Science and Art: A Future for Stone

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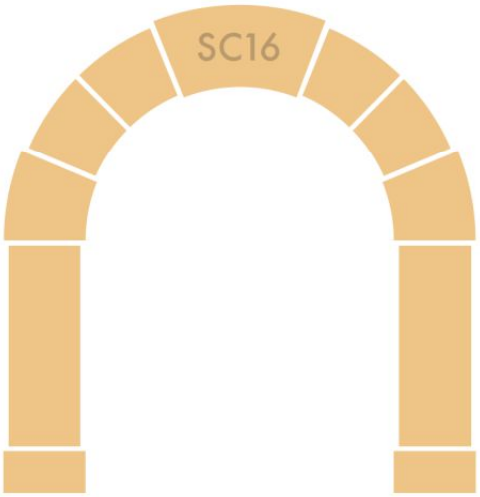

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Cover image: The front door of the Paisley Technical College building, now University of the West of Scotland. T.G. Abercrombie, architect 1898. Photograph and cover design by T. Howind.

SMART HYDROPHOBIC TIO_2-NANOCOMPOSITES FOR THE PROTECTION OF STONE CULTURAL HERITAGE

F. Gherardi[1*], A. Colombo[2], S. Goidanich[1] and L. Toniolo[1]

Abstract

This study presents the set-up of photocatalytic hydrophobic TiO_2-nanocomposites and the assessment of their application in stone heritage conservation. TiO_2 nanoparticles were synthesized according to the non-aqueous route obtaining pure anatase phase nanoparticles with an opportune surface capping, which makes titania dispersible in aqueous systems and photo-active not only under UV radiation but also under solar light, thus enhancing its ability to degrade pollutants. Nanocomposite films were obtained by mixing different ratios of nanoparticle dispersions in commercial aqueous polymeric solutions. SEM analyses of the treated marble samples show crack-free coatings. The nanocomposites-based treatments do not affect the original colour of the specimens, which show a decrease in the water capillary absorption. By increasing the nanoparticles content, an enhancement of the static contact angles of the surfaces occurs, compared to both the untreated reference and the reference samples treated with the pristine polymers. The Rhodamine fading test after ageing in solar box with a Xenon lamp shows that the highest photocatalytic activity is achieved by specimens treated with the nanocomposites with the highest nanoparticles content. In order to evaluate the eventual degradation of the polymeric matrices due to the photoactive TiO_2 nanoparticles and the durability of the nanocomposites, accelerated ageing in a solar box were performed. The obtained results prove the effectiveness of the proposed TiO_2-based nanocomposites as protective coatings for stone surfaces of built heritage.

Keywords: self-cleaning, hydrophobic, TiO_2-nanocomposites, artificial ageing, marble

1. Introduction

In urban area, cultural heritage surfaces are soiled by the accumulation of pollutants, which can contribute to the formation of crusts, affecting the buildings from both the aesthetical and chemical point of view. In order to prevent the weathering of stone surfaces and protect them, water-repellent polymer coatings have been used, thanks to their ability to reduce the water-stone interface tension and to increase its water repellency. Different classes of polymeric coatings have been applied in the field of stone conservation (Tsakalof *et al.* 2007). Among them, acrylics have been used in the last decades even if the

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performances in terms of durability were not satisfactory (Favaro *et al.* 2006). Partially fluorinated and perfluoropolymers were developed with the aim to improve the water repellent behaviour and the resistance to photodegradation of nonfluorinated polymers (Ciardelli *et al.* 2000). Nowadays, alkyl-aryl-polysiloxanes products are the most used in the restoration field, since they show higher durability and stability than acrylics (Tesser *et al.* 2014), though they are not always appropriate for every lithotype (Tsakalof *et al.* 2007, Charola 2002).One of the strategy to enhance the hydrophobicity of the coatings is to increase the surface roughness, without changing the substrate morphology, by dispersing nanoparticles in polymeric films. If these surfaces are exposed to rainfall, water forms spherical droplets which roll away, removing dust and dirt. To achieve this goal, solutions of different polymer have been modified by adding different nanoparticles, increasing their protective efficiency, conferring super-hydrophobic (water contact angle > 150°) and self-cleaning properties (Manoudis *et al.* 2008). Different nanoparticles have been used for this aim and among them nano-TiO_2 are one of the most common, since their introduction into the polymeric matrix confers photocatalytic properties to the surface (Fujishima *et al.* 2008). Indeed, thanks to their photoactivity, nano-TiO_2 can lead to the breakdown both organic and inorganic compounds, which can be easily washed away by rainfall, with a reduction of time and costs for cleaning maintenance (Munafò *et al.* 2015). In the set-up of the proposed nanocoatings, TiO_2 nanoparticles have been selected because they contain pure phase anatase which are characterised by the presence of benzyl alcohol molecules anchored on their surfaces. This surface capping makes the nanocrystals photoactive even if exposed to solar irradiation, increasing their photoefficiency. Moreover, as reported in a previous study (Gherardi *et al.* 2015), the proposed nanoparticles allow to obtain highly stable dispersions in aqueous systems, preserving the aesthetic compatibility with stone substrates. The results obtained from the tests that are shown in this paper proved that the proposed nanocoatings present better effectiveness compared to pristine polymers commonly used as stone protective treatments as they demonstrate higher aesthetic compatibility, lower capillary water absorption and higher hydrophobicity of the stone surfaces.

