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# EVALUATION OF SILICONE BASED PRODUCTS USED IN THE PAST AS TODAY FOR THE CONSOLIDATION OF VENETIAN MONUMENTAL STONE SURFACES

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## ABSTRACT

The commercial consolidating siloxane compounds *EAS 40*, *Rhodorsil Consolidante RC90* and *RC80*, and the silicone water repellent agents *Rhodorsil H224* and *Hydrophase* were carefully applied to stone specimens and tested to ascertain their chemical nature and their stability under oxidative stress and degradative environments. The resins were applied to laboratory samples (Carrara marble and Vicenza white limestone specimens) and subjected to controlled natural weathering and artificial ageing. The film morphology and the penetration depth was observed and measured by SEM-EDS determinations, while the stability of the resins was monitored by FTIR, SEM-EDX, colorimetric measurements and sponge tests. The results were compared with those obtained from a spread sampling of Venetian surfaces treated in the second half of the XX c. with *Sogesil XR893* and *X54-802*, silicone resins which are no longer on the market. The overall results prompted a number of considerations on the effects of the resins applied to stone materials and offered the authors the opportunity to make a practical contribution to current practices in the consolidation of stone materials.

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**KEYWORDS:** stone conservation, strengthening agent, silicone resin, photo-oxidation, biodeterioration.

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## 1. INTRODUCTION

People have always attempted to protect architectural and decorative stones from their inevitable deterioration. In ancient times, there was the long-established tradition of the maintenance of original stone materials. During the XIX century and with the rapid development of the chemical industry and industrial complexes, the development of techniques and research into synthetic materials used for the preservation of immovable cultural heritage led to the advancement of new technologies and application methods, which were also adapted for the restoration and conservation of stone materials (e.g. Manoudis et al., 2017; Sabatino et al., 2016; El Darby et al., 2016; Samanian et al., 2012). Alkaline silicates and fluoro-silicates were suggested as strengthening agents due to their capacity to hydrolyze after application, with the consequent precipitation of silica in the pores of stone. At the end of the 1940s, architectural and sculptural conservators accepted the arrival and diffusion of polymeric materials with great enthusiasm. Acrylic and epoxy resins, silicon-based products, fluorinated compounds and polyester polymers were widely used. Restorers and conservators contributed to their diffusion and the related application methodologies, though preliminary experimental tests were not always undertaken to ensure their efficacy (Cavaletti et al., 1985; Ginell et al., 1998; Ferreira Pinto et al., 2008). This often led to the development of unexpected degradation mechanisms, such as the generation of secondary products, due to the chemical interaction between the product applied and the stone substrate or with the environment (Antonelli et al., 2016), which in turn compromised the stability and the aesthetic aspect of the artefact (Varas et al., 2007). In Venice, sensitivity towards conservation and restoration of monumental buildings increased on the 4th November 1966 when a sea flood threatened the city. On that occasion, the Italian government asked UNESCO to promote studies of the monuments in order to safeguard one of the largest and most untouched historical centres in the world, which has been preserved for centuries. Scientific researchers were encouraged and exhaustive reports were published regarding the general problems of the inner centre and the lagoon and, more specifically, stone conservation (Electa, 1986). It was an experimental time. During that period, the first treatments using synthetic polymers were carried out in Venice (Lazzarini, 1993). The study of the chemical stability and solubility of commercial products used in the past is, today, strongly recommended, in order to monitor the state of conservation of treated surfaces and to make informed assessments of when and where new treatments may

be necessary (Ferreira Pinto et al., 2008, Antonelli et al., 2016). Moreover, the knowledge of the mechanisms of alteration of commercial products allows for better understanding of the needs, purposes and limits of the products applied. However, assessing the resistance of a protective or strengthening agent to natural weathering or to microbiological attack is typically a lengthy process necessitating long-term field trials.

In this context, the present work aims to study 3 strengthening and 2 protective agents based on silicone, commonly used for the restoration and conservation of stone artefacts, for improving the understanding of the stability of these polymeric compounds after natural and artificial ageing. In order to compare the effectiveness of the treatments and their stability under oxidative stress and degradative environments, the resins were applied to veined Carrara marble and Vicenza white limestone specimens and subjected to different typologies of degradation: natural weathering in Venice and artificial ageing (Xenon irradiation). Fourier Transform Infrared Spectroscopy (FTIR) were of invaluable help in understanding the chemical characteristics and features of the resins, the sol-gel processes and the polymer structural changes due to ageing processes. Microscopic observations of cross-sectioned samples (especially by means of SEM-EDS analysis) were carried out to investigate the morphology of the stone after the application of the resin. In addition, colorimetric and water absorption measurements (sponge-contact method), were used to verify chromatic alterations and variations of water repellency of the treated surfaces, connected to the degradation of the polymer. The results obtained were compared and contrasted with the evaluation of past conservative treatments based on silicone resins (*Sogesil XR893* and *X54-802*) applied on stone monumental surfaces in Venice during the 1960s and the 1970s (Tesser et al., 2017).

