

## Biodegradable Polymers on Cementitious Materials

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**Abstract.** *Nowadays the sustainability and safety requirements of structures inspire the study of new self-healing materials and preventive repair methods on cementitious elements. To achieve this undertaking, this research replaces widely employed synthetic polymers by biodegradable ones as consolidants and water-repellents, and assesses the protection and consolidation effect of biopolymers (obtained by using waste biomass of mixed microbial cultures from polyhydroxyalkanoates production processes) as eco-friendly healing agents by analysing the water absorption of two kind of materials. The first group of samples are cement mortar specimens whose external surface has been treated with biopolymer products and subsequently evaluated by water drop absorption test. The second group of samples are cement mortar specimens formulated with biopolymer products included in its mixing water and later the waterproofing efficiency is analysed by capillary water absorption tests. The water absorption behaviour of both kind of samples shows a potential improvement of cementitious elements durability, since water absorption results have decreased for treated samples in comparison with untreated ones.*

**Keywords:** *Repair Methods, Self-Healing, Polyhydroxyalkanoates, Durability, Cement Mortar.*

### 1 Introduction

During historic and prehistoric period, the use of biopolymers from plants and natural sources was a common technique in the manufacture of construction materials. They developed suitable behaviour in terms of reducing the water content of the binding materials, accelerating the hardening process of the binders and achieving a compaction desirable in the production of compacted hardened structures with appropriate durability. Thereby a suitable binder to keep the structural integrity of aggregate-based materials used in ancient structures is reaching. In addition, these natural biopolymers can exhibit biocidal and insecticidal properties leading to resistance of the constructed structure to bio-corrosion as well as termite resistance (Karandikar *et al.*, 2014). However, nowadays the usage of biopolymers has disappeared in the most of developed countries around the world, only in some rural areas of underdeveloped countries these eco-friendly techniques are still practised, where the knowledge has been inherited from one generation to another.

Demand for construction materials has been rising in recent decades in many countries, with

the intense industrialisation and urban development induced by economic and demographic growth, then self-healing materials and repair methods are required in construction sector.

Cement-based materials are inert, however, currently a number of chemical products are generally added to mortar and concrete mixes to control several parameters (plasticity, pumpability, setting time, water content, freeze-thaw resistance, strength, colour, etc.) Because of these chemical admixtures, today cement-based materials could become more harmful to the environment. They require more energy to be produced and more raw materials. The use of various synthetic admixtures in cement-based materials has been proved to have contributed to the emission of toxic species into the atmosphere (Hazarika *et al.*, 2016).

The replacement of synthetic admixtures by natural polymers would pave the way for more green construction. The use of natural materials as opposed to non-renewable and petroleum-based products has been identified as a potential means for reducing the embodied energy and carbon footprint of buildings, as well as helping to create healthy and comfortable indoor environments (Dove, 2014; Felton *et al.*, 2013). Natural polymers are polymers synthesized by living organisms (plant, animal, algae, fungus or bacteria) and consist of long chains made of repeating, covalently bonded units, such as nucleotides, amino acids or monosaccharides. Biopolymers have the potential to reduce carbon emissions since the CO<sub>2</sub> released when they degrade can be reabsorbed by crops grown to replace them, making them close to carbon neutral.

Several publications have studied the usage of these natural products in the production of earthen buildings: vegetable oils (Ogacho *et al.*, 2003; Balo and Yucel, 2013), plant gums and resins (Ruskulis, 2002), molasses (Vilane, 2010) or animal products (Ruskulis, 2002; Eires *et al.*, 2013; Beas, 1991). However, there are few studies where this kind of additions are used on cement-based materials. In this study, the potential of a novel biopolymer from biodiesel by-product is evaluated to realize self-sealing of cement-based materials, on one hand, and surface repairing development of cement mortar samples, on the other hand.

## 2 Material and Methods

The bioproducts used as surface repairing agents were eco-friendly, being obtained by waste biomass from a microbial mixed culture (MMC) for polyhydroxyalkanoates production using crude glycerol (biodiesel by-product). MMC cell walls were disrupted by sonication (Sonicated bioproduct, B-S) or not (Non-sonicated bioproduct, B-NS). For comparison, different control samples were prepared: i) untreated; ii) specimens in which the bioproduct was replaced by the same volume of tap water. Table 1 shows the different treatments for external addition of biopolymers.

