CHARACTERIZATION OF HYDRAULIC MORTARS CONTAINING NANO-TITANIA FOR RESTORATION APPLICATIONS

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Abstract

In this work nano-titania of anatase form has been added in mortars containing (a): binders of either lime and metakaolin or natural hydraulic lime and, (b): fine aggregates of carbonate or silicate nature. The aim was to study the effect of nano-titania in the hydrolysis and carbonation of the above binders widely used in the design of restoration mortars, as well as the mechanical properties of the derived mortars. The nano-titania proportion was 4.5-6 per cent w/w of binders. The physicochemical and mechanical properties of the nano-titania mortars were studied and compared to the respective ones, without the nano-titania addition, used as reference. DTA-TG, FTIR and XRD analyses indicated the evolution of carbonation, hydration and hydraulic compound formation during a one-year curing. The mechanical characterization indicated that the mortars with the nano-titania addition showed improved mechanical properties over time when compared to the specimens without nano-titania. The results evidenced carbonation and hydration enhancement of the mortar mixtures with nano-titania. The hydrophylicity of nano-titania improves the humidity retained in mortars, thus facilitating the carbonation and hydration process. This property can be exploited in the fabrication of mortars for adhering fragments of porous limestones from monuments, where the presence of humidity controls the mortar setting and adhesion efficiency. A specifically designed mechanical experiment based on the direct tensile strength proved the suitability of these mortars with nano-titania as adhesive materials for restoration applications.

Keywords: adhesive mortars, nano-titania, metakaolin-lime, hydraulic lime, hydration, mechanical properties

1. Introduction

The adhesion of mortars to 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 preventing from 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

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demonstrated excessive strength, high irreversibility and, if improperly applied, their removal may be more damaging to the historic fabric (Amstock 2000).

In this research work, two different kinds of stone from Piraeus, namely Aktites and Mounichea stones corresponding to a hard dolomitic limestone and a marly limestone of the area, respectively, were selected due to their common employment as main construction materials of the Athenian Acropolis building 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) physico-chemical and mechanical compatibility between repair materials and stone, (b) adequate strength to resist tensile and shear forces, (c) retreatability, (d) longevity, (e) affordability and (f) ease of installation.

The design of adhesive mortars with binders of either hydrate lime-metakaolin or natural hydraulic lime has been adopted with the aim of formulating a complex system characterized by the highest compatibility. Nowadays, both of hydrate lime-metakaolin and hydraulic lime mortars are widely used in the field of the restoration and conservation of architectural monuments, due to its capability to enhance the chemical, physical, structural and mechanical compatibility with historical building materials (stones, bricks and mortars) (Rosario, Velosa, Magalhaes, 2009). This compatibility is a very critical prerequisite for the optimum performance of conservation mortars considering the damages caused to historic monuments during the past decades, due to the extensive use of cement mixtures.

Into this framework, in special designed mortars consisting of binders of either lime and metakaolin or natural hydraulic lime and fine aggregates of carbonate nature, nano-titania of anatase (90 per cent) and rutile (10 per cent) has been added in 4.5-6 per cent w/w of binder. The aim was to study the effect of nano-titania in the hydration and carbonation of the above binders and to compare the physico-chemical properties of the nano-titania mortars with those mortars without nano-titania (used as reference). Thermal analysis (DTA-TG), infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analyses were performed to investigate the evolution of carbonation, hydration and hydraulic compound formation during a six-month curing period. Furthermore, the stone–mortar interfaces, the adhesion resistance to external mechanical stress as related to the physico-chemical characteristics of the stone-mortar system and the role of the nano-titania as additive were reported and discussed in this paper.

2. Experimental procedure

2.1 Design of adhesive mortars: binders, fillers and aggregates

Binders of either lime (L: by CaO Hellas) with metakaolin (M: Metastar 501 by Imerys), or natural hydraulic lime (NHL: NHL3.5z by Lafarge) as well as nano-titanium dioxide (T: nano-structured nano-titania by NanoPhos), used as filler due to its photocatalytic activity, are employed for the design of the adhesive mortars. The already established photocatalytic activity of nano-titania in anatase form (Hyeon-Cheol, Young-Jun, Myung-Joo et al. 2010) will significantly enhance the hydration and carbonation process, thus affecting the adhesion performance. Moreover, self-cleaning properties of the adhesive mortars can be also attained due to the photocatalytic action of the nano-titania. XRD, FTIR and DTA-TG techniques were used to characterize the raw products.

