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Sustainable cement mortar bioformulated with a bioproduct obtained from fermentation of biodiesel' crude glycerol

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ABSTRACT

This study analyses the potential of a new eco-friendly bioproduct to construction sustainability and its contribution for improving the fresh and hardened properties of cement mortar. The bioproduct was obtained from biomass grown using crude glycerol (biodiesel production waste). With similar functionality than petrochemical-based additions, these bioproducts encourage the decrease on the use of fossil-based raw materials with the concomitant reduction in their carbon footprint. The effect of bioproduct's sonication and storage for 3 day at 4 °C were assessed. Properties such as consistence, porosity, density, compressive and flexural strength, water droplet absorption, capillary absorption, drying rate, thermal conductivity and ultrasonic pulse velocity of the bioformulated mortars were compared with a control cement mortar. The findings show that the bioproducts can be used as renewable and eco-friendly alternative to petrochemical-based polymer admixtures to lengthen mortar service life, even after storage. Sonicated bioproduct improved the water related mortar properties, while non-sonicated bioproduct developed higher mechanical properties. Contributing for a cleaner production of cementitious products, an original waste from chemical industry was transformed into a valuable raw material for use in the construction industry.

1. Introduction

Biopolymers from plants and other natural sources were commonly used throughout history to manufacture construction materials. In some cases that practice lowered the water content in the composites mixing, enhancing durability (Karandikar et al., 2010). By hastening binder hardening it prevented rapid absorption-induced mixing water loss and raised the compaction and high performance pursued in the hardened material to build durable structures. The resulting mixes ensured the structural integrity of the aggregates used in ancient construction. A further advantage of natural biopolymers is that they may also feature biocidal and insecticidal properties, namely affording resistance to bio-corrosion and termite's action (Karandikar et al., 2010). However, natural biopolymers use has almost disappeared in today's developed societies and is now confined to rural areas in some developing countries where the skills needed to deploy such eco-friendly techniques are transmitted from one generation to the next.

In recent decades intense industrialisation and urban development induced by economic and demographic growth raised the demand for construction materials in many countries. A heavy burden on the environment in terms of both the natural resources consumed and the enormous flow of waste generated is then placed. Whilst cement-based mortar and concrete are the most widely used and deemed inert of all construction materials, certain chemicals are now routinely added to concrete mixes as admixtures to control plasticity, entrained air, pumpability, setting time, water content, freeze-thaw resistance, strength and colour. Their use may nonetheless diminish the eco-friendliness of cement-based materials, due to the higher energy and raw material consumption involved. Moreover, some concrete bearing synthetic admixtures has been shown to emit toxic substances into the

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atmosphere (Hazarikai et al., 2016).

Replacement of such synthetic admixtures with natural polymers could contribute to a greener 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, while generating healthy and comfortable indoor environments (Dove, 2014; Felton et al., 2014). These natural polymers are synthesised by living organisms (plants, animals, algae, fungi or bacteria) as long chains made of repeating, covalently bonded units, such as nucleotides, amino acids, monosaccharides and others (Luengo et al., 2003). Some biopolymers may even potentially lower carbon emissions, as the CO_2 released by their decomposition can be reabsorbed by crops to regenerate them, creating a nearly carbon-neutral cycle.

Although the market presence of bio-admixtures is practically imperceptible, a number of researchers have proposed their use in construction materials. Matsuoka et al. (Y. Matsuoka K. Yakota and S. Kusui, 1997) conducted studies on curdlan, a viscous polysaccharide, to improve concrete workability. Nara et al. (1994) confirmed β-glucan capacity to raise cement slurry viscosity and hence its fluidity. Chandra and Aavik (1983), using black gram (*Vigna mungo*) in cement mortar and in normal and structural lightweight aggregate concrete, described its air-entraining properties and concomitant improvement in bond strength and hydrophobicity. Hydrophobicity was further enhanced by the defoaming properties of oil when added in conjunction with the black gram. Chandra et al. (1998) added cactus mucilage to cement mortar to raise plasticity and thawing salt resistance, as well as to reduce absorption. Woldemariam et al. (2014) found cypress plant extract to induce rises in strength at a constant slump and workability at a constant liquid-cement ratio. Govin et al. (2015), studying the effect of guar gum derivatives on the fresh state properties of cement-based mortars, reported that these biopolymers were able to improve water retention while adapting cementitious paste rheology to specific applications. Otoko and Ephraim (2014), analysing the use of palm liquor as a concrete admixture, concluded that the polymer enhanced concrete workability and compaction, reduced honeycombing and retarded initial and final setting times. Dwivedi et al. (2008) observed black gram to be adsorbed onto cement, retarding cement hydration and favouring nanosize hydration product formation. Exploring the feasibility of using an okra (*Abelmoschus esculentus*) extract as a bio-admixture, Hazarika et al. (Hazarikai et al., 2016) observed a significative improvement of the fresh state properties and mechanical strength of cement mortars. Shanmugavel et al. (2020) noted improvements relative to a control cement concrete in the fresh properties, mechanical strength and durability of concrete containing cactus extract. Plank (2004) and Vieira et al. (2005), in turn, suggested that lignosulfonate, casein, starch and cellulose derivatives and other water-soluble polysaccharides can be used to modify the properties of cement-based products. Therefore, it can be assumed that waterproofing bioproducts are almost not currently significant in the construction sector, despite having a high potential to improve the fresh state properties and durability of cement-based materials.