2. Experimental procedure

2.1. Preparation of TiO_2-based nanocomposites and application on stone

TiO_2 nanoparticles have been synthetized according to a non-aqueous synthesis (Niederberger *et al.* 2002), by using benzyl alcohol and titanium (IV) tetrachloride, as solvent and precursor respectively, as reported in a previous paper (Colombo *et al.* 2012). This synthesis enables the formation of anatase primary nanocrystals of about 5–6 nm diameter which aggregate in elongated clusters whose the longest axis measures about 40 nm. Water dispersions of TiO_2 nanoparticles with a concentration of 3 % by weight were used for the preparation of nanocomposites. The pristine polymers used as references are commercial aqueous dispersion of fluoropolyethers (*Fluoline PE*, *CTS srl*, labelled as F REF) and aqueous dispersion of organosiloxanes (*Silo 112*, *CTS srl*, labelled as S REF). Nanocomposites were prepared by adding different ratios of the nanoparticles dispersion in the polymeric solutions. In particular, polysiloxane-based films were obtained with the following concentrations of nanoparticle in the polymer: 16 wt.%, 28 wt.% and 44 wt.% (labelled as S16, S28 and S44) whereas for fluoropolyethers-based only the nanoparticles concentration of 16 wt.% (labelled as F16) was used, since the use of higher concentrations did not allow the preparation of stable blends. Samples of Carrara marble with 50×50×10

mm and 50×50×20 mm sizes were washed with deionized water and dried at room temperature until a constant mass was achieved. Then, the nanocomposites were applied on their surfaces by brush. For comparison, untreated stone samples were analysed (named NT).

