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Advanced Mortar Coatings for Cultural Heritage Protection. Durability Towards Prolonged UV and Outdoor Exposure

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Advanced Mortar Coatings for Cultural Heritage Protection. Durability Towards Prolonged UV and Outdoor Exposure

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Abstract

In the present work two kinds of hybrid polymeric-inorganic coatings containing TiO₂ or SiO₂ particles and prepared starting from two commercial resins (Alpha®SI30 and Bluesil®BP9710), were developed and applied to two kinds of mortars (an Air hardening calcic Lime Mortar, ALM and a natural Hydraulic Lime Mortar, HLM) to achieve better performances in terms of water repellence and consequently damage resistance. The two pure commercial resins were also applied for comparison purposes. Properties of the coated materials and their performance were studied using different techniques such as contact angle measurements, capillary absorption test, mercury intrusion porosimetry, surface free energy, colorimetric measurements and water vapor permeability

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1 tests. Tests were also performed to determine the weathering effects on both the commercial and the
2 hybrid coatings, in order to study their durability. Thus, exposures to UV radiation, to UV
3 radiation/condensed water cycles and to a real polluted atmospheric environment have been
4 performed. The effectiveness of the hybrid SiO₂ based coating was demonstrated, especially in the
5 case of the HLM mortar.
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10 **Keywords**

11 Mortars; hybrid coatings; cultural heritage; surface modification; ageing; exposure.
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15 **1. Introduction**

16 The environmental conditions (*i.e.* temperature, humidity and air pollution) can seriously
17 affect the monumental stones and for this reason conservation of historical buildings is nowadays an
18 important issue. Among the main agents responsible for stones deterioration, atmospheric pollution
19 seriously affects buildings materials (Doehne and Price 2010; Toniolo et al. 2015). Carbon, sulphur
20 and nitrogen oxides together with aerosol particulate matter, such as smoke, provoke surface soiling
21 (Zielecka and Bujnowska 2006; Quagliarini et al. 2012; Goffredo 2013). Actually, the main
22 degradation product is calcium sulphate from the transformation of CaCO₃, induced by the reaction
23 with the acids, *i.e.* sulphuric acid and nitric acid, contained in rain.
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40 The presence of moisture can enhance the damaging activity primarily in the case of interior
41 with a high intrinsic porosity. Polymeric materials have been widely studied as protective coatings
42 to limit the process of deterioration of building materials exposed to the environment, due to
43 condensed water, pollution and salts formation. Thus, the protection of the cultural heritage
44 buildings and monuments by surface treatment with polymers is a convenient practice to reduce
45 maintenance problems. Their ability to form a protective layer on the monument surface limits the
46 transport of different fluids from the surface to interior. However the simultaneous fulfillment of
47 protection efficiency, transparency, stability and durability both to climate alteration and
48 chemical/mechanical attacks is nowadays a challenge (Toniolo et al. 2015). Traditionally acrylic
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1 and vinyl polymers, organosilicone compounds and fluorinated film forming agents have been
2 applied to stone monuments as protective hydrophobic coatings against deterioration (Zielecka and
3 Bujnowska 2006).
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7 Moreover, in the last few years, oxide-based nanomaterials have been frequently applied for
8 restoration and conservation of works of art. In this way transparent and self-cleaning treatments,
9 that ensure a better preservation of stone elements, may be obtained. Recently transparent-
10 hydrophobic mixed PDMS (polydimethylsiloxane)–TiO₂–SiO₂ coatings have been proposed and no
11 color modification of marble surface have been observed (Cappelletti and Fermo).
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19 In our previous study (Cappelletti et al. 2015b) an Air hardening calcic Lime Mortar (ALM)
20 and a natural Hydraulic Lime Mortar (HLM) were used as representative substrates for historical
21 mortars, and commercially available Si-based resins (Alpha®SI30 and Silres®BS16) were adopted
22 as protective agents to give hydrophobicity features to the artificial stones. In particular the
23 effectiveness of the two commercial resins in reducing salt formation (sulphate and nitrate), induced
24 by the interaction of the mortars with the atmospheric pollutants, was demonstrated in the case of
25 the HLM mortar.
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36 Here, the same mortars were used as substrates and two inorganic/organic hybrid coatings
37 (SiO₂ nanoparticles + alkylpolysiloxanes emulsion (Bluesil®BP9710) and nano-TiO₂ nanoparticles
38 + Alpha®SI30) were applied to increase the hydrophobicity features with respect to that of the pure
39 resins. The surface properties of the coatings and their performance as protective agents were
40 studied using different techniques such as contact angle measurements, test, colorimetric
41 measurements, capillary absorption and water vapor permeability tests and salt crystallization
42 resistance. Finally, the durability and the effect of aging caused by the prolonged exposure to
43 controlled and real environmental conditions will be discussed in details.
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2. Materials and methods

2.1 Mortars preparation

Samples of an Air hardening calcic Lime Mortar (ALM) and a natural Hydraulic Lime Mortar (HLM) were produced following the detailed procedure described in our previous work (Cappelletti et al. 2015b). Before any test, the substrates were previously seasoned for at least three months and then cut in the desired shape. ALM samples are white and brittle, whereas HLM samples are hard and brownish blocks.

2.2 Hydrophobic commercial resins

Two commercially available resins were used both to protect the substrates and to modify the wettability features of the pristine mortars. Alpha®SI30 (purchased by Sikkens) is a silicon based solvent-borne resin already characterized in our previous works (Fermo et al. 2014). It was found to be composed by a mixture of a trimethoxy silane, with a quite long chain (*i.e.* iso-octyl) and a PDMS (poly-dimethylsiloxane). The present resin was applied as it is without any further dilution. Instead, Bluesil®BP9710 (by Bluestar Silicones) is a concentrated of O/W emulsion (phase volume, $\phi = 0.44$) with an alkylpolysiloxane oligomer base, designed to protect surfaces against moisture. It is stabilized by exploiting a nonionic emulsifier at alkaline pH (around 10). It was applied after a 1:11 dilution in water.

2.3 Hybrid coatings

The hybrid coatings were produced by addition of inorganic nanoparticles to the resins in order to obtain a modification on the surface roughness of the mortars. Only two combinations between resins and inorganic nanoparticles were achieved to ensure the compatibility among the different raw materials of the formulation.

