IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

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To cite this article: M Roveri *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **364** 012070

Florence Heri-Tech – The Future of Heritage Science and Technologies IOP Publishing
IOP Conf. Series: Materials Science and Engineering **364** (2018) 012070 doi:10.1088/1757-899X/364/1/012070

Self-cleaning and antifouling nanocomposites for stone protection: properties and performances of stone-nanomaterial systems

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Abstract. The development of nanocomposites combining photocatalytic, antifouling and protective features has provided interesting and promising results in the last years. However, few data about the behaviour of the nanomaterials applied on stone surfaces are available in the literature. In the framework of the EU-Horizon 2020 project “Nano-Cathedral”, nanostructured protective treatments have been designed with different nanoparticles (TiO_2, Ag, ZnO), solvents and silane/siloxane-based polymeric matrices. The innovative formulations have been applied on 6 lithotypes, selected among the stones used in five medieval cathedrals (Vitoria-Gasteiz, Ghent, Cologne, Vienna and Pisa) and a contemporary theatre (Oslo Opera House), which are emblematic of different European geological and environmental areas. The treated stone specimens have been fully characterized to evaluate the surface optical and morphological compatibility, the reduction of water absorption by capillarity, the change in wettability and water vapour permeability properties. The selected treatments fulfil all these requirements and exhibit good photocatalytic and antifouling properties once applied on stone specimens. Different accelerated ageing procedures have also been performed in order to evaluate the stability of the polymeric matrices in the presence of photoactive TiO_2.

1. Introduction

The use of nanomaterials in the conservation of natural and artificial stone materials has been an active research topic over the last fifteen years, showing a potential for tackling different aspects of conservation, from consolidation to protection against chemical and biological decay agents.

In particular, the development of chemically stable nanocomposites based on the addition of inorganic TiO_2, ZnO or Ag nanoparticles (NPs) to silanic or acrylic matrices has provided an effective means of combining the water repellency features of siloxane, fluorinated and acrylic polymers with the photocatalytic activity of nano-TiO_2 [1], able to promote the solar-driven degradation of many pollutants, and the biocidal properties of Ag and ZnO [2].

“Nano-Cathedral”, a Horizon 2020 project currently in progress, is devoted to developing a systematic approach to the use of TiO_2, ZnO and Ag-based nanomaterials in the protection of European architectural heritage, by evaluating the performance of an array of innovative research products applied on natural stones with highly different properties.

In this work, three innovative nanocomposites based on different silicon-based matrices and containing different types and concentrations of NPs were set up with the contribution of companies and their protective performance was assessed on different stone substrates.

As stone substrates, three lithotypes with largely complementary properties were selected, i.e. Apuan marble, Balegem limestone and Schlaitdorf sandstone. These natural stones were employed in relevant historical buildings involved in the project: Apuan marble is used in the Cathedral of Pisa (Italy, XIII cent.) and in a contemporary high-standing building, the Oslo Opera House (Norway, 2008), Balegem stone is present in the Cathedral of Ghent (Belgium, XIII cent.) and Schlaitdorf stone in the Cathedral of Cologne (Germany, XIII cent.).

The performance of the selected nanocomposites was evaluated on fresh stone substrates in laboratory conditions according to the recent EN Standard Protocol for the assessment of protective treatments in the field of Cultural Heritage [3] and by assessing their photocatalytic/biocidal activity.

Moreover, three different artificial ageing protocols that take into account the separate effects of heat, UV light irradiation and meteoric run-off are currently being conducted in laboratory conditions, with the aim of investigating the durability of nanocomposites once applied on stone substrates and predicting their long-term response towards environmental exposure. Partial results from this investigation will be presented, including those related to the effects of heat and UV light irradiation.

As a final step of the Project, the nanocomposites were applied on deteriorated surfaces in pilot areas of the respective historical buildings and the evaluation of their performance is currently being performed in the real environmental conditions, which are very different from site to site. Results from this onsite experimentation will be complementary and determinant for a thorough evaluation of the effectiveness of the considered new protectives and will be available at the end of the Nano-Cathedral project.

2. Materials and methods

Three nanocomposites were selected, according to a preliminary screening protocol, among those prepared by the companies involved in the project. Owing to the confidential non-disclosure agreement signed within the Project, only partial information can be given about the products, as shown in table 1.

Table 1. Description of the nanocomposites.

