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Influence of polyurethane in the polymerization process for poorly graded sand stabilization and cementing

Amin Gholam-Abbas Shotorbani¹ · Nader Shariatmadari¹ · Mehran Karimpour-Fard¹ · Abdoullah Namdar¹ · B. P. Naveen² · Mohammad Aghaei Asl³

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Abstract

The weakness of the subsoil creates problems in both the construction process and structural serviceability. There is a need of introducing a new method with an acceptable advantage over the traditional method for soil stabilization. This study aims to introduce a suitable method for stabilizing poorly graded sand (SP) using a synthesized chemical additive. The specimens were prepared in three different environments, which are ambient air, air-water, and water with 5, 10, 15, and 20% of the designed additive. The optimized polymerization by synthesized chemical additive impacts modulus elasticity, the failure pattern, flexibility, compressive strength, and shear strength mechanism of the SP specimens. The SP was stabilized with enhanced mechanical properties and cementation particles through an adequate polymerization process that has taken place by innovated synthesized chemical additive. The finding of this study is applicable to the SP stabilizing with considering the construction project requirement.

Keywords SP · Synthesized additive · Optimized polymerization · Modulus elasticity · Flexibility

Introduction

Sand has several disadvantages as a construction site. These weaknesses of sand are lack of cohesiveness, high level of permeability, inappropriate saturated sand particles interactions, a large volume of porosity, easy excess pore water pressure owing to undrained conditions, and applying heavy cyclic loading and surcharge relaxed deformation and easy displacement under the saturated situation. Therefore, in geotechnical engineering, the improvement of the sand's mechanical properties is needed before using that as a construction material or soil foundation. In addition, the sandy subsoil and structure are vulnerable to liquefaction, erosion, multidirectional deformation, differential displacement, and

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- ¹ Iran University of Science and Technology (IUST) School of Civil Engineering, Narmak, Tehran 16846, Iran
- ² Amity University Haryana, Haryana, India
- ³ Payame Noor University-Dapertment of Civil Engineering, Tabriz, Iran

partial or complete collapse due to changing groundwater levels and heavy rainfall; these natural hazards can be prevented by improving the sand's mechanical properties ().

Autobire first discovered polyurethane in 1937 as a rubber substitute. Polyurethane foam is flexible and it has been used as an insulating material. Polyurethane can be produced by the reaction between isocyanate (NCO) and a hydroxyl group (OH) of polyol, and it is now used in various types of insulation such as buildings, tanks, pools, etc. (). Improving SP characteristics using polyurethane adequately has not been reported in the literature. Therefore, several factors need to be considered when SP's mechanical properties were strengthened using polyurethane. The quality of polymerization is an essential factor that needs to be investigated in detail. In addition, to maintain environmental quality needs to introduce novel and effective methods for soil improvement.

Numerous methods are presented in the literature for assessing and improving the mechanical properties of the different types of soils and construction materials (Eshghinezhad et al., 2021; Zokaei et al., 2021). The rice husk ash and calcium carbide residue have been investigated to improve expansive soil stabilization and cementation (). Applying soil mixture to enhance the bearing capacity of

Mehran Karimpour-Fard Karimpour_mehran@iust.ac.ir

the natural soil was reported (). Synthesizing polymerization from the kaolin-bentonite mix and using it as an additive for concrete has been investigated (). Introducing calcareous soil-tire mixtures (), sand-tire mixtures (Eshghinezhad et al., 2021), and marine soil-tire mixtures are reported (Zokaei et al., 2021). Among the available methods in the literature, polymerization is a complicated process for improving the mechanical properties of the soil and other construction materials and needs more attention. In the present work, with attention to the polymerization process of polyurethane, improving SP mechanical properties needs to be investigated in detail.

The concepts of strain and stress were discussed for the materials loads response, the material's brittle pattern, the prediction of strain energy, and the materials fracture mechanism (Ayatollahi et al., 2005; Foti et al., 2018; Vantadori et al., 2022). In specimen simulation using SP and polyurethane, the stress and strain level of the materials requires to be studied to realize the strength and stiffness of the materials.