## 2. EXPERIMENTAL

### 2.1 Materials

The siloxane strengthening agents considered were *EAS 40*, an orthosilicic acid ester (ethyl silicate 40) provided ready-to-use by Sinopia Restauro, *Rhodorsil Consolidante RC90* and *Rhodorsil Consolidante RC80*, both supplied by the Italian company Siliconi Padova. *Rhodorsil Consolidante RC90* and *RC80* are composed of tetraethylorthosilicate (TEOS) combined with a tin-siloxane catalyst and a water repellent component, which is a methyl resin in the case of *RC80* and a methyl-phenyl resin in the case of *RC90*. The solvent is white spirit with the addition of xylene only in the case of *RC90*, presumably to im-

prove dissolution of the methyl-phenyl resin (Siliconi Padova, 2000; Siliconi Padova, 1994). During the curing processes and the consequent polymerization mechanisms, the resins develop branched siloxane structures and provide waterproofing properties due to the hydrophobic feature of methyl groups in their formulation. They are both very durable with respect to UV and thermo-oxidation (Tesser et al., 2014). In the restoration field, *Rhodorsil Consolidante RC90* has replaced the old *Sogesil XR893* (Rhône Poulenc), an organosilicon compound manufactured by dissolving a methyl-phenyl-polysiloxane in benzene with a solid content of 50% (Marchesini et al., 1966).

The silicone water-repellent agents studied were *Rhodorsil H 224* and *Hydrophase*. The first product is a transpiring agent supplied by Siliconi Padova as a solution of alkyl polysiloxane polymer in a mixture of aliphatic hydrocarbons. For application on stone materials, the product has to be diluted by 10% using white spirit. *Hydrophase* is an alkyl-alkoxy silane with molecular dimensions similar to those of water (5-10 Å), produced by Phase Restauro and provided ready-to-use.

## 2.2 Methods

The resins were applied by brushing, to the point of complete absorption, on veined Carrara marble and Vicenza white limestone specimens measuring 5 cm x 5 cm x 1 cm. Two samples were prepared for each resins and stone substrates. After application of the strengthening agents, the samples were kept at room temperature until the curing of the polymer was achieved (15 days).

Natural weathering was developed by exposing ten treated and two untreated specimens to Venetian outdoor conditions, on a balcony at Palazzo Badoer (S. Polo, Venice), overlooking a garden, a long way from canals and water-bus pollution. The specimens were placed on a south-facing plastic support, inclined by 60°, and exposed for 12 months. The aging was monitored monthly for the first three months, then every three months.

Photo-oxidative weathering was carried out on five couple of treated specimens and a couple of untreated specimens in the laboratory using a SolarBox 3000 apparatus (CoFoMegra, Milan), equipped with a Xenon light source with one filter cutting both the wavelengths lower than 295 nm (outdoor simulation) and higher than 800 nm (IR radiation) thus avoiding the heating of the specimens. The irradiation was set to 500 W/m<sup>2</sup> for the duration of the test, which lasted for 1200 h (UNI 10925, 2001). Monitoring was performed every 200 h for the first 600 h and at the end (1200 h).

The surfaces of the treated samples were periodically observed during the ageing processes using a

Leica WILD M3Z stereomicroscope with increasing magnification (6.5x, 10x, 16x, 25x, 40x) in order to describe the physical and morphological characteristics of the samples. A polyethylene slide was used to make a mask with 5 holes, in order to take repeated pictures in a specific area of the sample's surface so as to be able to compare the results obtained throughout the ageing process. The camera used was a Leica CLS150E model.

Periodically,  $\mu$ FTIR analyses using a Jasco IRT-5000 Irtron Infrared Microscope were carried out in order to study the chemical nature and the state of conservation of the applied resin over time. A micro scale of the polymeric films was sampled from the stone surfaces, using a needle, laid and pressed on a standard KBr pellet, then analyzed in transmittance mode. In this case the spectral resolution was 1 cm<sup>-1</sup> and the consecutive scans were 120. The sponge test, carried out according to the UNI 11432 standard (UNI 11432, 2011), was applied to check the maintenance of the hydrophobic features of the treated stone surfaces. It consists of a 1034 Rodac\_contact-plate (5.6 cm diameter) containing a sponge (Calypso natural make-up Spontex), thicker than the height of the borders of the contact-plate after wetting with approximately 5 ml of water. During the tests, the contact plate was pressed against the treated surface, applying the maximum amount of pressure, which is determined by the contact of the borders of the contact plate with the examined surface. The contact time was 1 minute for Vicenza white limestone and 3 minutes for veined Carrara marble due to its low porosity. The initial and final weights of the contact-plate containing the damp sponge, before and after the contact with the surface, were measured using an analytical balance. The amount of water absorbed by the material being tested, was expressed by the mass difference as a function of area and time, using equation 1, where  $Wa$  is the water absorption per square metre and unit time,  $m_i$  is the initial weight of the sponge inside the contact-plate,  $m_f$  the final weight of the sponge inside the contact-plate after the test,  $A$  is the sponge area and  $t$  is the time contact:

$$Wa(g / m^2 s) = \frac{\Delta m}{A \cdot t} = \frac{(m_i - m_f)}{A \cdot t}$$

*Equation 1: mathematical formula to calculate the water absorption per square meter and time-unit (Wa)*

The sponge test was repeated 3 times for each specimen and the mean value calculated. Colour changes induced by degradation of polymers were evaluated by colorimetric measurements on treated specimens using a Konica Minolta CM-2600d colorimeter. The analyses were carried out according to the standard (EN 15886, 2010). A polyethylene slide

was used to make mask with 5 holes, to enable accurate repositioning of the instrument in the same area of the sample. The results were reported in the CIELab1976 system. Each set of data shown below is the mean value of the 5 areas for each sample. The total colour variation  $\Delta E$  was calculated according to Equation 2.

$$\Delta E^*_{ab} = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2}$$

*Equation 2: mathematical formula to calculate the total colour variation  $\Delta E$*

Morphological observations and detailed chemical microanalyses were used in order to measure the penetration depth of the products in the specimens. The cross-sections of the cut samples, coated with a thin gold layer, were studied with a Philips XL 30 SERIES SEM. The semi-quantitative elemental composition was measured by EDS with a EDAX X-ray dispersive spectrometer, equipped with a thin beryllium window. The accelerating voltage was 25 keV. The observations were carried out according to the Normal 8/81 recommendation (Normal 8/81, 1981).