2.2. Evaluation of the effectiveness of TiO_2-based nanocomposites applied to stones specimens

The morphology of the stone surfaces before and after the application of the nanocoatings was analysed by Environmental Scanning Electron Microscopy (ESEM) and EDS analyses, using a Zeiss EVO 50 EP ESEM, equipped with an Oxford INCA 200 - Pentafet LZ4 spectrometer. The evaluation of the aesthetical compatibility with the stone was carried out by spectrophotometric measurements by a Konica Minolta cm-600D instrument, with a D65 illuminant at 8°, wavelength range between 360 nm and 740 nm. The data were elaborated according to the CIE $L^*a^*b^*$ standard colour system and the average results of $L^*a^*b^*$ were used to calculate the colour difference ΔE* between treated and untreated areas: $\Delta E^* = [(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)2]^{1/2}$ *[Eq.1]*. Static contact angle and capillary water absorption tests were performed in room conditions, without exposing the samples to solar lamps or UV light in order to evaluate the wettability changes and water absorption of the stone surfaces after the application of the nanocomposites. Static contact angle was evaluated on 15 points for each sample, using an OCA (Optical Contact Angle) 20 PLUS (DataPhysics, Germany), with a drop volume of 5 µl, after 10 seconds. The drop shape was recorded with a camera and the angle between the substrate surface and the tangent from the edge to the contour of the water drop (contact angle) was evaluated. The capillary water absorption of the stone samples was performed on 50×50×20 mm stone samples before and after the application of the dispersions in room conditions. The capillary water absorption value per unit area (Q_i,expressed in mg/cm^2) is defined with the expression: $Q_i = (m_i - m_0)/A*1000$ *[Eq.2]*, where m_i is the mass (g) of the wet sample at time t_i, m_0 is the mass (g) of the dried sample, A is the surface area (cm^2) in contact with the water. The samples were weighed at the following time intervals: 10 min, 20 min, 30 min, 60 min, 4 h, 6 h, 24 h, 48 h, 72 h, 96 h. The relative capillary index (CI rel) was calculated with the equation: $CI_{rel} = \int_{t0}^{tf} f(Q_i)_{tr}dt / \int_{t0}^{tf} f(Q_i)_{ntr}dt$ *[Eq.3]*, where $\int_{t0}^{tf} f(Q_i)_{tr}dt$ is the area under the absorption curve of the treated specimen (tr) and $\int_{t0}^{tf} f(Q_i)_{ntr}dt$ is the area under the absorption curve of the untreated specimen (utr). The photocatalytic activity of the stone surfaces treated with nanocomposites was assessed by decomposition tests of an organic colorant, which was applied as aqueous solution of rhodamine B (0.05 g/l ± 0.005 g/l) to the surface of both untreated and treated samples. The degradation of the applied organic dye was monitored by evaluating the colour change of the surface (using a VIS spectrophotometer, as previously described) exposed in a Suntest CPS$^+$ solar box, equipped with a Xenon arc lamp source and a cut off filter for wavelengths below 290 nm. The irradiance was 765 W/m^2, at the temperature of 35°C. In literature, other authors performed the test with the explosion of the samples to UV light, however, Xenon lamp was selected to simulate the real conditions of outside exposed treated stones because it emits radiations similar to those of solar light. The colorimetric measurements were performed after 15, 30, 60, 90 and 150 minutes of irradiation. The chromatic coordinate a^* was used to evaluate the photocatalytic discoloration of stain D* over time, by the equation: $D^* = (|a^*(t) - a^*(rB)|/|a^*(rB) - a^*(0)|*100$ *[Eq.4],* where $a^*(0)$ and a^*(rB) are the average values of the chromatic coordinate a^* before and after the application of the stained solution and a^*(t) is

the a^* value after t hours of light exposure. Finally, in order to evaluate the eventual degradation of the polymeric matrices due to the presence of photoactive of TiO_2 nanoparticles in the nanocomposites, accelerated ageing of the nanocomposites cast on glass slides in a solar box were performed as described above, for 750 h. The ageing of the films was followed by Fourier Transform Infrared Spectroscopy (FTIR) by using a Nicolet 6700 spectrophotometer coupled with a Nicolet Continuum FTIR microscope equipped with a MCT detector (acquired between 4000 and 600 cm^{-1} with 128 acquisitions and 4 cm^{-1} resolution). Spectra of micro samples were recorded using a micro compression diamond cell accessory and they were normalized on the intensity of the Si-O stretching (at 1100 cm^{-1}) for polysiloxane-based films and on F-C stretching (at 1200 cm^{-1}) for fluoropolymer-based films.

3. Results and discussion

ESEM/EDS analyses were performed on treated and untreated surfaces of Carrara marble. Fig. 1 reports the images of Carrara marble treated with the fluoropolyether (F REF) and the fluoropolyether-based nanocomposite (F16): darker areas on the surface represent the areas where the coatings accumulate. Both the pristine polymer and the nanocomposite are not homogeneously distributed on the stone specimens (Doehne and Price 2010). On the contrary, organosiloxanes-based coatings create crack-free films, with a homogenous distribution of TiO_2 nanoparticles in the blends cast on the stone (Fig. 2).

To verify the respect of the original aesthetic properties of the surface, colour measurements were performed on stone specimens before and after the application of the treatments. Tab. 1 summarizes the value of colorimetric coordinates L^*, a^*, b^* and ΔE^* of the stone before and after the application of the fluoropolymer (F REF), polysiloxane (S REF) and the coatings with nano-TiO_2 (F16, S16, S28 and S44).The values of ΔE^* were lower than 4 for every treatment but, in general, the application of the nanocoatings leads to lower ΔE^* values compared to the polymers (F REF and S REF). In particular, among surfaces treated with polysiloxane-based nanocoatings, ΔE^* values decrease with the increase of the nano-TiO_2concentration, since they present lower differences of L^* and b^* compared to those of the surface before the application of the treatments. This is due to the whitening effect of nano-TiO_2 towards the slight yellow colour of the polymer.

