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A sustainable production of natural hydraulic lime mortars through bio-amendment

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ABSTRACT

This article examined the effect of a bioproduct suspension obtained from fermentation of biodiesel's crude glycerol when used to formulate natural hydraulic lime mortars, as a fluid replacing the mixing water. The bioproduct was used either sonicated or non-sonicated and two volumes of mixing fluid were tested. The aim was to assess the advantages and drawbacks that could be achieved with a waste-based bioproduct, instead of petrochemical-based additions. The investigation revealed a positive effect on workability, producing mortars with a lower mixing fluid content, improving the mechanical performance. Finally, the bioproducts reduced the mortar water absorption by gravity and capillary.

1. Introduction

Global climate change encourages the pursuit of a more suitable and ecological construction and building sector. In this emerging scenario, lime mortars play a vital role since these materials exhibit several potential advantages in terms of sustainability. Their manufacture produces less environmental impact than cement-based materials, due to a lower energy consumption and CO_2 emissions [1]. Besides, some lime-based composites, as hemp-lime concrete, can be considered carbon-negative building materials [2–4], using local available residues and their low processing level. In addition, it is important not to underestimate their chemical, physical and mechanical compatibility for restoration of historical masonries, due to their water vapor permeability and not very high compressive strength [5]. Due to their high porosity, relative low internal cohesion and slow carbonation, lime-based mortars frequently need to be mixed with different additives to improve some of their properties [6]. Many of those additives have petrochemical origin, the main ones being the superplasticizers.

In the past, several studies demonstrated that ancient formulations with organic additives were able to enhance the air lime mortar properties, such as workability, setting time, porosity, performance towards water and durability. Nunes and Slížkova [7,8] added linseed oil to air lime mortars and achieved a remarkable capillary reductions and, consequently, a greater resistance to NaCl cycles and to freeze–thaw ageing. The study developed by Fang et al. [9] showed that the air lime mortar formulated with tung-oil and calcium hydroxide had improved mechanical properties, and higher resistance to water and weathering. Lagazzo et al. [10] used different fatty acid soaps and concluded that all of them showed the ability to reduce the water absorption of hydraulic lime-cement mortars, despite producing a higher porosity. Izaguirre et al. [11] studied the effect of a commercial potato starch on the properties of hardened air lime mortars and observed that the matrix of the hardened mortar presented greater coherence, owing to its large density and low porosity, and consequently lower capillarity and

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permeability absorptions, better mechanical properties and improved durability.

These findings agree with the records in ancient applications. For instance, part of Nanjing old city wall was built with sticky rice-air lime mortar, and Yang et al. [12] proved that this organic addition delayed the decay of air lime mortars. That justified the incorporation of sticky-rice and tung-oil in air lime mortars used to build tombs or dams due to their good water-proofness [12].

Natural hydraulic limes (NHL) are binders with both air and hydraulic curing, considered alternatives to air lime-pozzolan based ones [13]. These limes belong to a larger family with hydraulic properties, subdivided in three classes - NHL2, NHL3.5 and NHL5 - exhibiting decreasing minimum content of calcium hydroxide [14]. NHL results from calcination of raw materials at a lower temperature when compared with cements and, since the 2010 version of the EN standard [14], no additives can be incorporated to the raw material collected from the quarry.

The addition of minerals to NHL mortars has been investigated, such as the replacement of lime by pozzolanic materials [15,16] or more innovative ones, such as addition of graphene oxide [17]. Research has also been conducted to evaluate the effect of aggregate size and type [18,19], the dosage and production process [20–23], on the performance of NHL mortars. However, not much has been tested concerning bio-based additions, vernacular or innovative, on NHL mortars. This may be explained by the fact that the NHL, commonly applied since the 19th century, started to be used much more recently than air lime mortars, which have been used for more than two millennia.

The present experimental study evaluates the bioformulation of NHL3.5 mortars to improve their fresh and hardened properties, with special focus on the hydrophobic effect, since water penetration through the NHL mortar matrix could promote the deterioration of the material. In the bio-modified formulation the mixing water was replaced by a bioproduct obtained from microbial mixed cultures waste biomass grown with crude glycerol, a by-product of biodiesel processing. Biodiesel production through transesterification can generate up to 10 % (w/w) of crude glycerol as a by-product, impacting on the refined glycerol market. Thus, development of technologies that utilize this by-product is of uttermost importance, converting it into new added-value products or materials [24].

This same bioproduct was previously used to formulate cement bio-modified mortars. The resulting materials presented advantages in terms of properties related with water absorption and mechanical characteristics [25]. However, the effect of the bioproduct on NHL mortars was, so far, unknown. Therefore, the aim of the present work was to assess the improvements (and drawbacks) on the performance of formulated fresh and hardened NHL mortars, when varying their preparation and content of the bioproduct. This type of innovative bioproducts can be a sustainable alternative to the addition of petrochemical polymers, associated with lower embodied energy substitutes. Their utilization would transform a waste of the chemical industry into an addition for the construction and restoration sectors.

2. Experimental procedure

2.1. Materials mortars and samples

The natural hydraulic lime NHL3.5 used in all the mortars is commercialized by Secil company according to the EN 459-1 standard [14]. The NHL loose bulk density was 0.73 kg/dm^3. The sand was a commercial siliceous sand, from Abrantes, Portugal with a bulk density of 1.47 kg/dm^3. The NHL mortars were dosed with a lime:sand ratio of 1:4 by volume, corresponding to 1:8 by weight, based on the NHL and sand loose bulk densities.

The bio-based agents used in the experimental study were retrieved from the biomass produced by mixed microbial cultures (MMC) present in the selection reactor of a two-step polyhydroxyalkanoates (PHA) production process. These cultures produce a mixture of compounds, including small amounts of PHA at this stage. The culture used a solution of crude glycerol diluted in tap water as growth medium. This impure glycerol was a derivative from transesterifications reactions occurring in biodiesel production [26]. Two distinct aqueous suspensions forms of the bioproduct were used in the present work: one composed of MMC whole cells (MMC) and a second one containing MMC lysed cells, obtained by sonication to disrupt the cell walls and membranes (MMC_S).

