PARTICLE MODIFIED CONSOLIDANTS IN THE CONSOLIDATION OF POROUS STONES

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Abstract

Conventional inorganic silicon-based consolidants, most widely used in stone conservation, present some serious limitations, such as the tendency to crack and shrink during drying. This deficiency has been the focus of several studies, aiming at modifying and improving their performance. The objective of this work is to investigate the performance of particle modified consolidants applied on two types of porous stones used in historical structures in Greece. Particle modified silicon-based consolidants (PMC) consist of a silicate binder loaded with titania (TiO_2) particles, combined with a nanosilica suspension. In order to evaluate the consolidation effect, changes in properties of treated specimens were estimated through several methods such as SEM, mercury intrusion porosimetry, water absorption by capillarity and water vapor permeability. Changes in appearance were also estimated by color measurements. PMCs appear to be promising in stone consolidation, as they show a reduction of the shrinkage during drying. In addition, PMCs do not cause significant changes to the physicochemical properties or the color parameters of the stone.

Keywords: particle modified consolidant, titania, nanosilica, stone consolidation

1. Introduction

One of the most serious problems facing conservation is the deterioration of carbonate stones used in construction. Where stone is weakened by environmental decay factors, consolidation may be necessary to reinforce the stone's cohesion. The majority of the materials used as stone consolidants have been both organic polymers and inorganic materials, such as calcium hydroxide. Silicon-containing polymers, such as tetra-ethoxysilane (TEOS) have been the most widely used consolidants (Rodrigues 2001, Price and Doehne 2010, Scherer and Wheeler 2009). The polymerization, initiated either by atmospheric humidity or water contained into the stone's porosity, occurs by hydrolysis and condensation (Horie 1987). More specifically, the alkoxysilanes are hydrolyzed by water to form silanols, which then polymerize to give a silicon polymer.

These materials present sevral positive aspects such as the ability to penetrate into porous materials due to their low viscosity. However, their commonly reported drawbacks of the poor chemical affinity between calcite and silica molecules and the tendency to crack during shrinkage and drying, have been the focus of several studies with the objective of modifying and improving alkoxysilane performance (Rodrigues and Pinto 2008). Previous work on nanoparticle modified consolidants

show that they may reduce cracking and shrinkage after solvent evaporation (Miliani, Velo-Simpson and Scherer 2007). These consolidants consist of a silicate binder loaded with titania particles (TiO_2) and silica (SiO_2) nanoparticles. Based on the fact that the specific surface area of a solid increases with the decrease of its volume, the use of nanoparticles offers the possibility of having a larger surface area for reaction to take place as well as a better penetrating ability, due to low viscosity suspensions.

The objective of this work is to investigate the performance of particle modified consolidants applied on two types of porous stones used in historical structures. Cubic samples were treated with PMC through capillary absorption and left to dry in laboratory conditions. Then the evaluation of the application followed, using various test methods according to the performance goals for stone consolidants (ASTM E2167-01, 2008).

2. Materials and Methods
2.1 Stone specimens

The treatments were carried out on two types of carbonate stones. One was a biocalcarenite from Rhodes (Rh), which contains ~70% of $CaCO_3$. It is composed mainly of marine shells fragments and microfossils, with secondary minerals such as quartz, biotite and feldspars. The other stone was a limestone from Crete (Re) which contains of ~90-95% of calcite. They have quite different porosities (Rhodes ~15%; Rethymno ~30%), as well as significant difference in the pore size distribution, where in case of RH, is shifted towards the area of larger pores (average pore radius ~31μm) while in RE, shows the presence of much finer pores (average pore radius ~1,7μm). Figure 1 presents the pore size distribution plots of the two types of stone. The stones also present distinct difference in appearance, as the RE stone has a light-creamy color, while RH is darker-colored (grey).
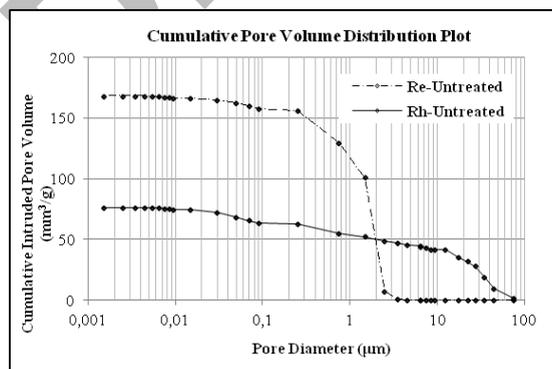