The present study assessed the potential of a bioproduct obtained from microbial mixed cultures waste biomass grown with crude glycerol, a by-product of biodiesel processing, for incorporation on cement mortars. The improved workability and induced self-sealing in cement mortars was evaluated on the grounds of their physical-mechanical properties. The effect of sonication (disruption of the cell walls) and storage (at 4 °C) of the bioproduct was also assessed. The novel bioproduct here studied would not only enhance mortar sustainability but might also constitute a lower cost alternative to petrochemical polymers, as it allows for transforming a waste of the chemical industry in a raw material in the construction industry. The obtained bioplastic is water insoluble and relatively resistant to hydrolytic degradation, offers good resistance to moisture, shows good ultra-violet resistance, is soluble in few organic solvents, mostly halogenated hydrocarbons, and is more dense than water (Serafim et al., 2019). These are several reasons why this bioproduct shows a great potential to be used as healing admixture on cement-based materials.

2. Materials, mortars and samples

To produce the mortars, a CEM II/A-L 32.5 N cement, classified according to EN 197-1 (CEN, 2011), supplied by Secil Group, Portugal, was used. The cement loose bulk density was 1.15 kg/dm^3.

A siliceous sand, from Abrantes, Portugal, was used. The sand loose bulk density was 1.47 kg/dm^3.

The bioproducts used in this study were obtained from the waste biomass generated by mixed microbial cultures (MMC) producing a mixture of compounds, where polyhydroxyalkanoates (PHAs) are present. The growth medium used consisted of crude glycerol diluted in tap water. This crude glycerol was in turn a by-product of the trans-esterification reactions involved in biodiesel production as described by Freches and Lemos (2017). The cells are selected by the operational conditions imposed to the reactor and are the best fitted organism that survive. The bacteria present balance between two-three main types in a dynamic process that changes over time. Aqueous suspensions containing whole (admixture MMC) or lysed cells after sonication to disrupt the cell walls (admixture MMC_S) were used as mixing liquid to prepare the mortars. The sonicated suspension contained the cell debris as well as the exposed intracellular content, namely proteins, nucleic acids, lipids, and PHAs. The effect of ageing of the MMC derivatives by storing the suspensions for 3 days at 4 °C prior to mixing with the mortar (subsequently labelled MMC_3 and MMC_S_3) was determined.

The cement mortars were prepared with a cement:sand volumetric ratio of 1:5. Based on the cement and sand loose bulk densities (aforementioned), this ratio corresponds to 1:6.4 in weight.

The tap water used to mix the control mortar (W) was replaced in the other four mortars (Table 1) by the respective bio-admixture: MMC, MMC_S, MMC_3 or MMC_S_3.

Prismatic samples produced on metallic moulds (40 mm × 40 mm x 160 mm) and samples simulating rendered bricks (Fig. 1) were manufactured. Previously to the application of the mortar layer to produce the render samples on brick, these were sprayed with tap water, reproducing what is currently performed in situ: spraying the brick masonry surface to limitate the water absorbed from the mortar by the brick masonry. A one-layer of mortar with 2 cm of thickness was applied, according with the common procedure used when this type of renders are tested (Silveira et al., 2021). The prismatic samples were demoulded after 2 days curing at 20 ± 2 °C and 60 ± 5% relative humidity (RH) and were kept in those conditions for 6 months. After this time, the different tests to characterize the mortars in the hardened state were initiated.

3. Testing methods

Fresh and hardened mortar properties were tested.

3.1. Fresh state testing

Mortar consistency was determined both on a flow table as per

Table 1
Mortars designation and batching.

Sample ID	Hydration fluid (mixing volume)	Cement wt. (g)	Sand wt. (g)
W	530 cm^3 of water	627	4000
MMC	530 cm^3 of whole MMC cell suspension		
MMC_S	530 cm^3 of sonicated MMC cell suspension		
MMC_3	530 cm^3 of whole MMC cell suspension stored for 3 days at 4 °C		
MMC_S_3	530 cm^3 of sonicated MMC cell suspension stored for 3 days at 4 °C		

Fig. 1. Examples of prismatic and render on brick mortar samples produced.

European standard EN 1015-3 (CEN, 2000a) and with the plunger penetration procedure described in EN 1015-4 (CEN, 1999).

Density of fresh mortars was assessed following the guidelines described in standards EN 1015-6 (CEN, 2007). It was calculated as the mass of each mortar divided by the volume occupied by the mixture in a 1-L container.

3.2. Hardened state testing

Apparent density of hardened mortars was determined geometrically based on EN 1015-10/A1 (CEN, 2000b) with three prismatic samples.

