Consolidation of Vicenza, Arenaria and Istria stones: a comparison between nano-based products and acrylate derivatives

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Abstract

Nano-based formulations are emerging as successful materials besides the use of conventional products for the consolidation of carbonate works of art e.g. stone, mortars or mural paintings. In this work, the physico-chemical characteristics, performances, and consolidation efficacy in terms of external appearance of commercial NanoRestore $Ca(OH)_2$ and NanoEstel SiO_2 dispersions were investigated and compared with two commercial acrylates derivatives, Acril 33 and Acril ME. The colloidal stability of the different consolidants was investigated by dynamic light scattering (DLS) and centrifugal separation analysis (CSA) techniques. As expected, acrylate emulsions showed a higher colloidal stability than the inorganic nanoparticle dispersions, with sedimentation velocity from 10^{-4} to 10^{-2} μm/s. The examined consolidants were applied on three different stones, widely used in historical buildings in Venice: Vicenza, Arenaria and Istria stones, representing macro-, meso- and micro-porous materials, respectively. The absorption capacity, colour and gloss variation of the different stone materials were comparatively evaluated after the consolidants application. An accordance among porous structure of the substrates, hydrodynamic particle size and amount of consolidants absorbed was observed for nano-based formulations. The weathering resistance under natural and UVB aging conditions were also investigated for the consolidated stone samples, and recorded as changes of colour, gloss and surface morphology. NanoRestore and NanoEstel showed the best performances under the natural aging while the UVB irradiation seemed to not induce significant modification in the surface morphology of the treated stone samples.

Keywords: Stone consolidation; Nano-based products; Acrylate derivatives; Natural and simulated UVB aging; Colour and gloss variations

1. Introduction

The persistent exposure to the combined action of natural weathering and anthropogenic pollution over time can cause several damages to lime- and silica-based porous materials used in both artworks and architectural manufacturing. Air pollution, the presence of soluble salts and biodeteriogens [1–5] can induce flaking of the surface layers, powdering, formation of small blisters and loss of large area of the artefact [6,7]. In this context, one of the main challenges in conservation and restoration field is the use of compatible consolidants which can avoid deterioration without altering the main characteristics of the stone materials restored. Furthermore, the durability of the treatment and the long-term stability of the consolidated substrates should be ensured [8–15].

In the field of stone conservation, calcium hydroxide is one of the most promising products suitable for consolidating calcareous materials (e.g. stone sculptures, monuments or wall paintings) because it is converted into calcium carbonate as a result of carbonation, when exposed to atmospheric CO_2 under moist conditions. $Ca(OH)_2$ is generally applied as a saturated aqueous solution, however, due to its low solubility, large amount of solution is needed. Consequently, the treatment of stone materials with large amounts of water could be detrimental to porous matrices, favouring the pore collapse through freeze–thaw cycles and the transport of soluble salts [16]. Additional drawbacks are

the incomplete conversion of calcium hydroxide into calcium carbonate, as well as the post treatment chromatic alteration and the low penetration depth [17]. Moreover, the stability of aqueous $Ca(OH)_2$-based dispersion is not always ensured, although few exceptions are reported in literature [18]. Fast clustering and sedimentation of the hydroxide particles can in fact occur, with scarce penetration and veiling of the treated surface [19].

To enhance the consolidant performances of $Ca(OH)_2$, engineered nanomaterials (ENM) based formulations have been developed [20]. In detail, dispersions of $Ca(OH)_2$ nanoparticles (NPs) in water or short-chain alcohols have been largely studied to establish their potential use for consolidation of limestone and carbonatic painted surfaces [16,21–23], wood [24], paper and canvas deacidification [25], as well as for archaeological bones treatment [26]. The nano-size of the particles eases the penetration of the product through porous substrates and increases the particle reactivity with respect to CO_2. Several methodologies of $Ca(OH)_2$ NPs synthesis have been reported [27–32], and the related formulations showed different features like degree of dispersibility, particle size distribution and particle structure, which are expected to affect the consolidation process. Literature studies showed that $Ca(OH)_2$ NPs dispersed in short-chain alcohols exhibited a higher colloidal stability than using water as dispersant, significantly improving the degree of consolidation by decreasing agglomeration rate of particles [21,33,34].

As far as silica-based stones consolidation, commercial products containing alkoxysilanes, such as tetraethoxysilane (TEOS), are commonly used [35]. These products, polymerizing in situ via a sol-gel process within the porous structure of the stone to be consolidated, increase the mechanical properties of the materials. However, they can form a dense microporous network of gel that tend to become brittle and susceptible to cracking. Moreover, this network can obstruct the porous of the materials promoting a significant reduction of water permeability [36]. To improve consolidation performances, nanosilica-based products were synthetized by a template synthesis in which a surfactant was used as structure-directing agent during the polymerization process. Following this procedure, silica nanoparticles with uniform size and ordered mesopores were obtained. The presence of surfactants avoids the cracking of the gel during the drying phase because of a coarsening of the gel network that reduces the capillary pressure [37,38]. Furthermore, the advantage of using nanosilica-based product with respect to the traditional solvent-based TEOS is the non-hazardous solvents employed and the reduced time necessary to obtain the gel network. On the other hand, the capability of silica nanoparticles to penetrate porous materials with respect to the solvent-based silica product have not been jet deeply investigated [39].

Acrylic resins have also been largely used in conservation practice. They are thermoplastics copolymers based on monomers derived from acrylic and methacrylic acid. Depending on the ratio of the monomers, it is possible to structure a resin with specific molecular weight and physico-chemical characteristics [40]. During the early 1930s, acrylic polymers started to be used as picture varnishes because of their initial resistance to yellowing, their solubility in hydrocarbons solvents, their ability to form flexible and transparent films and their glass transition temperature, preventing the dirty pick-up. Unfortunately, these resins resulted unsuitable for long-term uses, due to the unexpected cross-linking, cracking and yellowing exhibited when the polymers were exposed to natural light [41]. At the end of the 1940s, a more stable acrylic resin system was introduced with the commercial name of Paraloid. This acrylic polymer applied in solution was recommended for a wide range of applications, such as textile, wood and pigments consolidants, as adhesives for paper and, due to its hydrophobicity, as consolidant and water repellent for stones [42]. In particular, Paraloid B72, a co-polymers of methyl methacrylate and ethyl acrylate (P(MMA/EA)) soluble in organic solvents, showed an improved stability at different aging conditions [43,44]. In the last years, the growing attention towards human health and environment has led to water-based emulsions safer than the original formulations.

In this context, four different stone consolidants NanoRestore, NanoEstel, acrylic-based emulsion Acril 33, and micro emulsion Acril ME were investigated. The physico-chemical characterization of the commercial suspensions was performed by means of Dynamic Light scattering (DLS) and

Centrifugal Separation Analysis (CSA). The consolidants were then applied on three different stones, i.e. Vicenza, Arenaria and Istria stone, that are representative of macro-, meso- and micro-porous materials. These stones have been selected for their abundance in architectural decorative apparatus of numerous venetian palaces and churches such as the Basilica of San Marco and Palazzo Ducale [45]. Before the application step, Brunauer-Emmet-Teller (BET) analysis was carried out to evaluate the specific surface area and the total pore volumes of the three different stone materials. Afterwards, the consolidated stones samples were investigated under natural aging and laboratory test conditions, i.e. UVB aging. Stereomicroscopic measurements were carried out to observe the variations in the physical and morphological characteristics of the treated surfaces, while colorimetric and gloss [46] measurements were performed to evaluate the chromatic variations which can occur on the surfaces after the consolidation treatments due to natural and artificial aging.

2. Experimental section

2.1 ***Materials***

All the commercial products tested were provided by CTS (Altavilla Vicentina, Italy). NanoRestore is a 2-propanol dispersion of $Ca(OH)_2$ NPs (5 g/L solid concentration). NanoEstel is an aqueous colloidal dispersion of nano-sized silica (solid content 30%) stabilized with sodium hydroxide (NaOH < 0.5%). Acril 33 is an aqueous emulsion (solid content 46%) of ethylacrylate and methylmethacrylate co-polymer while Acril ME is a water based micro emulsion (solid content 41%) of the polymer poly(butyl methacrylate).

