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Soil Stabilization Using Zein Biopolymer

Quadri Olakunle Babatunde and Yong-Hoon Byun *

School of Agricultural Civil & Bio-Industrial Engineering, Kyungpook National University, Buk-gu,
Daegu 41566, Republic of Korea
* Correspondence: yhbyun@knu.ac.kr; Tel.: +82-53-950-5732; Fax: +82-53-950-6752

Abstract: The characterization and analysis of the cementation properties of novel biopolymer binders in soils are essential for their potential application in geotechnical engineering. This study investigates the cementation effect of a novel zein biopolymer binder on sandy soils. Soil specimens are mixed with various contents of zein biopolymer ranging from 0 to 5%. The mechanical and microscopic characteristics of the treated specimens are evaluated using unconfined compression tests and scanning electron microscopy, respectively, after curing for 3, 7, and 28 days. The results show a consistent increase in compressive strength and elastic modulus of treated soils with increasing curing periods and biopolymer contents. A small amount (1%) of zein biopolymer increases soil strength and elasticity regardless of gradation. Additionally, the bonding force between the soil–zein biopolymer increases linearly with soil uniformity. Therefore, the application of zein biopolymer can be potentially used as a binder for fine- and coarse-grained soils in geotechnical engineering considering its stabilization and sustainability properties.

Keywords: biopolymer; compressive strength; elastic modulus; soil stabilization; zein

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1. Introduction

Soil stabilization with improved mechanical properties and sustainability has been an essential factor in ecological protection. Two different approaches can improve soil strength in the field: (i) a mechanistic approach that uses heavyweight machines to compact and consolidate soils and (ii) a synthetic approach that employs conventional binders and polymers to enhance both the mechanical and chemical properties of soils [1,2]. Conventional binders, such as lime and Portland cement, have been extensively used to improve the mechanical properties of soil [3,4]. However, their contribution to environmental pollution and vegetation reduction has been a significant challenge [5–7]. Recently, environmentally friendly cementitious materials were introduced as potential soil stabilizers because of their sustainability and efficiency compared with conventional binders [8]. Microbially induced calcite precipitation (MICP) and enzyme-induced carbonate precipitation (EICP) have been used to increase the strength and reduce the permeability of cohesionless soils [9–12]. Nevertheless, the inability to reproduce microorganisms in dense soils is a major drawback of both MICP and EICP [13].

Bio-based polymers have recently been introduced as synthetic binders to improve the mechanical properties of soils. Biopolymers are non-traditional binders produced naturally without any detrimental effect on the environment [14]. Biopolymer binders have been extensively used to stabilize soils [15–18] and increase their erodibility resistance [19]. Several studies have shown that biopolymer binders enhance the strength of soils [20–23]. Hataf et al. [24] reported that the cementation of soil with chitosan biopolymer improved the stiffness of the specimen by bridging the soil particles. Starch and xanthan have been added to improve the cohesiveness of problematic soils [18]. Sulaimon et al. [25] performed a comparative study on two different biopolymers to enhance the strength of expansive soils. Nevertheless, the strength of biopolymer-treated soils was weakened when the soils were saturated owing to the interaction of these hydrophilic polymers with water [26].

Chang et al. [26] and Gao et al. [27] recently introduced a protein-based biopolymer, casein, extracted from bovine milk, which was hydrophobically linked to enhancing the strength of both dry and wet soils. However, understanding the cementation mechanism of cement substitutes (biopolymers) is essential for their potential applications.

The utilization of protein-based biopolymers as a binder for soil stabilization is limited in geotechnical engineering. This study envisioned filling the research gap and investigating the cementation effect of a newly suggested protein-based binder (zein biopolymer) to improve soil strength. The zein biopolymer is commercially extracted from maize and has been majorly used as a binder in various fields [28–30]. Zein is the protein part of maize, which controls the strength of the endosperm. It has been well known as a green bio-adhesive polymer because of its cementation behavior with biological walls and based on its reaction with hydrogen ions and its protein network [31]. The hydrophobicity of zein is associated with its large number of nonpolar amino chains [32]. Zein biopolymers are widely used in tissue engineering to increase the tissue interaction of bone scaffolds [33,34]. Zein has also been used for food preservation [35] and cementing the walls of medicines sensitive to microorganisms [36]. Furthermore, zein possesses adhesive and self-stabilization properties through the hydrophobic oligomers formed during reaction with solvents. However, it is essential to understand the cementation effect of a newly proposed zein biopolymer at various contents to emphasize its benefits as a sustainable soil binder.

