# Nano-$TiO_2$ coatings to support the preservation of the stone cultural heritage

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***Abstract* – The constant exposure of the stone cultural heritage to the combined action of atmospheric agents and pollution represents a threat to its conservation and protection.**

**Nano-sized titanium dioxide ($TiO_2$) materials have been widely used as protective coatings due to their ability to create self-cleaning surfaces, thus limiting maintenance costs and promoting the degradation of pollutants.**

**The present work aims to test innovative and self-cleaning products based on $TiO_2$ for applications in the field of cultural heritage. The properties of $TiO_2$-based materials were evaluated by capillary water absorption, accelerated aging test in a climatic chamber, colorimetric and contact angle measurements.**

## I. INTRODUCTION

In recent decades there has been a significant increase in research focusing on the degradation of stone cultural assets and methods for their conservation and protection [1, 2, 3]. Particular attention has been paid to carbonate rocks, as they appear to be severely affected by atmospheric agents and pollutants. Nanometric titanium dioxide is now a promising photocatalytic material due to its ability to degrade many organic contaminants and environmental toxins. Specifically, in this research, $TiO_2$ nanoparticles were incorporated into colloidal solutions of polyvinyl alcohol (PVOH) and polydimethylsiloxane (PDMS). Chemical compounds were then applied to the specimens of "Pietra di San Lucido", a limestone widely used in the historic centers of Calabria, particularly in the province of Cosenza.

Colorimetric test, static contact angle measurements and capillary absorption test were carried out in order to assess the hydrophobic properties and the colour variation induced by protective films on the stone surfaces and their stability under UV irradiation; for this reason, such tests were carried out both before and after treatment and ageing test.

## II. MATERIALS AND METHODS

$TiO_2$ nanoparticles (P25 type purchased by Evonic-Degussa, Germany), characterized by a specific surface area of 44 $m^2 \cdot g^{-1}$, a band gap 3.2 eV, a crystallographic phase of ca. 80% anatase and 20% rutile and an isoelectric point at pH of 6.8 [4], were embedded into two polymeric binders, respectively PVOH and PDMS (both purchased by Sigma Aldrich). The selected polymers exhibit distinct chemical and physical properties being: i) PVOH, a crystalline hydrophilic polymer with oxygen barrier properties, and ii) PDMS, is a mineral-organic polymer (containing carbon and silicon) of the siloxane family with high gas content and hydrophobic property. [5].

The colloidal solutions were prepared (Table 1, Table 2) by DIAm (Department of Environmental Engineering) at University of Calabria (Italy).

Initially, $TiO_2$ was dispersed in the solvent (e.g. water at 80°C for PVOH and heptane at 25°C for PDMS) via sonication (30 min), followed by the solubilization of the polymer at a concentration of 5wt% for PDMS and 2.5wt% for PVOH. In the case of the PDMS, the crosslinker was added with a concentration of 10wt% with respect to the polymeric binder. The crosslinker was sold together with PDMS, under the commercial name of Sylgard® 184. For Sylgard® 184 Base resin, the MSDS states that it contains 0.5 wt% xylene, 0.2 wt% ethylbenzene, >60 wt% dimethylvinyl-terminated dimethyl siloxane, 30 to 60 wt% dimethylvinylated and trimethylated silica and 1 to 5 wt% tetra(trimethylsiloxy) silane. For Sylgard® 184 Curing Agent, the MSDS states that it contains 0.19 wt% xylene, <0.1 wt% ethylbenzene, 55 to 75 wt% dimethyl, methylhydrogen siloxane, 15 to 35 wt% dimethylvinyl-terminated dimethyl siloxane, 10 to 30 wt% dimethylvinylated and trimethylated silica and 1 to 5 wt% tetramethyl tetravinyl cyclotetrasiloxane [6].