Vicenza, Arenaria and Istria stones 5 x 5 x 2 cm^3 were provided by Laboratorio Morseletto (Vicenza, Italy). Vicenza stone is a light ivory calcareous rock, principally composed by calcite and dolomite, extracted from the Oligocene horizons in Colli Berici (Vicenza, Italy). It is the result of the sedimentation of innumerable minute fossils, which create its texture, and it is usually used for stone sculptures. Arenaria is a clastic sedimentary rock composed mainly by sand-sized minerals or rock grains with a dark grey colour while Istria stone is a sedimentary compact rock with a micritic structure and a whitish colour, formed during the lower Cretaceous. All the stones type used in this study have been extensively used as building materials in venetian architectures.

2.2. ***Nano-based and acrylates consolidants characterization***

The dispersion stability of each consolidant was carried out by Dynamic Light scattering (DLS) and Centrifugal Separation Analysis (CSA). Hydrodynamic particle diameter was measured by DLS by means of a multi-angle Nicomp ZLS Z3000 (Particle Sizing System, Port Richey, FL, USA) with an optical fiber set at 90° scattering angle (W=25 mW, λ=639 nm, at 25°C). Particle sedimentation velocity was calculated by CSA, employing the Multiwavelength Dispersion Analyzer LUMiSizer 651 at λ=470 nm. Briefly, the samples were analysed in polycarbonate cuvette with 10 mm optical path every 50 seconds at 25°C and 2800 Rotation Per Minute (RPM). The transmission profiles, which are the raw data generated by CSA, moved from the lowest values of transmittance (indicating the highest amount of particles in the suspension) to the maximum transmittance, corresponding to the total sedimentation of particles in the cuvette (i.e. plateau). The variation of the transmission profiles over time and space allowed to calculate particle sedimentation velocity [47]. The overall results from DLS and CSA were reported as an average of three independent measurements.

After the physico-chemical characterization of the commercial dispersions, the consolidation test was carried out by applying Nanorestore, NanoEstel, Acril 33 and Acril ME on Vicenza, Arenaria and Istria stones. Before the consolidation treatment, the stone blocks were carefully washed and brushed in distilled water for 3 times in order to remove all the soluble salts and then dried in a static oven at 60°C. The consolidants were applied by brush until refusal and the samples were maintained in controlled conditions (T=25°C and UR=30%) until reaching a constant weight. The amount of absorbed product was estimate as the difference in weight between the consolidated and the untreated

stone samples for three independent measurements (10 weight measurements for each consolidated stone). Three samples for each substrate were prepared.

2.3. ***Stones characterization***

Stereomicroscopic measurements were carried out with a Nikon SMZ1270 with magnifications of 10 or 20x on the treated surfaces. The films morphology was recorded by a Nikon DS-Fi2 camera with Nikon Digital Sight DS-L3 software.

Brunauer-Emmet-Teller (BET) analysis was carried out using a ASAP 2010 of MicroMetrics to evaluate the specific surface area (m^2 g^{-1}) and the total pore volumes of the different stones using nitrogen multilayer adsorption measured as a function of relative pressure. Before BET analysis the samples were degassed at 10^{-3} Torr at 130°C for 12 hours. BET analysis was conducted at -196°C, temperature of condensation of the N_2. The total pores volume was determined at P/P_0 of 0.98.

The stones consolidated with the tested formulations were investigated as fresh and under natural and UVB aging conditions. Natural aging of the samples was carried out exposing the samples to Venice-Mestre (Italy) outdoor conditions in a rigid plastic support with an inclination of 60° over 2 years. UV accelerated aging tests were carried out in a UVB chamber, under a monochromatic UVB radiation (λ=254 nm) at 28 ± 2°C and relative humidity of 45% up to 1200 hours. The variation of treated samples color was monitored at incremental time intervals, monthly for natural aging and 100 hours for the UVB aging. The colour measurements were carried out by a Konica Minolta spectrophotometer according to CIE Lab colour space method [48,49]. The parameters L*, a*, b* were simultaneously collected. L* stands for the lightness (L*=0 corresponds to black, L*=100 corresponds to white), while a* and b* are the colour-opponent dimensions: a* is the red/green balance (-a* corresponds to green and +a* corresponds to red) and b* is the yellow/blue balance (-b* corresponds to blue and +b* corresponds to yellow). The total variation of colour (ΔE*) was calculated by the equation $[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)]^{1/2}$. The parameters ΔL*, Δa* and Δb* refer to the difference between the aged samples and the untreated ones ($\Delta L^* = L^*_{t=x} - L^*_{t=0}$; $\Delta a^* = a^*_{t=x} - a^*_{t=0}$; $\Delta b^* = b^*_{t=x} - b^*_{t=0}$).

The specular gloss of the untreated, treated and aged stone samples, i.e. the ratio of the luminous flux reflected from the samples in the specular direction for a specified source and receptor angle, was determined with a Picogloss 503 (Erichsen) at the incident angle of 20° with a resolution of 1 GU, according to ASTM D523-08, 2004 [28]. The gloss retention (Δgloss %) was calculated between the untreated and the consolidated surface as $[(gloss_{(untreated)} - gloss_{(treated)}) / gloss_{(untreated)} \times 100]$ and between the unaged and aged samples as $[(gloss_{(t=0)} - gloss_{(t=x)}) / gloss_{(t=0)} \times 100]$.

3. Results and discussion

3.*1.* ***Colloidal characterization of consolidants***

The colloidal stability of Nanorestore $Ca(OH)_2$ and NanoEstel SiO_2 NPs dispersions was investigated by CSA and DLS techniques. In detail, as far as particle sedimentation velocity, a method already developed [50] was applied to Nanorestore and Nanoestel, and the transmittance profiles of the two nano-based dispersions are displayed in Figure 1. As it can be clearly observed by transmittance profiles, the settling of Nanoestel NPs is very low if compared to Nanorestore results, showing sedimentation velocities ≤ 0.01 μm/s at gravity vs 0.04 μm/s calculated for Nanorestore. This indicates the higher stability of Nanoestel with respect to Nanorestore in alcoholic dispersion.

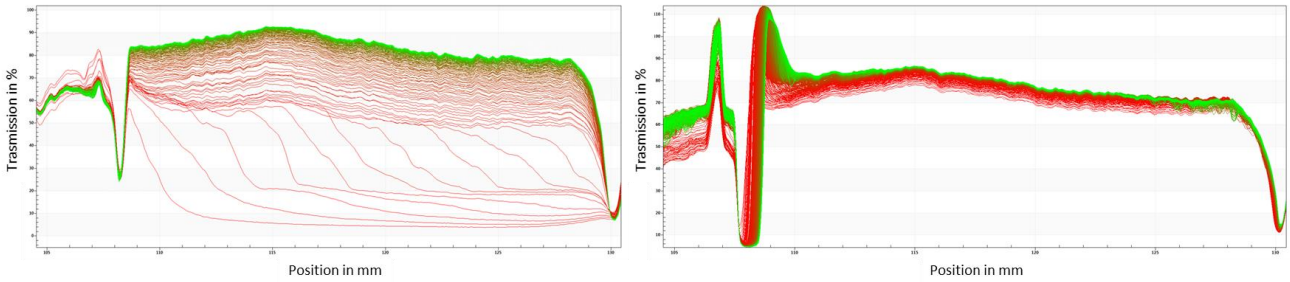


Figure 1 – Typical transmission profiles at 2800 RPM of Nanorestore dispersion (left) and Nanoestel dispersion (right).

Furthermore, hydrodynamic particle size of the tested dispersions was determined by DLS. A population with an average hydrodynamic particle size of 336±34 nm was detected for Nanorestore dispersion while 165 ± 28 nm was obtained for Nanoestel.

As far as the acrylic derivatives, the emulsions were opportunely diluted for CSA and DLS measurements (see Figure S1 in the Supporting Information). Sedimentation velocity values and average size distribution were $\leq 3x10^{-4}$ μm/s and 70 ± 15 nm for Acril 33 and $\leq 8x10^{-4}$ μm/s and 47 ± 7 nm for Acril ME. In conclusion, the highest colloidal stability of both acrylic emulsions with respect to the nano-based dispersions investigated was proved.

3.2. Stone surface characterization

3.2.1. Consolidated stones

The surface area and the total pore volumes of the different stones were investigated by BET method before the consolidants applications, and confirmed the micro- meso- and macro-porosity of Istria, Arenaria and Vicenza stone respectively (Table S1 in SI).

