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A state-of-the-art review of polymers used in soil stabilization
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Highlights

- The physicochemical properties of polymers used in soil stabilization are discussed.

- The interaction mechanisms between soil and organic- and geo-polymers are reviewed.

- The mechanical properties of polymer-stabilized soils are highlighted.

- The challenges and research gaps of polymer stabilization of soils are identified.

A state-of-the-art review of polymers used in soil stabilization

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Abstract

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1. Introduction

Chemical soil stabilization is the alteration of soil properties to improve the engineering performance of the stabilized soil over its un-stabilized counterpart. The major categories of concern for chemically stabilized soils include mechanical properties – mainly compressive strength and shear strength, permeability, volume stability and durability [1]. Numerous products have traditionally been used for chemical soil stabilization, among which Portland cement and lime are the most widely used backed by a long history and extensive studies. The exploration of new soil stabilizers is motivated by the pursuit of better engineering performance, the demands of various special soil conditions and projects, environmental concerns and cost. Soil stabilization using polymers has attracted considerable attention in the research arena with the aim of providing a more complete understanding of the expected properties of the polymer treated soils and the fundamental mechanisms governing the changes in engineering properties and performance.

In general terms, polymers are large molecules composed of repeating units called monomers. A polymer is usually formed through polymerization of monomers and exhibits physical and chemical properties that are different from the monomers. Both natural and synthetic polymers have reportedly been used to stabilize soils [2-5].

The first time polymers were used to stabilize soils was during World War II, when a water-soluble polymer was introduced to stabilize soils for road and runway construction for military vehicles [6]. Since then, research on polymer-soil interaction has transcended into engineering and agricultural applications [7]. Natural polymers including polysaccharides and synthetic polymers such as polyacrylamides have exhibited promising benefits in agricultural applications by enhancing soil aggregate stability and conserving water in addition to reducing the effects of water and wind erosion as well as harmful vegetation growth [8]. In contrast, the application of polymers in engineering has often been constrained due to their high cost and thereby has been overshadowed by the use of traditional stabilizers, mainly Portland cement and lime. That said, polymers have been successfully used to control dust at construction sites, reduce wind erosion of sand in arid and semiarid areas such as the Middle East, and improve slope stability [3, 7, 9, 10]. In successful applications, polymers have proven to be more environmentally friendly compared to cement and lime in terms of emission of greenhouse gases and the consumption of natural resources and energy. Carbon dioxide emissions due to the production of Portland cement are the second largest contributor (i.e., single industrial emitter) to global greenhouse gas release from human activities, second only to the combustion of fossil fuels [11]. Polymers, on the other hand, do not require such substantial energy consumption and emit much less greenhouse gases. Certain polymers are industrial by-products, which are abundant and would otherwise be treated as wastes. These include lignin, a biopolymer, from pulp and paper industry and fly ash, a precursor of geopolymer,

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generated from coal power plants [12, 13]. Biopolymers like polysaccharides occur naturally and have been widely used in food industry [14]. Synthetic polymers such as polyacrylamide have been used in irrigation for agricultural purposes for decades [8]. These polymers are proven to be environmentally friendly and boost the enthusiasm of designers and contractors to explore their uses in soil stabilization.

This paper provides a state-of-the-art review of the existing research regarding polymers used in soil stabilization. While there are numerous types of polymers, only those that have been used in soil stabilization are discussed. The properties of polymers and their applications in areas other than soil stabilization are beyond the scope of this work. The paper hence specifically discusses the physicochemical properties of the polymers used in soil stabilization, and investigates the likely mechanisms associated with polymer-soil interactions. Further, the paper examines the engineering properties of polymer stabilized soils contained in the current literature research methods and tools and identifies gaps in the current literature as well as the challenges that lie ahead. This set the stage to consider needed research directions.

2. Physicochemical Properties of Polymers

Numerous types of polymers have been investigated as potential reagents for soil stabilization. Considering the complexity of polymer structures and types of polymers available, they are classified, depending on the backbones of the structure and the source, into three categories: geopolymers, biopolymers and synthetic organic polymers. Geopolymers are a group of inorganic polymers that are developed from amorphous aluminosilicates activated by concentrated alkali solutions [15]. Biopolymers are produced from biomass or bacteria and are rich in nature, such as cellulose, lignin and polysaccharides. Synthetic organic polymers are human-made polymers with various main chain and side chain compositions. Commonly used synthetic organic polymers in soil stabilization include polyacrylamide (PAM), polyacrylate, poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc) and their derivatives. The compositions and physicochemical properties of these polymers are significantly different; therefore, they exhibit different interactions with soil minerals, which eventually determine soil stabilization performance.

2.1 Geopolymers

A geopolymer is an inorganic aluminosilicate material synthesized by mixing source materials (i.e., precursors) rich in amorphous silica and alumina with alkali activators. The silica and alumina in the precursors undergo a series of polymerization reactions with alkali polysilicates, yielding polymeric Si-O-Al bonds with Si and Al in IV-fold (tetrahedron) coordination with oxygen [16]. The resulting three dimensional aluminosilicate structures are the poly(sialate) type (-Si-O-Al-O-), the poly(sialate-siloxo) type (-Si-O-Al-O-Si-O-), and the poly(sialate-disiloxo) type (-Si-O-Al-O-Si-O-

1 Si-O-), which are normally amorphous to semi-crystalline [15]. The general empirical
2 formula of geopolymers is as follows:

$$M_n \left\{ -\left(SiO_2\right)_z - AlO_2 \right\}_n \cdot wH_2O$$
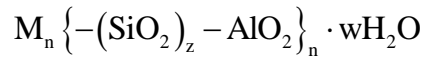
4 Where M is an alkali cation such as Na^+, K^+ or Ca^{2+}, n is the degree of polycondensation
5 and z is the Si/Al molar ratio which typically takes a value of either 1, 2 or 3 [15].
6 However, later studies reveal that z can significantly vary, ranging from <1 up to 300
7 [17, 18]. When $z < 1$, the mixtures set and harden but contain crystalline phases
8 including gibbsite [18]. When $1 < z < 3$, the geopolymer has a three dimensional, cross-
9 linked rigid network with stiff and brittle properties and thus cementitious and ceramic
10 material; while $z > 3$, structure of geopolymer tends to become two dimensional, linear
11 linked with adhesive properties and when $z > 15$, the geopolymer exhibits rubbery
12 properties [17].
13

14 Since geopolymers were introduced, many materials such as kaolinite, metakaolin, fly
15 ash, furnace slag, rice husk ash and red mud have been studied as potential precursors
16 to provide reactive alumina and silica sources [19-22]. Alkaline metal hydroxide
17 solutions, especially NaOH and KOH, together with sodium silicate (i.e., water glass)
18 are most widely used as activators to initiate the geopolymerization. The properties of
19 geopolymers vary greatly depending on the aluminosilicate source, alkali solution
20 concentration as well as the conditions under which the geopolymers are synthesized.
21 Si/Al molar ratio, among all the constituents, is known to have the most significant
22 effect [23, 24]. Significant improvement of properties of geopolymers can be obtained
23 when the Si/Al molar ratio is between 1 and 3, while the Na/Al molar ratio is maintained
24 at unity [15]. Alkali concentration determines the pH of the mixture, affecting the
25 solubility of the precursors as the alumina and silica tend to dissolve under high pH
26 conditions. However, despite the differences caused by the variances between
27 individual components, geopolymers in general exhibit some common physical and
28 chemical properties yet distinct from that of other stabilizers. Due to the unique three
29 dimensional cross-linked, zeolite-like structure from geopolymerization, geopolymers
30 have excellent chemical durability against sea water attack, acid attack, high
31 temperature and fire, frost attack and sulphate attack [25]. However, the resistance of
32 sulphate attack needs to be verified when calcium-containing precursors such as slag
33 are used for geopolymerization or when cement and lime are added as a supplement to
34 the geopolymer mixture because calcium can be easily attacked by sulphate, causing
35 the mixture to be less durable, as is the case for traditional stabilizers like lime and
36 cement.
37

38 **2.2 Biopolymers**

39 Biopolymers or microbial induced polymers have been introduced recently as a new
40 type of soil stabilizers and are actively investigated in soil stabilization. Common

biopolymers that have been studied for soil stabilization and their major physicochemical properties are summarized in Table 1.

Polysaccharides are the most widely used biopolymers across various industries [26]. Different types of polysaccharides, including agar gum, guar gum, gellan gum, beta-glucan and xanthan gum have been used as additives in food and medical applications and are environmentally friendly [14, 27]. They are also used in industrial applications as a flocculant, foam stabilizer, water treatment agent and filtration aid [28]. Further details of the properties of different polysaccharides used in soil improvement as well as their applications are documented in a recent review paper by Chang et al. [28].

Lignins are one of the most abundant organic polymers on earth, only second to cellulose, and it is mainly found in the cell wall of woody tree species [29]. Lignins are readily available as a byproduct of the pulping and papermaking industry and properties vary depending on the plant source and the isolation protocol [12]. Lignosulfonate is the most common byproduct lignin through sulfite pulping and is also the most widely investigated byproduct lignin in soil stabilization. It contains both hydrophilic functional groups including sulphonate, phenylic hydroxyl, and alcoholic hydroxyl and hydrophobic carbon chain [30]. Kraft lignins, also known as sulfate lignins, are extracted from the kraft cooking process. Sulfur-free lignins are also available from the bioethanol industry where a large quantity of lignins are left as a waste material. The lignins derived from bioethanol industry have a higher content of lignin, about 50 - 70%, compared to that from pulping, with a moderate macromolecular size, making it more similar to native lignin [31]. Therefore, scrutiny of the properties of lignins is necessary before stabilizing soils.

Although the properties of different biopolymers vary significantly, generally biopolymers have high specific areas with varying charges and different particle sizes. This characteristic enables them to interact with fine soil particles (i.e., silt and clay) directly through ionic bonds and hydrogen bonds [32]. Biopolymers dehydrate during drying and swell when rehydrated. The elastic properties of biopolymer hydrogels such as tensile strength and stiffness diminish exponentially with increasing water content [33]. However, the viscous swelled biopolymer hydrogels have the ability to coat the surfaces of large particles like sand and fill the pores between sand particles to reduce the permeability drastically [32, 34].

