1. Introduction
Conservation of historical buildings is an important issue. The environmental conditions seriously affect the monumental stones. The protection of the cultural heritage buildings and monuments by surface treatment with polymers is a common practice due to their ability to form a protective layer on the monumental surface as well as to control the transport of different fluids from the surface to monument interior [Price, 1996; Khallaf, 2011, 592]. Different classes of synthetic organic coatings have been used for this purpose and in particular acrylic and silane polymers, perfluoroethers, and fluorinated polyolefins. [Alessandrini, 2000, 962; Castelvetro, 2002, 57]

In nature many plant surfaces exhibit enhanced water repellency, which is attributed to their textured surfaces with hierarchical micrometer- and nanometer-sized structures in connection to hydrophobic surface components. [Wu, 2005, 198] In the case of water repellent leaves, airborne dust particles can be removed by water droplets that roll off the (self-cleaning) surfaces: this effect is called “Lotus-Effect”. [Chen, 2013, 1] This remarkable ability of nature has inspired numerous researchers to fabricate surfaces which could imitate these superhydrophobic features, by using numerous techniques such as the deposition of nanoparticles-polymer composites on smooth surfaces. [Zielecka, 2006, 160; Ono, 2008, 55] Because of the two-length-scale hierarchical structure and the hydrophobic character of the surface, enhanced water repellency (superhydrophobicity) is achieved. It is worth noting that inorganic nano-oxides, such as silica and titania, improve the performance of materials used in conservation field. [Licciulli, 2007, 437] In particular recently, the application of photocatalytic coatings on stone has been investigated for providing surface protection and self-cleaning properties. [Hsieh, 2005, 240]

In the present study a commercially available silane polymer, used as protective agents, have been tested on three different substrates, Carrara/Botticino marbles and Angera stone to improve their hydrophobicity features. Then the conservation effectiveness of inorganic nanoparticles/polymer composite coatings was evaluated when applied on the differently porous stone substrates.

2. Experimental
From each stone (Angera (A), Botticino (B) and Carrara (C)), small blocks were obtained and polished with commercial grade diamond abrasive disks. (Fig.1)
The stones were treated with commercial water-repellent protective agent: among the several commercially available resins, ALPHA® SI30 was adopted in the present work since it is soluble in aqueous medium and representing an eco-friendly solution (low toxicity for human health and environment). Moreover, the performance of superhydrophobic hybrid layers (titania nanoparticles + ALPHA® SI30) deposited onto the stone surfaces was evaluated in
order to have a comparison with what obtained by using only water-repellent protective agent. Different syntheses have been tested to improve the stability and the transparency of the titania sol. A solution of $\text{Ti(OC}_3\text{H}_7\text{)}_4$ in ethanol was stirred for 15 min at room temperature; then a fixed amount of HCl 37% and a non-ionic surfactant (Lutensol ON70), dissolved in ethanol were added to the alkoxide solution. The mixture was maintained under stirring for 10 min. Further, the titania sol was mixed with the siloxane polymeric agent ALPHA®SI30 (10 mL -7(Alpha):3(TiO$_2$). The as-prepared polymer-particle mixtures were sprayed onto three different samples through a nozzle of 700 μm using an airbrush system (Asturo airbrush). The quantity of the spraying mixture was kept steady by controlling the spray pressure (2.5 bars) and the spray time (3 s). The treated specimens were subsequently kept at room temperature for 5 days. After evaporation of the solvent, investigation of the surface properties and evaluation of stone protection efficiency were carried out. The bare and coated samples were characterized by several techniques, such as XRD, SEM-EDS, FTIR, TGA, IC, CIE-Lab colorimetric analyses and contact angle measurements.