Both bioproducts, MMC and MMC_S, were used as mixing liquid to prepare the NHL mortars, whose efficacy was compared with a control mortar mixed with tap water (W). In two mortar batches, the mixing water volume was replaced by MMC and MMC_S suspensions (MMC-1 and MMC_S-1) and, in other two batches, the mixing fluid was reduced (MMC-2 and MMC_S-2). Two mixing fluid/lime ratios were also studied as described in Table 1.

Standard 40 mm × 40 mm × 160 mm prisms were produced using steel molds, and samples simulating renders were manufactured on the surface of hollow bricks (Fig. 1). To limit the water absorption from the mortar by the brick masonry, and to simulate *in situ* applications, the bricks were sprayed with tap water prior to the application of the mortar layer to produce the render samples. Each brick was covered by one coat of NHL mortar with 20 mm of thickness. After 48 h of cure time at 20 ± 2 °C and 60 ± 5 % relative humidity (RH), the prismatic samples were demolded and retained in the same cure moisture and temperature conditions for 6 months. Afterwards, hardened state tests to analyze the NHL mortars properties were performed.

2.2. Test procedures

2.2.1. Fresh state

Consistency of fresh NHL mortar was measured by the flow table and the plunger penetration methods according to the standards EN 1015-3 [27] and EN 1015-4 [28], respectively.

Fresh mortar densities were determined as per the European standard EN 1015-6 [29], using a 1 L container.

2.2.2. Hardened state

Apparent density of three prismatic NHL mortar samples was assessed geometrically as stipulated in EN 1015-10/A1 [30].

Open porosity and bulk and real density values were tested based on standard RILEM Test N° I.1 and Test N° I. 2 [31]. Specimens were saturated by water immersion under vacuum and weighted. For each mortar, three 40 mm × 40 mm × 20 mm specimens cut from the prismatic samples were used.

Thermal conductivity was tested to evaluate the effect of the bioproducts on thermal insulation of the bioformulated NHL mortars, using an ISOMET 2104 portable Heat Transfer Analyzer fitted with a 60 mm diameter API 210412 contact probe. Thermal conductivity values were measured on the render on three brick samples per each NHL mortar at a temperature of 25 ± 2 °C and RH of 45 ± 5 %.

The compactness of the natural hydraulic lime renders on the brick

Table 1
Mortars designation, mixing fluid/lime ratio and composition in mass per unitary volume (g/dm^3).

Mortar ID	Mixing fluid/Lime (by volume)	Hydration fluid for mixing	NHL wt. (g)	Sand wt. (g)
W	1.06	174 mL water	121	969
MMC-1		174 mL MMC whole cells and water		
MMC_S-1		174 mL MMC sonicated cells and water		
MMC-2	0.88	150 mL MMC whole cells and water	124	998
MMC_S-2		150 mL MMC sonicated cells and water		

Fig. 1. Examples of the produced mortars as render on brick and prismatic samples.

samples were analyzed by Ultrasonic Pulse Velocity (UPV) with a Proceq Pundit Lab instrument according to the procedure described in standard EN 12504-4 [32]. Three samples of render on bricks were tested per studied mortar.

Flexural strength values of NHL mortars were analyzed as described in EN 1015-11 [33], employing a Zwick Roell Z050 equipment with a 2kN load cell, using three prismatic samples per NHL tested mortar. Following the same standard, the remaining halves of the prismatic samples resulting from the flexural test were subsequently subjected to compressive loading, using the same equipment, with a 50 kN load cell, to apply the force.

The water droplet absorption time was determined based on standard RILEM Test N° II. 8a [31], using the protocol described by Parracha et al. [34]. The assay was video recorded to optimize the accuracy of the measured time (seconds) required for the sample surface to completely absorb a drop of water, defined in terms of loss of sheen. The test analyzes the permeability changes in bioproduct-containing mortars by monitoring the absorption of a 0.1 cm^3 drop of water dropped onto the sample surface in laboratory conditions (temperature of 25 ± 2 °C and RH of 45 ± 5 %). This test was developed on 40 mm × 40 mm × 40 mm specimens, cut from the prismatic NHL mortar samples; three samples were evaluated per formulation.

The capillary water performance was assessed by following the standards EN 15,801 [35] and EN 1015–18 [36]. Three cube specimens with sides of 40 mm, prepared from the prismatic ones, were tested for each NHL mortar. To waterproof the four side faces of each analyzed specimen, they were covered with a layer of paraffin. Each tested face was immersed in tap water to 5 mm depth, then, the weight increased by water absorption was recorded every 5 min up to 45 min, and at 1 h, 2 h, 3 h, 4 h, 6 h, 24 h and 48 h after initial contact with water. Capillary water absorption and total absorbed water coefficients were calculated from the capillary curves.

The adhesive strength between rendering mortars and the substrate was determined based on standard EN 1015–12 [37]. Square subsamples (50 mm × 50 mm) were cut on the rendering mortar layer up to the limit of the hollow brick. Metallic pull-heads were fixed with epoxy glue to the mortar surface (Fig. 2). After 2 days of glue drying, tensile load perpendicular to the test area through the pull-head pins was applied using a Zwick Roell Z050 equipment, at a velocity of 1 mm/min and with a load cell of 2 kN. The adhesive strength was calculated dividing the maximal force registered by the equipment by the glued area. The pattern of mechanically induced fracture was registered, either adhesive, when the fracture occurred between the mortar and the substrate, or cohesive, when the fracture was developed in the mortar itself.