Table 1. Compositions and properties of common biopolymers used in soil stabilization

Category	Type	Compositions and major physicochemical Properties	Reference
Lignin	Kraft lignin	- Rich type diversity	[35]
		- Highly reactive with other chemicals	
	lignosulfonate	- Possess many active functional groups and high solubility	
	Hydrolyzed lignin	- Poor water solubility	
		- low chemical activity	
	New lignin derivatives	- Properties vary with the used pulp making methods	
Polysaccharides	Xanthan gum	- $C_{35}H_{49}O_{29}$ (monomer)	[36]
		- Pseudo plasticity	
		- Stable under a wide range of temperature and pH	
		- Highly viscous, hydrophilic colloid	
		- Anionic polysaccharide	
	Guar gum	- Rapidly hydrates in water, forming highly viscous solutions	[36]
		- Non-ionic, minimally affected by ionic strength or pH	
		- Degrade at extreme pH and temperature	
	Agar gum	- Consists of agarose and agaropectin, agarose is a firmly gelling complex sugar, while agaropectin is a weakly gelling charged polymer	[37]
		- Hydrophilic colloid	
		- Dissolve in boiling water at 85 °C and forms a gel when cooled to 32 - 43 °C	
		- A neutral polymer chain with a limited reactivity to other materials	
		- Biodegradation is minimized, but sensitive to polymeric additives	
	Gellan gum	- High molecular weight polysaccharide made of four molecules	[38]
		- Linear anionic heteropolysaccharide	

Category	Type	Compositions and major physicochemical Properties	Reference
	Sodium alginate	- Thermo-gelation behavior - Dissolve slowly in water, forming smooth-pouring solutions - Form gels by reaction with calcium and sodium salts	[36]
	Beta-glucan	- Various natural formations - Molecular weight 250 - 3000 kDa - Electrostatically neutral for natural beta-glucan, but can exhibit charges when modified	[4, 39]
New biopolymers	*R. tropici* EPS, *L. mesenteroides* EPS, Astragalus, Persian gum, Casein, Sodium caseinate	- Compositions and properties not fully investigated for soil stabilization	[40-43]

2.3 Synthetic Organic Polymers

Many synthetic organic polymers have been used in soil stabilization in the past decades, including polyacrylamide (PAM), polyacrylates, poly(vinyl alcohol) (PVA), poly(vinyl acetate) (PVAc), polyurethane, aldehyde, propylene, etc. Among all the synthetic organic polymers, the most commonly used polymers and their properties are listed in Table 2.

Polyacrylamide (PAM) and its Derivatives

PAM and its derivatives are the most widely used synthetic polymers in soil stabilization. PAM-based polymers were originally used in agriculture to control and manage erosion and infiltration. They were later deployed for uses beyond agriculture control, including construction site erosion, use in storm water runoff ponds to accelerate water clarification, soil stabilization and dust prevention in helicopter-landing zones, and various other high-traffic military situations [7]. It is noteworthy that cationic or nonionic PAMs are often toxic, while anionic PAMs are usually nontoxic to plants, animals and humans [8]. Therefore, most of the PAMs that have been used in soil stabilization are anionic. However, cationic PAMs were also reported to be used for stabilizing soils [44]. Table 2 also provides information on different properties of PAMs such as surface charge, molecular weight, viscosity and pH, which affect their interactions with soils.

Polyacrylate and its Derivatives

Polyacrylates, also known as polyacrylics or acrylate polymers, are a group of acrylate- or acrylic-based polymers. The compositions and properties of polyacrylates vary considerably, depending on the functional groups that are introduced to the basic acrylic acid structure, e.g. methyl acrylate, ethyl acrylate, butyl acrylates and isobutyl acrylate [45]. Poly(acrylic acid) among others is the simplest acrylate polymers.

Polyacrylates including acrylic acid and acrylic esters are flammable, volatile, mildly toxic, and colorless liquids, which can easily polymerize. Polymers of acrylic acid and its sodium salts are used as flocculants and dispersants. Acrylic esters are used exclusively for production of polymers and these polymers are used mainly for coatings, paints, adhesives and binders [45].

Poly(vinyl acetate) and Poly(vinyl alcohol) Based Polymers

Polyvinyl acetate (PVAc) is an aliphatic synthetic polymer with a high cold flow and can be easily polymerized. Therefore, PVAc is widely used in emulsion products, paints, adhesives, and textile finishing operations [46]. This adhesive property also makes it

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possible for PVAc to bind the soil particles together. Several studies have shown that they can improve the strength and reduce the swell-shrinkage properties of expansive clays [47-49].

Polyvinyl alcohol, also known as PVA, is a water-soluble synthetic polymer. It can be produced from polyvinyl acetate due to the sensitivity of the ester groups in PVAc. Different from PVAc, PVA is hydrophilic due to the presence of the hydroxyl groups. It is highly polar and can bond with hydroxyl groups in soil minerals through hydrogen bonding. Researches show that addition of PVA significantly improves the properties of soft clays [50, 51].

Additional Synthetic Polymers

Besides the polymers discussed previously, other synthetic polymers have also been investigated. Properties of these polymers are not well understood from the standpoint of soil stabilization. Polymers with different functional groups or compounds such as ester [52, 53], propylene [54], urethane [55, 56], carboxylic [50] and aldehyde [57] have been studied in the laboratory to evaluate their interactions with different types of soils. Other polymers including methylene diphenyl diisocyanate [58-60], resins [61-63], and CBR PLUS [64] have also been studied. For these new polymers, the lack of sufficient research to establish an understanding of stabilization mechanisms as well as to establish a mix or composite design approach has led to the addition of these polymers to soils at a wide range of dosages, from as low as 1% to as high as 45% [50, 65-67]. Some of the polymers have been reported to have potential to work as a soil stabilizer while the others fail to show significant improvement under certain circumstances [68-70].

Table 2. Summary of the physicochemical properties of major synthetic organic polymers

Type of Polymer	Composition and Synthesis Method	Physicochemical Properties	References
Polyacrylamide (PAM) $[CH_2=CHCONH_2]_n$	- Synthesized from acrylamide sub-units with a linear-chained or cross-linked conformation. - Anionic PAMs are produced if the amide functional groups ($-NH_2$) in part of the acrylamide subunits are released or substituted during polymerization. - Can also be synthesized as neutral, cationic or amphoteric.	- Cross-linked PAMs are water absorbent but are not water soluble, while the linear-chained PAMs can dissolve in water easily and once it dissolves, it stays linear, although it may coil or curled to varying degree. - The linear-chained PAMs are usually employed in soil stabilization. - The amount of the surface charge of PAMs can be made to vary through hydrolysis. - Molecular weight varies depending on the number of component monomers. Can have $\geq 2 \times 10^7$ g/mol for high molecular weight anionic PAM, or as low as 3.5×10^3 g/mol for a short-chained PAM molecule. - Becomes more viscous as molecular weight increases. - Viscosity increases with pH, especially at > pH 10.	[71] [72] [7]
Polyacrylates	- Composed of monomers of acrylic acid and esters ($CH_2=CHCOOR$). - Different types can be formed by replacing the H on the vinyl group ($-CH=CH_2$) and/or the H of the carboxyl group ($-COOH$) with other functional groups. - Have various compositions depending on the monomers.	- Monomers such as acrylic acid and acrylic esters are colorless liquids. - Highly reactive due to the vinyl and carboxylic groups. - Acrylic acid is hydrophilic and also miscible with alcohols and esters. - Acrylates can easily be polymerized with different functional groups, forming different polymers. - Adhesive and viscous.	[45]

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Type of Polymer	Composition and Synthesis Method	Physicochemical Properties	References
Poly(vinyl acetate) (PVAc) $[CH_2=CHOOCCH_3]_n$	- Synthesized from vinyl acetate monomer - Equal quantities of vinyl acetate and water stirred together with emulsifiers	- Molecular weight, charge and particle size vary depending on polymerization process. - Have atactic and amorphous structures. - Insoluble in water, but can be dissolved in benzene, acetone etc. - Have high cold flow, glass transition temperature of 28°C and most of the time is even lower. - Good adhesion. - Can be easily polymerized in bulk, solution, emulsion and suspension.	[46]
Poly(vinyl alcohol) (PVA) $[CH_2=CH(OH)]_n$	- Prepared by alcoholysis of a poly(vinyl ester) and in practice poly(vinyl acetate) is used	- Water soluble. - Have atactic but crystalline structures. - Molecular weight is lower than PVAc from which it is made. - Highly polar.	[46]

1

3. Polymer-Soil Interaction

3.1 Mechanisms

Inorganic: Geopolymers

Geopolymers are inorganic with different Si-Al backbone structures. Therefore, the mechanisms of geopolymers interacting with soil minerals are significantly different from those of organic polymers. Geopolymerization is the main mechanism for geopolymer stabilization. A series of reactions of the amorphous alumina and silica under alkali conditions result in cementitious materials which bind the soil particles and change the properties of the candidate soil, both the structure and the mineralogy.

The geopolymerization process has three phases: dissolution of source alumina and silica, gelation and reorientation of Si- and Al-complexes, and polycondensation [73]. Figure 1 presents a simplified reaction mechanism of this process.
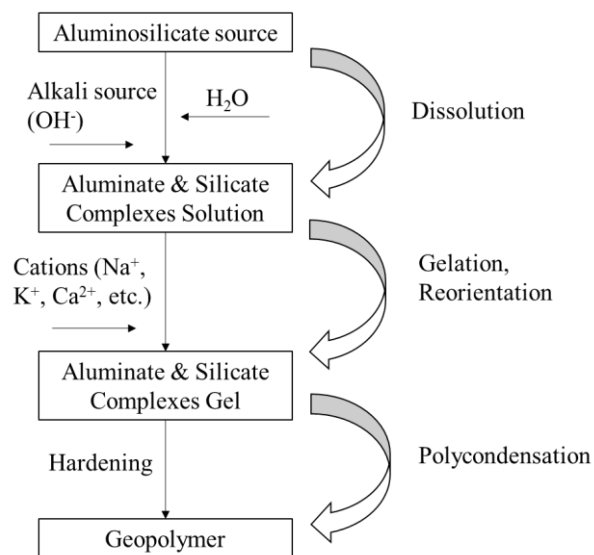

Figure 1. Schematic diagram of geopolymerization. Revised after Duxson et al. [73].

