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Physico-chemical and mechanical characterization of hydraulic mortars containing nano-titania for restoration applications

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ABSTRACT

In this work nano-titania of anatase and routile form has been added in mortars containing: (a) binders of either hydrated lime and metakaolin, or natural hydraulic lime and, (b) fine aggregates of carbonate nature. Mortar composition was tailored to ensure adhesion of fragments of porous limestones from the Acropolis monuments. The aim was to study the effect of nano-titania in the hydration and carbonation of the above binders, as well as the mechanical properties and the adhesive capability of the designed mortars, where the nano-titania proportion was 4.5–6% w/w of binder. The physico-chemical and mechanical properties of the nano-titania mortars were studied and compared to the respective ones, without the nano-titania addition. DTA-TG, FTIR, SEM and XRD analyses indicated the evolution of carbonation, hydration and hydraulic compound formation during a 1 year curing. Results indicate enhanced carbonation, hydration and modulus of elasticity of mortar mixtures with nano-titania. A specifically designed experimental procedure for measuring the direct tensile strength of the mortar–stone system proved that nano-titania mortars can be used as adhesive materials for porous limestones.

1. Introduction

The use of mortars for the re-adhesion of fragments of archaeological stone or other building materials is an important intervention, which results in a substantial structural integrity between the adhered materials, leading to the slowing or prevention of further decay. Treatment options include the application of adhesives and grouts, as well mechanical pinning repairs. Commonly used adhesives such as epoxy, acrylic and polyester resins demonstrated excessive strength, high irreversibility and, if improperly applied, their removal may be of great damage to the historic fabric [1].

Even though the design of the system stone-adhesive mortar might appear simple in concept, nevertheless, the physico-chemistry and mechanics is complex. Therefore, the proper design and application of the adhesive mortars can be considered a matter of prime importance, followed by understanding the adhesion mechanisms.

Two different kinds of stone from Piraeus, namely Aktites and Mounichea stones, corresponding to a hard dolomitic limestone and one soft, marly limestone of the area, respectively, were selected for this study due to their common employment as main construction materials of the Athenian Acropolis buildings during the Archaic period. The preferred treatment strategy for the reassembling and adhesion of these fragments was addressed through designing bonding mortars compatible to these stones. Repair criteria were as follows: (a) compatibility of repair materials and stone, including physico-chemical and mechanical factors, (b) adequate strength to resist tensile and shear forces, (c) retreatability, i.e. the ability to remove the adhesive mortar and reapply the same or a different repair material, (d) longevity, including resistance to corrosion and staining, (e) affordability and (f) ease of installation.

The design of adhesive mortars with binders of either hydrated lime–metakaolin or natural hydraulic lime has been adopted into this framework aiming to formulate a complex system characterized by the highest compatibility. Nowadays, hydrated lime–metakaolin or natural hydraulic lime mortars have been increasingly preferred in the restoration and conservation of architectural monuments, due to the enhanced chemical, physical, structural and mechanical compatibility of those mortars with historical building materials (stones, bricks and mortars) [2]. This compatibility is a very critical prerequisite for the optimum performance of conservation mortars, when considering (a) the damage caused to historic monuments during past decades, due to the extensive use of cement mixtures and (b) their disadvantages in terms of incompatibility with porous stones, high salt content, limited elasticity, etc. [3].

In the present study, nano-titania composed of anatase (90%) and rutile (10%) forms has been added in special designed mortars

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consisting of binders of either hydrated lime and metakaolin or natural hydraulic lime and fine aggregates of carbonate nature. The aim was to study the effect of nano-titania (4.5–6% w/w of binder) in the hydration and carbonation of the above binders, which are widely used in the design of restoration mortars. A comparison of the physico-chemical properties of the nano-titania mortars cured up to 1 year to mortars without nano-titania (used as reference) was carried out. The assessment of the evolution of carbonation, hydration and hydraulic compound formation during a six-month curing period was performed through thermal analysis (DTA-TG), infrared spectroscopy (FTIR), Energy Dispersive X-ray fluorescence (EDXRF) and X-ray diffraction (XRD) analyses. In this case, special emphasis was given to mortars tailored to ensure adhesion of fragments of porous limestones from the Acropolis monuments in Athens, Greece. Therefore, this paper also discusses stone–mortar interfaces and reports the adhesion resistance to external mechanical stress as related to the physico-chemical characteristics of the stone-mortar system and especially the role of the nano-titania additive.

2. Materials and methods

2.1. Design criteria: binders, fillers and aggregates

The design of the adhesive mortars involves binders of either hydrated lime (L: by CaO Hellas) with metakaolin (M: Metastar 501 by Imerys), or natural hydraulic lime (NHL: NHL3.5z by Lafarge), in which nano-titanium dioxide (T: nano-structured nano-titania by NanoPhos) was added as a filler for its photocatalytic activity. The already established photocatalytic activity of nano-titania in anatase form [4] was thought that will significantly contribute to the enhancement of the hydration and carbonation process, thus affecting the required bond strength. Furthermore, the nano-titania with its photocatalytic properties can assist to a self-cleaning process of the adhesive mortars.

Metakaolin is a highly active aluminosilicate material, which is formed by the dehydroxylation of kaolin $Al_2(OH)_4Si_2O_5$ that occurs by thermal treatment in the ~650–800 °C temperature range. The raw products were characterized by XRD, FTIR, DTA-TG and EDXRF techniques. Metakaolin presents a fine grain size distribution (cumulative passing from 24 μm: 100% and from 16 μm: 95.6%) as estimated by laser particle size analyzer (Mastersizer 2000 particle analyzer, Malvern). X-ray diffraction analysis revealed that metakaolin is amorphous with minor content of mica, quartz and feldspar. As far as the pozzolanic activity of MK is concerned, the percentages of total silica and active silica (according to EN 197-1 and EN 196-2) were determined as 54.2% and 44.6%, correspondingly [5]. The pozzolanicity of metakaolin (according to Greek Presidential Decree 244/1980, article 8) is determined up to 13.1 MPa [5].