**Table 1.** Description and short names of bioproducts/biotreatments and controls.

	Surface treatments	Short name
<i>Controls</i>	Control (no treatment)	Control
	Reference (tap water)	H <sub>2</sub> O
<i>MMC-glycerol bioproducts</i>	MMC grown with crude glycerol	B-NS
	MMC grown with crude glycerol after sonication	B-S

Cement mortar to test the surface repair effect was produced with a cement CEM II/A-L-32.5 N (EN 197-1, 2011), from Secil Group, Portugal, with a loose bulk density of 1.18 kg/dm<sup>3</sup>. The mortar was formulated with a cement:sand mass proportion of 1:1.9, that corresponds to a volumetric proportion of 1:3.

Triplicate specimens were prepared and tested. Bioproducts were applied onto the surface of mortar samples by dropping into a 3 x 3 grid of 9 addition points in a surface of 40 mm x 40 mm in a total of 2 cm<sup>3</sup> of each bioproduct suspensions using a pipette. To simulate degraded surfaces, a cut surface of samples was treated. Samples were located on a test room one week before biotreatments to establish uniform laboratory conditions (20 ± 2 °C and 40 ± 5% relative humidity).

Five days after the treatment, the repairing effect was assessed by a water-drop absorption test. This test allows evaluating the permeability variation of biotreated surfaces by monitoring the rate of absorption of a 0.1 cm<sup>3</sup> drop of water, that is, the time required for a material to fully absorb a water drop under open air conditions (Figure 1). The absorption period of time was video-recorded.



**Figure 1.**Steps of water drop absorption test.

Regarding internal addition of bioproducts, the cement mortar samples to test the self-healing effect of the biopolymer at different ages was bioformulated with the composition shown in Table 2.

**Table 2.** Composition and code of the cement mortar samples.

Sample	Code	Sand (g)	C (g)	Water(ml)	B1 (ml)	B2 (ml)
Control (Cement mortar with water formulation)	CW	4	627.13	530	0	0
B1 (Cement mortar with bioproduct formulation)	CB1	4	627.13	0	530	0
B2 (Cement mortar with older bioproduct-3 days old formulation)	CB2	4	627.13	0	0	530

Six months after the cement mortar manufacture, the healing effect was assessed by a water-drop absorption test, following the same steps explained previously for the surface treatment

samples. Triplicate specimens were tested, which were located on a test room one week before measurements to establish uniform laboratory conditions ( $20 \pm 2$  °C and  $40 \pm 5\%$  relative humidity).

### 3 Results and Discussion

The results of the water drop absorption time of surface biotreated samples are represented in Figure 2, which showed that the samples exposed to only water (H<sub>2</sub>O sample) reduced the time until water drop absorption, being a negative effect on the mortar durability, as expected. However, when the cement mortar was treated with non-sonicated bioproduct (B-NS), a waterproof effect was observed, since the water drop absorption time increased 601% in comparison with control sample. If the mortar surface is treated with the sonicated bioproduct (B-S), the waterproof response is even greater, since B-S sample showed a water absorption time 912% higher than the control sample. The development of a waterproof film in the external part of the sample (surface and external cracks), due to the biopolymer deposition is the reason of the better performance of treated samples in comparison with Control and H<sub>2</sub>O samples.