Product	Composition	Solvent	Property
WNC	alkyl alkoxy silane oligomers (15% w/w) with TiO_2 NPs (0.96% w/w)	water	photocatalytic
ANC	alkyl alkoxy silane monomers (40% w/w) with TiO_2 NPs (0.12% w/w)	2-propanol	photocatalytic
TNC	hydrophobized silica with AgO and ZnO nanoparticles (0.2% w/w)	2-propanol	anti-bacterial

The stone substrates belong to three different lithotypes, i.e. Apuan marble, Balegem limestone and Schlaitdorf sandstone, whose main characteristics are summarized in table 2.

Table 2. Main characteristics of lithotypes (porosity data are from mercury intrusion porosimetry measurements).

Lithotype	Provenance	Description	Open porosity (%vol)
Apuan marble	Carrara region, Italy	Metamorphic rock with almost purely calcitic composition and highly compact texture	0.7±0.1
Balegem limestone	Ghent region, Belgium	Sedimentary rock with large siliceous clasts in calcitic matrix; compact texture	9.9±0.8
Schlaitdorf sandstone	Neckar area, Germany	Sedimentary rock with chiefly siliceous composition and coarse texture	16±1

5x5x1 cm and 5x5x2 cm specimens (6 for each size) of fresh lithotypes were gently polished with abrasive paper (P180 carborundum paper), washed and kept in deionized water for 1 hour in order to remove possible soluble salts and then dried in oven at 50 °C until constant weight (a minimum of 48 hours). The nanocomposites were applied by capillary absorption for 6 hours, using a filter paper pad saturated with the treating material, according to EN 16581:2014 standard [3]. The time of application was defined after checking the time necessary to allow for the penetration of the products inside the depth of lithotypes. A commercial protective treatment based on silanes and siloxanes, Silres BS 290 (Wacker Chemie, dil. 8 wt.% in white spirit), was used as reference material for comparison. In order to determine the amount of absorbed dry matter, all stone specimens were weighed before the treatment and then after solvent evaporation until constant weight was achieved (a minimum of 48 hours). For all products, the amount of dry matter per unit area is reported in table 3.

Table 3. Dry matter (mg/cm^2) absorbed by the fresh stone specimens.

Treatment	Apuan Marble	Balegem	Schlaitdorf
WNC	0.3±0.2	16±1	26±4
ANC	1.3±0.1	10±3	18±10
TNC	4.5±0.2	7±1	7.7±0.5
Silres BS 290	2±1	12±8	18±7

The colour change of stone specimens after the application of the products was measured with a Konica Minolta CM-600D Vis spectrophotometer with a D65 illuminant at 8°, in the 360-740 nm wavelength range. 25 measurements were performed on each specimen before and after the treatment. The results were expressed in the CIE L*a*b* colour space and the average values of L*, a* and b* were used to calculate the colour change ΔE*. A threshold value of ΔE*=5 was set as requirement for aesthetic compatibility [4].

Static contact angle test was performed on 15 points for each sample, according to EN Standard Protocol [5], using an OCA (Optical Contact Angle) 20 PLUS (DataPhysics, Germany) equipment, with a drop volume of 5 µl, after 10 seconds. The test was carried out before and after the application of the treatments.

The capillary water absorption of the stone specimens was measured following the EN Standard Protocol [6] on untreated and treated specimens. The data were elaborated according to the literature [7]. In order to evaluate the reduction of water absorption, two parameters were considered: the relative capillary index (CIrel) and the ratio of the absorption coefficients of treated and untreated specimen (ACt/ACnt).

Water vapour permeability tests were performed according to the EN Standard Protocol [8] on the specimens before and after the application of the treatments, using the “wet cup” system described in [9]. In order to evaluate the retention of permeability, the ratio of the permeability values of treated and untreated specimen (δt/δnt) was calculated.

The photocatalytic properties of the products were assessed through the Rhodamine discolouration test, according to the laboratory procedure and data elaboration described in [9]. The extent of discolouration (D*) of specimens treated with WNC and ANC was divided by that of specimens treated with Silres BS 290, which has no photocatalytic properties and can be used as blank.