This study aims to investigate the unconfined compressive strength and elastic modulus of zein-biopolymer-treated soils. First, the gradation and compaction properties of the sandy soils are examined based on a sieve analysis and standard proctor tests. Subsequently, the strengthening mechanism and elements of the zein biopolymer are established. After specimen preparation, unconfined compression tests are conducted to evaluate the mechanical properties of the zein-biopolymer-treated soils, such as the stress–strain relationship, compressive strength, and elastic modulus. Finally, several relationships are analyzed between the index and mechanical properties and the microstructures of the biopolymer-treated soils with the biopolymer content.

2. Materials

2.1. Zein Biopolymer

Zein is a protein-based biological polymer that constitutes 44–79% of maize endosperm [37]. Zein, also known as prolamin, contains a high level of glutamic acid, leucine, proline, and alanine, whereas it is deficient in basic and acidic amino acids [38]. Commercial zein is extracted from maize kernels using benzene or ether solutions to remove oily and fatty substances, as shown in Figure 1 [32]. Zein can be categorized into four groups based on its hydrophobic properties and formation of a protein network: α-zein, β-zein, γ-zein, and δ-zein [39,40]. α-zein, also known as commercial zein, has strong hydrophobic interactions, forming a protein network [39]. The hydrophobicity of zein is ascribed to its small number of polar amino groups [41]. Previous studies have found that zein can be dissolved using a nonpolar solvent, ethanol, a strong alkali solution, and urea in high concentrations [32,38].

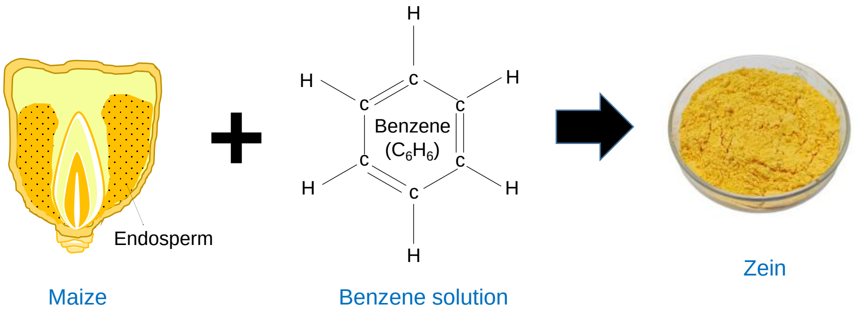


Figure 1. Zein extraction from maize.

The amphiphilic property of zein, which results in low permeability and improved strength, has been a driving force governing its application in various fields. The adhesive characteristics and electrosteric stabilization of zein depend on the solvent concentration and the curing temperature [32]. The biopolymer used in this study was formed using commercial zein, ethanol, deionized water, and polyethylene glycol. Commercial zein was used as a binder, and ethanol/deionized water was used to enhance the solubility of zein. Polyethylene glycol was selected as the superplasticizer to improve the adhesive strength of the zein biopolymer. Figure 2 shows the preparation and reaction chain of the solvent with the zein biopolymer during the curing period. Ethanol, polyethylene glycol, and deionized water are mixed to prepare the solvent. Ethanol and polyethylene glycol form a polar solvent, whereas water is a nonpolar one. Ethanol and polyethylene glycol in the mixture react with the nonpolar amino groups of the zein biopolymer, exposing the polar amino groups to deionized water. The polar solvent exposed nonpolar and polar amino groups in the mixture, forming a large zein nanoparticle with a cementation effect [42]. During the dehydration process, the solvent gradually evaporates, enhancing the cementation effect of the zein biopolymer. The induced cementation effect shows an increase in the protein network and hydrophobic interactions between the zein molecules and the functional structure [43].

