

# Effect of the acetylation on the water resistance of biopolymer stabilised soil

## Effet de l'acétylation sur la résistance à l'eau des sols stabilisés par des biopolymères

X. Yu\*

*University of Sheffield, Sheffield, UK*

S.J. Armistead

*University of Colorado, Boulder, USA*

J. McGregor, N. Martsinovich, C.C. Smith

*University of Sheffield, Sheffield, UK*

\**xinyuan.yu@sheffield.ac.uk*

**ABSTRACT:** The global soil stabilisation market is forecast to grow to \$35 billion by 2027 driven primarily by infrastructure and construction activities and exacerbated by the increasingly urgent need to adapt to climate change. Naturally sourced biopolymers are a promising low carbon 'green' stabilising agent, achieving higher strength in stabilised soils than cement and at similar cost. However, widespread uptake of biopolymers is impeded by the fact that they typically suffer from (a) poor water resistance and (b) poor resistance to biodegradation over time. This paper presents interim results from a research study into novel biopolymer treatment processes which are applied at or subsequent to the soil/biopolymer mixing stage with the aim of enhancing resistance to water and biodegradation while involving the addition of only small volumes of natural materials. The specific approach described in this paper aims to minimize the interaction of vulnerable hydrophilic functional groups in the biopolymers with water through acetylation, whereby the hydrophilic groups are replaced by natural hydrophobic acetyl groups. Three mixing protocols are proposed and this paper examines the first protocol where the acetylation agents are added at the same time as the biopolymer is added to the soil. While this is the simplest process procedurally, results demonstrate that the strength on wetting is lower than non-acetylated chitosan treated soil. Improved performance is anticipated for the other protocols.

**RÉSUMÉ:** Le marché mondial de la stabilisation des sols devrait atteindre 35 milliards de dollars d'ici 2027, principalement en raison des activités d'infrastructure et de construction, et exacerbé par le besoin de plus en plus urgent de s'adapter au changement climatique. Les biopolymères d'origine naturelle constituent un agent stabilisateur "vert" prometteur, à faible teneur en carbone, qui confère aux sols stabilisés une résistance supérieure à celle du ciment, pour un coût similaire. Cependant, l'adoption généralisée des biopolymères est entravée par le fait qu'ils souffrent généralement (a) d'une faible résistance à l'eau et (b) d'une faible résistance à la biodégradation au fil du temps. Cet article présente les résultats provisoires d'une étude portant sur de nouveaux procédés de traitement des biopolymères appliqués au stade du mélange sol/biopolymère ou ultérieurement, dans le but d'améliorer la résistance à l'eau et à la biodégradation tout en n'impliquant l'ajout que de faibles volumes de matériaux naturels. L'approche spécifique décrite dans cet article vise à minimiser l'interaction des groupes fonctionnels hydrophiles vulnérables des biopolymères avec l'eau par acétylation, les groupes hydrophiles étant remplacés par des groupes acétyles hydrophobes naturels. Trois protocoles de mélange sont proposés et cet article examine le premier protocole dans lequel les agents d'acétylation sont ajoutés en même temps que le biopolymère est ajouté au sol. Bien qu'il s'agisse du processus le plus simple d'un point de vue procédural, les résultats montrent que la force de mouillage est inférieure à celle d'un sol traité au chitosane non acétylé. Des performances améliorées sont attendues pour les autres protocoles.

**Keywords:** Biopolymer; soil stabilisation; chitosan; water resistance.

## 1 INTRODUCTION

The global soil stabilisation market is expected to experience substantial growth, increasing from \$25 billion in 2019 to an estimated \$35 billion by 2027

(Emergen Research, 2020) with soil-chemical stabilisation, anticipated to be the fastest-growing sector. This growth is primarily attributed to heightened infrastructure and construction activities,

further fueled by the urgent imperative to address climate change, flood risk, and rising sea levels.

Despite this growth, there are environmental concerns associated with conventional commonly used chemical additives such as cement and lime. Biopolymers have been advocated as an alternative low-carbon sustainable stabilisation agent (Chang et al., 2020). Existing research has demonstrated that biopolymers can achieve considerable soil strength improvements with low additive dosage compared to traditional stabilisers such as cement or lime, while at similar cost. The potential for biopolymers to naturally degrade over time may also be seen as beneficial for temporary and semi-permanent works (lifetimes of decades), however there is a need to develop robust controls on the degradation process.