In order to determine the antibacterial activity of TNC, sterilized stone samples of the three chosen lithotypes were treated with the products and, after the complete evaporation of the solvent, were incubated with fresh Bacillus cereus or Pseudomonas putida cultures for 16 h at 28 °C. As controls, untreated stone samples were also incubated with the bacterial strains. After the incubation, the stone samples were washed once with fresh medium to remove unattached cells. Remaining bacteria were collected by scratching an area of 5 cm^2 with a sterile swab. The swab was then transferred to 3 ml fresh medium and vortexed to release the bacterial cells in the medium. Serial dilutions of this suspension were placed on solid medium plates and incubated at 28 °C for another 16 h. Afterwards, single colonies could be observed and were counted to determine the number of CFU (Colonie Forming Units).

The artificial ageing of stone specimens in laboratory conditions was conducted for 750 hours through two different protocols: one thermal ageing in oven at 65 °C and one UV light ageing in an irradiation chamber (Suntest XLS$^+$, URAI S.p.A) equipped with a Xenon arc lamp (cut-off filter for λ<295 nm, 765 W/m^2 irradiance). Two specimens per lithotype and treatment were selected for each protocol, among the six specimens that were characterized in the former part of this investigation. At the end of the first ageing cycle, the stone specimens were characterized through the static contact angle and capillary water absorption tests, according to the previously described methodologies. A complete testing procedure including all the tests will be carried out in the next few months, after another ageing cycle of 750 hours has been finished.

3. Results

The results of the colour measurements on fresh stone specimens are summarized in table 4.

Table 4. Total colour difference (ΔE^*) between treated and untreated specimens.

Treatment	Apuan Marble	Balegem stone	Schlaitdorf
WNC	1.5±0.5	3.4±0.4	1.5±0.2
ANC	2.8±0.8	1.7±0.5	7.1±0.6
TNC	4±1	4.5±0.8	2.6±0.5
Silres BS 290	1.8±0.9	3±2	8±2

It can be observed that all treatments preserve the original surface colour on Apuan marble and Balegem stone. On Schlaitdorf stone, WNC and TNC show excellent colour compatibility, whereas ANC and Silres BS 290 produce a colour change higher than the threshold value of 5, due to a darkening and yellowing effect. In both cases, the application of a lower amount of product would probably ensure a lower chromatic alteration.

The results of water absorption measurements on treated and untreated specimens are reported in table 5.

Table 5. Relative capillary index (CIrel) and relative absorption coefficient (ACt/ACnt) of treated specimens.

Treatment	Apuan Marble		Balegem stone		Schlaitdorf	
	CIrel	ACt/ACnt	CIrel	ACt/ACnt	CIrel	ACt/ACnt
WNC	0.75±0.05	0.4±0.4	0.35±0.07	0.1±0.1	0.44±0.05	0.11±0.05
ANC	0.13±0.02	0.19±0.03	0.07±0.01	0.02±0.01	0.08±0.02	0.028±0.009
TNC	0.5±0.2	0.03±0.02	0.19±0.09	0.01±0.01	0.09±0.01	0.031±0.007
Silres BS 290	0.2±0.3	0.05±0.07	0.5±0.3	0.6±0.3	0.11±0.07	0.02±0.01

On Apuan Marble, ANC shows the best results in terms of water absorption reduction. Good results were obtained by Silres BS 290 but the very high standard deviation values of both CIrel and ACt/ACnt is an indication of the heterogeneity of the treatment applied on different marble samples. TNC proves to be a good water repellent product especially after a short time interval of contact with water (30 min), whereas WNC is not effective in water absorption reduction. On Balegem stone, the best effectiveness was obtained by ANC both after 4 days (CI rel) and after 30 min (ACt/ACnt) compared to the other treatments. Good results were obtained by TNC and WNC, whereas Silres BS 290 shows poor effectiveness in the reduction of the water uptake. Finally, on Schlaitdorf stone, excellent results in terms of water absorption reduction were obtained from specimens treated with ANC, TNC and Silres BS 290, with CIrel values of about 0.1. WNC shows rather good reduction as well, especially within 30 min of contact with water.

The results of water vapour permeability measurements on treated and untreated measurements are reported in table 6.

Table 6. Ratio of water vapour permeability values of treated and untreated specimens (δt/δnt).