The mechanism of geopolymerization was first investigated by studying the behaviors of low-calcium materials, mainly metakaolin and Class F fly ash under high alkaline conditions [23, 24, 74-77]. Reactions start immediately when the precursor (Al and Si source) comes into contact with the alkali activator [78]. The aluminosilicate minerals dissolve in the highly concentrated alkaline solution with silicate being IV-coordinated upon dissolution while V- and VI-coordinated Al are converted to IV-coordination [79]. The dissolved small species of alumina and silica (tetrahedra coordination) along with the silicate initially supplied by the activating solution begin to form aluminosilicate oligomers by sharing corner oxygen [77]. When the solution reaches saturation, an aluminosilicate gel starts to form, diffuse, migrate, reorganize and eventually reach

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equilibria and precipitate [75, 80]. During this process, the cations in the solution fill in the cavities to balance the negative charge of Al^{3+} in the tetrahedron coordination [15]. The geopolymer sets at ambient temperatures and thus has an amorphous to semi-crystalline structure [15]. Setting can be almost instantaneous, or can take several days, depending on the mix design and the curing conditions [77]. This mechanism between low-calcium precursors and alkaline activators is now more frequently referred to as the formation of N-A-S-H (sodium aluminosilicate hydrate) gel, analogous to C-S-H (calcium silicate hydrate), the cementitious product of Portland cement [75]. This term has been widely accepted within the field since it was first introduced in 2005 by Fernandez-Jimenez and Palomo [81].

Compared to N-A-S-H gel, another model of (N, C)-A-S-H was proposed after calcium -based materials were used for geopolymerization. (N, C)-A-S-H gel model involves more complicated reactions than the N-A-S-H gel model by the introduction of calcium into the geopolymer system and is currently less well understood. It is believed that (N, C)-A-S-H system consists of multi phases: C-S-H gel and N-A-S-H gel [20, 82-85]. The source of calcium could be from the use of calcium-containing precursor materials such as slag and Class C fly ash, from calcium silicate activators, or from addition of Portland cement, lime and calcium carbide [86-89]. The phases of C-S-H and N-A-S-H in the calcium-based geopolymer system are believed to coexist with each phase forming separately at varying rates [20, 87]. The coexistence of both C-S-H and N-A-S-H gels in the geopolymer system both contribute to the strength development of geopolymers [90].

The chemical reactions involved during geopolymerization are rather complicated. It should also be noted that most of the current literature focusing on geopolymers are actually about "geopolymer concrete" or "geopolymer mortar". As this paper focuses on the interactions between geopolymer and soils, only selected key literature are discussed to provide the fundamental knowledge of geopolymerization for further understanding of geopolymer-soil interactions.

The application of geopolymers in soil stabilization is investigated recently when Cristelo et al. [91] used alkaline activated fly ash in grouting technique in place of cement and achieved a soil strength of 16.7 MPa in the laboratory and 26.4 MPa in field application after being cured for 90 days . The improvement of soil strength is attributed to the cementitious geopolymerization products (eg. N-A-S-H or (N, C)-A-S-H gel, depending on the source materials), which bind the surrounding soil particles during gelation and eventually harden into a denser, stronger and chemically stable matrix [91]. Based on this mechanism, different aluminosilicate materials, mainly metakaolin [92, 93], Class C fly ash [94-96], Class F fly ash [13, 93, 97, 98] and blast furnace slag [97, 99] have been studied for soil stabilization. New silica and alumina source materials such as palm fuel ash are also being investigated for feasibility of geopolymer

stabilization [100, 101]. However, the mechanism between soil-geopolymer interaction should be investigated further. Although geopolymer as a material is already quite complicated, the application of geopolymers to soil gives rise to additional complexity. Geopolymerization is sensitive to many factors such as the alkaline concentration, silica and alumina source and moisture content, all of which could be changed due to the presence of soil, especially when the proportion of geopolymer in the geopolymer-soil system is relatively small. A high dosage of geopolymer for soil stabilization would not be cost effective. Therefore, the quality control of geopolymerization in the geopolymer-soil system will be much difficult than in a pure geopolymer system. Besides the effects of soil acting on the geopolymers, the components in the geopolymer could also change the behaviors of the soil due to the high alkaline environment. For example, soils are Al and Si rich materials, and the alumina and silica can dissolve in an alkali solution, resulting in the change of soil properties. Therefore, when geopolymer is mixed with soils, reactions such as cation exchange on soil mineral surfaces or in double layer should be expected, especially when calcium-rich precursors (e.g., Class C-Fly ash) or a KOH activator are chosen. This could also contribute to the change of soil properties, including strength improvement. In addition, one can expect that soils with varying mineralogy could behave completely different even when treated with the same geopolymer. Investigating these issues is essential for a thorough understanding of the mechanisms of geopolymer stabilization. However, studies on this aspect of geopolymer stabilization is very limited.

### *Organic: Biopolymers and Synthesized Polymers*

For organic polymers, either biopolymers or synthesized organic polymers, the change in functional groups from one monomer to another results in polymers with different conformations and properties. Although it is virtually impossible to figure out how each functional group interacts with soil minerals and how each polymer performs differently from each other, the interaction mechanisms between organic polymers and soil minerals follow some general principles due to the physicochemical nature of polymers.

Electrostatic interaction is one major mechanism for polymer stabilization, especially between cationic polymers (polycations) and clays as the surfaces of clay minerals are generally negatively charged. The polycations adsorb easily onto the surfaces and edges of clay minerals, modify the water sorption near the clay surface and result in large, stable flocculated particles [2].

In neutral polymers, the adsorption of uncharged polymers by clays is largely entropy-driven. An increase in entropy occurs due to a combination of adsorption of the polymer on the clay colloidal surface and concomitant desorption of water from the clay surface, as shown in Figure 2, adapted from Theng [102]. This is especially true for high

molecular weight polymers. Theng [102] explains that surface conformation is one of contiguous sequences of adsorbed segments or "trains", which alternate with three-dimensional "loops" that extend away from the surface. The polymer then terminates, according to Theng [102], in two free-dangling tails (see Figure 2). One would expect that the desorption of water from the clay surface that accompanies the polymer sorption would break the sequential hydrogen bonding of water molecules extending from the clay surface, thus increasing entropy. Theng [102] continues to explain that total energy of adsorption can be very large because of so many adsorbed segments. Consequently, the rate of desorption is low, and the process may be considered to generally be irreversible because of the low probability of all trains simultaneously detaching.
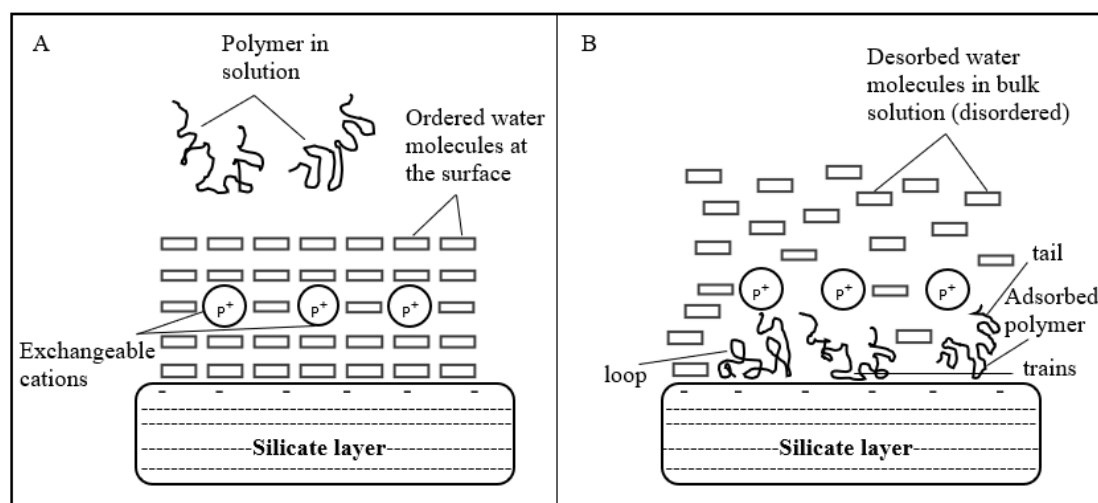
Figure 2. Diagram illustrating the adsorption of neutral polymer molecules onto a clay surface and change in conformation of polymers and the desorption of water molecules. (A) Before adsorption; (B) After adsorption. Adapted from Theng [102].

Anionic polymers (polyanions) are effective flocculants, especially in the presence of polyvalent cations [103]. Because only a few segments of the polymer chain are involved in adsorption, the majority are associated with long loops and tails. This leaves polyanions to develop a large "grappling distance" facilitating the interparticle bridging effect. The interactions between anionic polymers and clay minerals depend on the ambient pH. Theng [102] explains that under acidic conditions, anionic polymers can intercalate into the clay interlayers and behave similarly to neutral polymers. Here, electrostatic interaction could take place between anionic groups and aluminum exposed at the edges of the clay minerals, which under acid conditions acquires a positive charge. Under alkaline conditions, anionic polymers bind with clay minerals primarily through cation bridging, either displaced from the interlayer or externally supplied. This is promoted by the large "grappling distance" due to the electrostatic repulsion. The cationic bridging process results in an increase in entropy initially during complexation but ultimately results in strong clay mineral-polymer complexes.

