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# The potential use of chitosan as a biopolymer additive for enhanced mechanical properties and water resistance of earthen construction

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## HIGHLIGHTS

- Chitosan successfully improved the engineering behavior of earthen construction.
- Coating with 0.5% chitosan solution protected earthen materials from water erosion.
- Earthen material with 1%–3% chitosan admixture had high water erosion resistance.
- Samples with 3% chitosan admixture showed improved mechanical properties.

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## ABSTRACT

The study investigates the feasibility of using chitosan biopolymer as an admixture, or as an external coating, for earthen constructions to improve their resistance in two components: water induced degradation and key mechanical properties. The resistance to water induced degradation was evaluated in terms of contact angle and drip erosion tests, while the influence on mechanical properties was measured through compressive, tensile and three-point bending tests. The results indicate that the use of low concentrations of chitosan can improve significantly the performance in the two components and therefore was found to be a promising treatment for new or existing construction.



## 1. Introduction

Earth has been used as a construction material since ancient times to build houses, archaeological, and historical monuments over the world. It is estimated that approximately 30% of the world population live in unreinforced earthen houses located principally in developing countries primarily due to economic considerations [1]. In recent years the use of earthen construction has seen an increase in popularity as an eco-friendly sustainable architectural approach. Its ability to be recycled indefinitely and aesthetic benefits have resulted in increased popularity of earth architecture with many museums, embassies, and other building types made of earth [2–4]. Additional benefits of building with earth, beyond economic considerations, include low ecological impact due to reduced greenhouse gas emissions during construction [2] as well as facilities with good thermal and acoustic behavior [5].

Different techniques have been reported for earthen construction primarily depending on the region of the world where it is used. According to [1], earthen construction techniques can be divided into three main groups: structure, monolithic and brickwork. Rammed earth walls (monolithic) and adobe masonry (brickwork) are the most widespread methods. As an example, in Peru, 34% of the houses are built with these two techniques [6].

Unfortunately earthen buildings can have some disadvantages. From a mechanical perspective, they are usually heavy, brittle, and present low tensile resistance which makes them especially vulnerable to seismic events [7]. For example, as shown in Fig. 1a, after the 2003 earthquake of Bam, Iran, historical earthen buildings were severely damaged [8]. Another negative aspect to consider

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when dealing with this material is its hydrophilic and porous nature making buildings vulnerable to erosion and severe degradation upon water exposure [9]. As shown in Fig. 1b, rising damp and rain penetration can severely affect the exposed structural elements reducing their strength and affecting the structural stability [10]. Finally, it has also been reported that earthen buildings can be susceptible to extensive cracking, due to drying and desiccation, which not only affects the structural performance of the earthen building but also provides an attractive habitat for insects and fungus that can pose a serious health risk to the inhabitants since they may transmit diseases. For example, millions of human deaths has been reported in Central and South America due to the Chagas disease transmitted by Triatomine bugs that are often found inside cracks in adobe walls as shown in Fig. 1c [11].

The improvement of the mechanical properties of earthen constructions has been the subject of study by many research groups using various approaches. Several studies have focused their attention on improving the mechanical properties of earthen constructions using additives applied during material fabrication. For example, notable increases in the compressive strength of adobe blocks (more than 80%) were reported when two types of polymeric agents (cationic amine and emulsified asphalt) were added as solutions during the mixture process [12]. This same study reported a reduction of the levels of water absorption of the treated adobe blocks from 80% (percentage by weight) to 10%. Other authors recommended the use of emulsified asphalt for the stabilization of soil in earthen construction with high silt content [13]. Another popular approach to improve mechanical properties of earthen constructions has involved the inclusion of synthetic or natural fibers. Quagliarini et al. [14] successfully showed how the inclusion of fibers may contribute to control the plastic behavior of earthen blocks and to prevent cracking due to shrinkage in the drying process. Aymerich et al. [15] also reported the benefit of increased capacity for energy absorption when wool fibers were added to earthen materials. The use of polymeric fibers for the fabrication of compressed earth blocks also evidenced positive influence in the increment of the compressive and flexural strength up to 22.5% and 22%, respectively [16]. The same study reported that the addition of these fibers also allowed reaching considerable levels of deformation compared to unreinforced specimens.

The literature review also revealed several studies that have explored solutions to improve the durability of earthen materials to water degradation. Most of the studies report the use of stabilizers for enhancing the durability of these types of materials. As summarized by [17], different types of additives such as lime, pozzolan, cement, biopolymers (e.g., tuna cactus mucilage, nopal and agave cactuses; linseed and cooking oils; seaweeds fibers, etc.), and mineral composites have been successfully used for the protection of earthen construction materials against rainfall erosion.

The focus of this paper is on the use of the biopolymer chitosan to enhance mechanical and water durability properties of earthen materials. A review of the literature on modification of earthen construction using biopolymers revealed some preliminary applications using a few types of biopolymers but not chitosan. For example [18] used alginate for modifying the mechanical behavior of fiber treated adobe blocks and the results showed that its addition can improve the flexural and compressive strength of the final product. Another biopolymer reported in the literature for the improvement of water resistance of earthen construction materials is the cactus mucilage, which according to several studies [19–21] has positive effects on the water protection and conservation of earthen constructions.

The research presented in this paper investigated the use of chitosan for the modification and improvement of earthen construction materials such as rammed earth and adobe blocks. Chitosan is a biopolymer composed of 2-amino-2-deoxy-D-glucose and 2-acetamido-2-deoxy-D-glucose units linked through β-(1 → 4) bonds and it is derived from alkaline deacetylation of chitin, one of the most abundant natural polysaccharides. The chemical structure of chitosan is shown in Fig. 2. Due to its high percentage of nitrogen (around 6.89%), chitosan is of commercial interest compared to synthetically substituted cellulose (1.25%) [22]. Another attractive feature of chitosan is its low cost as it usually is obtained from discarded crab and shrimp wastes processed from canning industries or from crustacean shells obtained from the food industry [22]. Chitosan has attracted attention as a material and potential additive due to its proven advantageous properties such as biodegradability, antibacterial activity, non-toxicity and high charge density [23]. Due to its polymeric and chemical nature it has been used for surface modification of materials such as textiles, films and others, transferring its functionalities and properties [24–26].

For this work different solutions of chitosan biopolymer were used either as an additive introduced during the fabrication process of new earthen specimens or as an external coating applied to existing earthen materials. The effect of chitosan biopolymer treatment on earthen materials focused on evaluating: i) susceptibility to water induced degradation, and ii) mechanical properties. The susceptibility to water induced degradation was evaluated in terms of sessile drop contact angle measurements and drip erosion tests. The influence of chitosan biopolymer treatments on the mechanical properties of earthen materials was measured through an experimental program designed to assess the compressive, tensile and flexural behavior of the treated and untreated earthen


**Fig. 1.** Typical problems of earthen houses: (a) earthen structure after the 2003 Bam earthquake [8]; (b) adobe wall eroded by water (http://emeraldcut.blogspot.pe/2015/10/nevada-fort-churchill-state-park.html); and (c) Triatomine bug living in an earthen wall and carrying the parasite that causes Chagas disease (http://archivo.elsalvador.com/).

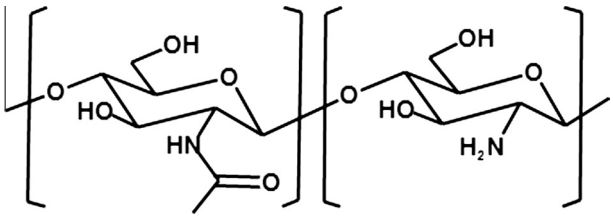


**Fig. 2.** Chitosan chemical structure.

material samples. The following sections describe the experimental study and results.