Treatment	Apuan Marble	Balegem stone	Schlaitdorf
WNC	1.2±0.4	0.9±0.3	0.8±0.3
ANC	0.9±0.2	0.6±0.3	0.9±0.2
TNC	0.5±0.3	0.2±0.1	0.4±0.2
Silres BS 290	0.3±0.2	0.3±0.2	0.436±0.2

On Apuan marble, both WNC and ANC do not affect the original vapour permeability, since the δt/δnt values are about 1. Further investigations would be necessary to explain, in the adopted treatment conditions, why WNC increases the mean values of vapor permeability of the stone. However, a similar effect has been reported in the literature concerning other coating materials [10]. TNC leads to a reduction of about 50% of permeability, whereas Silres BS290 significantly reduces it, indicating that probably the product is partially occluding the pores of the stone. On Balegem stone, WNC does not significantly affect the original water vapour permeability (reduction of about 10%), while ANC reduced the permeability of about 40%. Silres BS 290 and TNC show the highest reduction of permeability (about 70-80%). It is important to notice that, except for TNC, high values of standard deviation could be observed, indicating a high heterogeneity of the treated stones. On Schlaitdorf stone, WNC and ANC do not significantly change the original water vapour permeability; Silres BS 290 and TNC show comparable results with a reduction of the permeability of about 60%.

The results of static contact angle measurements on treated and untreated specimens are reported in table 7.

Table 7. Static contact angle (θ) of treated and untreated specimens (expressed in degrees); on untreated Schlaitdorf stone the contact angle could not be measured due to the very fast absorption of the drop.

Treatment	Apuan Marble		Balegem stone		Schlaitdorf	
	untreated	treated	untreated	treated	untreated	treated
WNC	66±10	113.8±0.7	71±8	116±4	-	128±2
ANC	72±18	140±10	37±7	143±3	-	137±3
TNC	55±7	129±12	54±10	149±3	-	133±7
Silres BS 290	58±11	101±5	32±8	125±12	-	127±6

In the case of Apuan marble, the application of all the new products reduces the surface wettability compared to the result obtained from Silres BS 290, with static contact angle values higher than 100°. In particular, ANC and TNC show a significant increase in the values of static contact angle (about 130-140°). On Balegem stone, all the products change the original surface wettability. In particular, specimens treated with TNC and ANC reach values of static contact angle of about 140-150° and the low standard deviation proves the homogeneity of this surface property of the treated stone. Finally, all the treatments applied on Schlaitdorf stone show water repellent properties, with contact angle values higher than 100°. In particular, ANC and TNC lead to a significant reduction of the surface wettability (about ɵ=140°), with low standard deviations proving the homogenous distribution of the products on specimens.

The results of the Rhodamine discolouration test are reported in table 8.

Table 8. Ratio of D* values of specimens treated with WNC/ANC and specimens treated with Silres BS 290 at 150 min (D^*_t/D^*_{SILRES}).

Treatment	Apuan Marble	Balegem stone	Schlaitdorf
WNC	1.34	2.08	3.04
ANC	1.30	1.40	3.90

It can be observed that, on Balegem stone, WNC produces a higher discolouration compared to ANC. This is readily explained by its higher TiO_2 concentration. However, when it comes to Apuan marble, the photocatalytic performances of the products are comparable and the performance of ANC is significantly better in the case of Schlaitdorf stone, indicating that this product, despite a lower nanoparticle concentration, has a better performance compared to WNC once applied on certain substrates.

Concerning the results of the test for the antibacterial activity of TNC (table 9), it can be observed that Apuan marble specimens show minor reduction of the CFU number for both Bacillus cereus and Pseudomonas Putida. This could be explained either by the small amount of protective product absorbed by the marble, or by the small amount of bacteria able to attach to the marble surface. On the other hand, the antibacterial activity of Balegem and Schlaitdorf specimens prove the effectiveness of TNC in the reduction of CFU compared to the respective untreated specimens, especially regarding Bacillus cereus.

Table 9. CFU values of untreated specimens and specimens treated with TNC (/10^6 counts/mL).

Treatment	Apuan Marble		Balegem stone		Schlaitdorf	
	Bacillus cereus	Pseudomonas putida	Bacillus cereus	Pseudomonas putida	Bacillus cereus	Pseudomonas putida
TNC	1.9±0.4	4.4±0.4	7±1	10.4±0.3	5.7±0.1	11.2±0.7
untreated	1.9±0.4	4.9±0.4	21±3	12.0±0.9	57±8	17±1

In conclusion, the laboratory tests conducted on fresh stone specimens showed that on Balegem and Schlaitdorf stones, ANC and TNC prove to be the best products regarding both protection efficacy and photocatalytic/antibacterial activity. In the case of Apuan marble, ANC has a comparable performance, while TNC shows only poor effectiveness in antibacterial activity.