The amount of Nanorestore, Nanoestel, Acril 33 and Acril ME adsorbed on the three different stone substrates was measured as weight difference and the overall data are reported in SI (Table S2). Adsorption results (Figure 2), according to BET measurements, showed as Vicenza stone is the material with the highest capacity to adsorb the consolidants investigated because of its biggest pores size. On the other hand, Istria stone showed the lowest adsorption of consolidants, as expected for a micro-porous material. Comparing the recorded amounts of the different consolidants adsorbed, Nanorestore and Nanoestel showed the lowest values of adsorption (< 0.04 g) for each stone investigated, except for Nanoestel which was strongly adsorbed on Vicenza stone (0.80 g). Acril 33 and Acril Me were instead absorbed in relevant amounts with respect to inorganic nano-based materials by all the stones investigated. This finding can be ascribed to the different way in which inorganic NPs and acrylates interact with the substrates, acrylates in fact usually form a film on the surface of the stones.

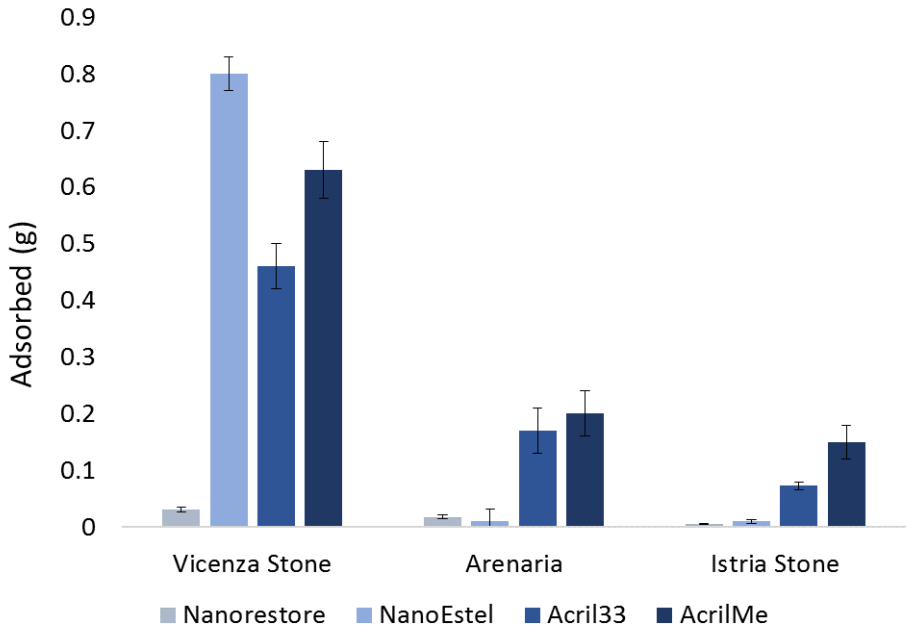
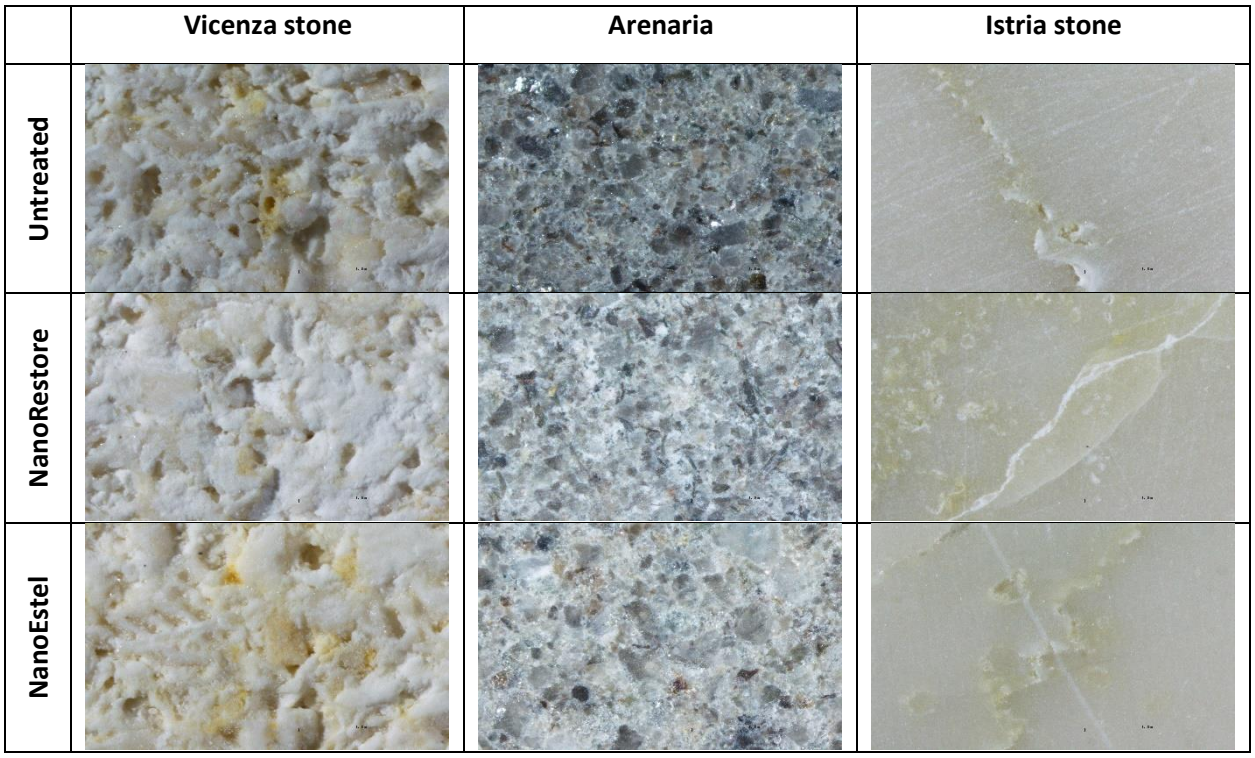


Figure 2. Comparison among NanoRestore, NanoEstel, Acril 33 and Acril ME adsorption from Vicenza, Arenaria and Istria stones.

To better understand this behaviour, the surface morphology of Vicenza, Arenaria and Istria stones was further investigated by Stereo Microscope analysis (Figure 3), before and after each consolidation treatment. The results highlighted that the stone samples treated with NanoRestore underwent a slightly whitened of the surface. As far as the surface treated with NanoEstel, a thin homogenous transparent and bright film without cracks was observed, while Acril 33 and Acril ME completely changed the original aspects of the stone supports creating a transparent, bright and thick film with a large number of air bubbles. In result, the polymeric layer covering the surface appeared to change the natural morphology of the stone and to occlude the pores.



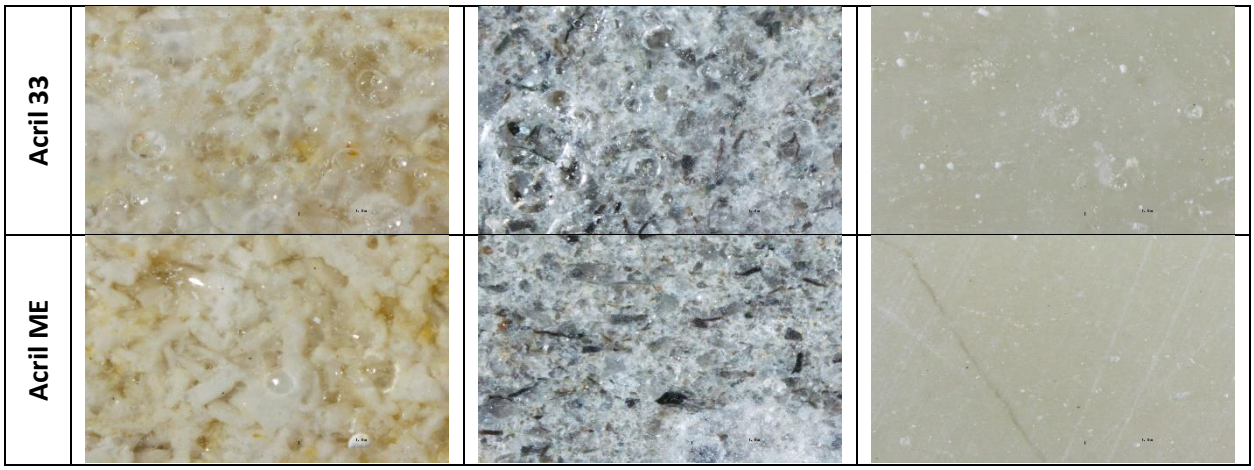


Figure 3. Micrographs (20x) of the surface morphology of the stone samples before (untreated) and after the consolidation treatment with NanoRestore, NanoEstel, Acril 33 and Acril ME.