The abrasion resistance was measured according to the standard DIN 18947 [38]. A metallic hard rotating brush was pressed against the surface of the mortar, with a constant applied pressure produced by a mass of 2 kg and 20 rotations, to simulate wear conditions (Fig. 3). The loose particles were cleaned from the surface with a brush and the deep of the abrasion mark was measured.

3. Experimental results and discussion

3.1. Fresh state results

3.1.1. Consistency

The consistency results obtained for the control and bioformulated mortars (Fig. 4), showed that for equal dosage (mortars W, MMC-1 and MMC_S-1), the addition of the bioproducts increased the workability of mortars. It was noticeable the effect in mortars with non-sonicated bioproduct (18 % by flow table and 129 % by penetrometer), and even higher in mortars bioformulated with the sonicated bioproduct (22 % by flow table and 151 % by penetrometer), both relative to the control mortar. These improvements encouraged the evaluation of mortars manufactured with a smaller volume of mixing fluid (MMC-2 and MMC_S-2, with 120 cm^3 less of mixing fluid than the control mortar, W). These two mortars, MMC-2 and MMC_S-2, developed consistency values similar to the control mortar. For MMC-2 mortar, results were 11 % lower by the flow table and 20 % lower by the penetrometer in comparison with W, and for MMC_S-2, the flow decreased 8 % while the penetration even increased 9 %, compared with control mortars. The positive effect on the consistency observed for the mortars bioformulated with the sonicated products may be explained by the fact that the suspension of the sonicated bioproduct was more fluid and

Fig. 2. Square pull-head plates glued on the rendering mortar surface and adhesive test set-up.

Fig. 3. Abrasion test equipment and relief (left) on a mortar sample.

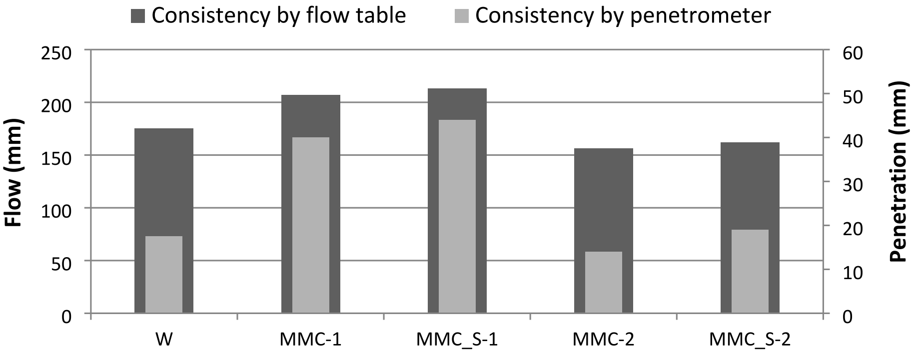

Fig. 4. Flow table and penetration consistency of the control and bioformulated NHL mortars.

homogeneous than the non-sonicated one. Furthermore, cell disruption released the intracellular content, namely different polymers as proteins, lipids, nucleic acids and PHA that may have improved the workability of the mortar. On a previous publication by García-González et al. [25], where the same bioproducts were tested on cement mortars, lower consistency improvements were observed for non-sonicated bioproducts (almost the same flow, 0.3 % increase, in comparison with the control mortar, and 30 % higher of penetrometer deep). However, for the sonicated bioproduct, the improvements on cement mortar consistency were comparable to the values achieved in the present study for the NHL mortars, with 18 % of flow increase and 150 % by penetrometer. Contrarily, Oliveira et al. [39] tested this type of bioproducts, produced by MMC using crude glycerol, on air lime mortars and observed that those seemed to need a higher liquid content to achieve an adequate workability, although after increasing the mixing liquid/binder ratio (from 2.4 on the control air lime mortar to 2.5 on bioformulated air lime mortar), the highest flow table consistence was obtained for the later ones.

3.1.2. Density of the fresh mortar

All the values of density on fresh bioformulated NHL mortars were slightly reduced (between 4.3 % and 7.9 %) in comparison with the control NHL mortar (Fig. 5), more significant on mortars with higher volumes of bioproduct as mixing fluid. Between sonicated and non-sonicated bioproducts, the variation of fresh density was almost unnoticeable, and if a greater lowering was detected, it was in samples with sonicated bioproduct, since broken cells exhibited lower level of aggregation. These results can be due to a lower density of the bioproducts in comparison to water, as well as to the air entrainer effect resulting from the addition of the bioproducts. Similar effects were observed by García-González et al. [25], who also detected a decrease between 2.2 % and 7.8 % on all the samples of bioformulated cement mortars, with slightly higher decreases on the sonicated ones.

3.2. Hardened state mortar results

3.2.1. Density and porosity

Comparable to the density results of the fresh mortars, the presence

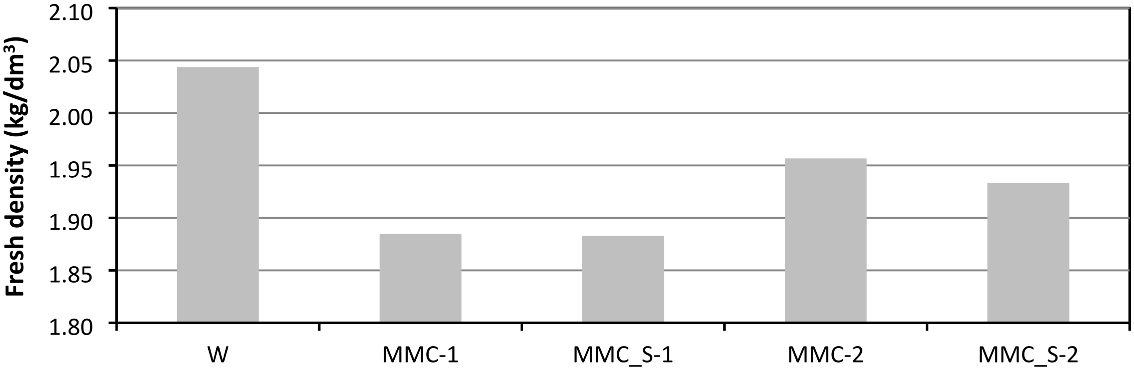

Fig. 5. Density of the control and bioformulated NHL mortars in the fresh state.

of the bioproducts slightly reduced (between 1.9 % and 6.8 %) the apparent density of mortars in the hardened state (Fig. 6). The effect was probably owing to the same reason, a more porous microstructure on bioformulated NHL mortars due to an air entrainer effect of the bioproducts.