SI30 TiO₂ hybrid was prepared by adding home-made TiO₂ nanoparticles to Alpha®SI30 resin. the titania synthesis was carried out by simple hydrolysis and poly-condensation of a titanium alkoxide, to obtain a stable and transparent sol (Cappelletti et al. 2015a), stable for several weeks at

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2 room temperature and without any control of atmospheric humidity. The mixture of the obtained
3 titania sol and the siloxane polymeric agent (1 : 1) was stirred vigorously to obtain a homogeneous
4 dispersion.
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7 Instead, BP9710 SiO₂ hybrid was obtained by mixing Bluesil®BP9710 with a transparent
8 suspension of SiO₂ nanoparticles (LUDOX®LS, from Sigma Aldrich, $\phi = 0.30$). The latter
9 powders, electrostatically stabilized at pH 8, have an average particle size of 12 nm with a specific
10 surface area of 220 m² g⁻¹. The final concentration of the silica nanoparticles in the hybrid
11 formulation was around 1%.
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19 The application of coatings on mortars surfaces was carried out by using a brush in a
20 homogeneous manner, in order to reproduce everyday working conditions. All the clad mortars
21 were dried for 24 hours in an oven at constant temperature (50°C).
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27 *2.4 Sample characterizations*

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29 Water Static Contact Angle (SCA) measurements of water on bare and coated mortars were
30 performed on a Krüss Easy instrument. A drop of 3 μ L was gently placed on the surface; the drop
31 profile was extrapolated using appropriate fitting functions depending on the drop shapes.
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67 SFE (Surface Free Energy) and the relative polar and disperse components were evaluated
68 by using the Owens–Wendt–Rabel–Kaelble (OWRK) method (Owens DK 1969; Cappelletti et al.
69 2013), by using different high purity solvents (*i.e.* diiodomethane, glycerol, ethylene glycol,
70 diethylene glycol).
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73 Colorimetric measurements were performed to verify the color modification of the
74 protective films after both the deposition of the protective coatings and the various aging tests (see
75 in the following). The chromatic coordinates were calculated according to the Commission
76 Internationale d'Eclairage (CIE Lab method) (Cappelletti et al. 2015b), starting from diffuse
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1 reflectance spectra acquired in the UV/vis spectral range from 800 to 350 nm with a
2 JASCO/UV/vis/NIR spectrophotometer model V-570 instrument. According to the literature, no
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4 significant variation occurs when $\Delta E^* < 3$ (La Russa et al. 2012; Esposito Corcione et al. 2014).
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7 The Water Vapor Permeability (WVP) of bare and coated mortars was evaluated by means
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9 of the methodology described in the European Standard Norma EN 15803 (Manoudis et al. 2009;
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11 UNI EN 2009).
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14 Capillary water absorption measurements were performed on bare and coated materials by
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16 the gravimetric sorption technique, as described in the Italian protocol Norma UNI 10859 “Cultural
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18 Heritage – Natural and artificial stones – determination of water absorption by capillarity”
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20 (NORMA UNI 2000; Cappelletti et al. 2015b).
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24 Porosity and pore size distributions were determined by MIP (Mercury Intrusion
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26 Porosimetry), through a Micromeritics Autopore IV with a maximum pressure of 400 MPa,
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28 according to the procedure reported in a previous work of some of the co-authors of this paper
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30 (Ruffolo et al. 2014). Measurements were performed on samples with the same weight (1.5 g) to
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32 standardize testing and minimize errors. This technique allowed to determine pore sizes ranging
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34 from 0.003 to 40 μm .
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39 *2.5 Controlled aging tests and exposure*

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42 Various aging tests were performed to evaluate the stability of the protective coatings: *i*)
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44 under UV irradiation (500W halide lamp, 215-365 nm, for 50 h) and *ii*) by using a QUV/basic
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46 accelerated weathering tester, equipped with UVA-340 lamps (optimal sunlight conditions in the
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48 critical short wavelength region in the range 295 – 365 nm) for a period of about 1000 h. This kind
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50 of test was used to simulate the critical conditions through cycles of moisture condensation and UV
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52 irradiation.
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56 Finally, the samples were exposed in a typical urban environment in Milan. The exposure
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58 site was in the Milan University Campus, an area quite far from the city centre, which is considered
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1 representative of a typical urban background. The exposure tests were carried out for 7 months
2 during winter (15 November 2014 - 15 May 2015). Ion Chromatography (IC) was employed for the
3 analysis of soluble salts (Cl^- , NO_3^- and SO_4^{2-}) in the exposed mortars. The samples were prepared
4 according to a procedure reported elsewhere (Cappelletti et al. 2015b).
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10 **3. Results and discussion**