Table 1 reports the mortar mixes. A water to binder (W/B) ratio from 0.8 to 0.6 was used for all mixes. The mixing tools and materials were stored at a constant temperature of 23 °C for 24 h before mixing. The quantity of hydrated lime that will react with metakaolin was fixed in a weight ratio equal to 1.5, ensuring the pozzolanic reaction, while any unreacted quantity of hydrated lime, after its carbonation, provides elasticity to the final mortar. This excess of hydrated lime after its carbonation, enables the mortar to acquire a pore size distribution similar or compatible to porous stone, thus facilitating the homogeneous distribution of water and water vapor in the complex system. In addition, the enhanced derived elasticity can function as a tool for the arrangement and absorption of external stresses, which otherwise could lead to the mechanical failure of the mortar. For the NHLT mortars the binder to aggregates ratio (*B*/*A*) is equal to 1 or 2. Preliminary tests on the adhesive capability of the designed mortars with fragments of porous limestones pointed out the inefficient performance of natural hydraulic lime (NHL) mortars without the nano-titania addition. Thus it was decided to exclude NHL mortars without nano-titania from further study.

Table 1
Mortar mixes (composition in mass%).

Samples	Sand	Binders			Filler	*B*/*A*	*W*/*B*
		NHL	M	L	T		
NHLT1	48	49			3	1	0.7
NHLT2	33	64			3	2	0.6
ML1	50		20	30	0	1	0.8
MLT1	47		20	30	3	1	0.8

Sand: limestone sand; NHL: natural hydraulic lime; M: metakaolin; L: hydrated lime; T: nano-titania; B: binder; A: aggregates; W: water.

In order to overcome the increased water demand, the additive of TiO_2 nano-powder was dispersed into water under ultrasonic treatment for 15 min to disperse the agglomerates. The obtained TiO_2 colloidal solution was subjected to UV radiation (365 nm) for 30 min to activate the nano-titania. Then it was added to the other raw materials and stirred with a handheld mixer for 5 min.

Taking into account that fine aggregates can contribute to the avoidance of shrinkage and cracking during the setting process, it was deemed important to add sand of carbonate nature with fine grains in the mix design. Therefore, aiming at improving the bond strength between mortar and porous stone, equal proportions of carbonate sand passing through the 125 and 63 μm sieves, were subjected to thorough water washing to free the harmful soluble salts before adding to the mix.

2.2. Testing procedures

2.2.1. Physico-chemical testing

When binders of powdered pozzolans, such as metakaolin are mixed with hydrated lime, or natural hydraulic lime is mixed with water, they produce a new binder that exhibits a hydraulic character, due to the reaction among the amorphous phase of pozzolans and hydrated lime [5]. On the other hand, the natural hydraulic lime binder when mixed with water produces similar components to hydrated lime–metakaolin mixtures [6]. Previous studies have shown that the pozzolanic and hydration reactions, which take place in room temperature and in conditions of high relative humidity, lead to the formation of a hydrous gel of calcium silicate (CSH) and calcium aluminate (CAH) hydrated phases, which modify the microstructure of the paste and increase both the hydraulic properties and the strength of the mortar [7]. Therefore, the study of the hydration is essential in order to evaluate the performance of the mortar, in terms of physical and mechanical properties, which are also interrelated to the longevity of the mortar [8].

The above mixtures (Table 1) were molded in prismatic and cubic moulds, with dimensions of 4 × 4 × 16 cm and 5 × 5 × 5 cm, respectively and then placed in a curing chamber for setting, at RH = 65 ± 3 % and *T* = 20 2 °C, according to the procedure described in the EN 196-1 standard. Pastes of these mixtures with and without nano-titania, with dimensions of 5 mm in diameter and 30 mm in height, were also prepared and sealed into ceramic tubes using Parafilm® membrane to avoid moisture loss and drying and were then maintained at the same curing conditions with the studied mortars. The setting process of the paste was interrupted at preset time periods, of 1, 3, 5, 7, 11, 21, 28 and 90 days according to a hydration stop procedure, which involved the immersion of the sample in two stop-bath solutions (acetone and diethyl-ether) for 60 min each, and then drying at 70 °C for 30 h.

In powder samples the development of the hydration and carbonation were examined with XRD, mercury intrusion porosimetry (MIP), FTIR, DTA-TG and scanning electron microscopy (SEM). By identifying CSH and CAH at different ages, not only qualitatively, but also semi-quantitatively, the hydration and carbonation process can be monitored. The mineralogical analysis was carried out by X-ray powder diffraction analysis (XRD) on a Bruker D8 Advance Diffractometer, using Ni-filtered Cu Kα radiation (35 kV 35 mA) and a Bruker Lynx Eye strip silicon detector. Data was collected from 3° to 70° 2θ with a step size of 0.02° and a count time of 0.1 s per strip step. The crystallize phases were identified using the Diffrac plus Software (Brucker AXS) and the JCPDS database. The quantitative XRD analysis was performed by the RIETVELD method using the software TOPAS from BRUKER. A crystal structure Data Base from BRUKER was used for the crystalline phases, which were analyzed by the Rietveld method. SEM examination was carried out in fractured surfaces, using a FEI Quanta Inspect scanning electron microscope. DTA-TG was operated with a Setaram LabSys Evo 1600 °C thermal analyzer; in static air atmosphere up to 1000 °C at a rate of 10 °C/min. FTIR analysis was operated in a FTIR Perkin–Elmer 1000 spectrometer with 4 cm^{-1} resolution in the spectral range of 400–4000 cm^{-1}. The samples were homogenized with KBr and pressed to obtain a pellet with the aid of a vacuum hydraulic press. MIP measurements were recorded using a Quantachrome Autoscan 60 porosimeter, in the range of 2–4000 nm. Physical properties of the stone and mortars were further studied by water absorption by saturation according to EN 13755:2002, as well as capillary water absorption measurements for mortars according to EN 1015-18:1995 and for stones according to EN 1925:1999.