### 2.3 Evaluation of conservation treatments

In order to investigate the alterations suffered by silicone-based compounds and caused by the Venetian environment after several decades from their application, a fragment from the Lunette above the portal of Corner chapel "Madonna con bambino e angeli" (Lamberti, Maestro dei Mascoli, Bartolomeo Bon) of S. Maria Gloriosa dei Frari basilica - (Sestiere S. Polo - Venice) was collected from the lowest left part of the mantle of the Virgin Mary, adjacent to a previous broken area, using a scalpel in accordance with the Normal 3/80 recommendation (1980). The area of the sampling was finally covered by brushing with *Rhodorsil RC90* resin. In 1973-1974 K. Hempel and G. Musumeci cleaned the surface of Candoglia marble with pure water, sepiolite poultice and micro-sandblasting. The marble was lightly heated, treated with the solvent and consolidated using X54-802 (Rhone Poulenc) 1:0.1:0.04:1 in propan-2-ol and pure water (Lazzarini, 1979). The micro-fragments collected were studied by optical microscopy,  $\mu$ FTIR, FTIR and SEM-EDS analyses and particular attention was devoted to assess the stability of the resin. Taking into consideration also the results obtained in Tesser et al. (2017) from the evaluation of efficacy of

the polysiloxane *Sogesil XR893* used for the consolidation of stone materials in Venice, a thorough comparison with the results obtained from the laboratory examinations undertook.

## 3. RESULTS

### 3.1 Natural weathering

After outdoor exposure in the Venetian environment, the treated samples suffered gradual decay. The excess of silicone strengthening agents formed on the specimens showed diffuse craquelure after the first month of outdoor exposure and by the sixth month it was possible to observe the presence of biological microorganisms with different growth rates, especially on stone surfaces treated with *EAS 40*. In time, the superficial aspects of the stones progressively changed and, after 12 months, the samples completely lost the superficial film, as also confirmed by SEM investigation, permitting the gradual increase of the hydrophilicity of the surfaces (figures 1-2). In particular, the surfaces treated by *EAS 40* absorbed water more and more over time, due to the general tendency to crack of TEOS and to the absence of hydrophobic chemical groups, such as methyl and phenyl groups that characterize *Rhodorsil* resins.

Only observing the surfaces with a high magnification stereomicroscope, it was possible to see the presence of light yellow powder in the inter-grain spaces in case of *RC80*, and micro-scales of transparent resin in case of *RC90*. Mapping cross-sections of the samples by EDS analysis, the products showed little or no penetration in Carrara marble, whereas in the case of Vicenza limestone the penetration of the resins seemed to be dependent on the dimension of the macromolecules (figure 2). In fact, *EAS 40* showed the most homogeneous distribution in the sample section and it penetrated almost the entire thickness of the Vicenza limestone specimen (2 cm), while *RC80* penetrated to 7,5 mm and *RC90* to 4,5 mm.

In all specimens treated with *Rhodorsil RC90*, darkening of the surfaces was visible to the naked eye after 12 months, with deposition of atmospheric particles as well as biological growth on the surfaces. *Rhodorsil RC80* tended to turn yellow when exposed to outdoor conditions.

