Use of nanosilica- or nanolime-additioned TEOS to consolidate cementitious materials in heritage structures: physical and mechanical properties of mortars

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ABSTRACT

Tetra-ethoxysilane or tetraethyl orthosilicate (TEOS), also known as ethyl silicate, traditionally applied to consolidate stone, has recently begun to be used on Portland cement mortars and concrete with promising results. TEOS not only fills the pores in the substrate, but reacts with the cement favouring the precipitation of new C-S-H gels that densify and strengthen the materials. This study explored the effectiveness of new TEOS-based treatments bearing nanosilica (NS) or nanolime (NC) in and their compatibility with cement materials found in the built heritage, given the participation of the various products in the pozzolanic reactions that may induce additional C-S-H gel. The physical and hydric properties (mechanical strength, porosity, surface gloss and colour, water vapour permeability and low pressure water absorption) of a Portland cement mortar were determined before and after applying the consolidants. Ethyl silicate, alone or in conjunction with nanolime (4:1), proved to most effectively raise material strength and improve water repellence while conserving the original colour and gloss.

Keywords: Portland cement; mortar; heritage; consolidant; TEOS; nanosilica; nanolime

1. Introduction

Concrete attained noble architectural status in the twentieth century, when it began to be used on building exteriors and in sculpture [1]. While durable if properly designed, produced and maintained, in practice concrete often needs to be repaired [2,3], as it is subject to cracking or spalling attributable to a variety of causes [4,5]. European standard EN 1504 [6] defines the requirements that must be met by products and systems to protect and repair concrete structures in terms of the degree of deterioration (including products to be injected into the concrete, adhesives, products to protect reinforcement and surface treatments). However, intervention to conserve cultural assets is subject to very specific principles [7,8] that reject overly aggressive treatments, recommend action only where and to the extent strictly necessary with products that alter neither the physical-chemical properties of the materials nor overall aesthetics and call for pre-testing, along with other requisites.

Material consolidation, understood to consist in the application of a product to a crumbling surface to improve cohesion, mechanical properties and the adherence of the altered layers to the healthy substrate, is a common practice in heritage stone conservation and restoration. Tetra-ethoxysilane (TEOS), also known as ethyl silicate ($Si(OEt)_4$), is one of the most widely used consolidation products [9] for its compatibility with and stability in [10] such substrates.

It hydrolyses in the presence of water (moisture in the atmosphere or in the pores of the material), generating silanol groups (Si-OH) that polymerise to form siloxane bonds (Si-O-Si) and ultimately inducing the precipitation of a silica gel that raises stone strength.

This gel fills the pores and adheres to substrates with a Si base, also by forming siloxane (Si-O-Si) bonds [11]. It consequently adheres poorly to non-siliceous materials (such as limestone or marble). The treatment layer may also crack during drying on a number of types of substrates. Strategies developed to prevent this latter difficulty envisage combining the material with surfactants [12], additives [13] or nanoparticles [14,15,16,17].

Recent studies on the consolidation of cement-based materials, less intensely researched to date [18,19,20], have assessed the effect of TEOS on the physical properties of mortars with promising results: mechanical strength and durability (reduction of chlorides and carbonation depth) were enhanced with no significant alteration of surface colour or gloss. Nonetheless, TEOS has been shown to penetrate compact materials in depth [19] and in early age (1 day) cements the formation of alcohols during TEOS hydrolysis retards hydration and favours the formation of a more porous, weaker structure [21].

Nanosilica (nano-SiO_2, NS)-based surface consolidating treatments [22], on the grounds of the reactivity of two of the main products of Portland cement hydration, portlandite ($Ca(OH)_2$) and C-S-H gel [10,20,23], and their ability to fill the pore systems, have been attempted, with varying success on hardened concrete and cement mortars, for whilst they can densify these materials, their penetration capacity is lower than in TEOS. In fact, NS compared with a variety of organic or inorganic surface treatments has been found to be less effective in reducing water absorption [24], chloride migration or CO_2 penetration [19; 24] or in raising mechanical strength

[25]. Nonetheless, results are quite dependant on the microstructure of the coated materials since in more porous substrates nanoparticles are able to penetratete deeper and therefore act more effectively on reducing the migration of water and aggressive agents [26]. Like this, Sanchez et al. [27] by forcing the migration of nanosilica under the action of an electric on a cement mortar enhanced the surface of the material and thus the durability of the entire bulk and confirmed the sealing ability and pozzolanic activity of the nanoparticles [28].

