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Monitoring long run performances of multifunctional coatings for environmental protection of stone building surface

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Abstract
In this study, multifunctional TiO_2 NPs/fluoropolymer coatings with self-cleaning and hydrophobic properties applied to a calcareous stone are investigated for long run performances in outdoor conditions. The coated samples were exposed over one year to an urban environment and their physical and photocatalytic properties were monitored.
The study provides better insights on the real performances of nanostructured TiO_2-based coatings for stones in buildings.

I. INTRODUCTION

Since last years, nanostructured titanium dioxide based coating of natural stone has been explored to obtain material surfaces with photocatalytic properties, namely self-cleaning and depolluting abilities.

TiO_2-based coatings for natural stone surfaces include two main categories: hydrophilic nano-TiO_2 dispersions [1-3] and nanocomposites [4-7] addressing hydrophobic properties along with photocatalytic abilities.

Coating performances have been investigated with promising results in laboratory conditions, but their assessment in real conditions for the potential of use in the context of the built heritage is quite limited.

In this study, a TiO_2 NPs/fluoropolymer product is used for self-cleaning and hydrophobic coating of a calcareous stone. It was developed in a previous research [8] by mixing TiO_2 nanoparticles in a water dispersion with a commercial product Fluoline PE, a hydrophobic fluoropolymer by CTS (Altavilla Vicentina, Italy). Coatings obtained with this product are investigated for long run performances in outdoor conditions, compared to those obtained with the use of the polymer alone, and the first results are presented here.

II. EXPERIMENTAL PART

A. Materials and treatments

A compact limestone, named Trani stone [8], having a very low porosity (2%), was selected for this study. Prismatic specimens with dimensions of 5 × 5 × 2 cm^3 were prepared according to the UNI10921 standard protocol [9] and treated by brush. Only one 5 × 5 cm^2 side of each specimen was treated. Details about the samples, the applied products and the treatments are listed in Table 1. Additional information on the preparation of the applied products were described in a previous paper [8].

Table 1. Nomenclature of the samples and details of the treatments.

Sample	Applied product	Applied amount [mg/cm^2]
Pol	Perfluoropolyether in water dispersion (10% wt)	24
Pol+Ti	Perfluoropolyether/ TiO_2 water susp. (3% wt) 1:0.067	24

All the samples were exposed outdoor in Bari, a port city in the South-eastern Italy, from February 2016 to January 2017. The samples, placed in an unsheltered area near the city centre, were affected by the environmental agents and by the pollutants from the vehicular traffic. Periodic controls were performed every 4 months.

The data about the environmental conditions and the air quality status during the exposure are summarised in Table 2.

Table 2. Average (max-min) values of the environmental parameters recorded at the exposure site (data provided by ARPA Puglia): temperature T (°C), relative humidity (RH), solar radiation SR (W/m^2), precipitation P (mm), particulate matter $PM_{2.5}$ ($\mu g/m^3$) and PM_{10} ($\mu g/m^3$), nitrogen oxides NO_x ($\mu g/m^3$).

	E1 (Feb-May)	E2 (June-Sep)	E3 (Oct-Jan)
T	16 (31-7)	25 (34-16)	13 (27- -1)
RH	66 (96-21)	63 (96-22)	68 (97-27)
SR	150 (966-0)	215 (972-0)	58 (718-0)

P	0.1 (7.2-0.0)	0.1 (26.0-0.0)	0.1 (8.8-0.0)
$PM_{2.5}$	14 (32-6)	15 (29-5)	16 (43-5)
PM_{10}	27 (95-12)	24 (45-11)	27 (58-11)
NO_x	81 (861-11)	62 (312-1)	78 (665-6)

B. Techniques and methods of analysis

Contact angle and colour measurements were carried out on the stone samples before the outdoor exposure. The same investigations were repeated at the end of each period of exposure. Evaluation of the self-cleaning ability and water absorption by capillarity were evaluated before the exposure and after 1 year outdoor.

Water-stone static contact angle measurements [10] were carried out using a Costech apparatus (Costech International S.p.A.). For each specimen, 30 micro-drops of deionised water were deposited with a syringe on different positions of the surface. The shape of the drop was recorded with a camera and its contact angle was calculated.

Colour measurements [11] were performed with a tristimulus colorimeter (Minolta Chroma Meter CR300, Konica Minolta Inc.), using CIE Standard illuminant C. Ten measurements were performed on each specimen and the colorimeter was recalibrated to a calibration plate at the start of each measurement session. The colour changes (ΔE^*_{ab}) were calculated through the L*a*b* (CIE 1976) system, using the following formula:

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

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).

Photocatalytic activity of the stone-coated surfaces in terms of self-cleaning abilities and its evolution was evaluated by degradation test of Rhodamine B (RhB) aqueous solution. A RhB aqueous solution (dye concentration = 0.05 g/l) was spread on both uncoated and coated surfaces until it was refused by the specimens; 24 mg/cm^2 were applied. After drying (24 hours in laboratory), colour measurements were performed; then, the samples were exposed to light using a solar simulator Solarbox 1500e R.H. (Erichsen Instruments), under a Xenon lamp (1500W power), located in the upper part of the exposure chamber, in the axis of a parabolic mirror that guarantees irradiation uniformity. A glass filter ensured irradiation in the range 275 - 825 nm, simulating outdoor exposure. Light irradiance and temperature were 450 W/m^2 and 30 °C, respectively. Colour measurements were performed before the staining, after the application of RhB without irradiation up to 7.5 hours of exposure in solarbox. Due to the red colour of RhB, parameter a* evolution can be used to control the photodegradation activity, which was expressed as percentage of discoloration (D) over time and calculated as:

$$D = [\,|a^*_0 - a^*_t| \,/\, |a^* - a^*_0|\,] \times 100 \qquad (2)$$

where a^*_0 and a^*_t are the values measured at the beginning of the test and at time t of irradiation, respectively; a* is the value obtained by colour measurements before the RhB application.