In Table 1, the mortar mixes are presented, where the ratio of water to binder (W/B) ranges from 0.8 to 0.6. The required quantity of lime that will react with metakaolin was fixed in a weight ratio equal to 1.5, ensuring the pozzolanic reaction. Any unreacted quantity of lime, after its carbonation, provides elasticity to the final mortar and enables the mortar to acquire a pore size distribution similar or compatible to porous stone, thus allowing a homogeneous distribution of water and water vapor in the complex system. Furthermore, 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.

Table 1: Mortar mixes (composition in mass %)

Samples	**Sand**	**Binders**			**Filler**	**B/A**	**W/B**
Code	Cc	NHL	M	L	Nano-titania		
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

Preliminary tests on the adhesive capability of the designed mortars with fragments of porous limestones pointed out the inefficient performance of NHL mortars. Thus it was decided to exclude this formulation from further study. TiO_2 nano-powder dispersion in a small amount of water was achieved through ultrasonic treatment for 15 min; afterwards the obtained TiO_2 colloidal solution was subjected to UV radiation (365 nm) for 30 min to activate the nano-titania. Then the dispersed TiO_2 solution was mixed with the other raw material and stirred with a handheld mixer for 5 min. Due to the fact that the fine aggregates can contribute to the avoidance of shrinkage and cracking during the setting process, the addition of sand with fine grains was deemed essential. Consequently, equal proportions of sand passing through the 125 and 63 μm sieves were added in the mix, which were previously washed by water to free the harmful soluble salts.

2.2 Assessment of the adhesive mortars

2.2.1 Physico-chemical properties of mortars

When binders of powdered pozzolans, such as metakaolin are mixed with lime, or natural hydraulic lime is mixed with water, they produce a new binder that exhibits a hydraulic character due to reactions among the amorphous phase of pozzolans and lime (Aggelakopoulou, Bakolas and Moropoulou 2011), as well as hydration of NHL (Maravelaki-Kalaitzaki Karatasios Bakolas *et al.* 2005). 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 hydrate (CSH) and calcium aluminate hydrated phases (CAH), which modify the microstructure of the paste and increase both the hydraulic properties and the strength of the mortar (Tziotziou Karakosta Karatasios *et al.* 2011). 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 (Papayianni and Stefanidou 2006).

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 ^{o}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 ^{o}C for 30 h.

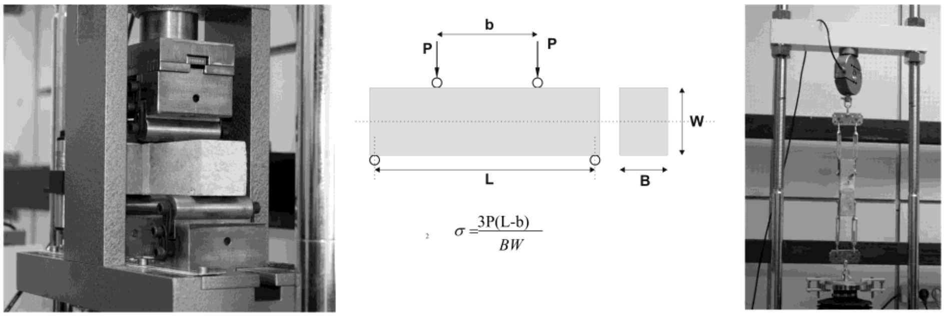
The development of the hydration and carbonation of powder samples were carried out by XRD, mercury intrusion porosimetry (MIP), FTIR, DTA/TG, EDXRF and scanning electron microscopy (SEM). By identifying CSH and CAH at different ages, not only qualitatively, but also semi-quantitatively, the hydration and carbonation process can be monitored. The mineralogical analysis was investigated by XRD with a Siemens D-500 diffractometer (40 kV/35 mA) and the spectra were collected between 5^{o} and 60^{o} 2θ scale, with a step of 0.03^{o}/5s. SEM analysis was carried out in fractured surfaces, using a FEI Quanta Inspect scanning electron microscope. DTA/TG was operated with a Setaram thermal analyser; in static air atmosphere up to 1000 ^{o}C at a rate of 10 ^{o}C/min. The FTIR analysis of KBr pellets was operated in Perkin-Elmer spectrophotometer in the spectral range of 400-4000 cm^{-1}. 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 estimation of the designed adhesive mortars

The Aktites and Mounichea stone samples were cut and shaped into specimens with dimensions of: (a) 4x4x4 cm used to measure the compressive strength of the stone and (b) 4x4x8 cm used to bond them with the designed mortars. The mechanical properties of the designed mortars were characterized by measuring the uniaxial compressive strength (Fc) and the flexural strength (Ff-3pb) according to EN 1015-11:1999.