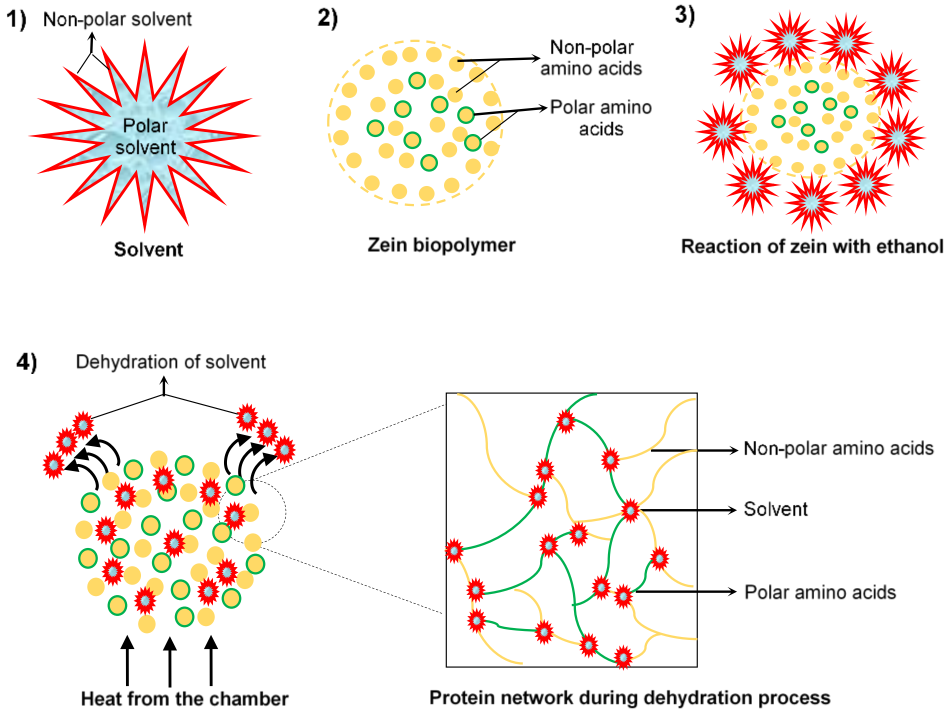


Figure 2. Zein biopolymer reaction for strength improvement.

2.2. Soils

Silica sand incorporated with silt fractions was selected for this study due to its susceptibility to failure, such as erosion. The cementation effect of the zein biopolymer was investigated using different soils. Five sandy soils were prepared by mixing different proportions of silt with sand, ranging from 10 to 90%. After the sieve analysis, the index and gradation properties were determined, as summarized in Table 1. The specific gravity and mean diameter of each specimen ranged from 2.63 to 2.69 and from 0.19 to 1.15 mm, respectively. The maximum dry unit weights and optimum moisture contents of the specimens were evaluated through the Proctor test, according to ASTM D698 [44]. For the compaction test, soil specimens were prepared with five different moisture contents. The soils with selected moisture contents were compacted at three equal layers using a standard proctor mold. After finishing the compaction, the maximum dry density corresponding to the optimum moisture content was measured.

Table 1. Index and compaction properties of soils.

Specimen ID	**D_{10}**	**D_{30}**	**D_{50}**	**D_{60}**	**C_u**	**C_c**	**#200 (%)**	**G_s**	**USCS**	**MDD (kN/m^3)**	**OMC (%)**
S1	0.32	0.80	1.15	1.32	4.1	1.5	4.3	2.63	SW	20.1	10.4
S2	0.09	0.56	1.01	1.21	13.1	2.8	9.6	2.64	SW-SM	19.8	13.2
S3	0.07	0.24	0.67	0.80	11.2	1.0	14.6	2.67	SM	20.5	10.3
S4	0.09	0.23	0.59	0.72	8.0	0.8	13.1	2.69	SM	19.9	11.5
S5	0.08	0.13	0.19	0.22	2.8	1.0	13.4	2.69	SM	17.2	10.4

D10 = 10% cumulative passing; D30 = 30% cumulative passing; D50 = 50% cumulative passing; D60 = 60% cumulative passing; C_u = coefficient of uniformity; C_c = coefficient of curvature; #200 = percent passing No. 200 sieve; G_s = specific gravity; USCS = unified soil classification system; MDD = maximum dry unit weight; OMC = optimum moisture content.

2.3. Mixing Process

The effects of the zein biopolymer on the mechanical behavior of the soils were prepared in two different forms: treated and untreated soils. The untreated specimens without the zein biopolymer were prepared at the optimum moisture content. Each biopolymer-treated specimen was formed by mixing commercial zein with soil at the maximum dry unit weight. The mixing process was performed for 5 min to achieve a homogenous soil-zein mixture as suggested by Hataf et al. [24]. The solvent solution was prepared by mixing ethanol, deionized water, and polyethylene glycol. The volume ratio of ethanol: water: polyethylene glycol was 4:5:1. The solvent was continuously stirred for several minutes to obtain a stable solution. Each biopolymer content was a predetermined mass of zein in percentage relative to the mass of the corresponding soil specimen, and each treated specimen was prepared at the optimum moisture content with the solvent using an automatic mixer.