Key to this is to address the issues of biodegradation and strength reduction on exposure to water. This paper describes a systematic approach for improving the water/biodegradation resistance of biopolymer stabilised soils and reports initial results from an 18-month UK EPSRC funded research project.

## 2 BIOPOLYMER SOIL STABILISATION AND INFLUENCE OF WATER

Typically, biopolymers are dissolved in water, forming a viscous fluid, before thorough mixing with soil. On drying, the functional groups on the long chain structure can bind with other biopolymer molecules or soil particles giving rise to a significantly improved strength and stiffness after drying. Additions of 1-3% biopolymer by weight have been shown to give rise to strengths exceeding those achieved by e.g. addition of 8-10% of cement (Chang et al., 2015 and Muguda et al., 2017).

Biopolymer stabilisation will significantly depend on the mineralogy of the soil and the properties of the biopolymer involving either direct biopolymer-soil binding or physical coating of soil particles by biopolymer and biopolymer-biopolymer binding.

However some of these binding mechanisms can be weakened/outcompeted by water molecules. Experimental measurements on xanthan gum stabilised soils have previously demonstrated a loss of compressive strength upon exposure to water (Chang et al., 2015, 2020). Biopolymer tensile strength and stiffness can diminish significantly with increased water content (Yakimets et al., 2007). Elsewhere the addition of de-acetylated chitin has been shown to improve the mechanical properties of clay-based soils, however this effect is significantly reduced in the presence of water (Hataf et al., 2018).

## 3 DESIGN APPROACH

The approach described in this paper has been previously described in Smith et al. (2023) and is briefly summarized here. It is hypothesised that the biopolymer functional groups within a stabilised soil which may otherwise preferentially bind to water, can be treated post mixing to negate their vulnerability to water and biodegradation without affecting the soil-biopolymer binding. In this paper the conversion of 'vulnerable' functional groups utilising acetylation is examined.

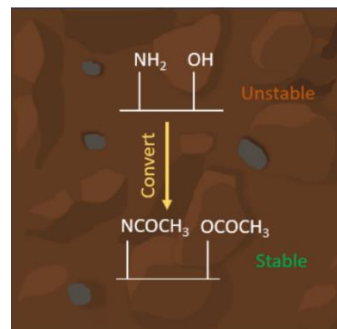


Figure 1. Enhancing biopolymer resistance to water and biodegradation through acetylation (after Smith et al., 2023).

Acetylation is a chemical process that has seen success as a non-toxic and environmentally friendly timber treatment technology (Mantanis, 2017). It involves replacing vulnerable hydrophilic functional groups with natural hydrophobic acetyl groups (shown in Figure 1). Re-acetylation can typically be carried out through the addition of acetic anhydride.

While this paper reports interim results based primarily on macro-geotechnical results from unconfined compression tests, and initial FTIR studies, additional studies will be carried out using XRD, GPC, zeta potential, TGA, and SEM to identify and characterize the binding and chemical reactions that occur.

Treatments agents will include various acetylation agents. In the wider project, three treatment protocols will be investigated:

1. Acetylation of the dissolved biopolymer immediately prior to soil mixing.
2. Mixing of the dissolved biopolymer with the soil followed by acetylation but prior to sample curing.
3. Mixing of the dissolved biopolymer with the soil followed by acetylation after sample curing.

It is anticipated that better performance will be seen in Protocols 2 and 3, however these will be more complex to apply in the field. This paper reports results from the evaluation of Protocol 1.

## 4 EXPERIMENTAL STUDY

### 4.1 Materials

Silica sand sourced from Cheshire, UK was purchased from Minerals Marketing Ltd, and was chosen for its local abundance. The particle sizes ranged between 0.06-0.5mm and the chemical composition is listed in Table 1.

Table 1. Chemical composition of soils.

Chemical composition	Typical (%)
SiO <sub>2</sub>	94.68
Fe <sub>2</sub> O <sub>3</sub>	0.28
Al <sub>2</sub> O <sub>3</sub>	2.52
K <sub>2</sub> O	1.47
LOI	0.24

Chitosan biopolymer was utilised for the current study. Chitosan was selected due to its significant strengthening potential in soil stabilisation (Hataf et al., 2018; Adamczuk and Jozefaciuk, 2022), and its production route via de-acetylation of chitin, a material used by insects and crustaceans for exoskeletons and which has inherent water resistant properties. Chitin itself is a significant bi-product of the food industry. It is hypothesised that re-acetylation of chitosan, post soil treatment, will revert chemical bonds unused for soil binding to the chitin form and benefit from its associated properties such as high stability. The chitosan used in the study was purchased from Acros Organics, having a molecular weight ranging from 100000-300000 Da.