11 *3.1 Properties of bare and coated mortars*

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13 ALM and HLM substrates show a hydrophilic character ($\theta < 90^\circ$) leading to the complete
14 and almost immediate absorption of water drops. For this reason the evaluation of the water static
15 contact angles (Table 1, 2nd column) has been performed by using the first frames taken by the
16 video registration of deposition procedure. Both the substrates were produced with the same coarse
17 aggregate ($0.5 \text{ mm} < d < 4\text{mm}$) demonstrating an intrinsic variability, which is reflected in high
18 standard deviations (Table 1). Moreover, SFE determination through the OWKR method leads to
19 consistent values determining high polar surfaces for both the bare substrates (Table 1, 3rd and 4th
20 columns).
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35 After the treatment with all the pure water-repellent agents (Alpha@SI30 and
36 Bluesil@BP9710), a successful hydrophobization of the substrates occurs ($\theta < 140^\circ$, Table 1, 2nd
37 column), as already pointed out in our previous work (Cappelletti et al. 2015b). Particularly, both
38 the hybrid coatings increase the surface hydrophobicity reaching the superhydrophobic properties
39 only in the case of HLM substrate (Table 1, 2nd column), hence highlighting, once again, the pivotal
40 role also played by the intrinsic variability of AL and HL mortars themselves.
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50 Furthermore, SFE evaluation, carried out for the samples treated with the commercial resins
51 SI30 and BP9710, shows a drastic decrease in the polar component of the total surface free energy
52 (Table 1, 2nd column), as it was expected. On the contrary, for hybrid systems, it has not been
53 possible to calculate the SFE, since contact angles with water and highly polar solvents could not be
54 determined ($\theta > 150^\circ$).
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1 Thus, by comparing the performances of the two commercial resins, Alpha®SI30, as
2 reported in our previous work, gave the best results especially when applied onto the hydraulic lime
3 mortar, probably due either to the presence of an adequate micro-porosity (Cappelletti et al. 2015b)
4 or to the different interaction with the resin in the presence of silicates (Fermo et al. 2014).
5 Moreover, as concern the hybrid coatings performance, the combination of the intrinsic porosity of
6 HLM with the nano- and micro-scale surface roughness (induced by the introduction of
7 nanoparticles) has probably led to the super-hydrophobicity features ($\theta > 150^\circ$). This is an
8 interesting result, especially for water-based system, since the environmental issues arising from the
9 use of a solvent-borne system are a well known drawback (Zeno W. Wicks et al. 2007).
10 Furthermore, all the protective coatings are invisible to naked eye ($\Delta E^* < 3$).
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24 Moreover, since the water vapor transmission rate through the mortars must not be reduced
25 after the coating treatments (Zielecka and Bujnowska 2006), a little change in the samples pore
26 structure is an important result. In Figure 1, as result of the WVP test, the cumulative mass change
27 is shown ($|\Delta m| = m_i - m_0$, where m_i and m_0 is the mass of the test assembly respectively at time t_i
28 and t_0 , in kg) for each set of successive weighing of the specimens versus time. Surprisingly, both
29 the hybrid systems showed a better behavior than the two commercial resins. Among the applied
30 coatings, the smallest reduction in WVP was given by the hybrid SI30 TiO₂, which reaches a vapor
31 flow comparable with that of the reference. The commercial silicon aqueous emulsion BP9710,
32 applied on both mortars, showed a sensible reduction with respect to water vapor permeability, thus
33 leading to a decrease that can be still considered acceptable in materials transpiration. Furthermore,
34 this is fully in accordance with what is already reported in the literature for highly hydrophobic
35 silane- and silicone-derived coatings, which are known to be able to maintain a high degree of water
36 vapor permeability (Zielecka and Bujnowska 2006). Indeed, these resins allow stones to breathe
37 and, at the same time, they prevent deterioration phenomena caused by external agents, such as
38 atmospheric pollution (see the following).
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As commonly reported in the literature (Bortolotti et al. 2006; De Ferri et al. 2011), the prevention of water rising by capillary absorption plays a pivotal role in the conservation of historical buildings. This phenomenon is one of the main responsible of mortars degradation, since water freeze-thaw cycles can cause cracks, and the transport of salts inside the materials can lead to crusts formation. Figure 2 shows the amount of water absorbed per unit area over time (Q_i) for all the adopted mortars. Typical parameters of the present analyses, including the capillary absorption coefficient (CA) and the capillarity index (IC, which gives information about the resistance to capillary rise when prolonged contact with water occurs) were calculated and reported in Table 2. For the untreated mortars the rise quickly arrives to a plateau that corresponds to the water saturation equilibrium of the sample. On the contrary, when the pure resins are applied on the mortars surface, a dramatic decrease in the capillary rise parameters (Table 2 and Figure 2) occurs for all of the treated substrates: the final Q_i collapses, CA reduces of about two orders of magnitude and IC is halved, confirming the hydrophobic performances of both the resins. Comparing the two commercial resins, Alpha®SI30 shows the best behavior with both the types of mortars and the water absorption is further reduce in the corresponding hybrid systems. Commercial BP9710 shows, by contrast, an opposite behaviour: higher CA and Q_i values are obtained with pure resin, whereas the addition of silica nanoparticles strongly improve its performances, making it competitive with the solvent-based system. Overall, all the samples showed promising protective properties.

3.2 *Controlled aging tests and exposure*

In order to evaluate the coatings stability, all the samples were treated both under direct UV lamp irradiations and in a QUV/basic machine for 1000 h accelerated aging test (Figures S1 and S2). The latter is equipped with UVA lamps, alternating 8 h of light with 8 h of water vapor condensation (in the dark). These conditions can reproduce well the aging due to external physical agents, excluding the contribution of chemical reactions occurring in a polluted environment

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2 (TECHNICAL BULLETIN LU-8052; TECHNICAL BULLETIN LU-8010 1987; TECHNICAL
3 BULLETIN 1993; Fedor and Brennan 1996).

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5 As shown in Figure 3, all the samples show no-significant ΔE^* variations after the aging,
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7 and only a slight loss of hydrophobicity has been observed, with exception of the SI30 TiO₂ hybrid
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9 coating, for which a significant decrease in the SCA values has been noticed for both the mortars.
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11 This fact could be easily explained considering the TiO₂ photoactivity, which could have promoted
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13 the degradation of the organic resin (Morikawa et al. 2006; Fujishima et al. 2008; Irie et al. 2009;
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15 Ohtani 2010; Kaur and Singh 2012). On the contrary, BP9710 SiO₂ has seemed to be well
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17 performing, since it shows both small ΔE^* and SCA variations.
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22 Furthermore, the comparison between this kind of test and the UV aging has shown that the
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24 main reason for coating deterioration is the UV light, whereas high humidity and condensation
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26 cycles seem not to affect the stability of the commercial and the hybrid coatings. Taking into
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28 account the lower power of the QUV lamp than the used halide lamp, the faster decrease in the SCA
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30 values of the UV irradiated samples can be easily explained (Figure 3).
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34 Another issue of interest in historical building is related to salt crystallisation occurring into
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36 porous structure of the material, which exerts the so-called crystallization pressure on the pore walls
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38 leading to the degradation of the material. In this study salt crystallization tests were performed, in
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40 order to assess the effect of the treatment on the resistance against salt weathering (Flatt 2002; Zeno
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42 W. Wicks et al. 2007; Yu and Oguchi 2010; La Russa et al. 2012; Caruso et al. 2014). In Figure 4, it
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44 has been reported the mass variation of samples after each weathering cycle. All specimens, after 3-
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46 5 cycles, showed an increase in weight related to the salt precipitation inside the pore structure.
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48 After the fifth-seventh cycle all samples start to loose material. Treated specimens, show a better
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50 behaviour, since after fifteen cycles they suffer less variation of mass (ranging from 8 to 10%). An
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52 exception is represented by HLM BP9710 sample; in this case, the behaviour against salt
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54 crystallization is quite similar to the untreated sample. In order to better understand the resistance of
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56 samples toward salt weathering, a calculation of the crystallization pressure has been performed
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1 from MIP measurement and applying a thermodynamic model proposed by Wellman and Wilson
2 (1968). The model predicts that porous material with larger capillaries connected to smaller ones
3 are the most susceptible to damage (Arnold and Zehnder 1989). The pressure that builds up between
4 two such connected pores, once crystallization takes place, is given by following the equation
5 proposed assuming a spherical geometry (Everett 1961): $\Delta P = 2\gamma (1/r - 1/R)$, where $\Delta P =$
6 crystallization pressure (dyne/cm²); $\gamma =$ crystal-solution surface tension (dyne/cm); $r =$ smaller pore
7 radius (cm); $R =$ larger pore radius. The calculation has been done following the method employed
8 by (Rossi-Manaresi and Tucci 1991). In Table 3, it has been reported the porosity values calculated
9 from MIP measurements, it can be noticed that only small variations of porosity have been detected
10 after the treatment of the samples. In Figure 5, it has been reported the pore size distribution of the
11 ALM and the HLM series, which show a quite different distribution. The treatments are able to
12 change slightly the pore distribution of the materials, this changing can influence significantly the
13 crystallization pressure. In Table 3, it has been reported the values of the crystallization pressure,
14 calculated from the pore size distributions. The treatments scarcely influence the ALM in term of
15 crystallization pressure. On the contrary, the HLM series seem to suffer the presence of SiO₂, since
16 treatments induce an increase in crystallization pressure (61.5 MPa), while in bare samples the
17 pressure is 17.0 MPa. This increase in pressure is partially compensated by the hydrophobicity
18 induced by the treatment that reduce the amount of water absorbed by the treated sample and this
19 lead to a lower amount of salt introduced into the stone porous structure. This two effects, higher
20 crystallization pressure and lower amount of salt into the stone, make the bare HLM and the SiO₂
21 hybrid coating similar against salt weathering.