Static contact angle measurements were carried out on Carrara marble specimens in order to monitor the wettability change of the surface after the application of the treatments. As presented in Tab. 1, compared to the untreated specimen (NT), the treated specimens show higher value of contact angle θ, since the polymers reduce the wettability of the surface. Moreover, compared to the surfaces treated with the pristine polymers (F REF and S REF), the application of the nanocomposites (F16, S16, S28 and S44) increases the contact angle values, as the nanoparticles creates surface nanoroughness. Indeed, by increasing the nanoparticles concentration in the blends, higher values of contact angles were measured.

To study the change of water absorption by capilalrity, the relative capillary index (CI_{rel}) was selected as representative parameter. As shown in Tab. 1, the values of $CI_{rel,}$ obtained from specimens treated with the nanocomposites are lower compared to the pristine polymers, indicating that the addiction of nanoparticles further inhibit the water absorption by the stone surfaces. The reduction of water absorption is less evident in fluoropolymer-based nanocomposite (F16) compared to polysiloxane-based nanocomposites (S16, S28 and

S44), probably due to the poor distribution of the film on Carrara marble surface. Moreover, no relevant changes in CI_{rel} were obtained by increasing the concentration of TiO_2 nanoparticles in the blends.

Fig. 3 reports the trend of rhodamine B discoloration (D*%) with time, after pre-fixed intervals of exposition to Xenon lamp irradiation, of stone specimens either untreated (NT) or treated with pristine polymers (F REF and S REF) and with the nanocomposites (F16, S16, S28 and S44). Compared to both the untreated specimen and the specimens with the pristine polymers, the D* values are higher for nanocomposites, confirming the photocatalytic properties of nano-TiO_2. In addition, the photocatalytic activity of specimens increases with the increase of nano-TiO_2 in the blends. However, a less photo-efficiency is achieved by F16 compared to S16 as the maximum D*% value obtained by specimen treated with F16 is 56% whereas for S16 is 81%. This is probably related to the lower amount of nanocomposite on the surface and able to confer photoactivity to the stone surface.

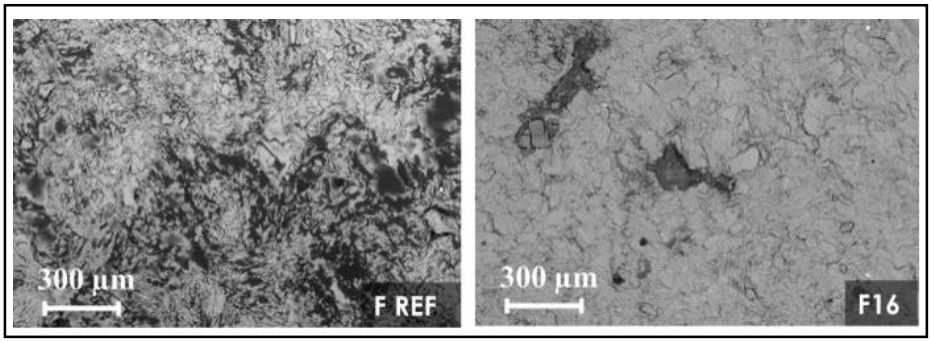

Fig. 1: ESEM/EDS characterization of Carrara marble surface treated with F REF (left) and F16 (right).

