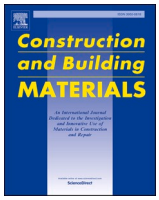
Construction and Building Materials 456 (2024) 139307

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat



New methodological approach for the mechanical testing of aerial lime-based binders and mortars: the effect of PEG-1000 addition

Paulina Guzmán García Lascurain, Luca Andena *, Elena Hitthaler, Maria Sugari, Lucia Toniolo, Sara Goidanich

Dipartimento di Chimica, Materiali e Ingegneria chimica "Giulio Natta", Politecnico di Milano, Milan 20133, Italy

ARTICLE INFO

Keywords:
Lime-based mortars
Aerial-lime binders
Mechanical testing
PCMs
Scratch test

ABSTRACT

So far, the mechanical testing at the macro scale of aerial lime-based materials has mainly been focused on the analysis of mortars, while binder specimens have not been studied as much. In the present work an alternative, material-effective and low-waste methodology to evaluate the mechanical properties of aerial lime binders and mortars is proposed. The core of this methodology is based on specimen size reduction, minimizing quantities of material required during development and testing. In particular, the proposed methodology is aimed at studying the interaction of different quantities of a phase change material (PCM) with aerial lime binders and mortars. The mechanical properties of pure aerial lime binders were successfully characterized, whereas mortar specimens provided less detailed information. The mechanical characterization showed that aerial lime binders, and consequently mortars, are weakened in the presence of Poly(ethylene glycol) - PEG, a PCM. It was observed that 8 % of PEG in the binder lower the resistance to compression by 36 %, resistance to scratch on 76 % and flexural resistance by 32 %. Finally, this study also proposes a model for the physical interaction between the PCM and the aerial lime-binder to explain the observed weakening mechanism: PEG can hinder the correct crystalline interlocking between the calcite crystals in the carbonated binder, and act as a lubricant promoting their sliding under compressive forces.

1. Introduction

Aerial lime-based mortars are one of the oldest construction materials manufactured by humans [1,2]. Currently, the slow setting via carbonation of these mortars, their low mechanical properties compared to concrete, and loss of traditional know-how for their manufacturing, have resulted in a reduction of their use. Nevertheless, these mortars remain relevant for the restoration of built heritage. Their physico-chemical and mechanical characteristics make them compatible with the historical original masonry [2,3]. Also, thanks to their reduced environmental footprint, if compared to concrete, these mortars are becoming an interesting alternative for sustainable architecture. Generally, aerial lime-mortars are used in construction and restoration for non-structural applications (plasters, renders, beddings, or pointers to join elements of masonry) given their low compression strength in the order of a few MPa [4].

To overcome these limitations and promote the use of lime-based mortars, the introduction of additives in lime-based mortars has increased significantly over the previous decade. Small amounts of additives in the mortar improve its processing and final properties [5]. Among various types of additives Phase Change Materials (PCMs) [6,7], often polymeric in nature, are thermal energy storage systems (TES) able to increase the thermal capacity of the mortars (plasterings). They melt or crystallize at specific temperatures, meanwhile capturing or releasing thermal energy [8]. The phase-change temperatures are often correlated with the day/night cycles, helping control of the interior temperature and reducing the intense need ~~of~~ for conventional thermo-regulation systems. However, many authors have reported that when PCMs are introduced in mortars, they tend to reduce the mechanical performance of the latter [6,7]. Particularly, when the PCMs are included in the mortars as Form-Stable Phase Change Material aggregates (FS-PCM) impregnated with Poly(ethylene glycol) (PEG) as active PCM, the mechanical properties can be reduced by 50 % with respect to the control [6]. In this regard, a previous work [9] revealed that the lack of confinement of PEG inside the FS-PCM aggregates leads to its dispersion in the binder phase. It was then hypothesized that this lack of

* Correspondence to: Dipartimento di Chimica, Materiali e Ingegneria chimica, Politecnico di Milano, 20133, Milano, Italy.
E-mail address: luca.andena@polimi.it (L. Andena).

https://doi.org/10.1016/j.conbuildmat.2024.139307
Received 3 October 2024; Received in revised form 19 November 2024; Accepted 20 November 2024
Available online 23 November 2024

confinement and the consequent mixture of PEG with the binder could be one of the reasons behind the reported weakening of the mortars [6,7]. However, until now this hypothesis has not been demonstrated, and the interaction between PEG and binder phase is not fully understood. To this aim, the mechanical testing of pure aerial lime-binder specimens and lime-based mortars in the presence of PEG could provide fundamental information to explain the reported mortar weakening.

Currently, the standard-regulated mechanical testing of lime-based mortars consists of evaluating the strength characteristics of the mortar (compression and tensile strength) and is performed according to EN 1015–11 [10]. Furthermore, the adhesive strength and elastic modulus of renders and plasters are studied using the EN 1015–12 [11]. In the present work, only the compressive and flexural strength characteristics were considered.

As defined by the EN 1015–11 standard [10], all mortars where the binder content is at least 50 % aerial lime are classified as lime-based mortars. This means that the category of "lime-based mortars" consists of those where the binder can be made of pure aerial-lime or up to a blend of 50/50 lime:cement. Under this definition, the mechanical resistance of this category can cover a wide range [4,12,13], where the strength of the mortar highly depends on that of the binder [4]. It has been recently underlined that current mechanical testing methods are basically designed for cement-based mortars and, therefore, they might not be fully suitable for characterising lime-based ones, to assess plaster and renders [14].

The current standard (EN 1015–11) requires performing the tests on at least 3 mortar specimens cast on steel moulds of 160 ×40 ×40 mm^3. These dimensions are problematic since:

(a) They are not representative of the real dimensions of lime-based mortar applications, which are normally applied as thin layers, around a few mm thick [14].
(b) Casting these large specimens requires a large amount of material. According to the standard, the fresh paste needs to be 1.5 times larger than the required amount to perform 3 replicas of each sample. These quantities are not always easily available, especially at the research laboratory developing phase.
(c) Particularly for aerial lime-based mortars, which harden via carbonation, the necessary time required to have a fully carbonated specimen of such dimensions will most probably exceed the 28 days required by the EN 1015–11 [15]. If the test is performed before the mortar is fully carbonated, the mechanical resistance will be a fraction of the one achieved once carbonation is complete.
(d) To cast aerial lime-based mortars of this geometry and prevent micro-cracking, a common practice is to use superplasticizers which perhaps are not necessary when making a layer a few mm thick.
(e) Under the current climate crisis, the large production of waste material and its correct disposal at the laboratory level is an urgent problem that universities and research entities should consider [16,17]. Large specimens also imply large material quantities, and after the test is performed, these materials are disposed, generating equal amounts of laboratory waste.

Moreover, based on the standard, the specimens should be cast in steel moulds, which are non-porous materials, unlike the common substrates where lime-based mortars are normally applied. These non-porous substrates drastically impact the porosity of the mortar [18–20]. Consequently, the mortars cast in porous substrates present a higher mechanical resistance [18–20]. A different European standard dedicated to mortars in the field of cultural heritage, the EN 17187 [21], briefly mentions the mechanical characterization of lime-based mortars. In this standard, it is advised to perform the mechanical characterization only if enough material is available, but no reference to any testing methodology is present.