3. Experimental Study

3.1. Specimen Preparation

All specimens were compacted in detachable cylindrical MC-nylon molds with a height of 100 mm and an internal diameter of 50 mm. Each mold was supported by two adjustable stainless-steel cable ties at the upper and lower parts to hold it tightly during the curing period. The inner walls and joints of the detachable molds were lubricated with vacuum grease to enable easy removal of the specimen and prevent water leakage from the joints. For compacting each specimen, 25 blow counts per layer were applied with a hammer of weight 5.4 N at three different uniform layers of a specimen. The compacted specimens were demolded after curing for 2 days to mitigate the heat loss through the insulated mold, and the specimens were then cured at a constant temperature of 40 °C and humidity of 30% for the desired periods.

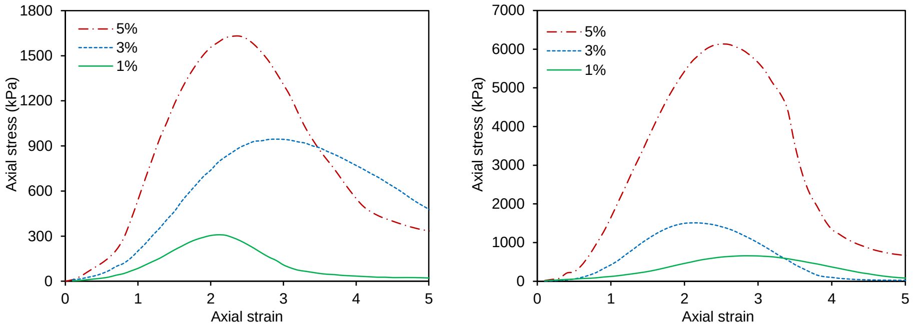
3.2. Unconfined Compression Test

Unconfined compression tests evaluated the compressive strength and elastic modulus of all specimens after curing for 3, 7, and 28 days. Axial loading was applied on the top of each cylindrical specimen at a strain rate of 1 mm/min up to an axial strain of 5%. All specimens' compressive strength and secant modulus of elasticity were evaluated as suggested in previous studies [45–47]. Half of the unconfined compressive strength and the corresponding strain was used to determine the secant modulus of elasticity. All untreated specimens could not resist axial loading under the unconfined compression test because of the lack of compressive strength.

4. Results and Discussion

4.1. Stress–Strain Curve

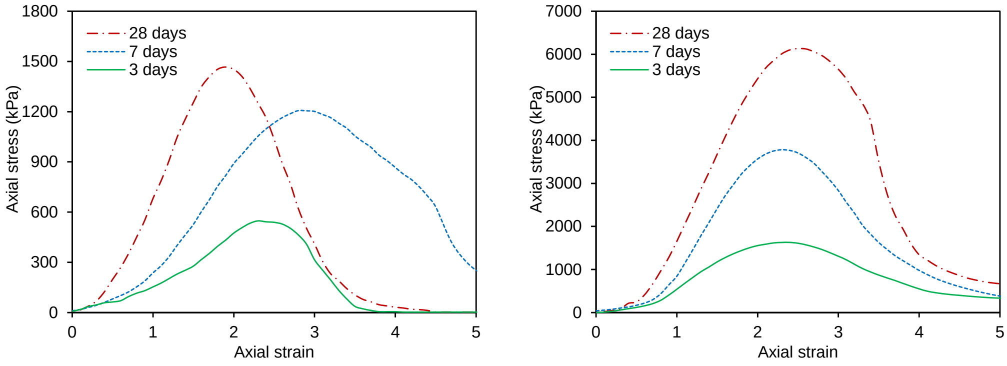
The stress–strain curves of the treated specimen were evaluated from the unconfined compression tests. Typical stress–strain relationships of the treated specimens (S3) with three biopolymer contents after curing for 3 and 28 days are plotted in Figure 3. For the five different sandy soils, the axial stress initially increases with an increase in the strain and subsequently reaches the peak stress, which is determined as the unconfined compressive strength. The weak crosslinking of the treated soil at the initial curing state (3 days) resulted in lower compressive strength. The moist inner part of the specimen at the early curing stage leads to the weak shear strength of the specimens. Continuous dehydration during the curing period gradually increases the bonding properties of the biopolymer. For the specimens (S3), the axial stress rapidly rises with increasing axial strain, and the unconfined compressive strength increases with an increase in the biopolymer content, regardless of the curing period. The treated specimens cured for 28 days show higher compressive strength than those cured for 3 days, regardless of the biopolymer content. The improved compressive strength with the curing period can be attributed to the increase in the specimen's particle size and molecular weight of the zein biopolymer [42].



(**a**) (**b**)

Figure 3. Typical stress–strain curves of treated specimens with different biopolymer contents at two curing periods: (**a**) 3 days; (**b**) 28 days.

