

Article

Performances and Coating Morphology of a Siloxane-Based Hydrophobic Product Applied in Different Concentrations on a Highly Porous Stone

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Abstract: Many polymers, able to confer a hydrophobicity to treated surfaces, have been proposed for the restoration and conservation of civil and monumental buildings. Polysiloxanes, and their precursors, the silanes, have been frequently employed for stone protection. To avoid decay of the treated surfaces, the effectiveness and harmlessness of the treatment need to be carefully evaluated before application in the field. In this study, a commercial alkyl-siloxane was tested as a protective treatment on a highly porous stone, starting from water solutions with different contents of the product. The treatments have been devised to try to balance the requirements and the sustainability of the conservative actions. Sustainability, in terms of costs and environmental impact, is regarded as a key factor in the 21st century. Morphological observations of the stone surface, static contact angle and colour measurements, water vapour transmission test, and tests of water absorption were carried out to characterize the untreated and treated stones. A concentration below the minimum level suggested by the manufacturer was still able to act as a good barrier against water. More concentrated solutions produced polymer accumulation and coatings with extended cracks. The properties of the treated stone were affected by the presence of cracks in the coating.

Keywords: stone protection; siloxanes; hydrophobic coating; ESEM-EDS; permeability to water vapour; water absorption; contact sponge test

1. Introduction

During the last few decades, great attention has been devoted to the restoration and conservation of buildings, especially in the case of monuments and historic built heritage, which are perceived as having cultural value and are potential tourist attractions.

Stone materials used in monuments and buildings generally deteriorate under environmental conditions. The penetration of water through the exposed surfaces is one of the main causes of degradation and damage [1]. The highly porous materials, which are able to absorb larger amounts of water, usually suffer from faster degradation [2]. To limit the ingress of water—and, consequently, to minimize the decay phenomena—suitable preservation remedies are used. The application of coatings, to stop the liquid water entry and let it escape as vapour, is the preferred solution.

Over the years, many polymers, able to confer a hydrophobic character to treated surfaces have been proposed [3–5]. These materials most often are obtained from acrylic, fluorinated, and silicon-based monomers. Among them, polysiloxanes, and their precursors, the silanes, have been frequently used [6–10] and have also recently been proposed as nano-composites by introducing nano-particles of inorganic oxides into hybrid siloxane or silicone polymers [11–15].

However, while some treatments have given good results, others have altered the properties of the stone [16], leading to decay or accelerated degradation processes. For this reason, nowadays,

the effectiveness and harmlessness of the treatment are carefully evaluated and monitored by *in situ* investigations [17–20]. In addition, the sustainability of the treatments, in terms of costs and environmental impact, has become a key consideration in the 21st century and it is taken into account when selecting the most appropriate conservation solution.

Starting from these considerations, this study deals with the application of hydrophobic coatings on a highly porous stone widely employed in southeastern Italy, but representative of building materials in many regions of the Mediterranean basin. A siloxane-based product requiring dilution in water was selected, to try and fulfil the requirement of low environmental impact. Different quantities of the product were investigated to find the minimum amount able to provide a suitable hydrophobicity to the tested surfaces.

Preliminary tests verified acceptable colour changes and hydrophobicity of the surfaces after the treatments. Then, investigations of the morphological features of the surfaces were carried out, since as described in the literature, the treatments that give the best results in the protection against water are not those that penetrate deeper into the stone material, but those that adapt their morphology and coat crystals as a film [21,22]. Finally, the variations in some properties (water vapour transport and water absorption) of the treated stone samples were examined.

The obtained results highlighted that the application of higher quantities of the product did not yield the best performances. In addition, the properties of the treated stone were strongly dependent on the characteristics of the coating.

2. Materials and Methods

2.1. Materials

A commercial product, consisting of organic-modified alkyl-siloxanes having a low molecular weight (trade mark: VP 1805), was investigated. This material (WR) is able to generate hydrophobic coatings and is suggested for the protection of mineral building materials and for stone conservation. As reported in the technical sheet, a dilution with water is necessary before use. Solutions from 5% to 20% w/w are suggested. No additional information on the amount to apply is given.

The WR product was tested on a highly porous calcarenite, named “Lecce stone”. This stone has been widely employed for a long time, as a construction material in southeastern Italy and it is typical of the baroque monuments and buildings of the region. Calcite is its principal constituent, along with very small quantities of clay and other non-carbonate minerals [23,24]. “Lecce stone” has a very high porosity, usually ranging from 30% to 45% [25–27], and has a unimodal porosity distribution. In our case, the used samples exhibited a porosity of 42%, with pore sizes mainly between 0.3 and 10 μm , as analysed by mercury-intrusion porosimetry [28]. Due to its characteristics, “Lecce stone” can be considered as representative of the porous materials used for historic and civil buildings in many countries of the Mediterranean basin.