The incising of stone faces by special mechanical tools to provide a rough surface and the wetting of these surfaces, were prerequisite before the application of the mortars. 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.

Home designed equipment for both the four point flexural strength (Ff-4pb) (Fig. 1a, b) and the direct tensile strength test (Ft) (Fig 1c), were used for measuring the adhesive performance of the bonded stone-mortar specimens (4x4x17 cm) (Whittaker, Singh and Sun 1992).



(a) (b) (c)

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

3. Results and discussion

3.1 Stones and raw materials characterization

Table 2: Mineralogical composition and properties of the stones and raw materials.

Stone	*Cc*	*Do*	*Cl*	*Qz*	*Kl*	*Il*	*Alb*	*Fc (MPa)*	*WCC (g cm^{-1} s$^{-1/2}$)*	*WSC %*
D1	6.2	83.0	0.6	3.7	1.8	4.2	0.5	42.3	0.0026 (±0.001)	3.7 (±0.1)
D2	1.5	78.7	2.8	6.1	2.5	7.8	0.5	28.7	0.0141 (±0.004)	13.1 (±2.8)
D3	12.0	80.0	0.9	2.7	2.4	1.9	0.1	107.0	0.0011 (±0.0002)	2.3 (±0.2)
D4	4.2	80.0	1.3	3.3	3.3	7.0	0.9	6.6	0.0007 (±0.0004)	2.9 (±0.9)
K	11.1	70.9	1.1	5.4	0.9	8.1	2.2	22.7	0.0211 (±0.005)	8.3 (±2.0)

Cc: Calcite; Do: Dolomite; Cl: Chlorite; Qz: Quartz; Kl: Kaolinite; Il: Illite; CH: Calcium Hydroxide; C_2S-beta: Larnite; C3S: Alite; At: Anatase; Rt: Rutile; Fc: Compressive Strength; WCC: Water Capillary Coefficient; WSC: Water Saturation Coefficient

Mineralogical composition and properties, both of raw materials and stones, determined by XRD and thermal analyses are presented in Table 2. According to these results, 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); (b) marly limestone/dolomitic limestone with an oolitic texture, brownish or yellowish to light grey-color with a low to medium porosity and low values of mechanical strength (D2, D4, K).

Furthermore, Table 2 reports the values of the compressive strength, as well as mean values of water capillary and water saturation coefficient calculated in three stone specimens. 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 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 D4 stone, on the absence of inter-connected pores, which affect the stone hygric behavior.

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 ^oC corresponds to the dehydration of calcium silicate hydrates (CSH), calcium aluminate hydrates (CAH) and the residual bound water (Aggelakopoulou, Bakolas and Moropoulou 2011). The dehydration of $Ca(OH)_2$ (CH) occurred in the temperature range ~480 – 500 ^oC, while the decomposition of $CaCO_3$ took place at a temperature higher than 600 ^oC.

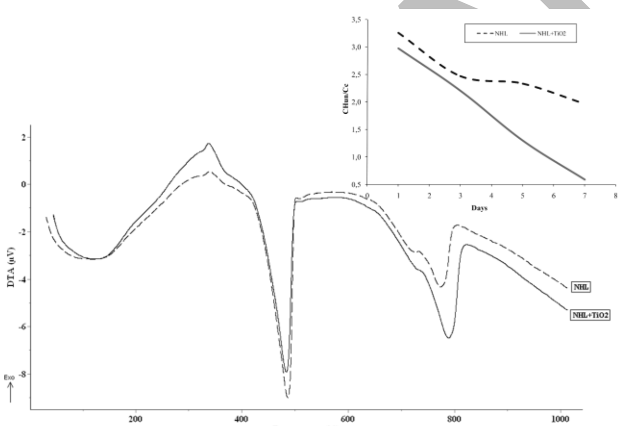


Figure 2. DTA curves for NHL mortars without nano-titania (dashed line) and with nano-titania (solid line) at 7 days of curing along with the evolution of carbonation illustrated in the inset plot.