Figure 4 shows the variations in the stress–strain curves of treated specimens (S1 and S3) with 5% biopolymer content. For both specimens, after a longer curing period, the axial stress rapidly increases with increasing axial strain, and the unconfined compressive strength increases with increasing curing period. For all curing periods, the unconfined compressive strength of S3 is greater than that of S1. Considering that S3 has a higher coefficient of uniformity than S1, the interparticle bonding induced by the zein biopolymer may be significantly influenced by the coefficient of uniformity of S3.



(**a**) (**b**)

Figure 4. Variation in stress–strain curves of two treated specimens with curing period: (**a**) S1; (**b**) S3.

4.2. Strength

The unconfined compressive strength of all specimens treated with various biopolymer contents after curing periods is shown in Figure 5. Overall, the unconfined compressive strength increases with an increase in the curing period, regardless of biopolymer content. The increased compressive strength rate with the curing period depends on the biopolymer content and the grain size distribution of soils. For all specimens, the unconfined compressive strength increases with increasing biopolymer content. A higher biopolymer content induces more interparticle bonding in the zein-treated specimens. Increasing the biopolymer simultaneously improves the viscous gel of the zein biopolymer connecting the soil particles. This finding agrees with the strengthening properties of biopolymer-treated soils from previous studies using a different biopolymer binder [23,48,49]. The dehydration of the solvent in the treated specimens enhances the protein–protein network, which results in adhesive interaction between the soil particles [43], as shown in Figure 2. At the biopolymer contents of 1 and 5%, S3 shows the highest compressive strength after 28 days of curing ranging from 320 kPa to 3065 kPa. This indicates that a small biopolymer content (1%) has a significant strength improvement on sandy soils. At a biopolymer content of 3%, S2 presents the highest compressive strength for all curing periods. The strength improvement of S2 and S3 can be attributed to their grain size distribution, with the highest coefficient of uniformity. Moreover, in previous studies [50], the peak compressive strength of a soil mixture was found at the optimum fines content. The obtained compressive strength shows a more stabilization efficiency with similar biopolymer contents and soil type compared with results obtained by Sulaimon et al. [25].