22 The interaction with atmospheric gases and aerosol deposition is one of the main processes
23 of environmental degradation, occurring on the exposed surfaces of monuments and historic
24 buildings. For this reason, both bare and treated samples have been exposed in a typical urban
25 polluted environment at the Milan University Campus and the concentration of the main anions
26 (Figure S3), typically found in degraded stones, has been monitored as in our previous work (Watt
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1 et al. 2014; Cappelletti et al. 2015b). In particular, sulphate is the main product of carbonate
2 degradation due to pollution, whereas nitrate and chloride are mainly due to atmospheric
3 depositions (Fuente et al. 2011; De et al. 2013). As shown in Figure 6a, in HLM coated samples the
4 overall absorption of anions was strongly reduced. Nitrates and chlorides were found in much lower
5 concentrations than sulphates, but it is well known that sulphatation process is the main degradation
6 reaction of calcium carbonate. Either nitrates or chlorides concentrations were reduced with the
7 application of both resins, with a slight further decrease for the hybrid coatings. It is also worth
8 noting the drastic decrease in the sulphate concentrations, in particular for the hybrid BP9710 SiO₂.
9 As previously demonstrated (Cappelletti et al. 2015b), the two resins BS16 and SI30 were not
10 effective in the protection of ALM mortar and the same thing has been observed for the resin
11 BP9710. Moreover, SI30 TiO₂ coated samples were not exposed since they did not show good UV
12 resistance in the controlled aging tests, which does not make them feasible candidates for
13 environmental protection. Colorimetric measurements (CIELab) were carried out to verify the color
14 alteration of the protective films. The results, shown in Figure 6b, highlight how both the BP9710
15 the hybrid coating containing SiO₂ coated mortars showed no significant variations in the color,
16 even after 7 months of exposure (only a slightly decrease of brightness has been determined). The
17 SCA measurement showed a similar trend (see Figure 6c): the BP9710 coated materials retained the
18 hydrophobic behavior better than the SI30 ones, indicating better resistance of the water-based
19 system, and the high performing BP9710 SiO₂ coating remained stable maintaining a high surface
20 hydrophobicity.

21
22 In conclusion, with respect to the results previously reported in the literature for mixed
23 coatings, the present hybrid films are clearly more stable (Manoudis et al. 2009).
24

25 **4. Conclusions**

26 In the present work, two already characterized artificial stones (Cappelletti et al. 2015b), an
27 air hardening calcic lime mortar (ALM) and a natural hydraulic lime mortar (HLM), were used.
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1 Alpha®SI30 and Bluesil®BP9710 resins were applied to the bare mortars to give
2 hydrophobic features; these Si-based polymers were used as base to prepare hybrid organic-
3 inorganic coatings, through the addition of oxide nanoparticles. Comparing the commercial
4 polymers with the modified ones, the latter show better features in hydrophobicity, transpirability
5 and capillarity rise. Although, SI30 TiO₂ shows lower chemical stability after UV and QUV aging
6 (higher ΔE^* values and appreciable contact angle lowering) with respect to the relative commercial
7 resin. On the contrary, the hybrid coating BP9710 SiO₂ shows promising aging resistance,
8 comparable with BP9710, retaining its superior characteristic in terms of water protection. Salts
9 crystallization resistance tests were carried out and the final performances of the coatings in terms
10 of reduction of salts formation (*i.e.* sulphate and nitrate formation) were studied after a prolonged
11 exposure to a polluted environment (Unimi campus in Milan). All of the treated samples show a
12 reduction in terms of both nitrates and sulphates formation. The combined effect of these factors
13 indicates that BP9710 modified with the addition of SiO₂ nanoparticles seems to be a novel
14 promising protective coating agent in the field of historical building reconstruction. The results
15 obtained have shown that HLM samples coated with the hybrid systems achieved super-
16 hydrophobicity. In particular, the water-based system shows promising results, being ecofriendly,
17 invisible to naked eye, superhydrophobic and aging resistant.
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Sample	θ / deg	γ / mN m ⁻¹	γ_P / mN m ⁻¹
ALM	70 ± 10	37 ± 7	13 ± 3
ALM SI30	116 ± 8	15 ± 6	< 1
ALM SI30 TiO2	129 ± 4	*	*
ALM BP9710	114 ± 7	12 ± 3	< 1
ALM BP9710 SiO2	126 ± 9	*	*
HLM	65 ± 10	33 ± 10	15 ± 5
HLM SI30	137 ± 7	< 10	< 1
HLM SI30 TiO2	> 150	*	*
HLM BP9710	130 ± 7	< 10	< 1
HLM BP9710 SiO2	> 150	*	*

Table 1. Static contact angles (θ) and Surface Free Energy (SFE, γ) values (with relative standard deviations) by Owens, Wendt, Rabel and Kaelble (OWRK) method with its polar component (γ_P). * = for hybrid coatings the OWRK method was not applicable since $\theta > 120^\circ$

Sample	IC	CA / mg/cm ² s ^{-1/2}	Q _{tf} / s ^{1/2}
ALM	0.97	17.24	747.4
ALM SI30	0.43	0.12	81.0
ALM SI30 TiO2	0.51	0.08	77.0
ALM BP9710	0.46	0.21	314.2
ALM BP9710 SiO2	0.51	0.10	119.1
HLM	0.96	11.45	725.0
HLM SI30	0.53	0.12	138.8
HLM SI30 TiO2	0.49	0.09	144.3
HLM BP9710	0.46	0.37	292.2
HLM BP9710 SiO2	0.53	0.13	144.6

Table 2. Water Capillary Index (IC), Absorption Coefficient (CA) and amount of water absorbed at the final time (around 8 days, Q_{tf})

Parameters		HLM	HLM BP9710	HLM BP9710 SiO2	ALM	ALM BP9710	ALM BP9710 SiO2
Porosity	%	23.3	23	22.8	28	27.7	27.6
Crystallization Pressure	MPa	17.0	34.0	61.5	2.6	4.9	2.2

Table 3. Mercury Intrusion Porosimetry parameters

Figure captions

Figure 1. Water Vapour Permeability curves showing the variation of cumulative mass for all the samples (both **a**) air hardening calcic lime (AL) and **b**) hydraulic lime (HL) mortars).

