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TiO_2–SiO_2–PDMS nanocomposite coating with self-cleaning effect for stone material: Finding the optimal amount of TiO_2

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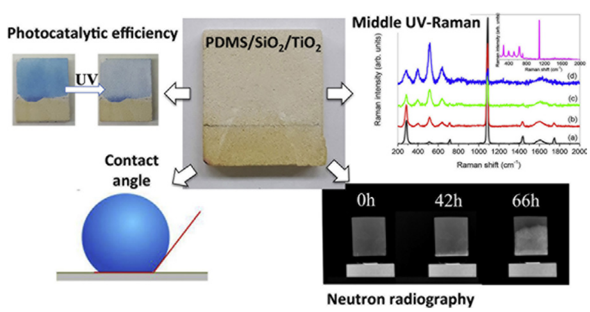
HIGHLIGHTS

- The effect of variable amounts of TiO_2 in TiO_2–SiO_2–PDMS nanocomposite coatings has been investigated.
- 23.7 g/m^2 of TiO_2 on Modica stone maximize the photo-catalytic features of TiO_2 modified treatment.
- TiO_2–SiO_2–PDMS nanocoating has been applied on stone and the features have been investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano-sized TiO_2 is widely used as photocatalysts for many applications; however, some aspects in the application in cultural heritage conservation are still unresolved. In particular, in this research, we focused our attention on nanostructured product composed by silica, polydimethylsiloxane (PDMS) and TiO_2 nanoparticles. We explored the effect of variable amounts of nanoparticles on the features of coating, since this issue still has some unclear aspects. Several samples of limestone have been treated, and then, analysed. The chromatic variations induced by the treatments have been measured by colorimetric analysis, while the hydrophobic properties of coatings have been evaluated by contact angle measurements and capillary water absorption. The photocatalytic efficiency has been evaluated by methylene blue staining. In addition, two large facilities have been involved in this study, in order to obtain accurate results in a non-invasive way. On one side, middle-UV Raman spectroscopy measurements at IUVS beamline@Elettra (Trieste), by using UV synchrotron radiation (SR) source, revealed successful, with respect to conventional set-up, in order to quantify the amount of the anatase on the surface. On the other side, neutron radiography measurements at RAD Radiography Station@BNC (Budapest) permitted a sensitive monitoring of the water absorption dynamics on untreated and treated samples.

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1. Introduction

Stone decay represents a crucial issue in the field of preservation of historic structures; a large number of studies is addressed to conservation and restoration of stone materials. In particular, carbonate-based rocks, such as calcarenite, are seriously affected by alteration and decay phenomena produced by the constant exposure to combined action of natural weathering and urban pollution. In this regard, bio-deterioration and air pollution are two of the main causes of decay, producing blackening of the surface layers, biological patina, black crusts, formation of small blisters and loss of parts in the artefacts [1–7]. The consolidation and the protection of such degraded materials represent a crucial task for their conservation [8–10].

Nanoparticles represent a challenge for stone conservation aims. For example, calcium and strontium nanoparticles have been used for calcarenite consolidation [11]. In particular, nanometric TiO_2 represents an effective material thanks to its high chemical stability, non-toxicity and high photo-reactivity; these properties make it potentially useful for conservation aims. Nanoparticles of TiO_2 can be dispersed in an organic binder [12], or applied as nanosols or dispersions, without any binding agent [13–15]. In a more recent approach TiO_2 is mixed with SiO_2 leading to a hybrid coating [16–19]. Moreover, it is extensively used as biocide against several biofoulers [20–25].

When TiO_2 is exposed to ultraviolet (UV) light ($\lambda < 400$ nm), holes (h+) and excited electrons (e−) are generated. The holes are capable of oxidizing water or hydroxide anions into hydroxyl radicals (–OH) [26]. Free radicals produced can decompose a wide range of organic compounds. The photocatalytic efficiency is determined by the competition between the recombination (nanoseconds) of photo-excited charge carriers, electrons and holes, and the transfer of those to the organic compound.