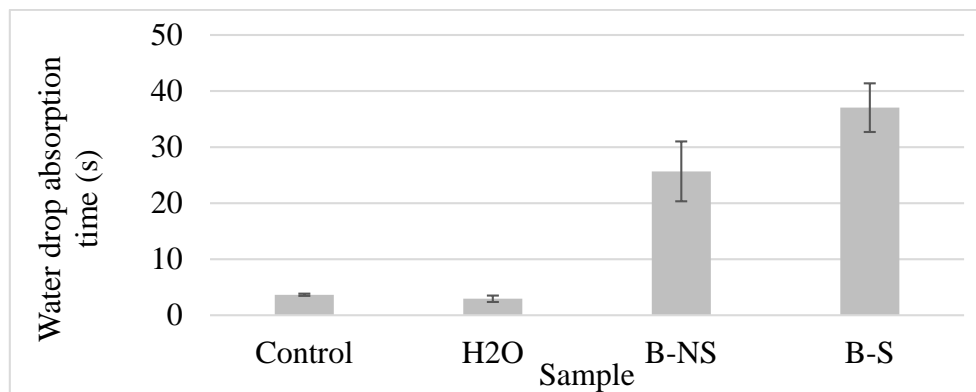
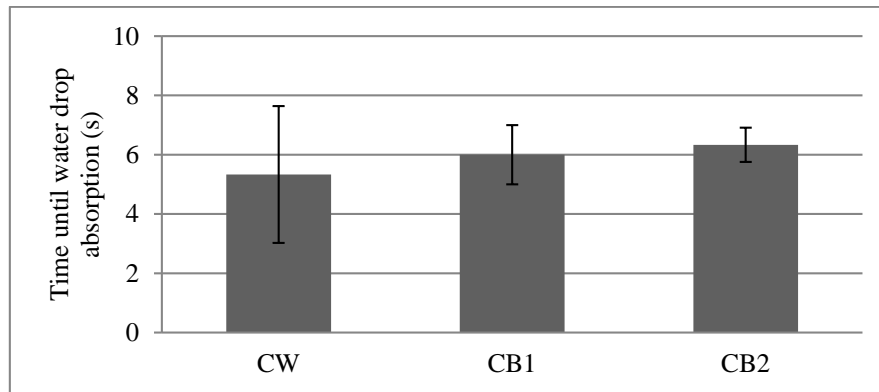


Figure 2. Water drop absorption time of surface treated cement mortar samples.

Authors as Subbiah *et al.* (2018) used silane enriched with nanomaterials as water-repellent on cement mortar, obtaining a 10% water absorption decrease. Treatment of cement mortars with nano-silica was tested by Hou *et al.* (2014) and they observed a water permeability decrease, by reducing the volume of pores larger than 50 nm and the threshold value of the pore network. Other authors as Chandra *et al.* (1998) applied water extracts of cactus to biotreat the surface of Portland cement mortar samples, achieving up to 83% improvement in water resistance.

The Figure 3 shows the water drop absorption time for the cement mortar with water (CW) and the bioformulated cement mortar with the biopolymer at different ages (CB1 and CB2). Although, deeper studies should be developed to decrease the standard deviation in the data, the results of this test state that the self-healing effect of biopolymer presence, since CB1 samples spend 12,5% more time to absorb the water drop than the CW sample. When the age of the biopolymer is increased (CB2 sample), the self-healing effect is even greater, raising the water drop absorption time until 16,7% in comparison with the control sample (CW). The better performance of bioformulated cement mortar than the conventional mortar in water drop

absorption test can be related with the low water accessible porosity on bioformulated samples due to the polyhydroxyalkanoates production on cement paste, which apparently increased over time, considering short periods of time.



**Figure 3.** Time until water drop absorption of CW, CB1 and CB2 samples.

Previous results have already shown that addition of ecofriendly polymers on cement-based materials generated positive findings on material durability, such as Chandra et al (1998), who used the water extract of cactus in preparation of Portland cement mortar and this natural polymer improved water absorption and freeze-salt resistance. Also Chandra and Aavik (1983) used black gram as binder in cement mortar and stated that it worked like air entraining agent, improving the hydrophobicity of cement mortar. They also tested the addition of oil along with black gram, which worked as a defoaming agent and substantially improved the hydrophobic property of cement mortar. Hazarika *et al.* (2018) used a plant based polymeric material as a low cost chemical admixture in cement mortar and concrete preparations. The addition of this bio-admixture decreased the water absorption capacity as well as the porosity of the mortar samples.

In addition, the two approaches tested on this study showed that external treatment of mortar samples with biopolymers are more effective than when bioproducts are incorporated like mixture addition (bioformulation).

## 4 Conclusions

- The treatments with MMC bioproduct from glycerol showed a significant decrease of the permeability on the surface biotreated samples. The sonicated biopolymer exhibited a greater repairing effect than the non-sonicated one.
- Addition of MMC bioproduct on the formulation of cement mortars implied a positive effect on its durability and this result was greater when the bioproduct solution was older, involving a relatively short period of time (few days).

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