Nanolime (nano-$Ca(OH)_2$, NC), traditionally used to consolidate carbonate-based materials [29], has also been tried recently as a surface treatment for porous cement mortar in conjunction with nanosilica (a coat of NS followed by a coat of NC) with promising results in terms of mechanical strength [25].

In the pursuit of the most ideal surface treatments to consolidate heritage cement assets by capitalazing the advantages of the aforementioned products (i.e. TEOS is more effective in filling pores smaller than 50 nm [22]; NS has a extremely high pozzolanic reactivity [22]); and their physicochemical compatibility and feasible synergy potential, this study explored the performance of TEOS and NS or NC blends on a cement mortar. In fact, recent studies have shown that nanoparticles can improve the performance of coatings on cement-based materials, by increasing their surface roughness and thus water repellency [30], or vice versa, the performance of nanoparticles can be enhanced by coatings like in a recent study of Hou et al. [31] in which nanosilica particles coated with polymethylhydrosiloxane enhanced the water proofing properties of a cement mortar.

The effectiveness and compatibility of the new explored consolidating blends were assessed in keeping with heritage intervention criteria and the possible changes in the physical and hydric properties of a Portland cement mortar: mechanical strength, porosity, surface gloss and colour, water vapour permeability and low pressure water absorption.

2. Experimental

2.1. Materials and treatment application

Portland cement (CEM I 42.5N/SR; Table 1) specimens of two sizes, 10x10x60 mm and 60x70x10 mm, were prepared with a water/cement ratio of 1:2 and a cement/sand ratio of 1:5. The fines (Ø < 1 mm) were removed from the standardised sand to favour mortar porosity. This is a way to simulate the porosity of a degraded mortar in need of consolidation. TEOS (CTS ESTEL 1000), used as a reference, and combinations of the product with two proportions of nanosilica (BASF MEYCO MS 685) and nanolime (CTS NANORESTORE) (Table 2) were drip-applied to one side of specimens (previously cured in a humidity chamber at RH>95 % and a temperature of 21(±2) °C for 28 days) until apparent saturation, defined as the point when the surface remained moist for at least 1 min. Inasmuch as TEOS and NS could not be blended due to differences in the polarity of their respective solvents, NS was applied first, followed by TEOS. Manufacturer recommendations were followed to apply NC in conjunction with TEOS to prevent the appearance of carbonate veils on the surface, namely by placing a moist paper pulp poultice for 8 h on 9 g Japanese paper over the surface to be treated, all covered by polyethylene terephthalate film. In Table 3, the total amount of products consumed by the mortars either in one step (TEOS; TEOS and NC) or two (NS followed by TEOS) is listed. Used ratios were based on preliminary application tests and represent the volume of each product blended together before application for TEOS and NC mixes or individually applied for NS and TEOS treatments.

The physical properties of the specimens were characterised after curing the treatments for 5 weeks at 21(±2) ºC and relative humidity of 45(±5) %

2.2. Methods

Pore size distribution in the mortars before and after application of the treatments was found on a Mercury Micromeritics Autopore IV 9500 V1.05 porosimeter, applying a maximum intrusion pressure of 22 749.92 MPa, which corresponds to a pore diameter of 0.0067 µm. Since treatments were applied to one side of the specimens, porosity results of 1cm^3 fragments were just used for comparison purposes, in no case as absolute values.

Possible variations in water vapour permeability were determined to RILEM recommendations [33]. To ascertain material resistance to water absorption, Karsten tube tests were performed [34]. The latter test is particularly apt in studies of protective treatments for the historic heritage since can be carried out in situ.

After 28 days of initial curing, the untreated and treated 10x10x60 mm specimens were tested for compressive and flexural strength, respectively on an IBERTEST Autotest 200/10SW frame and a NETZSCH 6.111.2 device [35]. The resonant frequency signals generated in flexural mode vibration (Young's modulus or the dynamic modulus of elasticity) were recorded as specified in international standard UNE-EN ISO 12680-1: 2007 [36] on a GrindoSonic MK5 “Industrial” analyser.