Figure 2. Capillary absorption for **a**) air hardening calcic lime (AL) and **b**) hydraulic lime (HL) mortars.

Figure 3. ΔE^* (above) and Static contact angle (below) variations after controlled accelerated aging tests.

Figure 4. Mass loss vs cycles number showing the resistance of the hydraulic lime mortar towards salts crystallization.

Figure 5. Pore size distribution measured by means of mercury porosimetry (MIP) for **a**) AL and **b**) HL mortars.

Figure 6. **a**) Anions concentration determined by Ion Chromatography (IC) in HLM exposed samples; **b**) ΔE^* and **c**) static contact angles variations and after HLM samples exposure.

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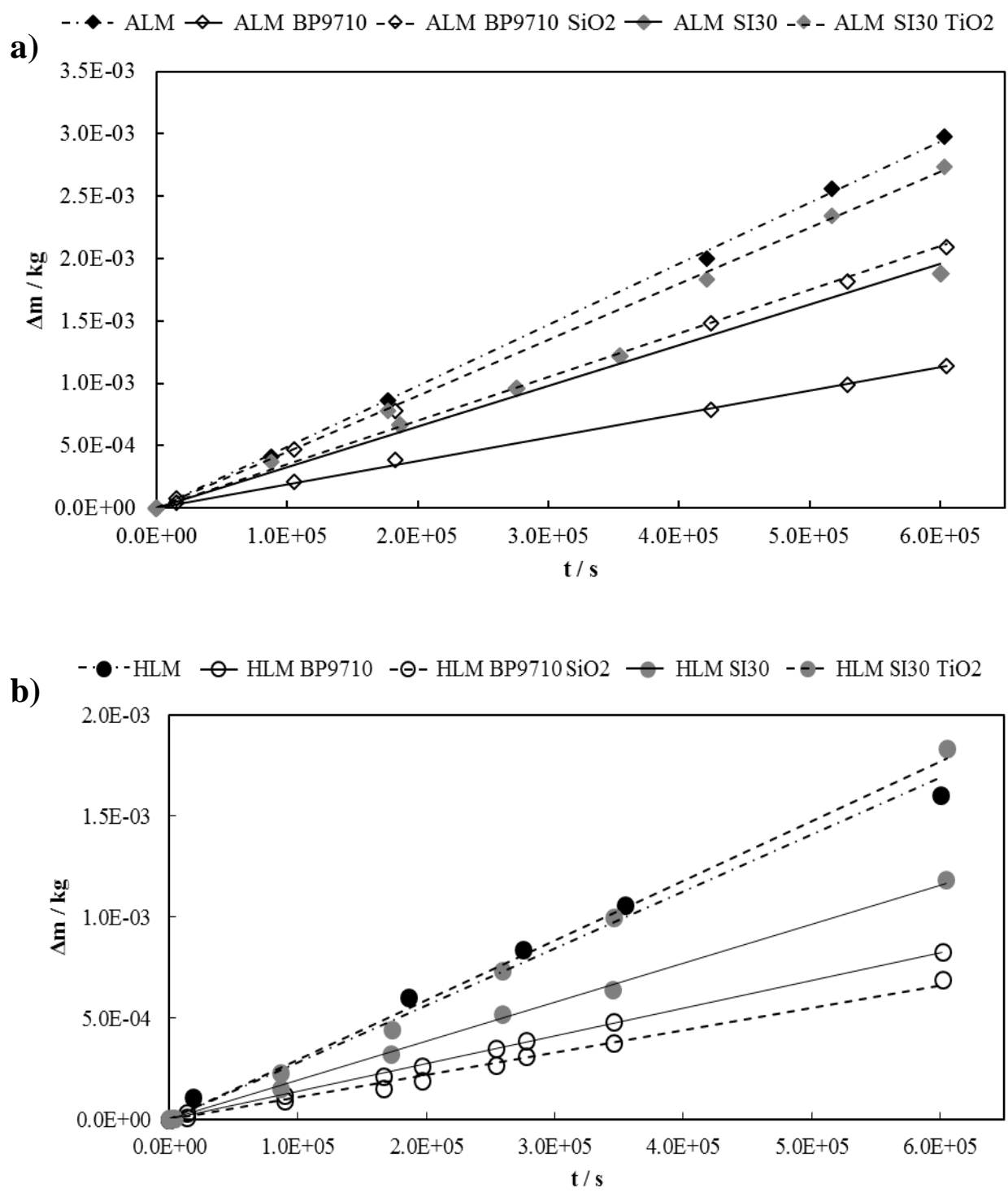


