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Nano-TiO_2 coatings for cultural heritage protection: The role of the binder on hydrophobic and self-cleaning efficacy

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ABSTRACT

Nano-sized titanium dioxide has demonstrated its efficiency in many application fields thanks to its photocatalytic features that provide self-cleaning properties to the materials with simple and non-expensive procedures. For this reason, it has been successfully used also for the practice of restoration of stone built heritage. However, some aspects are still unresolved and need to be further investigated, such as the method for binding these particles to stone surfaces.

In this work, nano-TiO_2 was combined with three different binders and applied on two stone substrates, namely the Carrara marble and the Noto calcarenite, two lithotypes extensively used in built heritage. The performance of all tested coatings was evaluated by scanning electron microscopy (SEM), roughness measurements, capillary water absorption test, static contact angle calculation, colorimetric measurements, UV aging and self-cleaning test. Results suggested the key role of interaction between coating and stone surface in terms of penetration of the product, hydrophobicity, variations of surface roughness and durability, which define the performance of the coatings. Specifically, among the three tested products, the best behaviour in terms of hydrophobicity, durability and self-cleaning properties was shown by both the acrylic (Fosbuild) and fluorinated (Akeograd P) suspensions. Conversely, the Paraloid id B72 - TiO_2 mixture led to an intense superficial alteration of both stones and showed scarce water-repellent and photo-degrading effect.

1. Introduction

In recent decades, an apparent acceleration in the rate of stone decay and the growing worldwide interest in preserving historic structures are promoting a significant increase in the number of studies addressed to conservation and restoration. In particular, many authors state that carbonate-based rocks, such as calcarenite and marble, 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, soluble salts, bio-deterioration and air pollution, are the main causes of decay, producing flaking of the surface layers, powdering, black crusts, formation of small blisters and loss of parts in the artefacts [1–8]. Many alteration processes are driven by water, which is one of the most important abiotic factors of decay in porous materials [2,9]. Once it penetrates the pores by capillary force, water carries out its deteriorating effect through: (a) the chemical dissolution of the carbonate component of the stone; (b) physical phenomena such as freezing/thawing cycles, salt crystallization and deposition; and (c) microorganisms growth, whose colonisation contributes to deteriorative processes [10–12].

For these reasons, any protective treatment should be targeted to reduce the surface wettability of the stone substrate. Besides a good water repellence feature, a protective coating should also have a good resistance against aging and, at the same time, induce negligible colorimetric variation on the treated surface.

In the last 50 years, synthetic polymers have been widely employed as adhesive, consolidating and protective products on the stone built heritage [11,13–15]. Among these, acrylic and fluorinated resins are used as protective coatings for stones, due to their suitable hydrophobicity and adhesion to the surface [14,16–25]. Recently, the use of nanoparticles is spreading increasingly in the field of cultural heritage conservation as it allows enhancement of treatment performance. Nanostructured materials, if properly dispersed in coatings, can offer outstanding properties and performances. For instance, by exposure to light, photoactive materials

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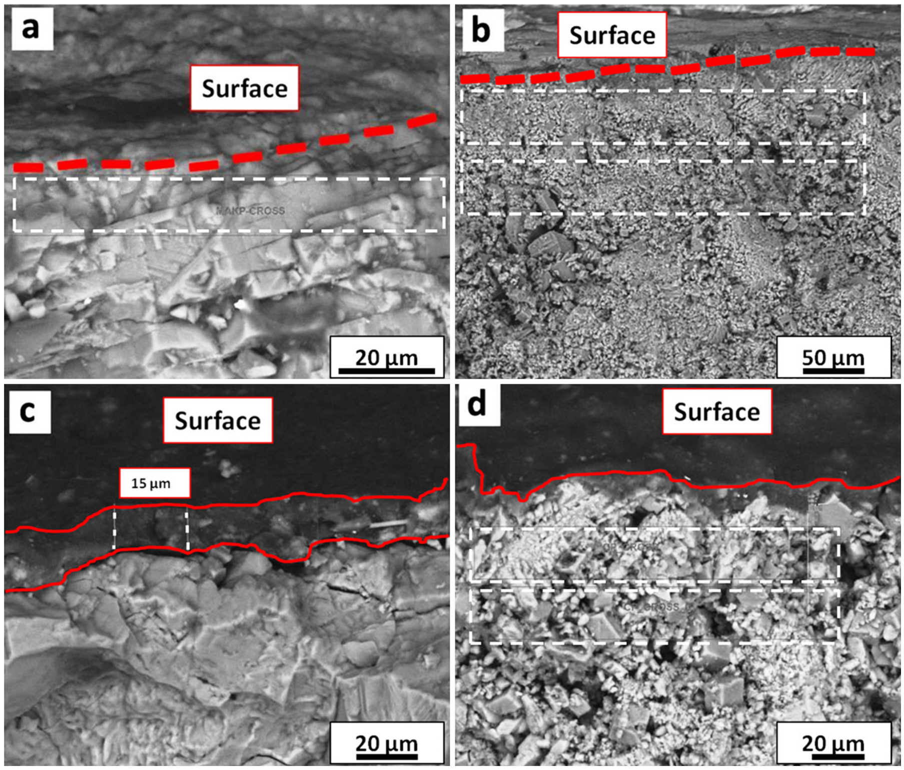