The mechanisms between organic polymers and coarse grains such as sands are less investigated and less understood compared to clay. Different from clay minerals, the surfaces of large grains of sands are usually neutral. Mohamed [9] believes the mechanisms between polymers and sand particles are analogous to that of asphalt emulsion. According to Mohamed [9], three types of structural changes after introduction of polymer to sand were observed: (1) the covering of the sand particles with a thin film; (2) the formation of polymer ties connecting neighboring sand particles which are not in direct contact; and (3) the development of adhesion between neighboring sand particles in contact. Mohamed [9] attributes the improvement of properties including hydraulic conductivity and mechanical strength to these three structural changes, which is consistent with other studies [34, 104, 105]. Liu et al. [55, 56, 106, 107] believe that the sand reinforcement mechanisms of polymer includes filling, chemical reaction, and enwrapping, after investigating the interactions between polyurethane and sand,. The authors continue to explain that the polymer solution fills up the voids and adsorbs ions on the surface of sand particles to form physicochemical bonds between molecules. The elastic and viscous membrane is formed through the bands of long-chain macromolecules to interlink the sand particles. The hydrogel, formed by the polymer and water, absorbed on the surface of sand grains via hydrogen and inter-molecular force, and the hydrogel gradually turned to a thin and hardened polymer membrane with the evaporation of water, which resulted in an improvement in elasticity, flexibility, and strength [108].

3.2 Factors Influencing Polymer-soil Stabilization

Geopolymers

The efficacy of geopolymers in soil stabilization significantly rely on both the inherent properties of the geopolymer constituents (i.e., precursor and activator) and ambient conditions such as temperature.

The structures and mineralogy of source alumina and silica are of vital importance in affecting the properties of the geopolymer. Among natural Al-Si minerals, framework silicates, compared to chain, sheet and ring structures, show a higher extent of dissolution in alkaline solution and generally demonstrate better engineering properties after polymerization [80]. For the same reason, many waste materials or industrial byproducts such as fly ash, metakaolin, slag and rice husk are considered as a good source material to produce geopolymers. The higher content of amorphous silica and alumina in these materials resulting from high-temperature burning makes these by-product materials dissolve in alkaline solutions easily [21, 23, 99].

The activators used in geopolymer production are mainly sodium or potassium hydroxide with sodium silicate. Xu and Van Deventer [80] claim that the use of KOH

instead of NaOH favors the geopolymerization after testing fifteen natural Al-Si minerals. However, potassium hydroxide has a higher cost than sodium hydroxide, thus sodium based alkali solution is recommended [109]. As a matter of fact, most of the literature used sodium hydroxide as alkaline source in soil stabilization [13, 91, 93, 94, 99, 101, 110, 111]. The ratios of alkali to silicates (e.g. $NaOH/Na_2SiO_3$) within the activator, of Si/Al in the precursor, of precursor content to soil, and alkali concentration and content simultaneously affect the stabilization result [91, 111]. A higher precursor and alkali content and higher alkali concentration normally impact geopolymer-stabilized soil positively since more silica and alumina are available for dissolution, which contributes substantially to the improvement of soil properties. However, no consensus has been achieved on the optimum amount of precursor content, alkali content and concentration. This is understandable as too many factors contribute to the performance of geopolymer stabilization and the mechanisms are not fully understood.

The strength of the geopolymers is also affected by the curing temperature which eventually influence the stabilization efficacy. Geopolymerization can occur below 100 °C. A previous study showed that metakaolin-based geopolymers cured under higher temperatures (60 - 80 °C) acquired higher early strength but lower long-term strength compared to those cured at lower temperatures (10 - 40 °C) [112]. The author believes high temperature leads to rapid formation of large pores and the increase of cumulative pore volume, which results in a weaker final geopolymer material [112]. In addition, different precursors also require different curing temperatures to initiate the reactions. For example, alkali activation of low calcium contents such as metakaolin or Class F fly ash requires an elevated temperature and high alkalinity compared with activation of high calcium components [90].

Biopolymers and Synthetic Organic Polymers

Composition, conformation, molecular weight, molecule size, pH, concentration and charge density are the major factors impacting the functioning of polymers. As for soils, particle size distribution, water content and mineralogy dictate the efficacy of stabilization with polymers.

Varying the chemical composition of monomers results in polymers with different properties such as solubility, hydrophilicity and hydrophobicity, and viscosity. These have significant impact on their suitability for soil stabilization. Molecular weight and molecule size of the polymers play a key role in defining the nature of interactions with various soils and soil minerals. Organic polymers usually have a broad range of molecular weight. For example, PAM has a molecular weight ranging from 3.5×10^3 to 2×10^7 g/mol [71, 72]. The increase of molecular weight gives rise to a sharp increase of viscosity and significant reduction in solubility. Moen and Richardson [113] found that small-sized polymers distribute more evenly in the microaggregate fraction of soils

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because of their greater ability to penetrate the fine pores. Richardson et al. [114] also found that high molecular weight polymers may maximize soil-polymer interactions; however, the effectiveness could be affected by limited polymer penetration of the soil surface and failure to attain uniform aggregation adsorption. On the other hand, they found that small-sized polymers could create a more homogeneous soil stabilizing polymer network.

Polymer conformation also impacts their effectiveness. During polymerization, chains of monomers interact with each other and result in different chain conformations: linear, branched or cross-linked chains. Linear chains of polymers are more effectively adsorbed onto soil particles if a certain critical molecular weight is exceeded. This is because the long chains could tend to extend and are adsorbed over larger areas of the particle's surface compared to branched and cross-linked chains [114]. The length of the chains also affects the interactions among soil particles and polymers with a long, straight-chained and widely spaced structure bonding groups tend to create large stable aggregates; the short-chained are inclined to form small aggregates which could reduce plasticity in clay [114].

The structures and mineralogy of soils especially clays also impact the effectiveness of polymer-soil stabilization by influencing the adsorption of polymers onto clay surfaces. Theng [102] explains that the uptake of the polymer decreases in "condensed" systems such as kaolinite, where bonding among repeating structures is hydrogen bonding; in illite, where potassium is the interlayer cation forming a unique dative, covalent bond; and montmorillonite saturated with, for example, calcium, divalent cations. In such cases, the ability of large polymer chains to enter interstitial space among repeating clay units is too restricted to allow migration and configurational changes.

Ambient solution pH and concentration affects the surface charge and conformation of charged polymers and therefore influence polymer adsorption onto soil particles [2]. Higher concentration of the polymer solutions enables sufficient active functional and structural groups in the polymer to be available for interaction with soil particles and therefore could increase the efficiency of polymer stabilization. However, the increase of concentration normally causes increased viscosity of pore fluid and could make penetration into the soil particles difficult. A balance between the concentration and the consequent viscosity should be found to ensure the proper application of polymers.

Moisture is another major factor that can impact the efficacy of polymer-soil stabilization in both positive and negative ways. On one hand, moisture is needed at the initial stage of the polymer stabilization to help the polymers distribute evenly into the soil particles and contributed to the bonding between polymer molecules and soil minerals. In fact, some level of solubility of the polymer in water is required for effective distribution (mixing). Previously-formed bonds are strengthened as a result of

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water evaporation [115]. Santoni et al. [116] also conclude that moisture evaporation or drying is required for strength improvement of nontraditionally stabilized soils after investigating six different polymers (compositions not revealed) and other nontraditional stabilizers. However, excessive moisture can weaken the polymer stabilized soils similar to the effects observed in cement and lime stabilized soils. Most of the research in the literature comparing dry and wet polymer-stabilized samples have shown varying degrees of strength loss with increase in moisture content of the soils [9, 34, 116-119]. The key to successful polymer-soil interaction from mixing and distribution to the durability of the final product may be the kinetics of the polymer's reaction with water during transient wetting and drying periods that affect the pavement.

4. Engineering Properties of Polymer-Stabilized Soils

The main goals of soil stabilization are to improve mechanical properties, control permeability, resolve volumetric instability and enhance durability. The major properties and tests investigated in the literature for evaluating polymer stabilization quality are summarized in Figure 3.
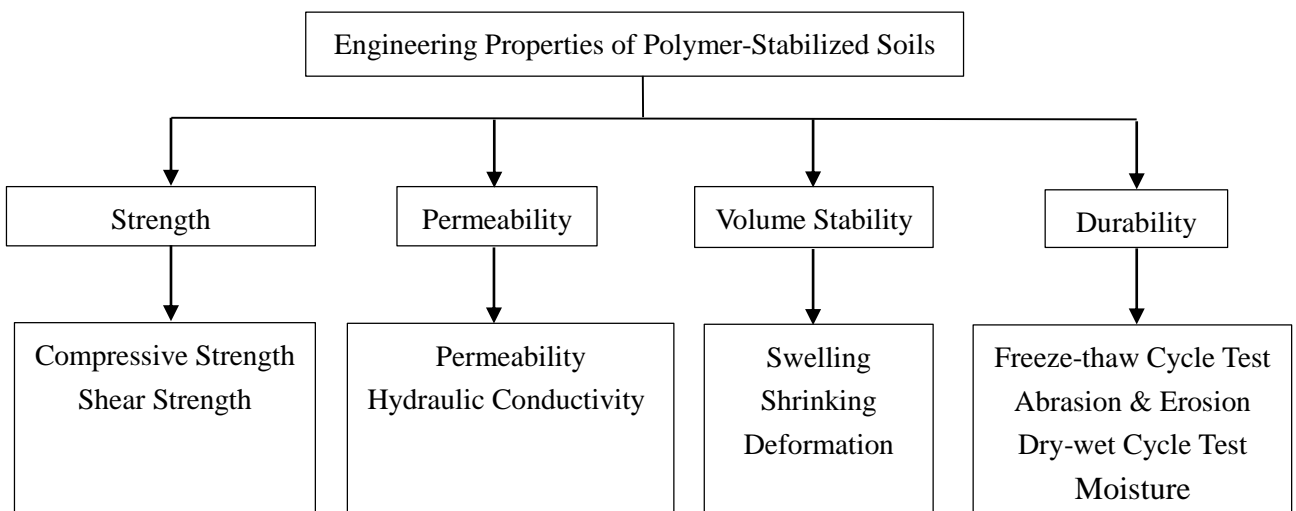

Figure 3. Tests for evaluating the effectiveness of polymer-stabilized soils.