## 2. Materials

### 2.1. Chitosan biopolymer

The chitosan biopolymer used in this study was purchased from Sigma-Aldrich Corporation. Chitosan has low solubility and is a high viscosity substance. The molecular weight of the chitosan, measured by means of a capillary viscometry, was 1370 kDa. The chitosan used in this study had a degree of deacetylation of 65%, therefore still has remaining 35% of non-free amino groups in its structure provoking low levels of solubility and high levels of viscosity when dissolved in a 1% of acetic acid solution [27]. For this experimental study, several concentrations of an aqueous acidic chitosan solution were used for the treatment of the earthen materials. The different concentrations of the chitosan admixtures were prepared in all cases by dissolving a predetermined mass of chitosan in a 1% (volume to volume) acetic acid solution. The concentrations of chitosan used in this study ranged from 0.5% to 3% mass to volume, which correspond to a range of 5–30 mg of chitosan per liter of the 1% acetic acid solution. The two main solutions investigated are termed Solutions A and B which corresponded to concentrations of chitosan of 0.5% and 3% of chitosan in the 1% acetic acid solution, respectively.

### 2.2. Base soil used for fabrication of earthen materials

Soils used for earthen construction can have a high variability in terms of particle size gradation, chemical composition, mineralogy, and others [30]. To a great extent, the soil characteristics and properties will depend on the available local soil sources of the area where the earthen materials are fabricated. For the present study the base soil was selected to represent a typical Peruvian coastal region soil that is commonly used for fabrication of adobe bricks for building earthen houses in the rural areas near Lima. The following subsections describe in more detail the base soil used in this study.

#### 2.2.1. Gradation and index properties of the base soil

The base soil was a dark brown, low plastic silty clay with sand and some traces of fine gravel. The grain size distribution curve of the base soil was obtained by means of sieve analysis coupled with hydrometer testing carried out in general accordance with ASTM D2487 [28]. The gradation curve for the base soil is shown in Fig. 3. As shown in this gradation curve the base soil has 1% by weight of gravel sizes, 20% of sand content, 43% of silt sizes, and 36% of clay content based on soil particle size ranges recommended in ASTM Standard D422 [29]. Typically adobe construction uses base soils with different proportions of sand, silt and clay that can vary widely based on local experience and available soil sources. For example

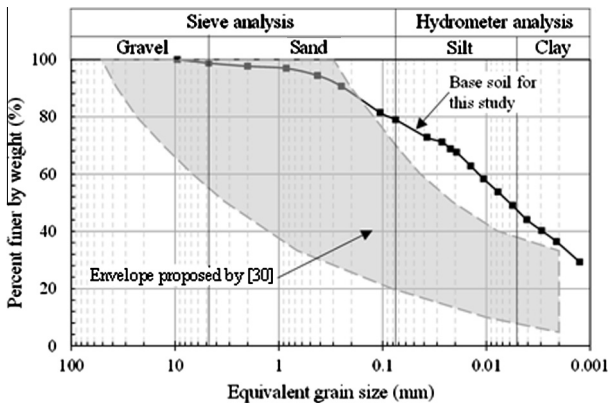


**Fig. 3.** Grain size distribution of base soil.

Jimenez Delgado and Guerrero [30] after reviewing a wide range of adobe bricks around the world suggested that most base soils used for the adobe fabrication fell within the range of the grain size distributions shown as a shaded grey area in Fig. 3. It can be seen that the base soil used in this study is slightly outside the range of gradation curves reported by Jimenez Delgado and Guerrero [30], however this is not a concern as this range is not a requirement but rather the range that corresponds to the database of adobe projects they compiled in that study.

The Atterberg plastic and liquid limits of the base soil were found to be 17% and 33%, respectively. These limits correspond to a low plastic clay. Based on the gradation curve and Atterberg limits the base soil was therefore classified as low plastic clay (CL) as per the Unified Soil Classification System [28].

#### 2.2.2. X-ray fluorescence tests on the base soil

The X-ray fluorescence testing (XRF) of the base soil was carried out using a portable X-ray fluorescence spectrometer model Bruker Tracer III-SD which was equipped with a rhodium tube under vacuum mode at 40 kV and 10.3 mA to delimit the main elements. XRF tests were performed on a small soil sample that was first manually ground with an agate mortar and then pelletized. Pellets were produced using a 13 mm die under a uniaxial load of 10 tons sustained for 5 min to obtain dense samples. The resulting XRF spectrum is shown in Fig. 4(a). The XRF results provide evidence of the presence of Al, Si, P, S, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Pb. The most abundant elements are Fe, Ca, Sr, Ti and Si. Small quantities of Ni, Mn, P and Cu were detected below the levels where exact amount can be quantified and thus were labeled as present as trace elements. Due to the equipment parameters, the presence of the following elements, typically present in most soils, cannot be discarded (light elements): H, C, N, O, F, Na and Mg.

#### 2.2.3. X-ray powder diffraction tests on the base soil

The X-ray powder diffraction test (XRPD) was performed on the ground, dry base soil using a Bruker D8 XRD device. XRPD data was collected for phase angles (2θ) ranging between 5° and 80°, with a 0.02° step and an integration time of 4 s. The identification of the different crystalline phases was carried out using the X'Pert High Score 2.0 software from Philips Analytical with the PDF-2 database. Only the elements previously detected using XRF and all light elements not detected by the instrument (H to Mg) were used for the identification. The XRPD pattern together with the identification of the main peaks are shown in Fig. 4(b).

Table 1 summarizes the main minerals detected with the XRPD test and also compares the results (wt%) with values reported in the literature similar adobe materials from other regions of the world. Mineral quantification was carried out by the Rietveld method using GSAS software [31] and the EXPGUI interface [32]. The base soil seems to be a granitoid in which the main phases are quartz, an albite/anorthite mixture (feldspar) and muscovite (mica). It also contains a small portion of an amphibole and chlorite minerals (clinochlore and vermiculite, a degraded chlorite). Minor phases such as calcite and orthoclase were also identified. Due to the complex mixture present and the preferred orientations found in some minerals, mass percentages should be considered as approximate. Muscovite, for example, might be overestimated due to its strong (0 0 1) preferred orientation.

## 3. Experimental program

The experimental program involved investigating the influence that the use of a chitosan biopolymer had on earthen materials in the following two aspects: i) susceptibility to water induced degradation, and ii) mechanical properties. The chitosan biopolymer solutions were applied in two different manners. One as an admixture that was added during the fabrication of the earthen material samples and the second mode of application was as an external coating that was applied to the outside surface of an existing earthen material sample. The following subsections describe the test procedures used for the assessment of these two components. Results and discussions are presented in Section 4.