To complement the aforementioned data, open porosity and bulk and real density were determined as described in standard RILEM Materials and Structures 75 (RILEM, 1980), which recommend vacuum-treating and soaking the specimens prior to the analysis. Small specimens resulting from one half of the prismatic samples after the flexural strength test were used. Three of these subsamples with dimensions around 40 mm × 40 mm x 20 mm were tested for each mortar formulation.

The effect on thermal insulation was determined by measuring thermal conductivity on an ISOMET 2104 portable Heat Transfer Analyser fitted with a 60 mm diameter API 210412 contact probe. The tests were performed on the render samples on brick at a temperature of 25 ± 2 °C and RH of 45 ± 5%. Three samples of renders on brick were tested per studied material.

The cementitious renders on brick were analysed for compactness with ultrasonic pulse velocity (UPV) with a Proceq Pundit Lab tester following the protocol set out in standard EN 12504-4 (CEN, 2006). Each material was tested using three samples of renders on brick.

The mortar flexural strength was assessed as stipulated in standard EN 1015-11 (CEN, 2000c) with three prismatic samples per mortar. Based on the same standard, half samples resulting from the flexural test were used for compressive strength testing. A load cell of 50 kN was used.

The water droplet absorption test, consisting of measuring the time in seconds required for the mortar surface to completely absorb a drop of water, defined in terms of loss of sheen, was one of the methods used to assess bioproduct-induced self-sealing (Parracha et al., 2019). This test assesses the variation in bioproduct-bearing mortar permeability by monitoring the absorption of a 0.1 cm^3 drop of water dripped onto the surface in laboratory ambient conditions. Monitoring was video-recorded to optimise measurement accuracy. This test was developed on 40 mm × 40 mm x 40 mm mortar specimens, cut from the prismatic ones. Three samples were tested per mortar formulation.

The capillary water absorption curves and coefficients, along with capillary water penetration, were determined as per standard EN 15801 (CEN, 2010) and EN 1015-18 (CEN, 2003) using cubic specimens (40 mm × 40 mm x 40 mm) cut from the prismatic samples. Three specimens were used for each mortar formulation. The four side faces of each specimen were waterproof with paraffin. The tested face of each specimen was submerged in water with a depth of 5 mm. Weight increase by water absorption was registered at 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 35 min, 40 min, 45 min, 1 h, 2 h, 3 h, 4 h, 6 h, 24 h and 48 h after contact with water.

The same specimens, fully saturated after the capillary absorption test, were tested for drying capacity as described in standard EN 16322 (CEN, 2016). The face that was previously in contact with water was now the drying face; the drying by the opposite face was blocked by contact with a metallic surface. Weight decrease by drying was measured at 15 min, 30 min, 45 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 24 h, 48 h, 72 h, 96 h, 120 h, 144 h, 168 h, 192 h, 216 h. The drying curves allowed to assess the drying rate in the first drying stage, characterised by transport of liquid water to the surface followed by evaporation (initial linear part of the drying curve with time in abcissae), and the drying rate in the second drying stage, characterised by a decline in liquid water transport and a rise in water vapour diffusion governed by the material's hygric properties (linear leg of the absorption/$t^{1/2}$ curve).

To check the possible microstructural or chemical alteration in bioformulated mortars, preliminary SEM and EDS analyses were developed by a Hitachi S-4800 scanning electron microscope fitted with a tungsten X-ray emitter and Si/Li detector, and coupled to a Brucker XFlash 5030 energy-dispersive X-ray analyser.

4. Results and discussion

Results and discussion of the tested parameters is showed in this section:

4.1. Consistency

As Fig. 2 shows, both methods (flow table and penetrometer) used to measure mortar consistency showed improvements in the bioformulated mortars, in particular for the samples containing the sonicated bioproducts (MMC_S and MMC_S_3). The gap in consistency values between the sonicated and non-sonicated biopolymers was wider in the mortars formulated with the readily available, fresh, bioproducts (MMC and MMC_S) than the ones after 3 days storage at 4 °C (MMC_3 and MMC_S_3). That effect may be attributed to variations in the suspensions

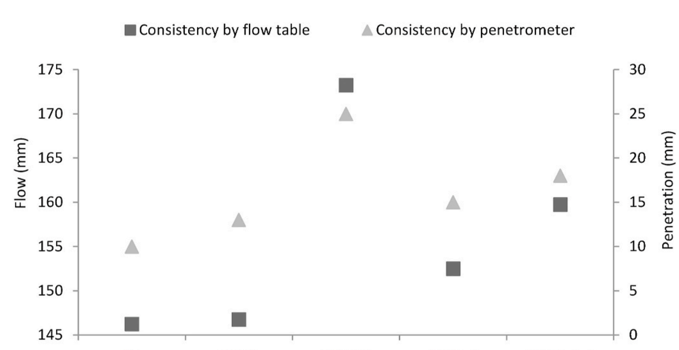

Fig. 2. Flow table and penetration consistency of the control and bio-formulated mortars.

over time. While the sonicated product was initially more fluid and uniform after cell lysis, over time both the cells debries and the cell content released during sonication tended to aggregate, rendering the suspension denser and non-uniform and, consequently, less fluid. Thus, the MMC-S formulated samples presented higher fluid consistencies due to the fact that the sonicated fresh bioproduct was more homogeneous. In contrast, when the suspensions with non-sonicated MMC were stored outside the reactor under the controlled conditions in which they were generated, cell clusters broke up, raising fluidity. Earlier researchers found mortar and concrete workability to improve in the presence of other types of biological admixtures such as curdlan (Y. Matsuoka K. Yakota and S. Kusui, 1997), β-glucan (Nara et al., 1994), cypress plant extract (Woldemariam et al., 2014), cactus extract (Shanmugavel et al., 2020), palm liquor (Otoko and Ephraim, 2014) or guar gum derivatives (Govin et al., 2015).