4.1 Soil Strengthening
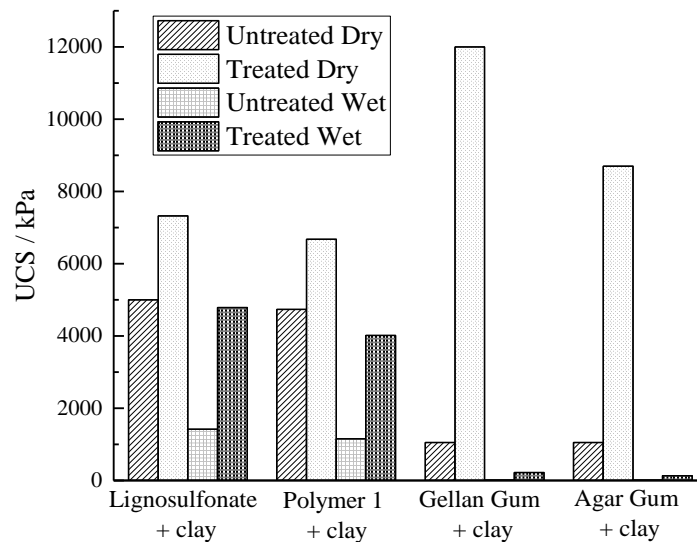
Compressive Strength

Extensive practical testing has been performed to investigate the strength improvement of both the coarse (e.g., sands) and fine soils (i.e., silts and clays) when stabilized with different polymers. Despite the differences in basic properties of the major organic polymers that have been investigated, most of the polymer-stabilized soils exhibit immediate strength improvement. Some polymers that show a significant increase of the unconfined compressive strength of different soils are shown in Figure 4. The value

of compressive strength varies significantly in different scenarios and thus the relative strength increases compared to each control sample (untreated soil) are also presented in Figure 4. One can see that polymers can increase the strength of weak soils by 16 % [120] up to 1000 % [38, 121]. Many other researchers reported an increase of soil strength by using various polymers. Tables 3 and 4 summarize the compression test results for soils treated with synthetic organic polymers and biopolymers, respectively.
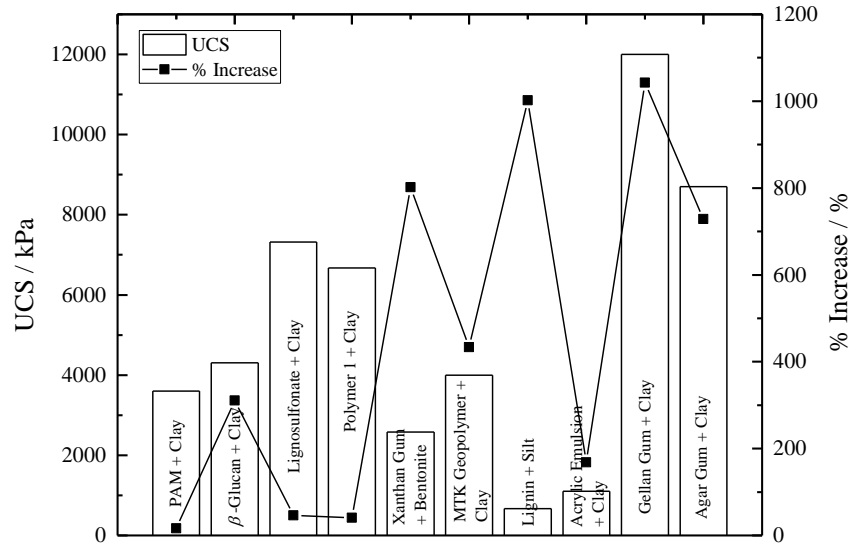
Figure 4. Unconfined compressive strength of soils stabilized by different polymers after 28 days and the percentage increase versus control samples. Note: the figure was created with data derived from [4, 11, 38, 92, 117, 120-122].

Figure 5. Comparison of unconfined compressive strength of polymer stabilized clay soils in dry and wet conditions after 28 days. Note: the figure was created with data derived from [38, 117].

However, it should be noted that most of the compressive strengths reported in the literature are tested in the dry state where moisture in the samples is minimized, which

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is not representative of the actual state of soils in the field. For example, clay normally has a much higher compressive strength when dried than that of a wet condition. Selected literature on polymer-treated clay with a dry and wet state comparison is presented in Figure 5.

Tingle and Santoni [117] tested soils treated with multiple polymers and the result revealed a significant drop in strength under wet conditions. However, the strength improvement relative to untreated soil due to polymer addition was still much higher in wet conditions than that of dry conditions for these polymers. Chang et. al. [38] observed substantial strength loss upon wetting when studying biopolymer treated clays. As shown in Figure 5, even though the strength of gellan gum treated clay was as high as 12 MPa in dry state, it dropped to 220 kPa after wetting. Similarly, a drop in strength in the mount of 8 MPa was recorded for agar gum treated clay under wet conditions. Therefore, more attention should be paid to the strength of polymers treated soils under wet conditions, instead of only dry compressive strength, which may overestimate the strength of some soils and neglect the possible effects of moisture on polymers. Once again, these data do not address how quickly the polymer-soil bonding mechanism deteriorates as moisture enters the stabilized soil and how quickly the polymer-soil system can release the moisture during a drying period. Finally, does the polymer-soil system recover all or part of its original, pre-wetting, strength? A systematic wetting and drying test that mimics field conditions is needed.

For geopolymer stabilized soils, the unconfined compressive strength was reported to significantly improve, but the extent of this improvement varies greatly depending on the geopolymer compositions and dosages as well as soil types, as shown in Table 5. Two categories of geopolymers, calcium free or low calcium based geopolymers, mainly Class F fly ash and metakaolin, and calcium containing geopolymers such as slag, are currently being used in soil stabilization. Both categories of geopolymers are effective in improving soil strength. Cristelo et al. [91] reported a UCS of 11.4 MPa of sandy clays treated with Class F fly ash based geopolymers activated by sodium hydroxide and sodium silicate. This combination has been studied by other researchers since then and also showed effectiveness in stabilizing silty and sandy soils [111, 123]. Zhang et al. [92, 110] used metakaolin instead of fly ash as the precursor to stabilize the clay soils and a strength improvement of up to 4 MPa was recorded. However, smaller strength values were also reported when using a similar metakaolin-based geopolymer to stabilize clay soils with high plasticity [93]. Calcium-containing geopolymers were also investigated. Phummiphan et al. [94] stabilized silty clay with Class C fly ash and strength of the treated soil was significantly improved. Yu et al. [124] used slag based geopolymer to treat kaolin and a strength value of 2.5 MPa was recorded after 7 days of curing [124]. Besides the precursors, the effects of activator concentrations on stabilization effectiveness were also being investigated. A high alkaline concentration is generally preferred for geopolymer stabilization since more

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silica and alumina can be dissolved under such conditions; however, there seems to be a limit to the alkali concentration, beyond which the improvement of soil strength becomes less significant [91].

The current research also starts to explore new materials as potential precursors and activators for geopolymer stabilization. The most common combination is fly ash with slag [99, 125-127]. Other materials such as palm fuel ash, volcanic ash and rice husk ash were also reported as aluminosilicate source. Lime, carbon carbide residue and cement were also studied as potential activators [101, 111, 125, 128, 129]. For these new combinations, the unconfined compression test is nearly the only test that has been carried out. Therefore, more tests are necessary to fully evaluate the effectiveness of these new geopolymers.

Synergistic effects between polymers and traditional stabilizers have been recently investigated. Ayeldeen and Kitazume added polypropylene fibers and liquids to cement stabilized soft kaolin clay and a remarkable strength improvement was observed [54]. The Strength of a cement-kaolin mixture reached a peak with the addition of 0.5% polymer fiber and was sensitive to the amount of liquid polymer added [54]. Bulanov et al. modified cement treated clay with polycarboxylate ether with the result that the compressive strength increased by up to 102% [130]. However, the mechanisms of polymer and cement stabilization are quite different and the effects of each component on different soils and in combination are not well understood, making this a fertile area for further research.

Shear Strength

Standard direct shear test and triaxial shear test are also frequently used to evaluate the efficacy of polymer stabilization. Many previous studies have confirmed that polymers can improve the shear strength of soils. Indraratna et al. [131] used lignosulfonate to treat sands and silts, immediate improvements of shear strength were observed with the addition of only 1.2% for silty sand and 2% for sandy silts [132]. Chang et al. [34] added 0.5 - 5% gellan gum to sandy soils and the peak shear strength was significantly increased. Also, the cohesion and friction angles of the treated sand were also noticeably improved, which according to the authors is due to the binding effects of the gellan gum hydrogels. The viscous biopolymer provides interparticle cohesion that strengthens with condensation and eventually binds particles into agglomerates through interparticle connections and interparticle bridging [34]. The significant improvement of cohesion was also confirmed in organic peat soil, kaolinite, bentonite [11, 133], and sand [134] when treated with xanthan gum. Further details on the improvement of shear strength, cohesion and friction angle of different soils using various biopolymers can be found in a recent review paper by Chang et al. [28]. Soils treated with synthesized

1　organic polymers also showed such an improvement [135-137]. However, shear

2　strength tests on geopolymer-treated soils are rarely addressed.

