A superhydrophobic and oleophobic composite coating for the protection of marble

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Abstract. A superhydrophobic and highly oleophobic coating was produced on marble by embedding silica (SiO_2) nanoparticles and a C6 fluorocarbon polymer into a polysiloxane binder. Nanoparticles were responsible for the formation of a two-length-scale hierarchical structure whereas fluoropolymer lowered the surface energy of the composite, resulting in extreme wetting properties which were evidenced by the large contact angles of water (=160°) and oil (=137°) drops. The distinctive roles of the nanoparticles and fluoropolymer on the wettability of the composite coating were elucidated using Scanning Electron Microscopy. The superhydrophobic coating offered good protection against water penetration by capillarity and had practically no significant effect on the original colour of marble substrate. Finally, it is reported that the composite coating maintained enhanced hydrophobic character, after multiple cycles of the tape peeling and the sandpaper abrasion tests.

Keywords: Superhydrophobic, Conservation, Marble.

1 Introduction

Stone-built cultural heritage is usually exposed to outdoor conditions and it is therefore subjected to decay processes, raised by the direct and indirect effects of water (rainwater or humidity), extreme temperatures and temperature fluctuations, solar radiation, micro-organisms and pollution. In the last three decades several tools and methods have been developed and devised to control the matter at the nanoscale, thus opening new avenues in conservation science and practice [1,2]. Photocatalytic and self-cleaning materials [3-5], antimicrobial nanomaterials [6-8], anti-graffiti coatings [9-11] and superhydrophobic nanostructured materials [12-14] are some examples of the enormous progress which has been recently achieved.

Superhydrophobic materials and materials of enhanced hydrophobicity, defined in Figure 1 according to the contact angle of water drop (WCA), have recently attracted considerable attention [12-14] as they are advantageous over the typical hydrophobic materials which have been suggested in the past (e.g. [15]) to impede water-induced degradation of stone-built cultural heritage. Conservation materials should meet several requirements with respect to their effects on the properties of natural stone. For example, a protective coating should not cause significant change to the original colour of stone. Consequently, a logical approach to produce superhydrophobic coatings for the protection of natural stone is to start with materials that are already recommended and used in conservation practice, such as silanes and siloxanes [16], and to try to modify their wettability. Following this approach, engineering nanoparticles (NPs) have been widely used, as additives to solutions or emulsions of silane/siloxane conservation products, to enhance surface roughness of the resulting polysiloxane+NPs composites e.g. [12,14,17-19]. Enhanced roughness is a key feature of superhydrophobic surfaces in which the Cassie-Baxter scenario is realised [20]. Moreover, a rough superhydrophobic surface is usually consisted of low surface energy materials, such as epicuticular waxes which are present on the surface of superhydrophobic plant leaves [21]. Careful selection of low surface energy agents can lead to the production of superamphiphobic surfaces which combine superhydrophobicity (WCA>150°) and superoleophobicity [22]. The latter is described by the large contact angle of oil drop (OCA>150°) and can be useful to protect buildings of the cultural heritage which are threatened by oil-based pollutants, particularly in urban areas.

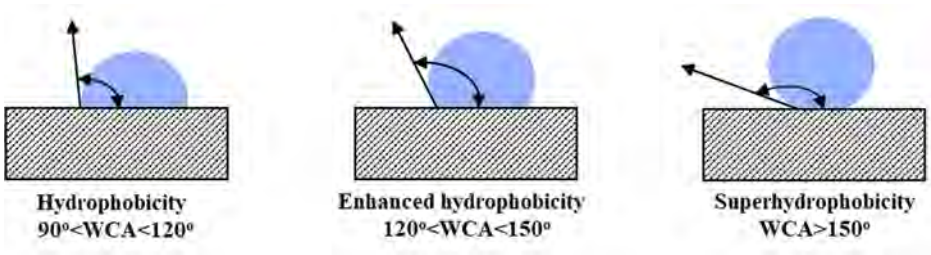

Fig. 1. Wettability regimes of hydrophobic surfaces, defined by the contact angle of water (WCA) drop on the surfaces.