4.2. Fresh and hardened density, effective porosity, bulk and real density

The inclusion of bioproducts in the mortar formulations induced a decrease in both fresh and hardened states density (Fig. 3). That finding was not unexpected. Considering that PHA could be present in the waste MMC biomass, with density normally on the order of 1.25 kg/dm^3 (Vandi et al., 2018), a value substantially lower than the 2 kg/dm^3 usually found for cement mortars was observed in the present study. The fresh state mortars prepared with non-sonicated admixtures (MMC and MMC_3) with whole, intact cells (unbroken by sonication and denser than the components of the sonicated suspensions) exhibited larger level of aggregation of components than the sonicated materials (MMC_S and MMC_S_3) when observed under a microscope. Those differences could have affected mortar density. As in the case of consistency, the narrower difference in fresh state density values between the later (MMC_3 and MMC_S_3) and former (MMC and MMC_S) age mortars may be attributed to properties intrinsic to the suspensions. Most probably, over time the sonicated product tended to rise in density due to cell fragment aggregation, whereas the non-sonicated material grew less dense with storage time due to the decline in intercellular tension. These results revealed an inverse relationship between mortar consistencies (Fig. 2) and mixture densities (Fig. 3). Studies such as the one conducted by Jasiczak and Zielinski (2006) on other types of organic admixtures observed the same behavior.

The findings for the tests to determine effective porosity and bulk and real density values graphed in Fig. 4 showed that the real and bulk density tendency determined for saturated specimens in vacuum were equivalent to the fresh and hardened state values measured under environmental conditions. Density was lower in the samples with bioproducts than in the control, whilst the lowest values were observed for the mortars with the sonicated products. Those findings further support the existence of a direct correlation between density and mechanical strength in all the mortars studied.

However, mortar and concrete durability is usually less dependent on the density of these materials than on porosity and pore size

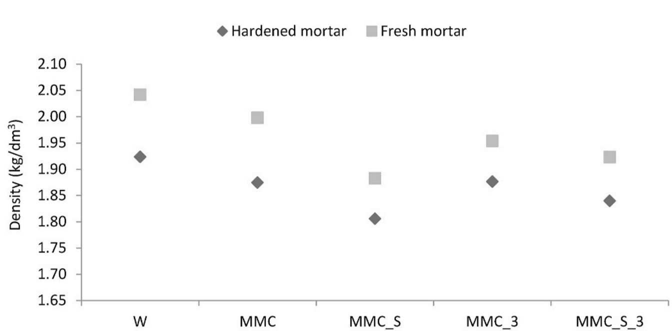

Fig. 3. Density of fresh and hardened states of the control and bioformulated mortars.

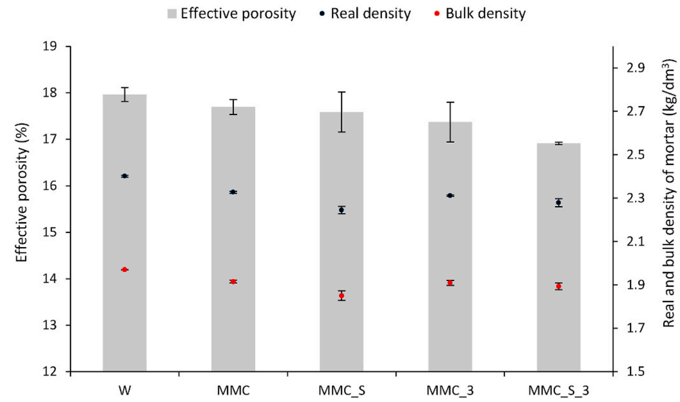

Fig. 4. Effective porosity, real and bulk density in the control and bioformulated mortars.

distribution, specially mesopores and macropores (pore size higher than 0.1 μm) (Gómez-Soberón, 2002; Kumar and Bhattacharjee, 2003), which defines their resistance to attack or penetration by external agents, but also their behaviour related to water such as absorption and drying. The percentage of effective porosity in the samples (Fig. 4) predicted the beneficial effect of bioproducts on mortar durability. The bioformulated mortars had 1.5%–5.9% lower effective porosity than the control. Sonicated MMC_S bioproduct-containing mortar had 0.6% lower effective porosity than the MMC ones, whilst that parameter was 2.7% lower in MMC_S_3 than MMC_3 mortar. Short storage periods, in turn, were observed to raise the protective effect of the admixture, as effective porosity was 1.8% lower in MMC_3 than in MMC, and 3.8% lower in MMC_S_3 than in MMC_S samples.