FIGURE 1

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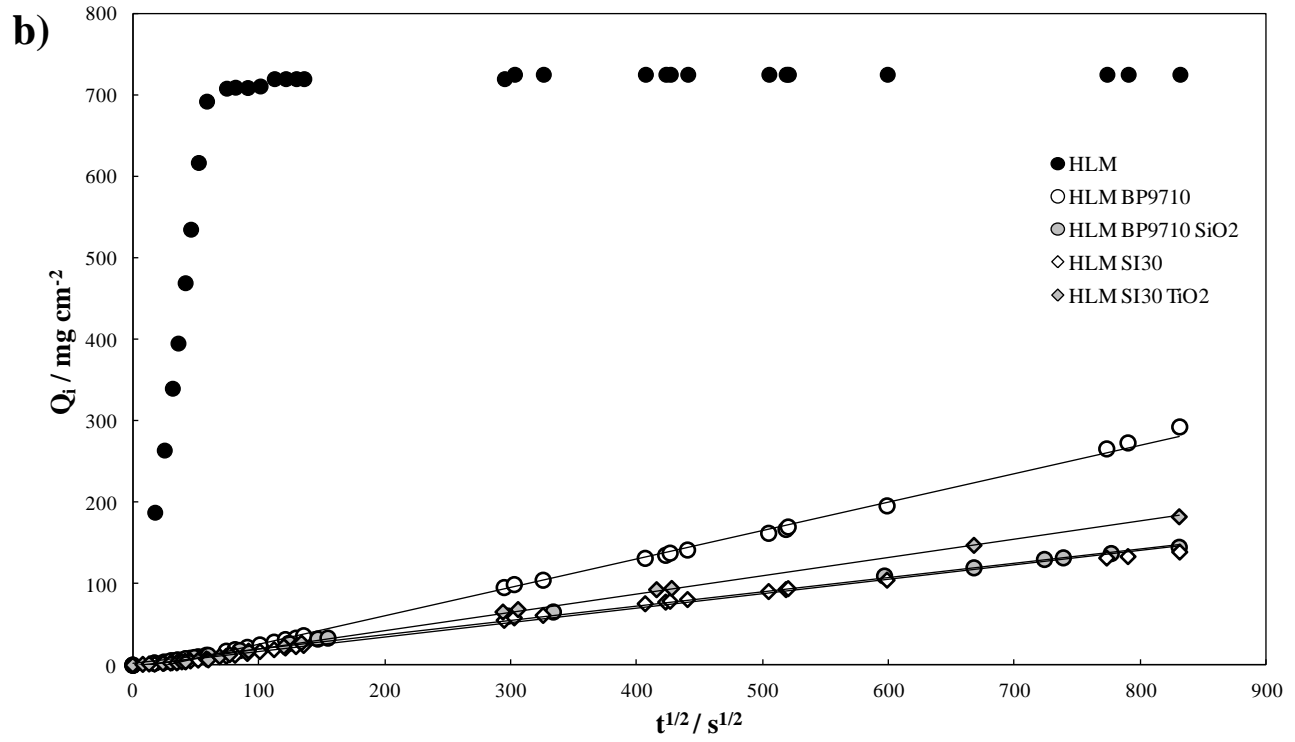
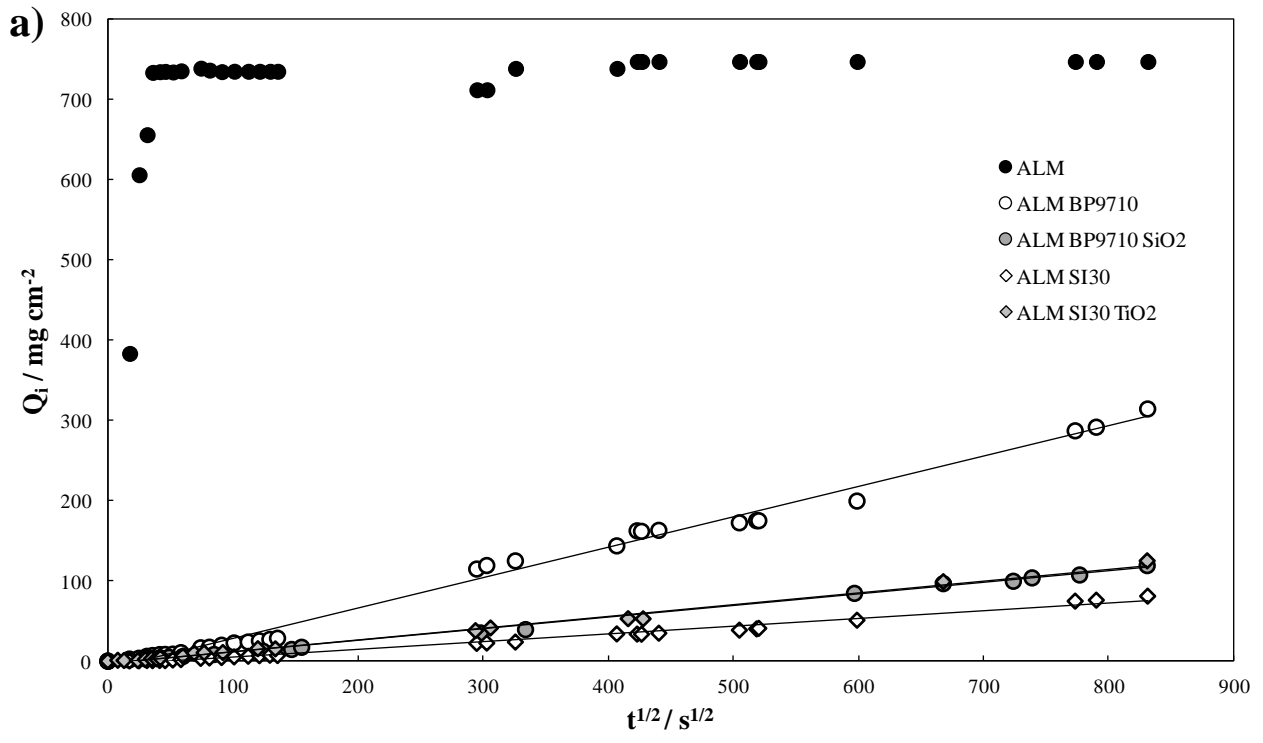