The chromatic coordinates (L*, lightness, and hue, a* (red+/green-) and b* (yellow+/blue-)) were measured in 60x70x10 mm mortar specimens before and after treatment with a Minolta CM 2500 D spectrophotometer. The total colour variations (ΔE*) were calculated from the following equation ($\Delta E^* = (\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2)^{1/2}$) [37]. Surface gloss was determined on the same surfaces at an 85° angle using a Minolta Multi Gloss 268 glossimeter sensitive to variations in scantly glossy surfaces (0-160 µm gloss units).

3. RESULTS AND DISCUSSION

3.1 Porosity

The cement mortar prepared had an open porosity of 12.85 % (vol,), with pores of a diameter of over 10 µm (entrained air pores) accounting for 24.78 % and capillary pores, the ones that decrease over time as cement reacts with capillary water, i.e., with a diameter of 0.01 µm-10 µm (Table 4, Fig. 1), for 73.1 %. The remaining 2.2 % consisted of pores of C-S-H gel [38].

Whilst all the treatments lowered total mortar porosity, the ones with the highest TEOS content were particularly effective, reducing the value by 20 % to 32 % (NS+TEOS (1:1), TEOS and TEOS+NC (4:1)) (Table 4), while also filling entrained air pore more intensively.

TEOS and the TEOS+NC blends were most effective in lowering mortar capillary porosity, especially in respect of the smallest capillary pores (1-0.01 µm), and the only ones to reduce the mean pore size. Such pore structure refinement, which favours material durability by hindering the diffusion of aggressive ions, is the result of the physical pore filling (Hou et al. [22] reported that TEOS may penetrate pores under 50 nm) and the precipitation of C-S-H gel, the product of the pozzolanic reaction between TEOS and the cement matrix [10,20,21] and TEOS with nanolime [20].

The two combinations of TEOS and NS induced a substantial rise in the number of the smallest capillaries (1-0.01 µm), the outcome of the conversion of larger pores, and a considerable decline in gel pores (<0.01 µm). Unlike NC, the application of NS before ethyl silicate would not favour the formation of pore gels. The failure of NS to penetrate in the pore matrix, as illustrated by SEM micrography and Ca and Si elemental mapping on the mortar surface (Fig. 2), would hamper subsequent access by TEOS which ultimately could fill larger pores.

3.2 Water vapour permeability

The treatments lowered the water vapour transmission rate by 50 %-63 % (Table 5). Hou et al. [26] observed steeper declines in porosity in specimens made with higher w/c ratios in cement pastes treated with TEOS and a colloidal nano-SiO_2.

At 59 %-63 %, the TEOS+NC blends induced the steepest declines, followed by the treatments with a higher ethyl silicate content, namely TEOS and NS+TEOS (1:9), with similar values (54 %-56%) (Table 5). Generally speaking, the greater the pore structure refinement the greater was the reduction in permeability (with the exception of treatment NS+TEOS (1:9)). Whilst reductions of over 25 % are not recommended for heritage stone conservation [39], that threshold is not applicable to cementitious materials, in which the pores in the paste become more refined as the hydration reactions progress: the volume of capillary pores, which primarily govern the transport properties of cement-based materials [26], declines while the volume of gel pores rises. Material durability is in fact enhanced with such refinement, given the lesser possibility of expansion or contraction due to moisture gradients or acidic gas migration [26].

3.3. Low pressure water absorption

The possible changes in the surface characteristics of the mortars after application of the treatments, i.e., TEOS-prompted water repellence [40] and pore filling, were determined with the low pressure water absorption test.

The water absorbed by the specimens through Karsten tubes before and after applying TEOS+NS or TEOS+NC are shown in Figure 3, while Table 6 gives the values for each product of the two coefficients traditionally used to determine water repellence in historic materials on the grounds of those curves. All the products applied induced substantial declines in water absorption, ranging from 62% to 83%. De Witte et al. [41] deemed that a material is resistant to water penetration when amount of water absorbed measured by a Karsten tube is greater than or equal to 0.5 cm^3 between 5 and 15 minutes after starting the test (period of time in which the absorption rate is highest). Further to that criterion, the untreated mortar would itself be rainwater-resistant (Table 6). However, according to the Nwaubani and Dumbelton´s [42] threshold value ($\leq$0.35 kg/m^2h) for assessing water repellency, only the mortars treated with NS+TEOS (1:9) and TEOS+NC (4:1), the combinations with the highest TEOS content, would be effectively protected.