Researchers such as Torres-Acosta and Díaz-Cruz (Torres-Acosta and Alejandra Díaz-Cruz, 2020) found that prickly pear mucilaginous exudate and cooked mucilage used in concrete formulation likewise induced a decline in their effective capillary porosity (pores with radius from 0.01 μm to 10 μm), irrespective of the test age (30, 90, 180 or 400 days).

4.3. Thermal conductivity and ultrasonic pulse velocity

The thermal conductivity findings (Fig. 5) were consistent with the effective porosity values achieved by the bioformulated samples, as all four bioformulated mortars exhibited higher values than the control, an indication of greater continuous cement paste, since more porous materials transmit heat less efficiently (Wang et al., 2020). A comparison of the four bio-admixtured mortars showed that samples with

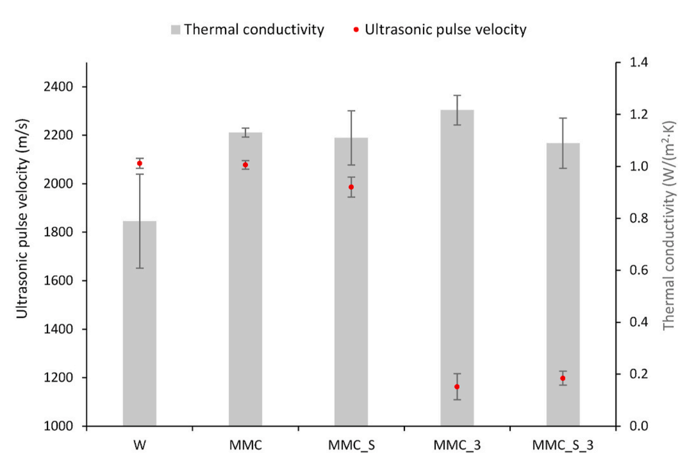

Fig. 5. Ultrasonic pulse velocity and thermal conductivity in the control and bioformulated mortars.

non-sonicated bioproduct (MMC and MMC_3) to be better thermal transmitters, perhaps due to the presence of denser cell clusters, disaggregated by sonication in mortars MMC_S and MMC_S_3. Conducting an accelerated chloride penetration test, Shanmugavel et al. (2020) observed chloride permeability in concrete prepared with a viscous cactus extract biopolymer to decline by 8%–10% with rising admixture concentration. They attributed that effect to the bonding properties of the polysaccharides in the cactus extract, which generated a more compact microstructure than that found in the reference concrete. The behaviour observed in this study was similar, as the biopolymers in the bio-admixtures induced microstructural compaction.

The results of the UPV test (Fig. 5), a procedure frequently applied to study mortar and concrete uniformity (Nazari et al., 2010), showed in turn that the use of early age biopolymers scarcely altered the cementitious matrix (0.3% in MMC and 4.7% in MMC_S), whereas the samples containing bioproducts stored for a longer time prior mixing had a larger impact on cement matrix behaviour. The lower uniformity induced might be more likely the result of changes taking place in the microstructure prior to inclusion in the mortar than to chemical alterations in the cementitious product, since no adverse effect was observed on mortar properties (see the foregoing discussion of the mechanical strength findings). Other bio-admixtures, such as arabic gum biopolymer included in concrete (Mustafa Mohamed et al., 2020), raised the compressive strength in parallel with the UPV values recorded, the highest of which were observed for biopolymer concentrations of 0.9%.

4.4. Compressive and flexural strength

Further to the compressive strength findings (Fig. 6), the use of bio-admixtures had scarcely any effect on mortar bearing capacity. Strength was highest in the mortars containing the later age non-sonicated bio-product (MMC_3) and slightly greater than in the control mortar (W). The least favourable effect (21.5% lower strength) was foreseeably observed in the mortar prepared with the early age sonicated biopolymer (MMC_S), showing the lowest density material (Fig. 3).

The present findings were similar to or even more favourable than those reported in earlier analyses of the use of bio-admixtures in mortars, as several authors reported minor strength loss in mortars containing such products. Mignon et al. (2016), using alginate as superabsorbent polymers, observed no or only a scant (<15%) decline in compressive strength when the biopolymer was added at 1% by cement mass. Shanmugavel et al. (2020), adding cactus extract to concrete, observed early age (7th day) compressive strength to decline with rising biopolymer content. In contrast, the 28th, 56th and 90th days strength values were favoured by rising amounts of the extract, with improvements of up to 30% for 10% concentrations in the total mixing water.

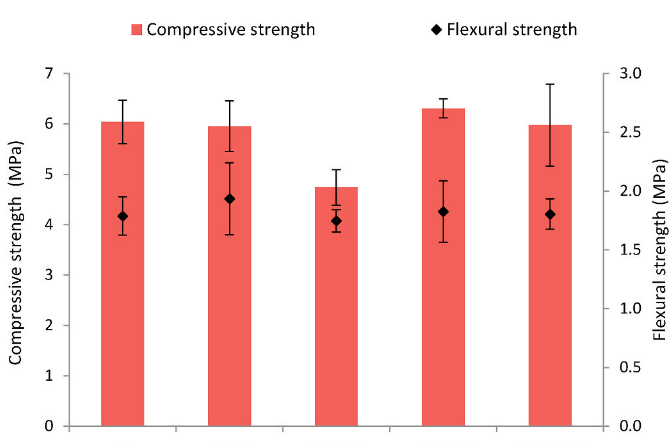

Fig. 6. Compressive and flexural strength in the control and bioformulated mortars.

