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Performance evaluation of a commercial protective coating through field-exposure tests on three stone substrates

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ABSTRACT
In the last decades, there have been several studies on Cultural Heritage regarding the performance of protective and consolidating coatings for the prevention of decay. A coating must have several characteristics such as efficiency, breathability, and must be durable and reversible. In this research work, the performance of a commercial protective product (Fosbuild FBLE 200) was evaluated. This coating is composed of a TiO_2 nanopowder dispersed in an aqueous solution of an acrylic polymer. The product, which exhibits depolluting, antimicrobial, water-repellent and self-cleaning properties, has been applied on three different lithotypes: Carrara marble, Noto stone, and Comiso stone. Field-exposure tests were carried out in two different outdoor environments (Catania and Palermo) in order to assess its suitability. Promising results were obtained for the Carrara marble after one year of exposure; however, a decrease in effectiveness was observed at the end of the second year.

Section: RESEARCH PAPER

Keywords: Coatings; Fosbuild FBLE 200; stone; field-exposure tests

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1. INTRODUCTION

In the field of cultural heritage, protective coatings play a key role in the preservation of monuments, statues, and many other works of historic and artistic interest. These treatments are necessary [1]-[6] in order to prevent the development of numerous possible degradation phenomena, such as the formation of black crusts, chromatic alterations, detachment of the substrate, erosion, and many other effects [7]-[10]. The main factors which give rise to these processes are: the interaction between the substrate and air pollutants (sulphur dioxide, particulate matter, and nitrous oxides), the crystallization of soluble salts, and biodeterioration [1], [11], [12]. Stone materials are amongst the substrates which mostly suffer from the degradation phenomena and for this reason they have been, and still are, at the centre of attention in this field [13].

For a product to act as a protective coating in the field of cultural heritage, it needs to possess several qualities such as: good adhesion to the substrate, water repellence, natural water vapour permeability, transparency, easiness of use, durability, reversibility, compatibility with the surface, and also needs to be easy to synthesize, of low-cost and non-toxic [1]-[11]. The substances which have been used in the last decades for the protection of stone substrates have been: acrylic polymers, partially-fluorinated acrylic or methacrylic-based copolymers, polyester resins, vinyl polymers and bio-films [1]-[12]. However, no one of these options seems to fully satisfy all the requirements of an ideal coating [12].

Nano-composites are being advanced as possible alternatives to traditional polymeric coatings due to their superhydrophobic character and photocatalytic action, which enhances water repellence and helps contrast the damaging effects of air pollutants [12]. In fact, many products now used in conservation, such as composite-based polymeric materials, are being studied and tested in various research areas and then readapted to the needs of the cultural heritage sector [5], [14]. Titanium dioxide (TiO_2) is one of the substances which is being mostly employed due to its great photocatalytic activity, sterilizing, deodorizing and anti-fouling properties [11], [12]. As for the traditional coatings, extensive and continuous application in the protection of cultural heritage will require thorough analytical research in order to assess their potentialities and possible risks [1]-[6].

The aim of the present work is to evaluate the performance of a commercial protective polymeric coating, namely Fosbuild FBLE 200, which is composed of a TiO_2 nanopowder dispersed in an aqueous solution of an acrylic polymer. Laboratory tests have highlighted disinfectant, antimicrobial, water-repellent and self-cleaning properties of the product, along with potent biocidal effects [12], which make this product very promising for specific applications in the cultural heritage field. However, no field-exposure test was carried out in order to confirm the applicability of this product on samples exposed to real-life conditions. The present article represents an extension of a previously published extended abstract [15].

Fosbuild FBLE 200 was tested through an outdoor exposure study carried out in two Italian cities, Palermo and Catania, which are characterized by different environmental conditions and sources of air pollution. Three different stone substrates of carbonate nature were examined: Carrara marble, Noto stone and Comiso stone. The first is one of the most widespread stone materials in Italian statuary and monumental architecture, whilst the following two are calcarenites characteristic of Sicilian architecture. Both treated and untreated samples were exposed for a 2-year period in both sites and analyses were carried out at the end of the first and the second year to evaluate the performance of the coating. In order to evaluate the effectiveness of the coating, the results were compared with the ones obtained from a previous exposure study of the untreated specimens [14].