In particular, Figure 2 depicts the DTA curves for the NHL mortars with and without nano-titania at 7 days of curing. The inset plot illustrates the evolution of the ratio unreacted-CH (CHun) to formed-Cc(Ccf) for a curing period of 1, 3, 5 and 7 days. As the setting process proceeds mass losses attributed to the release of 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 lime consumption and the formation of hydraulic phases are more pronounced for the nano-titania mortars at different curing times. The same observation was also obtained from the thermal analysis of metakaolin-lime mortars with and without nano-titania.

SEM micrographs of the mortars ML1 without- (Figure 3a) and with nano-titania MLT1 (Figure 3b) after one year of curing corroborate the results of DTA analysis. SEM micrograph of MLT1 (Figure 3b) shows that a dense network of hydraulic amorphous components was formed providing more elasticity to the mortar matrix. Moreover, characteristic hexagonal crystals of portlandite were located in both SEM micrographs; nevertheless in the case of MLT1 mortar the portlandite crystals are obviously fewer. The FTIR spectra of the above studied mortars are in full accordance with the SEM micrographs, showing after curing of one year traces of portlandite and enhanced hydraulic compound formation (Maravelaki-Kalaitzaki, P. Lionakis, E. Agioutantis, Z. *et al.* 2012).

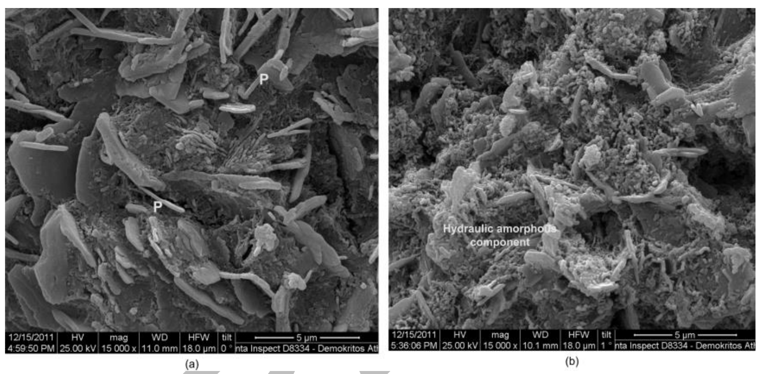


Figure 3. SEM micrographs of (a) ML mortar and (b) MLT mortar showing portlandite crystals (P) and the hydraulic amorphous components.

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 (Jayapalan, Lee and Kurtis 2009).

3.3 Mechanical Evaluation

Table 3 reports the physical and mechanical properties of the designed mortars. The physical properties of the designed mortars differed insignificantly indicating that the nano-titania addition neither modified the microstructure nor affected the hygric behaviour of the materials. The lowest Fc values were recorded for the NHL samples, while the Fc values decreased with curing time in the ML1 samples. Even though, the Fc values recorded at four 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 three months and one 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 authors (Aggelakopoulou, Bakolas and Moropoulou 2011, Velosa Rocha and Veiga 2009) and was most probably attributed to the microcracking formation due to shrinkage during the curing. Figure 4 depicts typical stress-strain curves of hydrated lime-metakaolin with (MLT1) and without nano-titania (ML1), in two time intervals of 4 weeks and 3 months.

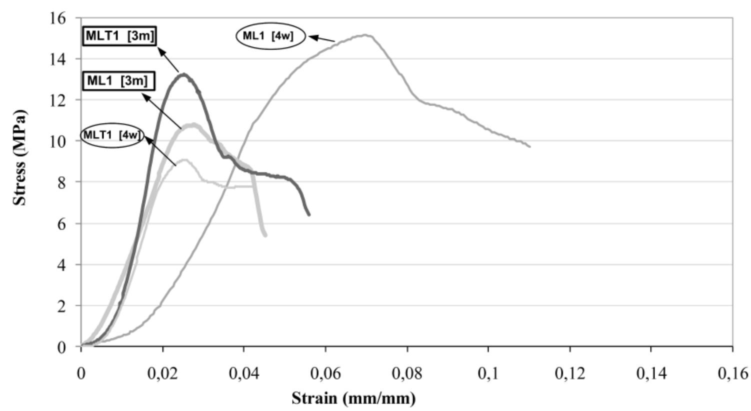


Figure 4. Stress-strain diagram of samples without nano-titania at 4 weeks (ML1 [4w]) and 3 months (ML1 [3m]) curing time and with nano-titania at 4 weeks (MLT1 [4w]) and 3 months (MLT1 [3m]) curing time.