In the present work, the synthesized additive and optimized polymerization were studied for analysis of the stress, strain, modulus elasticity, flexibility, shear, and compressive strengths of the SP specimens. Considering the engineering properties of the polyurethane and the weak point of the SP mechanical properties, a polyurethane-SP mixture needs to be designed.

Materials

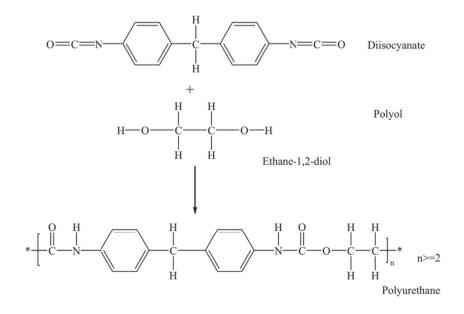
The polyurethane was created from a mixture of isocyanate-polyol. The percentage of isocyanate mixed with polyol has a significant impact on the characteristics of Arab J Geosci (2023) 16:380

polyurethane in terms of chemical reaction, structural flexibility, and strength. In the laboratory, the polyurethane was made by using a mixture of polyol-isocyanate. The designed polyurethane material used in this study activates fast, and the polymerization process is associated with the percentage of the mix of isocyanate with a polyol. Figure 1 presents the isocyanate-polyol mixture and the creation of the polyurethane. Under a controlled synthesis environment, the isocyanates linearly influence polyol binder in producing polyurethane.

The polymerization process of polyurethane foam has been performed in three stages; the first stage is cream time; in this stage, the polymerization has not been started, and the mixture is liquid. Cream time for polyurethane foam varies between 5 and 240 s. The polymerization begins with the end of the cream time, the stage known as gel time. In the third stage (free time), the substance solidifies, and the polymerization ends after 18-24 h that the mechanical strength of most polyurethane foams reaches its maximum value (Fakhar & Asmaniza, 2016; Rezaeimalek et al., 2017a). The mixture ratio of the isocyanatepolyol is responsible for the polymerization process time and quality. It requires considering that the strength of the polyurethane to the thermal changes, freezing, humidity, flexibility, and cracking is higher in comparison to the natural stone materials.

Today, due to the appropriate physical and mechanical properties of these materials, such as high tensile strength, low weight, good stability and durability against climatic factors, environmental compatibility, and easy implementation without any problem in saturation media, it has gained a pervasive application in soil improvement (Barden et al., 1969; Hardin & Drnevich, 1972; Rogers, 1995; Elkady, 2002). In the present study, SP has been mixed with

Fig. 1 Chemical reaction for polyurethane synthesis (Saleh et al., 2019)



polyurethane. The mixture's mechanical behavior has been analysed using a uniaxial compressive strength test and Scanning Electron Microscope (SEM) images.

Soil

To identify the sand particle's size, the sieve analysis results have been presented in Figure 2. Particle size varies from 0.7 to 2.9 mm and D50 = 1.6 mm, and the Uniformity Coefficient, Cu = 1.8, and gradation coefficient, Cc = 1.09 were calculated. According to the Unified Soil Classification System (USCS), sand has been classified as poorly graded sand (SP). The engineering properties of the SP are presented in Table 1. The specific dry unit weights of the SP are 1.57 and 1.33 tons/m³, respectively. The emax and emin for SP are 0.99 and 0.69. The void ratio of the SP is an effective factor in the injection of polyurethane in SP for polymerization and cementation. Considering the quality of SP stabilization requirements in the construction site, the rate of the polyurethane injection in the SP needs to be investigated.