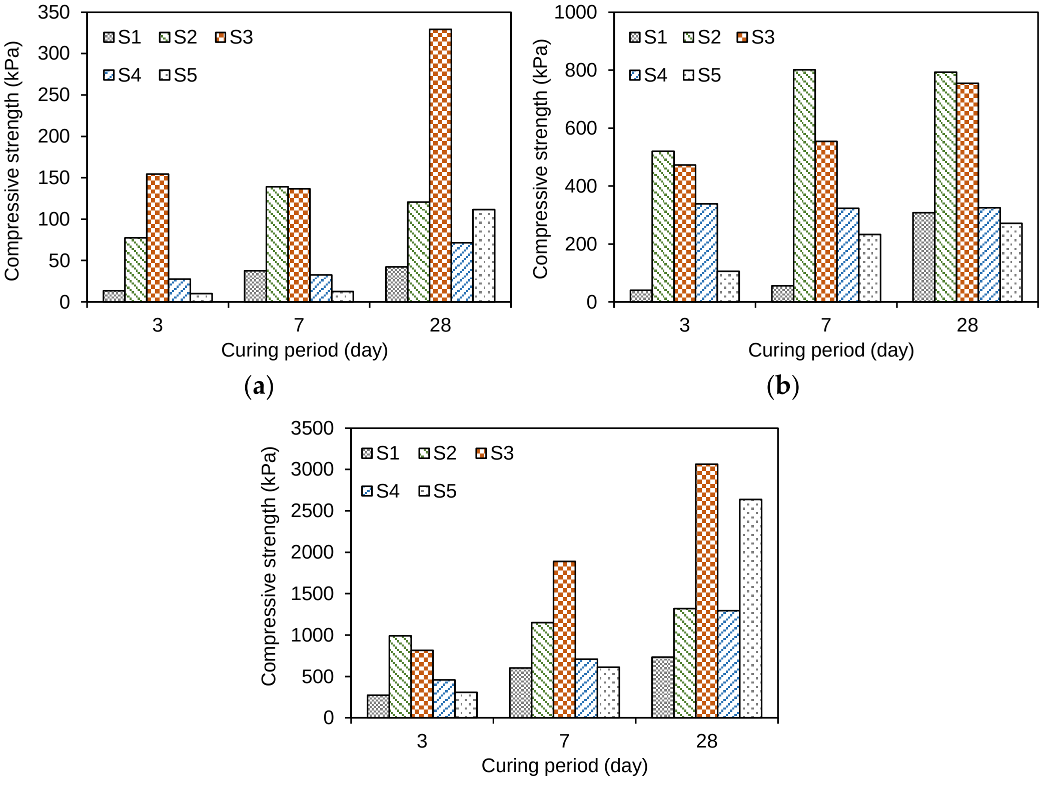
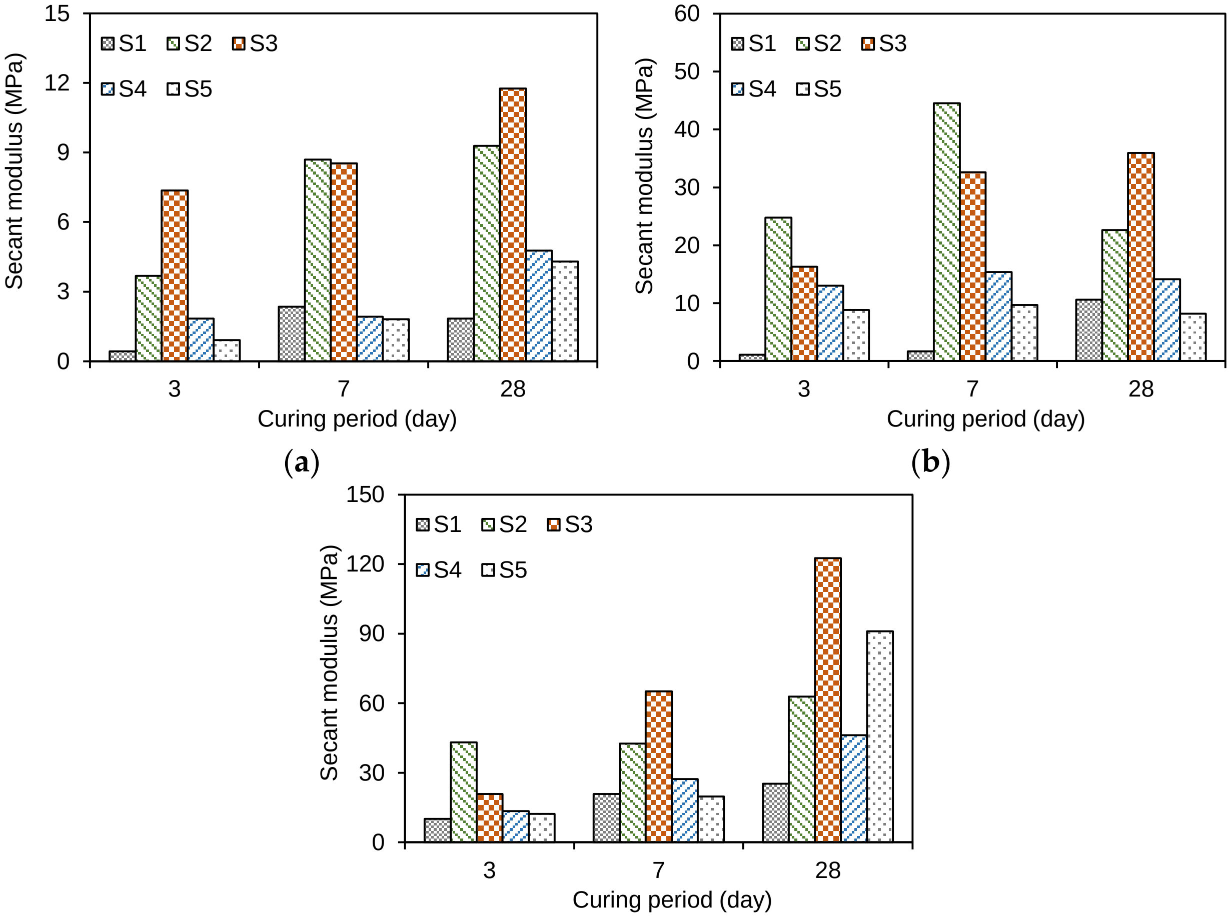


Figure 5. Unconfined compressive strength versus curing period of all treated specimens with three biopolymer contents: (**a**) 1%; (**b**) 3%; (**c**) 5%.

4.3. Stiffness

The secant modulus of elasticity of all treated specimens for the three curing periods is plotted in Figure 6. Overall, the secant modulus significantly increases with the curing period and the biopolymer content. The increased stiffness of the treated specimens indicates electrosteric stabilization of the zein biopolymer, which results in bio-filling between the silt and sand particles [49]. The zein biopolymer improved the cohesiveness of all treated specimens, contributing to an increased secant modulus. The increased stiffness of each specimen can be attributed to the hydrolysis of more amide bonds, which transforms the amide groups in the zein biopolymer into acidic groups [42]. Moreover, this transformation increases zein's tensile characteristics, improving the stiffness of the treated specimen [42,43].