Figure 1. Cumulative Pore Volume Distribution Plots of untreated Rethymno and Rhodes stones

2.2 Consolidants and application method

Monomer tetraethoxysilane (TEOS, purity ≥ 98%, Fluka Chemika) catalyzed by di-n-butyltin dilaurate (DBTL) was used in order to prepare the binder solution, while, an ammonia solution 25% (ammonium hydroxide) was used as a catalyst for the preparation of the nanosilica suspension. Titanium oxide powder (Aldrich, Titanium (IV) Oxide, powder, 99,8%, particle size ~ 150-200 nm) was added into the silica suspension, while the solvents used were ethanol (absolute) and isopropanol.

The consolidants were applied by contact capillary absorption both in dry cubic 5x5x5 cm specimens and in 5x5x1.5 cm samples (for the water vapor transmission tests) in laboratory conditions (T=25-27°C). Specimens were positioned vertically in the base of a vessel containing a small amount of the consolidant solution, and left to absorb the consolidant by capillarity for several hours, supplying the container with the solution at regular intervals. The vessel and specimens under consolidation were surrounded by a plastic container to minimize solvent evaporation. Excess material was gently removed with ethanol (absolute) using a sponge at the end of the application, in order to avoid blocking of the surface, or the formation of superficial deposits that may affect the appearance of the stone surface.

2.3 Evaluation methods

Stone samples were observed in a scanning electron microscope (SEM-EDX) in order to evaluate the penetration depth and to determine the elemental analysis of treated substrate.

The mass gain of dry stone was measured. The treated samples were allowed to cure until constant mass. The consolidant remaining on the dried stones is the difference in weight of specimens before and after treatment and is expressed as a percentage of the specimen's weight before treatment.

The water absorption coefficient was estimated through capillary rise tests (UNI 10859:2000). The samples were dried at 60°C, weighed, treated and then tested. The amount of water absorbed per unit area was then calculated and reported as a function of the square root of time.

For the determination of water vapor transmission rate through the stone, the "water method" was performed on treated and untreated samples, according to a standard test method (ASTM E96). Each test specimen of 1.5 cm in thickness is sealed to the mouth of a test dish containing distilled water. The test dishes were placed at a controlled temperature of 23±2 ^{o}C and in an environment of 50±5% relative humidity. The test dishes were weighed every 24 hours and the water vapor transmission rate was determined by the change in mass at the steady state of the system. The test was run for 10 days, then the water vapor transmission, permeance and permeability values were calculated.

The microstructural study, in order to investigate variations in the stone porosity and the pore size distribution, was performed by mercury intrusion porosimetry (Porosimeter Pascal 140 & 440 series, Thermo Electron). The ultrasound velocity was measured with a US instrument (PUNDIT 6, CNS Farnell), which measures the transmission time of the pulse source 54 kHz. The elastic

modulus, E, was calculated from the equation $E=dV^2$. The changes of thermal expansion coefficient are examined by thermomechanical test (TMA 402, Netzch).

The effect of the treatment on the optical appearance of the stones was measured using a portable Spectrophotometer (Dr. Lange Spectro-color, LMG183) before and after the treatment. Color values were obtained in the CIELab space. Mean values of L*, which refers to the brightness (0 for black−100 for white), the red-green component a* (positive for red and negative for the green colors) and the yellow-blue component b* (positive for yellow and negative for the blue colors), were used to obtain the average color difference ΔE*, through the equation $\Delta E* = [(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)^2]\,\frac{1}{2}$.

3. Experimental procedure
3.1 Consolidants preparation

Two types of PMC were prepared in the laboratory using two different solvents, ethanol (absolute and isopropanol, respectively. The consolidants consist of a silicate binder, plus colloidal particles as well as the solvent. Titania particles (TiO_2) were added into nanosilica suspensions and then mixed with the binder solution. Table 1 represents the composition of the PMC consolidants.