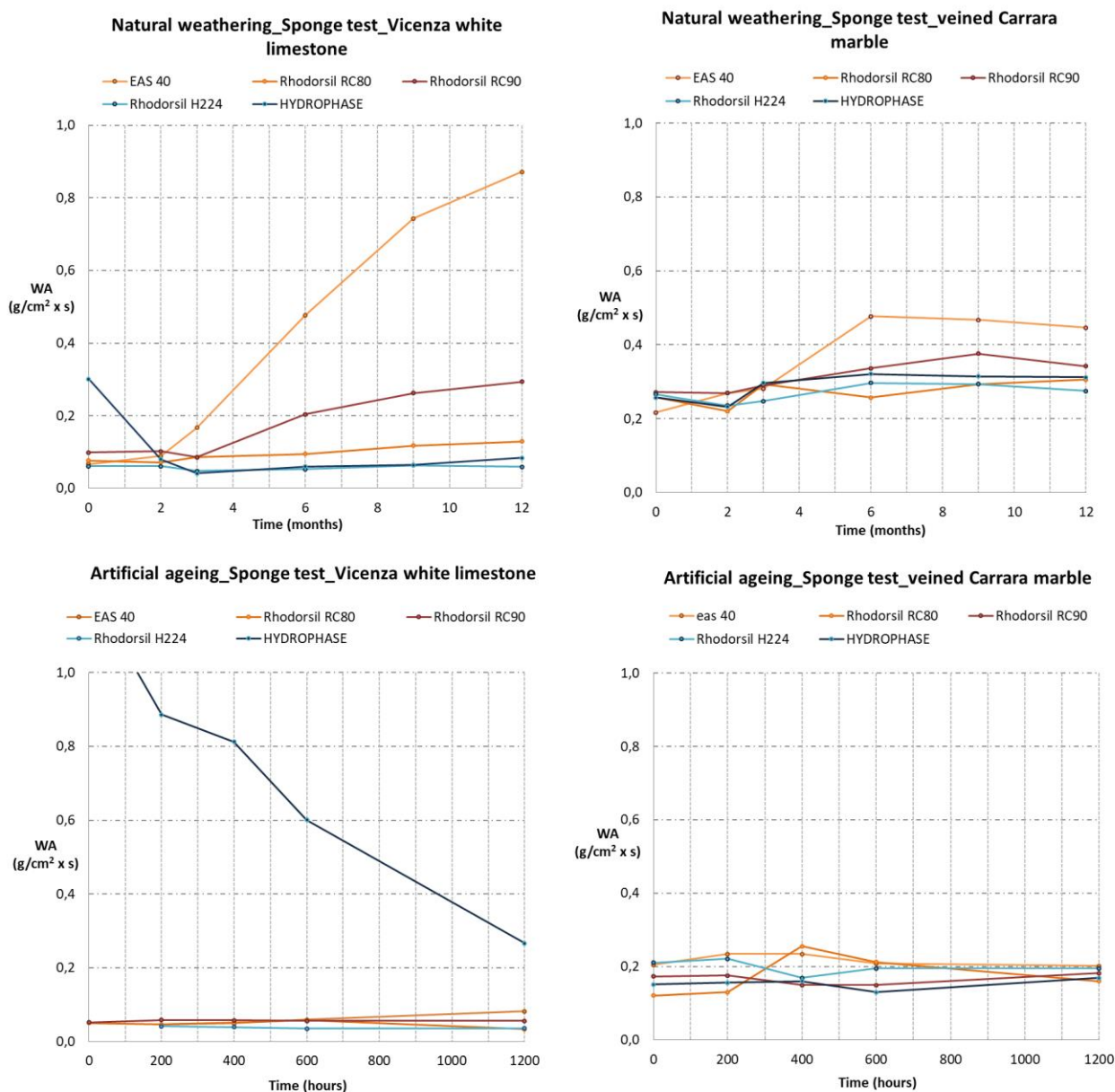


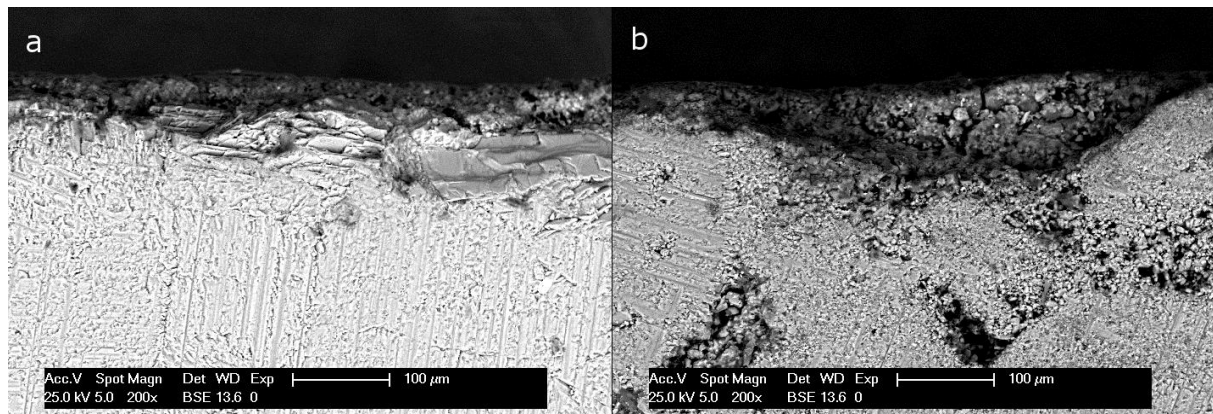
Figure 1: Results of sponge tests on treated specimens during natural weathering and artificial ageing.

All the products appeared chemically stable. The  $\mu$ FTIR spectra collected did not show any peculiar changes in the form of the appearance or disappearance of particular peaks or bands. In general, a shift was observed towards higher wavenumbers for all peaks related to the C-H chemical bond. According to the literature, this trend suggests a shortening of the chemical bond due to the lower degree of liberty of the molecules during the polymerization process (Whang et al., 2001; Orcel et al., 1986). In the case of the Si-O-Si chemical bond, the strengthening agents tested behaved differently. In particular, in the spectra of RC90 applied to a Carrara marble specimen (figure 3), the doublet at 1070-1051  $\text{cm}^{-1}$ , related to the symmetrical stretching of the Si-O-Si chemical bond in a branched structure, shifted gradually to-

wards lower values of wavenumber and definitely became a singlet at 1053  $\text{cm}^{-1}$ . Further evidence of the cross-linked siloxane chain, due to the polymerization process, derives from the broadening of this peak and the appearance of a shoulder at 1134  $\text{cm}^{-1}$ , which is probably due to the presence of the phenyl group. These results are in accordance with published studies of the polymerization process of RC90 resin on a slide (Tesser et al., 2014). In contrast, the spectra of RC90 applied to Venezia limestone showed higher intensity for those peaks related to C-H chemical bond (1431, 1450, 1471  $\text{cm}^{-1}$ ), with a shift of the peak related to the Si-O-Si chemical bond towards higher wavenumbers, from 1053 to 1078  $\text{cm}^{-1}$ . This may be related to a different interaction between the product and the substrate and it could

form an interesting topic for more detailed research in the future.