(**a**) (**b**)

(**c**)

Figure 6. Elastic modulus versus curing period of all treated specimens with three biopolymer contents: (**a**) 1%; (**b**) 3%; (**c**) 5%.

The relationships between the unconfined compressive strength and secant modulus of elasticity of the zein-treated specimens are plotted in Figure 7. Generally, the unconfined compressive strength increases linearly with the secant modulus, regardless of the biopolymer content, grain size distribution, and curing period. The conversion of the amide groups to acidic groups in zein during the solvent's dehydration process improves the compressive and tensile strength properties of the treated specimens. Zhang et al. [39] also reported that the transformation of amide groups in zein enhances the stability of the zein biopolymer.

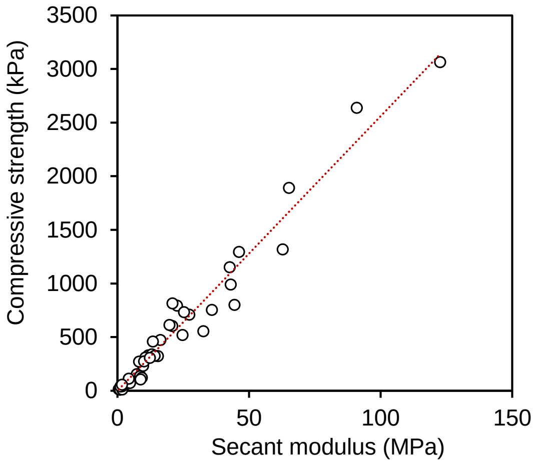


Figure 7. Relation between unconfined compressive strength and elastic modulus of zein-treated specimens.

4.4. *Effect of Gradation*

Understanding the critical parameter that influences the engineering properties of a material is important for a potential application. The relationships between the unconfined compressive strength and coefficient of uniformity of the specimens treated with 3% biopolymer content are plotted in Figure 8. Generally, the unconfined compressive strength increases with the coefficient of uniformity, and the increasing rate of the unconfined compressive strength depends on the curing period. The linear relationship between the obtained unconfined compressive strength (q_u) and the coefficient of uniformity (C_u) can be represented as follows:

$$q_u = \alpha \cdot C_u \quad (1)$$

where α is the slope of the linear relationship. The slope and coefficient of determination of the relationships for the three curing periods are summarized in Table 2. The slope of the linear relationship increases with an increase in the curing period. The relationship demonstrates a significant influence of soil uniformity on the cementation of the zein biopolymer used in this study. It can be inferred that the strength improvement induced by the zein biopolymer can be more effectively applied to specimens with a higher coefficient of uniformity under a longer curing period.

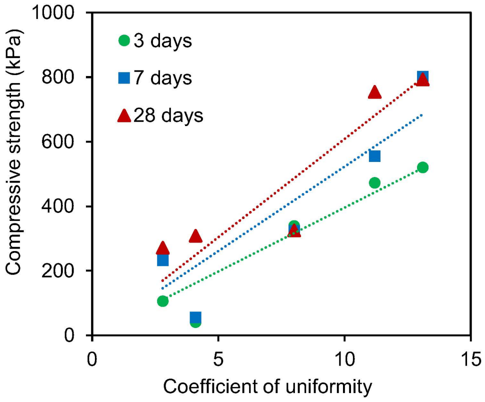


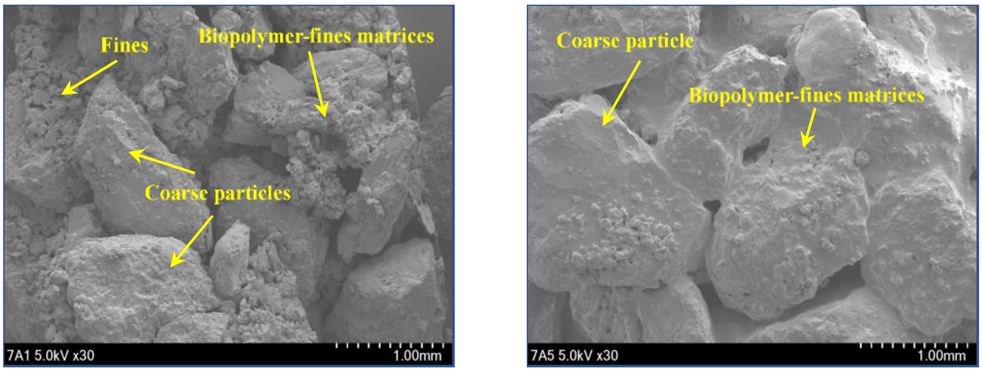
Figure 8. Relation between unconfined compressive strength and coefficient of uniformity of specimens treated with 3% biopolymer content.