Furthermore, colorimetric and gloss analysis allowed to observe variations in terms of ΔE and Δgloss % with respect to the untreated stones (Table 1). A general tendency of the treated stone samples to yellowing was observed and, as it can be seen in the color graph of Figure 4, this chromatic variation induced the simultaneous decrease of a* values (shift to green shades) and the increase of b* values (shift to yellowing shades). On the other hand, the lightness variations (i.e. increment in the L* values), as shown in Table 1 indicated a slightly shift towards clearer shades (whitening effect of the consolidants). This behavior was shown mostly for the stone samples consolidates with $Ca(OH)_2$ NPs. In general, the overall results in Table 1 for Vicenza stone highlighted the best performances of NanoRestore in terms of colour and gloss retention among the consolidants tested, showing the lowest ΔE (7.96) and Δgloss % (-13) values. Small colour and gloss variations (ΔE= 8.78 and Δgloss %= 33) were also recorded after NanoEstel treatment. Thus, both the inorganic NPs exhibited good consolidant performances by maintaining the original characteristics of the untreated surface. However, they presented opposite trends in term of gloss variation. NanoRestore in fact, induced a slightly decrease in the gloss of the treated surface (negative values of Δgloss %, indicating an increase of the surface brilliance), while NanoEstel showed positive values of Δgloss % (indicating more opacity than the untreated material). On the other hand, significant variations of colour and gloss retention were recorded for Vicenza stone treated with the two acrylic-based consolidants. In particular, the highest values of Δgloss % (-173) recorded for Vicenza stone treated with Acril 33, highlighted a surface modification after the treatment.

As far as Arenaria, even if Acril 33 and Acril ME seemed the most compatible consolidants with ΔE values of 6.67 and 6.63 respectively, they formed a glossy layer on the surface of the stones that changes significantly the gloss values of the original materials with extremely high Δgloss % variations in both cases.

Finally, taking into account Istria stone, the most compatible consolidant was also in this case NanoRestore (Table 1), which induced a slightly whitening of the surface but not a significant variation in the colour parameters (ΔE=7.57) and in the gloss values (Δgloss %= -18). The nanosilica-based consolidant induces similar variation in the colour parameters (ΔE = 9.44) but higher gloss variations (Δgloss %= -51) with respect to Nanorestore. Acrylates present high gloss variations of the treated surfaces towards highly negative values, indicating an increase of the surface brilliance after the stone treatment. In conclusion, the overall results in Table 1 suggested that the inorganic NPs consolidants showed the lowest colour and gloss surface variation for all the treated stones.

Table 1. Colour parameters Δa*, Δb*, ΔL* and ΔE and gloss variation (Δgloss %) values determined for Vicenza, Arenaria and Istria stone after the consolidation treatments with NanoRestore, NanoEstel, Acril 33 and Acril ME.

Stone sample	Consolidant	Δa*	Δb*	ΔL*	ΔE	Δgloss%
Vicenza	NanoRestore	-1.59	5.89	5.11	7.96	-13
	NanoEstel	-0.97	8.17	3.08	8.78	33
	Acril 33	-0.62	11.25	1.90	11.42	-173
	Acril ME	0.30	13.58	-1.94	13.72	-39
Arenaria	NanoRestore	-1.10	5.46	5.43	7.78	-22
	NanoEstel	-0.83	7.11	0.29	7.16	-54
	Acril 33	-0.82	6.56	0.88	6.67	-1109
	Acril ME	-0.70	6.59	0.11	6.63	-1256
Istria	NanoRestore	-0.74	6.64	3.55	7.57	-18
	NanoEstel	-0.58	9.15	2.25	9.44	-51
	Acril 33	-0.85	8.56	2.24	8.89	-666
	Acril ME	-1.16	8.39	0.85	8.51	-527

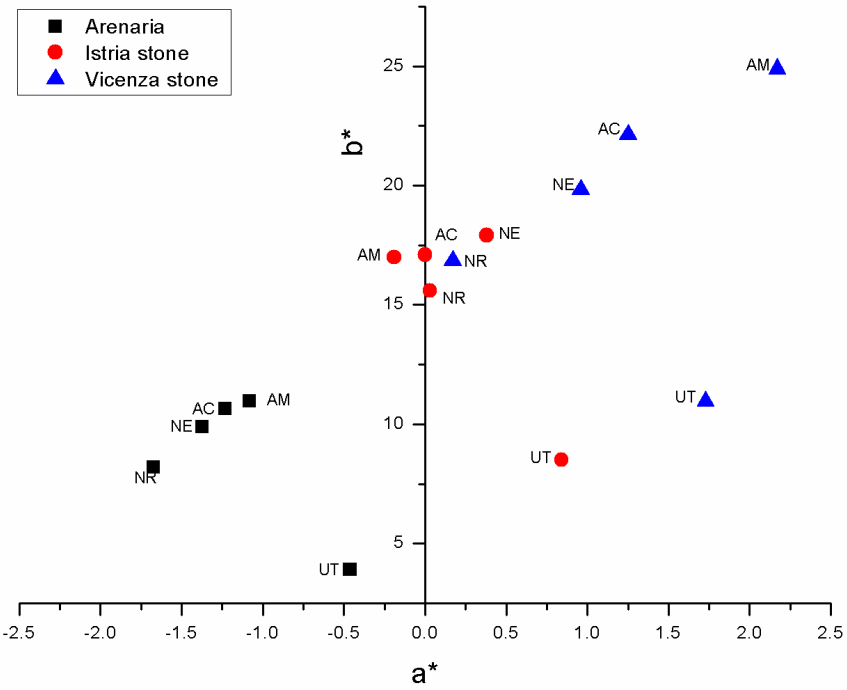


Figure 4. Plot of a* *vs* b* values (color graph) determined for untreated (UT) Vicenza stone (Δ), Arenaria (□) and Istria stone (O) and treated samples with NanoRestore (NR), NanoEstel (NE), Acril 33 (AC) and Acril ME (AM).

3.2.2. Natural and UVB aging of treated stones

Stone samples treated with NanoRestore, NanoEstel, Acril 33 and Acril ME were exposed to different aging environments, a natural outdoor aging over 2 years (in Venice-Mestre, Italy), and an artificial (UVB) aging for 1200 hours. Total color (ΔE) and gloss (Δgloss %) variations values obtained after both aging experiments are reported in Table 2.

Table 2. ΔE and Δgloss % values determined for Vicenza, Arenaria and Istria stone after natural outdoor and UVB aging.

Stone sample	Consolidant	Natural aging		UVB aging	
		ΔE	Δgloss %	ΔE	Δgloss %
Vicenza	NanoRestore	24.21	61	3.94	-8
	NanoEstel	21.63	50	2.98	-25
	Acril 33	25.61	59	4.88	-37
	Acril ME	24.18	75	4.18	-75
Arenaria	NanoRestore	9.90	33	1.51	-16
	NanoEstel	8.88	25	1.84	-37
	Acril 33	17.59	97	3.15	-17
	Acril ME	24.85	97	2.79	-24
Istria	NanoRestore	9.78	44	3.73	-22
	NanoEstel	11.43	40	2.67	-7
	Acril 33	22.43	91	2.85	-34
	Acril ME	18.39	87	3.85	-57

As far as natural aging, Vicenza stone treated samples showed the highest ΔE variations regardless the consolidant applied, with values ranging from 21.6 to 25.6, while for Arenaria and Istria stones, the lowest ΔE values were observed for samples treated with nano-based consolidants (values ten times lower than those obtained for the treatment with acrylate derivatives). Furthermore, ΔE variations over time were also investigated along the two years of aging experiments performed, and the overall results obtained for each consolidant are reported in Figure 5. From these data it can be clearly observed the highest and fast increment of ΔE for all the stones samples treated with Acril 33 and Acril Me emulsions.