As these treatments induced consolidation rather than water repellence strictly speaking, they proved to be highly effective in terms of lowering water ingress and with it the amount of any dissolved aggressive ions, observation reported by other authors after the application of only TEOS [18,26,40].

3.4 Colour and gloss

The values of the 5 week chromatic parameters ($\Delta E^* = (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$) and gloss ($\Delta G$) in the mortars are given in Table 7.

With the exception of the blend with a high nanolime content (TEOS+NC (1:4)), all the treatments darkened the mortar surface (decline in L*). In the products with a high TEOS content in particular, the colour change was perceptible to the naked eye, assuming a threshold of $\Delta E^*>3$ (for colour change in general [43]). Nonetheless, all but one of the colour variations were wholly acceptable for the purposes of ancient building material conservation ($\Delta E^*\leq 5$; [43]). The exception was the change prompted by the NS+TEOS (1:9) blend, where $\Delta E^*>10.50$. The results of applying TEOS separately were consistent with those reported by Pigino et al. [18] for Portland cement concretes, with ΔE^* values of around 5 or even lower ($\Delta E^*=2.6$), depending on the water/cement ratios in the cement mixes. In an earlier study, Barberena-Fernandez et al. [24] found that separately, nanosilica and nanolime induced much lower, imperceptible ($\Delta E^*<2$) variations in colour in the same type of substrate. They also observed that nanosilica modified surface gloss slightly, albeit perceptibly to the naked eye, assuming the $\Delta G^*>2$ threshold established by García and Malaga [44]. TEOS+NS-based treatments also affected surface gloss, more intensely at higher proportions of NS ($\Delta G=2.5$-3.9). Such variations may nonetheless be regarded as acceptable.

3.5 Mechanical properties

Further to the pre- and post-treatment mortar mechanical strength findings, at 37.71 MPa, untreated compressive mortar strength was slightly lower than specified in European standard EN 197-1 [45] for a 28 day, type I 42.5 cement (42.5 MPa-62.5 MPa). That was attributable to the low cement/sand ratio and the removal of fines during cement preparation to favour treatment penetration (Fig. 4). Flexural strength was 7.88 MPa (Fig. 4). Both types of strength rose after application of all the treatments without exceeding the limits recommended for the conservation of stone materials (treated specimen strength/untreated specimen strength <1.5) [46].

The greatest rise in compressive (46 %) and flexural (36 %) strength was observed in the specimens with ethyl silicate (TEOS) as the sole component, which was consistent with the fact that they also exhibited the steepest decline in total and entrained air porosity, corroborated by the excellent linear correlation between the latter and compressive strength (Fig. 5). The next strongest specimens were the ones treated with ethyl silicate-high blends: (TEOS+NC (4:1) and NS+TEOS (1:9)). The rise in compressive and flexural strength in the former was respectively 36 % and 33 % and in the latter 39 % and 35 %.

The separate application not only of nanolime but also of nanosilica to the same substrate in a prior study by Barberena-Fernández et al. [25] prompted moderate (14 %) to low (3 %) rises in compressive strength. Nanosilica ineffectiveness was due either to surface carbonation, which would impede the pozzolanic reaction due to the lack of portlandite on the surface, or to treatment viscosity (Table 2), which would hamper its penetration into the substrate. Nonetheless, when used in appropriate proportions (1:5:1) [25], due to the pozzolanic reaction between the two types of nanoparticles, they induced greater rises than the combinations containing low concentrations of ethyl silicate studied here (NS+TEOS (1:1) and TEOS+NC (1:4)).

The results of the acoustic resonance spectroscopic trials, a non-destructive method particularly apt for architectural heritage conservation studies, showed that at 31.5 GPa, Young's modulus or the dynamic modulus of elasticity was high in the untreated specimens (Fig. 6). The products that induced the steepest increase in material stiffness (rises in Young's modulus of 13%-18 %) were, logically, the same ones that prompted the highest rises in mechanical strength: those with more ethyl silicate in their composition, TEOS, TEOS+NC (4:1) and NS+TEOS (1:9), which filled the entrained air pores most effectively.