The bulk and real densities of tested NHL mortars, measured under water saturation of samples, showed a similar tendency (Fig. 7) than fresh and hardened state values determined in laboratory conditions. Bulk and real densities slightly decreased in bioformulated MMC-1 and MMC_S-1 mortars (reductions between 3 % and 7 %), and a minor reduction, between 2 % and 4 %, for samples with smaller volumes of mixing liquids (MMC-2 and MMC_S-2). As expected, due to their characteristic lower density, samples MMC-1 and MMC_S-1 presented higher effective porosity values: 9 % for samples with non-sonicated bioproduct and 11 % for sample with the sonicated one. However, the mortars prepared with smaller volumes of the mixing fluid (720 cm^3 versus 600 cm^3) achieved better results, since not only the effective porosity of the mortars did not increase, but also, they achieved similar porosity values: reduction of 1 % for MMC-2 and 4 % for MMC_S-2.

Pahlavan et al. [6] studied the effect of used cooking oils in hydrophobic NHL mortars for conservation renders and observed that this addition increased the total open porosity of mortars. However, all the NHL mortars presented values commonly considered compatible for conservation. Izaguirre et al. [11] studied the effect of a commercial starch, on air lime-based mortars and noticed that, like in the present study, the density of all mortars on the hardened state decreased with increasing amounts of the bioagent. The same authors claimed that the open porosity of the air lime mortars with potato starch was lower than the reference one. Also, García-González et al. [25] observed an effective porosity reduction on cement mortars manufactured with bioproducts obtained from the fermentation of biodiesel's crude glycerol, sonicated and non-sonicated bioproducts, as well as with bioproducts with different ages. Another study, where prickly pear mucilaginous exudate and cooked mucilage were used in the production of concrete [40], stated that the additions of these bioagents reduced the effective capillary porosity (pores radius between 0.01 μm and 10 μm) of the concrete samples, irrespective of the testing time (from 30 days to 400 days).

3.2.2. Compressive and flexural strength

According to the mechanical characterization tests, both compressive and flexural strength (Fig. 8) followed a similar tendency: the replacement of water by the bioproduct suspensions caused a decrease on the mechanical resistance of NHL mortars, 8 % and 15 % for MMC-1, and 19 % and 21 % for MMC_S-1, respectively. However, when the volume of mixing fluid was smaller (600 cm^3 instead of 720 cm^3), both compressive and flexural strength were benefited: for MMC-2, the compressive strength increased 26 % and the flexural resistance increased 25 %, relative to the control mortar. When the sonicated bioproduct was used, MMC_S-2, the compressive resistance increased up to 31 % and the flexural strength raised 22 %, also versus the W mortar. This fact agreed with the results of effective porosity of NHL mortars with mixing fluid adjustment, since lower quantity of open-air pores gives rise to a more compacted NHL mortar matrix, able to support higher strengths.

When these types of bioproducts were tested in cement mortars [25], they did not substantially affect their mechanical behavior (compressive and flexural strength), with values ranging from 22 % to 5 %. Mignon et al. [41], that added 1 % of alginate by cement mortar samples (w/w), observed small reductions of the compressive and flexural strength (<15 %) when the biopolymer was added.

Other studies, as the research developed by Oliveira et al. [39], who also replaced the mixing water by MMC from biodiesel's crude glycerol and by *Escherichia coli* cultures, verified that these type of organic additions reduced the compressive strength of air lime mortars, 58 % for the air lime mortar with *E. coli* and 42 % for the mortars with MMC bioproducts, both compared with a control mortar. Nunes and Slížková [8] used linseed oil on air lime and lime-metakaolin mortars to improve their hydrophobic properties and showed that these organic products caused a reduction of 16 % and 17 % on flexural and compressive strength of the lime mortars, whereas the same additions increased the flexural and compressive strength, 15 % and 9 % respectively, of metakaolin-lime mortars.

Izaguirre et al. [11] tested the influence of different dosages of a commercial starch additive on the properties of air lime mortars, showing an improvement in the flexural and compressive strength. Therefore, the results of the present work indicate that both bioproducts tested (sonicated and non-sonicated) improved the workability of mortars, allowing to reduce the mixing fluid content, and increased their mechanical performance. Furthermore, the better mechanical properties occurred in parallel with a decrease in the density, which is an advantage for the application of mortars. Finally, this benefit seems to be more significative on NHL mortars in comparison to air lime or cement ones.

3.2.3. Adhesion and resistance to abrasion

Figure 9 presents the results obtained for adhesive strength of control and bioformulated NHL mortars. The addition of MMC bioproducts, either sonicated or non-sonicated, replacing the mixing water or with adjustment of the quantity of bioproduct added, increased the ability of NHL mortar to bond to a brick substrate, as well as the cohesion of NHL mortars. Non-sonicated bioproducts improved the adhesion strength in 9 % and 14 % (relative to the W sample), for the MMC-1 and MMC-2, respectively. More significant, the used of sonicated bioproducts, MMC_S-1 and MMC_S-2, augmented the adhesion values in 16 % and 22 %. This fact can be justified by the greater homogeneity of the sonicated