Liquid polymers

The main components of polyurethane are polyester polyol and dimethyl diphenyl diisocyanate (as the primary bonding agent) (Buzzi et al., 2010; El-Ehwany, 1989; Han & Ye, 2006; Nie et al., 2011; Scucka et al., 2015). To have a reactive polyester polyol, we must have a substance as a precursor in the chemical reactions. In this study, dimethyl diphenyl diisocyanate (MDI) has been used for this purpose (Rezaeimalek et al., 2017a). The combination of polyester polyol with dimethyl diphenyl diisocyanate in the presence of foaming agents can lead to the production of hard polyurethane foams, which can be helpful in improving the soil properties (Fakhar & Asmaniza, 2016; Rezaeimalek et al.,

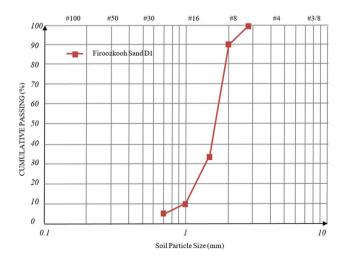


Fig. 2 Particle size distribution curve for the SP

Table 1Characteristics of thesands used in this research

Sand	Firooz- kooh Sand D1
D50 (mm)	1.6
Cu	1.8
Cc	1.09
Gs	2.65
emax	0.99
emin	0.69
$\gamma min(ton/m^3)$	1.33
$\gamma max(ton/m^3)$	1.57

2017a; Keene et al., 2014; Komurlu & Kesimal, 2015; Lee et al., 2017; Rezaeimalek et al., 2017b; Valentino et al., 2014). In addition, the polymerization process of polyure-thane that influences the mechanical properties of the SP has not been reported in the literature in detail. Therefore, it needs more investigation before applying this method for soil improvement (Table 2).

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It should be noted that ester groups can reduce the flexibility of polyurethane chains due to the creation of solid electrostatic bonds along the chain. There are also polyurethane and polyurea groups formed along the coiled and intertwined polymeric chain that build the complex parts of chains. Between these challenging sections, different chains can form hydrogen bonds and create a separation between the hard and soft phases of the polyurethane compounds. This phenomenon can, in turn, act as a physical crosslinking agent (Gisselfält & Helgee, 2003; Landers et al., 2014). Furthermore, the polyurethane characteristics have the advantage of injecting into the soil to control permeability and modification of mechanical properties of the soil.

Hydrogen bonds created between the complex parts of the polyurethane chains and the corresponding physical crosslinking have been shown in Figures 3 and 4 (Landers et al., 2014).

Methods

As previously discussed, the primary purpose of this study is to determine the methods of sample processing in different environments. Also, to investigate the effect

Table 2 Physical properties of the MDI-based stabilizer

Property	Polyol	Isocyanate
Density 25°C (g/cm3)	1.10	1.23
Viscosity 25°C (mPa.s)	300-400	220
Cream time (s)	40–54	
Gel time (s)	120-125	

Fig. 3 (a) Fuzzy separation between the hard and soft parts of polyurethane chains due to the formation of strong hydrogen bonds between the hard parts of the chains (b) as well as the presence of three-factor cross-linking agents

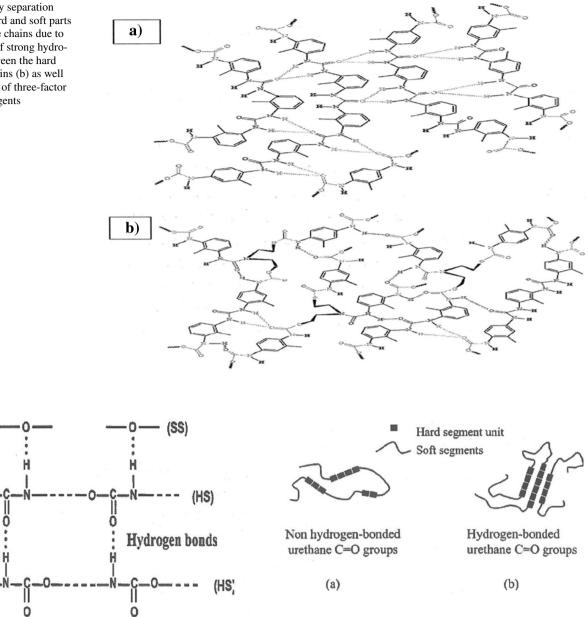


Fig. 4 (a) Fuzzy separation created between the hard and soft parts of polyurethane chains due to the formation of strong hydrogen bonds between the hard parts of the chains, (b) the presence of three-factor cross-linking agents