In the present study, we investigate the synergistic effect of silica (SiO_2) NPs and a fluoropolymer, used as low surface energy agent, on the wetting properties of siloxane-based coatings. The latter are deposited on marble and originate from aqueous dispersions, thus avoiding the use of organic solvents. Superhydrophobicity (WCA>150°) and enhanced oleophobicity (120°<OCA<150°), are achieved on the surface of coated marble, by tunning the relative amounts of the three constituents, that are a water-borne silane system (Dynasylan SIVO 121), SiO_2 NPs and a C6 fluorocarbon polymer. Wetting properties are discussed in light of Scanning Electron Microscopy (SEM) images which reveal the surface structures of the produced coatings. Furthermore, the effects of the produced coatings on the capillary water absorption and colour of marble are

investigated. Finally, the mechanical durability of the superhydrophobic coating is tested.

2 Experimental

Dynasylan SIVO 121, which is a water-borne silane system that contains fluoroalkyl-functional groups, was diluted in distilled water to prepare a stock solution of 20 wt% (solution D). Fumed silica (SiO_2) nanoparticles (NPs) with a 7 nm mean diameter were obtained from Aldrich. NPs were dispersed in solution D. Two dispersions were produced with NP concentrations of 1% w/w (dispersion D/S) and 2% w/w (dispersion D/2S). A fluoropolymer (C6 fluorocarbon polymer, cationic) was added to dispersion D/S to the final concentration of 5% w/w (dispersion D/S/F). The dispersions were stirred vigorously for 30 min and were then sprayed for 2 s onto white marble specimens using an airbrush system (Paasche Airbrush) with a nozzle diameter of 733 μm, which was held at a distance of 20 cm from the marble surface. For comparison, solution D was also sprayed on marble. The treated marble specimens were annealed at 60° for 1h to remove residual solvent and accelerate curing.

Drops (8 μL) of distilled water and olive oil (purchased from the local market) were placed onto coated marble samples and contact angles were measured using the ImageJ software. The reported angles of water (WCA) and oil (OCA) drops are averages of five measurements. Scanning electron microscopy (SEM; TM3000, HITACHI) was employed to study the surface structures of the treated marble samples. The L*, a*, b* colour coordinates of the CIE 1976 scale were measured using a PCE-CSM 2 spectrophotometer (PCE Instruments Corp). The reported results are averages of three measurements, which were carried out on three different spots of each sample.

Absorption of water by capillarity was measured by the gravimetric absorption technique, according to the EN 15801 (CEN, 2009) standard using dried weighted coated and uncoated marble blocks (5x5x2 cm). The treated samples were placed with the coated surface (5x5 cm) onto a filter paper pad (Whatman paper, No. 4) and were partially immersed up to about 0.3 cm in distilled water. The four lateral faces (5x2 cm) of each specimen were covered by waterproof Teflon tape. The same procedure was applied to test uncoated marble. Weight increase by water absorption was measured periodically for 48 h in total.

The marble sample with the D/S/F coating was subjected to the tape peeling and sandpaper abrasion tests. WCA was measured for several cycles until WCA on the D/S/F coating became <120°, suggesting that enhanced hydrophobicity was lost. The tape peeling test was applied using a Scotch Tape 600 (3M) according to the specifications described in ASTMD-3359 97. Twenty-five (25) cycles were applied in total. WCA was measured in three different areas of the sample after each cycle. For the abrasion test, the sample was placed face-down to sandpaper (mesh 180) with a weight of 100 g placed on top of it, corresponding to a total pressure (including the weight of the sample) of about 0.92 kPa. Then, the sample was moved for 10 cm along a ruler, rotated by 90° and moved for 10 cm along the ruler again. This process was defined as one complete abrasion cycle which guarantees that the specimen is both longitudinally

and transversally abraded in each cycle while maintaining movement in one direction. Fifteen (15) cycles were applied in total. WCA was measured in three different areas of the sample after each cycle.

3 Results and discussion

3.1 Wetting properties and structure

Figure 2 shows the results of contact angle measurements of water (WCA) and oil (OCA) drops on marble specimens coated by (i) Dynasylan (D), (ii) Dynasylan with 1% w/w SiO_2 NPs (D/S), (iii) Dynasylan with 2% w/w SiO_2 NPs (D/2S) and (iv) Dynasylan with 1% w/w SiO_2 NPs and fluoropolymer (D/S/F). For the D surface, WCA and OCA are 116° and 88°, respectively, and they increase to 133° and 112°, when 1% w/w NPs are added to the preparative dispersion of the deposited coating (D/S surface). Further increase of the NP concentration to 2% w/w has practically no effect on WCA which, according to Figure 2, is stable for the D/S and D/2S surfaces. A slight increase of OCA is observed when the NP concentration increases from 1 (D/S) to 2% (D/2S) w/w but this difference is almost within the experimental error.