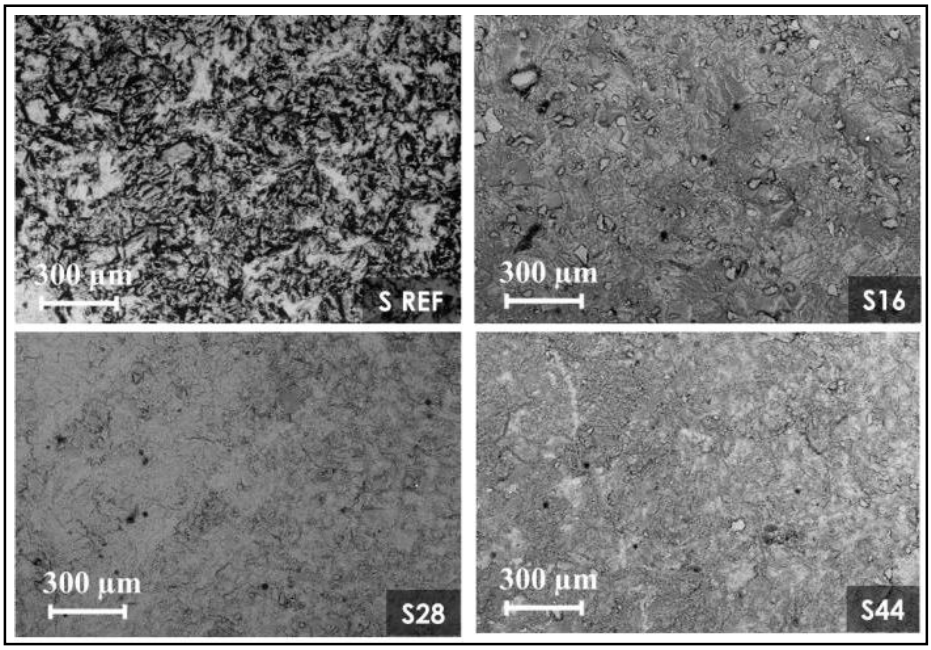

Fig. 2: ESEM/EDS characterization of Carrara marble surface treated with S REF, S16, S28 and S44, from left to right, from top to bottom.

Tab. 1: Colorimetric coordinates L, a*, b* and ΔE* of the stone before and after the application of fluoropolymer (F REF) and polysiloxane (S REF) and nanocoatings (F16, S16, S28 and S44) and average values of static contact angle (ϑ) and relative capillary index (CI_{rel}) of untreated and treated specimens.*

	Before the treatments			**After the treatments**					
	*L**	*a**	*b**	*L**	*a**	*b**	*ΔE**	*θ*	CI_{rel}
F REF	87.17	-0.77	0.35	85.39	-0.94	2.49	2.79	106.13	0.77
F16	89.24	-0.68	0.21	89.01	-0.68	0.33	0.26	135.68	0.73
S REF	86.90	-0.65	0.21	83.21	-0.77	1.20	3.82	95.34	0.78
S16	87.65	-0.74	0.45	85.09	-0.84	1.17	2.66	128.79	0.52
S28	87.27	-0.64	-0.14	85.37	-0.65	0.44	1.99	138.40	0.44
S44	86.21	-0.76	0.74	84.60	-0.83	1.41	1.75	142.49	0.48
NT								48.31	

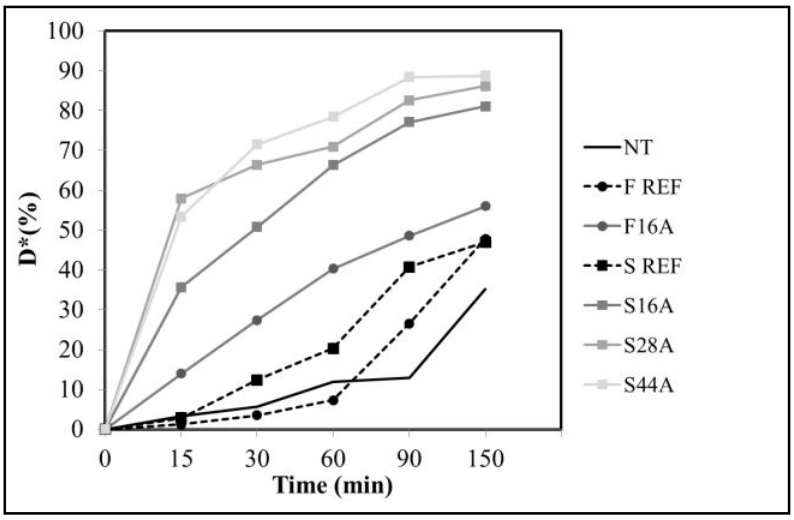

Fig. 3: Stain discoloration values D (%) as a function of time (min.) for untreated and treated Carrara marble after pre-fixed intervals of irradiation in solar box.*

Finally, both the pristine polymers and the nanocomposites were cast on glass slides and artificially aged in a irradiation chamber with a Xenon arc lamp source. The films were analysed by FTIR spectroscopy after 750 h of accelerated ageing. After the ageing, both siloxanes and fluorinated nanocomposites showed stability, due to the fact that no macroscopic defects (yellowing, cracks) were observed. As reported in Figures 4 and 5, compared to the spectra obtained from unaged film, the spectra from both aged pristine polymers (F REF and S REF) and aged nanocomposites (F16 and S16), show the presence of peaks at 1720 and 1740 cm^{-1} (C=O stretching) and the increase of the wide band between 3100-3400 cm^{-1} (OH stretching), due to the formation of new compounds (esthers). However, the chemical changes in nanocomposites are more evident compared to the aged pristine polymers.