### 3.1. Evaluation of susceptibility to water induced degradation

As mentioned earlier, earthen-based construction materials are hydrophilic and porous, thus present low durability when exposed to water. For example [37] reported significant erosion of adobe walls when exposed to rainfall. Permeability issues need also to be addressed because water penetration and moisture entrapped inside may adversely affect the aesthetic, biological, and structural performance of earthen buildings, e.g., efflorescence, mildew, and freeze/thaw damage [38]. The susceptibility to water induced degradation was quantified in this study using two indicators,

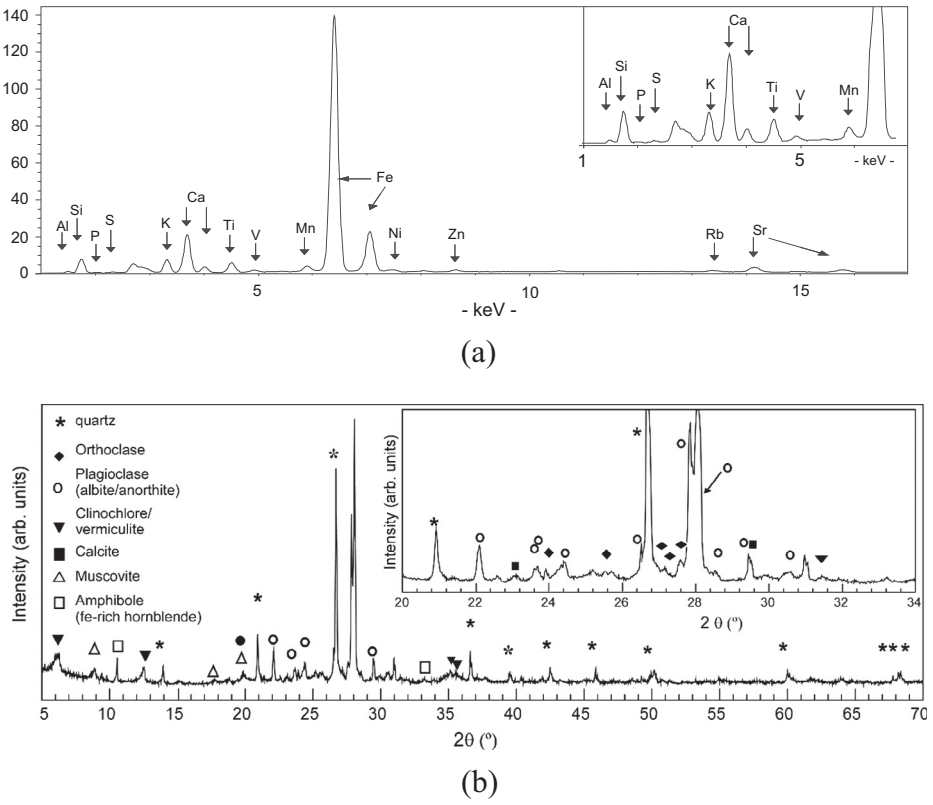


**Fig. 4.** Chemical and mineralogical analyses of base soil: (a) X-ray Fluorescence spectrum and (b) X-ray powder diffraction pattern.

**Table 1**
Mineral composition of some soils used for adobe building blocks compared to base soil analyzed in this study.

| Main mineral | | | | Mineral amount (wt %) Reference | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | [33] | [34] | [35] | [36][a] | This study |
| Phyllosilicates | Muscovite-illite ($K_{1-x}Na_x$)($Al_{1-x-y}Mg_xFe_y$)$_2$($Si_3Al$)$O_{10}$(OH)$_2$ | | | 15(2) | – | 14 | – | 32(3) |
| | Kaolinite ($Al_2Si_2O_5(OH)_4$) | | | – | 30 | 45 | X | – |
| | Clinochlore/vermiculite (($Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$)/($Mg,Fe^{+2},Fe^{+3}$)$_3$[($Si,Al)_4O_{10}$](OH)$_2$·$4H_2O$ | | | – | – | – | – | 4(2)/2(1) |
| | Fe-rich magnesiohornblende ($Ca_2(Mg,Fe^{+2})_4Al(Si_7Al)O_{22}(OH)_2$) | | | – | – | – | – | 1.0(1) |
| | Talc ($CaSO_4·2H_2O$) | | | 6(1) | – | – | – | – |
| Tectosilicates | Quartz ($SiO_2$) | | | 13(3) | 65 | 23 | X | 32(2) |
| | Feldspars | Potassium | (Microcline) | 6(1) | (2) [c] | – | – | – |
| | | | (Sanidine) | 24(3) | | – | – | – |
| | | | (Orthoclase) | – | – | – | – | 5(1) |
| | | Plagioclase | (Albite) | – | – | – | – | 21(4) |
| | | | (anorthite) | – | – | – | – | |
| Non silicate minerals | Brushite ($CaHPO_4·2H_2O$) | | | 11(1) | – | – | – | – |
| | Indigirite ($Mg_2Al_2(CO_3)_4(OH)_2·15H_2O$) | | | 4(1) | – | – | – | – |
| | Calcite ($CaCO_3$) | | | 6.3(6) | – | 4 | – | 3(1) |
| | Goethite (FeO(OH)) | | | – | 2 | 7 | X | – |
| | Gibbsite ($Al(OH)_3$) | | | – | – | – | X | – |
| | Magnetite ($Fe_3O_4$) | | | – | – | – | – | [b] |

*Notes:*
[ ] Numbers in brackets indicate references.
[a] Amounts were not quantified in the original paper (X denotes presence of mineral).
[b] Soil sample slightly magnetic so magnetite presumed to exist but not detected in the XRPD test.
[c] Data given as "potassium feldspar", without specifying the exact mineral.

namely the water contact angle and performance of samples in drip erosion tests.

### 3.1.1. Contact angle and drip erosion tests

The wettability of porous materials is often assessed using contact angles measured using the sessile drop method [39]. The contact angle in this test method is defined as the angle formed by the liquid from the sessile drop and the surface of the material (see Fig. 5a). Materials with contact angles less than 90° are considered to have high wettability, while contact angles above 90° correspond to materials with low wettability [39]. For this study, the contact angle was measured from digital photographs taken with

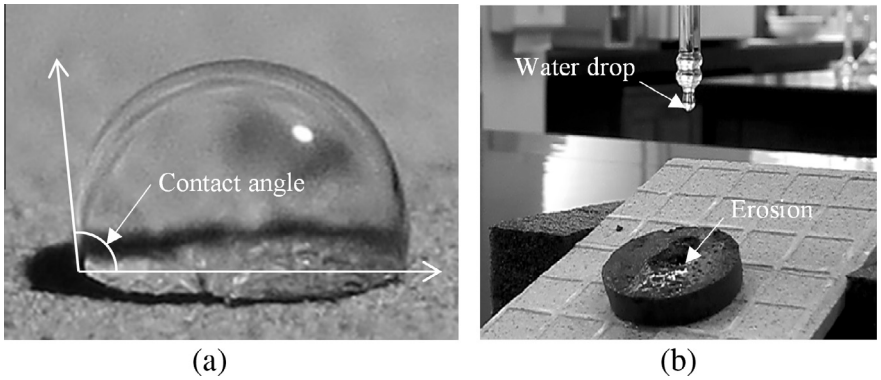


**Fig. 5.** Assessment of water induced degradation: (a) contact angle test; and (b) drip erosion test (the needle position is only referential for illustration purposes; the height in all tests was of 1 m).

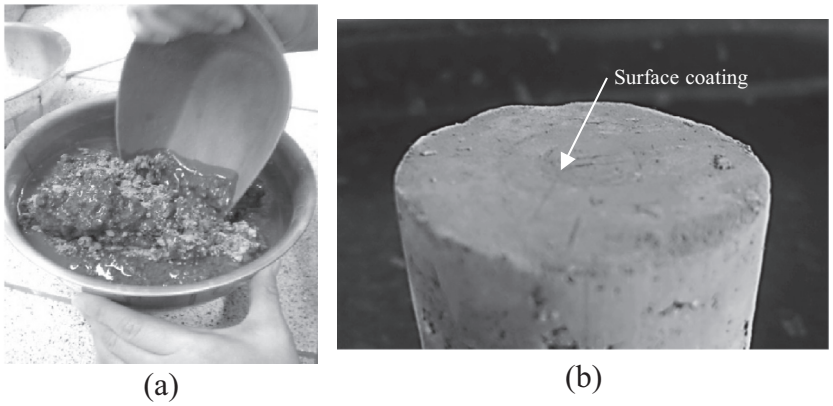


**Fig. 6.** Preparation of specimens for water induced degradation tests: (a) hand mixing process; and (b) cylindrical specimen with surface coating of chitosan biopolymer.

appropriate light contrast immediately after a 10 μL drop of distilled water was deposited on top of the earth surface using a micro-syringe.