of material density on the strength and stiffness of samples. Figure 5 shows the entire research work in form of a flowchart. The uniaxial compressive strength device is shown in Figure 6.

There was no information about the optimal amount of polymer additive in the first step. Therefore, in the second step, the processing conditions of the samples in different environments and different percentages of additives (5, 10, 15, and 20 %) were examined.

Deringer

Sample preparation

After controlling the test equipment and preparing the required soil, now it is time to pour the weighed soil into the mould. The Knocking method has been used for sampling and to obtain the weight of the soil poured into a mould with a diameter of 5 and a length of 10 cm, the specific gravity of the soil has been determined. The weight of the soil has been distinctly based on the particular weight of the soil and the

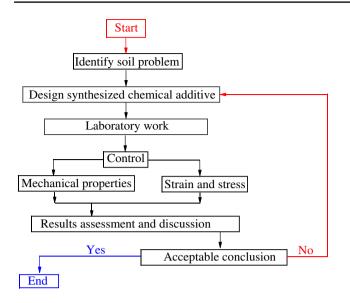


Fig. 5 The flowchart for research work

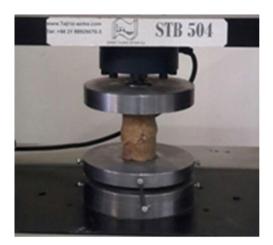


Fig. 6 Uniaxial compressive strength measuring device

mould volume. Then the polyurethane additive was added in different percentages; according to the weight percentage, the same amount reduced the soil weight. Then, the sandpolymer mixture is poured into the mould in 5 equal layers

Fig. 7 Specimens for unconfined compressive strength testing

(measured with a caliper) and is uniformly compacted by the cylindrical mould. It is poured into a mould and compacted with equal compaction energy (35 blows for each soil layer). The samples should be made uniformly and in similar sizes (Rezaeimalek et al., 2017a). Figure 7 shows the specimens for unconfined compressive strength testing using uniaxial compressive strength measuring device.

After preparing, the samples should be kept inside the mould for 20 min because isocyanate and polyol can lead to different setting speeds. Then the samples are taken out of the mould, and exposed to air at room temperature (20–25 °C) for 1 day. After this period, the samples treated in water are removed from the mould. Finally, it was immersed immediately in water. It was stored for 1 day, and then a uniaxial compression test on the samples was done (Rezaeimalek et al., 2017a; Komurlu & Kesimal, 2015; Rezaeimalek et al., 2017b) to identify the mechanical properties and the level of the failure strain, stress, and modulus elasticity of the specimens.

Evaluation of the mixing method

All sand-polymer mixing was performed in a 4-speed automatic mixer to achieve a uniform mixture. This reaction takes place between polyol, isocyanate, and sand, which is very intense, and it usually reaches 60% of its final strength in less than 15 min, and its maximum final strength is obtained in 24 h (Rezaeimalek et al., 2017a; Barden et al., 1969; Rezaeimalek et al., 2017b). The morphology of sand particles in polymerization has not been investigated, and it could be an intersecting research topic in the future.

Processing methods and time duration

After selecting the mixture and compressing methods, cylindrical samples are prepared and then removed from mould carefully to avoid sample damage, deformation, and cracks. A series of samples were processed at room temperature for 1 day, and other samples were processed at room temperature for 24 h and then immersed in water and the third group, the remaining samples were immediately submerged



in water for 24 h after being removed from mould and then were subjected to the uniaxial test.