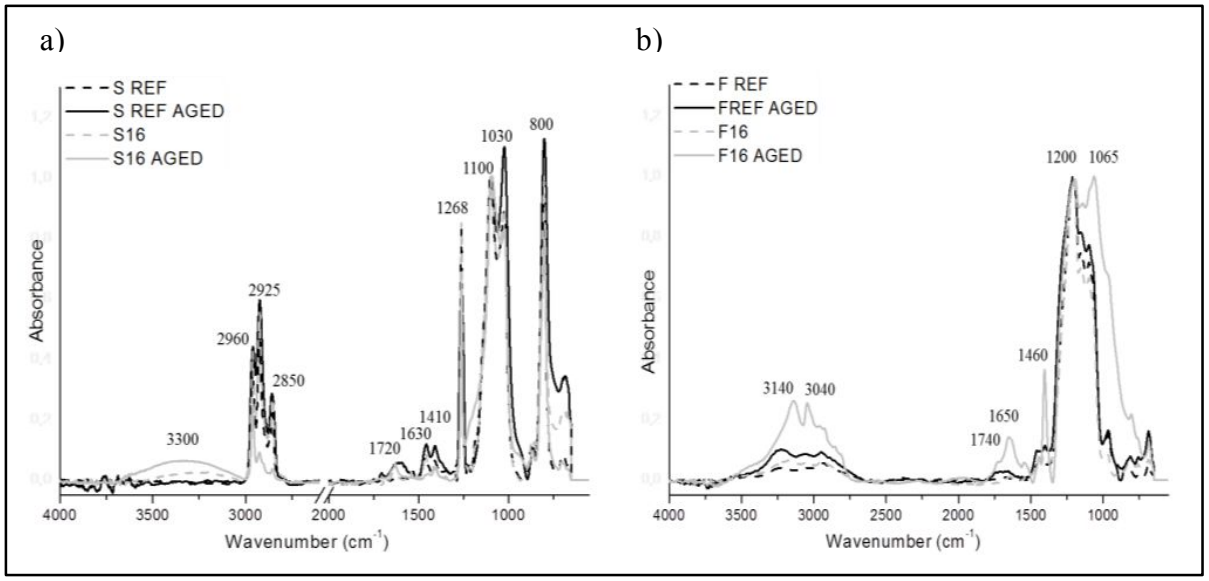

Fig. 4: FTIR spectra of F REF and F16 before and after 750 h of accelerated ageing in a Xenon solar irradiation chamber (a), FTIR spectra of S REF and S16 before and after 750 h of accelerated ageing i in a Xenon solar irradiation chamber (b).

4. Conclusions

The present study reports the development of formulations of nanocomposites, obtained by mixing different ratios of nano-TiO_2 dispersions in commercial aqueous polymeric solutions. According to ESEM/EDS analyses, both fluoropolymer (F REF) and fluoropolymer-based nanocomposite (F16) provide inadequate treatments from the morphological point of view, due to their poor distribution on the stone surfaces. On the contrary, polysiloxane-based nanocomposites are homogeneously distributed on the surfaces. Both the fluoropolyether and organosiloxanes-based nanocomposites do not affect the original colour of the specimens, which show also a decrease in the water capillary absorption. By increasing the nanoparticles content, an increase of the static contact angles of the surfaces occurs due to the increase of the surface roughness. Moreover, polysiloxane-based nanocoatings show higher photo-efficiency compared to the fluoropolymer-based coatings. Accelerated ageing prove that both siloxanes and fluorinated nanocomposites show stability, as no macroscopic defects are observed. However, FTIR spectra demonstrate that the presence of TiO_2 nanoparticle accelerate the degradation of the nanocomposites compared to the polymers, with the formation of new compounds. The results obtained from accelerated ageing of the nanocomposites will be compared with those obtained from nanocoatings applied on marble blocks in a pilot-areas on the façade of Duomo di Monza, where monitoring tests to assess their durability are currently underway. Nevertheless, the preliminary results prove the effectiveness of the proposed polysiloxane-based nanocomposites as self-cleaning and protective treatments for marble surfaces.

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