*Rhodorsil RC80* applied to Carrara marble as well as to Vicenza limestone, confirmed the same situation



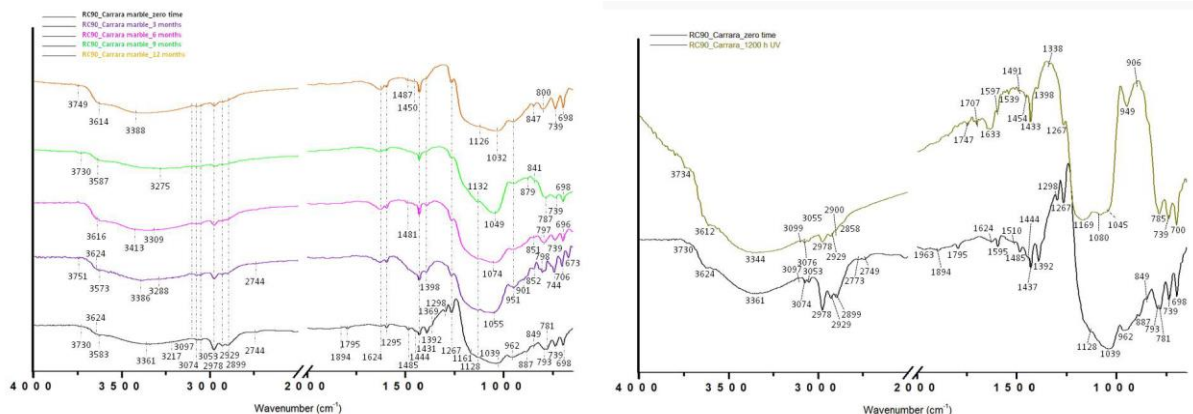
**Figure 2:** SEM micrographs of Carrara marble (a) and Vicenza limestone (b) cross-sections treated with Rodorsil Consolidante RC80 after 12 months of exposure to natural weathering. The product interacted in different way due to the different texture and porosity of the substrates.

Concerning water-repellent agents, throughout the ageing processes, *Rhodorsil H 224* appeared on Carrara marble specimens as a homogeneous, bright and transparent film, whereas on Vicenza limestone the resin seemed to react with the stone substrate. In fact, in the latter, after the application of the treatment, white crystals filled the pores of the stone and formed a superficial white patina, which during 12 months of exposure turned yellow and cracked. SEM-EDS analysis of the samples cross-section confirmed the probable alteration of the surface after application and curing of the resin, showing a thick superficial layer with a silicon content (1.9%) lower than that of the original composition of the resin (2.4%) distributed into the porous network of the stone. It was considered that the superficial layer

observed for *RC90* applied to Carrara marble. In this case too, a gradual shift of the peak related to the Si-O-Si chemical bond was observed towards lower values of wavenumbers, from 1082 to 1049  $\text{cm}^{-1}$ .

was composed not only of the resin, but also of an incoherent material made up of an aggregation of calcite and resin.

*Hydrophase* applied to both Carrara marble and Vicenza limestone showed the formation of a bright, homogeneous and thin polymeric film, which developed white particles and wore thin during natural ageing. Both *Hydrophase* and *Rhodorsil H224* showed diffuse fungal growth but they maintained hydrophobicity during ageing process assuring good protection effect. In particular, the behaviour of *Hydrophase* applied on Vicenza limestone is distinct, as the value of superficial hydrophobicity increased with time.  $\mu\text{FTIR}$  analysis ascertained the chemical stability of *Hydrophase* and *Rhodorsil H224* during the exposure of the resins to outdoor conditions.



**Figure 3:** On the left:  $\mu\text{FTIR}$  of Rhodorsil RC90 resin, applied to Carrara marble and exposed to outdoor conditions. Monitoring was undertaken at zero time (black line), after 3 months (violet line), 6 months (pink line), 9 months (green line) and 12 months (orange line). On the right:  $\mu\text{FTIR}$  of Rhodorsil RC90 resin, applied to Carrara marble and exposed to UV rays for 1200 hours. Monitoring was undertaken at zero time (black line), and after 1200 h of exposure (dark yellow line).