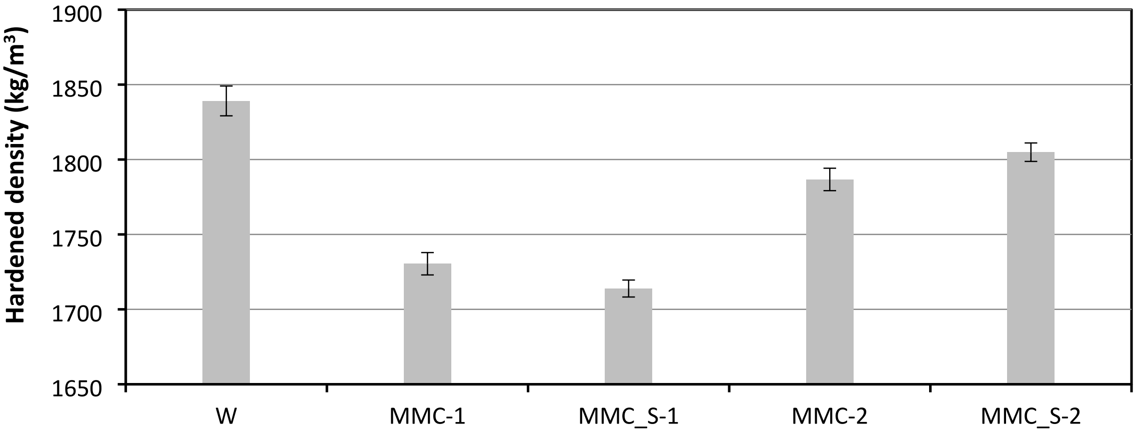

Fig. 6. Apparent density of the control and bioformulated NHL mortars in the hardened state.

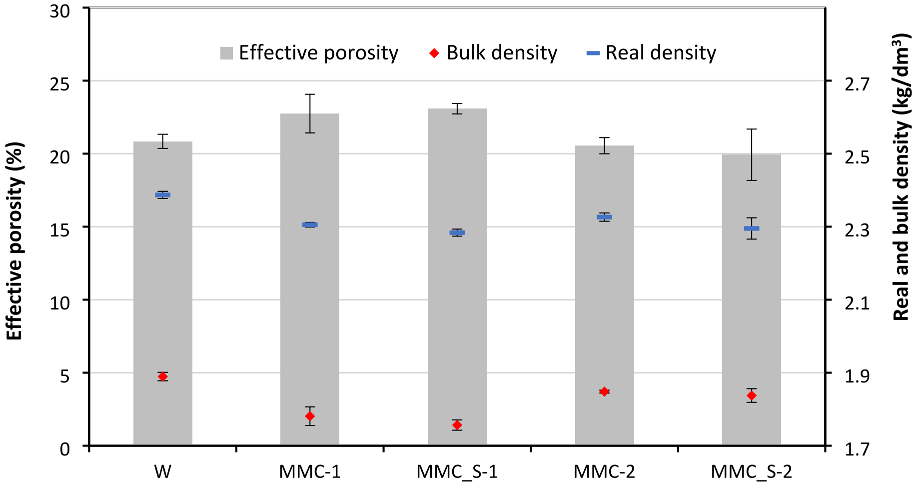

Fig. 7. Effective porosity, real and bulk density of the control and bioformulated NHL mortars.

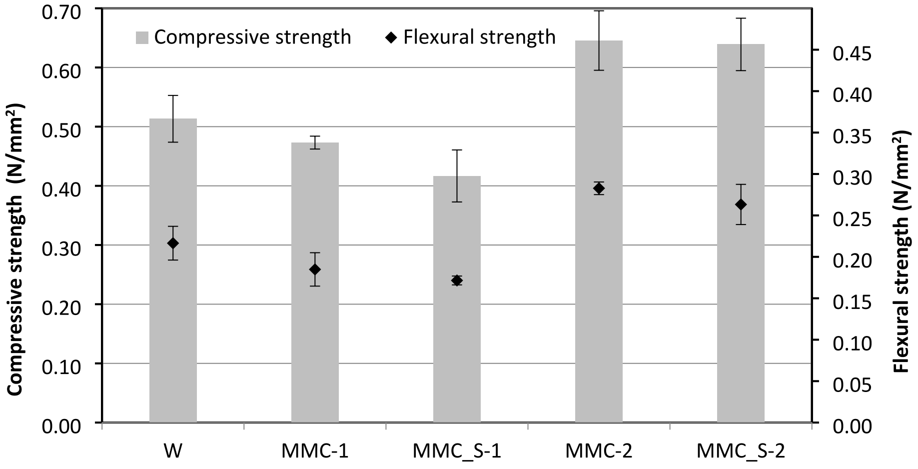

Fig. 8. Compressive and flexural strength of the control and bioformulated NHL mortars.

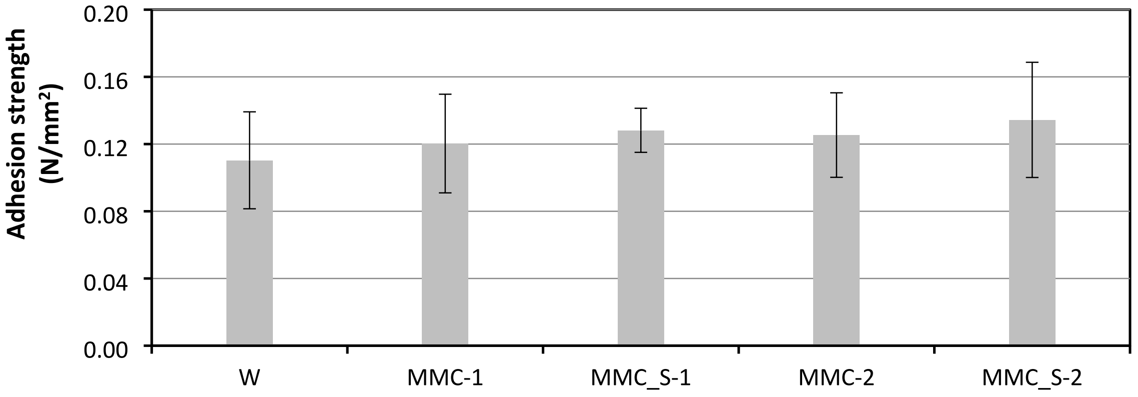

Fig. 9. Adhesion strength of the control and bioformulated NHL mortars.