Effect of polymer content

The optimal mixing ratio of polyol-isocyanate is unknown. We have prepared samples with 1.2:1 polyol to isocyanate ratio. In the present study, the amount of polymer has been selected to be 5%, 10%, 15%, and 20%, which is mixed with soil in a ratio of 1.2:1 polyol to isocyanate. A polyol-isocyanate mixture can produce polyurethane in a different ratio. The polyol-isocyanate mixture influences polyurethane and the quality of mixing with sand and injection of polyurethane underground.

Discussion and results

Introducing an acceptable composite material for improving soil stability is essential for geotechnical engineering. To achieve suitable results for strengthening soil, advanced methods are needed. In addition, when a new additive or method is used for soil improvement, it needs to evaluate which strength parameter of soils has more impact on soil strengthening. Figure 8 shows the results of uniaxial compressive strength tests of curing samples in three environments: air, air-water, and water. The samples that were cured at air-water, in all different percentages of combination, have shown a higher maximum uniaxial compressive strength compared to the other methods. According to the experimental results, the specimens prepared in air and the air-water with 5% polyurethane have exhibited acceptable results in developing compressive strength.

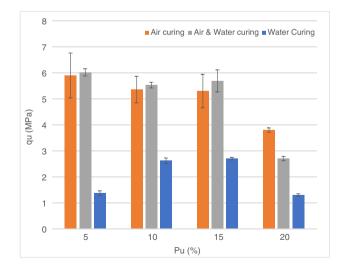


Fig. 8 Results of uniaxial compressive strength tests for curing samples in three environments: air, air-water, water

Fig. 9 Specimen collapse and shearing paths failure



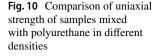
Figure 9 shows specimen collapse and cracking failure paths. The failure mode is a combination of the compressive and shearing failure paths. The failure pattern of the modified SP has significantly improved compared to the unmodified SP, compared to the applied load and time of the collapse. The additive changes the compressibility mechanism of the specimen with the chemical reaction developing in an environment.

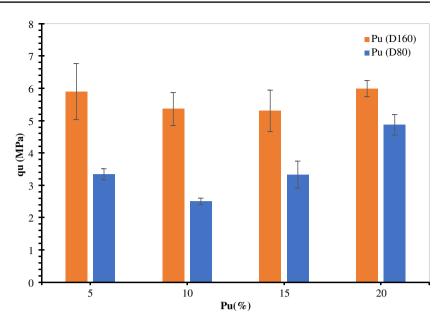
Effect of polymeric material density

Polyurethane with two densities of 160 and 80 kg/m³ was mixed with 131 Firooz Kooh sand to determine the effects of polyurethane density on developing the compressive strength of SP specimens under different preparation conditions. It expects a stronger bond between the grains with a select appropriate density for the specimen. Figures 10, 11, and 12 show the effect of polyurethane density on the uniaxial strength of the elastic modulus, stress, and strain, respectively. Because soil stabilization is the main objective of this research work, E50 was studied. As the density of polyurethane increases, the samples' uniaxial strength and hardness increase. The higher than 5% polyurethane used in enhancement SP causes a reduction of the modulus elasticity and increases specimen flexibility. Therefore, the SP subsoil with an injection of different levels of polyurethane will exhibit the load's sustainability and response differently.

Effect of mixing ratio of polyurethane

The gel-like state is known as gel time. The gel time entirely depends on the values of the various initial ratios of polyolisocyanate. The shorter gel time corresponds to a higher reaction rate. Therefore, reaction rates and bond formation can vary in a wide range. The rate of reactions can be controlled by controlling the material temperature so that in lower ambient temperatures, the rate of reaction will be decreased, and conversely, the gel time will be increased.