Table 3. Summary of the compressive strength of soils treated with synthetic organic polymers

Reference	Polymer Type	Polymer Dosage	Soil Type	Compressive Strength
[138]	Acrylic	2%	Silty clay	2.82-3.57 MPa (7d)
[9]	Styrene-acrylic / Vinyl-acrylic emulsions	0.5, 1, 1.5, 2, 3, 5%	SP	0.8-10.2 MPa (7d)
[139]	Acrylic-acrylamide copolymer	0.5, 1% + 5% calcium carbide	Clay	434.4 kPa, 468.9kPa
[140]	Acrylate emulsion	0.25, 0.5, 1, 2%	GM-GC	2-3 MPa (7d); 2-3.8 MPa (28d)
[141, 142]	Polymer emulsion; Emulsion + Sulfonated oil	1, 2, 3, 4, 5x recommended dosage	CL	2.4-4.8 MPa (28d)
			CH	4.8-7 MPa (28d)
			Sandy Gravel	0.2-2.5 MPa (28d)
[143, 144]	PAM	0.002%	GM	7.7 MPa
			SC	7.9 MPa
			GC	5.9 MPa
[50, 145]	PVA	0.1, 0.3, 0.5, 1, 1.5%	CH	Dense: 710.1 kPa Loose: 116.8kPa
[146]	Acrylic polymer	2, 3, 4, 5%	CH	868.88-898.39 kPa (7d);
			MH	3199.79-3901.47 kPa (28d)
[147]	Acrylic copolymer + ionic stabilizer	0.25, 0.375, 0.5% P + 0.5, 0.75, 1% Ionic	CI (IS1498)	1.7-7.0 MPa (>7d)
[148]	Styrene acrylic emulsion	10, 15, 20, 22.5, 30, 35%	SP	6 MPa
[149]	PAM	0.1, 0.2, 0.4, 0.6 g/L	CH	96.87-138.34 kPa (1-14d)
	PAM + Ground rubber	0.2% PAM + 5, 10, 20, 30% GR	CH	106.18-211.09 kPa (7d)
[44]	Cationic PAM	2, 8, 16 g/L	Fine-grained soil	280-460 kPa (7-28d)
[150]	Acrylate polymer	0.3, 0.6, 0.69, 1.2, 1.5%	Saline soil	1085-1561 kPa (7d); 1453-1930 kPa (28d)

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Reference	Polymer Type	Polymer Dosage	Soil Type	Compressive Strength
[49]	PVAc	1.5, 3.75, 5%	CH	900-1300 kPa
[115]	Urea / Phenol formaldehyde resins	3, 4, 5%	SP, ML, CH, MH-CH	0.05-1.7 MPa (7d); 0.3-3.4 MPa (28d)
[68]	Polybutadiene	1-5, 10%	CL, CH	78.4-117.6 kPa (7d); 49-166.6 kPa (28d)
[53]	Acetic-ethylene-ester	5, 10, 20, 30%	Clay	180-245 kPa (1-3d)
[151-154]	Polypropylene	3, 5, 6, 10, 15%	Swelling clay	90-189 kPa
[155]	Polyethylene	4%	Laterite soil	510-831 kPa
[118]	Epoxy resin	6, 7, 8%	Saline soil	419-897 kPa
[52]	Polyester	10, 20, 30%	SP	10-45 MPa (1-28d)
[156]	SS 299	3, 6, 9,12, 15%	MH	221-377 kPa (7d); 224-385 kPa (28d);
[59, 60]	Methylene Diphenyl Diisocyanate	5, 10, 15%	SP	700-4700 kPa
		10% polymer + 10% water	CH	1.50-3.42 MPa (7d)
[61]	Epoxy resin	1, 2, 3, 4, 5%	Sand	2-10 MPa
[51]	Polyvinyl chloride; polyethylene	3, 6%	Clay	600-2700 kPa
[157]	TS-SS liquid polymer	0.25, 0.5, 1%	Crushed limestone + sulphate	4619 kPa
[158]	HPAM	2%	GM-GC	1700 kPa (7d) 3700 kPa (28d)
	TPAM			1800 kPa (7d) 3600 kPa (28d)

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2

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Table 4. Summary of the compressive strength of soils treated with biopolymers

Reference	Polymer Type	Polymer Dosage	Soil Type	Compressive Strength
[4]	Glucan	0.05, 2.46, 4.92 g/kg	Residual clay	1- 4.4 MPa (28d)
[34]	Gellan gum	0.5, 1, 1.5, 2, 5%	SP	130.2-434.6 kPa (28d)
[42]	Xanthan gum	0.5, 1, 1.5, 2, 3%	CL	470.52-569.55 kPa (7d); 612.74-823.19 kPa (28d)
[159]	Casein and sodium caseinate	0.5, 1, 2, 3, 5%	Dune sand	450-1700 kPa (14d)
[160]	Sodium alginate	1, 2, 4% of OMC	CH	830 kPa
		2, 4, 6% of OMC	ML	390 kPa
[161]	Xanthan gum	0.5, 1, 1.5%	Laterite soil	220-335 kPa (7d);
[162]	R. tropici exopolysaccharide	0.3, 1, 3, 10, 15, 20 mg/mL	Silt	120-1560 kPa (4d)
[37]	Agar only Agar + starch	1, 2, 4% 1% agar + 0.5% starch	Sand	158- 487 kPa
			Organic peat	15-100 kPa
[11, 133]	Xanthan gum	0.5, 1, 1.5, 2, 2.5%	Bentonite	286- 2580 kPa
			kaolinite	150-1180 kPa
[163]	Chitosan	0.02, 0.04, 0.08, 0.16%	CL	1500-3000 kPa (7d)
[164]	Xanthan gum	0.5, 1, 1.5, 2, 2.5%	CH	600 – 1800 kPa (7d) 600 – 2941 kPa (28d)
[165]	Xanthan gum	1, 1.5, 2%	SM	4200-4900 kPa (28d)
[166]	Guar gum	0.5, 1, 1.5, 2%	MH-CH	170- 390 kPa (7d) 196- 418 kPa (28d)
[167]	Biofuel coproduct A	1, 3, 6, 12, 15%	CL	300- 1000 kPa (7d)
	Biofuel coproduct B	1, 6, 12%	CL	300- 600 kPa (7d)
[105, 121]	Lignin	2, 5, 8, 12, 15%	ML	180 - 330 kPa (7d) 220 - 680 kPa (28d)

Table 5. Summary of compressive strength of soils treated with geopolymers

Reference	Precursor	Activator	Precursor Dosage	Soil Type	Compressive Strength
[91]	FAF	Na_2SiO_3 + NaOH	20, 30, 40%	Sandy Clay	11.4 MPa (28d)
[110]	MK	Na_2SiO_3 + NaOH	3 - 15%	CL	1.5-3.5 MPa (7d); 1.3-3.8 MPa (28d)
[92]	MK	Na_2SiO_3 + NaOH	8, 13%	CL (sulphate-rich)	2.5-4 MPa (28d)
[111]	FAF	Na_2SiO_3 + NaOH	25, 35, 45%	Coode Island Silt	100 kPa - 1200 kPa (28d)
	FAF + CCR		35%, CCR = 3-15%		400 kPa - 2000 kPa (28d)
[94]	FAC	Na_2SiO_3 + NaOH	30%	Silty Clay	5 - 7.5 MPa (7d Wet); 8.5 - 10.5 MPa (28d Wet)
[101]	PFA	NaOH, KOH	15 - 30%	CH	400 - 700 kPa (7d); 800 kPa - 1200 kPa (28d)
[123]	FAF	Na_2SiO_3 + NaOH	10, 20%	Silty Sand	2 - 6 MPa (28d)
[168]	GGBS	CCR + Na_2SiO_3	40%	CL	400 - 1200 kPa (7d); 600 -1300 kPa (28d)
[99]	FA + GGBS	Na_2SiO_3 + NaOH	20, 30%	Coode Island Silt	4-7 MPa (28d)
[128]	VA	NaOH	5, 10, 15%	CL	6 MPa (7 & 28d) (dry); 1-1.5 MPa (7d) OMC 2-3 MPa (28d) OMC
[93]	MK/FAC	Na_2SiO_3 + NaOH	3- 15% (total)	CH	650-900 kPa (7d)
[169]	FAF	Lime + Na_2SiO_3	18%	Sulphate-rich, saline soil	6 MPa (30d)
[125]	FAC + GBFS	Na_2SiO_3 + NaOH	FA 30% + GGBS 10 - 30%	SC-SM	4-9 MPa (7d Wet) 8-16 MPa (28d Wet)
[170]	RGP	NaOH	3 - 25%	CL	400- 800 kPa (7d); 600- 1700 kPa (28d)

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Reference	Precursor	Activator	Precursor Dosage	Soil Type	Compressive Strength
[97]	FAF + GGBS	NaOH, KOH, Na$_2$SiO$_3$ + NaOH,	20% (total)	Coode Island Silt	100 - 3700 kPa (7d) 1600 -5800 kPa (28d)
[171]	FAF + GGBS	Na$_2$SiO$_3$ + NaOH	10, 20, 30% (total)	Coode Island Silt	3 - 6MPa (7d) 4 - 10 MPa (28d)
[172]	RHA + CKD	NaOH	14 - 20% (total)	Clayey soil	270 kPa (Wet)
[173]	GGBS + PF	Na$_2$SiO$_3$ + NaOH	10, 20, 30%	CH	400 - 2500 kPa (7d); 800 - 4000 kPa (28d)
[126]	FAF + GGBS	Na$_2$SiO$_3$ + NaOH	30%	A-4 (AASHTO)	3.1 MPa (7d); 4.33 MPa (28d) 2.04 MPa (7d Wet); 2.34 MPa (28d Wet) 0.9-1.1 MPa (7d); 3.1-3.8 MPa (28d) 0.5 MPa (7d Wet); 0.6 - 2MPa (28d Wet)
	FAF + lime		20, 30%		
[127]	FAF + GGBS	Na$_2$SiO$_3$ + NaOH	20, 25, 30% (total)	Coode Island Silt	0.5-3 MPa (7d)
[124]	GGBS	Na$_2$SiO$_3$ + NaOH	2.5 - 25%	Kaolin	1.3-2.5 MPa (7d); 3-4.5 MPa (28d)
	GGBS	ASM			1.2-2 MPa (7d); 2.5-4.1 MPa (28d)
[174]	GGBS	NaOH	10 - 50%	CH	2.4 -4.4 MPa (14d)
[175]	CMT + SF	KOH	10, 15, 20% (total)	Sandy soil	6-10 MPa
[176]	MK + BF	Na$_2$SiO$_3$ + CaO	10 - 18% (total)	CL	930 kPa
[177]	MK	NaHCO$_3$ + CaO	6-12%	Clay	400-800 kPa (7d)

1 FAC: Class-C fly ash; FAF: Class-F fly ash; MK: Metakaolin; PFA: Palm Fuel Ash; GGBS: Ground granulated blast furnace slag; FA: Fly ash – unclassified;
2 VA: Volcanic ash; CCR: Calcium carbide residue; RHA: Rice husk ash; CKD: Cement kiln dust; RGP: Recycled glass powder; PF: Polypropylene fiber; BF:
3 basalt fiber; CMT: copper mine tailing; SF: silica fume; ASM: anhydrous sodium metasilicate

4.2 Permeability and Hydraulic Conductivity

Permeability is defined as the property which allows the seepage of fluids through its interconnected void spaces [9]. When the fluid is water, the coefficient of permeability is also called hydraulic conductivity.