bioproduct suspension, with a better distribution of MMC biomolecules that improve the interactions between the mortar's particles and/or the mortar and the substrate, contrarily to the non-sonicated bioproducts, MMC-1 and MMC-2. The latter, as non-disrupted whole microbial cells, may exhibited larger level of aggregation of components, developing a more heterogeneous distributions throughout the mortar matrix. Regarding the pattern of mechanically induced fracture, all the tested mortars but MMC_S-1, registered adhesive fractures, showing the forced splitting in the transition zone between the mortars and the brick used as substrate. A different pattern of fracture was recorded on MMC_S-1 mortar, produced with a higher amount of sonicated bioproduct, where the failures occurred in the mortar thickness, close to the glue surface, registering cohesive fractures. In this mortar, the adhesive strength between the mortar and the substrate is in fact higher than the registered value, limited by the mortar cohesion.

The results of the abrasion test (Fig. 10) showed a similar NHL

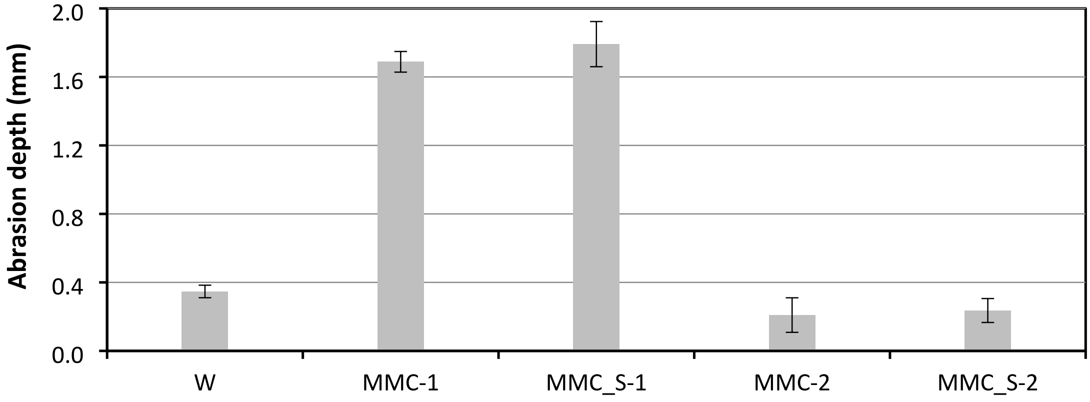

Fig. 10. Abrasion depth of the control and bioformulated NHL mortars.

mortars behaviour as for the mechanical strengths and effective porosity when the bioproduct was added. The direct replacement of mixing water by bioproducts, either sonicated or non-sonicated, significantly declined the resistance to abrasion wear. However, the reduction of mixing fluid was able to increase the abrasion resistance of mortars MMC-2 and MMC_S-2, by 40 % and 32 %, respectively.

3.2.4. Thermal conductivity and ultrasonic pulse velocity

Thermal conductivity of NHL mortars is displayed on Fig. 11, showing that the direct replacement of water by the MMC bioproducts reduced the thermal conductivity of NHL mortars (MMC-1 and MMC_S-1), with greater decrease in mortars with the sonicated bioproduct (MMC_S-1). However, this reduction was almost unperceived when the mixing fluid content was adjusted on NHL mortars bioformulation. Heat transmits more efficiently in dense materials and less efficiently in porous materials [42]. Oliveira et al. [39] also detected reductions of 20 % when using MMC bioproducts on air lime mortars bioformulation. However, García-González et al. [25] observed opposing findings, since the addition of MMC bioproducts to the rest of the cement mortar components resulted in an effective porosity reduction on all samples tested, and in accordance with these results, their thermal conductivity was increased in all the bioformulated mortars.

Like thermal conductivity, NHL mortar compactness and uniformity were also tested by UPV, and the results (Fig. 11) showed that the addition of MMC bioproducts caused an ultrasonic velocity decrease when mixing water was replaced directly by the sonicated and non-sonicated bioproducts, in accordance with the thermal conductivity results in mortars with higher effective porosity (Fig. 7), MMC-1 and specially MMC_S-1. Likewise, in concordance with the slightly reduction obtained on the effective porosity of NHL mortars prepared with smaller volumes of bioproducts, the UPV was faintly increased (2–4 %). These findings agree with the densities and the mechanical strengths data, as expected due to the larger effective porosity, as in the case of MMC_S-1 (Fig. 7).

A predictable higher compactness and uniformity developed by MMC-2 and MMC_S-2 mortars, considering UPV results (Fig. 11), in conjunction with a lower effective porosity (Fig. 7) may explain the positive performance of these mortars on the abrasion test.

3.2.5. Water droplet absorption

The time for water droplet absorption measured for each mortar is presented in Fig. 12. It can be observed that the replacement of mixing water by the non-sonicated MMC bioproduct was not able to improve the resistance to water ingress capacity of the NHL mortar, decreasing the water droplet absorption time 14 % on MMC-1 mortar compared with the W mortar. This fact was probably due to the effective porosity increase developed by this mortar formulation, in combination with the heterogeneity of the non-sonicated bioproduct, in which the larger aggregation level of the MMC component was not able to fill enough the pore network of NHL mortar paste. In contrast, the addition of the sonicated bioproduct (MMC_S-1) was able to reach a higher volume of the pore network, increasing the water droplet absorption time up to a 57 % compared to the control sample. This bioformulation was a more homogeneous suspension in spite of the MMC_S-1 sample achieving a higher effective porosity than the control NHL mortar. A positive effect was also observed in cement mortars by García-González et al. [25], using the same kind of bioproducts, that attained an increase of the resistance to water ingress capacity on all the bioformulated samples, from 8 % to 83 % of improvement. Air lime mortar developed by Oliveira et al. [39], with the MMC bioproducts from crude glycerol, also achieved significant improvements on the waterproofing effect of the bioformulated samples, increasing the times of water droplet absorption