The $TiO_2$ concentration with respect to the polymeric binder was varied at a concentration of 2.5 (L) and 5wt.% (H). For reference purposes, a solution without $TiO_2$ (W) was used and a specimen was left untreated (TQ). Solutions were applied on 5x5x2cm specimens.

*Table 1. Summary of PDMS-based colloidal solutions prepared. (W)=$TiO_2$-free; (L)=lower concentration of $TiO_2$; (H)=higher concentration of $TiO_2$*

| | PDMS (W) $TiO_2$ (0%) | PDMS (L) $TiO_2$ (2.5%) | PDMS (H) $TiO_2$ (5%) |
|---|---|---|---|
| Solvent Heptane (g) | 9.47 | 9.448 | 9.425 |
| Polymer PDMS (g) | 0.475 | 0.5 | 0.5 |
| Active filler $TiO_2$ (g) | 0 | 0.00125 | 0.025 |
| Crosslinker (g) | 0.0475 | 0.05 | 0.05 |

*Table 2. Summary of PVOH-based colloidal solutions prepared.*

| | PVOH (W) $TiO_2$ (0%) | PVOH (L) $TiO_2$ (2.5%) | PVOH (H) $TiO_2$ (5%) |
|---|---|---|---|
| Solvent $H_2O$ (g) | 9.75 | 9.743 | 9.737 |
| Polymer PVOH (g) | 0.25 | 0.25 | 0.25 |
| Active filler $TiO_2$ (g) | 0 | 0.0062 | 0.0125 |

### *A. Capillary water absorption*

Measurements of water absorption were performed by capillary test in order to evaluate the amount of water absorbed by a stone specimen per surface unit (Qi) over time, before and after a treatment [7]. Qi is defined as: $Qi=(m_t-m_0)/S$, where S is the area of the base of sample, $m_t$ and $m_0$ are the sample weights measured during the test, respectively, at the time t and the time 0.

### *B. Colorimetric measurements*

Colorimetric tests were carried out using a CM-2600d Konica Minolta spectrophotometer, to assess chromatic variations [8]. Chromatic values are expressed in the CIE L*a*b* space, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and −a* green) and b* the yellow/blue coordinate (+b* indicating yellow and −b* blue). Colour variation where calculated as (1):

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (1)$$

where $\Delta L^*$, $\Delta a^*$ and $\Delta b^*$ represent the difference between the value of each chromatic coordinate in treated samples and the value in untreated ones.

### *C. Contact angle measurements*

Contact angle measurements were carried out in order to determine the wettability [9]. Contact angle represents the angle between the substrate surface and the tangent from the edge to the contour of a water drop of defined volume (10μl). Drop shape was recorded with a camera and automatically evaluated in terms of contact angle.

### *D. Artificial accelerated aging tests*

Artificial accelerated aging tests for simulation of solar radiation were performed using a SUNTEST XLS+ (Atlas, USA) in order to evaluate the stability of the $TiO_2$ coating. For a better assessment of the autocleaning function, samples were stained with methylene blue. Test lasted for 500 hours.

## III. RESULTS

The absorption test showed that for the samples treated with PVOH, the Qi values range from 507g/cm$^2$ to 555 g/cm$^2$, while for the samples treated with PDMS, the values range from 36 g/cm$^2$ to 51 g/cm$^2$ (Fig. 1).