2.2.2. Mechanical testing

The mechanical properties of the designed mortars were characterised by measuring the uniaxial compressive strength (Fc) and the flexural strength (Ff-3pb) according to EN 1015-11:1999. Stone samples of Aktites and Mounichea collected from the Athenian Acropolis monuments (*D*) and other monumental complexes close to this area (*K*) were cut into specimens of 4 × 4 × 4 cm to measure the compressive strength of the stone and into 4 × 4 × 8 cm specimens to bond them with the designed mortars.

The adhesive performance of the bonded stone-mortar specimens (4 × 4 × 17 cm) was measured using specially designed equipment for both the four point flexural strength (Ff-4pb) (Fig. 1a and b) and the direct tensile strength test (Ft) (Fig 1c) [9]. Four point bending tests were selected instead of typical three-point bending tests in order to apply the loading forces only on the stone pieces and not on the mortar. The tests were conducted using displacement control with a displacement rate of 0.02 mm/s. The loading pins were supported by a spring mechanism, so no pre-loading was applied to the specimen. In all cases the majority of the cracks appeared at the interface between stone and mortar. The direct tensile tests were also performed using displacement control with a displacement rate of 0.02 mm/s. Cracks appeared at the stone-mortar interface. Conventional pull-out tests are used to measure the shear strength of the interface while this test was designed to measure the direct tensile strength of the same interface. The mounting brackets were designed to eliminate out of plane bending and to balance eccentric loading. To avoid shear forced due to grips, a hole was drill in each of the stone pieces and the specimen was pulled apart through pins inserted in these holes. For these measurements, the stone faces were primarily incised by special mechanical tools to provide a rough surface. Furthermore, prior to applying the adhesive mortar, the stone surfaces were wetted. The mortar was partially applied to the stone surface and then the stone specimens were filled with mortar by placing them levelly with the aid of special joint clamps. The joint was kept moist with damp cotton gauze and a polyethylene sheet. The specimens were then placed in a storage chamber for 28 days, according to the conditions described in EN 1015-11:1999.

3. Results and discussion

3.1. Raw materials characterization

The thermal analysis of the hydrated lime, revealed that the percentage of $Ca(OH)_2$ (CH) and $CaCO_3$ (Cc) was up to 89.12% and 5.98%, respectively. Quantitative analysis of XRD data using the Rietveld method revealed that the NHL binder consists of 19.0% C_2S, 40.5% CH, 3.5% Qz, 24% Cc, 12% C_3S, while the nano-titania used consisted of 88.8% anatase and 11.2% rutile. The crystallite size of nano-titania calculated from XRD data following the Scherrer formula [10] is 54 nm for rutile and 27 nm for anatase. The carbonate sand contains a 90.5% quantity of calcite, 9.1% dolomite and 0.4% quartz. XRD analysis revealed that, except the main amorphous content, the mineral phases identified in metakaolin were illite and quartz.

Table 2 reports the mineralogical composition of the Piraeus stones from Acropolis, Athens, along with mean values of the compressive strength, water capillary and water saturation coefficients calculated in three stone specimens. The Piraeus stone can be classified in: (a) micritic dolomitic limestone hard and compact, with a low to medium porosity, small grain size and high values of mechanical strength (D1, D3) and (b) marly limestone/dolomitic limestone with an oolitic texture, brownish or yellowish to light

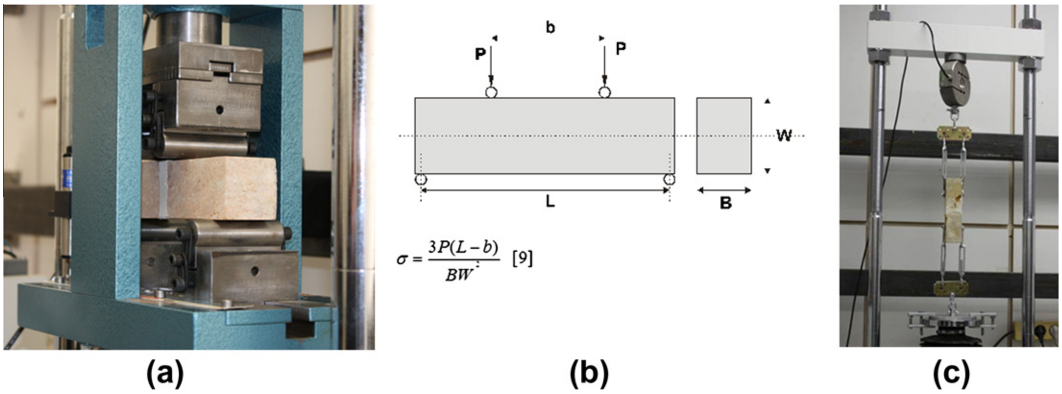

Fig. 1. (a) Four point bending apparatus with variable support spans, (b) geometry and calculations for four-point bending test and (c) direct tensile test apparatus for stone mortar specimens.

Table 2
Mineralogical composition and properties of the Piraeus stone from Acropolis, Athens, monuments.