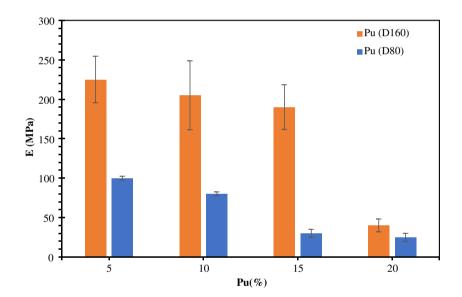


Fig. 11 Comparison of modulus of elasticity of samples mixed with polyurethane in different densities

Another point is that after creating the gel, maybe there was not the possibility of mixing or injecting, and the viscosity increased. So, the composition ratios should be selected in such a way that the gel allows mixing and, at the same time, stronger bonds can be formed.

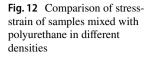
Strength of air-treated samples

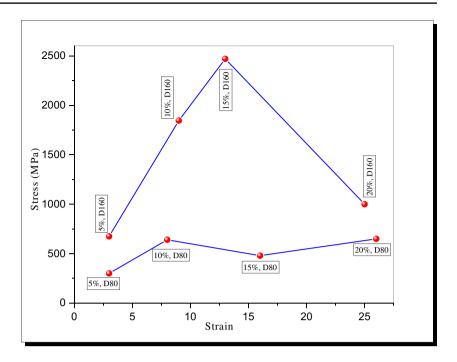
The samples (with 5%, 10%, 15%, and 20% additives) were kept for 24 h at 25 °C after being taken out of the moulds and then subjected to the uniaxial compressive strength test. As can be seen in the diagram in Figure 10, the uniaxial strength decreases by increasing the percentage of additive. This decrease relates to the volumetric nature of polyure-thane. An increase in the percentage of the additive has

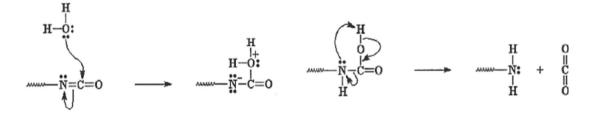
caused a distance between the sand particles and interlocking between the particles has been destroyed, and further expansion of the urethane groups (while creating more urethane bonds between the polyol chains) caused the polar groups to increase, which are trapped between interconnected polyurethane chains.

By increasing polar groups, strong electrostatic attraction between them is being created, and it causes the formation of more hydrogen bonds between them, as can be seen in Figure 13. These electrostatic attractions can bring polar groups closer to each other. Also, hard parts are created between the polymer layers (connecting the aggregates) due to their high polarity (Gisselfält & Helgee, 2003; Landers et al., 2014).

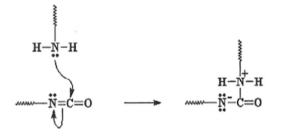
According to the uniaxial strength bar graph in Figure 8, the strength samples decrease by increasing the additive





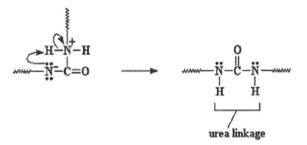


Step1: A water molecule attacks the isocyanate carbon, giving us an ionic species.



Step 3: The new amine attacks another isocyanate, just like the water attacked the old isocyanate.

Step 2: The nitrogen swipes *another* hydrogen, making an amine and carbon dioxide.



Step 4: The nitrogen swipes a hydrogen from the amine, creating a urea linkage in the polymer.

Fig. 13 Effect of reaction between water and isocyanate in the sample after immersion in water

percentage. In contrast, their strength is increased compared to the samples processed at room temperature due to the formation of hydrogen bonds between water and unreacted isocyanate inside the samples. N-C-O isocyanate agent reacts with the hydroxyl (OH) agent of water and forms methane and COC. In the second stage of polymerization, methane reacts with the water hydroxyl (OH) agent and develops polyuria. It should be noted that stress nodes could decrease the flexibility of the polyurethane chain due to the creation of solid electrostatic dipoles along the chain. In addition, polyurethane and polyuria groups formed along the coiled and intertwined (knotted) polymer chains will construct the complex parts of the chains. Between these hard parts, different chains can create hydrogen bonds with each other, which in turn cause a phase separation between the hard and soft phases in polyurethane compounds. This phenomenon acts as a physical crosslinking agent. The hydrogen bonds formed between the hard parts of the polyurethane chains and the formation of the physical crosslink. In Figure 13, the same hydrogen bonds have been shown while the 3-agent crosslinking composition is also used in the formulation, which causes the formation of a much more substantial part, and all of these factors can increase the mechanical strength of the specimens (Gisselfält & Helgee, 2003; Landers et al., 2014).