The second test used to assess the susceptibility to water induced degradation was the drip erosion test. These tests were carried out in general accordance with recommendations from the AENOR Spanish standard [40] and the Australian standard described in [41]. This test entails placing a sample on a surface inclined at an angle of 27° with respect to the horizontal. The specimen is then subjected to water drops released from a point exactly 1 m above the center of the test specimen. The drops are released at a rate of 50 mL per minute. A photo of the test is shown in Fig. 5 (b). In this test, the time elapsed was measured up to a maximum exposure time of 10 min or until the test specimen reached a state of significant erosional damage, whichever occurred earlier.

*3.1.2. Sample preparation and water induced degradation assessment test program*

The base soil, described earlier, was first sieved using the sieve No. 4 (opening = 4.75 mm) to remove any gravel size particles. The earthen material samples were then prepared manually by mixing the base soil with either water or with chitosan biopolymer solutions. The samples prepared with water used a base soil to water ratio of about 4:1 by weight (i.e., 20% of the total sample weight was water). This ratio is based on local practice to ensure adequate workability. The earthen samples prepared using chitosan solutions as the liquid during mixture preparation used a base soil to chitosan solution ratio by weight of about 3:1 (i.e., about 25% of the total weight of the sample corresponded to the chitosan solution). The higher amount of liquid in the earthen sample mixtures that used chitosan solution was found to be necessary to achieve a similar consistency and workability to the control samples that only used water. This was attributed to the high levels of viscosity of the aqueous acidic chitosan solutions. The earthen sample preparation involved thorough hand mixing of the base soil and water, or the base soil and aqueous chitosan solution, using a metal trowel for a period of about five minutes until a homogeneous mixture was achieved (Fig. 6a). The earthen mixture was then placed inside a cylindrical mold and air cured for a period of about 7 days in a controlled environment at a 60% relative humidity and a temperature of 20 °C. The cylindrical earthen specimens used for the erosion tests had a diameter of 55 mm and a height of 10 mm (Fig. 6b).

The samples with chitosan biopolymer solutions involved primarily two concentrations: i) Solution A prepared at a concentration 0.5% mass to volume ratio of chitosan to 1% acetic acid solution; and ii) Solution B corresponding to a concentration of 3% mass to volume ratio of chitosan to 1% acetic acid solution. However, after a first round of tests, two additional solutions with concentrations of 1% (Solution C*) and 2% (Solution D*) were added to the test program to determine the minimum concentration of biopolymer to provide an effective protection to the specimens. The test matrix of the water induced degradation component of this study is shown in Table 2.

The contact angle and erosion tests were carried out on earthen samples treated with chitosan in two different ways. The first one consisted on applying the biopolymer as a surface coating that was applied by briefly dipping one face of the untreated earthen

**Table 2**
Test matrix for the water induced degradation experimental component.

| Test type | Sample type | Description | N° of specimens |
|---|---|---|---|
| Contact angle | Control sample | Mixture proportion 4:1 (earth/water) | 1 |
| | Surface coating | Solution concentration: Solution A, Solution B, Solution C*, Solution D* | 3 for each solution |
| | Admixture | Solution concentration: Solution A Mixture proportion 3:1 (earth/solution) | 1 |
| | Admixture | Solution concentration: Solution B, Solution C* and Solution D* Mixture proportion 3:1 (earth/solution) | 3 for each solution |
| Drip erosion | Control sample | Mixture proportion 4:1 (earth/water) | 1 |
| | Surface coating | Solution concentration: Solution A, Solution B, Solution C*, Solution D* | 3 for each solution |
| | Admixture | Solution concentration: Solution A, Solution B, Solution C* and Solution D* Mixture proportion 3:1 (earth/solution) | 3 for each solution |

*Notes:* Mixture proportions correspond to dry base soil to liquid ratios by weight.
Solution A: 0.5% mass to volume ratio of chitosan to 1% acetic acid solution.
Solution B: 3% mass to volume ratio of chitosan to 1% acetic acid solution.
Solution C*: 1% mass to volume ratio of chitosan to 1% acetic acid solution.
Solution D*: 2% mass to volume ratio of chitosan to 1% acetic acid solution.

specimen into the corresponding chitosan solution to completely wet its surface. The increase of sample weight after this procedure was minimum and estimated to be between 0.5% and 1%. The other technique consisted in preparing the earthen material by mixing the dry base soil and the corresponding chitosan solution. In both the contact angle and drip erosion tests, untreated control samples were included to properly assess the influence of the chitosan biopolymer treatment.

### 3.2. Evaluation of influence on mechanical behavior

#### 3.2.1. Mechanical behavior testing

The influence of the chitosan additives on the mechanical properties of earthen specimens was evaluated through compression, split, and three point bending tests. Schematic drawings of these three mechanical tests are shown in Fig. 7. All mechanical tests were carried out as displacement controlled with a constant displacement rate of 1.27 mm per minute. For the uniaxial compression tests, a fine sand layer was placed on both ends of the cylindrical specimens to help reduce friction end effects and to minimize stress concentrations as per suggestions made by [42]. Displacements for all mechanical tests were recorded using a calibrated Linear Variable Differential Transducer (LVDT).

#### 3.2.2. Sample preparation and mechanical behavior assessment test program

Samples for mechanical testing were prepared using a procedure similar to the one used for fabricating the specimens for the erosion tests. The dry base soil was first sieved through a sieve No. 4 (opening of 4.75 mm) to remove any fine gravel sizes. All samples were manually mixed with a metal trowel for about five minutes, using either water or chitosan solution, until a homogeneous mixture was obtained and then placed in one of the different formworks shown in Fig. 8. Samples prepared with water represented the control reference for the samples prepared with chitosan as the admixture. The dry base soil to liquid proportions were the same as described before, i.e., about 4:1 by weight for the control samples prepared with water and about 3:1 by weight for the samples prepared using the chitosan solution as the liquid during mixture preparation. For compression and split tests, cylindrical specimens of 34 mm diameter and 71 mm of height were fabricated (Fig. 8a). The three-point bending tests involved prismatic beam samples with a cross section of 42 mm by 44 mm

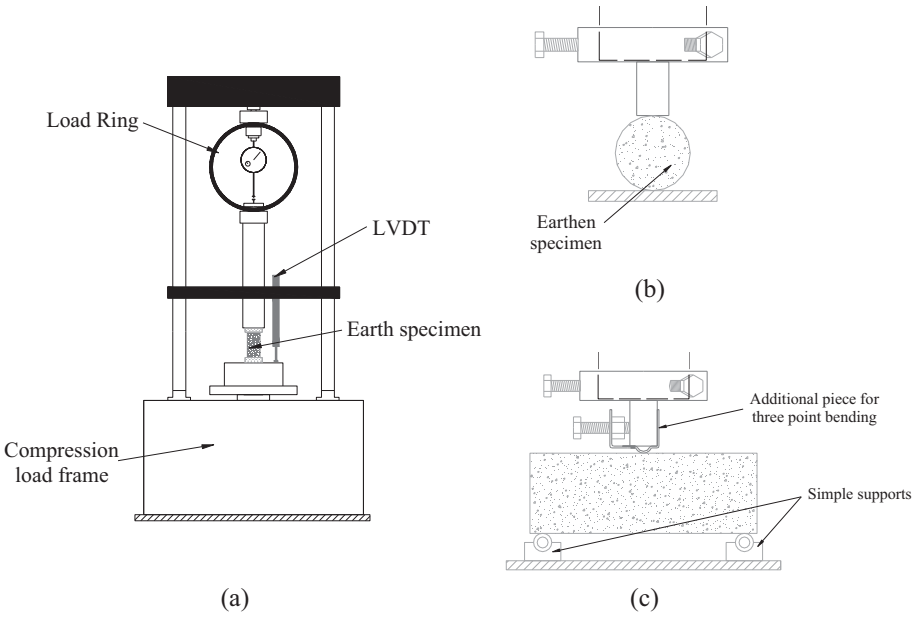


**Fig. 7.** Setup details for the mechanical characterization tests: (a) compression test; (b) split test; and (c) three point bending test.