Sample	Calcite	Dolomite	Chlorite	Kaolinite	Illite	Albite	Quartz	Fc (MPa)	WCC (g cm^{-1} s$^{-1/2}$)	WSC (%)
D1	6.2	83.0	0.6	1.8	4.2	0.5	3.7	42.3	0.0026 (±0.001)	3.7 (±0.1)
D2	1.5	78.7	2.8	2.5	7.8	0.5	6.1	28.7	0.0141 (±0.004)	13.1 (±2.8)
D3	12.0	80.0	0.9	2.4	1.9	0.1	2.7	107.0	0.0011 (±0.0002)	2.3 (±0.2)
D4	4.2	80.0	1.3	3.3	7.0	0.9	3.3	6.6	0.0007 (±0.0004)	2.9 (±0.9)
D7	1.0	76.0	1.2	0.9	8.2	2.2	10.5	21.5	0.0074 (±0.0003)	11.6 (±1.3)
K	11.1	70.9	1.1	0.9	8.1	2.2	5.4	22.7	0.0211 (±0.005)	8.3 (±2.0)

Fc: compressive strength, WCC: water capillary coefficient, WSC: water saturation coefficient.

grey-color with a low to medium porosity and low values of mechanical strength (D2, D4, D7, K).

The results of the water capillary and water saturation tests indicate that the pore system of the studied stones differed significantly and therefore the designed mortars should be adapted accordingly. Stones with high compressive strength, such as D1 and D3 absorb a low water amount correspondingly to their low quantity of aluminosilicates. However, in the D2, D4, D7 and *K* stones no clear relationship exists between compressive strength and hygric properties. Even though these stones contained similar amounts of aluminosilicates, they differed both in the absorbed quantity of water and the values of the compressive strength. This relies on the structural inhomogeneity of the samples and especially, as in the case of the D4 stone, on the absence of inter-connected pores, which affect the stone hygric behavior. Fig. 2a shows the thin section of the D4 stone, which is a micritic dolomite with few pores of small diameter. The minerals identified in the D4 sample were illustrated in the X-ray diffratogram of Fig. 2b.

The correlation between the pore size determined in the thin section study and the values obtained by the water total immersion and water capillarity can be used as indices of the microstructure evaluation of the studied stones. This property was successively correlated to the corresponding microstructure of the designed mortars, thus facilitating the mortar selection.

3.2. Physico-chemical evaluation of mortars

The total bound water (Htb) identified in the studied samples in the temperature range from 100 to 460 °C corresponds to the dehydration of calcium silicate hydrates (CSH), calcium aluminate hydrates (CAH) and the residual bound water [5]. The dehydration of $Ca(OH)_2$ (CH) occurred in the temperature range ~480–500 °C, while the decomposition of $CaCO_3$ is located at a temperature higher than 700 °C.

Fig. 3 depicts the DTA curves for the hydrated lime–metakaolin pastes without and with nano-titania at 4 weeks of curing. As the setting process proceeds the mass loss attributed to the release of Htb, as well as CO_2 from $CaCO_3$, increased, while the mass loss of CH dehydration decreased, due to the transformation of CH into hydraulic components and calcite. The hydrated lime consumption was completed, while the formation of hydraulic phases is more pronounced for the nano-titania pastes at 4 weeks curing time than the corresponding without nano-titania.

In the MLT1 mortars after 28 days of curing, the quantitative Rietveld analysis revealed higher amount of vaterite and aragonite, which are crystalline modifications of calcite (Table 3). This finding indicated that an enhanced carbonation process took place in the presence of nano-titania, since vaterite and aragonite have been considered indicative minerals of an intensive carbonation of portlandite [11]. In Fig. 4 the XRD patterns of the hydrated lime–metakaolin without (a) and with nano-titania (b) showed the full carbonation and absence of portlandite in the nano-titania samples.

SEM observations of the interior part of the MLT mortars after 1 year of curing indicated that a dense network of hydraulic amorphous components had been formed providing more elasticity to the mortar matrix (Fig. 5b). Characteristic hexagonal crystals of portlandite were predominately located in the studied areas of the ML samples after 1 year of curing (Fig. 5a), while these portlandite crystals were fewer in the MLT samples.

FTIR analyses of the interior of the hydrated lime–metakaolin samples illustrated in Fig. 6 corroborated the SEM observations. The sample without nano-titania (a) after 1 year of curing still showed portlandite, while the corresponding sample with nano-titania (b) was more carbonated, as it can be concluded by the identification of aragonite and vaterite with characteristic absorptions at 1082 and 857 cm^{-1}, respectively and the absence of portlandite (Fig. 6b) [12].

Fig. 7a illustrates the infrared spectra of natural hydraulic lime pastes with nano-titania (NHLT) at different hydration ages. In order to quantify the CSH evolution, the intensity ratio of CSH over the most intense SiO_2 transmittance peaks (at ~949 and 995 cm^{-1}, respectively) was plotted versus hydration time for hydraulic lime pastes with (NHLT2) and without nano-titania (NHL2) (Fig. 7b). On the FT-IR spectra (Fig. 7a) and the plot (Fig. 7b) it is evident that the absorbance peak at 949 cm^{-1}, attributed to CSH, makes its appearance around the 5th day of hydration and increases as the hydration proceeds [13]. The peak at 3640 cm^{-1} attributed to CH decreases as the carbonation and hydration proceed. Comparing the evolution of the hydraulic component formation for the NHL pastes with and without nano-titania in Fig. 7b, the slightly increased ratio of the intensities at the early stages of hydration of NHL clearly demonstrates the beneficial effect of nano-titania.

These variations can be explained by the TiO_2 photocatalytic action for the mixtures with nano-titania which leads both to calcite formation and enhanced hydration of CSH and CAH products, similar to what was observed on the early age hydration of Portland cement by adding increased dosage of fine titanium oxide [14].