To overcome some of these issues, alternative methodologies to characterize the mechanical properties of lime-based mortars have been proposed. A very popular one is the Drilling Resistance Measurement System (DRMS) [22,23], which correlates the resistance to drill of a material with its compressive strength. The drilled orifices are often only a few millimetres ~~of~~ in diameter [4], and they can be done in the laboratory and *in situ*. Another technique of increasing interest is the scratch resistance test [24–26], where the scratch resistance is correlated to the compressive and flexural strength of mortars. Both DRMS and scratch test are complementary techniques that allow to characterize the bulk and surface of the materials respectively. Besides, they can work on mortars with different and irregular dimensions, thus eliminating the specimen-size problem. However, in both cases when these measurements are made on heterogeneous materials (such as mortars), the results are difficult to interpret and often present a high noise-to-signal ratio. Another alternative method to determine the compressive strength of non-standard specimens is the double punch test (DPT) [27]. It consists of loading a small mortar (around 40 x 40 x 10 mm^3) between two circular plates of smaller diameter (20 – 30 mm). In this way, the compressive strength is calculated as the ratio between the failure load and the regular cross-section of the plates, instead of that of the specimen. Nonetheless, the results obtained strongly depend on the size of the mortars and of the punches [28]. Lastly, a modern minor-destructive test, has been applied by Łątka [29] on lime-based mortars, which is similar to DRMS since it consists of recording the resistance of a material to penetration with a hammered needle. Sample size and availability is a common challenge in the analysis of historical mortars. This issue has been overcome by cutting the samples to obtain semi-regular shapes of non-standard sizes [30] or mounting them in "support" materials that correct their irregular geometry while sustaining the small sample [31,32]. In these cases, the cutting action may affect the sample's integrity and using of the additional material must be considered when deriving the realistic mechanical performance of the tested mortar.

To the knowledge of the authors, currently, there is no mechanical study performed on specimens made exclusively of aerial lime-binder (without aggregates). The objective of the present work is to investigate the mechanism of weakening of lime-based binders with the introduction of this specific PCM: PEG. Moreover, this work aims to propose an alternative methodology to evaluate the mechanical properties of pure lime-based materials, where both binder and mortar samples can be tested on small sample sizes.

2. Materials and methods

2.1. Materials

Both binder and mortar specimens were prepared using aerial lime (*Calce idrata Fiore di idrato purissimo extra ventilato*, Fassa Bortolo Srl, Italy) composed of 89 % $Ca(OH)_2$ and 11 % $CaCO_3$ according to XRD analysis (see below). The carbonate content is associated with accidental carbonation during transportation and measurement. The aerial lime powder had a granulometry of <0.1 mm and a density of 450 kg/m^3. For the mortar specimens, silicate sand (granulometry 0.1 – 0.3 mm) was used instead of carbonate sand, to ensure that the CO_3 ~~so it~~ FTIR signal would be associated unequivocally with the binder. Silicate sand is mainly composed of silicon dioxide and is characterized by the Si – O FTIR vibrational signal at ~ 1100 cm^{-1}, which does not overlap with the CO_3 vibration at 1420 cm^{-1}. The PCM of interest was Poly(ethylene glycol) (trade name PEG-1000) supplied by Sigma–Aldrich (Germany). This PCM has a melting point between 37°C and 40°C and a solidification temperature around 18–20°C [6]. PEG-1000 was stored in a sealed container at room temperature and 50 % humidity; consequently, it is safe to assume that it was in the solid state before its dispersion in water and subsequent introduction in the specimens. PEG-1000 was introduced in both binder and mortar specimens in the following percentages

Table 1
Proportions (kg/m^3) to manufacture the different types of specimens. In both cases (B and M) specimens with all 4 concentrations of PEG-1000 and a control without the polymer were made.

Specimen type	Binder	Aggregates[a]	Water
Binder (B)[b]	310	0	310
Mortar (M)[b]	209	491	230

Notes: In binder specimens, water to binder ratio was 1:1. In mortar specimens, water to binder ratio was 1:1.1 and binder to aggregate ratio was 1: 2.35. For all specimens, the Binder to PEG ratios were: 1:0.05 ; 1: 0.08 ; 1: 0.1 and 1: 0.15 for 5, 8, 10, and 15 % of PEG respectively.

[a] The density of the silicate sand is 1604 kg/m^3

[b] The included PEG % (5, 8, 1,0 and 15 %) were weighted as the corresponding percentage fraction of the total mass weight of the binder.

by mass weight of the binder: 5, 8, 10, and 15 %. The selected percentages for this study allowed a distribution of values that would elucidate the effect that PEG has on the binder for a mix-design similar to the one used in the previous studies [6,9]. PEG-1000 was dissolved in the water used to make the specimens, to obtain a complete dispersion of this polymer in the whole volume of each specimen. For each type of specimen (binder and mortar), five sets were made: a control set without any PEG-1000, and four sets with the above-mentioned percentages. The proportions for each of the specimen types (binder and mortar) are reported in Table 1. The binder specimens were made by mixing the total mass of aerial lime with distilled water, or distilled water with the respective PEG %, in proportion 1:1. The mortar specimens were prepared by first mixing the dry components (binder and aggregates) in a clean plastic bag. Once the dry components were homogeneously mixed, distilled water, or distilled water with the respective PEG %, was added in the proportion specified in Table 1. The binder specimens were cured for 1 day at 20°C with 65 % RH and removed from the casts. The mortar specimens were cured in a controlled room at 20°C with 90 % RH for 3 days and at 65 % RH for 7 days before being removed from the casts (except for the carbonation specimens that remained in the casts to promote the carbonation from a single face – see carbonation).

In binder specimens, water to binder ratio was 1:1.

A series of preliminary tests were performed to optimise the shape and size of the different specimens depending on the type of test and material (mortar or neat binder). Different dimensions of the specimens were then selected depending on the specimen type and the specific test performed. In Table 2 the geometrical parameters are reported for each type of specimen, and in Fig. 1 the different moulds and specimens are shown. Moreover, for mechanical testing and porosity measurements, all the specimens were artificially carbonated in a chamber saturated by CO_2 (above 50000 ppm) for fifteen days. FTIR measurements performed before the mechanical measurements confirmed that the specimens were fully carbonated. The accelerated carbonation process would modify the structure of the resulting $CaCO_3$, hardened binder, and thus its mechanical performance [33]. However, since all the tested specimens were subjected to the same conditions, this process does not affect the comparative discussion of the results, but is important to consider this before extrapolating the obtained values to other conditions.

2.2. Methods

2.2.1. Aerial lime characterization - X-ray diffraction (XRD)

The material characterization of the aerial lime was conducted on a Panalytical X'Pert Pro diffractometer equipped with Ni filter, working at 45 kV and 40 mA, Cu Kα radiation (λ = 1.5405 Å), in a 2θ range of 20–40°. XRD patterns were analysed using HighScore Software (Malvern Panalytical).

2.2.2. Micro-Scratch test

Scratch tests were performed on binder specimens (B) on a micro-scratch tester (CSM Instruments / Anton Paar) using a Rockwell tip

Table 2
Dimensions of the different tested specimens. All measurements are expressed in mm. The crossed cells indicate tests that were not performed on a specific type of specimen. *The porosity measurements were only performed on the binder control specimen, 8 and 15 %w/w of PEG-1000.