Consequently, ANC and the reference Silres BS290 were chosen to undergo the ageing protocols on all three lithotypes, while TNC was only selected for Balegem and Schlaitdorf stones.

The results of the water absorption tests after 750 hours of thermal and UV light ageing are reported in figure 1. By comparing the values of CIrel before and after the ageing, it can be observed that thermal ageing does not produce negative effects on the protective performance, while in the case of UV light ageing, some differences can be highlighted in the behavior of the products. Indeed, no effect is observed in the case of TNC, while the effectiveness of Silres and ANC in the reduction of water absorption is slightly reduced, but the change is not remarkable. The results prove that the addition of nanoparticles in the formulations does not negatively affect the protective properties of the treated specimens.

The results of the static contact angle tests after the ageing are reported in figure 2. It can be observed that in all cases thermal ageing does not significantly affect the surface water-repellency of the treated stones. On the other hand, UV light ageing leaves the specimens treated with TNC unaffected, but it produces a visible effect in the case of Silres BS 290 and has a very strong impact on specimens treated with ANC in the case of Apuan Marble and Balegem, where substantially the surface wettability of untreated stone is reverted, while on Schlaitdorf stone the loss of hydrophobicity is much less pronounced. This significant decrease observed on specimens treated with ANC may be related to the photocatalytic activity of TiO_2 nanoparticles towards the polymeric matrix in which they are embedded. These results indicate that, although photocatalytic treatments applied on stone are predictably affected by a certain extent of degradation under UV light, this degradation remains largely a surface effect and the ability of the treatment to reduce water penetration is not significantly impaired.

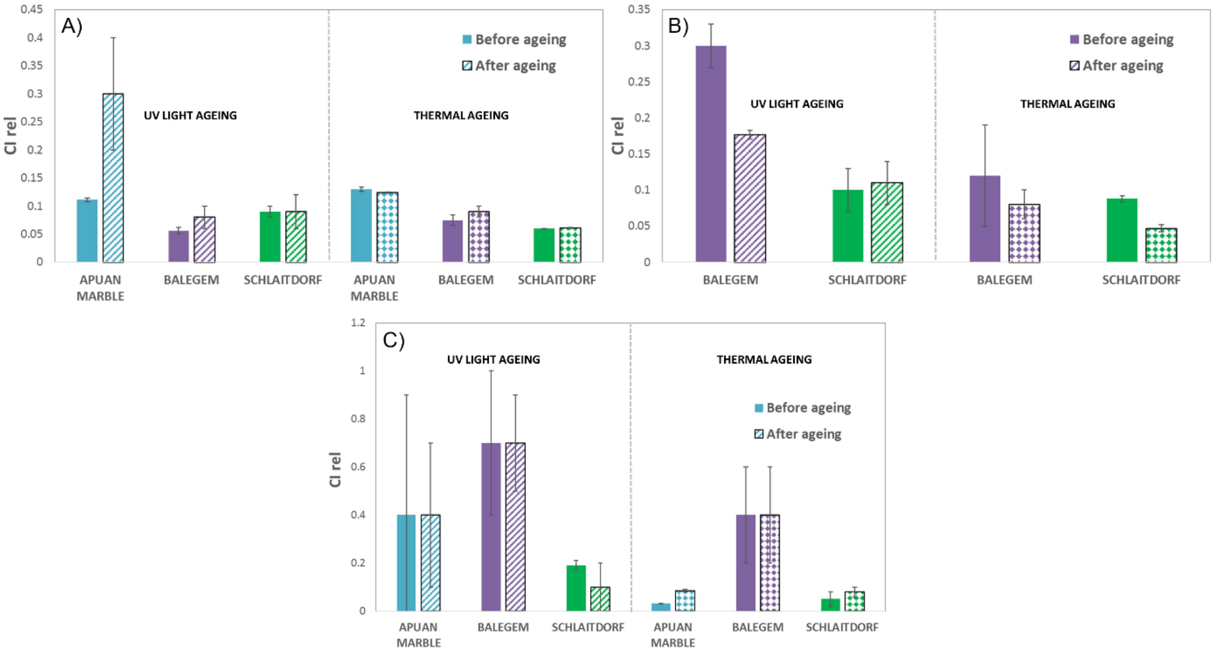

Figure 1. CIrel values of specimens treated with A) ANC, B) TNC and C) Silres BS 290 *before* and *after* the two ageing protocols.