Table 1. PMC Composition Table

PMC Composition	Particles suspension (SiO_2+TiO_2)	TEOS[a]	EtOH	Isopropanol	Total
PMC1 Volume (cm^3)	179.5	67.08	88.92 (B[b]) + 64.5 (S[c])	169.2 (Sil.[d])	400
PMC2 Volume (cm^3)	179.5	67.08	88.92 (B) +169.2 (Sil.) +64.5 (S)	-	400
Mass Solids (g) (in both)	SiO_2 1.35 TiO_2 6.74	0.77	-	-	8.87

[a] 43% TEOS into EtOH for the preparation of the binder solution,

[b] (B) included in the Binder solution,

[c] (S) added as a solvent at the final PMC solution,

[d] (Sil.) Included into the silica suspension

3.1.1 Synthesis of the binder solution

The binder solution consists of TEOS in ethanol (absolute), where di-n-butyltin dilaurate (DBTL) was used as a catalyst.

3.1.2 Synthesis of the particles suspension

Two different nanosilica suspensions were prepared using tetraethoxysilane as precursor into two different alcoholic media, ethanol (absolute) and isopropanol, while ammonia solution (ammonium hydroxide) was used as a catalyst. The TEOS solution was added dropwise over 20 minutes into the solvent containing the ammonia solution catalyst, under vigorous magnetic stirring.

Next step was the addition of titania particles into the silica suspension. Titanium oxide powder was added at a rate of 5:1, with respect to solids

(TiO$_2$:SiO$_2$). According to previous studies, the ratio of TiO$_2$ to nano-silica has to be no greater than 9:1, or the viscosity increases drastically (Scherer, Flatt et al. 2002)

3.1.3 PMC composition

The binder solution and the solvent were mixed together. The particles (particle suspension) were added to this solution in three steps under magnetic stirring followed by an ultrasonic treatment (100W/cm^2, 15 minutes). During ultrasonic treatment, the mix had to be placed in an ice-containing vessel to prevent solvent evaporation.

The mix prepared did show a segregation tendency for the first (2-3 approx.) days. Total shrinkage can be measured by taking a known volume of liquid polymer and measuring the volume after setting (Horie 1987). It was found that in an equal period of time, PMC1 has the most reduced shrinkage with respect to the PMC2 and the binder solution.

3.2 Application on stone specimens
3.2.1 Capillary height versus time during application

The consolidants show different behavior in each stone, mainly due to the different microstructural characteristics of the stones. Figure 2 represents the capillary height of the sorption during treatment versus time, for the first 3 hours of treatment. As seen in Fig.2, both stones have a faster absorption capacity in the binder solution, while no significant differences have been observed between the two PMCs. In case of Rh stone, the adsorption seems to reach to the top of the sample in a shorter time than Re stone (Figure 2), as the sorption curves of Re stone almost reach the maximum height within the first 3 hours of treatment.
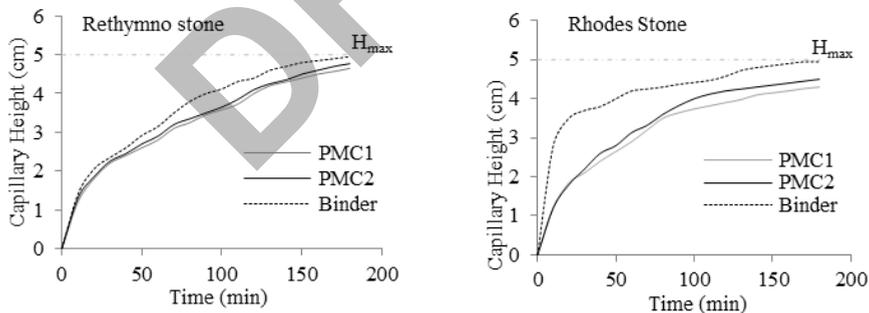

Figure 2. Capillary height versus time during application for Rethymno and Rhodes stones. Treatments with PMC1, PMC2 and the Binder solution. H$_{max}$ corresponds to the top of the specimens.