2. MATERIALS AND METHODS

In this work, a photo-catalytic formulation based on TiO_2 (titanium dioxide) nanoparticles, known as Fosbuild (FBLE 200), was tested. The research was aimed at evaluating the inhibitory capacity, in an outdoor environment, of this product, and therefore its effectiveness as a depolluting, antimicrobial, water repellent and self-cleaning agent. The product is distributed by the company Steikos srl (Italy) and is composed of a titanium dioxide nanopowder (anatase crystalline phase with mean particle diameter of 20 nm) dispersed in an aqueous suspension of an acrylic polymer (polymer 4 wt%, TiO2 0.3 wt%). The product was applied with the aid of a brush for each lithotype using two different quantities: high quantity (T1) and low quantity (T2) [16].

Three different stone substrates of carbonate nature were treated and exposed: Carrara marble, Noto stone, and Comiso stone. Carrara marble is one of the most common substrates in European cultural heritage, whereas Noto and Comiso stone are two lithotypes frequently found in Sicilian architecture [14]. The main features of these lithotypes are well described in the work of Comite et.al. (2017). These were then exposed outdoors in two Italian sites, Catania and Palermo, which are characterized by different environmental conditions and pollution. Both cities are influenced by pollution produced by vehicular traffic [17], [18], rather than by industry or domestic heating. Precisely, Catania is located on the Sicilian east coast overlooking the

Table 1. Number and type of samples treated with Fosbuild (FBLE 200) that underwent field exposure tests.

Sample ID	Lithotype	Number of samples (Catania)	Number of samples (Palermo)	Quantity of product applied / g
MC-T1	Carrara marble	3	3	0.500
MC-T2	Carrara marble	3	3	1.000
NO-T1	Noto stone	3	3	0.500
NO-T2	Noto stone	3	3	1.000
CO-T1	Comiso stone	3	3	0.500
CO-T2	Comiso stone	3	3	1.000

MC = Carrara marble
NO = Noto stone
CO = Comiso stone

Ionian Sea, at the foot of Etna, which is the largest active volcano in Europe that releases gaseous and ash emissions (plumes) that hit the city several times a year. Instead, Palermo is located in a large gulf of the north-western Tyrrhenian coast of Sicily. The most important natural contribution to the total aerosol particulate matter in the city of Palermo derives from the erosion of outcropping rocks, as well as from soils and sea spray [19], [20].

A total of 36 specimens (5 × 5 × 2 cm^3) underwent the field-exposure tests (Table 1). For the same reasons outlined in Comite et.al. (2017), the specimens were exposed at 24 m above ground level. Specifically, the locations of the exposure were: in Catania, the "Dipartimento di Scienze Biologiche, Geologiche e Ambientali – Sezione Scienze della Terra" of the University of Catania; in Palermo, the "Dipartimento di Giurisprudenza" of the University of Palermo. The locations were chosen in order to reproduce the real-life exposure conditions of buildings and monuments to the main sources of pollution present in the two cities, such as vehicular traffic (Figure 1). Overall, the duration of the experimental campaign was of 2 years (July 2011- July 2013).

Samples were then characterized using a multi-analytical approach. In order to evaluate the suitability of the product applied to the treated specimens, measurements were carried out, before exposure, for the determination of the contact angle (to evaluate the permeability to liquid water) and colorimetric tests (to estimate the chromatic alteration of the stone material after application), according to the regulations in force (Uni NorMal 20/85). In particular, the contact angle determines the wettability of the treated surfaces (NorMal 33/89).

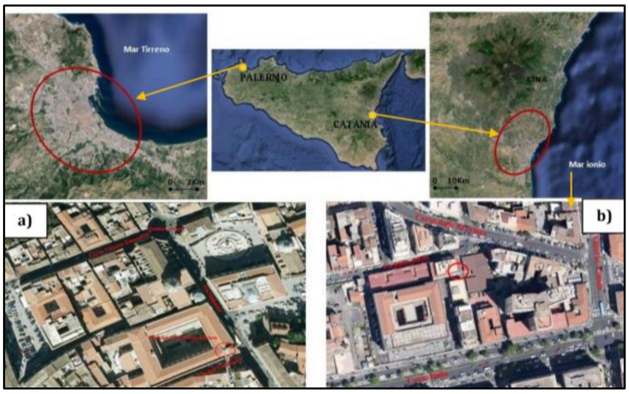

Figure 1. Satellite images of the cities of Palermo and Catania and of the exposure sites: a) "Dipartimento di Giurisprudenza", University of Palermo; b) "Dipartimento di Scienze Biologiche, Geologiche e Ambientali – Sezione Scienze della Terra".