Specimen type	Test performed				
	Microscratch	Compressive strength test	Flexural strength test	Carbonation	Porosimetry*
Binder (B)	20 ×10 x 2	10 ×10 x 5	20 ×10 x 2		15 ×5×2
Mortar (M)		10 ×10 x 5	40 ×10 x 5	10 ×10 x 10	

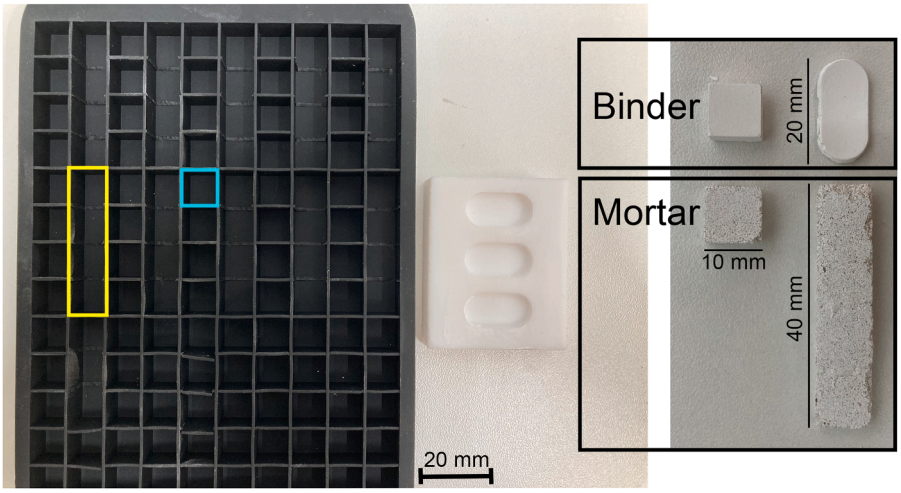


Fig. 1. Photo of moulds and specimens used. In yellow an example of the silicon mould used for mortar's flexural test is highlighted. In cyan, an example of the silicon mould used for both binder and mortar compression test is highlighted. The white PTFE mould was used for the binder flexural and scratch specimens. An example of all the specimens is also shown on the right.

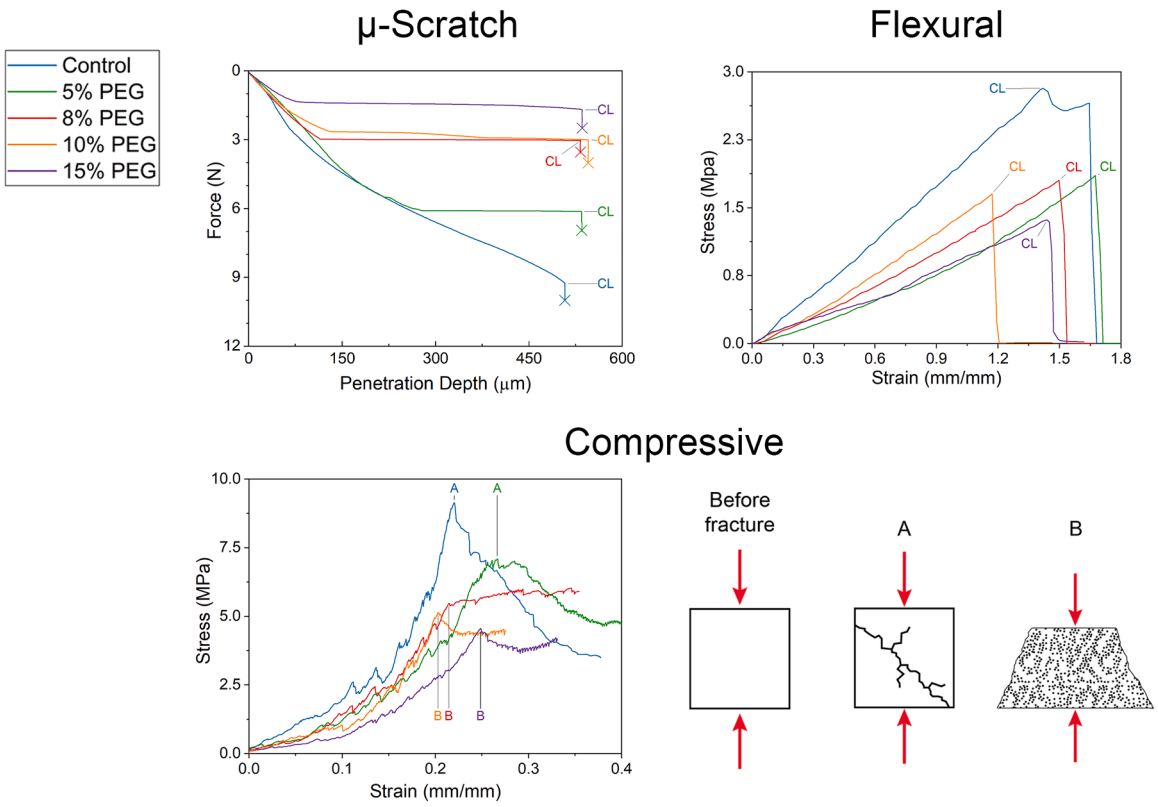


Fig. 2. Selected curves of each of the tests performed on binder-only specimens with different percentages of PEG-1000. The critical load corresponding to the fracture onset of the material is marked as "CL" for μ-scratch and flexural strength tests. For uniaxial compression testing, the critical points are marked with A and B, depending on the observed failure behaviour. The diagrams on the right represent a sketch of the two relevant failure modes.

with 120° cone angle and 800μm tip radius. The scratches were performed to promote fracture of the specimens with a progressive load from 0.03 to 15 N at a rate of 20 N/min for a full scratch length of 3 mm. A pre-scan was made with the lowest force (30 mN) to measure the individual profile of each specimen, and apply a correction to the measured penetration depth values. In a similar fashion, post-scan (always at 30 mN) allowed measurement of the residual depth after scratch. Oscillations in the initial profile due to surface roughness and non-perfect planarity were limited to a few μm, as opposed to the characteristic dimensions of the scratch process of several hundred μm (for both the scratch tip radius and the penetration depth). The test was performed on sets of specimens with increasing PEG-1000 concentration and a control set without PEG-1000. A total of 3–7 replicas for each set were performed. All the measurements were consistently made in the surface of the specimens that was in contact with air upon curing, since the bottom surfaces (in contact with the mould) presented an imprint of the mould's texture, especially in the control and low PEG percentage specimens. Some specimens containing different percentages of PEG broke during hardening because of production defects (e.g. bubbles trapped in the bottom of the cast) and the intrinsically weakened PEG-containing binder, thus the broken specimens were not analysed. Only specimens without visible fractures were tested. For each measurement the critical force value obtained at fracture was considered.

2.2.3. *Compressive strength test*

Compressive strength tests were performed on both binder (B) and mortar (M) specimens. The samples were tested on an Instron 1185R5800 electromechanical dynamometer equipped with a load cell of 10 kN at a displacement rate of 0.1 mm/min, until failure of the specimen. The deformation of each specimen was measured using an Instron strain gage extensometer 2620–601, with a range of ± 5 mm. The nominal compressive strength was calculated by dividing the measured load by the initial surface area of the tested specimen. Moreover, the total strain was calculated by dividing the measured displacement by the initial height of the tested specimen. The elastic modulus was calculated by performing a linear interpolation in the region of the stress-strain curve before the maximum, where contact conditions between the sample and the compression plates are optimal and the behaviour is truly linear. A total of ten replicas were performed for each set of specimens at the different concentrations.

2.2.4. *Flexural strength test*

The flexural strength tests were performed on both binder (B) and mortar (M) specimens. The test was performed on a TA Instruments RSA3 machine in transient mode. The distance between the lower supports used for the binder specimens was 10 mm, while that used in the mortar specimens was 25 mm. Both types of specimens were tested at a displacement rate of 0.3 mm/min until failure of the specimen. The flexural strength was calculated considering the maximum value of stress calculated according to beam theory. A total of ten replicas were performed for each set of specimens at the different concentrations.

2.2.5. *Carbonation test*

To monitor over time the level of carbonation of the mortar specimens and therefore to determine if PEG-1000 may affect this process, a series of measurements were performed over a period of 44 days. Twenty cubic specimens for each concentration of PEG-1000 (4 concentrations plus a control specimen without PEG-1000) were mixed and cast on the same day, and were carbonated under room conditions (~25 °C, 40 – 70 % RH, and ~400 ppm atmospheric CO_2) with only one face exposed to the air. In this case, the natural carbonation process was followed to follow in detail the kinetics of the reaction and see the effect that PEG-1000 had on it.

