5% APEC0.4 (diluted)
2% Cement
Toughness (J/m^3)
100
90
80
70
60
50
40
30
20
10
0
7
28
Curing Period (d)

Fig. 9

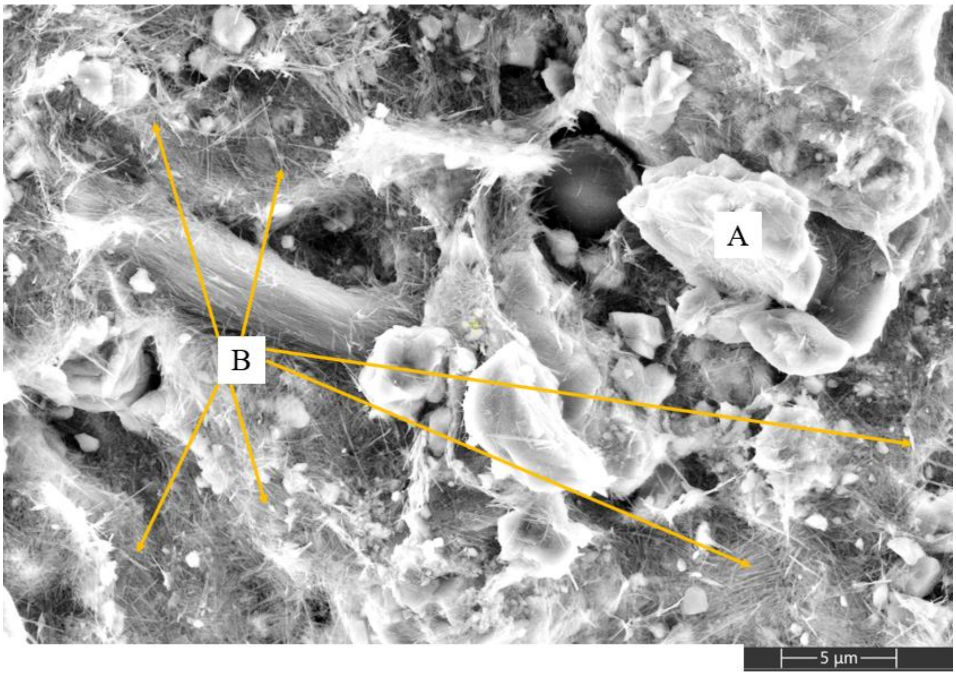


Fig. 10

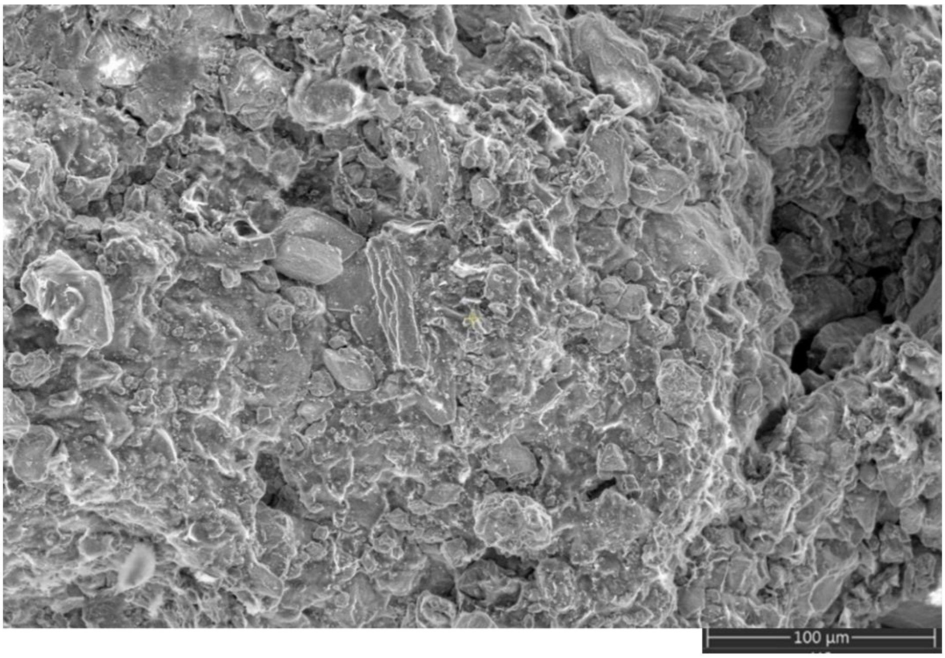


Fig. 11

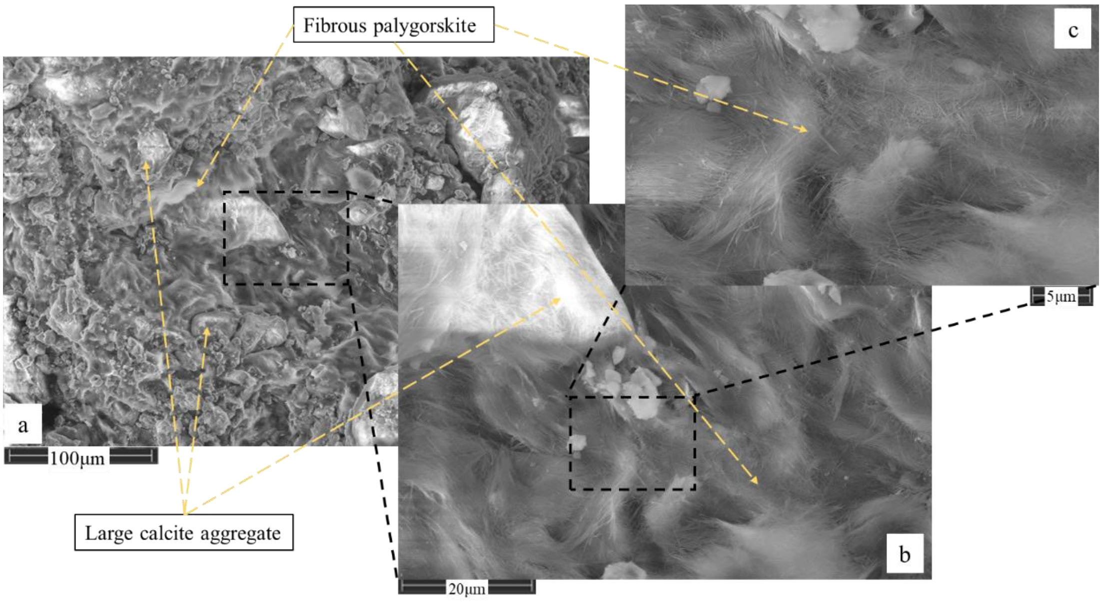

Fibrous palygorskite
c
5µm
a
100µm
Large calcite aggregate
b
20µm

Fig. 12

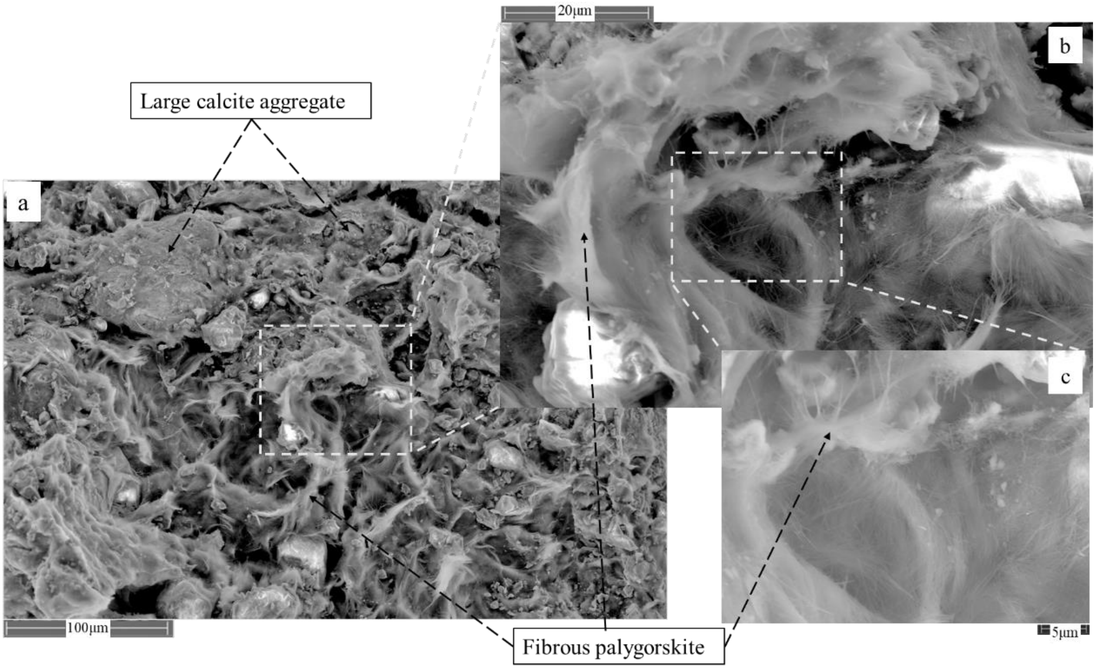

Large calcite aggregate
a
b
c
20μm
100μm
5μm
Fibrous palygorskite

Fig. 13

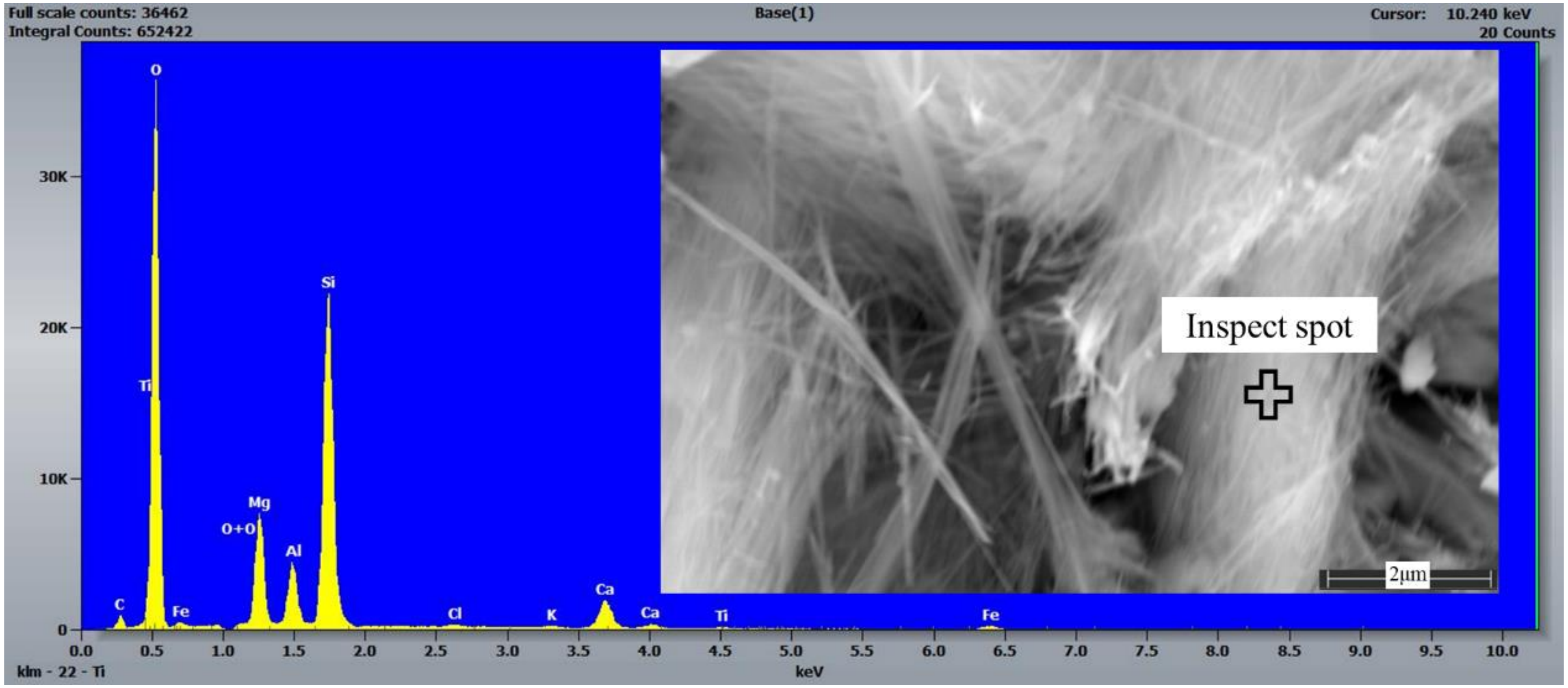

Full scale counts: 36462
Integral Counts: 652422
Base(1)
Cursor: 10.240 keV
20 Counts
30K
20K
10K
0
O
Ti
Si
Mg
O+O
Al
C
Fe
Cl
K
Ca
Ca
Ti
Fe
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