4. Evaluation of Treated specimens
4.1 Depth of penetration

After mass stabilization of the treated specimens (10-15 days after treatment), samples taken from three different height zones, zones a, b and c of the stone specimens (0<a<1.5 cm, 1.5 <b<3 cm and 3<c<5 cm, where zero corresponds to the

contact sorption area and the H_{max}= 5 cm) were examined with a SEM-EDX, in order to investigate the treated substrates elemental analysis in different capillary heights, as well as to evaluate the penetrating ability of the PMC to the specific types of stone. The penetration depth was estimated based on the detection of Ti, not contained in the original composition of any of the two stones.

According to the SEM-EDX results, in case of Re stone, PMC has been detected in all three height zones. Figure 3 shows the deposition of particles in a pore (of approximate diameter size ~3-4 μm) in zone "a" of Re stone, confirmed by the EDX analysis, with the detection of Ti and Si elements (Table 2). As shown in Table 2, in zone "a" of Re stone, the initial ratio of the particles is maintained (TiO_2:SiO_2 = 5:1 approximately). In addition, the concentration of Ti and Si reduces with increasing the height of the specimen. On the other hand, in Rh stone, PMC seems to have penetrated only up to the first zone (up to 1.5 cm height), which is mainly due to the different porosity and pore size distribution between two types of stone. Also, the particles ratio is not obvious in the elemental analysis of this stone, as it contains considerable amount of silicon-based compounds. Figure 4 shows the treated surface of Rh stone, where has been also detected an amount of Ti (Table 2). In both cases, the surface presents continuity and no signs of cracks have been observed through SEM examination. The penetration depth is highly related both with the liquid's properties as well as the microstructural properties of each substrate. It should also be noted that when using a material suspended in an alcoholic medium, is often not certain whether the consolidant (particles) penetrates as far as the solvent. A sample prewetting with solvent could assist the penetration into the pores network. The type of application may also affect to some extent the penetration.
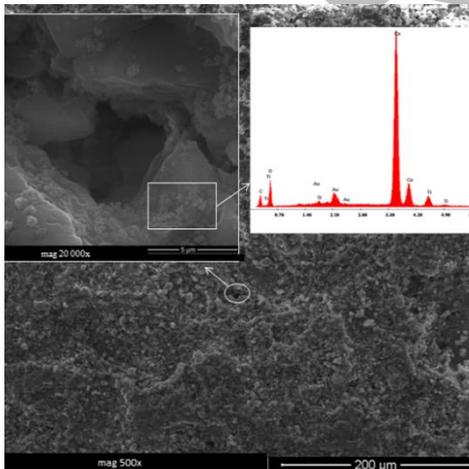

Figure 3. SEM image and EDX analysis of Rethymno stone treated with PMC. Zone "a" (0>a>1.5cm)

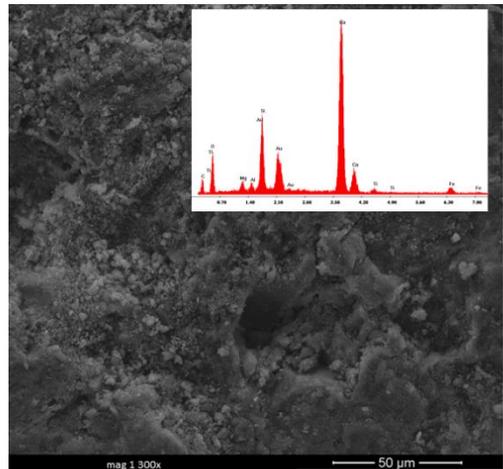**Figure 4**. SEM image and EDX analysis of Rhodes stone treated with PMC. Zone "a".

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Table 2. Wt% Elemental analysis.
Results of the EDX analysis in different height zones of samples treated with PMC.