After the exposure period, respectively after the first and second year, the samples were characterized by means of different analytical techniques:

- A ZEISS 47 50 52 stereomicroscope was used for surface observations, with optics from 0.8x to 10x, equipped with a digital camera for image acquisition;

- Colorimetric analyses were carried out by means of a Konica Minolta CM 2600d portable spectrophotometer, referring to the CIE *L** *a** *b** chromaticity diagram and the NorMal 43/93 standard. *L** is luminosity or brightness, which varies from black (value = 0) to white (value = 100); *a** ranges from +*a** (red) to –*a** (green) and *b** varies from +*b** (yellow) to -*b** (blue).

- Ion chromatography was carried out with a Dionex 4000i instrument, equipped with a gradient pump, a conductivity detector (CDM-1), and eluent gas module (EDM-2), with accuracy of 1.5 %. $SO4^{2-}$, NO_3^-, and Cl^- were quantified. The separation columns used for the anions were a Dionex AS4A or AS5A-5 mm (AMMS-1 micromembrane suppressor) [15]. For the preparation of test solution, reference was made to UNI 11087 (2003) technical standard.

- FT-IR spectroscopy was used to identify the main mineralogical phases constituting the particulate deposited on stone surfaces using a Perkin Elmer Spectrum 100, equipped with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded in ATR mode, in the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. The analysis was carried out on around 1 mg of powder.

3. RESULTS

3.1. Pre-exposure tests

Samples treated with Fosbuild (FBLE 200) were analysed prior to exposure using colorimetry and contact angle measurements in order to assess the suitability of the coating, following the Uni NorMal 20/85 technical standard. Chromatic variation (ΔE*) of the treated specimens were calculated with respect to the untreated samples using (1):

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{\frac{1}{2}} . \quad (1)$$

Table 2 shows the average chromatic variation after application of the protective coating.

All samples displayed values of Δ*E** below the threshold value of 5, under which the colour variation is imperceptible to the human eye [12], proving the suitability of the product.

With regards to the contact angle, the results of the tests conducted on the treated samples are displayed in Table 3.

Table 2. Average Δ*E** values for each sample.

Sample ID	Exposure site	Δ*E**
MC-T1	Catania	1.17
MC-T1	Palermo	2.19
MC-T2	Catania	1.01
MC-T2	Palermo	3.93
NO-T1	Catania	1.11
NO-T1	Palermo	1.92
NO-T2	Catania	1.87
NO-T2	Palermo	1.60
CO-T1	Catania	0.95
CO-T1	Palermo	1.53
CO-T2	Catania	1.83
CO-T2	Palermo	1.48

Table 3. Average contact angle values for each sample.

Sample ID	Exposure site	Contact angle / °
MC-T1	Catania	85.7
MC-T1	Palermo	86.2
MC-T2	Catania	90.3
MC-T2	Palermo	90.2
NO-T1	Catania	106.0
NO-T1	Palermo	126.0
NO-T2	Catania	106.0
NO-T2	Palermo	127.0
CO-T1	Catania	104.0
CO-T1	Palermo	127.0
CO-T2	Catania	105.2
CO-T2	Palermo	126.0

The Carrara marble specimens treated with low quantities of coating showed partial wettability, with acceptable contact angle values close to 90°; whereas the specimens treated with higher quantities showed lower wettability (contact angle > 90°). Thus, applying greater quantities of coating makes the surface more hydrophobic and therefore more suitable for applications in the protection of cultural heritage. With regards to the other two lithotypes, all specimens showed contact angle values greater than 90°, indicating poor wettability and good hydrophobicity.

3.2. Post-exposure tests

At the end of the first and second years of exposure at the two sites, some specimens were taken and subjected to a series of investigations in order to evaluate and compare any physical, chemical, and mineralogical changes that occurred after prolonged exposure. When necessary, comparisons were made between the data obtained for treated and untreated [14] samples.

Stereomicroscopic observations were carried out on the samples in order to examine the exposed surfaces. Specifically, a 5x magnification was used to obtain an overview of the sample, and a 7.5x magnification was selected to examine in detail the deposited atmospheric particulate matter. Images taken at the end of the first year of exposure show a limited amount of deposited particulate matter, with an overall good performance of the coating regardless of applied quantity, substrate, or exposure site. Differently, after two years of exposure, the amount of particulate matter deposited on the surface increased significantly for all samples and was clearly visible via stereomicroscope (Figure 2).

The largest amounts of deposited particulate matter were observed for the Noto stone samples (Figure 3).