Along those lines, other studies such as those authored by Mohamed et al. (Mustafa Mohamed et al., 2020), who used arabic gum biopolymer as an admixture in concrete, showed an 8% rise in compressive strength in concretes prepared with mixing water containing 1.1 wt% of the polymer. Otoko and Ephraim (2014) also raised concrete compressive strength by replacing 16% of the mixing water with palm liquor. Other researchers, such as Torres-Acosta and Díaz-Cruz (Torres-Acosta and Alejandra Díaz-Cruz, 2020), analysing the inclusion of prickly pear (*Opuntia ficus indica*) derivatives (mucilaginous exudate, cooked mucilage and powder), reported findings similar to the present results; i.e., the compressive strength developed by the samples did not vary significantly from the values exhibited by the control concrete, with rises or declines depending on curing time and type of bio-admixture.

Flexural strength (Fig. 6) in the samples containing bioproduct was 0.9%–8.3% higher than in the reference mortar, with the exception of sample MMC_S, where it was 2.2% lower. Otoko and Ephraim (2014) reported similar improvements in concrete flexural strength with a 16% concentration of palm liquor in the mixing water. Shanmugavel et al. (2020), in turn, observed 28th, 56th and 90th days concrete flexural strength to benefit from the addition of cactus extract. Although their results were less satisfactory, Mignon et al. (2016) did not rule out the use of alginate as superabsorbent polymers in mortars, as flexural strength was scantly impacted by their inclusion in the mix.

Both compressive and flexural strength (Fig. 6), as found here, were closely related to the density of mortars (Fig. 3).

4.5. Water droplet test

According to the data graphed in Fig. 7, the time needed to absorb a water droplet was longer in all the bioformulated mortars than in the control. Earlier age bioformulated mortars MMC and MMC_S lengthened absorption time less effectively than mortars bioformulated with 3 days stored cultures, MMC_3 and MMC_S_3. The 8.3% rise in absorption time prompted by the use of early age, non-sonicated bioproduct, in MMC mortar afforded further support for sonicating the bioproduct in this type of applications. The mortar bearing sonicated product MMC_S, raised absorption time up to 50% relative to the control sample. The mortars with the two bioproducts applied after 3 days storage, MMC_3 and MMC_S_3, proved to be equally effective, with absorption times 83.3% longer than the observed for the mortar W (control sample), providing a waterproofing effect. The findings discussed in this section are consistent and reciprocate with effective porosity. That result was both logical and expected, for samples with higher effective porosity (mortar W) would require less time to absorb a water droplet than those with lower porosity, such as mortars MMC_3 and MMC_S_3. BET (Brunauer–Emmett–Teller) or MIP (Mercury Intrusion Penetration) analysis could be interesting to compare in more detail the porous dimensional distribution of bioformulated mortars.

Other researchers achieved similar results with other bioproducts. Chandra and Aavik (1983) reported that when added with the black gram as a defoaming agent, the oil substantially improved concrete

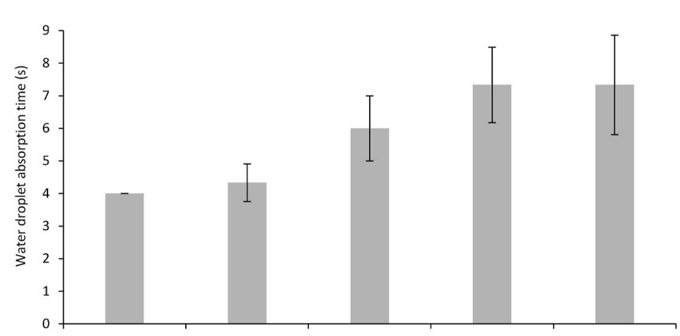

Fig. 7. Droplet absorption time in the control and bioformulated mortars.

hydrophobicity. Chandra et al. (1998), in turn, including cactus water in cement mortar, enhanced plasticity and raise absorption and thawing salt resistance. Torres-Acosta and Díaz-Cruz (Torres-Acosta and Alejandra Díaz-Cruz, 2020) reported a considerable improvement in chloride ion resistance in concretes containing admixtures such as prickly pear mucilaginous exudate or cooked mucilage, which they attributed to the cactus polymer's sponge-like pores behaviour in the cementitious matrix.

4.6. Capillary absorption and drying

The curves in Fig. 8, plotting the variation in the amount of water absorbed by each sample over time, attest the effectiveness of the biotreatments from the outset, as well as the beneficial effect of sonicating the mixed microbial cultures, irrespective of the age of the bioproduct.