Stone / zone	C	O	Mg	Al	Si	Sn	Ca	Ti	Fe
Re Stone									
Zone a (Fig 3)	13.68	35.70	-	-	0.75	-	45.49	4.38	-
Zone b	21.88	43.28	-	0.94	2.31	-	30.62	0.98	-
Zone c	19.68	41.04	-	0.45	1.88	-	36.23	0.72	-
Rh Stone									
Zone a (Fig 4)	18.99	31.94	2.51	1.51	10.26	-	31.01	0.96	2.82
Zone b	22.87	33.24	1.49	-	9.98	0.61	30.77	-	1.04
Zone c	24.98	43.02	0.77	0.45	6.57	-	24.21	-	-

4.2 Weight variation after treatment

The % mass gain of dry specimens following treatment was calculated by weight: % MG = $((w_{un} - w_{tr})/w_{un})*100$, where w_{un} is the initial mass of the specimen and w_{tr} is the dry mass as marked after constant mass was achieved. Similar values were obtained for both types of consolidants tested. Treated RE stone's mass gain was found to be ~ 0.34%, higher than the RH's, which stands at ~0.16%. The lower final mass gain of the Rh stone indicates that the specific stone has a lower absorption capacity in PMC, which agrees with the results from SEM.

4.3 Water Absorption

Capillary absorption measurements were carried out to investigate the difference in water absorption by capillarity between untreated and treated samples. Both consolidants showed similar behavior in the capillary rise tests. In Table 3 are reported the average values of the water absorption coefficient for three samples of each type of stone for the two treatments (tested before and after treatment). The slight reduce of the capillary absorption coefficient (C) after the treatment indicates that the treatment causes little changes in the hygric behavior of the stone. From the % amount of water absorbed also reported in Table 3, it is shown that for all stone species the treatment gives an amount of the absorbed water by capillarity slightly lower compared with the untreated samples (Table 3). However, the % water uptake is not reduced substantially by the treatment.

Table 3. Water absorption coefficient (C), amount of water absorbed (WA %) by capillary rise tests on untreated and treated samples. Water vapor transmission (WVT) rate, permeance and permeability values, as calculated by the water method.

Type of stone	C (mg/cm^{2}s$^{1/2}$)	WA (%)	WVT (g/h$*$m^2)	Permeance (g/Pa$*$s$*$m^2)	Permeability (g/Pa$*$s$*$m)
RH					
Untreated	26.2 ($\pm$ 0.01)	5.93 ($\pm$0.9)	6.77	1.23×10^{-8}	1.84×10^{-10}
Treated	23.2 ($\pm$ 0.01)	5.24 ($\pm$0.5)	4.89	8.93×10^{-9}	1.34×10^{-10}
RE					
Untreated	16.1($\pm$0.002)	11.65 $\pm$0.77)	10.35	1.89×10^{-8}	2.83×10^{-10}

Treated	15.4(±0.001)	11.05(±0.04)	9.26	1.69×10^{-8}	2.54×10^{-10}

4.4 Water Vapor Transmission

According to the performance goals for stone consolidants, the treatment should not appreciably affect the water vapor transmission rate (WVT) of the stone. The values of WVT, permeance and permeability (Table 3) of treated values present a reduction with respect to the untreated ones. The highest reduction of the WVT is observed in the Rh stone while for the Re stone the reduction is smaller. In any case, treatment does not seem to affect the transpiration rate of the stone.

4.5 Changes in stone porosity and the pore size distribution

Treatment causes slight variations in the characteristics of the stone's microstructure. After treatment, the Rh and Re limestones show a slight decrease in the total cumulative volume, the porosity, while small changes were observed in the bulk density values. The results also showed a reduction in the average pore radius values possibly due to deposition of the consolidant into the pores. The largest decrease has been observed in Rh stone, where the average pore radius values decrease in some cases from ~30 µm to ~8 µm. Similar characteristics were also observed with SEM (Figure 5). Combination of mercury intrusion porosimetry with SEM, water absorption characteristics and ultrasonic velocity data can provide information on how the pore structure changes could affect weathering resistance [ASTM E2167-01]. Ultrasonic velocity and elastic modulus did not show significant changes after treatment, although there was a tendency of increasing velocity in all tested samples, giving a slight increase in the elastic modulus, up to ~5%.