**Fig. 8.** Preparation of earthen specimens: (a) cylindrical specimens and formwork; (b) placing mixture in the formwork; and (c) prismatic specimens.

**Table 3**
Test matrix for the mechanical behavior assessment.

| Sample type | Description | Performed tests | N° of specimens |
|---|---|---|---|
| Control sample | Mixture proportion 4:1 (earth/water) | Compression | 8 |
| | | Split | 6 |
| | | Bending | 8 |
| Admixture | Solution concentration: Solution B Mixture proportion 3:1 (earth/solution) | Compression | 10 |
| | | Split | 6 |
| | | Bending | 4 |

*Notes:* Mixture proportion measured by weight.
Solution B: 3% chitosan dissolved in 1% acetic acid.
Only Solution B added as admixture was evaluated based on contact angle and drip erosion tests results presented in Section 4.

and a length of 125 mm (Fig. 8b and 8c). For mechanical testing all specimens were air cured for a period of about 14 days in environmental conditions. Given that mechanical properties of earthen materials are heavily influenced by sample moisture content [10] the actual curing duration for each sample was such that a residual gravimetric moisture content of approximately 4% was obtained. The actual moisture content of all specimens was measured immediately after testing by drying tested samples in an oven for 24 h at 110 °C and as shown later the sample moisture contents were very uniform and close to the target value of 4%. Additionally the density of all test specimens was documented by carefully recording the mass and dimensions of each sample at the time of testing.

The mechanical evaluation test program involved comparison of test results obtained from untreated (control) samples with corresponding results obtained from specimens prepared using the base soil mixed with Solution B of the chitosan biopolymer which corresponded to a concentration of 3% mass to volume ratio of chitosan to 1% acetic acid solution. The test matrix of the mechanical testing program is shown in Table 3.

## 4. Results and discussion

### 4.1. Assessment of water induced degradation

#### 4.1.1. Contact angle measurement results

Contact angle measurement results on surface treated samples, employing Chitosan Solutions A and B, are shown in Fig. 9. Specimens coated with Solution A yielded contact angles of 94° ± 9° which corresponds to a hydrophobic or water repellent condition. For Solution B, the contact angle results were 85° ± 5°. Both solutions resulted in surface treatments which are moderately water repellent based on contact angle values near 90°. However it is important to point out that tests using the higher concentration solution (i.e., Solution B) resulted in slightly lower contact angles. This reduction of the contact angle could be attributed to the differences of film thickness for both solutions. The coating film thickness was greater for the higher concentration solution. Since the surface coating involves a strong attachment between the soil

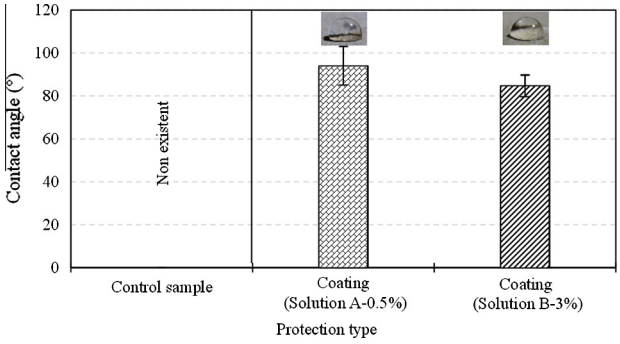


**Fig. 9.** Contact angle tests results in coated specimens.

particles and the more polar functional groups of the thin polymer layer, this leaves the less polar groups on the surface. In other words, the lower contact angles measured when a higher concentration is used, is due to the thicker film on the surface of the specimen, which leaves the superficial polymer chains less attached and with more freedom to move and attract water with their polar groups. Additionally a thinner polymer film (Solution A) will produce a rougher surface which yield increased contact angles in similar fashion to the lotus effect. However, both of these hypotheses should be corroborated with further studies. Nevertheless, these results demonstrate that the surface treatment using even very low chitosan concentration can have a positive impact on increasing the contact angle to values close to 90°. These results are in agreement with other references that show that chitosan films and the modified materials (e.g., fabrics) with chitosan generally shows high contact angles and thus are highly hydrophobic depending on the degree of deacetylation and crystallinity of chitosan [43–46]. Tests on untreated control earthen samples showed that measurement of the contact angle was not possible given the highly hydrophilic condition. In other words, for most control samples the water drop was immediately absorbed by the sample impeding measurement of the contact angle. This is as expected

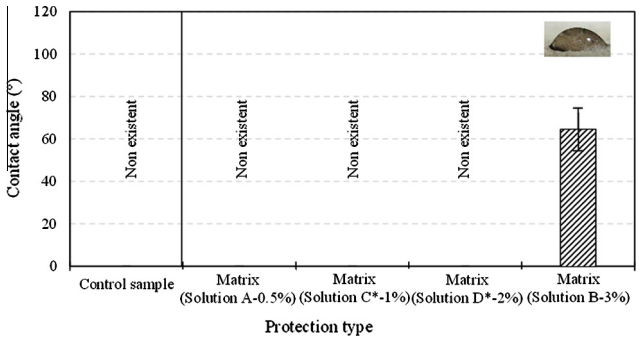


**Fig. 10.** Contact angle tests results for earthen materials prepared with chitosan biopolymer as an admixture.

as untreated earthen materials are porous and with a high water absorption rate [12].

The above results corresponded to tests on earthen specimens with surface coating of chitosan. The second set of contact angle tests involved testing earthen material samples where the preparation involved mixing the base soil directly with the chitosan biopolymer. Fig. 10 summarizes the results obtained for this type of sample treatment. As shown in this figure, no contact angles were measurable for the untreated control samples and for the samples prepared with Solution A (0.5% solution) of the chitosan biopolymer. This was due to the fast infiltration rate of the water sessile drop. Contact angle measurements were only possible for earthen samples prepared with Solution B of the chitosan biopolymer (3% solution) which has the higher chitosan concentration. Fig. 10 also includes contact angle results for samples prepared with two intermediate concentrations of chitosan of 1% and 2% which are labeled in this figure as Solutions C* and D*, respectively. Of the four chitosan concentration levels evaluated, only the samples prepared with the highest concentration, i.e., prepared with Solution B at 3% chitosan, permitted measurement of contact angles. The contact angles recorded for samples prepared with Solution B ranged within 65° ± 10° which show some water resistance but still correspond to a hydrophilic condition. These contact angle measurements suggest that earthen material prepared with a soil similar to the base soil used in this study would require mixture with a chitosan solution concentration of at least 3% in order to start recording contact angle values approaching 90° which is the minimum required for a hydrophobic behavior. Based on these contact angle results the test matrix for the mechanical tests, presented in Subsection 3.2.2, involved only earthen material specimens prepared with Solution B of the chitosan biopolymer (3% solution).

*4.1.2. Drip erosion test results*

The results of the drip erosion tests on untreated control earthen samples were as expected given the well documented poor water resistance of untreated earthen materials. Fig. 11 shows photos of an untreated sample after 1, 3 and 5 min of exposure to water dripping. The photos show substantial erosion even after only one minute of water dripping. After five minutes of exposure the specimen was almost completely disintegrated.