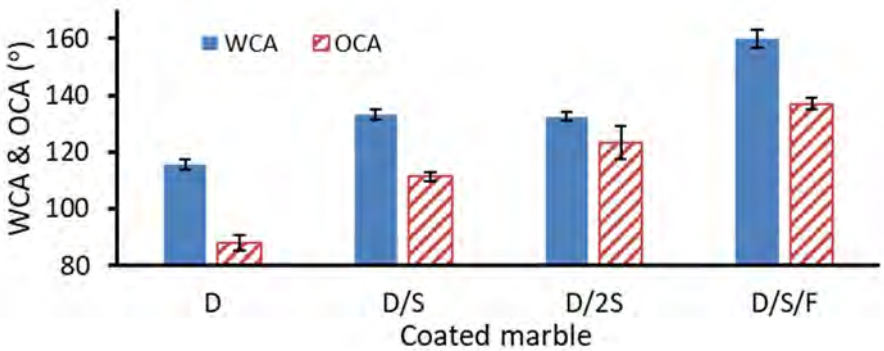

Fig. 2. Contact angles of water (WCA) and oil (OCA) drops on marble samples coated with four different materials: (i) Dynasylan (D), (ii) Dynasylan with 1% w/w SiO_2 NPs (D/S), (iii) Dynasylan with 2% w/w SiO_2 NPs (D/2S) and (iv) Dynasylan with 1% w/w SiO_2 NPs and fluoropolymer (D/S/F).

The effect of the concentration of the SiO_2 NPs is revealed in the SEM images of Figures 3a, 3b and 3c. No particular structure is observed on the D surface (Figure 3a) which is affected only by the spraying deposition process and the roughness of the underlying marble substrate. The D/S surface (Figure 3b) is structured, as micro-clusters are formed which consist of nanostructures [14,17]. Therefore, a two-length-scale hierarchical structure is formed on the D/S surface [14,17] which is responsible for the large WCA and OCA, reported in Figure 2. The SEM images of Figures 3b and 3c suggest

that there is an almost negligible difference in the structures of the D/S and D/2S surfaces: the micro-clusters in the D/2S surface are slightly larger compared to the D/S surface. This small difference had no effect on the WCA which, according to Figure 2, was practically the same for the D/S and D/2S surfaces. OCA, however, slightly increased with the NP concentration (Figure 2) as oil drops are more sensitive to slight changes of the surface structure compared to water drops [22]. In sum, it is reported that the structures of the D/S and D/2S surfaces are overall quite similar. Previously published studies on the wetting properties of polymer+NPs composites, showed that at a specific-critical value of NP concentration, the hierarchical structure becomes almost saturated [23,24]. Further increase of the NP concentration, beyond this critical value does not affect dramatically the surface structure and the WCA of the composite material [14,17,23,24]. The critical value of the NP concentration depends on the type of the polymer and the NPs which are selected for the production of the composite coating. The SEM images of Figures 3b and 3c suggest that for the composite studied herein, the 1% w/w NP concentration is adequate to reach the saturation point, as no major difference is observed between the structures of the D/S and D/2S surfaces and their corresponding WCAs. Taking into consideration that (i) the wettabilities of the D/S and D/2S coatings are similar and (ii) the increasing concern about the potential health and environmental risks associated with the use of NPs [25,26], the low NP concentration of 1% w/w was selected to prepare the fluorinated D/S/F coating.