To measure the carbonation level, FTIR measurements were

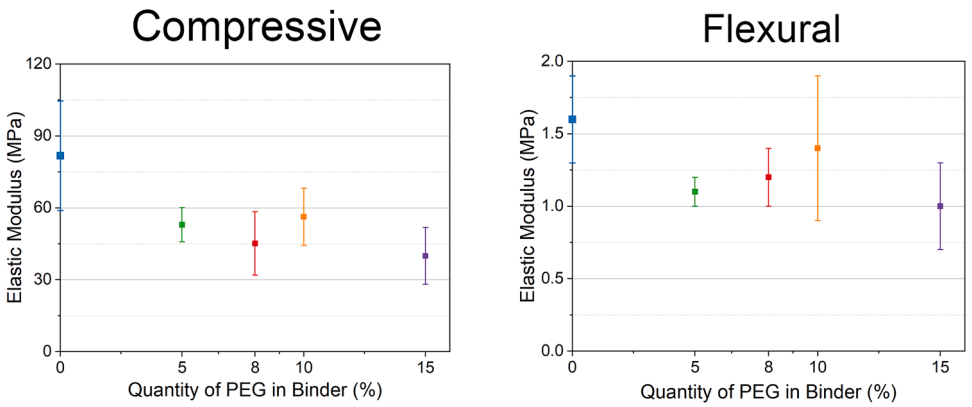


Fig. 3. Elastic Modulus of the binder specimens with different percentages of PEG-1000.

performed in attenuated total reflectance (ATR) mode on powder samples collected from the ground mortar specimen. After each measurement, the specimen was discarded. The measurements were made using a NicoletTM iS20 spectrometer (ThermoFisherTM Scientific), equipped with a DTGS detector and a diamond itXTM Smart accessory for ATR in the spectral range 4000–400 cm^{-1}, collecting 64 scans for each measurement with a 4 cm^{-1} spectral resolution (diameter of the crystal 2 mm). Each measurement was performed in triplicate and the average of the spectra was considered. To normalize the spectra, 10 % by weight of Potassium ferricyanide ($C_6N_6FeK_3$) was ground together with the specimen; all spectra were normalized by the $C_6N_6FeK_3$ peak at 2117 cm^{-1}. The proportion between the hydroxide peak at 3640 cm^{-1} and the carbonate peak at 1420 cm^{-1} was used to measure the progression of carbonation. The presence of CO_3 in these samples can only come from $Ca(OH)_2$ which has been converted to $CaCO_3$ via carbonation, thus this ratio serves as a good indicator for carbonation.

2.2.6. Porosity test

The effect that PEG-1000 has on the porosity of the binder was studied with Mercury Intrusion Porosimetry (MIP) in an Autopore IV 9500 (Micromeritics). For each measurement, the total weight of the binder specimen was approximately 1.5 g. The porosity measurements were performed in fully carbonated specimens by duplicate to ensure the reproducibility of the results.

3. Results and Discussion

3.1. Binder mechanical performance

Three testing methods were used to evaluate the mechanical performance of the binder: micro-scratch resistance, uniaxial compressive strength test, and flexural strength test. Representative results are presented in Fig. 2. In all the performed tests, it was observed that the presence of PEG-1000 in the binder reduced the maximum load that the specimens could bear. The results from the μ-scratch test revealed that as the quantity of the polymer increases, the material resistance decreases. Moreover, the fragile nature of the specimens can be clearly observed in the results from the μ-scratch test, evidenced by the sudden failure, as ~~it was~~ expected. The same brittle failure occurs in the flexural strength tests, with the exception of the control specimens which exhibit a very limited degree of ductility after the onset of fracture; those with PEG-1000 fail catastrophically immediately thereafter, instead. The limited ductility of the control is observed in Fig. 2, with a limited degree of deformation even after the critical load value (CL in the figure). Instead, in the PEG-containing specimens, once the critical load is reached (CL), the specimen breaks suddenly, as noted by the drop in the stress signal at the maximum deformation. This type of behaviour under flexural stress was also identified in gypsum-rich plasters [34], and was identified by the authors as a consequence of the pore collapse of the plaster. Lastly, during the uniaxial compression experiments, it was observed that for a critical PEG concentration of 8 % there is a change in the failure mode (from A to B in Fig. 2), which becomes more *plastic-like*. As can be observed in the diagram, the binder specimens, at these high concentrations, show an apparent *yielding*. As a matter of fact, the specimen progressively disintegrates into a compact and *plastic* mass of powder, with a behaviour similar to *kinetic sand* (see graphical diagram in Fig. 2). As the test proceeds, this powder is progressively compacted, thus showing large deformations developing at fairly constant stress values between 4 and 6 MPa. Once cohesion is lost (B in Fig. 2), the resulting binder+PEG powder is responsible for the observed *plastic-like* response.

To quantitatively describe the mechanical behaviour, the critical loads and elastic modulus (for compressive and flexural tests) were evaluated. The elastic modulus (E) (Fig. 3) for flexural strength tests, shows a decrease of E with the presence of PEG, and a slight increment at 10 % of PEG. The same behaviour is even clearer in the case of the compressive test. Moreover, the introduction of PEG in the binder, irrespectively of the amount, caused an average decrease in of the flexural E of 0.4 ± 0.2 MPa and of the compressive E of 33.2 ± 7.4 MPa. The latter corresponds which corresponds to a drop with respect to the control's elastic modulus of c.a. 27 % tested in flexural mode and 40 %, when tested under compression.

The strength values of the binders, presented in Fig. 4, also highlight that the presence of PEG-1000 reduces the mechanical performance of the binder. However, two different behaviours are observed depending on the type of test performed: a gradual decrease with increasing PEG-1000 concentration for the compression-dominated test configurations (scratch and compression), and a sudden drop in the case of flexural strength. This suggests that PEG-1000, even in very small quantities, has a deleterious effect on the binder tensile strength. Furthermore, for micro-scratch and compression testing, the trend seems to approach a plateau for higher percentages of PEG-1000. The good correlation of the results for these two configurations is related to the fact that, as already mentioned, the specimens are subjected to a similar (compressive) state of stress. It has indeed been demonstrated that scratch resistance can be correlated with the uniaxial compression strength of various types of materials [26–28].

The critical stress of the control binder in uniaxial compression is 8.2 ± 2.0 MPa. This value is within the range expected for the mechanical resistance of lime-based binders, based on a few studies made in lime plasters substituted with gypsum and pozzolan [34,35]. It remains important to highlight that further studies are needed to characterize mechanical properties of pure aerial lime binders. The observed reduction in the presence of PEG corresponds to a drop of the fracture stress of around 37 %, similar to the obtained drop in the elastic modulus. Numerically, this is a reduction of 1.9 MPa for binders with 5 % of PEG and 3.8 MPa for binders with 15 % of PEG; the reduction for