The first set of drip erosion tests was carried out on earthen material samples treated with chitosan biopolymer applied externally as a coating. Fig. 12 shows photos of drip test results for coated specimens with Solutions A and B. Both of these surface treatment levels passed the 10 min time limit of this test suggesting a good resistance to water induced erosion. These results suggest that even a very small concentrations of chitosan coating of 0.5% (Solution A) would be enough to protect the earthen samples by making its surface more hydrophobic and more resistant to water induced erosion. The effectiveness of chitosan for providing water protection can be explained because this biopolymer forms a hydrophobic barrier keeping soil particles bound and preventing them from breaking apart which is due to the strong dipole-dipole hydrogen bonding and ionic intra and inter molecular interactions of the polymer chains.

The second set of drip erosion tests was carried out on earthen samples prepared using the chitosan solution as an admixture. The drip erosion test results for specimens prepared with chitosan biopolymer in the earthen mixture are shown in Fig. 13. The earthen samples prepared with the lowest concentration level of chitosan (Solution A at 0.5%) showed significant erosion after 5 min of water dripping. It should be noted, however, that the erosion was different from what was observed in the control sample, as in this case the erosion observed to be localized and affected only the immediate area around the contact point where the water drops impacted the sample (see left photo in Fig. 13). In contrast, the drip erosion tests results for the specimen prepared with the highest concentration level of chitosan (Solution B at 3%) resisted the full test duration of 10 min thus denoting a good water erosion resistance. An additional test with an intermediate solution of 1% of chitosan (Solution C*) was carried out and the results showed that the 1% concentration level was also able to resist the full 10 min of water dripping. Therefore for earthen materials prepared by mixing the base soil and chitosan biopolymer solutions of at least 1% concentration (Solution C* and Solution B) is required to reach the 10 min exposure time requirement of the drip erosion test. However, based on the contact angle measurements on earthen samples prepared with chitosan biopolymer as an admixture, a 3% concentration (Solution B) was required in order to measure contact angles. Based on the combined observations from the

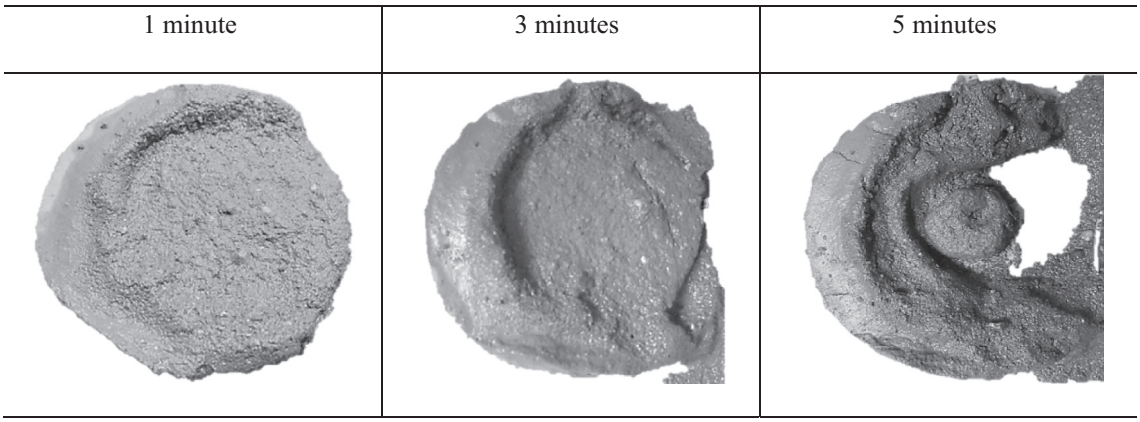


**Fig. 11.** Drip erosion test results for an untreated earthen specimen at different times of water drop exposure.

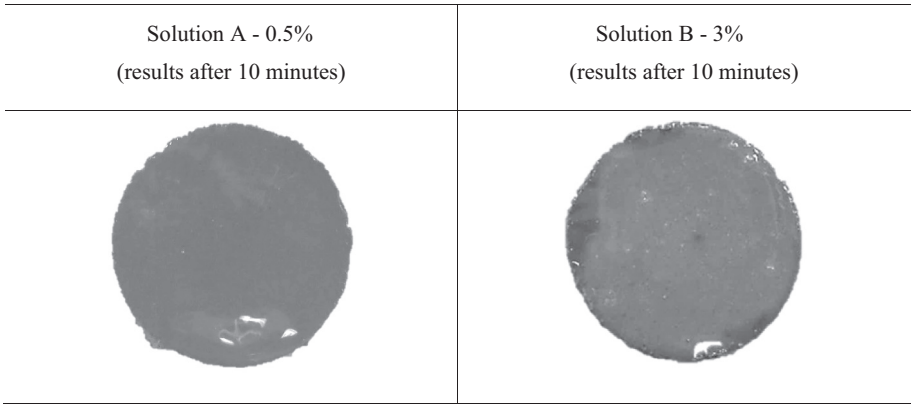


**Fig. 12.** Drip erosion test results of earthen specimens coated with chitosan solutions.

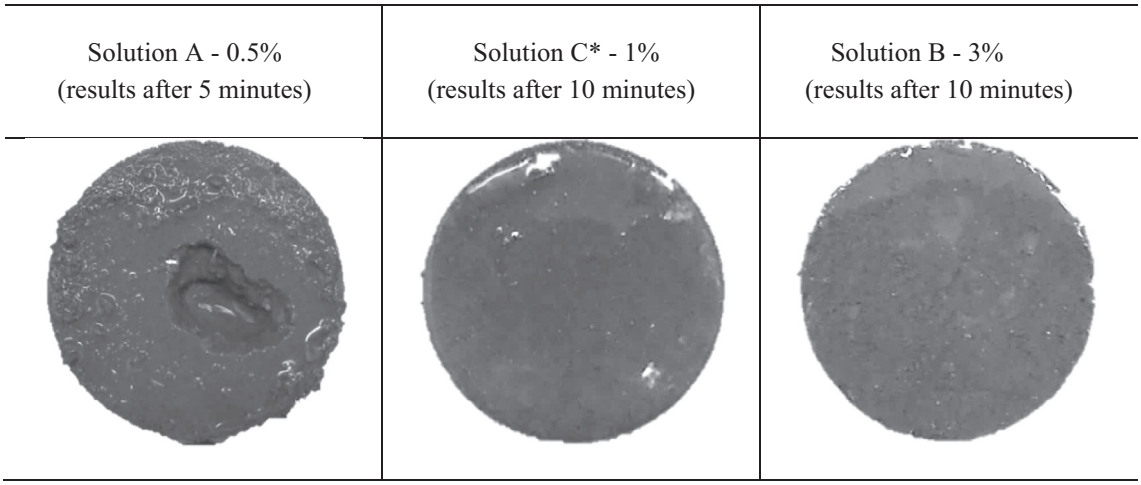


**Fig. 13.** Drip erosion test results for earthen materials prepared with chitosan biopolymer as an admixture.

contact angle measurements and the drip erosion tests it was decided that only earthen materials prepared with Solution B of the chitosan biopolymer as an admixture was adequate to yield reasonable improvements in water resistance. Therefore the mechanical test program only involved tests on treated samples with Solution B.

### *4.2. Assessment of influence on mechanical behavior*

The results of all three types of mechanical tests, for treated and untreated earthen specimens, are presented in Fig. 14. This figure also shows photos of the typical failure modes observed in each of the tests. As mentioned earlier, mechanical properties were measured only for the admixture type treatment (no coating treatment) and for samples treated with Solution B (3% concentration) which was found to be the concentration level that provided both hydrophobicity and resistance to water erosion in the water induced tests presented in the previous section.