### 4.2 Sample preparation

The sample preparation process was divided into four stages: 1) preparation of the chitosan solution; 2) addition of the acetylation agent; 3) mixing with soils; 4) compaction into cylindrical specimen for testing.

Chitosan itself is insoluble in water, therefore the chitosan solution was prepared by dissolving chitosan powder in a 0.1M aqueous acetic acid solution. Following this, the acetylation agents were mixed in after a period of 5 minutes followed by mixing with the soils. 50 grams of final soil-biopolymer mixture was compacted into 38 mm diameter cylindrical hollow mould by a tamper to produce final specimens of 38 mm diameter and 25 mm height for testing. The samples were then cured by air drying in the laboratory over a 24 hour period at an average relative humidity of 50% and average temperature of 20°C.

Initial test sets utilised 25 mm height specimens to permit greater throughput of samples for parametric studies while providing semi-quantitative data.

Verification of identified optimal treatment processes will be undertaken with 76 mm height samples in the future.

The chitosan to soils ratio was set at 1% by mass. The control test involved 1% chitosan treated soils without any acetylation agent ('1%CS'). Two different acetylation approaches were involved in the study: (a) '1%CS-MeOH-Ac<sub>2</sub>O': the addition of methanol (MeOH) with acetic anhydride (Ac<sub>2</sub>O), allowing acetyl groups to replace only the amino groups on the chitosan chain (Lavertu et al., 2012). This method is a common way to transform the structure of chitosan into chitin; (b) '1%CS-Ac<sub>2</sub>O': the addition of Ac<sub>2</sub>O alone for uncontrolled acetylation.

### 4.3 Test program

The test programme was designed to assess the mechanical behaviour, water resistance and mechanical recovery after wetting of chitosan treated specimens following different treatments.

The mechanical behaviour of specimens was primarily evaluated through unconfined compression testing using a loading rate of 0.2 mm/min.

Water resistance was gauged through a simple water immersion test. The initial tests reported here utilised a two-hour immersion as an initial indicator of behaviours following water exposure. Specimens then underwent unconfined compression testing directly after the 2-hour immersion. Additionally, specimens subjected to a 2-hour wetting immersion followed by curing were tested to further assess their ability to recover mechanical properties post-wetting.

## 5 INITIAL RESULTS

### 5.1 Mechanical behaviours under dry condition

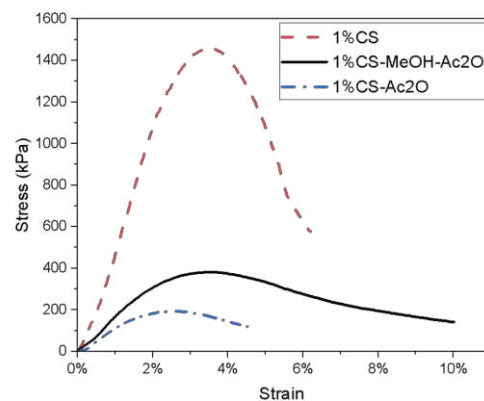


Figure 2. Stress-strain curves of 1% chitosan treated soil following 24 hours curing.

Figure 2 illustrates the stress-strain curves for specimens treated using the two reacetylation approaches following curing. The current reacetylation processes appear to reduce the strength of chitosan-treated soils, but this reduction is partly mitigated by approach (a) with the inclusion of methanol. This phenomenon could be attributed to the introduction of inactive acetyl groups, which may weaken the interactions between the biopolymer and the soil particles.

## 5.2 Water resistance

To assess water resistance, samples were immersed in water for 2 hours, and the results are shown in Figure 3. Both the 1%CS and 1%CS-MeOH-Ac2O specimens retained their shape in water, while the 1%CS-Ac2O specimen disintegrated. The resilience of 1%CS in water within the initial 2 hours can be attributed to the low solubility of chitosan, which only dissolves under acidic conditions. In contrast, the 1%CS-MeOH-Ac2O specimen absorbed a significant amount of water, behaving like a soft clay. While this reacetylation approach for this specimen should revert chitosan back to chitin, it may lead to randomly distributed acetyl groups (Gatto et al., 2019) that could lead to different characteristics compared to the original chitin, such as water absorbancy.