This is probably due to the greater intrinsic roughness and porosity [13] of the material which allows the deposited particulate to be captured and retained more easily. Unlike the exposure site of Palermo, the specimens exhibited in Catania showed a greater abundance of black particles, most likely attributable to the explosive activity of the Etna volcano (greater deposition of volcanic ash). Moreover, the specimens treated with low quantities of protective coating showed yellowing of the surface probably due, not only to the deposited particulate matter, but also to the partial degradation of the applied product.

With regards to colorimetric analyses, almost all the samples from Catania and Palermo exhibit the same trends: a decrease in the value of L^* and an increase in the values of a^* and b^* after exposure (Table 4). These variations indicate a decrease in luminosity probably due to the deposition of particulate matter and a yellowing effect probably due to the partial deterioration

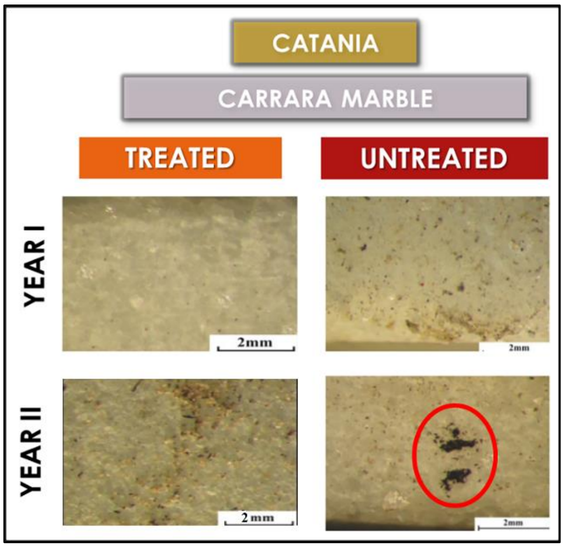

Figure 2. Surface observation under stereomicroscope of the treated (MC-T2) and untreated samples of Carrara marble taken at the end of the first and second year of exposure in Catania.

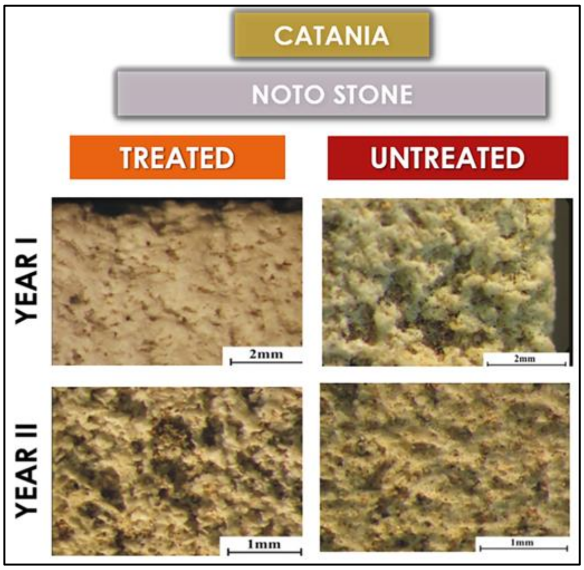

Figure 3. Surface observation under stereomicroscope of the treated (NO-T2) and untreated samples of the Noto stone taken at the end of the first and second year of exposure in Catania.

of the coating; in agreement with the stereomicroscopic observations.

Also in this case, comparisons were made between treated and untreated samples. Despite showing slight blackening and yellowing of the surfaces, the Carrara marble samples are the ones that showed the most promising results after one year of exposure. Indeed, the variation of the luminosity (ΔL^*) was lower in treated samples (-1.41) with respect to untreated ones (-2.84), highlighting at least a partial self-cleaning power of the coating (Figure 3). Instead, no significant differences could be observed for the Noto and Comiso stone samples. Almost all the specimens exposed in Catania and Palermo show moderate blackening and yellowing of the same entity on both treated and untreated samples.

Moving on to the chromatographic analyses, low concentrations of ions were found in the Carrara marble samples treated with the protective coating after one year of exposure.

Table 4. Variations in the L^*, a^* and b^* parameters after one and two years of exposure of treated samples.