klm - 22 - Ti
keV
Inspect spot
2μm

Fig. 14

Figure Captions

Fig. 1. Particle size gradation curves of the studied subgrade soil.

Fig. 2. XRD diffractogram of calcareous Qatari subgrade soils. Only soil particle sizes smaller than 2 mm were used.

Fig. 3. Chemical structures and bulk solutions of (a) PSS and (b) PDADMAC. Concentration of PSS solution was 0.07 g/mL with MW = 1,000,000 g/mol; Concentration of PDADMAC was 0.1 g/mL with MW = 275,000 g/mol.

Fig. 4. Compaction curves of the untreated and polymer treated subgrade soil.

Fig. 5. Unconfined compressive strength of subgrade soil treated with anionic and cationic polyelectrolyte complexes (APEC0.4 and CPEC0.4) at dosages of 5 % and 10 % after 7 and 28 days of curing.

Fig. 6. Comparison between compressive strength of the subgrade soil treated with diluted and concentrated APEC0.4. Dosages: 5 wt.% of diluted (0.07 g/mL) APEC0.4 vs. 2 wt.% of concentrated (0.2 g/mL) APEC0.4. Total content of effective polymers added to the soils was 0.0035% vs 0.004% (mass of solid polymer contents in the solution to the mass of dry soil).

Fig. 7. Comparisons between Portland cement, PECs and their constituent polyelectrolytes: PSS and PDADMAC (Dosage: 2 % by dry weight of soil).

Fig. 8. Stress-strain curves of the untreated and treated subgrade soils: (a) 7 days; (b) 28 days.

Fig. 9. Comparison of toughness of soil specimens treated by PSS, PDADMAC, APEC0.4 and cement after 7 and 28 days.

Fig. 10. SEM image of untreated calcareous subgrade soil. (A) prismatic calcite/dolomite; (B) fibrous/needle-shaped palygorskite, in bundles or on the surfaces and edges of calcite/dolomite. Magnification: 10,000X.

Fig. 11. SEM image of the subgrade soil at low magnification level (1,000x).

Fig. 12. SEM images of PSS-treated subgrade soil under varying magnification levels: (a) 1,000X, (b) 5,000X, (c) 10,000X.

Fig. 13. SEM micrographs of PDADMAC-treated subgrade soil with different magnification level: (a) 1,000X, (b) 5,000X, (c) 10,000X.

Fig. 14. EDS spectrum of the fibers in the PDADMAC-treated subgrade soil.