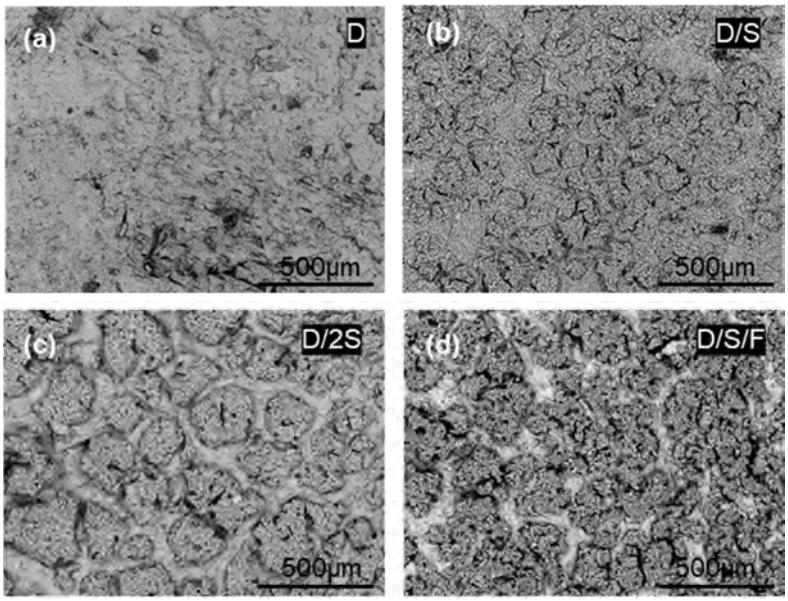

Fig. 3. SEM images showing the surface structures of coated marble samples; their wettabilities were revealed in Figure 2.

According to the results of Figure 2, elevated WCA (=160°) and OCA (=137°) were measured on the D/S/F surface suggesting that superhydrophobicity (WCA>150°) and

enhanced oleophobicity (120°<OCA<150°) were achieved [2]. The structure of the D/S/F surface is revealed in the SEM image of Figure 3d and shows no difference from the structure of the D/S (Figure 3b) surface. Consequently, the fluoropolymer did not have any noticeable effect on the structure of the composite coating. However, the fluoropolymer reduced the surface energy of the surface and induced superhydrophobicity to the D/S/F surface, as evidenced by the extremely large WCA and the elevated OCA which were reported in Figure 2.

The non-wetting properties of the D/S/F coating are demonstrated in the photographs of Figure 4. In Figures 4a and 4b resting water drops are shown. The drops were carefully placed on the surface of marble specimens, treated with D/S/F coating. In the subsequent snapshots of Figure 4c it is shown that a drop bounces off when it impacts a tilted marble sample, treated with D/F/S coating.

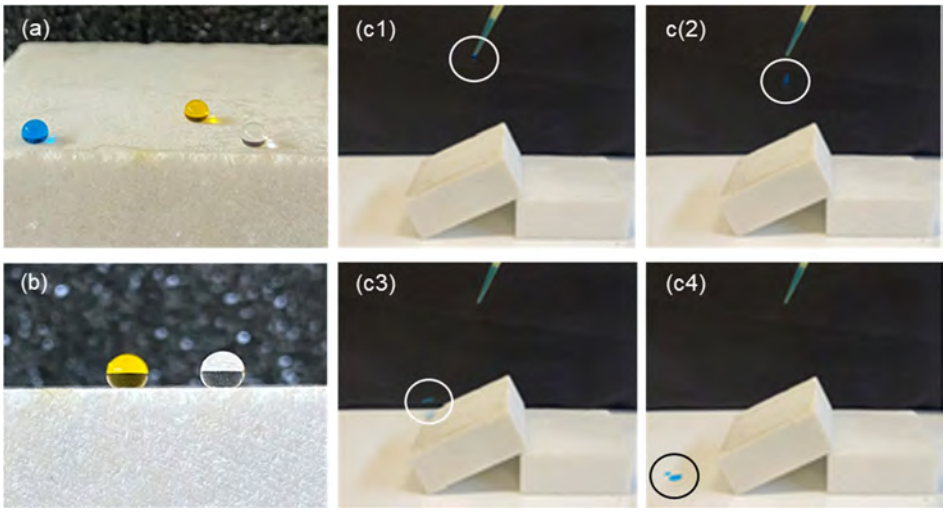

Fig. 4. (a,b) Photographs which show resting coloured water drops on the superhydrophobic D/S/F surface. (c1-c4) Subsequent snapshots of a water drop bouncing on D/S/F coating on marble. The motion of a water drop is captured by the circles.

3.2 Colourimetry and capillary water absorption

The colour changes (ΔE*) of marbles due to the deposition of the D, D/S and D/S/F coatings were calculated using the following formula:

$$\Delta E^* = \sqrt{(L_c^* - L_u^*)^2 + (a_c^* - a_u^*)^2 + (b_c^* - b_u^*)^2} \quad (1)$$

where L*, a* and b* are the brightness, the red–green component and the yellow–blue component of the CIE 1976 scale, respectively. The "c" and "u" subscript characters indicate the coated and uncoated samples, respectively. The results are summarized in Table 1. The applications of the D and D/S coatings have a negligible optical effect on the appearance of white marble, as both treatments lead to colour changes, lower than

the ΔE* limit which can be perceived by human eye (ΔE*=3) [27]. The application of the superhydrophobic D/S/F coating causes a noticeable colour change to marble (ΔE*=3.61) which, however. is lower than the acceptable limit for conservation purposes (ΔE*<5.0) [5,28].