Several studies have been devoted to understand the suitability of titanium dioxide nanoparticle as additive for coatings of stone materials, with particular attention of built heritage. It has been studied the biocidal effect of nanostructured coatings [13,24], as well as the influence of the binder on the efficacy of the treatments [27]. However, some aspects of the influence of nanoparticles on the hydrophobic features of the coatings, as well as understanding the long-term behaviour of such treatments are still unclear. Moreover, the behaviour of coatings at increasing amounts of nanoparticles is important to establish the right quantities to apply on the surface. In order to clarify these points, 30 samples of limestone have been treated with mixtures of nano-sized TiO_2/SiO_2/PDMS, and then, analysed. The chromatic variations induced by the treatments have been measured by colorimetric analysis, while the hydrophobic properties of coatings have been evaluated by contact angle measurements. The photo-activity of the treated surfaces has been assessed by methylene blue staining. In addition, two large facilities have been involved for this research. Middle-UV Raman spectroscopy measurements were carried out on IUVS beamline@Elettra (Trieste), and allowed us to evaluate the coverage rate of titania on the surface. Dynamic neutron radiographic imaging measurements were performed at RAD Dynamic Radiography Station@BNC (Budapest). This technique has been previously proposed by several authors to investigate the porous structure of rocks [28], to monitor the water imbibition dynamics within stone [29] and to evaluate the interaction of stone with consolidating agents [30,31]; these features are not explorable by means of conventional techniques. In our case, by this technique we would achieve a deeper understanding of the behaviour of the coatings in terms of water distribution within the stone.

2. Materials

AEROXIDE P25 TiO_2 nanoparticles (powder) has been used. They have a mean particle size of 25 nm, and mineralogical phase of anatase. They were added to Estel 1100 (E1100), a siloxane consolidant/protective agent provided by C.T.S. (Italy). This product has been used as binder in order to bond properly the particles on the surface. This is a mixture of tetraethoxysilane (TEOS) and polydimethylsiloxane (PDMS) oligomer diluted in white spirit (an aliphatic organic solvent). PDMS/TEOS ratio is 1/1 wt The product has an amount of final polymer of 30%wt. E1100/TiO_2 formulations have been prepared by diluting E1100 1/3 in weight with white spirit. Then, different amounts of TiO_2 have been dispersed in the consolidant/protective product (0.5, 2, 4, 8% wt) by using ultrasonic bath.

Formulations have been applied by brush on stone samples having size 3.5 × 3 × 1 cm, the sides interested to treatments were a 3 × 1 face and, partially the two 3.5 × 3 and 3.5 × 1 faces, as shown in Fig. 1.

1.0 ± 0.1 g of each formulation was applied on 20 cm^2 of each specimen. According to this, once polymerized, the amount of polymer on the surface was 50 g/m^2, while, TiO_2 amounts were 2.5 g/m^2, 10 g/m^2, 20 g/m^2 and 40 g/m^2; each treatment has been applied on six samples. For comparison, a series of samples has been left untreated, while another series has been treated only with E1100, Treatment with only TiO_2 was not taken into account, since without any binder particles would not be properly bonded on the surface.

For the experiments, a limestone has been used to make stone specimens. This lithotype has been taken from a quarry located in Modica (Ragusa, Sicily, Italy). This stone is widely used as building materials in Modica and Ragusa cities [32–34], both included in the UNESCO's World Heritage List since 2002.

Modica stone appears white-cream coloured, having a homogeneous texture and medium-fine grain size. Petrographic analysis [32] revealed a grain-supported texture having about 30% of micritic matrix. The porosity is around 27%. According to Dunham (1962) [35], the Modica stone is classified as packstone.

Several measurements have been carried out on the sample in order to assess the features of the coating and their interaction with the stone substrate.

3. Analytical methods

Several analytical methods have been applied on treated and untreated samples. Each analysis have been performed on three samples for each treatment.

In order to map the distribution of elements on a microscopic scale, an Electron Probe Micro Analyzer (EPMA) – JEOL – JXA 8230 – coupled with a spectrometer EDS – JEOL EX-94310FaL1Q – Silicon drift type – has been used. Elemental maps have been acquired with the following parameters: HV- 15 keV; Probe current – 10nA; Working Distance – 11 mm; Take off – 40°; Live Time – 50 s.

The colour changes of stones were measured by a Konica Minolta CM-2600D spectrophotometer, through the determination of L^*, a^*, and b^* coordinates of the CIELAB space, and the global chromatic variation expressed as ΔE [36]. This latter was determined according to the following relation:

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

All the given results are average values of five measurements taken on each specimen.

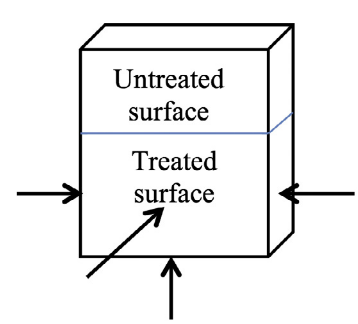

Fig. 1. Treatment scheme of samples. Arrows indicate the direction of treatment penetration.