3.3. Mechanical evaluation

In Table 4 the physical and mechanical properties of the designed mortars are presented. The physical properties of the designed mortars differed insignificantly indicating that the nano-titania addition neither modified the microstructure nor affected the hygric behavior of the materials. The lowest Fc values were recorded for the NHLT1 samples cured for 4 weeks. The Fc values increased with curing time for all types of tests with the exception of the ML1 samples, where the Fc values decreased. Even though, the Fc values recorded at 4 weeks curing for the MLT1 samples are lower than the corresponding values for samples without nano-titania (ML1), nevertheless, the Fc values of the MLT1 samples reached higher values than the ML1 samples after 3 months and 1 year curing, thus indicating the beneficial effect of the nano-titania in the compressive strength. The decrease of Fc values over time in the ML1 compositions has been already reported by other

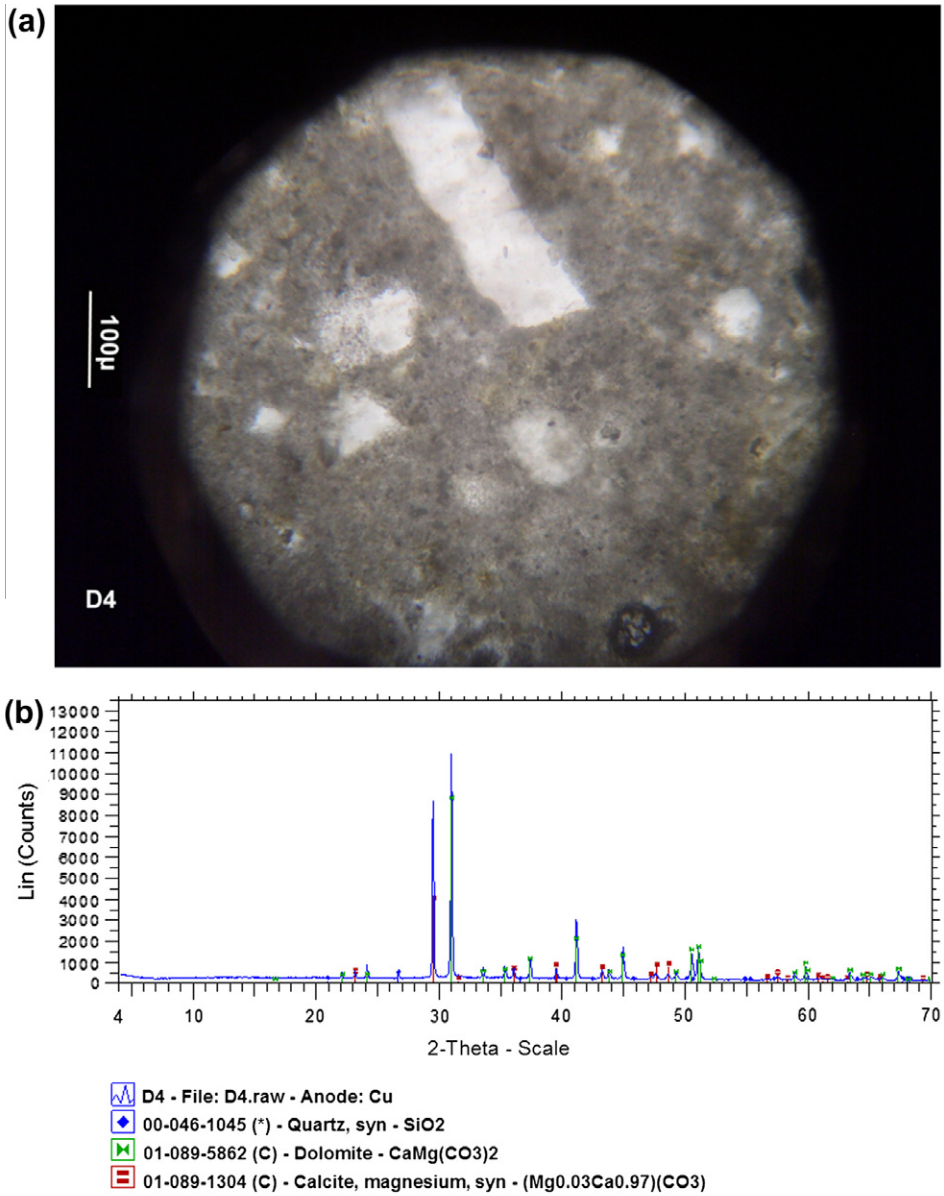

Fig. 2. (a) Thin section of sample D4 and (b) XRD of the sample D4.

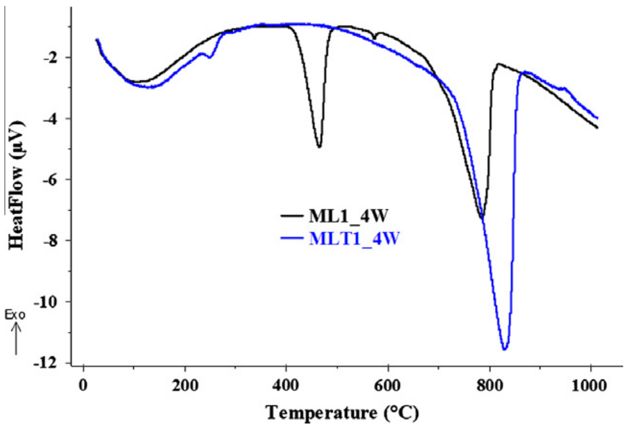

Fig. 3. DTA curves for hydrated lime–metakaolin pastes without (ML1) and with (MLT1) nano-titania at four weeks curing time.

Table 3
Quantitative Rietveld analysis of the designed mortars after four weeks of curing.