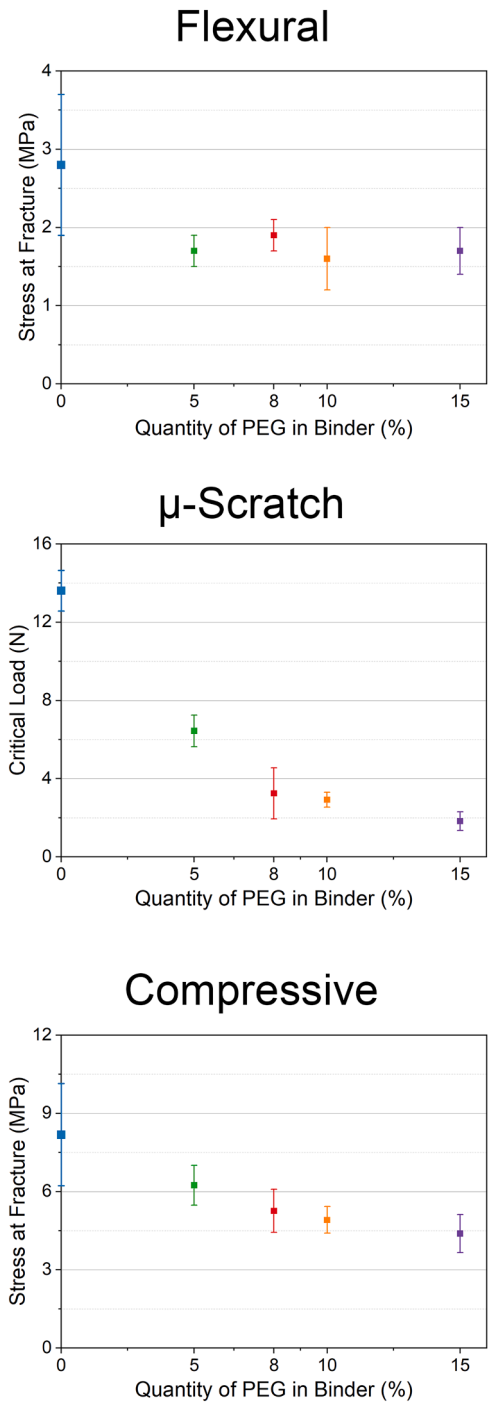


Fig. 4. Strength of the binder specimens at different concentrations of PEG-1000.

concentrations of 8 and 10 % obviously lie within these values. The results from the mechanical testing of the binder specimens in the presence of PEG are generally in line with previous ones [6,7]. However, the reduction in uniaxial compression resistance measured in a similar system using PEG was of 54 % [6]; in this case, the measured stress at fracture of the mortars was reduced from 0.52 ± 0.04 MPa to 0.24 ± 0.05 MPa. The difference with the values obtained in this study can be associated to the different nature of the samples (binder vs. mortar).

As mentioned before, in a previous work [9], two hypotheses were presented regarding the mortar's weakening in the presence of the FS-PCM aggregates: a) it is caused by the mixture of PEG and lime binder, and/or b) the poor compatibility between FS-PCM aggregates and binder causes internal fissures that overall result in a weakened mortar. The results presented here refer to binder-only specimens, where any effect related to the presence of aggregates can be excluded, and demonstrate, therefore, that the mixture of this polymer with the binder is an important reason behind the reduction of the mechanical properties of the mortars. Of course, this does not eliminate the possibility that a lack of compatibility between the FS-PCM aggregates and binder may further contribute to the mortar's weakening.

The present results show that the mechanical characterization of pure aerial lime binders is possible with the proposed specimen dimensions. As presented in the introduction, testing these types of materials is a challenging task. As a proof, all mentioned alternative methodologies consider only the mechanical characterization of mortars and not in the binders. Currently, only a few works are dedicated to the mechanical characterization of the binder phase of mortars, specially using nanoindentation, surface hardness, or penetration measurements [36,37], which give an important insight into the binder properties, but at a very small scale; also, some of these studies are performed on mixed binders containing only a percentage of aerial lime or mortars with a reduced quantity of aggregates. Another study uses standardized testing procedures with the aid of "confinement mortars" made of cement. However, a combination of such different materials could yield results that are difficult to compare with other studies. In contrast, recent works characterized the mechanical strength and surface hardness of gypsum plasters (without any aggregates) partially substituted with lime [34] and pozzolan [35]. These studies successfully measured the mechanical properties of gypsum/lime plasters and provided a methodology that allows for testing of both laboratory specimens and historical samples. The authors tested the plasters using an adaptation of standard EN1015–11, working on specimens that were 1/50th of the standard specimen dimensions. They showed that it is possible to obtain reproducible and realistic results with geometries that are a fraction of those recommended by the standard. However, they could not perform the measurements on specimens of pure lime plaster since these would disintegrate upon demoulding [34], thus they tested only specimens with at least 5 % of gypsum.

3.2. *Mortar mechanical characterisation*

Both flexural and compressive resistance tests were performed on mortar specimens of reduced dimensions. The results (Fig. 5) confirm that the presence of PEG-1000 weakens the mortar specimens, reducing the stress at fracture from the control value of 0.46 ± 0.13 MPa to 0.29 ± 0.15 MPa when 15 % PEG was introduced, which would reduce the minimal required mechanical resistance for its use in restoration [38]. For comparison, aerial lime mortars with the presence of PEG inside FS-PCM aggregates showed a flexural strength resistance of 0.20 ± 0.07 MPa [6], in line with the obtained results. Moreover, there is no apparent correlation between the reduction of the critical load and the quantity of PEG-1000 in the mixture. The mortar specimens display a general behaviour that is even more brittle than pure binder ones; this difference might be related to the higher influence of defects due to the presence of the aggregates in the mortar. The introduction of heterogeneities and defects can promote crack formation. This is more critical for flexural strength test, where a tensile component is present. Accordingly, results for this configuration showed low critical values and ~~a~~ high dispersion, and for this reason, they are not graphically presented. Instead, for the compression test, a critical load can be reliably identified. A marked change of the slope can be observed before failure, which could be associated with an increment of the apparent rigidity of the specimens when they are compacted.

Again, the average fracture resistance of the mortar specimens for each PEG-1000 concentration was calculated. As can be seen in Fig. 5b, a reduction of about 27 % with respect to the control is observed, irrespective of PEG-1000 concentration. This corresponds to a drop from the control value of 1.92 ± 0.37 MPa to an average of 1.40 ± 0.12 MPa for

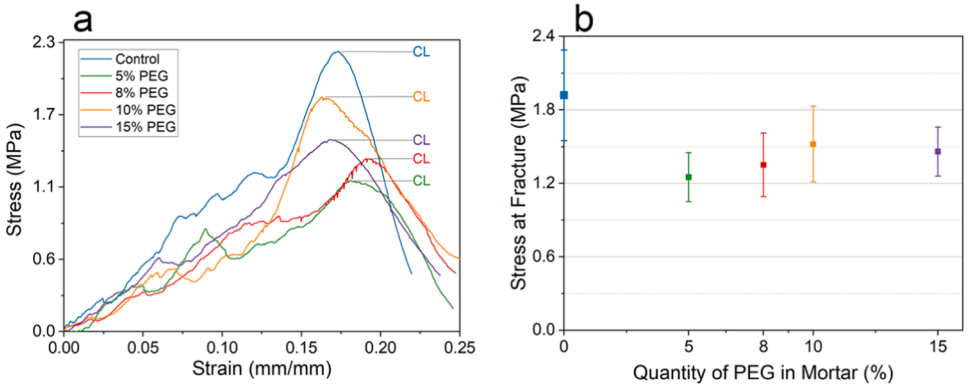


Fig. 5. Results from the compression test, a) representative curves of the test on mortar specimens with different percentages of PEG-1000; the points of failure of the material are marked as "CL"; and b) strength of the mortar specimens at different percentages of PEG-1000.

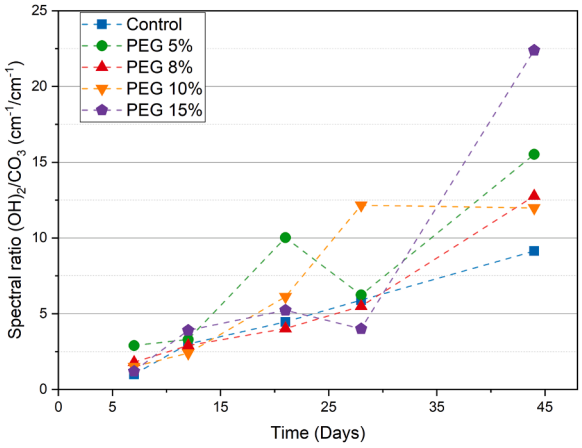


Fig. 6. Carbonation progression over 44 days of mortar specimens with different percentages of PEG-1000 included in the mixture.

the specimens with PEG. Again, the dominant failure mechanism remains brittle. However, the results obtained for the binder-only specimens (Fig. 3 and Fig. 4) provided more reproducible and reliable results, highlighting the advantage of working with binder-only specimens.