Significant and immediate reduction on permeability of polymer treated soils is reported in many studies. Al-Khanbashi and Abdalla [178] used three types of acrylic emulsions to treat sandy soil and they observed noticeable decreases in permeability with all three polymers, even at a rate as low as 0.5%. At a 5% application rate, the coefficient of permeability reduced by two orders of magnitude. For biopolymers such as guar gum, xanthan gum and sodium alginate, the hydraulic conductivity of the treated silty sand was further reduced, from 1×10^{-6} m/s to 2×10^{-7} m/s, 2×10^{-9} m/s, 4×10^{-11} m/s, respectively, after 7 days of curing with a dosage of 0.5% [36], which the authors believe is due to the pore-plugging effect of the organic polymers. Similar results are also reported by many other studies, and the polymers ranging from synthetic organic polymers like PAM to different biopolymers [5, 166, 179-181]. These viscous organic polymers increase the pore fluid viscosity in soil voids which in turn blocks the pores making movement of water more difficult and thus reduces the permeability of the treated soils [42]. Huang et al. [182] reported that addition of polyvinyl acetate-based polymer improved the soil microstructure and pore uniformity by blocking the small pores, increasing the water retention capacity.

On the other hand, the effect on permeability by geopolymer-stabilized soil has rarely been reported. Du et. al. [168] compared slag geopolymer treated soil with lightweight cement stabilized soil and found that geopolymer treated soil has larger air pores (>10 μm) than cement treated soil and the coefficient of permeability is 10 times higher, even though in the geopolymer treated soil, the soil aggregate was coated by a higher amount of hydration product. This result might be similar to the effects of lime stabilization. Although lime can substantially increase strength, lime typically changes, in some cases dramatically, the texture of clay soils. The textural change caused by flocculation of clay plates open the structure to flow of water as the water layers surrounding the clay plates are substantially reduced. This can increase permeability by several order of magnitude. Overtime the permeability of the lime-soil reduces as pozzolanic product fills voids, but never to the pre-stabilization level. The effects of geopolymer on soil permeability need further investigation.

4.3 Volume Stability

Swell and shrinkage of expansive soils have long been a problem for pavements and foundations. Expansive clays such as montmorillonite are notorious for their volumetric instability due to the potential of the highly active colloidal clay plate structure. Clay colloids have an enormous specific surface area, as high as several hundred square meters per gram. The clay colloids are also highly negatively charged thus providing a huge, active platform for the sorption of water resulting in expansion. Polymers have been studied to improve the volume stability by reducing the swell and shrinking potentials of these soils.

Inyang et. al. [183] evaluated the effects of three polymers including sodium carboxymethyl cellulose, PAM and polyethylene oxide on the volumetric swelling ratio

of Na-montmorillonite and all three polymers reduced the swelling of montmorillonite. PAM, as a cationic polymer, was the most effective compared to the other two polymers due to the strong electrostatic attractions between the positive polycation and the negative montmorillonite surfaces. Other organic polymers have also proven to reduce soil swelling and shrinkage, including but not limited to, formaldehyde [57], polypropylene [154], polyvinyl acetate [47], lignosulfonate [184] and xanthan gum [42, 180]. These organic polymers are believed to contribute to the reduction of soil expansion by repelling water from double layers and preventing water reabsorption if the polymer has hydrophobic functional groups [185]. Organic polymers could also reduce the thickness of the double layer of clay soils as polymers usually have a much lower dielectric constant compared to water, which results in a reduced double layer thickness [185]. Geopolymers are also reported to inhibit soil expansion. Khadka et. al. [93] used fly ash (FA) and metakaolin (MK) based geopolymers to treat highly plastic clay and observed a significant reduction of swell behavior in fly ash geopolymer treated specimens while no improvement was observed in MK treated soil. However, metakaolin geopolymer was reported to decrease the shrinkage strain of a low plasticity clay [110].

For soils rich in sulfate, traditional calcium-based stabilizers such as lime or cement can cause significant expansion due to the formation of ettringite and thaumasite [186]. Stabilization of sulfate-rich soils with polymers are also reported. A much lower swelling strain than that of 4% lime stabilized counterparts was observed when metakaolin geopolymer was used, and no ettringite formed through the geo-polymerization process [92]. Therefore, it can be expected that calcium-free geopolymers could be an alternative stabilizer for soils with high sulfate content. Gilazghi et al. [58] treated sulfate-rich clay with methylene diphenyl diisocyanate and a reduction of swelling was reported compared to untreated and 4% lime treated soils.

4.4 Durability

Freeze-thaw cycle test, dry-wet cycle test, abrasion test and erosion test have frequently been used to evaluate the durability of polymer stabilizers. Fungaroli and Prager [138] reported that acrylic polymer-modified soil-cement specimens were more resistant to freeze-thaw cycles than unmodified cement treated soils after curing for 7 to 91 days. Ayeldeen et al. [187] compared the effectiveness of xanthan gum, guar gum, carrageenan and modified starches to reduce soil erosion. They found that almost all the specimens treated with 0.5% biopolymer were able to resist five wet-dry cycles. Resistance of the silty sand to wind erosion was improved with treatment of these biopolymers. Arasan et al. [52] applied 10-30% of polyester (by dry weight of soil) to sand and reported no effects of 20 freeze-thaw cycles on samples cured for 28 days. Rezaeimalek et al. [148] reported a negative effect of freeze-thaw and dry-wet cycles on strength of acrylic emulsion treated sand, in which 41% strength loss and 9% of weight loss were observed after 24 freeze-thaw cycles, and 39% of strength loss and 7% weight loss after 24 dry-wet cycles. Compared to sand, the strength loss observed in clay specimens was more notable. However, although the strength loss of the specimens was significant, the residual strength was still considerable after the weathering scenarios [122]. Many other researchers observed the similar trends of strength reduction and mass loss of polymer treated soils [180, 188, 189].

Resistance to water erosion of polymer stabilized soils was also investigated. Indraratna et al. [104] studied the erosion characteristics of untreated and lignosulfonate treated silty sand using a process simulation apparatus for internal crack erosion. They found that lignosulfonate acted like a cementing agent to bind the soil particles together to form an erosion resistant surface and the coefficient of soil erosion dropped from 0.181 to 0.0021 even with the addition of 0.6% lignosulfonate. Similar trends were also observed for dispersive clays [190]. Chang et al. [191] used laboratory precipitation and stream erosion simulation to investigate the effects of two biopolymers, xanthan gum and β-glucan on erodibility of silty loam. Biopolymer treated soil demonstrated low erodibility compared to untreated natural soils for both the short and long term of water erosion. Other polymers including PAM, polysaccharide, casein and PVAc are also reported to increase the resistance of erosion of different soils [5, 48, 192, 193].

Similar to other stabilizers, polymers are impacted by excess moisture and intrusion of moisture into the soil matrix externally through cracks. Most researchers who have investigated moisture susceptibility of polymer-stabilized soils have reported strength loss when samples were wetted during the tests [9, 34, 116-118]. The degree of strength loss varied depending on the soil and polymer used; however, the wet strength of some polymer stabilized soils are favorable compared to wetted, untreated soils [119] and lime-treated soils [117]. Azzam [153] reported no visible or detrimental effect of submerging on polypropylene-stabilized clay after being soaked in water for 24 hours, which the author believed it was contributed to the hydrophobic components in the polymer. However, it is unclear how polymers with both hydrophilic and hydrophobic components will perform, and more research is therefore needed to fully understand the contribution of hydrophobic functional groups in polymers to moisture resistance. Compared with organic polymers, the durability of geopolymer treated soils is very limited in the literature.

5 Discussion

5.1 Comparisons with Cement Stabilization

Table 6 summarizes the major types of polymers used in soil stabilization versus the traditional stabilizer – Portland cement. Although cement has been widely used for the past decades and has proven successful in many real-world applications, polymers also exhibit potentials for soil stabilization application. Geopolymer stabilized soil can have comparable strength results with cement stabilization due to similar cementitious products. However, a thorough understanding of geopolymerization in soils has not yet been achieved and more research is needed to verify the effectiveness of geopolymers. Multiple biopolymers and synthetic organic polymers treated soils also exhibited comparable strength results with cement stabilization, nevertheless, like geopolymers, further investigation is still required.

Table 6. Comparisons between cement stabilization and polymer stabilization of soil [32, 194]

Properties	Cement	Geopolymer	Biopolymer	Synthetic Organic Polymer Solutions
Soil Competitiveness	Coarse- and fine-grained soils			
Mechanisms	Hydration	Geopolymerization	Ionic/hydrogen bonding, pore filling	
Main components	Cement, water	Pozzolans, alkali, water	Biopolymers, water	Synthesized polymers, water
Advantages	Strong, durable, sufficient, systematic case studies	Strong, durable, Low carbon footprint	Stronger in fine soils, environmentally friendly, low dosages	
Disadvantages	High carbon footprint, disposal issues, high alkalinity	limited application, high alkalinity, heat treatment, high dosages	Water sensitivity, new technique, limited application, high material cost, long-term durability concerns	

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5.2 Challenges of Polymer Stabilization

While the review of the existing research indicates great potential for the use of polymers in soil stabilization, the application of polymers faces many practical challenges.

The main reason for the reluctance towards the use of polymers is the lack of systematic, independent published research on polymer stabilizers [119, 142, 195]. In addition, the labeling of polymers in the market is unorganized and the names of polymers and suppliers change frequently, making it difficult to keep track of the assets and functionality of each polymer [196]. Another hurdle for the widespread use of polymers is the lack of proper standards for predicting the performance of polymer stabilizers [197]. The application rates provided by polymer suppliers vary and some researchers have found the recommended application rate not to be sufficient in order to provide the desired performance improvement [142].