Capillary water absorption [12] was measured up to 24 hours; the results before the exposure and after 1 year of outdoor exposure were compared. The amount of absorbed water (Q) was calculated as follows:

$$Qi = (w_i - w_0)/A \qquad (3)$$

where w_i and w_0 are the weight of the sample at time t_i and t_0, respectively, and A is the area exposed to water.

All weight measurements were registered using an analytical balance (Model BP 2215, Sartorius AG) with an accuracy of ±0.1 mg.

III. RESULTS AND DISCUSSION

The static contact angle decreased in all samples after the first period of outdoor exposure (Fig. 1). The reduction in contact angle values was also observed where TiO_2 was absent (Pol samples). Therefore, this result seems to be mainly ascribed to a modification of the wettability properties of the polymer. Being the wettability increase more pronounced in the presence of TiO_2, the hydrophilicity induced by the TiO_2 under solar radiation could have contributed to the lower contact angle values, which were recorded in this case in comparison to the coating with the polymer alone.

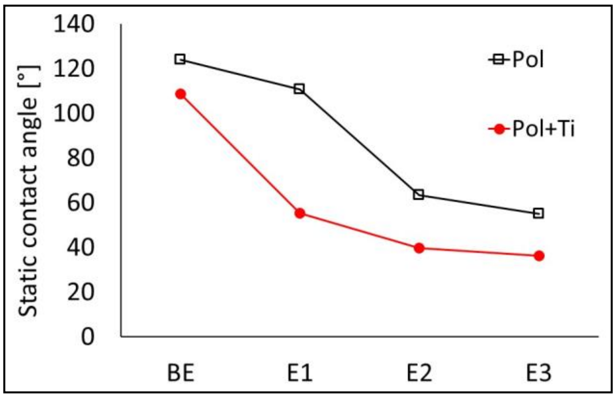

Fig. 1. Contact angle before (BE) and after outdoor exposures (E1, E2, E3).

In Table 3 the ΔE^*_{ab} are reported. The lowest colour variations were recorded for the mixtures TiO_2/polymer. The colour changes were small after the first exposure, then, the differences increased irrespective of the surface treatment, especially for Pol product.

Table 3. Colour difference (ΔE$_{ab}$) calculated by comparison with the un-exposed samples.*

Sample	E1	E2	E3
Pol	1.87	3.81	2.97
Pol+Ti	0.36	1.56	1.01

In Fig. 2 the decomposition of Rhodamine B after 7.5 hours of irradiation in solarbox, was reported. A decrease in the abatement of the used dye was measured after the outdoor exposure, proving a reduced efficacy of the photocatalytic coating. It is especially evident in a slowed kinetic of the degradation, while the final rate of abatement shows a lower decrease.

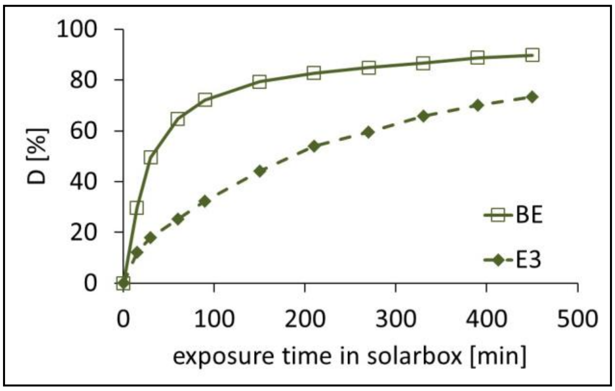

Fig. 2. Rhodamine B decomposition (as defined in Equation (2)), as a function of exposure time in solarbox, measured on Pol+Ti samples.

Table 4. Capillary water absorption: amount of water (mg/cm^2) absorbed after 24 h in samples before the coating (BT), before the outdoor exposure (BE), and after the 3rd exposure (E3).

Sample	BT	BE	E3
Pol	16.1	5.9	7.7
Pol+Ti	16.3	4.5	8.9

The absorbed water amount as measured by a capillary test show a significant abatement for the samples coated with the polymer/titania mixture and it is comparable to the water absorbed by the samples treated with the polymer alone. It showed a slight water absorption increase after one-year exposure. At this time, too, the water uptake was comparable to that measured for the Pol coated samples.

Conclusions

The monitoring of the stone surfaces coated with a TiO_2 NPs/fluoropolymer mixture in comparison with the mere F-polymer highlighted the coating performances in a real urban environment. The study showed that the titania based product better preserved the colour properties of the coated surface, likely related to the photocatalytic activity of the TiO_2 nanoparticles in the polymer. After one year of exposure, the stone coated surface preserved a photocatalytic ability, although with a decreased efficiency. Further research is in progress to account for the decrease of effectiveness under the real environmental conditions. Although wettability was higher for the polymer/titania coating, the capillary water absorption was comparable to that of samples coated with the mere polymer. Therefore, it seems that on the long run the mixture of the titania with the polymer does not affect the capability of the polymer to contrast water absorption by the coated stone surface.

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