Polymerization process

The synthesized polymerization was reported to improve the strength of the construction materials. The kaolin-bentonite mixture was thermally treated and used as a concrete additive. The produced additive improved the compressive strength of the concrete considerably by developing

Fig. 14 SEM micrographs of the sand-polymer composites. (A) 20%, (B) 15%, (C) 10%, (D) 5% (air processed) optimized polymerization (). The crystalline polyurethane products. Figure 14 shows types of polymerization quality by changing the sand-polyurethane mixture ratio. The quantity of polyurethane governs the polymerization densification and influences sand stabilization. The quality of the isocyanate-polyol mixture controls the polymerization process through the developed chemical reaction process and provides stiffness and strength for poorly graded (SP) sand. In addition, the modified specimen strength relates to the polymerization quality. The experiment results illustrate a maximum of 5% using polyurethane, showing the best shear resistance for the specimen. Using 10 % and more polyurethane causes high-level polymerization on SP specimens. In addition, it will be the reason for reducing the internal angle of friction of the SP and reducing the SP specimen's shear resistance.

With increasing the amount of polyurethane, the flexibility and deformation of the specimens were increased. The low thermal conductivity of the polyurethane is an advantage for poorly graded (SP) sand stabilizing use. The optimized amount of polyurethane in controlling thermal conductivity needs to be investigated in future research work.

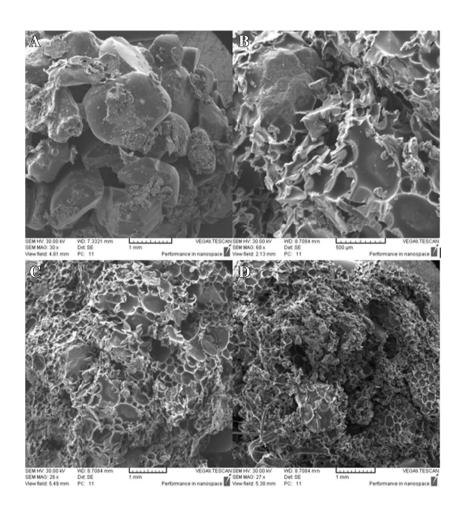
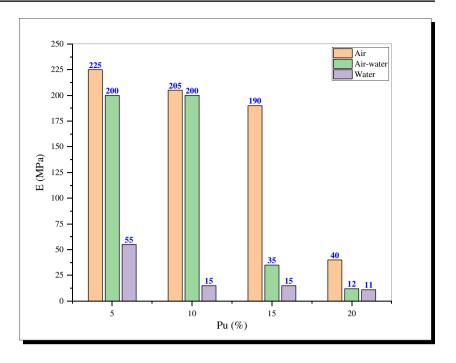
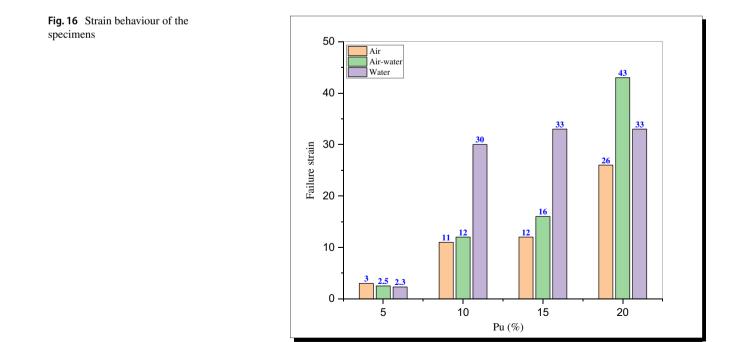