4. Conclusions

This study explores the potential of blends of TEOS with different amount of NS or NC particles for the consolidation of cement-based historic assets. Of all these treatments studied, only calcium hydroxide nanoparticles combined with ethyl silicate (TEOS) (TEOS+NC (4:1)) exhibited great affinity for conservation of cement mortar. Both, TEOS alone or combined with NC (4:1) raised mechanical strength by over 35 %, reduced the mean pore diameter and improved water repellence which would favour material durability by hindering the diffusion of aggressive ions. Furthermore, they did not perceptibly modify surface gloss or colour unlike the treatments with NS contrary, the presence of NS (NS+TEOS (1:9) and NS+TEOS (1:1)).

These results reveal the necessity of further exploring new blends that combine nanoparticles with either organic or inorganic coatings by optimizing the dosages of both components and the application procedures that ensure better penetration of the treatments.

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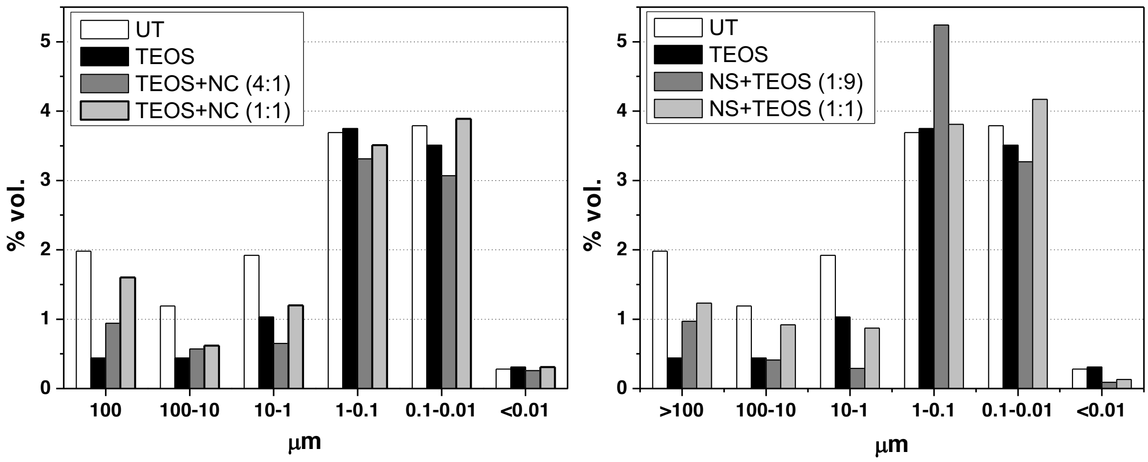

Fig. 1. Pore size distribution (vol.%) in untreated (UT) and, ethyl TEOS-treated and TEOS+NC (left) and TEOS+NS (right) -treated mortars.

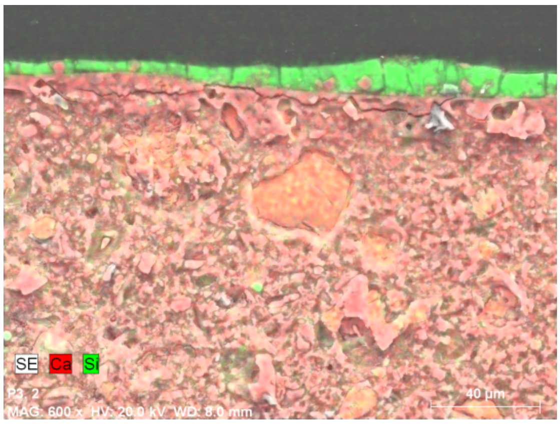

Fig. 2. BSEM micrograph and Ca and Si mapping in nanosilica-coated mortar.