Lithotype	Exposure Site	Year of exposure	ΔL^*	Δa^*	Δb^*
MC	Catania	1	-1.41	+0.53	+3.17
MC	Catania	2	-1.84	+0.44	+3.45
MC	Palermo	1	-4.82	+1.46	+6.38
MC	Palermo	2	-11.43	+1.32	+5.75
NO	Catania	1	-7.12	+0.59	-1.68
NO	Catania	2	-8.28	+1.08	-0.60
NO	Palermo	1	-7.32	+0.64	+2.27
NO	Palermo	2	-6.68	+1.22	+1.61
CO	Catania	1	-5.89	+0.87	+2.56
CO	Catania	2	-3.72	+0.69	+2.99
CO	Palermo	1	-10.31	+0.45	-3.45
CO	Palermo	2	-8.65	+2.52	+7.27

Compared to the very high values observed for the untreated samples, these results indicate a good performance of the coating (Figure 4).

Conversely, the data obtained at the end of the second year shows that the formulation no longer performs its self-cleaning function, probably aiding the deposition processes. In fact, not only the concentration of sulphates, nitrates and chlorides increases from one year to the next, but it also exceeds the values obtained for untreated specimens. It is possible that, once the effectiveness starts to decline, that the polymeric coating favours the adsorption of particulate matter onto its surface.

Instead, the data relating to the treated specimens of Noto and Comiso stone (Figure 5) shows a negative response already from the first year and, subsequently, also in the second exposure year, in both sites.

In fact, the concentrations of sulphates, nitrates and chlorides are very high if compared with those of the untreated specimens exposed to the same conditions.

Finally, FT-IR analyses were conducted in order to identify the mineralogical phases constituting the powders taken from the

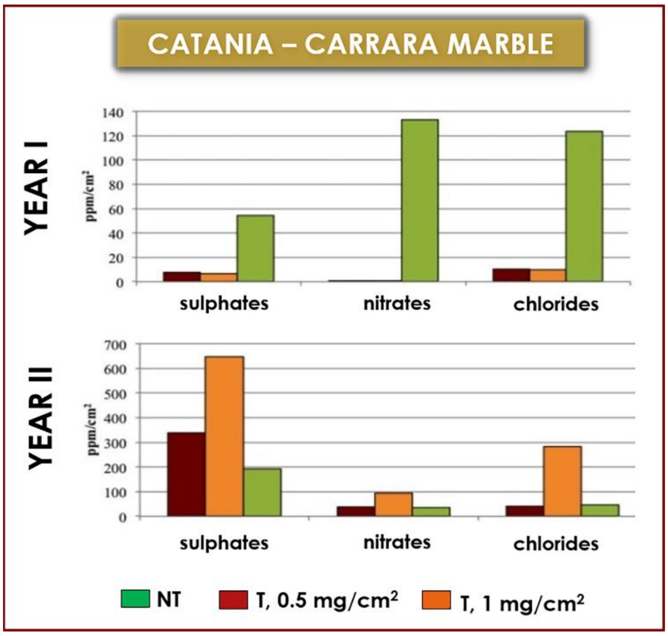

Figure 4. Bar graphs displaying the ionic concentrations of both treated (T, 0.5 mg/cm²; T, 1 mg/cm²) and untreated specimens (NT) after one and two years of exposure of the Carrara marble samples in Catania.

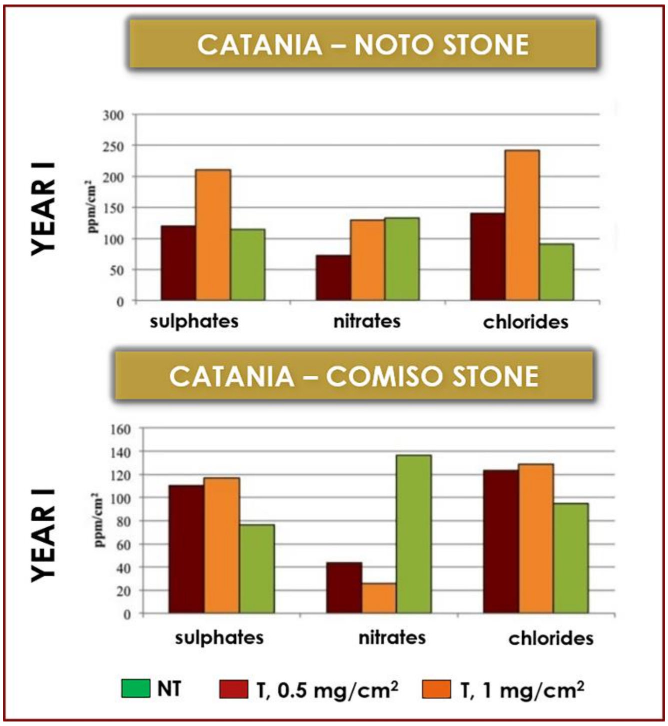

Figure 5. Bar graphs displaying the ionic concentrations of both treated (T, 0.5 mg/cm²; T, 1 mg/cm²) and untreated specimens (NT) after one year of exposure of the Noto and Comiso stone samples in Catania.