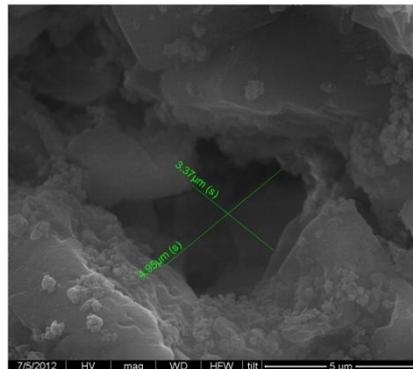**Figure 5**. SEM image of treated with PMC stone from Rhodes. Image indicates the pore diameter, Bar = 20 µm

Figure 6. . SEM image of treated with PMC stone from Rethymno. Image indicates the pore diameter, Bar= 5µm

4.6 **Thermal Expansion Coefficient** (TMA)

The determination of the thermal expansion coefficient allows the examination of the physico-mechanical compatibility between the stone and the conservation materials. The treated stone should have a coefficient of thermal expansion not significantly different from that of the untreated stone. The thermal expansion of Re stone ranges at ~6-x10^{-6} 1/K, while in case of Rh stone is about ~5x10^{-6}1/K, as calculated at a temperature range of 20-70°C. No considerable differences have been observed in the thermal expansion of treated stones, indicating that there is compatibility between consolidant and substrate.

4.7 **Appearance change**

The effect in the optical appearance of the studied treatments was evaluated by colorimetric measurements. Table 4 shows the changes of the chromatic coordinates for the treated stones. The ΔL^* value describes a change in brightness, where the positive values of ΔL^* indicate that treated samples reflect more light than untreated samples. Negative values of Δa^* and Δb^* indicate that the treated samples are less red and yellow, respectively, than the untreated. According to the Table 4, the treatment gives color changes that are within the generally accepted color change ($\Delta E < 5$) (Rodrigues and Grossi 2007). As mentioned, excess material was gently removed with ethanol using a sponge at the end of the application, in order to avoid an increase in specular reflectance or gloss that may be caused by the excessive surface deposition.

Table 4. Variation of the chromatic parameters of treated surfaces (sorption surface)

Stone /treatment	ΔL	Δa	Δb	ΔE*
Rh				
PMC1	0.66 ± 1.25	-0.45 ± 0.15	-1.88 ± 0.63	2.33 ± 0.26
PMC2	0.59 ± 1.04	-0.13 ± 0.15	-1.9 ± 0.55	2.16 ± 0.68
Binder (TEOS)	-0.48 ± 1.08	0.19 ± 0.36	-0.12 ± 1.11	1.41 ± 0.5
Re				
PMC1	1.31 ± 0.71	-0.1 ± 0.09	-1.71 ± 0.11	2.21 ± 0.37
PMC2	1.56 ± 1.28	-0.6 ± 0.99	-4.46 ± 2.51	4.86 ± 2.73
Binder (TEOS)	0.94 ± 0.34	-0.58 ± 0.37	-1.93 ± 1.2	2.24 ± 1.27

* $\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$

5. **Conclusions**

The above reported results show that it is possible to introduce oxide particles into silicon-based binder, obtaining good dispersions that penetrate into the substrate. The PMC presents a better penetrating ability, even though it shows a slower absorption rate, in case of Rethymno stone, which is finer-pored, also confirmed with the % mass gain of the dry specimens after treatment. SEM examination suggests that the consolidant does not show crack signs, as the observed surface presents continuity. Both consolidants (PMC1 and PMC2) seem to have caused some slight changes at the physicochemical properties of the stones after treatment. Water absorption coefficient showed a slight reduction after treatment, especially in Rh stone, while Re stone is less affected. Also, a slight

reduction was observed in the water vapor transmission rate of the treated stones, indicating that stone's transpiration is not highly hindered. In addition, there were some differences in the microstructure characteristics of treated stones, more noticeable in case of Rh stone. Ultrasonic velocity has a tendency to increase after treatment, giving a slight increase in the elastic modulus, while the thermal expansion of treated stones is not significantly affected, indicating that there is compatibility between consolidant and substrate. The color differences are within acceptable limits for both types of stone. Cleaning the treated surface after consolidation is recommended in order to avoid the formation of superficial deposits.

The penetration ability, especially in Rh stone can be assisted by prewetting of the surface before application. Also, other types of application must be examined in order to define the best treatment conditions that may lead to better consolidation effects. The consolidant's long-term performance in realistic environmental conditions must be also investigated. As a next step of research is included the introduction of other particles into silica matrix, such as alumina particles, as well as the assessment of the PMC's long term performance through accelerated weathering tests.

Acknowledgments

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