Fig. 14 shows that treated earthen samples had substantial strength gains for all three mechanical test types compared to the untreated control samples. Uniaxial compression test results showed strength gains of the treated samples of up to 170% with respect to control samples. On average the uniaxial compression strength increase was 85%. Similarly, the split and three-point-bending tests, showed a maximum strength increase of the treated versus untreated conditions of 250% and 175%, respectively. The average levels of strength increase, of the treated with respect to the untreated control condition, was 65% and 80% for the split, and three-point bending tests, respectively. The stress-strain curves (for uniaxial compression tests) presented in Fig. 14 also show increased values of the initial slope of these curves for the treated samples compared to the untreated samples. This would suggest that the chitosan treatment results in some stiffening effects of the treated earthen material. However, the most important improvement of the mechanical properties is in term of the strength (or peak values) of the different tests considered. This is consistent with [47] who reported that higher values of stiffness are correlated to higher strength in adobe bricks.

The increment of strength, and to a lesser extent on stiffness, is difficult to explain. The addition of the chitosan biopolymer admixture would result in a strong attachment between the polymer chains and the clay particles of the base soil, thus leading to an increment of the compressive strength. The addition of the polymer may also change the net air void space in the sample in a similar fashion as observed in bitumen treated soils [1]. The improved strength may also be related to the modification of the drying or curing process of the soil caused by the addition of the biopolymer. Earthen materials are sun or air-dried during curing, and not baked as in the case of conventional bricks, thus during curing they are susceptible to shrinkage and contraction which will often cause hairline internal and external micro-fissures [3,14]. Thus the second explanation for the observed improved mechanical properties of the chitosan-treated earthen material samples is the improved volume stability which resulted in reduced shrinkage and

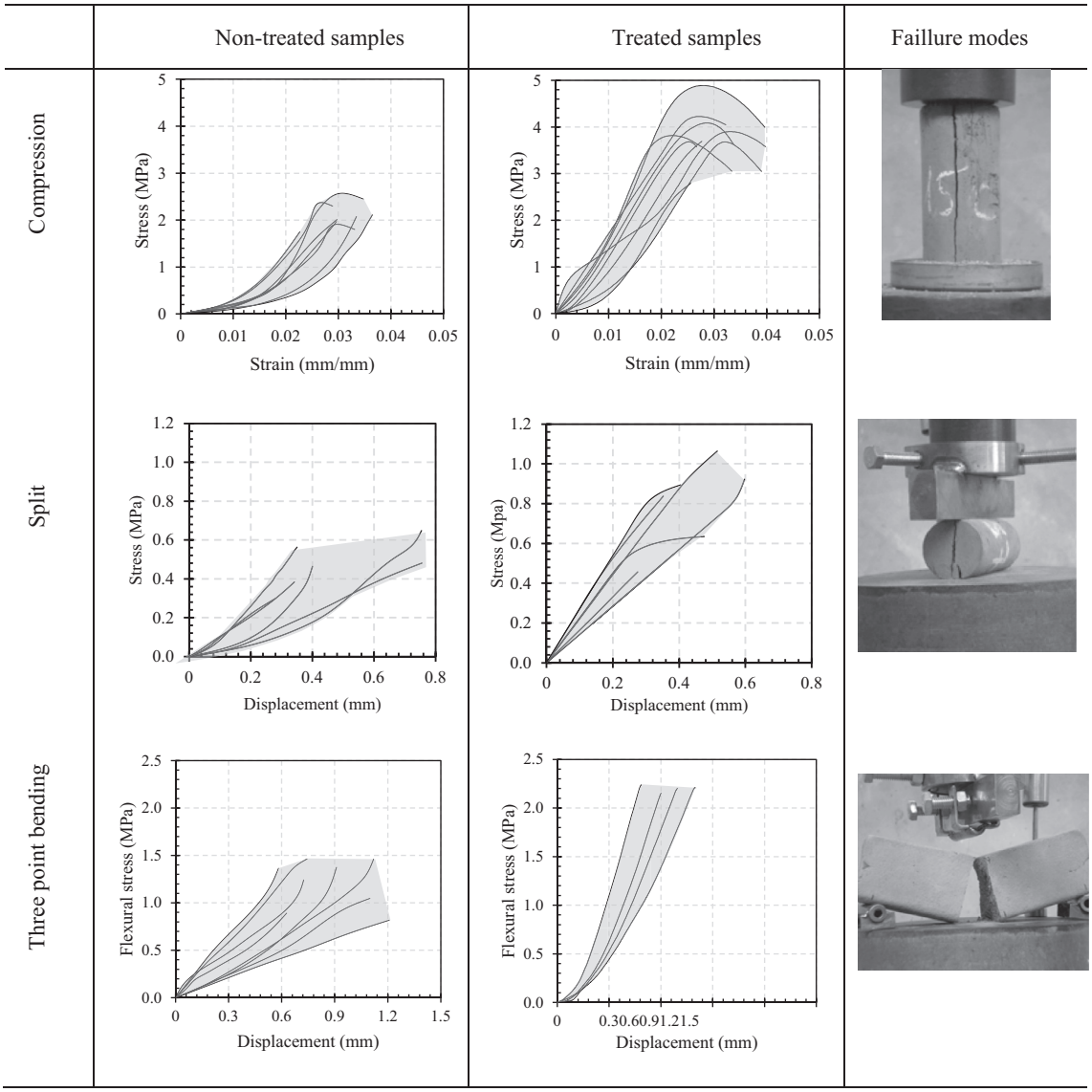


**Fig. 14.** Summary of the results of the mechanical tests in treated and non-treated specimens.

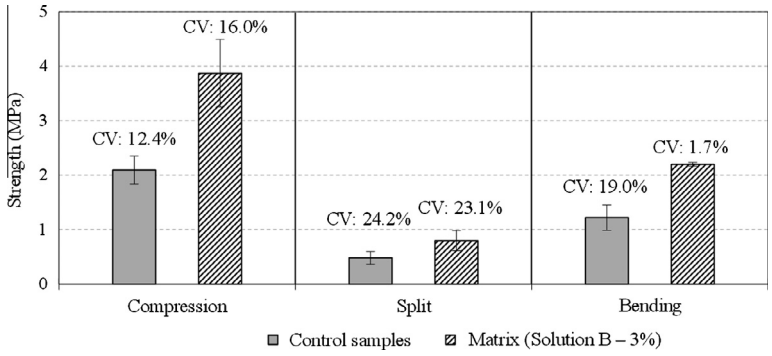


**Fig. 15.** Strength results from mechanical tests.

contraction during the air-dried curing process. This improved volume stability resulted in treated specimens with less microfissures and thus higher mechanical properties. In the present study, all samples were subjected to periodic examination during curing which involved tracking the residual moisture content and careful measurement of dimensions. The periodic sample examinations during the curing process revealed higher levels of contraction for the untreated control samples compared to the treated specimens. The results of this analysis showed that the untreated specimens presented an average volumetric reduction of 10.5%

from fabrication to testing time while the chitosan-treated specimens had only an average volume reduction of 8.7%. This observed decreased volume contraction for the treated samples likely resulted in a reduction of micro-cracking in the cured samples, as reported by [14], and thus offers an additional explanation for the higher values of strength and stiffness measured in the treated samples. However these two factors need to be further investigated using techniques such as detailed SEM microscopy, and careful sample volume change measurements during curing under controlled conditions.

