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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.