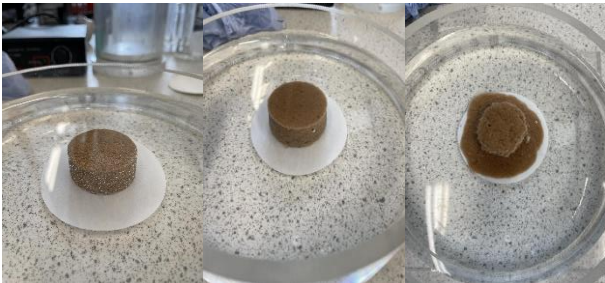


Figure 3. Specimens after two-hour water immersion test (a) 1%CS; (b) 1%CS-MeOH-Ac2O; (c) 1%CS-Ac2O.

Figure 4 presents a comparison of the unconfined compressive stress-strain responses of specimens after curing, wetting for 2 hours by immersion in a water bath, or wetting for 2 hours followed by a further curing stage. Both 1%CS and 1%CS-MeOH-Ac2O exhibit the ability to closely recover their stress-strain response after a single wetting and drying cycle. However, the failure modes of 1%CS and 1%CS-MeOH-Ac2O differ significantly as illustrated in Figure 5. While 1%CS experiences a compressive shear failure indicative of a peak material strength, 1%CS-MeOH-Ac2O displays a bulging response similar to a soft clay.

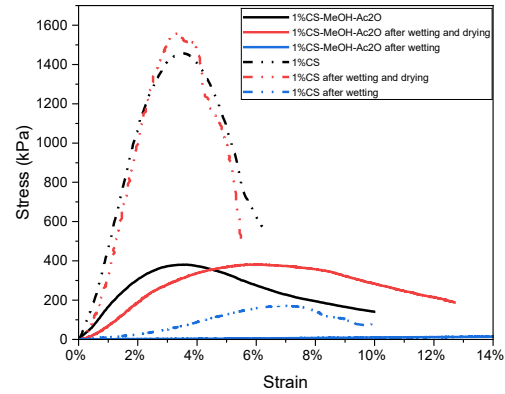


Figure 4. Stress-strain curve of specimen after drying, 2h wetting, 2h wetting and drying.



Figure 5. Failure mode of specimen after wetting (a) 1%CS; (b) 1%CS-MeOH-Ac2O.

## 6 DISCUSSION

FTIR results on pure re-acetylated chitosan samples have indicated the introduction of acetyl groups within the chitosan structure, and thus that the process appears to be able to regenerate the chitin structure (though with possible defects, Siripanich, 2023); however, the current mechanical testing indicates that it falls short of replicating certain anticipated properties. Notably, the water absorption ability increases, and the texture becomes softer upon exposure to water.

The initial re-acetylation methodology (Protocol 1) reported in this paper, while simple in operation suffers from the disadvantage that all agents are mixed together and that the reacetylation process may occur more rapidly than soil/biopolymer or biopolymer/biopolymer binding thus reducing strength gains. Further work will focus on the other staged protocols that provide more time for binding to develop before acetylation treatment.



## 7 CONCLUSIONS

The transformation of 'vulnerable' hydrophilic functional groups within a biopolymer through acetylation is hypothesised to hold significant promise in augmenting the biopolymer's resistance to both biodegradation and water. Three protocols are proposed:

1. Acetylation of the dissolved biopolymer immediately prior to soil mixing.
2. Mixing of the dissolved biopolymer with the soil followed by acetylation prior to sample curing.
3. Mixing of the dissolved biopolymer with the soil followed by acetylation after sample curing.

Results from initial studies on chitosan treated sandy soils reported in this paper focused on Protocol 1. While this is the simplest protocol operationally, the results were negative and indicated that while samples can retain their integrity on wetting they do not maintain their strength. On drying the strength characteristics are recovered. It is hypothesised that re-acetylation process may occur more rapidly than soil/biopolymer or biopolymer/biopolymer binding thus reducing strength gains. Further studies will investigate Protocols 1 and 2 which are anticipated to provide improved performance.

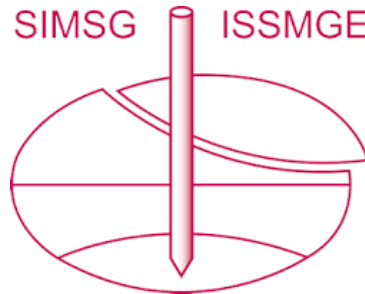
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