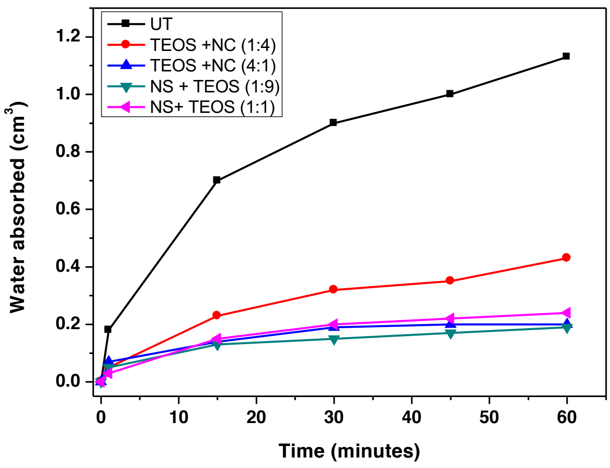

Fig. 3. Low pressure water absorption through Karsten tubes in treated and untreated specimens.

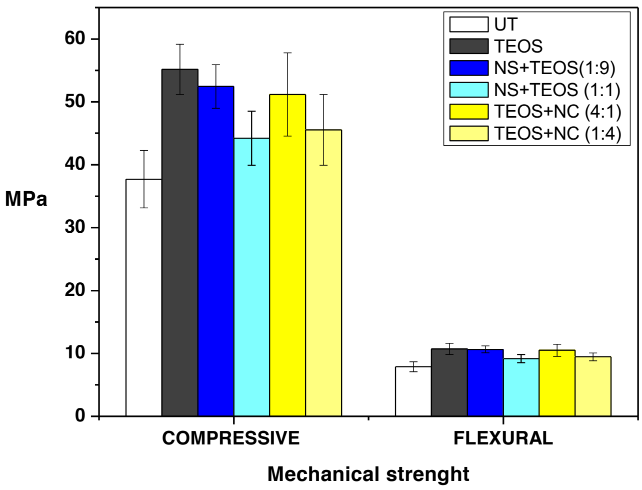

Fig. 4. Pre- and post-treatment compressive and flexural strength in cement mortar.

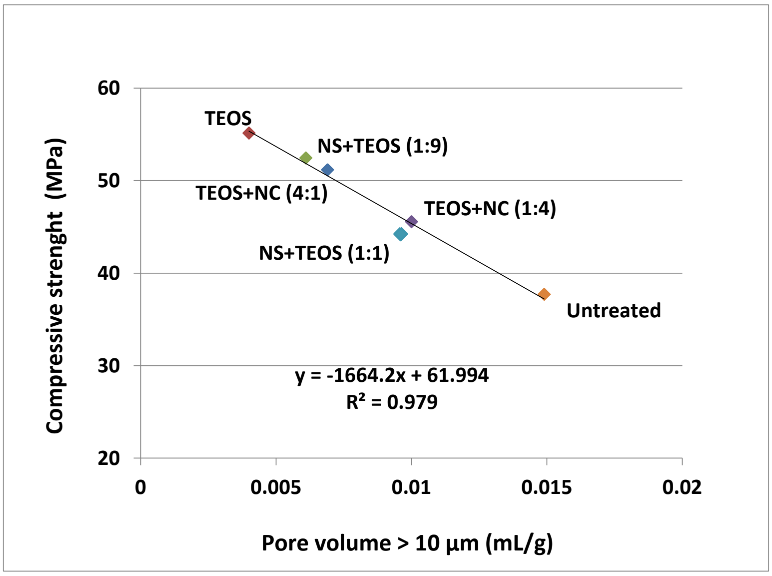

Fig. 5. Linear correlation between compressive strength and entrained air pore volume in untreated and consolidant-treated mortar.

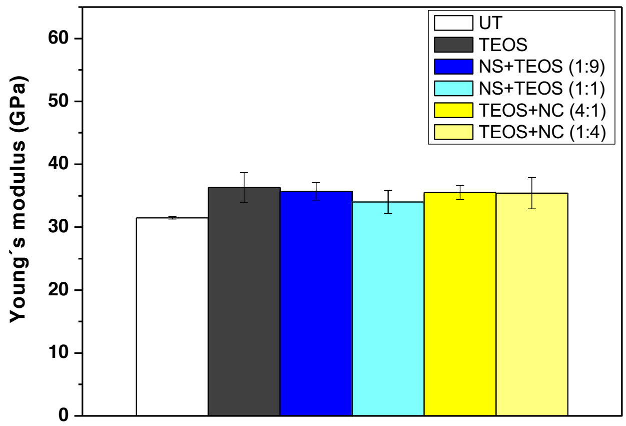

Fig. 6. Young's modulus in pre- and post-treated cement mortar specimens.