Code	Cc	Pt	V	Ar	Do	Cal	Qz	At	C2S	An
NHLT2_4w	64.1	24.9	–	–	–	–	2.7	–	4.6	3.7
ML1_4w	68.8	0.8	6.7	6.0	6.4	7.7	3.4	–	–	0.2
MLT1_4w	66.5	–	7.3	7.0	6.3	7.5	2.5	2.9	–	–

NHL: natural hydraulic lime; M: metakaolin; L: hydrated lime; T: nano-titania; w: week; Cc: Calcite; Pt: portlandite; V: vaterite; Ar: aragonite; Qz: quartz; At: anatase; C2S beta: larnite; An: anhydrite; Do: dolomite; Cal: monocarboaluminate.

authors [5,15] and was most probably attributed to the microcracking formation due to shrinkage during the curing.

Fig. 8 shows typical stress-strain curves of hydrated lime–metakaolin ML1 and MLT1 mortars tested in uniaxial compression. Performance at 4 weeks and 3 months curing time is compared for specimens with (MLT1) and without nano-titania (ML1). Higher values of the modulus of elasticity (E) were recorded for the MLT1 mortars (Fig. 8b) than the corresponding ones without

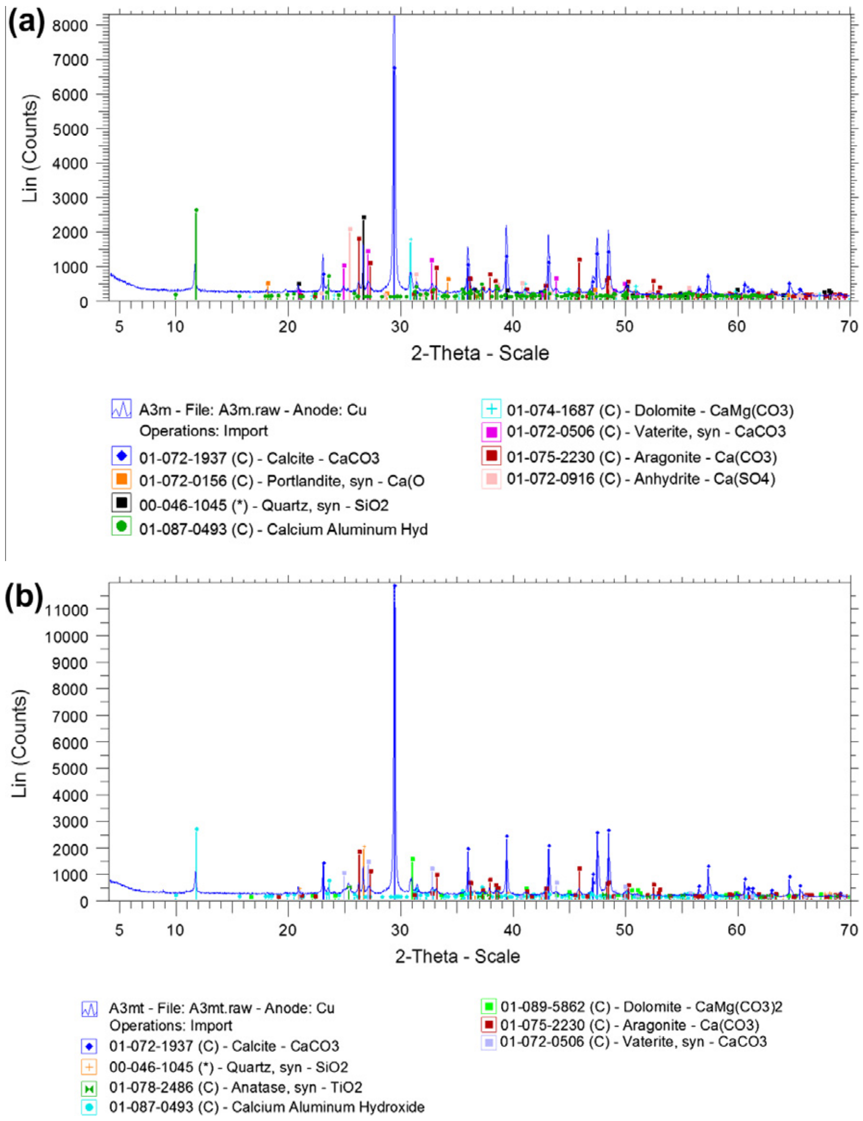

Fig. 4. XRD patterns for hydrated lime metakaolin mortars without (a) and with nano-titania (b) at four weeks curing time.

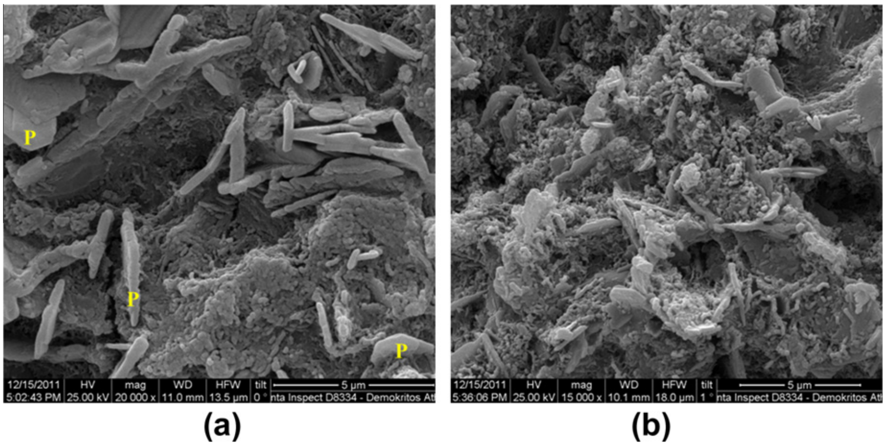

Fig. 5. (a) Hydrated lime–metakaolin sample without nano-titania showing portlandite crystals (P) and (b) hydrated lime–metakaolin sample with nano-titania at one year curing time.