Table 2. Slope and coefficient of determination for a linear relation between unconfined compressive strength and coefficient of uniformity of treated specimens with 3% biopolymer content.

Curing Period (Days)	Slope, α	Coefficient of Determination, R^2
3	39.6	0.974
7	52.3	0.949
28	60.8	0.969

4.5. Microscopic Interaction

Scanning electron microscopy images were captured to assess the microscale interaction between zein and soil particles at different biopolymer contents. Micrographs of treated specimens (S1) with two biopolymer contents are shown in Figure 9. The zein biopolymer covers the soils, connecting both fine and coarse particles in the mixture to fill the pore spaces. Figure 9a shows the soil particles in the treated specimen with a biopolymer content of 1%. The zein biopolymer mainly connects the fine particles to cause bio-clogging in the soil mixture. Furthermore, increasing the biopolymer content of the treated specimen enhances the interaction between the fine and coarse particles, as shown in Figure 9b. The microscopic observation demonstrates that a higher biopolymer content leads to a higher elastic modulus and compressive strength of the treated specimen. For the wide grain size distribution and higher dry density of sandy soils, the protein–protein network of the zein biopolymer may significantly enhance the interparticle bonding through electrosteric stabilization. Thus, the strengthening mechanism of the zein-treated specimens can be associated with the cementation effect of the zein biopolymer between the fine and coarse particles in the mixtures.



(**a**) (**b**)

Figure 9. Scanning electron microscopy images of treated specimens with two biopolymer contents: (**a**) 1%; (**b**) 5%.

5. Conclusions

The zein biopolymer is an environmentally friendly material due to the established waste management of maize and the reduced energy consumption and carbon dioxide emissions associated with its production. Establishing the optimized biopolymer binder content to improve soil strength is a critical parameter for potential applications. Therefore, this study investigated the potential of a novel zein biopolymer as a soil binder in geotechnical engineering. The effects of the grain size distribution, biopolymer content, and curing period were evaluated by preparing five sandy soils with different grain size distributions. Each specimen was mixed with varying contents of biopolymer at its maximum dry unit weight. Unconfined compression tests and scanning electron microscopy analyses were conducted to investigate the zein-treated specimens' strength, elastic modulus, and microstructure.

The stress–strain relationships of the treated specimens were analyzed to evaluate the compressive strength of the zein biopolymer. The incorporation of the zein biopolymer changed the soil structure by coating the particle surface with viscous gel. The biopolymer viscous gel filled in the soil voids, which significantly improved the strength and stiffness characteristics of the treated specimens. Furthermore, increasing the biopolymer content steadily enhanced the interparticle bonding in the soil mixtures which improved the compressive strength and elastic modulus. A small amount of zein biopolymer showed marginal strength and stiffness properties with soil specimens. Treated specimens showed little cementation effect at the initial state indicating a low compressive strength. With continuous evaporation of solvent during the curing period, the weak cross-linking between biopolymer and soil increased leading to improve soil stabilization. After curing for 28 days, the specimens with a higher coefficient of uniformity showed higher strength and elastic modulus. The wide grain size distributions of the sandy soils influenced the interparticle bonding of the zein-treated specimens, consequently accelerating the improvement in the compressive strength and the elastic modulus. Scanning electron microscopy images showed interparticle interaction of the zein biopolymer and the soils. The microscopic images demonstrated the performance of the zein biopolymer binder in the soil matrixes. The zein biopolymer mainly connected the fine particles, leading to bio-clogging in the soil mixture. The interaction between the zein biopolymer and fines bridged the coarse particles, thereby enhancing the interaction between the fine and coarse particles at higher biopolymer contents. The cementation of the biopolymer and sand varied with soil gradation. Therefore, the zein biopolymer investigated in this study can be a potential soil stabilizer for coarse and fine soils.

Author Contributions: The study was initiated by Y.-H.B.; Y.-H.B. and Q.O.B. designed the scope of the study. The experiment was performed by Q.O.B. and supervised by Y.-H.B.; Q.O.B. wrote the manuscript draft and Y.-H.B. reviewed the manuscript. All authors have read and agreed to the published version of the manuscript.

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