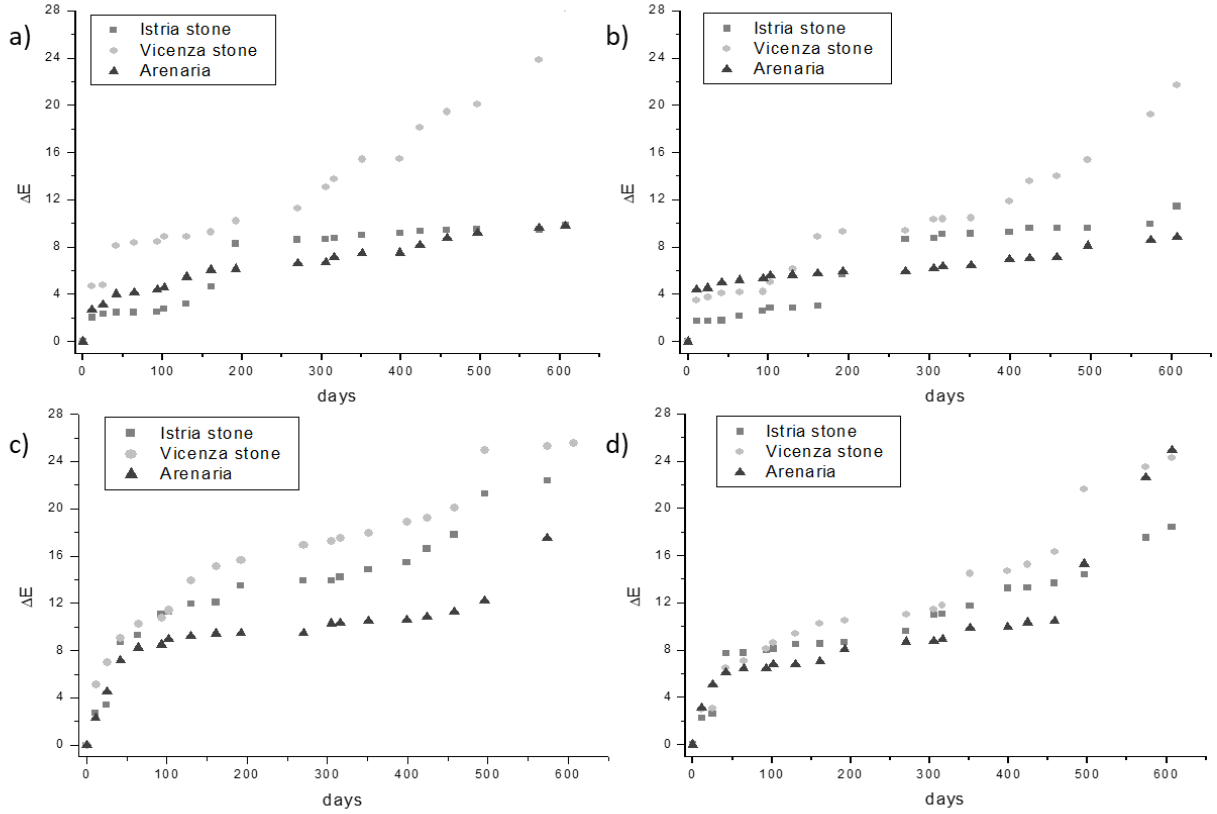


Figure 5 – ΔE parameter determined for the samples of Vicenza, Arenaria and Istria stone treated with (a) NanoRestore, (b) NanoEstel, (c) Acril 33 and (d) Acril ME and exposed at incremental time of natural outdoor aging conditions.

In detail, as displayed by the color graph reported in Figure S2 (SI), the total chromatic variations observed for the different stones are principally linked to a shift in the coordination color towards a red-brown dye. Moreover, as reported in Figure S3 and Figure S4 (SI), a decrease of L* values was recorded for Vicenza and Arenaria stones treated with the different consolidants, except for Arenaria with NanoEstel. In this last case, a whitening of the surface occurred, probably due to the formation of a thick silica-based layer derived from the crosslinking of the consolidants precursor. On the other hand, as showed in Figure S5 (SI), no significant variation in terms of lightness was determined for Istria stone exposed to natural aging, except for the samples treated with the two acrylic-based products, highlighting a massive darkening of the surface.

The colorimetric changes observed were mainly ascribed to deposition and entrapment of dust and atmospheric particles into the stone pores, as shown in Figure S6 (SI). In the specific case of aged Vicenza stone samples, the shift towards the dark red colour observed (Figure S2 in SI) was finally attributed to the presence and diffuse growth of freshwater *Chlorophyta* microalgae, from the family of *Haematococcaceae*. Optical microscope analysis (Figure 6) highlighted the presence of this unicellular microalgae (size ranging from 40 to 120 µm), which contains blood-red carotenoid pigment astaxanthin (3,3'-dihydroxy-β,β-carotene-4,4'-dione) in the cytoplasmic lipid globules of their cells. These pigments are produced and rapidly accumulated when the environmental conditions become unfavourable for normal cell growth [51,52], explaining the dark red colour observed in treated Vicenza stones after the natural aging process.

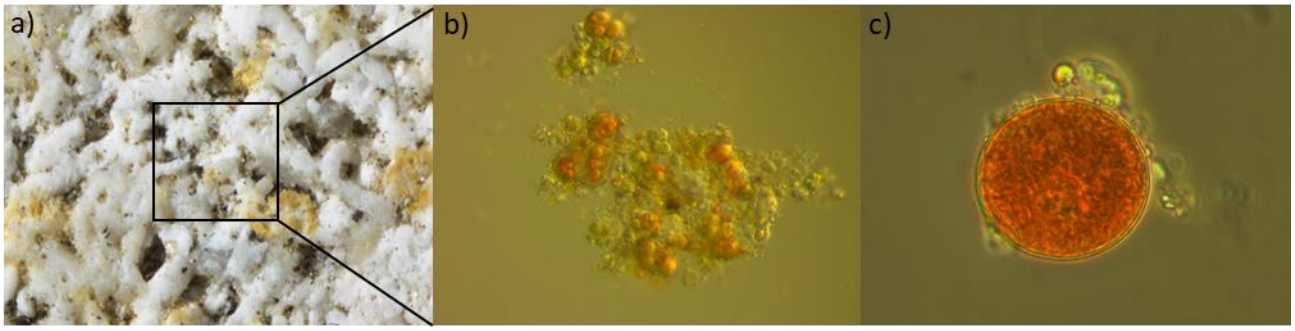


Figure 6- Micrographs of Vicenza stone treated with NanoRestore and exposed over two years to outdoor conditions. a) stone surface at 20x; b) *Chlorophyta* microalgae observed on the surface at 200x, c) *Chlorophyta* microalgae at 400x.

Concerning Δgloss % (Table 2), the natural aging induced a reduction in the gloss values for all the stone samples investigated (Δgloss % > 0). This indicate an opacification of the surface layers treated with the different consolidants. In detail, the inorganic NPs products, NanoRestore and NanoEstel, showed low gloss variations always < 50% for all the treated materials except for Vicenza stone treated with Nanorestore (61%). The best performances for these consolidants were obtained in the treatment of Arenaria. On the other hand, Acril 33 and Acril ME consolidants induced a highest opacification of the treated surfaces with Δgloss % ranging from 59 to 97%.

As far as UVB aging (Table 2), the laboratory conditions employed for the test seemed to not induce any significant color variation of the treated stone surfaces, showing ΔE always < 5. Also in this case, ΔE variations over time were investigated (Figure 7), confirming the low color alteration induced by UVB aging conditions over 1200 hours of analysis.

Moreover, according to the stereo microscope images (Figure S7 in SI), the surface appeared to be similar to the one of the original untreated stones, and the formation of craquelure or microfractures was not observed after 1200 hours of UVB aging.

As far as Δgloss % (Table 2), conversely to what observed during natural aging, UVB aging induced an increase in the gloss values of the surface. The increment of the brightness of the surface can be explained, in the cases of polymeric consolidants film of NanoEstel, Acril 33 and Acril Me, with an

increase of the degree of polymerization of the commercial products exposed to UVB irradiation [53]. Furthermore, in the case of the NanoRestore, the increment of gloss can be ascribed to a further conversion of $Ca(OH)_2$ NPs to $CaCO_3$ [18]. In general, a good resistance to photo-degradation was observed for all the stone surfaces treated with both the inorganic consolidants and Acril33, with Δgloss % values ranging from -37 to -7, while high variations were observed for AcrilMe (up to -75).