Table 1. Color changes (ΔE*) calculated using Equation 1.

Coating	ΔE*
D	0.82±0.37
D/S	2.00±0.46
D/S/F	3.61±1.41

The test for capillary water absorption was carried out for marble samples coated by D, D/S and D/S/F and, for comparative purposes, for uncoated bare marble specimen. The amount of the absorbed water at time t_i per unit area (Q_i) was calculated as follows:

$$Q_i = \frac{w_i - w_o}{A} \quad (2)$$

where, w_o is the initial weight of the sample prior to the test, w_i is the weight of the sample after being in contact with water for time t_i and A is the sample's area (5x5 cm) which had been in contact with liquid water during the test. The results are shown in Figure 5 and suggest that the amount of absorbed water initially increases rapidly with t_i and becomes constant for prolonged contact of the samples with liquid water. This behaviour of Q_i with respect to t_i has been commonly reported in several studies which investigated the capillary absorption of water by treated and untreated natural stones e.g. [4,18,27,28]. According to Figure 5, the D/S/F coating offered slightly better protection against capillary water absorption, compared to the D/S coating. This trend is in agreement with the hydrophobic characters of the two coatings which were evaluated through WCA measurements: the results of Figure 2 showed that a larger WCA was measured on the superhydrophobic D/S/F surface, compared to the WCA on the hydrophobic D/S surface. However, despite the large difference reported in the WCAs of the two surfaces (Figure 2), their corresponding difference in capillary water absorption (Figure 5) is extremely small. It is stressed that WCA is not a safe quantity to predict the wettability of a surface after being in prolonged contact with a large amount (and not just a drop) of water [14]. For example, it was shown that even a superhydrophilic composite material can offer protection against water absorption, provided that a hydrophobic component is included in the material's formulation [4].

Furthermore, Figure 5 shows that the D/S (or the D/S/F) composite coating gave better results than the D coating. Consequently, SiO_2 NPs contributed substantially to the reduction of water absorption, as the saturated Q_i measured for marble coated by D/S is lower than the corresponding result obtained for the marble sample coated by D. However, the effect of the fluoropolymer on capillary water absorption is not very significant as the values of the saturated Q_i measured for marbles coated by D/S and D/S/F are roughly comparable.

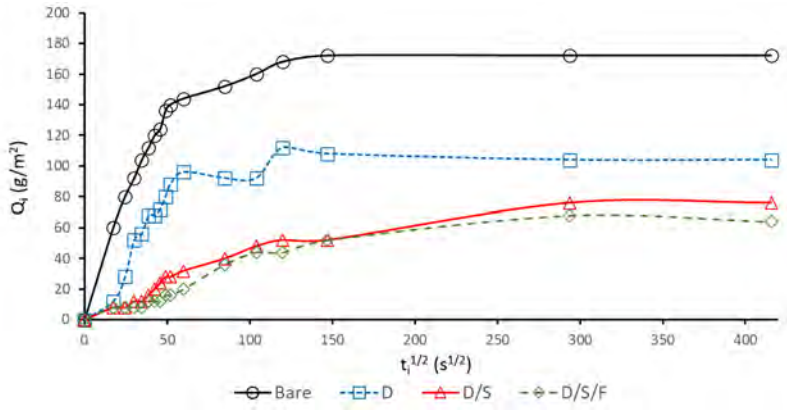

Fig. 5. Results obtained for the test of water absorption by capillarity: amount of water absorbed per unit area (Q_i) vs treatment time (t_i) for bare, uncoated marble and marble samples coated by D, D/S and D/S/F.

3.3 Mechanical durability

Coatings which are applied for the protection of stone-built heritage are usually not subjected to mechanical wear and are not designed to withstand loads. Hence, the mechanical durabilities of protective coatings for natural stones are usually not tested. Consequently, the mechanical test assessment of the D/S/F coating, described in the following, can be considered as an approach which aims to test the performance of the coating under extreme-severe conditions. The latter are unlikely to occur in real-life application (i.e. if, for example, the coating is applied on a heritage building) with the exception of building vandalism. In sum, the tests described below constitute a very rigorous evaluation of the coating performance which was designed for the protection of stone-built heritage.