3. Results and discussion

3.1. From hydrophobic to superhydrophobic behaviour

Static contact angle ($\theta$) measurements on the stone surfaces were performed in order to know their wetting properties. Figure 2 shows the water contact values measured on bare and treated samples. All the obtained values are averaged over ten different measurements and the relative standard deviation is $\leq 3^\circ$ for each set of analysis. The low values for the bare stones ($< 70^\circ$) defines a strong attraction between liquid and solid surface; the drop of water is often slowly absorbed from the stone, especially in the case of Angera, the stone characterized by the highest porosity. The application of AlphaSI30 coating leads to hydrophobic materials ($90^\circ < \theta < 100^\circ$).

In order to improve the water repellency of the coatings, nanoparticles deposition techniques was used to induce superhydrophobicity. This method leads to the formation of a rough two length-scale hierarchical structure that exhi-
bits completely water repellent properties. Static contact angle measurements show that all hybrid samples exhibited superhydrophobic behaviour with average contact angles higher than 140° (Fig. 2). Thus, self cleaning materials were obtained: the water drops, deposited on the layers, bounced and rolled off the stones.

3.1. Ageing test

In order to investigate the stability of the coatings, accelerated aging tests by UV irradiation (500W, 250-315 nm) were carried out. Colorimetric measurements (CIELab) were performed to verify the color modification (yellowing) of the protective film due to solar exposition.

Color and static contact angle measurements were carried out for hydrophobic (stone+AlphaSI30) and superhydrophobic (stone+AlphaSI30+titania sol) systems before and after 10h of UV exposure (Table 1). The treated samples did not show both a visible colour and contact angle variations even after UV irradiation (always $\Delta E^* \leq 4$, $\Delta \theta^* \leq 3$).

Finally, chemometric analysis was performed on reflectance spectra acquired for each stone before and after each treatment. This analysis allowed to bring out similarities and differences in the behavior of the material respect the different treatments (Figure 3).

As concerns Angera stone two main groups are present in the score plot: one formed by the bare samples and the other one composed by the stones covered either with the Alpha resin or by the resin Alpha with TiO$_2$ sol, both

![Fig. 3 - PCA score plot reporting the bare stones (A=Angera; B=Botticino; C=Carrara), the stones coated with Alpha resin, the stones coated with TiO$_2$ (defined sol in the graph) and the samples aged by UV radiation for 10 hours](image-url)

<table>
<thead>
<tr>
<th>Stone/treatment</th>
<th>$\Delta E$</th>
<th>$\Delta \theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A+AlphaSI30</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>A+AlphaSI30+titania sol</td>
<td>2.0</td>
<td>-2</td>
</tr>
<tr>
<td>B+AlphaSI30</td>
<td>1.9</td>
<td>-</td>
</tr>
<tr>
<td>B+AlphaSI30+titania sol</td>
<td>0.9</td>
<td>+3</td>
</tr>
<tr>
<td>C+AlphaSI30</td>
<td>3.1</td>
<td>-</td>
</tr>
<tr>
<td>C+AlphaSI30+titania sol</td>
<td>3.0</td>
<td>-3</td>
</tr>
</tbody>
</table>

Table 1 - Variation of CIELab parameters (DE) and contact angles before and after UV ageing for hydrophobic (stone+AlphaSI30) and superhydrophobic (stone+AlphaSI30+titania sol) systems
untreated (i.e. without UV) and exposed to UV radiation (10 hours). As already deduced from the values obtained from CIELab analysis, the samples change their color only slightly (ΔE<5) thus confirming the complete transparency of the protective treatments applied.

In the case of Botticino marble the points are all grouped in a single area denoting a strong persistence of the material color characteristics even after the treatments. Respect to Angera stone and Botticino marble, Carrara marble does not show a clear splitting of points in the graph probably due to the intrinsic properties of this material. In fact a great distribution of the points can also be observed for the bare samples due to the inhomogeneity of the marble color, sometimes characterized by grey veins.

This kind of approach could be very useful to monitor color variation of the materials during time especially if the aim is to control the degradation and alteration of the material once the protective coating was applied.

References