The current set of results from the mechanical tests highlights the detrimental effect that PEG-1000 has on aerial lime binders and mortars. To investigate its origin, two essential properties of lime-based materials, that have a direct impact on their mechanical response, were examined: the carbonation and pore microstructure.

3.3. PEG's influence on carbonation

Aerial lime-based mortars harden via carbonation. In this process, $Ca(OH)_2$ is slowly transformed into $CaCO_3$, incrementing its mineral hardness from ~2–3 in the Mohs scale. When these mortars are not fully carbonated, their mechanical resistance is also commonly lower [39]. Indeed, a plausible hypothesis for the reported reduction of the mechanical properties on aerial-lime mortars with FS-PCM aggregates [6] is that the PCM would hinder or slow the carbonation.

To understand the impact that PEG-1000 has on the carbonation of aerial lime-based mortars, long-term natural carbonation tests were performed. The results presented in Fig. 6 show that, contrary to what could be expected, PEG-1000 promotes the carbonation of the binder. Even at high percentages of the polymer, carbonation is apparently accelerated. Although no clear trend with PEG-1000 concentration can be identified, it is evident that the carbonation progression is always at least as fast as in the absence of the PCM additive. Further tests are

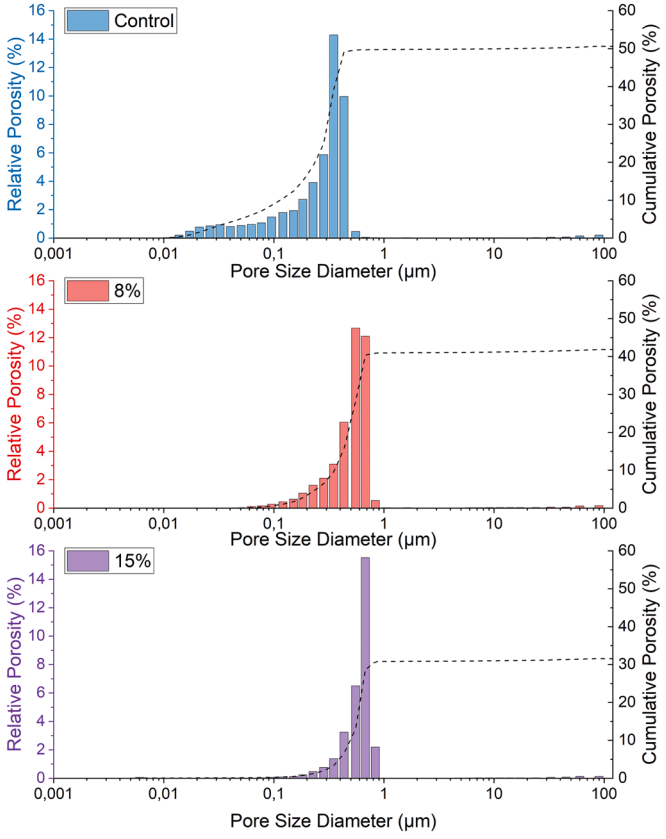


Fig. 7. MIP measurements of the binder only specimens for the control, 8 % and 15 % of PEG-1000. The bar plot represents the relative porosity, whereas the dotted lines indicate the cumulative porosity.

necessary to understand why, apparently, the presence of PEG favours the carbonation process. Nevertheless, the weakening of these mortars cannot be ascribed to a slowed-down carbonation.

3.4. Porosity

The porosity of the binder phase could give insight into the way the calcite clusters are interacting with the introduced PEG-1000, and the impact that this could have on the mechanical response of the mixture. It is important to highlight that the specimens tested were subjected to accelerated carbonation, which is known to have an impact on the porosity network and consequently on the mechanical properties of these types of materials [33]. Nonetheless, in the following section, a

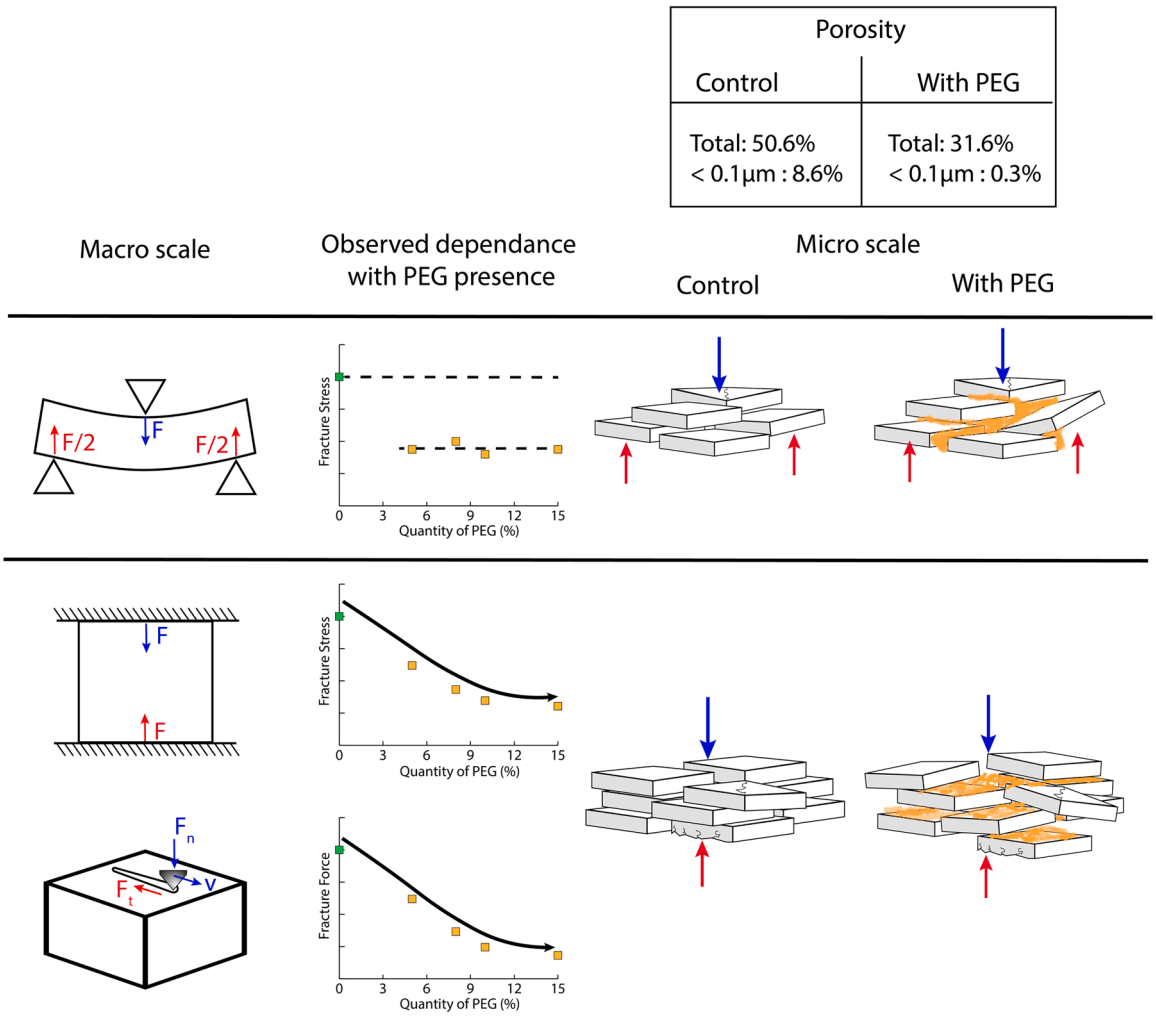


Fig. 8. Summary diagram of the proposed effect of PEG-1000 on lime-based binders and the weakening mechanism. The blue arrows represent the applied forces in the mechanical testing, whereas the red arrows indicate the material's reaction forces. Calcite crystals are represented as white rhombohedra while PEG-1000 is drawn in pale-orange.