Fig. 1. BSE-SEM images taken on cross section of AKP-nanoTiO_2 treatment on marble (a) and calcarenite (b); B72 and nanoTiO_2 applied on marble (c) and calcarenite (d). Concentration measurements were performed within the squares, except on marbles treated with B72 mixed with nanoTiO_2 where the product is concentrated in the superficial coating thick about 15 μm.

Table 1
samples ID and relative treatments.

ID calcarenite samples	Treatment
UC	–
CP-L	Paraloid B72 + nanoTiO_2
CP-H	Paraloid B72 + nanoTiO_2
CAKP-H	Akeogaard P + nanoTiO_2
CAKP-L	Akeogaard P + nanoTiO_2
CF-L	Fosbuild
CF-H	Fosbuild
(H) = high amount 1600 g/m^2 (L) = low amount 800 g/m^2	
ID marble samples	
UM	–
MP-L	Paraloid B72 + nanoTiO_2
MP-H	Paraloid B72 + nanoTiO_2
MAKP-L	Akeogaard P + nanoTiO_2
MAKP-H	Akeogaard P + nanoTiO_2
MF-L	Fosbuild
MF-H	Fosbuild
(H) = high amount 100 g/m^2 (L) = low amount 50 g/m^2	

can acquire photovoltaic properties and promote the photocatalytical degradation of volatile and water pollutants, as well as the deactivation of micro-organisms [26–29]. In particular, nano-titanium oxide, thanks to its photocatalytic behaviour, shows biocidal and self-cleaning properties potentially useful for conservation aims [30–35].

However, the suitability of nanoproducts and synthetic polymers to the stone materials used in the cultural heritage is not well defined, because of scarce knowledge with regard to the interaction between polymers and stone surfaces. It could influence the performance of the same product applied on different stone substrates [15,36].

In a previous paper [31] we assessed the antimicrobic and photo-degrading efficiency of a commercial mixture of acrylic binder and TiO_2, while the present work is focused on the role played by different binders on the coating performance. Specifically, the efficacy of three nanotitanium-based coatings has been assessed. These included: (a) an acrylic polymer in an organic solvent, Paraloid B72; (b) a fluorinated polymer in an alcoholic solvent; and (c) a commercial product based on an aqueous suspension of TiO_2 and an acrylic polymer. The choice of these products was based on their hydro-repellent, bonding and pre-consolidating properties; indeed, several papers have been devoted to the use of such products in the field of cultural heritage restoration [14,37–42].

The products were applied on two lithotypes largely used in the built heritage: the Pietra di Noto calcarenite, coming from the Val di Noto area (eastern Sicily, Italy) and extensively employed in Sicilian Baroque architecture [43–45], and the Carrara marble [43,46]. The stones were treated with polymer-TiO_2 mixtures and then, after the application, the performance of products and their suitability to the chosen substrates was evaluated by means of the following techniques: (a) SEM-EDS analysis, in order to determine the penetration depth and the morphology of the coatings; (b) roughness measurements, aimed at assessing the possible changes induced in the surface morphology by the different binders applied along with nano-titanium dioxide; (c) contact angle measurements; (d) capillarity water absorption test; (e) colorimetric measurements; (f) accelerated ageing test; and (g) self-cleaning test.

2. Materials and methods

2.1. Stone substrates

Carrara marble specimens come from quarries in the Apuan Alps, NW Tuscany, Italy. From a macroscopic viewpoint, the rock is quite homogeneous in colour, ranging from white to off-white, with some slightly faded greyish veins, usually isolated