The mechanical durability of the D/S/F coating was tested following the procedures of the tape peeling the sandpaper abrasion tests. WCA was measured for multiple cycles, until it became lower than 120° (WCA<120°) suggesting a transition of the wettability of the D/S/F coating from the enhanced hydrophobic to the hydrophobic regime (Figure 1). It is noted that the value of 120° is higher than the WCA (=115.6°) which was measured on the surface of the fresh D coating (Figure 2). The latter was applied on marble, using the solution which is provided by the manufacturer without any modification. The results are shown in Figure 6 and suggest that the D/S/F coating maintained an enhanced hydrophobic character (120°<WCA<150°) for 24 and 14 cycles, of the tape peeling (Figure 6a) and the sandpaper abrasion (Figure 6b) test, respectively. Consequently, the produced D/S/F coating showed a satisfactory mechanical durability. The D/S/F coating had to be subjected to 25 tape peeling cycles and 15 abrasion cycles to reach the WCA value of ≈115° which was measured on fresh D coating.

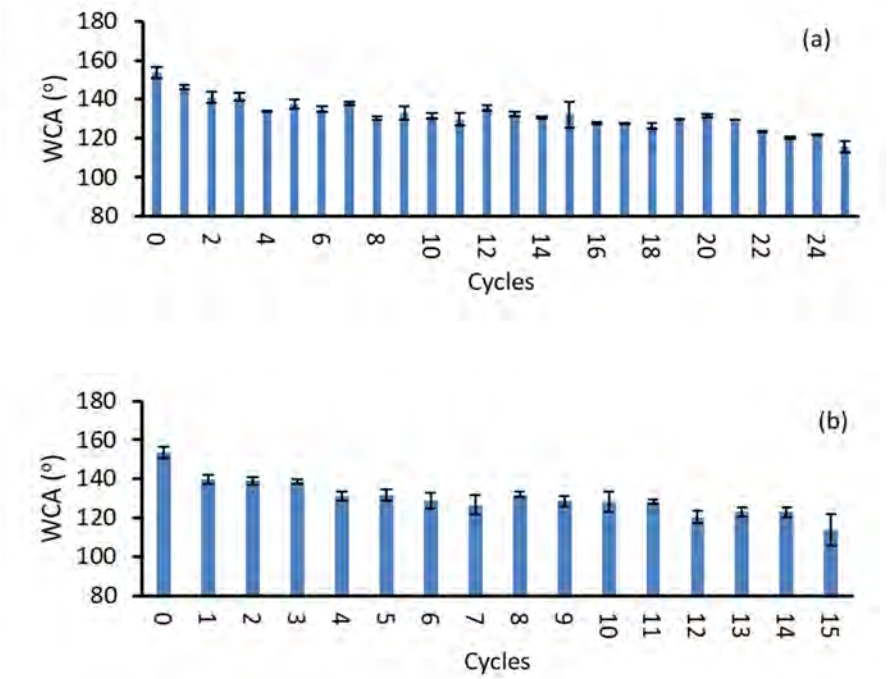

Fig. 6. Contact angles of water (WCA) drops on marble samples, coated by the D/S/F composite material, during (a) tape peeling and (b) abrasion cycles.

4 Conclusions

Non-wettable surfaces in nature consist of two-length-scale hierarchical structures and are coated by low surface energy materials. Following nature's example, a biomimetic route was devised to produce a superhydrophobic and highly oleophobic coating by embedding two additives, that were silica nanoparticles and a C6 fluorocarbon polymer, into a polysiloxane binder. The latter was the main component of the composite coating which was tested for the protection of marble. The colour change of marble induced by the superhydrophobic coating was ($\Delta E^*=3.61$) within the acceptable limit for conservation purposes ($\Delta E^*<5.0$). The superhydrophobic composite coating offered better protection against capillary water absorption, compared to the pure (without additives) hydrophobic binder. Considering that the potential application of the produced coating is the conservation of cultural heritage, it is reported that the coating exhibited very good mechanical durability, according to the results of the tape peeling and the sandpaper abrasion tests.

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