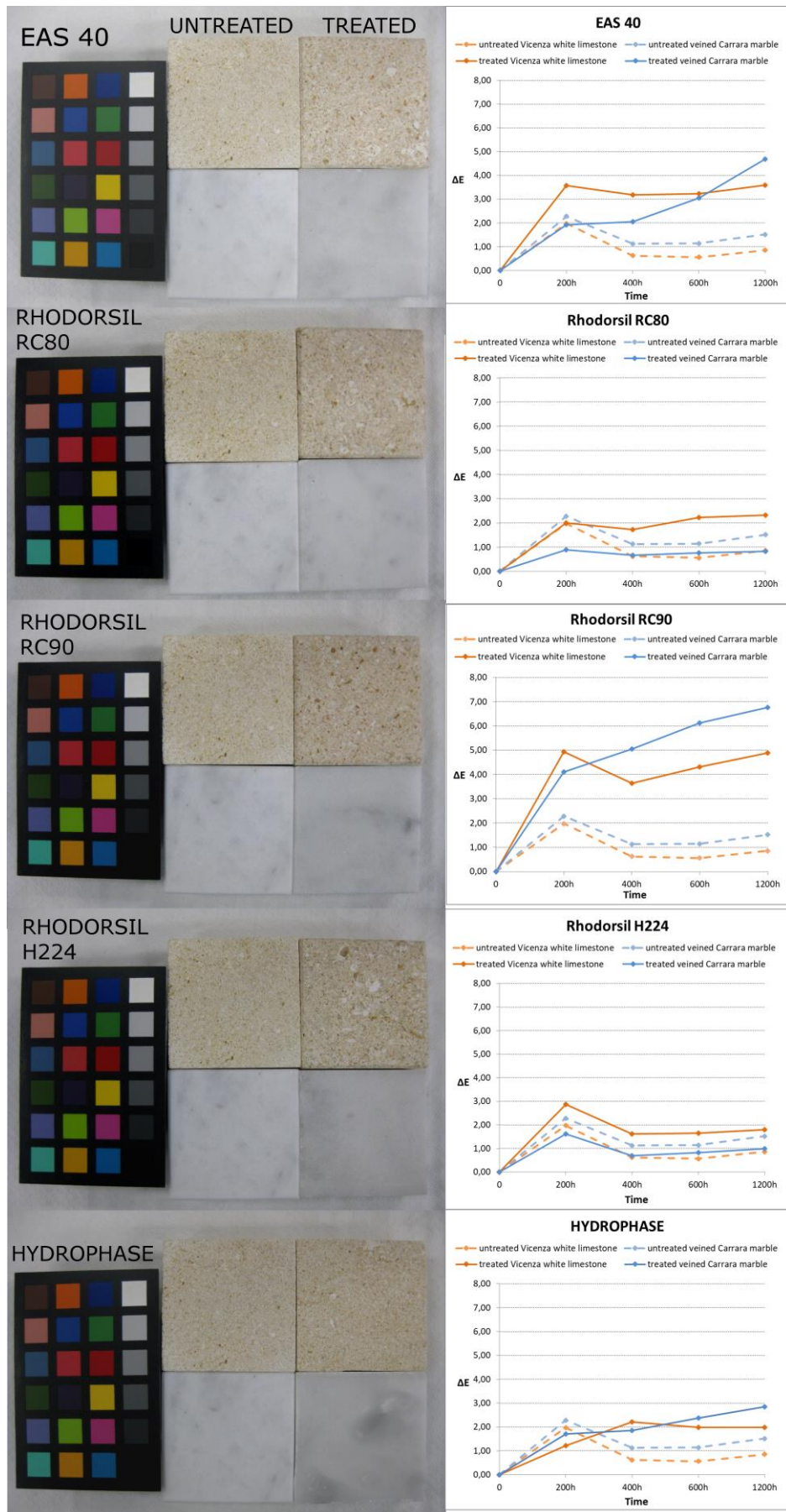


Figure 4: Results of colorimetric alteration analysis of treated specimens during artificial ageing.

### 3.2 Artificial ageing

The cured film of *Rhodorsil RC90* showed greater sensitivity to UV radiation than *RC80* and *EAS 40* due to the presence of phenyl groups in its macromolecules chemically linked to the siloxane chain. This colour alteration revealed a darkening of the polymeric film, even though no significant variation in the colour graph was observable (figure 4). When exposed to UV rays, all the treatments showed a constant hydrophobic feature for the entire exposure time. The FTIR spectra of the silicone-based strengthening agents examined and exposed to UV radiation showed the same trend observed for treated samples exposed to natural weathering. In general, the peaks related to the C-H chemical bond at about 1431, 1390  $\text{cm}^{-1}$  shifted towards higher wavenumbers (1450, 1416  $\text{cm}^{-1}$ ) and there was an increase in the bonds at 3440 and 1633  $\text{cm}^{-1}$ , related to Si-OH and O-H chemical bonds, respectively. In addition, all the collected spectra showed a variation of the main band associated to the Si-O-Si chemical bond. In fact, it was observed that the peak at 1030-1050  $\text{cm}^{-1}$ , related to branched siloxane chains in a cyclized structure, became a doublet at about 1110  $\text{cm}^{-1}$  and 1050  $\text{cm}^{-1}$ . This confirmed the cross-linking and the breakage of the siloxane chain induced by UV light with consequent formation of a linear chain (1110  $\text{cm}^{-1}$ ) and terminal groups Si-OH (3440  $\text{cm}^{-1}$ ). No differences were observed between Carrara marble and Vicenza limestone.

Comparing *Hydrophase* with *Rhodorsil H224*, the former appears more susceptible to UV radiation. However, both resins applied to Carrara marble showed a peculiar tendency to yellowing, more substantial in the case of *Rhodorsil H224*, whereas on Vicenza limestone the colour data tend to return to the untreated or zero value. The FTIR spectra of samples exposed to UV radiation showed decreasing and broadening of the main band at 1130-1020  $\text{cm}^{-1}$  related to symmetrical stretching of Si-O-Si chemical bond in the siloxane chain.