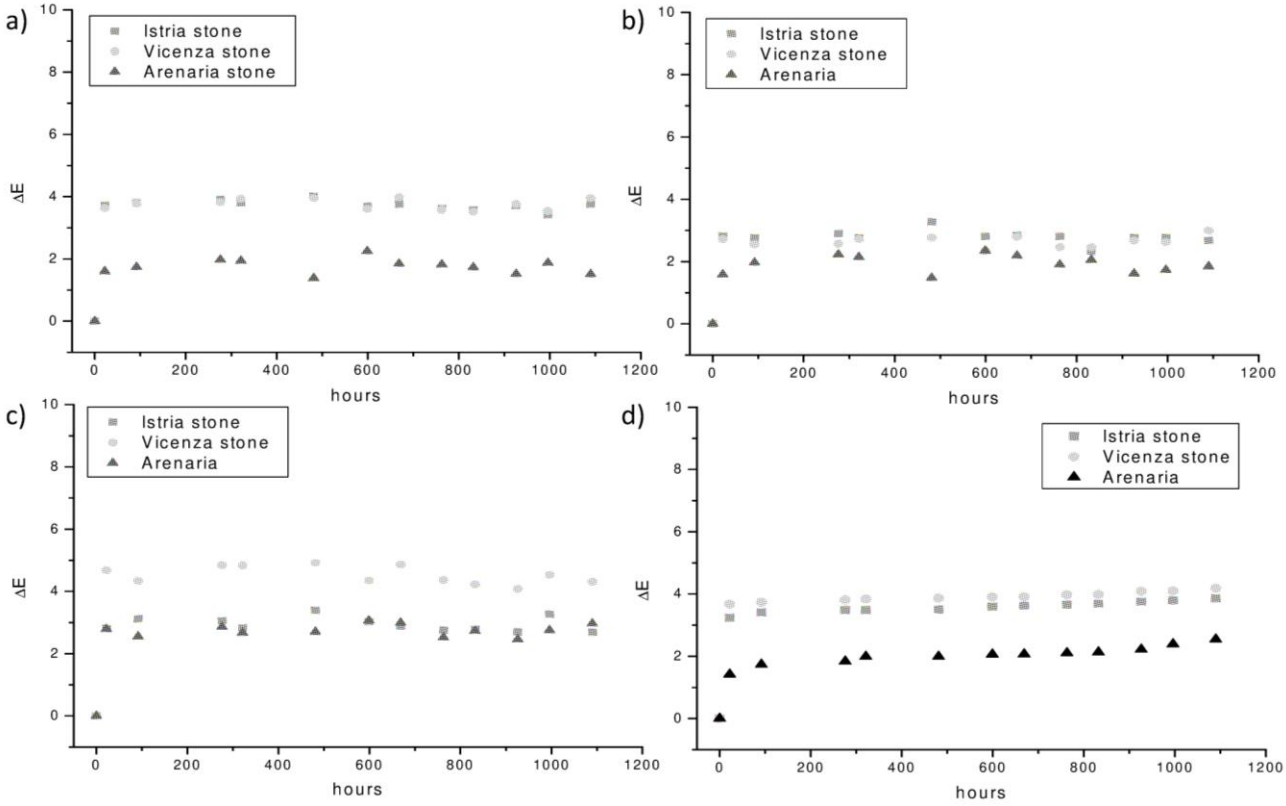


Figure 7 – ΔE parameter determined for the samples of Vicenza, Arenaria and Istria stone treated with (a) NanoRestore, (b) NanoEstel, (c) Acril 33 and (d) Acril ME and exposed at incremental time of UVB aging conditions.

4. Conclusions

In this study, commercial Nanorestore, Nanoestel, Acril 33 and Acril ME were applied on Vicenza, Arenaria and Istria stones, for investigating their surface appearance after the consolidation treatment. The overall results obtained by the followed approach, in which colorimetric and gloss measurements were combined with stereo microscope analysis and adsorption measurements, provided useful insights on the most suitable product in the stones consolidation with respect to Venice environment. In detail, the worst performances in terms of highest colour and gloss alterations of the stones surface were observed under natural aging conditions with respect to UVB. Among the three stones investigated, Vicenza stone resulted the most sensitive material towards aging degradation after the treatment with all the consolidants, while among all the consolidants applied, nano-based materials showed the best performances, highlighting the importance of nanotechnology in stone conservation field.

Conflict of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

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Supporting Information

Consolidation of Vicenza, Arenaria and Istria stones: a comparison between nano-based products and acrylate derivatives

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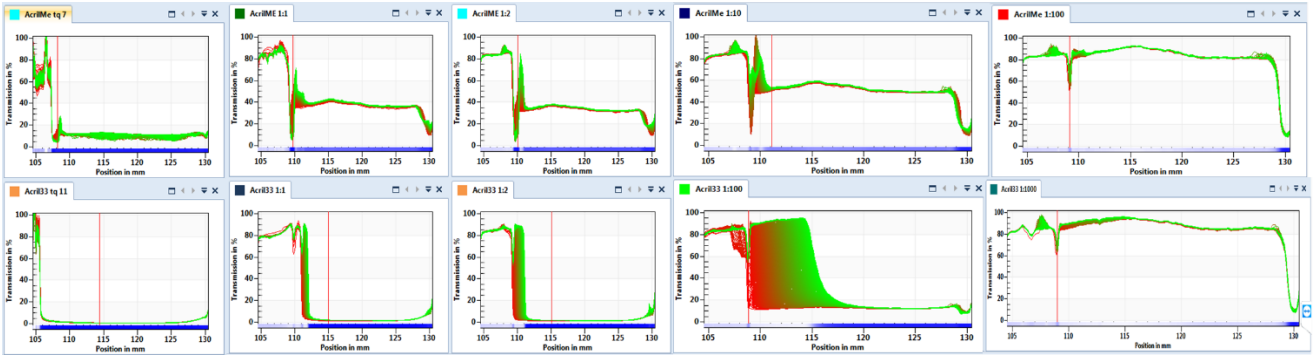


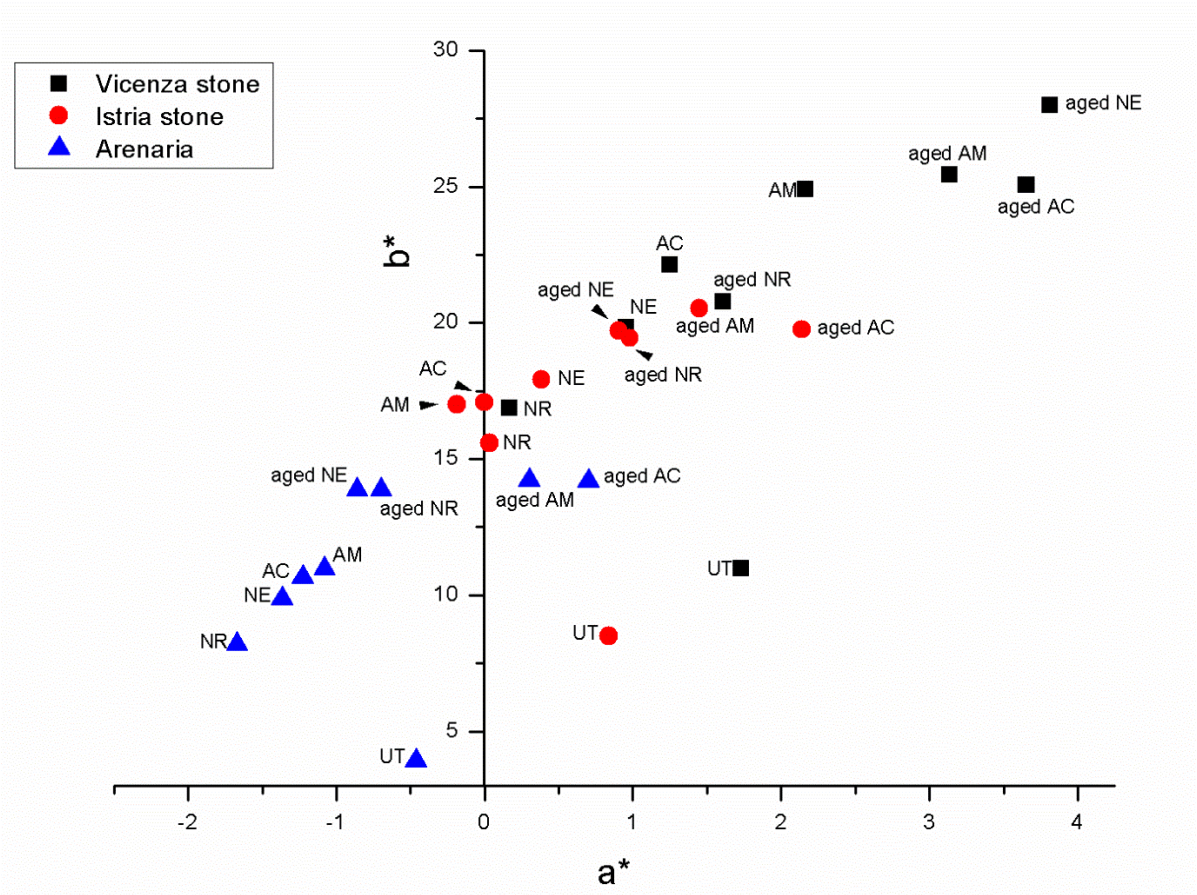
Figure S1 – Trasmission profiles of Acril Me fresh, 1:2, 1:4, 1:10 and 1:100 dilution with MilliQ water (top) and of Acril 33 fresh, 1:2, 1:4, 1:100 and 1:1000 dilution with MilliQ water (down).