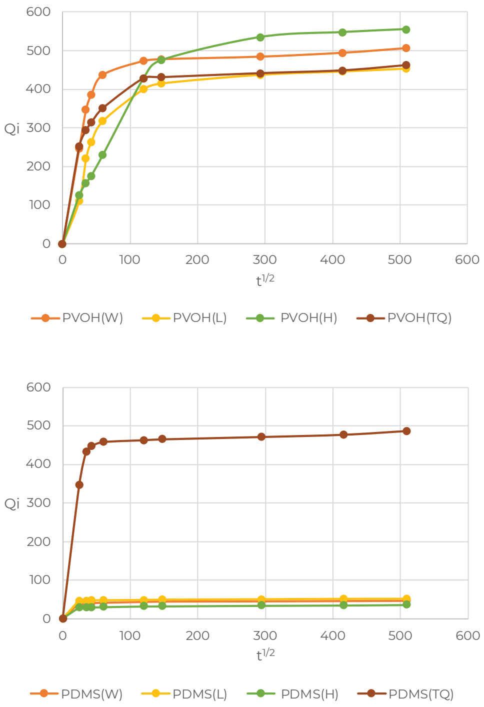

*Fig. 1. Capillary water absorption of PVOH and PDMS samples.*

Colorimetric measurements (Tab. 3) showed that PVOH-treated samples produced the least noticeable colour change after treatment (Fig. 3), although a small progression of the self-cleaning function of $TiO_2$ was noted for both PVOH and PDMS samples after aging test (Fig. 4, Fig. 5).

*Table 3. Colour variations after coating application and aging.*

| Samples | ΔE (Treated – untreated) | ΔE (Aged – untreated) |
|---|---|---|
| PDMS(W) | 16.53 | 30.7 |
| PDMS(L) | 14.22 | 27.1 |
| PDMS(H) | 13.06 | 28.9 |
| PVOH(W) | 5.68 | 19.1 |
| PVOH(L) | 3.10 | 14.2 |
| PVOH(H) | 3.82 | 13.5 |

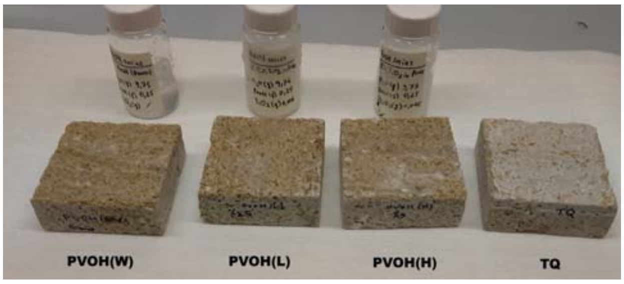

*Fig. 3. PVOH samples after treatment with colloidal solutions.*

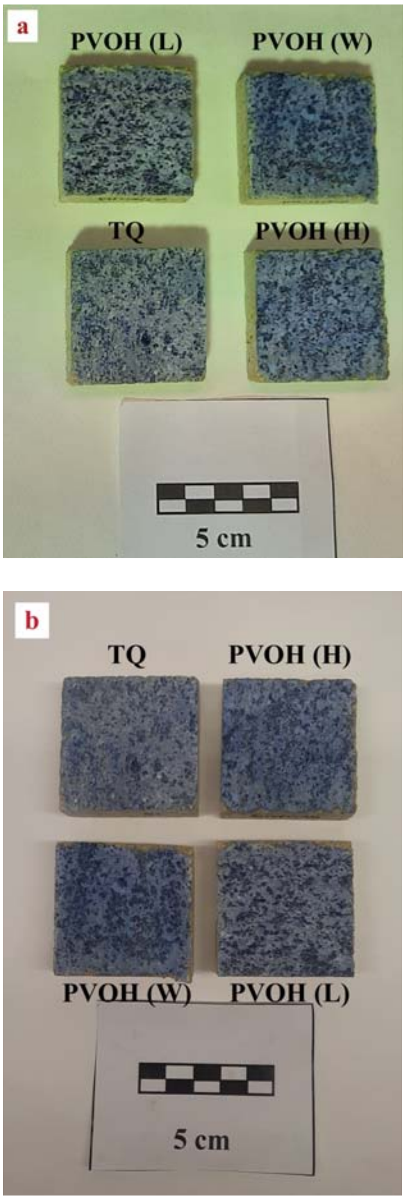

*Fig. 4. PVOH samples, stained with methylene blue, before (a) and after (b) accelerated aging test.*