The capillary absorption test-determined absorption coefficients, corresponding to the initial capillarity, and asymptotic value, corresponding to total absorption, presented in Table 2, showed that all the bioformulated mortars were less permeable than the control. The best results were recorded for mortars prepared with the pre-stored bio-admixtures MMC_3 and MMC_S_3, with 24% and 25% lower absorption coefficients, respectively, than sample W, and also considering the 20% decline found for the MMC and 16% for the MMC_S mortars. Those findings were consistent with the water droplet test results.

The drying curves by time and by square root of time (Fig. 9 a and b) together with the drying rates for the mortars in Table 2 showed that, in the first stage of the drying test, the presence of the sonicated bioproduct MMC_S and MMC_S_3 involved no additional barrier to water release by the mortar, for the D_1 values were similar to those observed for the control. In the MMC_S-bearing mortar the rate was 0.9% lower than in W, whereas bioproduct MMC_S_3 induced 3.3% greater water release in the respective mortar than found for the control. Those findings further support the potential of the sonicated bioproduct to lengthen mortar durability, the aim ultimately pursued. In the mortar with non-sonicated MMC_3 the drying rate in the first stage was altered slightly (D_1 was 3.5% lower than in W), whereas the decline in moisture release was much more accentuated in mortar MMC, where D_1 was 16.8% lower than in the control.

The drying rates recorded in the second stage of the test, D_2 (Table 2), were significantly lower in all the bioproduct bearing mortars than in the control. The presence of the bioproducts admixtures may have altered the mortar pore structure, lowering its sorptivity, as observed in the water droplet and capillary absorption tests. Under saturated starting conditions, then, the smaller pores in the mortars induced greater resistance against water flow, for adsorption forces retained hygroscopic and capillary water longer in the cementitious matrix, lowering the drying rates in the second stage of the test.

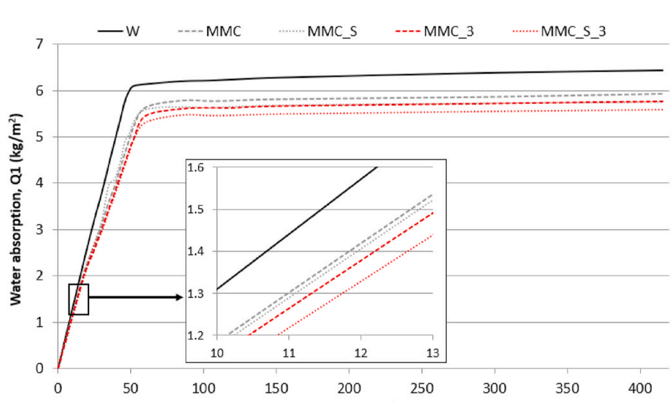

Fig. 8. Capillary water absorption curves in the control and bioformulated mortars.

Table 2
Capillary coefficient, absorbed water and drying rates of the control and bioformulated mortars.

Sample	Capillary coefficient (kg/m^2·s$^{1/2}$)	Absorbed water by capillary after 48 h (kg/m^2)	Drying rate 1 (kg/m^2·s)	Drying rate 2 (kg/m^2·s$^{1/2}$)
W	0.1233	6.43	0.0000422	0.0135
MMC	0.0988	5.93	0.0000351	0.0119
MMC_S	0.1032	5.74	0.0000418	0.0118
MMC_3	0.0943	5.76	0.0000407	0.0113
MMC_S_3	0.0927	5.58	0.0000436	0.0114

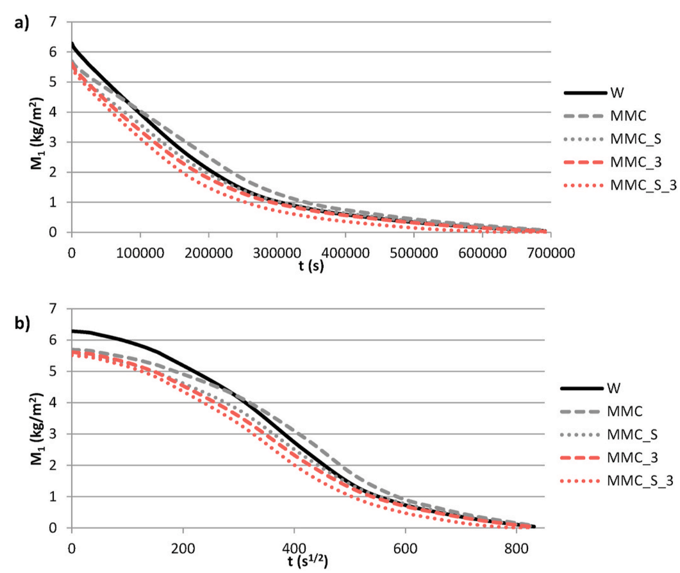

Fig. 9. Drying curves by time (a) and by square roof of time (b) in the control and bioformulated mortars.

During the drying tests no efflorescence occurred, showing that no problems of salts were induced by the bioformulation.