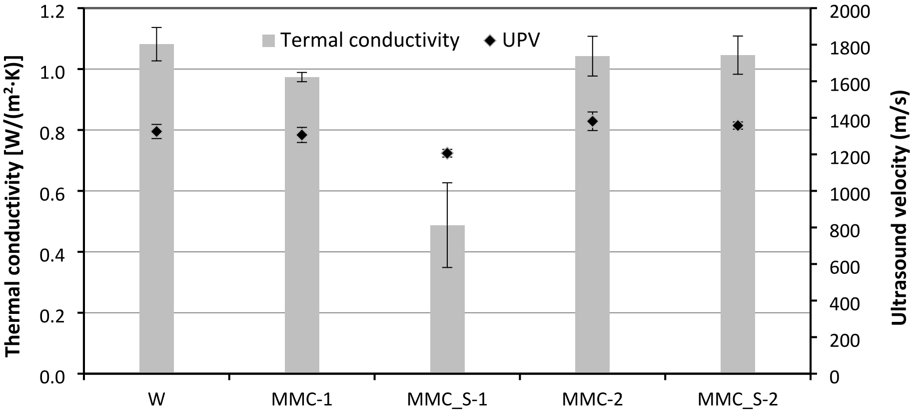

Fig. 11. Thermal conductivity and ultrasonic pulse velocity of the control and bioformulated NHL mortars.

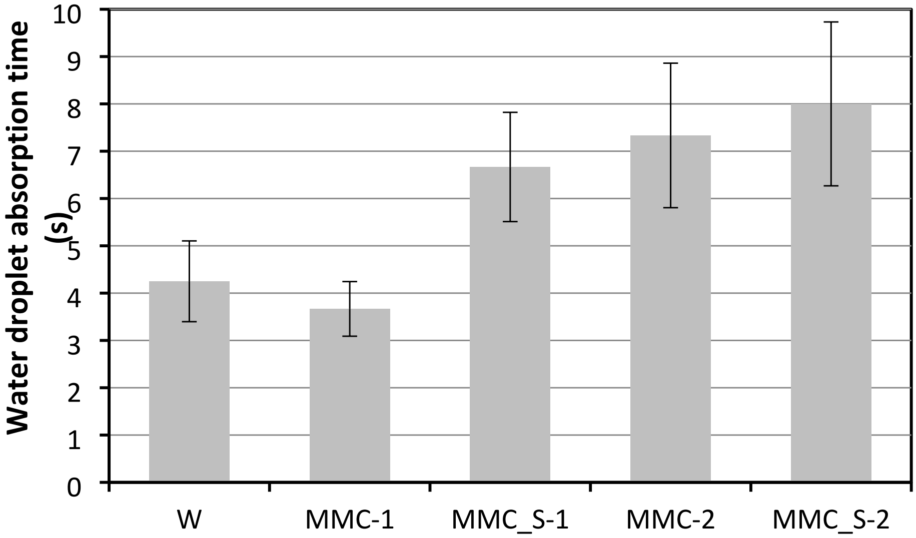

Fig. 12. Droplet absorption time of the control and bioformulated NHL mortars.

up to 700 % higher than the control air lime mortars.

Regarding the mortars MMC-2 and MMC_S-2 (prepared with smaller amounts of bioproducts), they exhibited an intensive increase in the water resistance effect, rising up to 73 % for the mortar with non-sonicated bioproduct, MMC-2, and 88 % for mortars with sonicated bioproduct, MMC_S-2, consistent with the results for the effective porosity obtained for these samples.

3.2.6. *Capillary water absorption*

The curves of weight increase registered during the capillary water absorption test (Fig. 13) and the capillary water absorption coefficients of control and bioformulated NHL mortars (Fig. 14) showed a beneficial effect of the use of all bioproducts, since the water absorption coefficient was decreased by 25 % and 20 % for mortars with direct mixing water replacement, MMC-1 and MMC_S-1, respectively. This improvement was amplified when the mixing fluid was reduced in the NHL mortar formulation, achieving 34 % and 33 % of reduction on the capillary water absorption coefficient compared with the control mortar for MMC-2 and MMC_S-2 mortars, respectively.

Observing Fig. 13 asymptotic part of the curves, also a reduction of the total absorbed water per contact area with water occurred when the water was replaced by the bioproducts, and the reduction was even higher when the volume of bioproduct reduced.

When García-González et al. [25] added the same bioproducts on cement mortars, the authors also observed that all the bioformulated mortars were less permeable than the control one. Oliveira et al. [39] tested similar glycerol-based bioproducts on air lime mortars and reached a 17 % reduction in the capillary coefficient compared with the control mortar. Pahlavan et al. [6], who evaluated the hydrophobicity of NHL mortars with addition of used cooking oils, reported that this addition exhibited a hydrophobic effect on the capillary phenomenon, due to the hydrophobicity of their vertical tunnels of pores (reduction from 30 to 60 times). According to these researchers, these bioadditives, especially high-linoleic acid oil, turned the hydrophilic cavities into hydrophobic ones due to their non-polar carbon-hydrogen bonds.