Table 1. XRF-based chemical analysis for cement CEM I 42.5N/SR.

(%)	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	SO_3	K_2O	TiO_2	LI*
Cement	19.01	4.06	4.73	0.03	1.64	62.4	3.19	0.66	0.23	3.02

LI*: loss on ignition at 1000 ºC

Table 2. Main physical-chemical characteristics of treatment products (manufacturers´ information).

	ESTEL1000® (CTS)	NANORESTORE® (CTS)	MEYCO MS 685® (BASF)*
Acronym	TEOS	NC	NS
Composition	Tetraethyl orthosilicate	Calcium hydroxide nanoparticles	Silicon dioxide nanoparticles
Solvent	White spirit D40	Denaturalised isopropyl alcohol	Water
Density (g/cm^3) (20ºC)	0.97	0.8	1.134 ±0.03
Viscosity (kg/(m s)	0.0049 (20ºC)	0.00275 (25ºC)	< 0.03 (20 ºC)
Active principle wt%	75	0.5	40
Particle dimensions	-	< 100 nm	98.7 nm (mean)**
pH	-	7.2	10 ±1
Liquid characteristics	Colourless	Opaque white	Opaque white

* Presently registered as MASTERROC® MS 685

** [32]

Table 3. Amount of product consumed by the mortars.

Treatment	Applied together (cm^3)		NS (1st product) (cm^3)		TEOS (2nd product) (cm^3)	
	a	b	a	b	a	b
TEOS	0.65	4.5	-	-	-	-
TEOS + NC (4:1)	0.49	3.37	-	-	-	-
TEOS + NC (1:4)	0.16	1.12	-	-	-	-
NS+ TEOS (1:9)	-	-	0.07	0.5	0.6	4.5
NS+ TEOS (1:1)	-	-	0.2	1.5	0.2	1.5

a= 10x10x60 mm; b= 60x70x10 mm

Table 4. Total porosity and mean pore size of treated and untreated cement mortars.

	Total porosity (vol. %)	Mean pore Ø (µm)
Untreated	12.85	0.0769
TEOS	9.47	0.0558
TEOS+NC (4:1)	8.80	0.0575
TEOS+NC (1:4)	11.13	0.0583
NS+TEOS (1:9)	10.27	0.0934
NS+TEOS (1:1)	11.14	0.0743

Table 5. Water vapour conductivity coefficients (δ) in untreated and consolidant-treated cement mortars.

	δ (Kg/m.s.Pa)	**% Reduction**
Untreated	$1.90E^{-12}$	-
TEOS	$0.87E^{-12}$	54.2
TEOS+NC (4:1)	$0.70E^{-12}$	63.1
TEOS+NC (1:4)	$0.77E^{-12}$	59.4
NS+TEOS (1:9)	$0.84E^{-12}$	55.9
NS+TEOS (1:1)	$0.95E^{-12}$	50.0

Table 6. Low pressure water absorption in untreated and consolidant-treated cement mortar specimens.

	Water absorption after 60 min ($kg/m^2 \cdot h$)	**Absorption (cm^3) from 5 min to 15 min**
Untreated	1.98	0.1
TEOS+NC (4:1)	0.35	0.03
TEOS+NC (1:4)	0.75	0.08
NS +TEOS (1:9)	0.33	0.02
NS+TEOS (1:1)	0.42	0.04

Table 7. Variations in lightness (L*), chromatic coordinates a* and b*, total colour (ΔE*) and gloss (ΔG).

	L*	**a***	**b***		**G**
Untreated	73.75	0.40	5.65	-	0.17
	ΔL*	**Δ a***	**Δ b***	**ΔE***	**ΔG**
TEOS	-4.87	0.10	1.13	5.03±1.01	0.13±0.05
TEOS+NC (4:1)	-3.14	-0.34	0.22	3.35±0.20	0.23±0.1
TEOS+NC (1:4)	0.82	-0.07	-2.03	2.32±1.03	0.08±0
NS+TEOS (1:9)	-10.38	0.20	1.57	10.50±0.29	2.48±0.35
NS+TEOS (1:1)	-0.26	-0.04	-1.31	3.07±0.16	3.93±0.8