comparative discussion between the tested specimens is presented, and since all of them were subjected to the same carbonation conditions, the relative change amongst the specimens is not attributed to the carbonation process, but to the presence of PEG. To understand this, Mercury Intrusion Porosimetry (MIP) measurements were performed on flexural binder specimens: the control, 8 %, and 15 % of PEG-1000. The results (Fig. 7) show that as PEG-1000 is included in the binder mix, the total porosity is reduced from 50.6 ± 0.1 % to 41.8 ± 0.3 % at 8 % of PEG and 31.6 ± 0.6 % at 15 % of PEG. The introduced PEG-1000 is apparently partially filling the pores of the binder. Moreover, when observing the relative porosity size distribution, a reduction of those pores smaller than 0.1 µm is observed. Pores under this diameter are associated, in lime-based mortars, with the binder, more specifically to the crystalline lattice [40]. When the water used to prepare the binder evaporates, the dissolved PEG-1000 can be accumulated at the border of the portlandite crystals. Later, when the portlandite crystals undergo carbonatation and become calcite, a size reduction is observed [41]. PEG-1000 that was surrounding the original portlandite crystals, now is filling the inter-crystalline spaces between calcite crystals. Indeed, this would impact only the intrinsic porosity of the crystalline lattice. This hypothesis is supported by the small shift to larger pores observed as the quantity of PEG in the binder increases (Fig. 7).

3.5. *Proposed mechanism of PEG weakening*

The gathered experimental evidence allows to propose a model for the weakening mechanism that lime-based binders undergo when PEG-1000 is poorly confined and therefore disperses inside the binder matrix. The proposed model (Fig. 8) suggests that when the binder is carbonated and PEG-1000 is accumulated in the inter-crystalline porosity, it hinders the crystalline interlocking, overall weakening the matrix. In fact, at 8 %, the pores below 0.1 µm are reduced from 8.3 % to 0.3 % of the overall porosity (Fig. 8). Therefore, the overall cohesiveness of the binder will be given by PEG-1000, which serves as a glue for the calcite crystals, instead of the crystalline interlocking. This modification in the matrix composition explains the observed change in the elastic modulus of the binder specimens and the disintegration into powder and "*plastic-like*" behaviour under compressive stress (Fig. 2).

The presence of PEG-1000 in the inter-crystalline porosity also serves as a *lubricant* that promotes the sliding of two neighbouring calcite crystals under a given force. The dependence of the PEG-1000 concentration is evident under compression forces since they induce this sliding movement between the crystals. Instead, in the flexural mode, the crystals do not slide under the applied force, and the overall material is only weakened by the reduction of the crystalline interlocking; thus, no relevant concentration dependence is observed.

4. Conclusions

In the present work, the weakening mechanism induced by PEG-1000 in lime-based binders and mortars was investigated. To this aim, a non-conventional mechanical testing methodology was proposed, that allows to successfully test the mechanical response of size-reduced specimens made of purely aerial lime binder. By reducing the otherwise inevitable formation of cracks and fissures, a reliable mechanical characterization can be achieved. This is a fundamental step ~~to~~ in studying the effect of additives on these types of materials at a laboratory scale. The core of this new methodology for the mechanical testing of aerial lime binders and mortars is based on the specimen's size-reduction, where the required material to test is overall reduced allowing to a) work in conditions of low availability of testing material, and b) reduce the laboratory waste. Future works should consider the comparison of the mechanical characterization using standard testing methodologies and the present one.

This new approach allowed to reach conclusive results and determine the detrimental influence that PEG-1000 has in aerial lime-based binders, leading to a weakening of their mechanical properties.

Moreover, based on the combined analysis of mechanical testing, carbonation, and porosimetry measurements, this work proposes an interpretation of the underlying weakening mechanism. When PEG is dispersed in the binder matrix, it hinders the crystalline interlocking of calcite, weakening the aerial lime matrix. Moreover, PEG acts as a lubricant that promotes crystalline gliding when compressive forces are applied.

Finally, in this work, it was evidenced that it is possible to obtain reliable and reproducible results of the mechanical performance of purely lime-based binders. The latter opens the possibility for future studies to work with these types of materials and study exclusively the macro-mechanical response of the binder phase in lime-based mortars.

Ethical approval

The authors hereby state that the present work complies with ethical standards.

CRediT authorship contribution statement

Lucia Toniolo: Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **Sara Goidanich:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Elena Hitthaler:** Writing – review & editing, Investigation. **Maria Sugari:** Investigation. **Paulina Guzmán García Lascurain:** Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Luca Andena:** Writing – review & editing, Validation, Supervision, Resources, Methodology.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Paulina Guzman Garcia Lascurain reports financial support was provided by PON Ricerca e Innovazione 2014–2020. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The present research was supported by the PhD Fellowship DOT1316197 (IMTR) CUP D45F21003710001 (Green) financed by Italian PON "Ricerca e Innovazione" 2014–2020 funding program.

Finally, the authors acknowledge the experimental support Prof. Cristina Tedeschi and Dr. Mariagiovanna Taccia for the Mercury Intrusion Porosimetry measurements, and Dr. Marco Contino for the Uniaxial Compression measurements. The authors also would like to thank Fassa Bortolo Srl for providing the aerial lime used in this work.

Data Availability

Data will be made available on request.