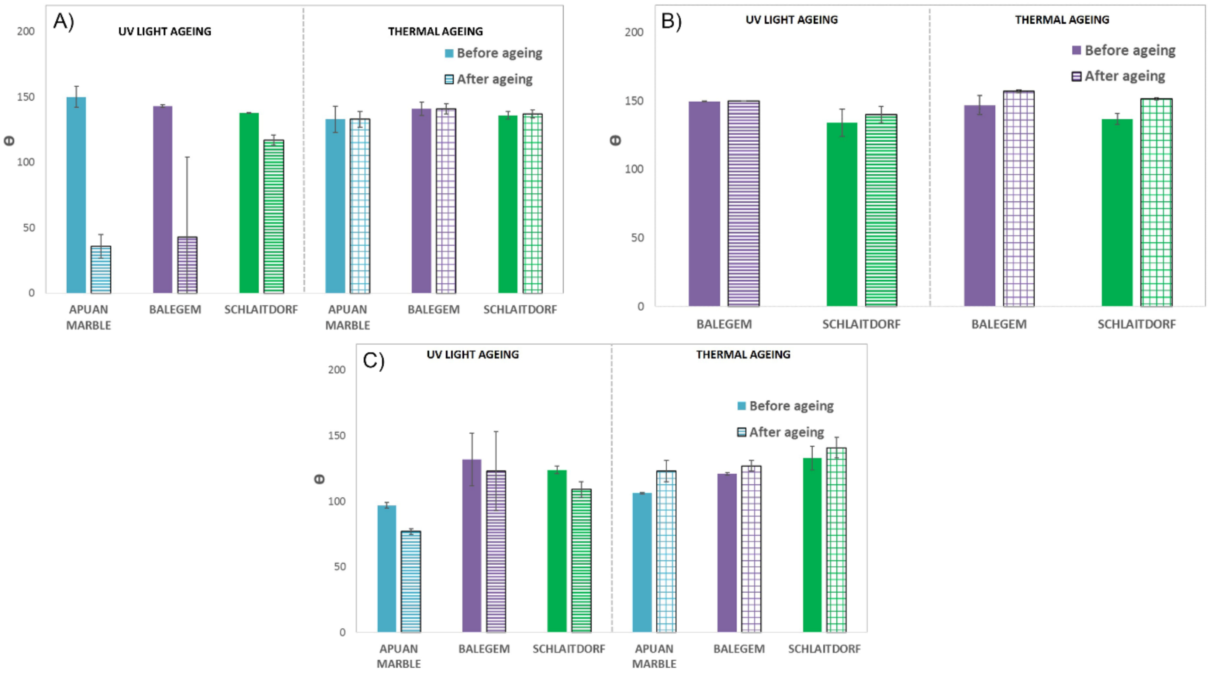

Figure 2. Values of static contact angle Θ (°) of specimens treated with A) ANC, B) TNC and C) Silres BS 290 *before* and *after* the two ageing protocols.

4. Conclusions

In this study, three innovative nanocomposites with photocatalytic or antibacterial properties, developed in the framework of the Nano-Cathedral H2020 Project, have been applied for protection purposes on three different lithotypes. The performance has been assessed through a set of laboratory tests and the durability has been evaluated by means of two different protocols of artificial ageing. The results indicate that two of the three products, one antibacterial and one photocatalytic product, show very high and promising protective effectiveness. The antibacterial product also showed excellent response in the durability tests, while the photocatalytic product proved to be able to retain much of its effectiveness in the reduction of water absorption but contact angle tests indicated a loss of hydrophobicity after the UV ageing protocol. This suggests the fact that, upon prolonged exposure to UV light, the product undergoes a degradation process, but this degradation, being a surface effect, does not significantly affect its effectiveness in reducing water absorption.

Acknowledgments

The Nano-Cathedral Project (Nanomaterials for conservation of European architectural heritage developed by research on characteristic lithotypes) is supported by the European program Horizon 2020 (GA n. 646178). The AA. wish to acknowledge the kind collaboration of the companies ChemSpec Srl (Italy), Colorobbia Srl (Italy) and Tecnan-Nanomat (Spain). Matea Ban from Technical University of Wien is gratefully acknowledged for Mercury Intrusion Porosimetry measurements.

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