4. Conclusions

This study examined the effect of a bioproduct obtained from the fermentation of biodiesel's crude glycerol (MMC) when used to formulate NHL mortars, replacing the mixing water. Two forms of the bioproduct were tested, sonicated and non-sonicated forms, and two

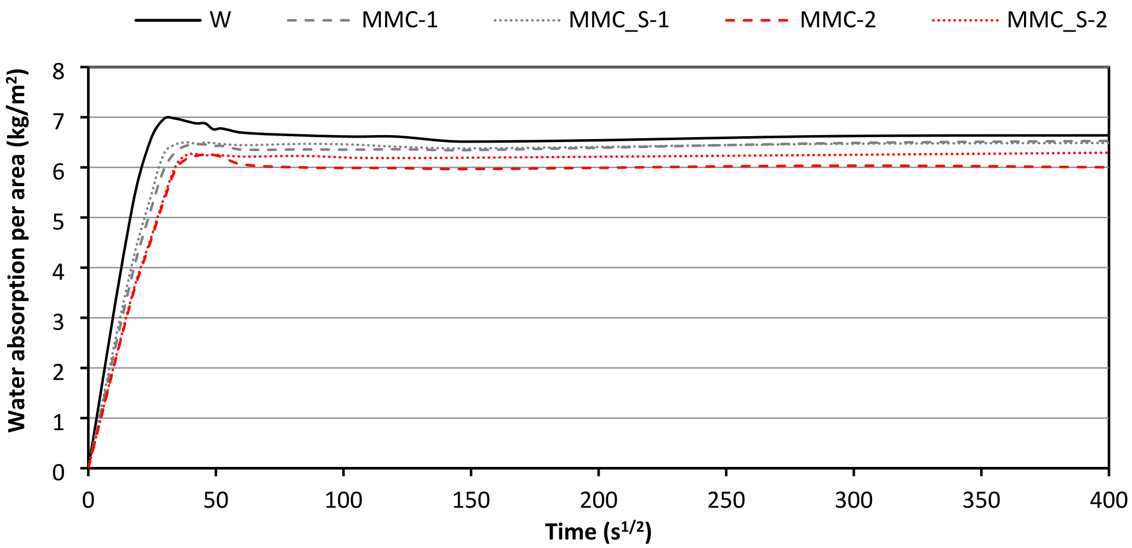

Fig. 13. Capillary water absorption curves of the control and bioformulated NHL mortars.

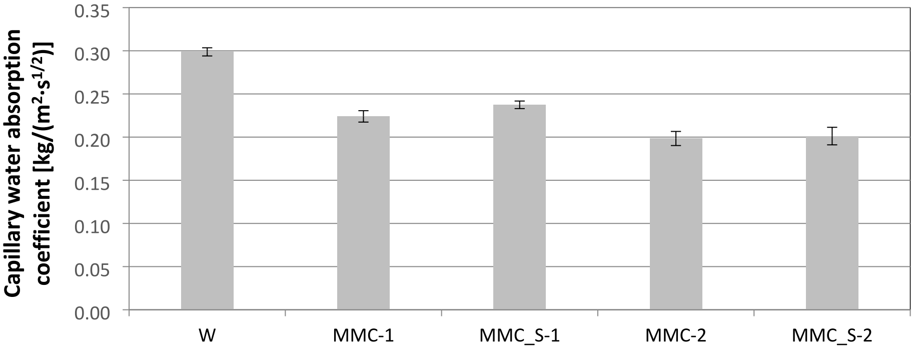

Fig. 14. Capillary water absorption coefficient of the control and bioformulated NHL mortars.

volumes of mixing fluid were used. The effects on both fresh and hardened mortar performance were tested and the experimental investigation revealed the following:

- The addition of the bioproduct significantly improved the workability of NHL mortars, either sonicated or non-sonicated, affording mixing fluid reductions on mortar formulation without declining their workability.
- All tested densities, on the fresh and hardened states, bulk and real, developed a slight reduction due to the bioproduct incorporation, smaller on mortars with less mixing fluid.
- The effective porosity was increased on mortars with direct substitution of mixing water by the sonicated and non-sonicated bioproducts; contrarily, the mortars with less mixing fluid reached a small reduction on the effective porosity.
- The mechanical strengths of NHL mortars were improved when the mixing liquid was smaller. In this case, the compressive strength was increased up to 26 % and the flexural strength up to 31 %.
- The addition of all MMC bioproducts increased the adhesion of the NHL mortars.
- The replacement of the mixing water by the same volume of bioproducts, either sonicated or non-sonicated, significantly declined the resistance to abrasion wear. However, when mortars were prepared with smaller volumes of mixing fluid, maintaining workability, their abrasion resistance increase up to 40 %.
- The replacement of the mixing water by the same volume of glycerol-based bioproducts, reduced the thermal conductivity and ultrasonic pulse velocity of NHL mortars. Contrarily, almost no changes were perceived when the mixing fluid content was adjusted on the NHL mortars bioformulation.
- Bioformulation of mortars lengthened the water droplet absorption time up to 57 % compared to the control mortar. The exception was the mortar with non-sonicated bioproduct added in larger volume, where the water droplet absorption time decreased 14 %.
- All the bioformulated NHL mortars were less hygroscopic than the control mortar, what should contribute to its durability when exposed to weathering, and to further increase their eco-efficiency.

The results were particularly interesting because the mechanical effect did not seem to have influence on compatibility issues, important when NHL mortars are intended to be applied on architectural heritage conservation. However, for this type of applications, it will be necessary to assess physical compatibility, namely in terms of water vapour permeability with the bioproducts added. Furthermore, the durability of these bioformulated NHL mortars should be further studied, namely concerning salts attack.

The waste-based bioproducts seem to be a promising alternative to raw materials-based additions. The air entraining effect should be deeper studied, namely by comparison with common air entrainer additions. To be used in pre-mixed mortars, the bioproducts should be in a powder form, for their effects to be reached when mixing with water *in situ*. That should be object of further research.

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, Writing – review & editing. **Alice S. Pereira:** Formal analysis, Funding acquisition, Resources, Software, Writing – original draft, Writing – review & editing. **Paulo C. Lemos:** Formal analysis, Funding acquisition, Resources, Software, Writing – original draft, Writing – review & editing. **Andrés Juan-Valdés:** Supervision, Funding acquisition, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

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