nano-titania (Fig. 8a). It seems that nano-titania with its hydrophylicity created an environment, which not only enhanced the hydraulic component formation, but also controlled the shrinkage, thus avoiding microcracking [16–18]. Further support to this statement is derived from the dense network of hydraulic components observed in the SEM micrographs (Fig. 5b) for the MLT1 samples,

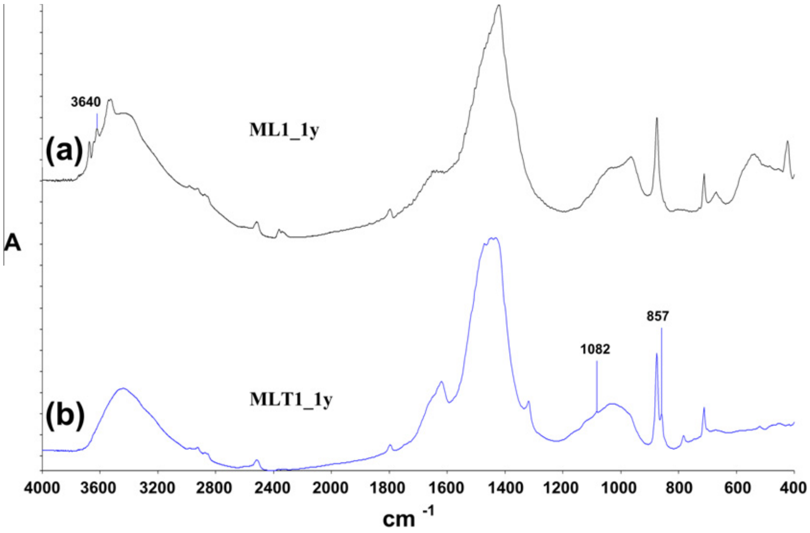

Fig. 6. FTIR absorption spectra for hydrated lime–metakaolin mortars without nano-titania (a) and with nano-titania (b) at one year curing time.

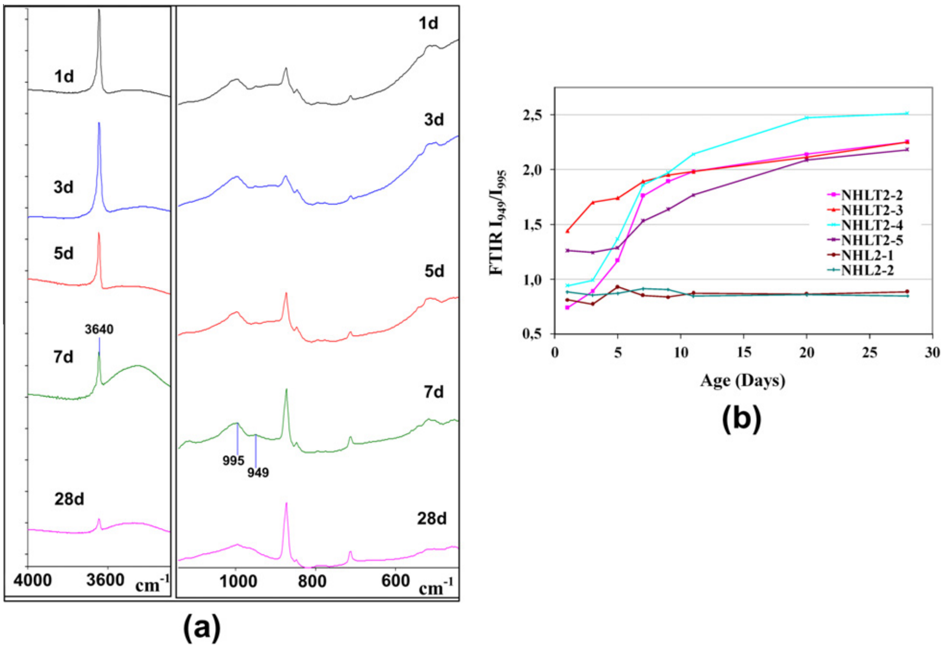

Fig. 7. FTIR absorption spectra for hydraulic lime pastes with nano-titania at different curing times (a) and, (b) the variation of the intensity ratio I_{949}/I_{995} as a function of curing time.

Table 4
Physical and mechanical properties of the designed mortars.

Code	WCC* (g cm^{-1} s$^{-1/2}$)	WSC* (%)	Total porosity (%)	Pore radius (μm)	Specific surface (m^2/g)	Curing	Fc^ (MPa)	Ff-3pb* (MPa)	*E* (GPa)
NHLT1	0.0149 (±0.007)	27.80 (±1.09)	33.0	0.30	12.0	4w	4.15 (±0.16)	1.16 (±0.05)	0.17 (±0.03)
						3mo	5.47 (±0.28)	1.69 (±0.40)	
						1y	5.51 (±0.95)		
NHLT2	0.0080 (±0.0004)	25.58 (±0.27)	37.8	0.09	12.8	4w	5.41 (±0.29)	1.03 (±0.12)	0.37 (±0.05)
						1y	7.22 (±1.61)		
ML1	0.0040 (±0.0001)	33.92 (±0.26)	31.5	0.03	14.0	4w	14.85 (±1.53)	1.15 (±0.14)	0.42 (±0.06)
						3mo	11.66 (±1.26)		0.76 (±0.29)
						1y	10.62 (±2.39)		0.56 (±0.22)
MLT1	0.0074 (±0.003)	29.52 (±1.07)	32.5	0.03	16.0	4w	9.08* (±0.89)	1.21 (±0.49)	0.59 (±0.09)
						3mo	14.19 (±0.70)		1.10 (±0.15)
						1y	15.40 (±1.87)		0.91 (±0.22)

WCC: water capillary coefficient; WSC: water saturation coefficient; w: week; mo: month; y: year; (∗) mean value of three samples; (^) mean value of 6 samples; Fc: compressive strength; Ff-3pb: flexural strength; *E*: elasticity modulus.