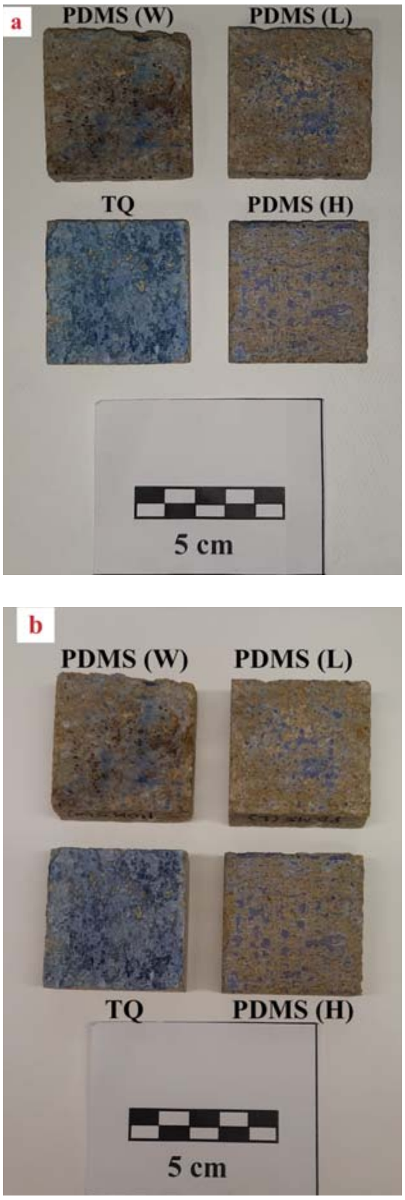

*Fig. 5. PDMS samples, stained with methylene blue, before (a) and after (b) accelerated aging test.*

Contact angle measurements pointed out the hydrophilic behavior of PVOH samples and the hydrophobic behavior of PDMS ones (Fig. 3) (Tab. 3).

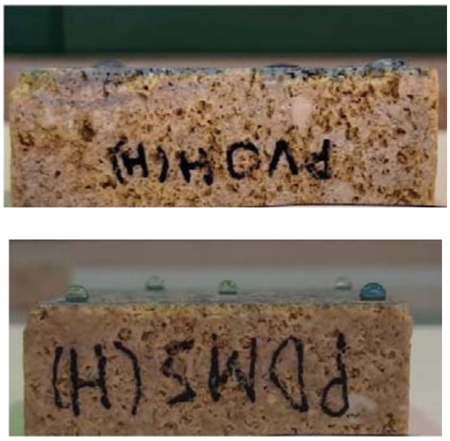

*Fig. 3. Contact angle evaluation of PVOH and PDMS samples.*

*Table 3. Contact angle measurements after treatment and after aging test.*

| Samples | Contact angle (◦) after treatment | Contact angle (◦) after aging |
|---|---|---|
| PDMS(W) | 108±11 | 105±6 |
| PDMS(L) | 111±2 | 107±7 |
| PDMS(H) | 113±15 | 111±3 |
| PVOH(W) | 53±5 | 39±2 |
| PVOH(L) | 53±3 | 36±12 |
| PVOH(H) | 64±10 | 37±4 |

## IV. CONCLUSIONS

The analysis performed pointed out a poor self-cleaning function of both PVOH and PDMS samples.

From absorption and contact angle measurements of PDMS, it’s possible to observe a hydrophobic behavior while PVOH showed a hydrophilic behavior. Colorimetric tests showed that PVOH leads to the least noticeable colour variation. The aging test showed a small progression of the self-cleaning function of $TiO_2$, and a decrease in contact angle values (most pronounced for PVOH samples). No significant differences have been detected between different amount of $TiO_2$ applied.

Proposed products should be further investigated for CH application. Although, in this case, the auto-cleaning function of $TiO_2$ nanoparticles didn’t highlight very clearly, this feature has already been demonstrated in literature; for what concerns the colloidal solution used, they represent versatile compounds with hydrophobic (PDMS) and hydrophilic (PVOH) properties usable in CH application field.

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