### 3.1 Comparison with past conservation treatments

In order to better compare the performance of silicone-based products examined as strengthening and protective agents, some microfragments were sampled from Venetian monumental surfaces treated in the past with *X54-802* (Rhone Poulenc) and *Sogesil XR893* (Rhône Poulenc), both today unavailable on the market (figure 5).

Close visual examination of the marble of the *Madonna con bambino e angeli* statues of *S. Maria Gloriosa dei Frari* basilica consolidated in 1973-1974 using *X54-802* (Rhone Poulenc) showed a good state of conservation; it appeared compact and cohesive, with no new losses, micro-cracks or powdering areas. Microscopically the cross-section of the microflake sampled showed the presence of non-homogeneous dark particles on the stone surface and that of a superficial polymeric layer, deemed a protective feature.



Figure 5: The four Venetian monumental surfaces considered here. (a) The angel on the front left, of the altar of the Holy Sepulcher in the Church of San Martino; (b) the statue of Sant'Alvise, on the main façade of the namesake church; (c) the statues located on the gable-end of the façade of the St. Mark Basilica; (d) the *Madonna con bambino e angeli* statues of *S. Maria Gloriosa dei Frari* basilica.

SEM-EDS analysis of the cross-sectioned sample confirmed the presence of a superficial layer made of silicone-based products rich in alumina grains, which could be related to the use of micro-sandblasting for the cleaning process (Figure 6). The

application method guaranteed a good penetration of the resin in the inter- and intra-grain spaces of the substrate. The FTIR spectra collected from the second conservative treatment showed all the characteristic bonds of siloxane resins. In particular, the



peaks at 2970, 2916  $\text{cm}^{-1}$  related to  $\nu_s$  C-H, those at 1410-1437 and 1323  $\text{cm}^{-1}$  associated to  $\nu_s$  C-H and  $\delta$  C-H, respectively, the peak at 1273  $\text{cm}^{-1}$  due to the symmetrical stretching of Si-CH<sub>3</sub> chemical bond, and, finally, those at 1034-1043  $\text{cm}^{-1}$  and 779-781  $\text{cm}^{-1}$  referring to  $\nu_s$  and  $\delta$  of Si-O-Si, respectively, in a siloxane chain, ensured the alkyl-alkoxy-silane formulation of the product. Moreover, FTIR analysis also allowed detection of the presence of gypsum (3541, 1408, 3246, 1684, 1622, 1124, 675  $\text{cm}^{-1}$ ) on the reverse of the sample where cleaning of the statue could not remove it.

Evaluation of the behaviour of *Sogesil XR893* siloxane-resin, applied to (i) a small column of the *Ca' d'Oro*, (ii) the Tullio Lombardo angels supporting the altar of the Holy Sepulchre inside the church of *San Martino*, (iii) the statue of *Sant'Alvise* (on the façade of the church dedicated to the saint), (iv) the statues located on the gable-end of the façade of the Basilica

of St. Mark, in the second half of the XX century, proved this siloxane resin has quite high chemical stability. The monumental surfaces appeared to be in a good state of conservation and the resin seems to continue its effectiveness more than forty years after its application. FTIR analysis of some sampled fragments confirmed the assumed chemical nature of the resin and the cross-linking tendency previously described for *Rhodorsil RC90* and *RC80*. Moreover, the spectra collected showed the partial breakage of the siloxane chain induced, upon the decay of the resin, by UV light with the consequence of linear chain and terminal groups Si-OH. The phenyl groups in the macromolecule cause a yellowing and, in some cases, browning of the treated surface after natural ageing and Xenon radiation. *Sogesil XR893* maintains its water repellent effect, as proved by sponge test (Tesser et al., 2017).

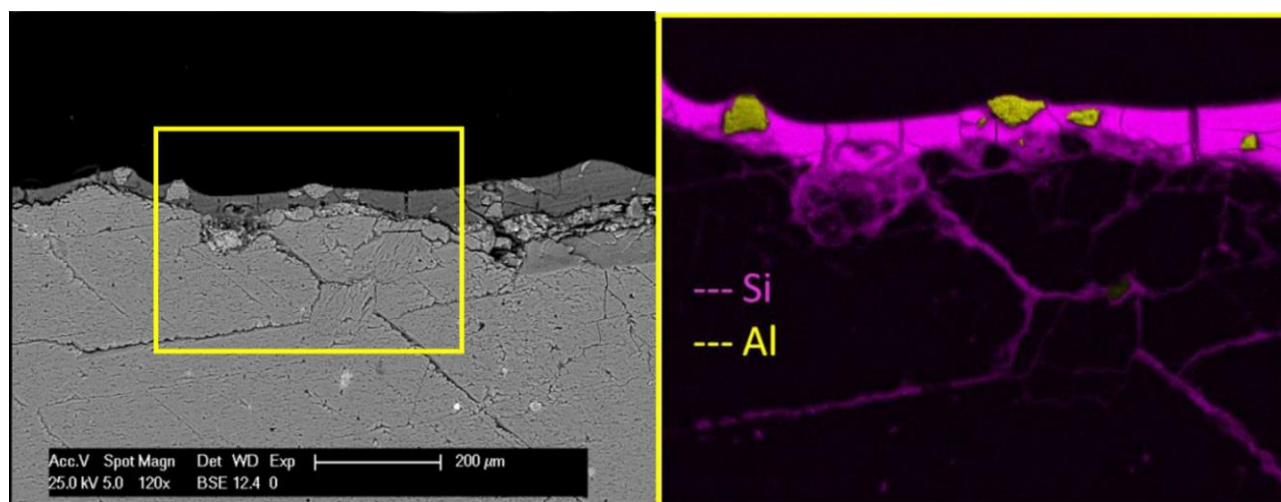


Figure 6: SEM micrograph (on the left) and elementary map (on the right) of a portion of the fragment sampled from the lowest left part of the mantle of the Virgin Mary of the Madonna con bambino e angeli statues of S. Maria Gloriosa dei Frari basilica.