The cost concerns of polymer stabilization is another important aspect that is restricting the broad application of polymers, especially organic polymers. Currently, the average marketing prices for the major polymers that have been used in laboratory research are significantly more expensive than traditional stabilizers such as cement and lime [32]. This is mainly due to the lack of mass production and food-grade high purity of the available polymers. However, the prices of polymers keep dropping in the past decades. Chang et al. [32] reported that the global market price of xanthan gum dropped from 13.4 USD/kg in the year 1990 to 2.6 USD/kg in 2014. It should also be noted that the marketing prices of polymers or cement are only one part of the total cost of soil stabilization. A proper and thorough life-cycle analysis and comparison integrating direct economic impacts, costs assigned to environmental impacts (recycling of waste materials, use of sustainable materials, etc.) as well as expenses related to durability and sustainability should be employed when comparing the costs of two different stabilizers [198]. Chang et al. [32] took the application dosage and the carbon trade exchange into consideration and reported a total cost of 12.50 USD for a 1-ton soil treatment with Portland cement. In contrast, it was 12.95 USD for xanthan gum, despite xanthan gum having a significantly higher material cost.

Moisture resistance of polymer-stabilized soils is also an issue that should be addressed. Improving the moisture resistance of polymer-soil mixtures will greatly increase the durability of polymer-stabilized soils and eventually reduce the long-term maintenance costs for infrastructures. Researches have already identified the potential for polymers to improve the moisture resistance [117, 119]. Soils stabilized by certain polymers containing hydrophobic components have exhibited better properties after wetting [151]. As discussed previously, it is imperative to understand how quickly the polymer-soil bonding mechanism deteriorates as moisture enters the stabilized soil and how quickly the polymer-soil system can release the moisture during a drying period.

Biodegradability of organic polymers could also affect the durability of polymer stabilized soils. Although the biodegradability of organic polymers has not yet been investigated in soil stabilization, several polymers such as polyacrylamide, polyacrylic acid, polyvinyl alcohol and all the biopolymers are known to be biodegradable under specific conditions in their applications in other areas [199]. The rate of deterioration of polymers varies depending on the polymer type, molecular weight of polymers,

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microorganism type and incubation conditions. For example, biodegradation of synthetic polymers having a hydrocarbon backbone, such as polyacrylic acid and polyacrylamide, seems to be restricted to polymer fractions having small molecular weight, while polyvinyl acid, also with a hydrocarbon backbone, can deteriorate even when having a high molecular weight [200]. However, it is noteworthy that although these polymers may eventually be mineralized, the conditions for such occurrence could sometimes be very restricted and may be uncommon due to the rare natural occurrence of the microorganisms that are capable of degrading these polymers [200]. Therefore, the biodegradability of polymer-stabilized soils require substantial investigation before conclusions can be made. Even though one polymer is biodegradable, its biodegradation rate in a natural setting should be considered from an engineering perspective to permit adequate evaluation of the durability of polymer-stabilized soils.

5.3 Future Research Needs

Establish Appropriate Protocols to Test Polymer Stabilizers

A systematic investigation of individual polymers and their effects on soils is critical. Currently there are no accepted testing protocols for evaluating the performance of polymers as soil stabilizers. Test procedures used for traditional stabilizers are adopted for polymer stabilizers. However, special properties of polymers such as viscosity are not considered in the tests designed for cement and lime stabilization. The high viscosity of polymers could lead to non-uniform mixing when in contact with soil, especially fine-grained clays. This could eventually affect the evaluation of certain polymers, which may have otherwise been effective. Curing of polymer-stabilized soils also plays a key role. Temperature and moisture clearly have significant impacts on the performance of polymers. The mixing sequence of polymer, water and soil could also present different results and hence the impact of these factors must be further evaluated.

Tests for geotechnical and mechanical properties other than the unconfined compression test should be more widely used to evaluate the effects of polymers properly. Although triaxial shear test, 1-D free swell, volumetric swell test, indirect shear test, erosion test and abrasion test were reported in the past ten years on polymer stabilized soils, they are still insufficient compared to unconfined compressive test. Most of these tests are only undertaken on a small number of polymers but are very limited on many others in the literature. Besides, properties such as toughness, fracture energy, dynamic responses of polymer stabilized soil should also be evaluated, which give insights into the performance of polymer treated soil under dynamic loads and are important in certain areas such as pavement engineering.

Investigate Mechanisms of Polymer Stabilization

Many theories were proposed, including electrostatic attractions, hydrogen bonding, van der Waals, entropy increase and physical binding as the mechanisms of polymer stabilization. However, these mechanisms have not been validated and are not fully understood. Techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR), among others, have been widely used to analyze the mineralogy, morphology and chemistry of soil minerals and polymers, as well as possible

interactions between polymer and soils. However, XRD is suitable for analyzing crystalline minerals such as soils, while FTIR and NMR are mainly used for polymer analysis only. Although understanding soil mineralogy and polymer chemistry is fundamental, it is only at the outset of investigating the possible polymer soil interactions. So far, SEM is nearly the only technique reported to analyze the soil-polymer mixture in the literature. The clear images of polymers wrapping the soil particles, binding the soil grains, and filling the voids contribute to the understanding of interactions. However, it remains unknown whether this type of interaction is purely physical or if some products are formed due to reactions between polymers and soils. How different functional groups of polymers interact with soil minerals, moisture, cations and ions is still unclear. Solving these issues would eventually unveil the mechanisms of polymer stabilization, understand the limitations and applications of different polymers, select the correct polymers based on different soil conditions.

Examine In-situ Properties

Assessing the field properties of stabilized soils based on laboratory testing results remains an important yet incomplete subject [195]. For polymers to be considered as a potential alternate stabilizer to cement or lime, the field performance of polymer stabilization needs to be fully understood and correlated with the appropriate laboratory tests. For example, use of a simple unconfined compression test for lime, cement and fly ash soil mixes has been reasonably well correlated to resilient modulus, flexural strength and other properties that impact field design. However, just how an unconfined compression test defines the in situ, field modulus of a polymer stabilized soil is not clear. The polymer stabilized soil may have properties such as visco-elastic effects that impact the time dependency of field moduli and responses based on in situ dynamic properties that may make a "world-of-difference" between cement and polymer treated systems. Another example is the difference between fracture energy in a cement treated soil and in a polymer treated soil. The ability of a polymer system to absorb energy due to polymer chain distortion and configurational entropy effects that does not translate into crack propagation may make a large difference in fatigue life of stabilized pavement layers. Carrying out well-designed in-situ field tests should contribute to the understanding of polymer-soil interactions and evaluate their performance in real field situations.

Resolve Durability Issues

Moisture susceptibility of polymer-stabilized soils is an issue remaining to be solved. This is possible through further study of polymers and their interactions with different soils, considering the vast varieties of polymers and the possibility of engineering new polymers when given the necessary target guidelines rather than simply using a by-product from another focus application. Current research has indicated promising properties of polymers that may improve their moisture resistance using the hydrophobic components in polymers [151]. New polymers could be engineered, which could form strong, durable and hydrophobic bonds with soil minerals against moisture while still meeting the required strength properties.

Assessment of the biodegradability of polymer-stabilized soils is also needed. Understanding of the conditions where a specific polymer could biodegrade and how

likely it is to occur in the field could help engineers and researchers to determine the appropriate polymers to choose under certain scenarios so the polymer stabilized soils could be durable for a designed period of time. Resolving the biodegradability concerns is also pivotal for the broad application of polymers in soil stabilization.

6 Summary

This paper reviewed different types of polymers (i.e., geopolymers, biopolymers and synthetic organic polymers) that have been utilized for soil stabilization in pavement and geotechnical engineering. The focus of the review is on the physicochemical properties of these polymers, the stabilizing mechanisms, as well as the engineering properties of different soils after polymer treatment.

Geopolymer is an inorganic polymer formed through geopolymerization between the activator (alkali) and the precursor (Al and Si source). The effectiveness of geopolymers is highly dependent on the activator and the precursor used, including the dosages, concentrations, as well as the aluminosilicate structures. The mechanism of geopolymer stabilization is geopolymerization in which the alumina and silica dissolve first under high pH condition and then form gel-like complexes and eventually harden.

Organic polymers including biopolymers and synthetic polymers are composed of monomers with different carbon backbones and side chains. The properties of organic polymers vary significantly depending on the composition and these properties, including molecular weight, particle size, charge, conformation, solubility, viscosity, and pH, are crucial for their interactions with soil minerals. Interactions between organic polymers and clay minerals vary depending on the charges of the polymers and the different modes of interactions of cationic, neutral, or anionic polymers. For coarse materials such as sandy soils, organic polymers change soil structures by covering sand grains with thin films, connecting noncontacted neighboring particles and developing adhesion between adjacent particles.

One focus of the current research is the exploration of novel polymers for soil stabilization. Dozens of polymers have been investigated, including but are not limited to, fly-ash geopolymer, metakaolin geopolymer, xanthan gum, guar gum, lignin, PAM, PVA and polyacrylate, and more novel polymers are being introduced, such as sulfur-free lignin, terpolymer and casein. These polymers are used to stabilize different soils, mainly sand, silt and clay, and the geotechnical properties of the stabilized soils are widely investigated. Among all the engineering properties, unconfined compressive strength was the most broadly studied and most polymers resulted in an increase of soil strength. However, the strength reported were mainly measured under a relatively dry condition, especially for a new polymer. The strength properties under wet conditions require further examination as many polymer stabilized soils are also reported to display a decrease in strength upon wetting, and some are even significant. Besides unconfined compressive strength, polymers are also reported to improve the shear strength, alter the permeability, inhibit the swelling and shrinkage, and enhance the durability of soils. However, these tests were only carried out on certain polymers by several researchers while for most of the polymers investigated, similar tests are rarely reported, especially for geopolymer treated soils.

The applications of polymers in soil stabilization face some challenges. The lack of systematic and independent published research, unorganized labeling of polymers in the market, lack of proper standards for evaluation of performances and inconsistency in suppliers' recommended application rate(s) make it difficult to use polymers broadly and confidently. The high cost of polymers, biodegradability and moisture susceptibility of polymer-stabilized soils are the other important factors that could limit their application if not solved properly. Therefore, this paper identifies future research needs such as establishing acceptable protocols for polymer evaluation, investigating mechanisms of soil polymer mixture, examining in-situ properties, and resolving durability issues.

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