Fig. 15 presents the statistical comparison of the mechanical tests results. The bar charts show the average strength obtained for each test type and for both types of specimens (control versus treated). All test types show the increase in strength discussed above, but also show the coefficient of variation measured for each set of tests. For example the results of uniaxial compression tests yielded coefficients of variations of 12.4% and 16% for the untreated and treated samples, respectively. These values of the coefficient of variation are considered reasonable given the inherent variability associated with earthen materials. For example in references [47,48], which involved samples retrieved from historical constructions, reported coefficients of variations ranging from 10.8 to 47%. Additionally [49], reported coefficients of variations from 2.6 to 27.5% for fabricated adobe bricks. The results from the split tests yield coefficients of variations with a range between 23.1% and 24.2% which are within the range of 10–73% reported by [47,48]. Finally, the coefficients of variation obtained from the three point bending tests for the admixture and control specimens were 1.7–19%, respectively. In [47] coefficients of variation between 24% and 51% were reported for three point bending tests which is slightly above the 19% obtained from control samples. This is somewhat expected as this study involved samples fabricated under more controlled conditions compared to [47] which involved field samples of diverse ages and conditions. The low coefficient of variation from the treated (admixture) samples evidence less variability in flexural strength which might be also due to the controlled fabrication process. However, it should be pointed out that only four samples were tested and that further investigation is needed to confirm this finding.

As mentioned in the previous section the sample moisture content was carefully monitored during curing in an attempt to minimize the influence of this variable in the mechanical test results. This was achieved by allowing some flexibility of the sample curing duration such that samples were only tested when their moisture content was close to 4%. This resulted in sample curing periods ranging from 7 and 14 days, with an average curing period of 8 days for the control samples and 10 days for the treated samples. This strategy was implemented because it is well known that sample moisture content can have an important influence on the mechanical properties of earthen materials. For example, Bui et al. [10] reported large reductions of compressive strength, ranging between 5 and 20%, for samples that had a water content increment as small as 2%. The measured moisture contents for all the specimens just before testing are presented in Fig. 16a. As shown, registered values for water content range from 4% to 6% with an overall average of 4.6% for the control samples and 5.0% for the samples prepared with Solution B as an admixture. Looking at each mechanical test type, the difference between average moisture content computed for untreated control samples and treated samples was found to be +1, +1.5, and −1.3 percentage points for the compression, split and the three-point bending tests, respectively. Although there were small differences in sample moisture contents between the control and treated samples, these were less than 1.5 percentage points and for the compression and split tests the treated samples had higher moisture contents than the corresponding controls. Therefore the moisture effects, if anything, would result in lower mechanical properties for the treated samples compared to the control given their higher moisture contents. From the moisture content monitoring it is a clear that the observed positive effect of the chitosan solution as admixture (Solution B) on increasing the mechanical properties of earthen specimens is not associated to moisture content variations, i.e. possible drier conditions of the treated specimens. This is based on the moisture content measurements which showed that in general treated specimens were at similar, or slightly higher moisture content compared to the control samples.

The sample homogeneity was also assessed based on sample dry density following suggestions by Adorni et al. [33]. The dry density ($\delta_d$) was calculated in terms of the bulk density ($\delta$) and the moisture content ($\omega$) as shown in Eq. (1).

$$\delta_d = \delta/(\omega + 1) \tag{1}$$

Dry density values for untreated (control) and treated samples for the three different test procedures are summarized in Fig. 16b. This figure shows dry density values were reasonably similar in all the tests thus confirming samples were prepared in a uniform fashion that achieved consistent dry density values. The differences in the average dry density values measured for the three test types

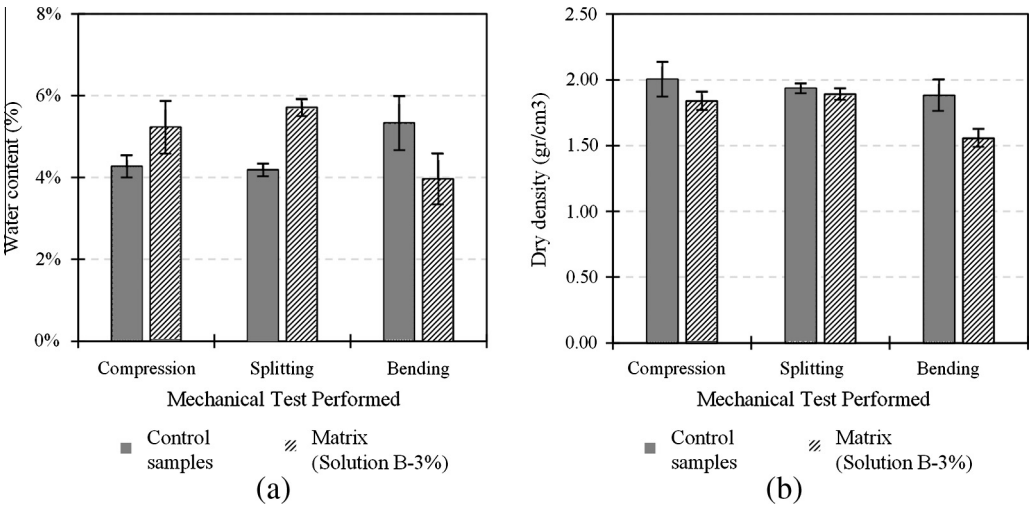


**Fig. 16.** Physical conditions of specimens after testing: (a) moisture content; and (b) dry density.

were 10%, 5%, and 15% for the compression, split and three point bending tests, respectively. These values are considered small and within typical variability for handmade earthen construction materials. These results further confirms that Solution B as an admixture in the preparation of earthen samples has very good potential as evidenced by a real positive effect in increasing the mechanical properties of the mixtures.

## 5. Conclusions

This paper describes a study carried out to investigate the feasibility of using chitosan biopolymer as a treatment for traditional construction materials to improve the resistance to water induced degradation and key mechanical properties. Chitosan in solution was used as an additive to provide water and mechanical resistance to earthen samples. The possibility of using the studied chitosan solutions as external surface coatings or as an admixture to be used during earthen material preparation was evaluated and some solution concentrations showed promising results in terms of improved water degradation resistance and mechanical properties.

The evaluation of the susceptibility to water induced degradation evidenced a positive influence of the presence of chitosan either as surface coating or admixture. Solution with low concentrations of this biopolymer (0.5% and 3%) applied as an external coating were found effective to create moderately water repellent sample surfaces based on contact angle values near 90°. Water drip test results showed that coating applications with low concentration chitosan solutions ($\geqslant$0.5%) were sufficient to provide protection against water drip erosion. When the chitosan solutions were incorporated as an admixture in the fabrication, the findings show that at least 3% is required to provide some hydrophobicity (contact angle values around 65°). Water drip erosion tests, on the other hand, revealed that the use of solutions with at least 1% chitosan concentrations is required to provide protection.

In terms of the influence of chitosan treatment on the mechanical behavior, the admixture of 3% chitosan solution used in the sample preparation showed significant increases in strength values of uniaxial compression, split, and three-point bending test results compared to the control untreated samples. Results of the uniaxial compression tests showed that the strength had an average increment of 85% with respect to the control tests. For the tensile strength measured from split tests, the results showed an average increment of 65% for the treated samples with respect to untreated. An average increase of 80% in the flexural strength was measured for the treated samples compared to control, untreated samples.

In summary the results of this study indicate that the use of chitosan biopolymer as a treatment to improve the resistance to water induced degradation and the key mechanical properties, for new or existing earthen construction, is feasible. However further studies are recommended to confirm the findings reported in this study to extend to different types of base soils and fabrication and curing conditions. It is important to also carry out a detailed study of the durability and long-term stability of the chitosan treatments, in particular when used as surface coating.

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