FIGURE 2

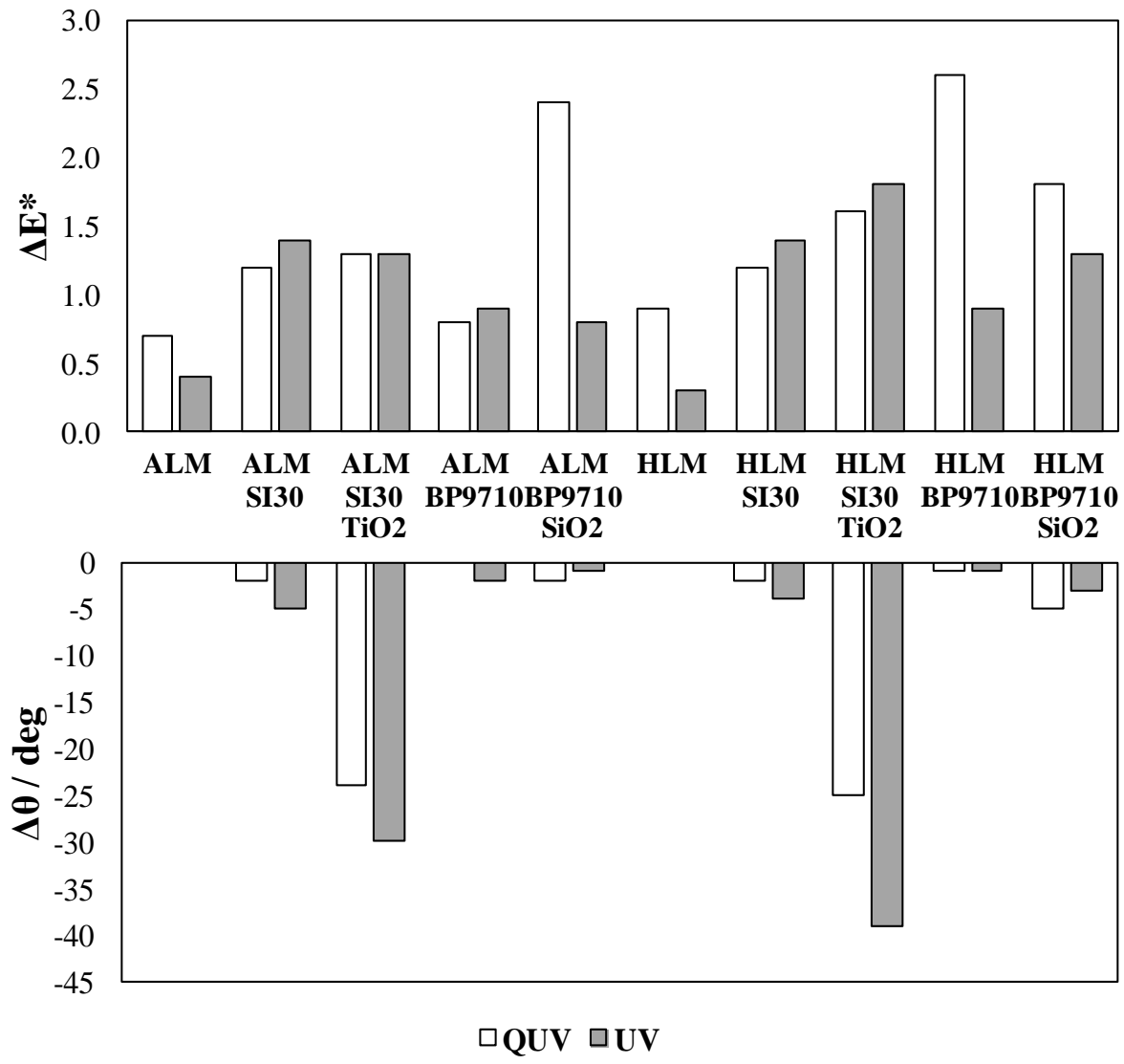


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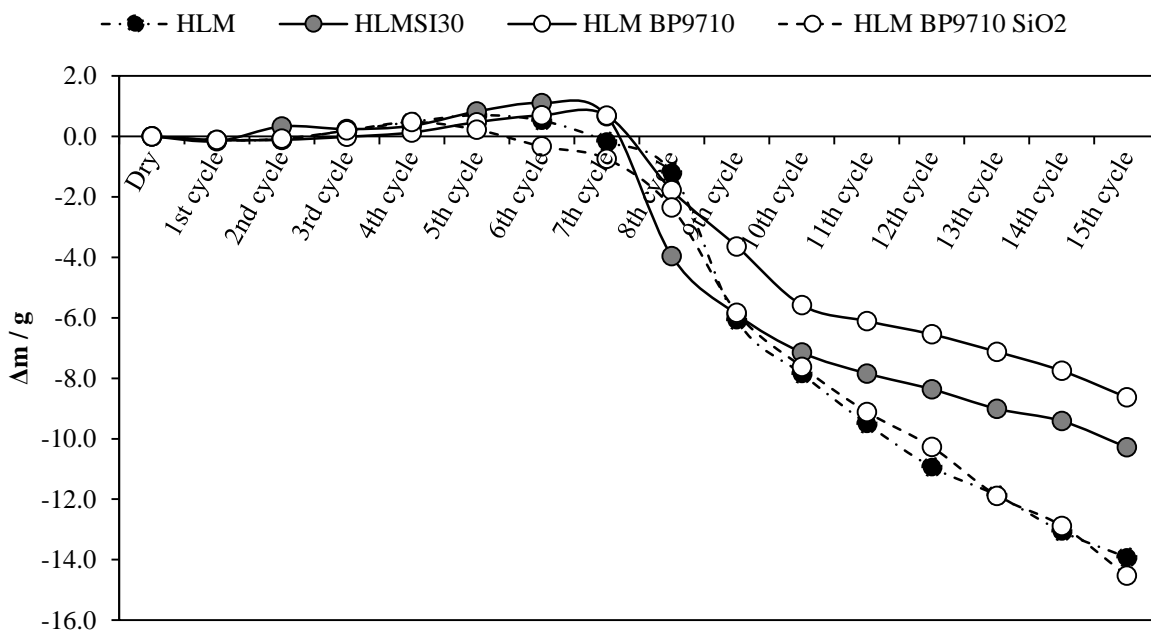


FIGURE 4

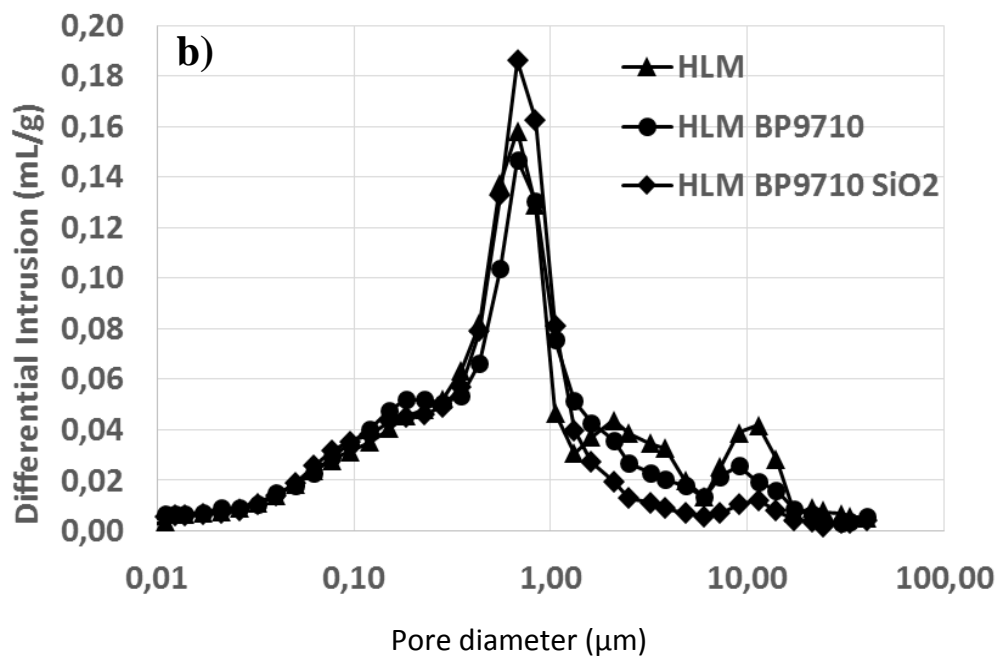
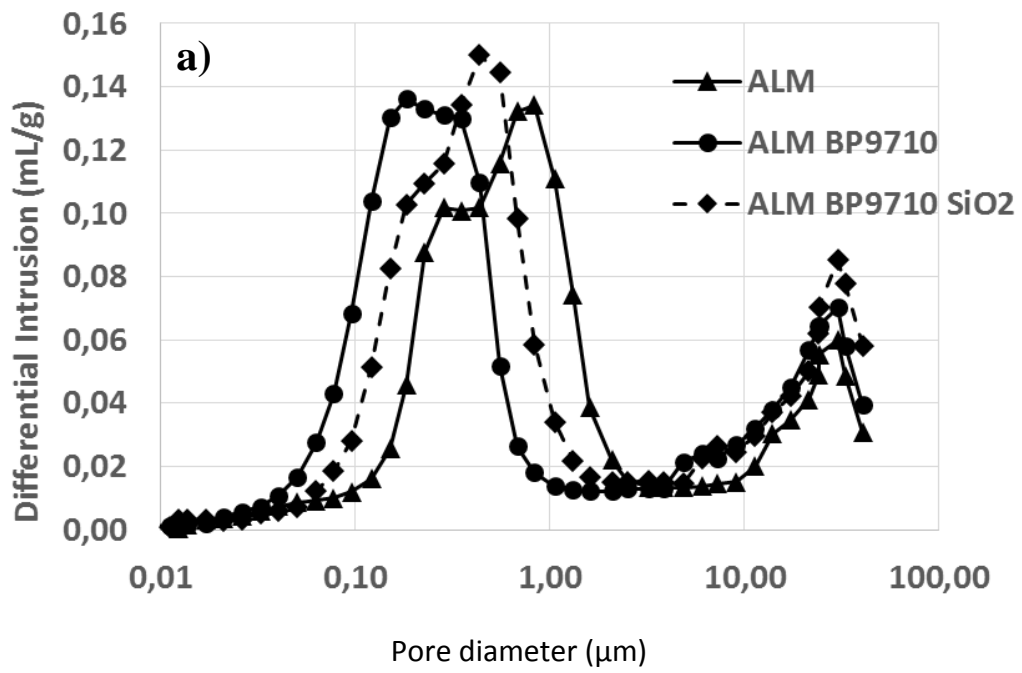