References

[1] D.Von Landsberg, The history of lime pro- duction and use from early times to the Industrial Revolution, Zem. Kalk. Gips 45 (1992) 199–203.
[2] K. Elert, C. Rodriguez-Navarro, E.S. Pardo, E. Hansen, O. Cazalla, Lime mortars for the conservation of historic buildings, Stud. Conserv. 47 (2002) 62–75, https://doi.org/10.1179/sic.2002.47.1.62.
[3] M. Apostolopoulou, E. Aggelakopoulou, A. Bakolas, A. Moropoulou, Compatible mortars for the sustainable conservation of stone in masonries BT - advanced materials for the conservation of stone, in: M. Hosseini, I. Karapanagiotis (Eds.), Advanced Materials for the Conservation of Stone, Springer International Publishing, Cham, 2018, pp. 97–123, https://doi.org/10.1007/978-3-319-72260-3_5.
[4] D. Ergenç, R. Fort, M.J. Varas– Muriel, M. Alvarez de Buergo, Mortars and plasters—how to characterize aerial mortars and plasters, Archaeol. Anthr. Sci. 13 (2021) 197.
[5] European Committee for Standardization (CEN), EN 16572:2015 Conservation of cultural heritage - Glossary of technical terms concerning mortars for masonry, renders and plasters used in cultural heritage, (2015).
[6] M. Frigione, M. Lettieri, A. Sarcinella, J. Barroso de Aguiar, Sustainable polymer-based Phase Change Materials for energy efficiency in buildings and their application in aerial lime mortars, Constr. Build. Mater. 231 (2020) 117149, https://doi.org/10.1016/J.CONBUILDMAT.2019.117149.
[7] S. Cunha, J. Aguiar, V. Ferreira, A. Tadeu, Mortars based in different binders with incorporation of phase-change materials: Physical and mechanical properties, Http://Dx.Doi.Org/10.1080/19648189.2015.1008651 19 (2015) 1216–1233, https://doi.org/10.1080/19648189.2015.1008651.
[8] S.R.L. da Cunha, J.L.B. de Aguiar, Phase change materials and energy efficiency of buildings: a review of knowledge, J. Energy Storage 27 (2020) 101083, https://doi.org/10.1016/J.EST.2019.101083.
[9] P. Guzmán García Lascurain, M. Frigione, A. Sarcinella, F. Linares, L. Schröer, V. Cnudde, L. Toniolo, S. Goidanich, Improving PEG confinement in smart aggregates for lime-based mortars, Constr. Build. Mater. 454 (2024) 138996, https://doi.org/10.1016/j.conbuildmat.2024.138996.
[10] European Committee for Standardization (CEN), EN 1015-11:2019 Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar, (2019).
[11] European Committee for Standardization (CEN), EN 1015-12:2016 Methods of test for mortar for masonry - Part 12: Determination of adhesive strength of hardened rendering and plastering mortars on substrates, (2016).
[12] M. Arandigoyen, J.I. Alvarez, Pore structure and mechanical properties of cement–lime mortars, Cem. Concr. Res 37 (2007) 767–775.
[13] A. Arizzi, G. Cultrone, Negative effects of the use of white Portland cement as additive to aerial lime mortars set at atmospheric conditions: a chemical, mineralogical and physical-mechanical investigation, Publisher: Nova Science Publishers, Inc., Editors: S. Manuel Rivera and AL Pena Diaz (2011) 231–243.
[14] R. Veiga, P. Faria, R. van Hees, M. Stefanidou, P.-N. Maravelaki, I. Papayianni, I. Ioannou, M. Theodoridou, V. Bokan Bosilijkov, B. Bicer-Simsir, RILEM TC 277-LHS report: properties of lime-based renders and plasters—discussion of current test methods and proposals for improvement, Mater. Struct. 56 (2023) 70.
[15] D. Ergenç, R. Fort, A.Santos Silva, R. Veiga, D.Sanz Arauz, The effects of DiloCarB as carbonation accelerator on the properties of lime mortars, Mater. Struct. /Mater. Et. Constr. 51 (2018) 1–16, https://doi.org/10.1617/S11527-018-1140-0/FIGURES/8.
[16] R.M. Izzo, Waste minimization and pollution prevention in university laboratories, Chem. Health Saf. 7 (2000) 29–33.
[17] N. Zhang, I.D. Williams, S. Kemp, N.F. Smith, Greening academia: developing sustainable waste management at Higher Education Institutions, Waste Manag. 31 (2011) 1606–1616.
[18] M. Philokyprou, I. Ioannou, A. Ilia, Design and Production of Repair Mortars for Historic Masonry Taking into Account the Characteristics of Old Mortars, in: J. Valek, C. Groot, J. Hughes (Eds.), RILEM Proceedings PRO 78 of HMC 2010 2nd Historic Mortars Conference & RILEM TC 203-RHM Repair Mortars for Historic Masonry Final Workshop, 2011: pp. 1051–1058.
[19] M.R. Veiga, A. Vilhena, Support for the rehabilitation of S. Francisco do Penedo fortress, : Luanda. 2nd Phase–Study Repair Conserv. Mortars Be Appl. Interv. Rep. (2019) 2019.
[20] T.J. Wijffels, R.P.J. Van Hees, The influence of the loss of water of the fresh mortar to the substrate on the hygric characteristics of so-called restoration plaster. Proceedings of the International Workshop on Urban Heritage and Building Maintenance VII, Aedificatio Publishers, Freiburg, 2000, pp. 49–54.

[21] European Committee for Standardization (CEN), EN 17187:2020 Conservation of Cultural Heritage - Characterization of mortars used in cultural heritage, (2020).
[22] D. Costa, A. Magalhães, M. do Rosário Veiga, Characterisation of mortars using drilling resistance measurement system (DRMS): tests on field panels samples, in: Historic Mortars: Characterisation, Assessment and Repair, Springer, 2012, pp. 413–423.
[23] J. Otero, V. Starinieri, A.E. Charola, Nanolime for the consolidation of lime mortars: a comparison of three available products, Constr. Build. Mater. 181 (2018) 394–407.
[24] L. Kyriakou, M. Theodoridou, I. Ioannou, Micro-destructive evaluation of the mechanical properties of lime-based mortars, J. Cult. Herit. 58 (2022) 219–228.
[25] A.-T. Akono, F.-J. Ulm, Scratch test model for the determination of fracture toughness, Eng. Fract. Mech. 78 (2011) 334–342.
[26] A.-T. Akono, F.-J. Ulm, Fracture scaling relations for scratch tests of axisymmetric shape, J. Mech. Phys. Solids 60 (2012) 379–390.
[27] J. Henzel, S. Karl, Determination of strength of mortar in the joints of masonry by compression tests on small specimens, Darmstadt Concr. 2 (1987) 123–136.
[28] E. Sassoni, C. Mazzotti, G. Pagliai, Comparison between experimental methods for evaluating the compressive strength of existing masonry buildings, Constr. Build. Mater. 68 (2014) 206–219.
[29] D. Łątka, Prediction of mortar compressive strength based on modern minor-destructive tests, Materials 16 (2023) 2402.
[30] J. Válek, R. Veiga, Characterisation of mechanical properties of historic mortars–testing of irregular samples, WIT Trans. Built Environ. 83 (2005).
[31] M. Drdácký, Z. Slížková, Mechanical characteristics of historical mortars from tests on small-sample non-standard specimens, Mater. Sci. Appl. Chem. 17 (2008) 20–29.
[32] A. Erkal, D. D'Ayala, Laboratory testing of non-standard original historic building materials and related implications for conservation, Q. J. Eng. Geol. Hydrogeol. 48 (2015) 15–28.
[33] C. Rodriguez-Navarro, T. Ilić, E. Ruiz-Agudo, K. Elert, Carbonation mechanisms and kinetics of lime-based binders: An overview, Cem. Concr. Res 173 (2023) 107301.
[34] K. Elert, R.A. Alaminos, C. Benavides-Reyes, M. Burgos-Ruiz, The effect of lime addition on weathering resistance and mechanical strength of gypsum plasters and renders, Cem. Concr. Compos 139 (2023) 105012.
[35] K. Elert, M.M.S. Jiménez, M. Burgos-Ruiz, Gypsum-based materials for exterior applications using lime and recycled pozzolanic additions, Constr. Build. Mater. 450 (2024) 138713.
[36] C. Nunes, Z. Slížková, M. Stefanidou, J. Němeček, Microstructure of lime and lime-pozzolana pastes with nanosilica, Cem. Concr. Res 83 (2016) 152–163.
[37] C. Rodriguez-Navarro, L. Monasterio-Guillot, M. Burgos-Ruiz, E. Ruiz-Agudo, K. Elert, Unveiling the secret of ancient Maya masons: biomimetic lime plasters with plant extracts, Sci. Adv. 9 (2023) eadf6138.
[38] European Committee for Standardization (CEN), EN 998-1 Specification for mortar for masonry - Part 1: Rendering and plastering mortar, (2016).
[39] Ba Silva, A.P.F. Pinto, A. Gomes, A. Candeias, Effects of natural and accelerated carbonation on the properties of lime-based materials, J. CO2 Util. 49 (2021) 101552.
[40] S. Maria, Methods for porosity measurement in lime-based mortars, Constr. Build. Mater. 24 (2010) 2572–2578.
[41] R.M. Lawrence, T.J. Mays, S.P. Rigby, P. Walker, D. D' Ayala, Effects of carbonation on the pore structure of non-hydraulic lime mortars, Cem. Concr. Res. 37 (2007) 1059–1069, https://doi.org/10.1016/J.CEMCONRES.2007.04.011.