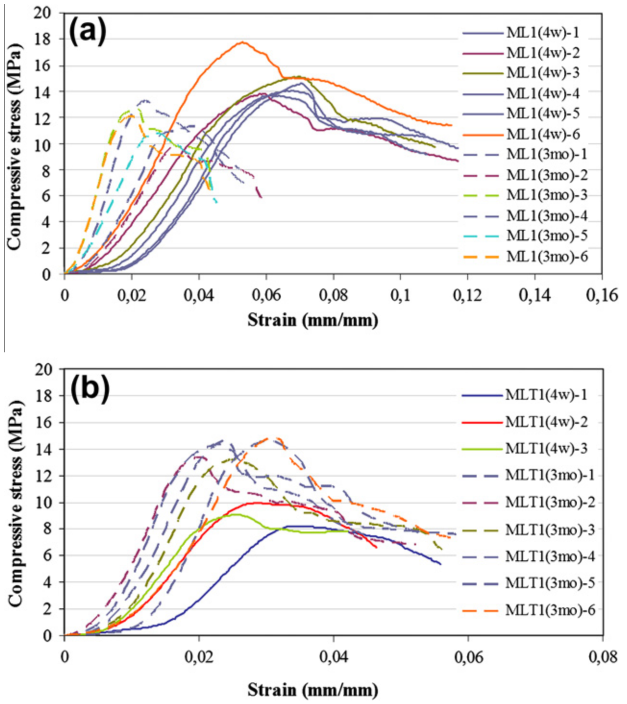

Fig. 8. (a) Compressive stress–strain diagram of hydrated lime–metakaolin (ML1) samples without nano-titania at four weeks (4w) and three months (3mo) curing time. (b) Compressive stress-strain diagram of samples with nano-titania (MLT1) at four weeks (4w) and three months (3mo) curing time.

Table 5
Mechanical properties of stone-mortar specimens cured for four weeks.

Mortar code	Ff-4pb adhered stone specimens (No)	Ff-4pb (MPa)	Ft adhered stone specimens (No)	Ft (MPa)
NHLT1	D7 (1)	1.36	D7 (1)	0.90
NHLT2	D1 (3)	2.39 (±0.70)	D1 (1)	0.70
NHLT2	D2 (1)	2.84	D2 (1)	0.33
MLT1	K (2)	1.41 (±0.64)	K (2)	0.15 (±0.08)
MLT1	D3 (1)	1.21	–	–
ML1	D4 (1)	1.07	D1 (1)	0.09

Ff-4pb: four point bending; Ft: direct tensile test; No: number of adhered stone-mortar specimens; NHL: natural hydraulic lime; M: metakaolin; L: hydrated lime; T: nano-titania.

along with the results of FTIR and XRD analyses which denoted the absence of portlandite and an enhanced carbonation level.

In this research work one of the principal objectives was to evaluate the adhesive performance of the designed mortars in the limited number of samples from the Acropolis monuments. Because of the limited number of stone specimens available and due to the un-even dimensions of such specimens, tests already established for measuring the bond between mortar and stone, cannot be considered, therefore tests for measuring the bending strength under 4-point loading and the direct tensile strength were carried out using the experimental apparatus presented in Fig 1. By combining the results of physical and mechanical properties the mortars NHLT2 and MLT1 were selected as adhesive means for the stones D3 and D1 showing the lowest clay content and water absorption. The other mortars (ML1, NHLT1) were used to join the marly dolomitic samples (D2, D4 and D7), while soft marly dolomitic stones (*K*) were also adhered with MLT1, given its good performance.

Table 5 reports the results of the 4-point bending test and the direct tensile test for the adhered stone-mortar specimens after 4 weeks curing time. In all tests, failure was observed at the interface between stone and mortar. This is a desirable finding, since it can guarantee that in cases of external pressure and forces the overall bonded system will fail within the mortar leaving integral the stone. The results revealed that high bonding strengths (flexural and tensile) were measured when applying the NHLT2 mortar to the hard Aktites samples (D1). In addition, MLT1 and NHLT2 mortars adhered successfully to both compact micritic dolomitic and marly dolomitic stones, and, therefore, were selected among the proposed adhesive mortars.

4. Conclusions

This research work addressed an important problem in the restoration sector concerning the reassembling of stone fragments from ancient monuments using non-cement mortars. The proposed adhesive mortars contain hydraulic lime or metakaolin and hydrated lime as binders, carbonate sand with grains smaller than 250 μm in a *B*/*A* ratio of 1 or 2, as well as nano-titania as additive in a binder replacement of 4.5–6%.

The mechanical characterization indicated that the mortars with nano-titania showed increased modulus of elasticity when compared to the specimens without nano-titania. The results also indicate enhanced carbonation and hydration of mortar mixtures with nano-titania. The hydrophylicity of nano-titania improves the humidity retention into mortars, thus facilitating the carbonation and hydration processes. This property was exploited in the fabrication of mortars tailored to adhering porous limestones, where humidity controls the mortar setting and adhesion efficiency. Specially designed equipment were applied to measure the bonding strength of stone-mortar systems and revealed that the nano-titania addition in both hydrated lime–metakaolin and hydraulic lime mortars improves the adhesive properties of the mortar when applied to porous stones.

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