4.7. Microstructural and chemical composition

Preliminary microstructural and chemical results of paste with MMC bioproduct, observed in the Fig. 10, showed that calcium (30–34%), silicon (24–29%) and aluminium (6–7%) were the majority components detected in bioformulated mortar samples, concurrently with data of conventional cement pastes, where Ca, Si and Al were the main components, originating from cement hydration products as Calcium Silicate Hydrates and Calcium Aluminium Hydrates (Hewlett and Liska, 2019). Displaying in a first approach that bioproduct addition did not lead to chemical alteration.

5. Conclusions

An innovative bioproduct obtained from a MMC using as substrate a diluted biodiesed by-product was developed and applied as mixing liquid to produce cement mortars. The effect of the sonication and storage for 3 days at 4 °C of the bioproducts was assessed, in comparison to a control mortar, wherein tap water was used for producing the fresh mortar.

The conclusions to be drawn from this study about the properties of mortars spiked with the bioproducts used as admixtures are set out below:

- The bio-admixtures studied enhanced mortar workability, with more suitable workability in the mortars prepared with sonicated

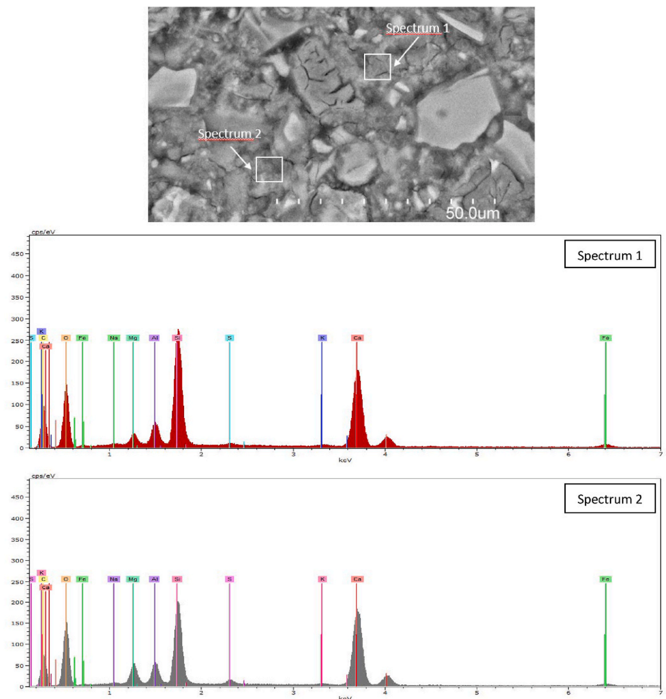

Fig. 10. SEM image and EDS spectrums of MMC mortar.

bioproducts, being a greener alternative to petrochemical-based additives as superplasticizers;

- Due to low bioproduct density and probable variation on porous microstructure, the mortars to which it was added, both when fresh and after hardening, were less dense than the control;
- Thermal conductivity and ultrasonic pulse velocity likewise ruled out any possible adverse effect of bioproduct on the internal uniformity of the material;
- The use of bio-admixtures did not greatly alter mortar compressive strength, with rises of 4.5% (for bioproduct agent without sonication at early age) and declines of 21.5% (for storage sonicated bioproduct);
- One of the most prominent findings was the effect of these admixtures on mortar pore structure; the decline in effective porosity relative to the control may have a potential beneficial effect on material resistance to penetration by aggressive external agents;
- The pore structure generated in the bioformulated mortars led to significantly more favourable water droplet and capillary absorptions in those new materials than in the control mortar;
- Early stage drying was scantly altered by the use of sonicated bio-admixtures, denoting the self-sealing potential of the product tested.

In light of the promising results of the present study, these bioproducts might well constitute an auspicious approach to enhance cement mortar durability, while slightly increasing mechanical properties. Simultaneously, they can contribute for the production of more eco-friendly cementitious products, one of the construction industry's aspirations in its relentless pursuit of sustainability. The bioproducts used have similar functionality than petrochemical-based additions of mortars or concretes and encourage the decrease on the use of fossil-based raw materials with the concomitant reduction in the carbon dioxide released into the atmosphere. Furthermore, the improved results in several of the tested parameters, which are associated with permeability and pore network of cement matrixes with MMC, entail a protective barrier against external attack, extending their service life. This implies a clear advantage in terms of optimizing natural resources and reducing waste production. Another highlight from this research is that an original waste from chemical industry was transformed into a valuable raw material for use in the construction industry.

Further studies should focus on the effect of these bioproduct on mortar microstructure and chemical composition, in order to ensure a suitable and complete characterization of this new and eco-friendly mortars.

CRediT authorship contribution statement

Julia García-González: Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Software, Writing – original draft, Writing – review & editing. **Paulina Faria:** Conceptualization, Funding acquisition, Resources, Software, Writing – original draft. **Alice S. Pereira:** Formal analysis, Funding acquisition, Resources, Software, Writing – original draft. **Paulo C. Lemos:** Formal analysis, Funding acquisition, Resources, Software, Writing – original draft. **Julia Mª Morán-del Pozo:** Project administration, Writing – review & editing. **M. Ignacio Guerra-Romero:** Project administration, Writing – review & editing. **Andrés Juan-Valdés:** Supervision, Funding acquisition, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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