Table S1. BET surface area and total pore volumes determined at P/P_0 of 0.98 for Vicenza stone, Arenaria and Istria stone.

Sample	**BET surface area (m^2/g)**	**Total Pore volumes (cm^3/g)**
Vicenza stone	$5.5 \cdot 10^{-2}$	$2.5 \cdot 10^{-3}$
Arenaria	4.3	$8.0 \cdot 10^{-3}$
Istria stone	$3.0 \cdot 10^{-2}$	n.d.

Table S2. Quantity (g) of absorbed product (NanoRestore, NanoEstel, Acril 33 and Acril ME) from the Vicenza stone, Arenaria and Istria stone.

Sample	**Vicenza stone (g)**	**Arenaria (g)**	**Istria stone (g)**
NanoRestore	0.031 ± 0.004	0.018 ± 0.003	0.006 ± 0.001
NanoEstel	0.800 ± 0.030	0.011 ± 0.020	0.010 ± 0.003
Acril 33	0.460 ± 0.040	0.170 ± 0.040	0.073 ± 0.007
Acril ME	0.630 ± 0.050	0.200 ± 0.040	0.150 ± 0.030



564
565 Figure S2- Plot of a* versus b* values determined for untreated (UT), fresh and aged at outdoor
566 Venezia Mestre environments treated samples with NanoRestore (NR), NanoEstel (NE), Acril 33
567 (AC) and Acril ME (AM). a= Vicenza stone (V); b= Arenaria (A); c= Istria stone (I).
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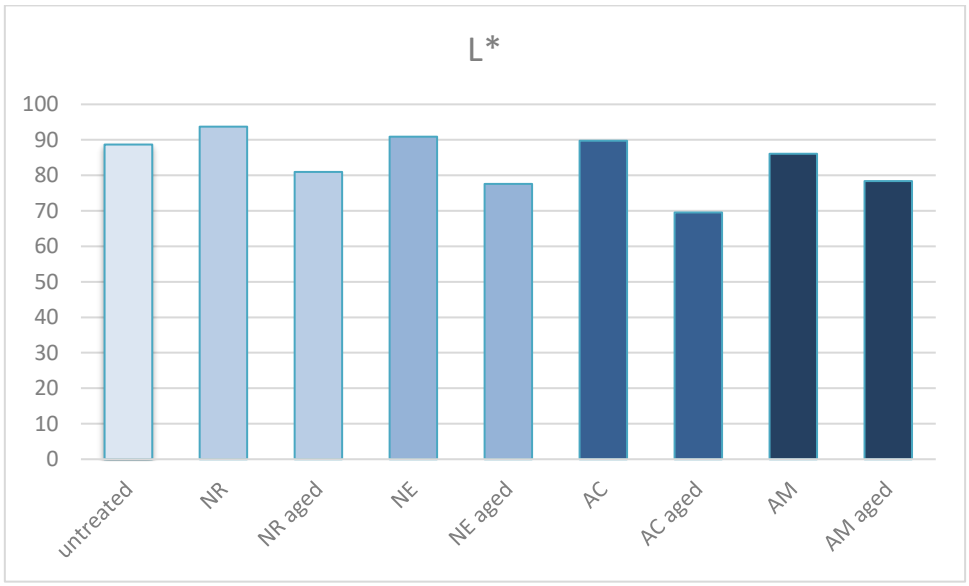

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571 Figure S3- Plot of L* values of untreated, fresh and aged (outdoor Venice-Mestre environment for
572 two years) Vicenza stone with NanoRestore (NR), NanoEstel (NE), Acril 33 (AC) and Acril ME
573 (AM).

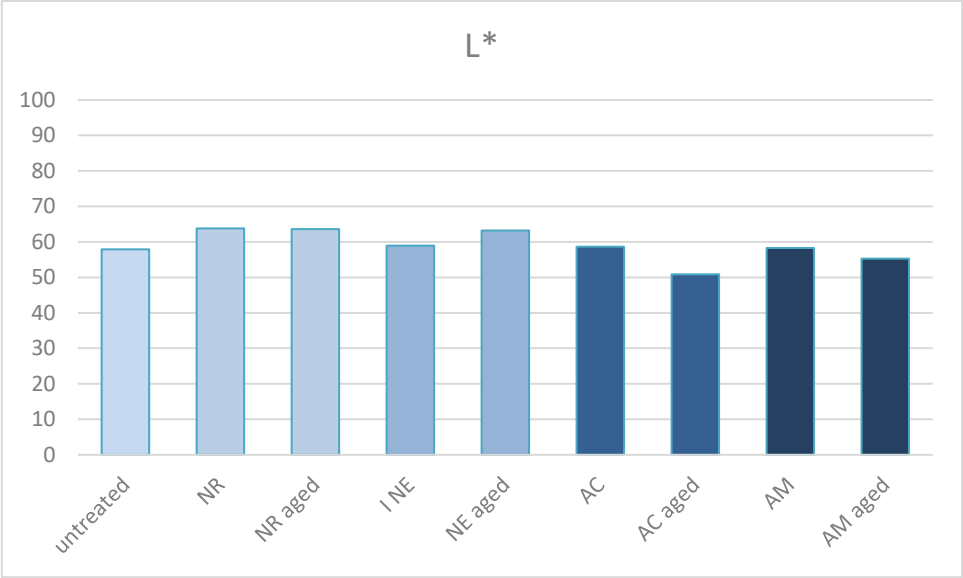

Figure S4- Plot of L* values of untreated, fresh and aged (outdoor Venezia Mestre environment for two years) Arenaria with NanoRestore (NR), NanoEstel (NE), Acril 33 (AC) and Acril ME (AM).

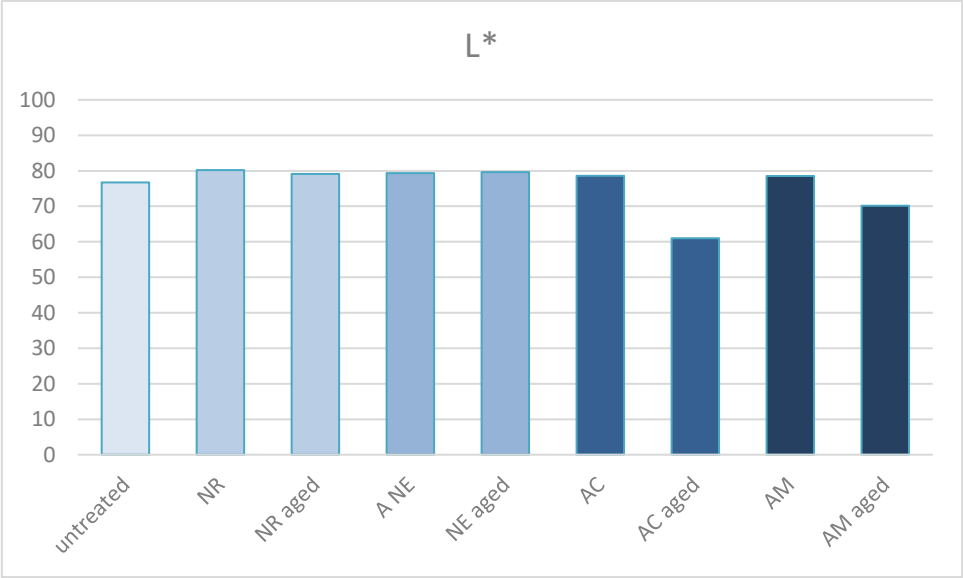

Figure S5- Plot of L* values of untreated, fresh and aged (outdoor Venezia Mestre environment for two years) Istria stone with NanoRestore (NR), NanoEstel (NE), Acril 33 (AC) and Acril ME (AM).