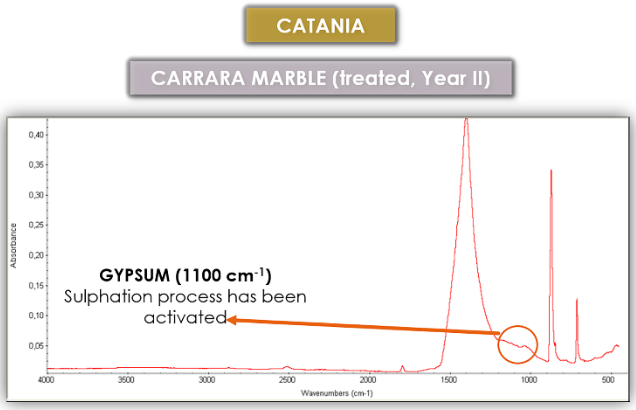

Figure 6. Representative IR spectrum of treated samples after two years of exposure.

surfaces of the specimens, both as treated and untreated, exposed in both sites. The results after one year of exposure showed a marked compositional homogeneity of all the samples. In fact, the acquired spectra revealed exclusively the presence of the characteristic bands of calcite at 1410-20, 871 and 710 cm^{-1}. In the second year of exposure, in addition to the calcite bands, a weak peak centred at 1100 cm^{-1} was also observed in all the samples (Figure 6) indicating the presence of gypsum. This result shows the initial formation of the sulphation process on the surface of the samples, which over time can lead to the formation of black crusts.

4. DISCUSSION

Probably due to the higher porosity which led to the penetration of the product in the bulk of the substrates, Fosbuild FBLE 200 proved to be not so efficient in protecting the calcarenites from degradation. A high concentration of inorganic salts, along with widespread deposition of particulate matter on the surface and darkening detected thanks to colorimetric measurements, are indices of the low performance of the tested product when applied to the Noto and Comiso stones. In fact, no significant differences were found with respect to the untreated samples.

On the other hand, results obtained from the Carrara marble samples revealed to be more promising. After one year of exposure, when compared to untreated samples, the concentration of sulphates, nitrates and chlorides is significantly lower in the treated specimen, highlighting the ability of the coating in blocking the interaction of the surface with airborne pollutants. Moreover, colorimetric analyses showed only a slight yellowing of the surface after one year, and no significant differences in terms of brightness, confirming the stability of the product. The same conclusions are further supported by the microscopic images, in which a clear difference between the treated and untreated samples can be seen.

However, results also showed that after two years of exposure, the performance of the product decreases. In fact, the concentration of sulphates, nitrates and chlorides increases, indicating the penetration of atmospheric pollutants. Also, microscopic images and colorimetric measurements showed darkening and yellowing of the surface; where the latter could be also due to partial degradation of the polymer itself. Finally, the FT-IR spectra show a weak peak around 1100 cm^{-1} which, in accordance with the high sulphate concentration detected via ionic chromatography, underlines the activation of the sulphation process.

Different application techniques and methods can be tested in the future in order to overcome the problem of pore penetration of the coating. In this regard, only two different amounts of polymeric coating were tested in this work, whereas a more thorough study needs to be conducted in order to determine the ideal quantity to be applied. Therefore, further developments include the optimization of the system employed, especially in terms of amount of product used per unit area of substrate. Instead, if the problem resides in the nature of the polymer itself, regardless of the amount used, new coatings will need to be tested and their performance compared to Fosbuild FBLE 200.

5. CONCLUSIONS

The results of this study revealed that the performance of polymeric coatings to be used in the field of cultural heritage depend on a variety of parameters, such as the nature of the coating itself, the intrinsic characteristics of the substrate and the environmental conditions surrounding the exposure site. Moreover, this study shows that, in order to evaluate the performance of a specific coating, it is crucial to perform outdoor exposure studies and not limit the evaluation to laboratory tests, which may be misleading. With regards to Fosbuild FBLE 200, this polymeric coating revealed to have possible applications for Carrara marble, whereas the performance on calcarenites is less promising.

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