Fig. 15 Modulus elasticity of the specimens



Comparative results

Figure 15 shows the modulus elasticity of the specimens in three conditions ambient air, air-water, and water. Figure 15 shows, according to the experimental results, samples processed at room temperature, and air-curing polyurethane display higher modulus elasticity than the other method. Figure 16 shows the strain of the specimens in three conditions ambient air, air-water, and water. The higher modulus elasticity causes the increasing solidity of the material and improves the specimens' mechanical properties. With increasing polyurethane in the specimens, the deformation capacity without cracks in the specimens was increased. In all specimens, the nonlinearity of the stress-strain relationship was changed with an associated increase in the percentage of polyurethane.



Considering Figures 8, 15, and 16 for poorly graded sand stabilization, using 5 % polyurethane shows the best results of the polymerization process and increases the compressive strength of the model. Using 20% polyurethane enhances the strength of the specimens owing to the polyurethane characteristics.

Environmental impact of PUs

PUs is a group of synthetic polymers that are known for their one-of-a-kind properties as well as their high degree of versatility. This category of polymer can be quickly manufactured and processed on a large scale using a variety of different techniques.

PUs is a key component of modern materials and are widely used. Uses include furniture coatings, construction materials, flame retardants, synthetic skins, and elastomeric components. They are also used in tissue engineering, pericardial patches, and synthetic skin coverings.

Pollution from production processes and materials is a major concern. Toxic substances in PU production are a concern. These materials can affect soil and water. PUs is cheaper for some processes, but they harm the environment, especially soil quality. New international regulations make PUs a safer option. Sand-reinforced with PU. PU and fibre materials improve sandy soil ductility for wider engineering use.

PU improves the soil's mechanical behaviour. Soil mechanical quality has improved. Because they are versatile, PU-based fibres are widely used in geotechnical processes. When introduced into the soil, they can improve strength isotropy and reduce the formation of parallel weakness planes. Using PU to improve soil's mechanical properties has environmental implications and challenges. Microplastics cause pollution. This is exacerbated when effective measures to minimize environmental contamination are not implemented.

Poor engineering and physical properties of soil affect construction use. To reduce damage from weak soils, various techniques and processes have been implemented. PUs is essential for improving soil quality. PUs effectively stabilizes and improve soil properties. This reduces soil compression and increases performance strength.

Conclusion

A synthesized chemical additive was designed by polyurethane-sand mixture design, for stabilizing SP through the optimizing polymerization and cementation of SP particles which leads to improving mechanical properties of the SP specimens. The modulus elasticity, failure pattern, flexibility, compressive strength, and shear strength mechanism of the SP specimens were investigated. Improving specimen stiffness and strength is related to the polymerization quality in the SP layers. An appropriate percentage of polyurethane creates optimized polymerization and leads to producing suitable SP stabilization. In addition, optimized chemical reaction provides acceptable stiffness and strength for poorly graded (SP) sand. The flexibility of SP is associated with the percentage of using synthesized chemical additives. In addition, polymerization quality is related to the environment. The optimized polymerization modifies the compressibility mechanism and sand particles' interaction with the associated chemical reaction developing in an environment.

The multidirectional deformation of the subsoil and cracking of the soil could be controlled or designed with an injection of synthesized chemical additive. The introduced method is applicable in improving the strength and stiffness of loose soils. The new composite material helps enhance the safety of the earth's structure. Appropriate synthesized chemical additive helps in minimizing environmental pollution from the construction industry activities. Using synthesized chemical additives is able to mitigate the liquefaction magnitude. Future research needs to consider polyurethane injection in the subsoil using different methods, for improving loose sandy subsoil stabilization.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

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