#### 4. DISCUSSION

From the results obtained it was observed that strengthening agents based on TEOS tended to crack due to the evaporation of ethanol during the hydrolysis chemical reaction and the large amount of catalyst in the case of *RC80* (Tesser et al., 2014). This produced the progressive disappearance of the superficial coatings and the decrease of the superficial hydrophobicity as time passed, especially in the case of *EAS 40*. However, the products remained in the porosity of the stone and, especially in the case of *Vicenza white limestone*, the penetration depth seemed dependent on the dimension of the macromolecules of the product applied. In fact, *EAS 40*, which is based on pure TEOS, showed a good, homogeneous penetration and distribution in all the

sections of the sample. *RC80*, which is based on TEOS combined with a methyl resin, reached 7500  $\mu\text{m}$  of penetration depth, whereas *RC90*, which is composed of TEOS combined with a methyl-phenyl resin, stopped at 4500  $\mu\text{m}$ . *RC90* is more sensitive to UV radiation, due to the presence of phenyl groups in its macromolecule, chemically linked to the siloxane chain. FTIR analysis showed a general chemical stability of the resins, and confirmed the cross-linking of the polymers by a shift towards higher wavenumbers for all the peaks related to the CH chemical bond. This trend suggests a shortening of the chemical bond due to the lower degree of liberty of the molecules during the polymerization process.

The same chemical stability was showed also by the two protectives tested. Both *Rhodorsil H224* and *Hydrophase* formed a thin superficial layer on the

specimens and conferred to the stone water-repellent properties stable through time. *Hydrophase* applied to Vicenza limestone showed a long polymerization process and the value of superficial hydrophobicity of the stone increased with time under natural aging processes. This could be related to environmental condition, especially humidity, which could interact with unreacted silanol groups increasing the polymerization process.

Both products applied to Carrara marble tended to yellow, either during natural or artificial ageing.

The good performance of silicone based products has been proved also by the evaluation of past treatments in Venice using two siloxane resins no longer available on the market. In particular, the artefacts treated using the water-repellent agent X54-802 showed a good state of conservation and a high penetration of the treatment into the stone porosity, probably due to the effectiveness of the application method. The resin still protects the stone surface and seems unaltered. On the other hand, the siloxane resin *Sogesil XR893* guaranteed the good state of conservation of the artefact for 40 years. However, the presence of phenyl groups in the molecule conferred a particular sensitivity to UV rays and the treated surfaces tended slightly to yellow and/or brown.

Comparing these results with those obtained from a similar experimentation on a cycloaliphatic epoxy resin (Tesser et al. 2018), it is possible to emphasise the better properties of silicone based products for the consolidation and protection of stone. In fact, the cycloaliphatic epoxy resin *EP2101*, widely used for the consolidation of stone substrates, showed different behaviour when applied to veined Carrara marble and Vicenza white limestone. In general, the resin penetrated much less deeply than the silicone resins tested and it displayed a greater chromatic alteration due to UV rays. The excess jellified resin tended to lift from the stone surfaces increasing the hydrophilicity of the treated surface; however, no cracking phenomena have been observed. The  $\mu$ FTIR spectra collected during the monitoring of the ageing process showed that a degradation mechanism began

for all the treated specimens and increased during the ageing time through the opening of the cyclic structure in the macromolecule and chain scission. The results were confirmed by the study of micro-fragments of the *Vereri column* on the Island of Murano and a Proconnesian marble fragment obtained from a stone substitution during restoration work on St. Mark's Basilica, which were both treated in the past with *EP2101* resin. The polymeric film still conferred cohesion to the superficial grains of the stones but appeared dark and raised from the stone surface in some places

## 5. CONCLUSIONS

In recent decades, art conservators have constantly required new products for coatings and strengthening agents to be applied to outdoor stone monuments. However, the experience of recent years has clarified that an ideal product suitable for all problems cannot exist. The lithotype, the state of conservation, the kind of artefact and the environmental conditions will determine a treatment from amongst those already subjected to experimentation in the past, or recently produced. This study reports the chemical investigation of the stability and alteration morphologies of 5 silicone-based products, namely 3 consolidants based on TEOS (*EAS 40*, *Rhodorsil RC90* and *Rhodorsil RC80*) and 2 water-repellent agents (*Rhodorsil H224* and *Hydrophase*), in order to evaluate their stability and to promote their conscious use in the future. The results obtained proved the chemical stability of silicone-based products over time and encourage their application for future restorations. Finally, the re-examination of past treatments, namely two siloxane resins no longer available on the market (*Sogesil XR893* and *X54-802*), allows the evaluation of their stability and comparison with new products, facilitating the monitoring of the state of conservation of monuments treated in the past and the devising of future restoration approaches.

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