Table 3: Physical and chemical properties of the designed mortars.

Code	WCC* g cm^{-1} s$^{-1/2}$	WSC* %	P %	Pr µm	SSA m^2/g	Cur-ing	Fc^ MPa	Ff-3pb* MPa	E GPa
NHLT1	0.0149	27.80	32.96	0.295	12.0	4w	4.15 (±0.56)	-	0.17
	(±0.007)	(±1.09)				3m	5.47 (±0.28)	1.69	
						1y	5.51 (±0.95)	-	
NHLT2	0.0080	25.58	37.79	0.092	12.84	4w	5.41 (±0.29)	-	0.37
	(±0.0004)	(±0.27)				3m	7.22 (±1.61)	-	
						1y		-	
ML1	0.0040	33.92	31.46	0.031	14.02	4w	14.85 (±1.53)	1.15	0.42
	(±0.0001)	(±0.26)				3m	11.57 (±1.39	-	0.76
						1y	10.62(±2.39)	-	0.56
MLT1	0.0074	29.52	32.54	0.031	16.01	4w	9.08* (±0.89)	1.21	0.59
	(±0.003)	(±1.07)				3m	14.19 (±0.70)	-	1.10
						1y	15.40(±0.70)	-	0.91

(*) mean value of three samples; (^) mean value of 6 samples; Fc: compressive strength; Ff-3pb: Flexural strength; E: Elasticity modulus, [4w]: 4 weeks; [3m]: 3 months; [1y]: 1 year; -: n. a.

By combining the results of physical and mechanical properties the mortars NHLT2, ML1 and MLT1 were selected as adhesive means for the stones under consideration (Table 4). The mortar NHLT1 showed similar values to others except for its high water coefficient capillary, which can be considered of secondary importance for the adhesive ability. However, NHLT1 exhibited difficulty in joining the stone specimens and therefore was not included in the finally selected mortars.

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 (Karatasios Katsiotis Likodimos, *et al.* 2010). Further support to this statement is derived from the dense network of hydraulic components observed in the SEM micrographs (Fig. 3) for the MLT1 samples.

Table 4: Mechanical properties of stone-mortar specimens cured for four weeks.

Mortar Code	Number of Ff-4pb adhered stone specimens	Ff-4pb (MPa)	Number of Ft adhered stone specimens	Ft (MPa)
NHLT2	4 (D1, D2)	2.39 (±0.7)	2 (D1, D2)	0.51 (±0.26)
MLT1	3 (D3, K)	1.34 (±0.47)	2 (K)	0.15 (±0.08)
ML1	1 (D4)	1.07	1 (D1)	0.09

Table 4 reports the results of the 4-point bending test and the direct tensile test for the adhered stone-mortar specimens. In all tests, failure was observed at the interface between stone and mortar. The results revealed that the higher bonding strength (higher flexural and tensile) was measured when applying the NHLT2 mortar as compared to the MLT1 and ML1 mortar.

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 lime as binders, carbonate sand with grains smaller than 250 μm in a B/A ratio from 1 to 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 compressive and flexural strength and 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, facilitating thus the carbonation and hydration processes. This property can be exploited in the fabrication of mortars tailored to adhering porous limestones, where humidity controls the mortar setting and adhesion efficiency. Home-designed equipment applied to measure the bonding strength of stone-mortar systems revealed that the nano-titania addition in both metakaolin-lime and hydraulic lime mortars improves the adhesive property of the mortar when applied to porous stones.

Acknowledgements

This work was carried out in collaboration with the The Akropolis Restoration Service (YSMA) of the Hellenic Ministry of Culture and Tourism. The authors would like to thank Emeritus Prof. Vasileia Kasselouri-Rigopoulou, (Committee for the Restoration of the Acropolis Monuments-ESMA) for collaboration and scientific support, the Committee for the Restoration of the Acropolis Monuments and Dr E.

Aggelakopoulou Head of the Technical Office for the Acropolis Monuments' Surface Conservation. This research has been co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: **Heracleitus II**, Investing in knowledge society through the European Social Fund.

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