FIGURE 5

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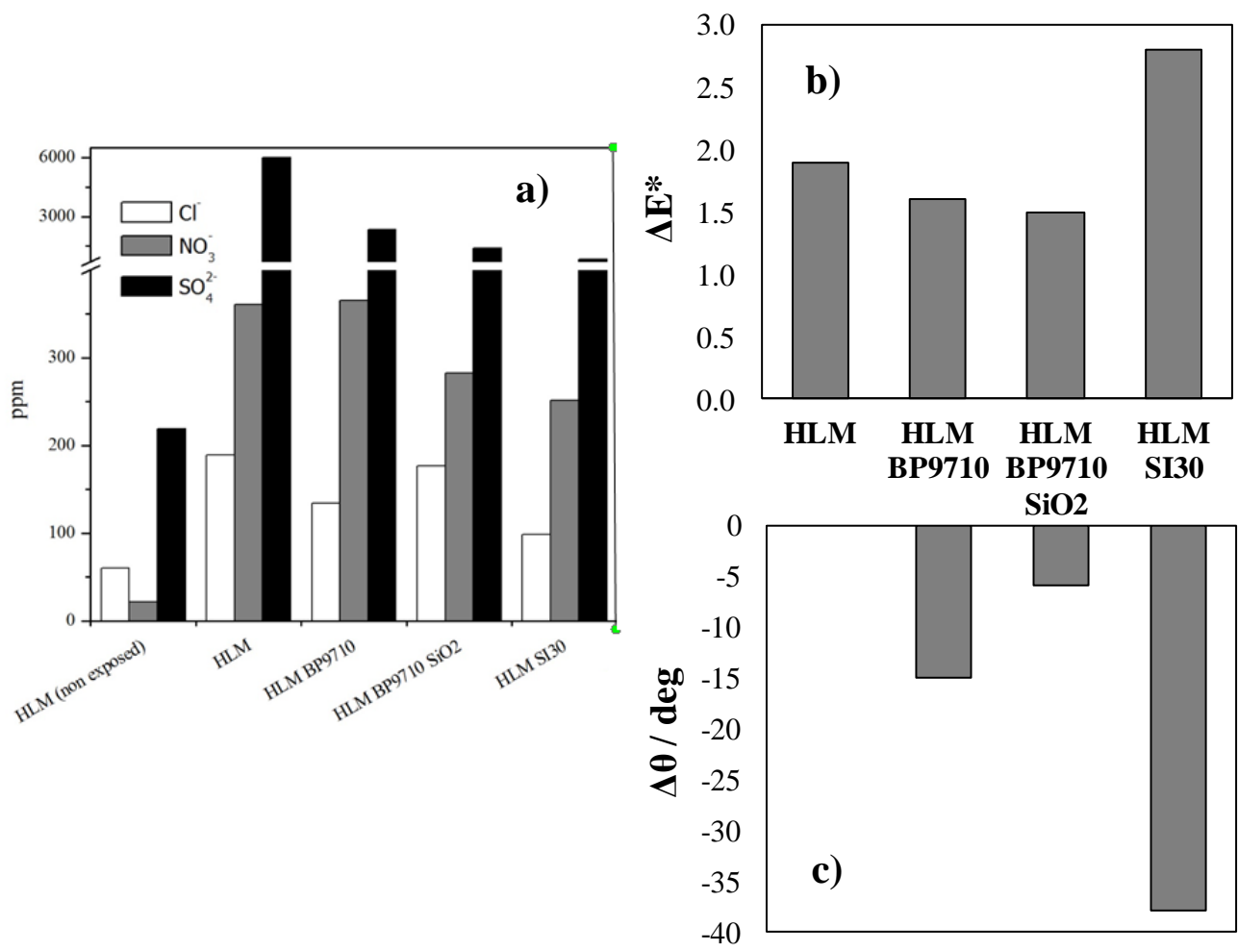
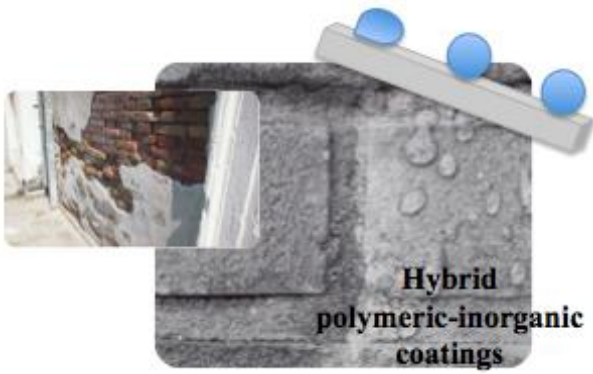


FIGURE 6

Table of Contents Image

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