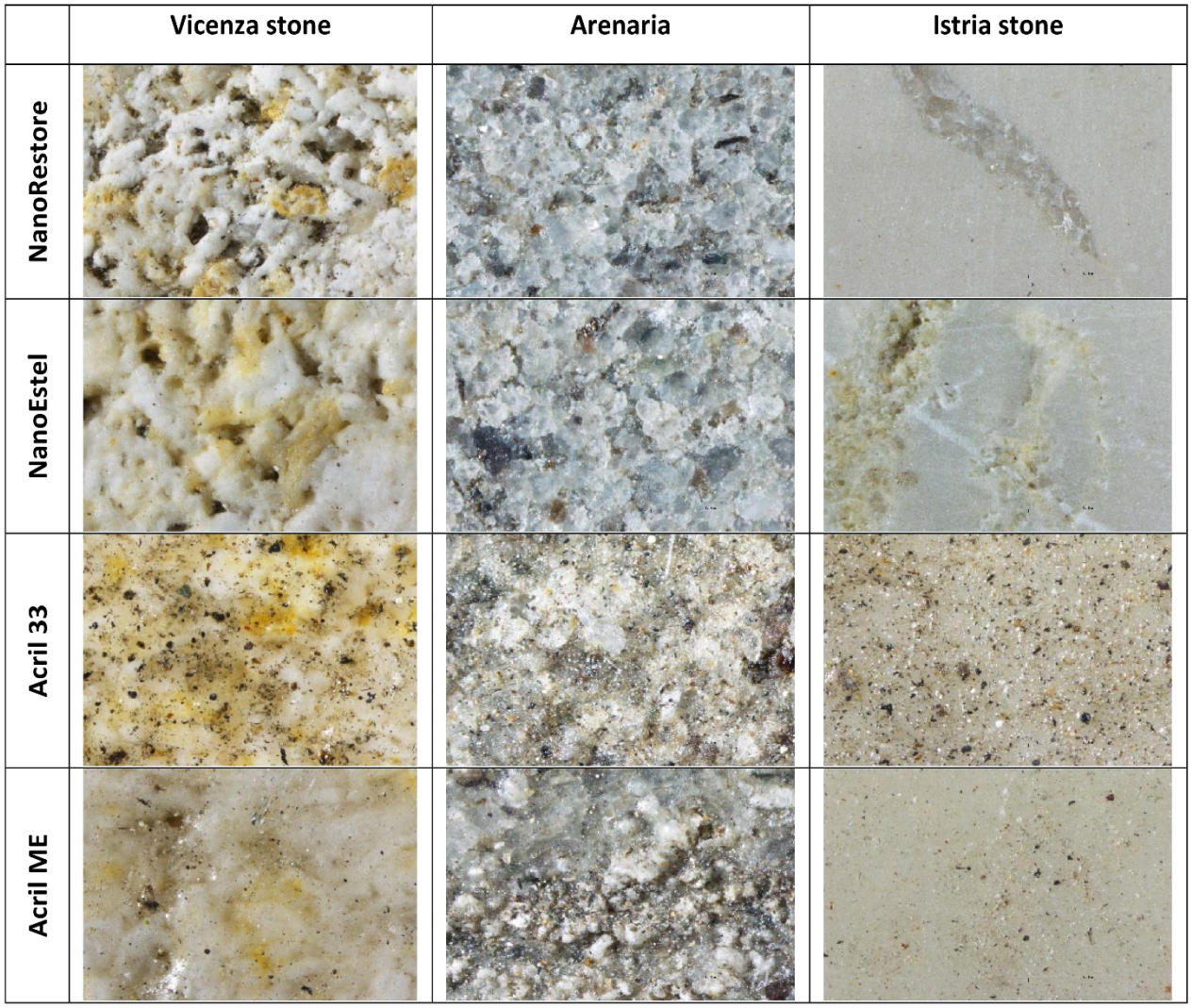

Figure S6. Micrographs (20x) of the surface morphology of the stone samples treated with NanoRestore, NanoEstel, Acril 33 and Acril ME and exposed at Venezia Mestre outdoor condition for two years.

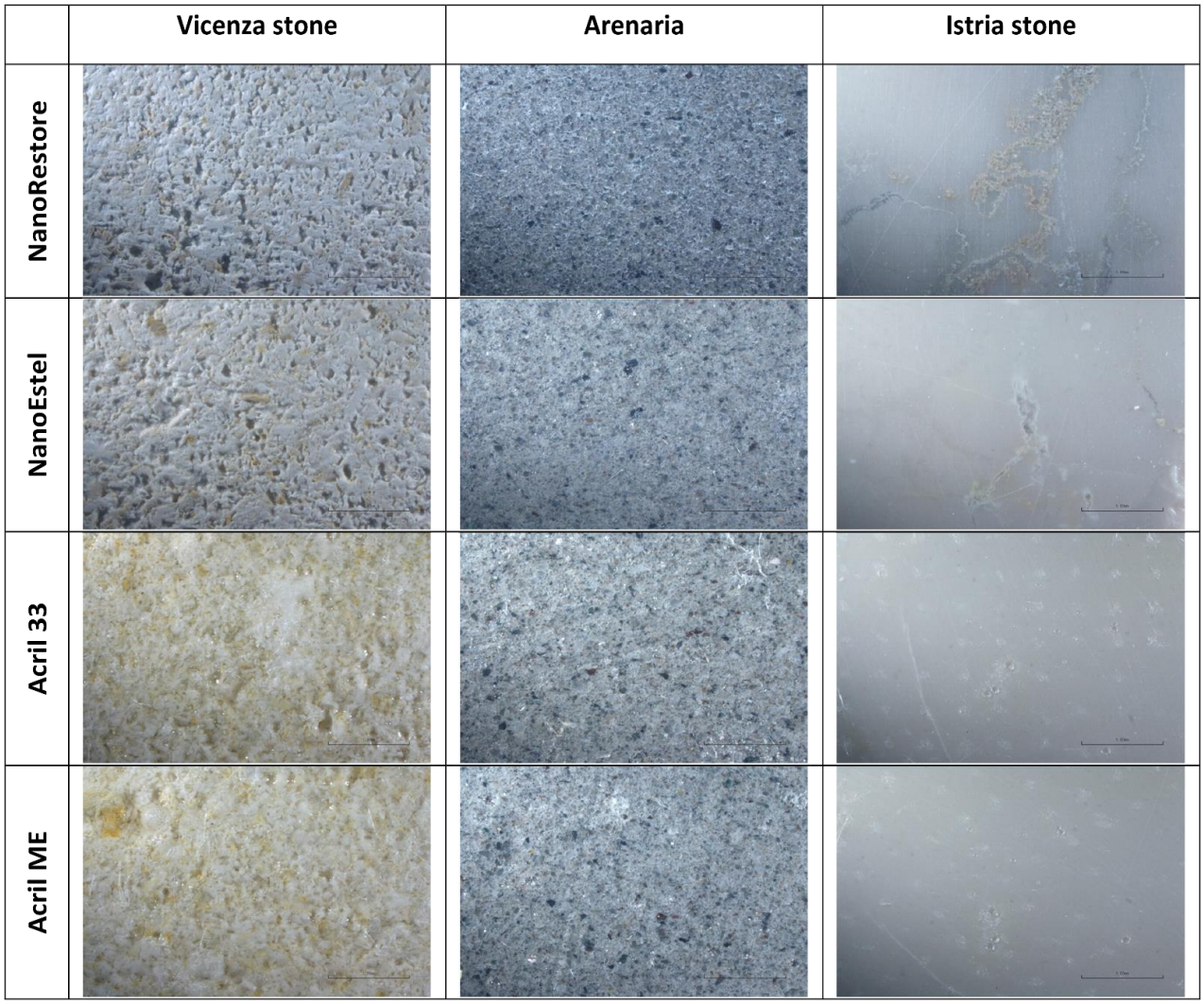

Figure S7. Micrographs (10x) of the surface morphology of the stone samples treated with NanoRestore, NanoEstel, Acril 33 and Acril ME and exposed at UVB aging for 1200 hours.