2.2. Treatments

Prismatic stone specimens, with dimensions of $5 \times 5 \times 1 \text{ cm}^3$ and $5 \times 5 \times 2 \text{ cm}^3$, were cut by a saw from a quarry block. According to the UNI10921 standard protocol [29], the samples were smoothed with abrasive paper (180-grit silicon carbide), cleaned with a soft brush, and washed with deionised water in order to remove dust deposits. The stone specimens were completely dried in an oven at 60 °C, until the dry weight was achieved, and stored in a desiccator with silica gel (relative humidity (R.H.) = 15%) at $23 \pm 2 \text{ °C}$.

Before the application of the product, the stone specimens were conditioned in equilibrium with the surrounding environment (24 h in the laboratory, at $23 \pm 2 \text{ °C}$ and $45 \pm 5\% \text{ R.H.}$).

The treatments were performed, on 5 specimens of each dimension, by brush, to simulate the methodology of application more commonly used in field conditions. Only one $5 \times 5 \text{ cm}^2$ side of each specimen was treated.

As previously reported, dilution of the WR in water was necessary. Solutions containing 5%, 10%, and 20% w/w were prepared and applied. Also solutions with 2.5% and 40% w/w of product—beyond the recommended range of dilution—were also proposed for the treatments. Each solution was prepared immediately before use, by adding the proper quantity of pure product into 5 g of water. For each specimen, the application of 1 kg/m² of the final solution was planned and the quantity used was controlled by weight measurements.

It is worth mentioning that the application of the solution at 20% w/w was not feasible in the selected dose, that is, 1 kg/m². Less than a third of this quantity saturated the superficial layer of the stone, thus hindering any further absorption. Furthermore, it was impossible to prepare the solution at 40% w/w, because a fast condensation of the polymer (with precipitate formation) took place just a few seconds after mixing with water. Therefore, the solutions at 20% and 40% w/w were not further investigated in this study.

Details about the treatments are listed in Table 1.

Table 1. Nomenclature of the treated samples and details of the treatments.

Samples	WR Concentration [w/w %]	Applied Solution [g]	Treated Surface [cm ² Per Specimen]
T _{2.5}	2.5	2.5	25
T ₅	5	2.5	25
T ₁₀	10	2.5	25
T ₂₀	20	0.8	25
T ₄₀	40	–	–

In order to allow both the solvent evaporation and the completion of condensation reactions, after the application of the solutions, all the specimens were kept in the laboratory at 23 ± 2 °C and 45 ± 5% R.H. for 30 days, and then they were dried in the oven at 60 °C until the weight stabilization was achieved; the stabilization was controlled by periodical measurements of weight.

2.3. Techniques and Methods of Analysis

Colour and contact angle measurements, morphological observations of the stone surface, water vapour transmission test, and tests of water absorption were performed to characterize the untreated stone material. The same investigations were repeated after each treatment.

All weight measurements were registered using an analytical balance (Model BP 2215, Sartorius AG, Göttingen, Germany) with an accuracy of ±0.1 mg.

During the preparation of the specimens, the treatments, and the tests, the environmental conditions were monitored by means of a thermo-hygrometer (Mod. EMR812HGN, Oregon Scientific, Kowloon, Hong Kong). It can collect temperature data from −50 °C to 70 °C (with a resolution of 0.1 °C) and relative humidity data in the range 2%–98% (with resolution of ±1%).

2.3.1. Preliminary Tests: Static Contact Angle and Colour Measurements

Before and after the protective treatments, colour and water-stone static contact angle measurements were performed on the stone surfaces. Colour measurements [30] were performed with a Minolta Chroma Meter CR300 tristimulus colorimeter (Konica Minolta Inc., Tokyo, Japan), using CIE Standard illuminant C. Ten measurements were performed on each specimen and the colorimeter was recalibrated to a calibration plate at the start of each measurement session. The colour changes (ΔE^*_{ab}) were calculated through the $L^*a^*b^*$ (CIE 1976) system, using the following formula:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where L^* is the lightness/darkness coordinate, a^* the red/green coordinate ($+a^*$ indicating red and $-a^*$ green), and b^* the yellow/blue coordinate ($+b^*$ indicating yellow and $-b^*$ blue).

Water-stone static contact angle measurements [31] were carried out using a Costech apparatus (Costech International S.p.A., Cernusco sul Naviglio, Milan, Italy). For each specimen, 30 micro-drops of deionised water were deposited with a syringe on different positions of the surface. The shape of the drop was recorded with a camera and its contact angle was calculated by means of the “anglometer 2.0” software (Costech International S.p.A., Cernusco sul Naviglio, Milan, Italy). The water-stone static contact angle was used as indirect evidence of a hydrophobic layer on the surface, since the contact angle cannot be evaluated on the untreated “Lecce stone”. Due to intrinsic characteristics of this material, the water absorption is very high and rapid and the drops of water do not remain on the surface [32]. The mechanisms behind the hydrophobic character of the coatings were not investigated in this study.

2.3.2. ESEM-EDS Analyses

The morphological features of both the untreated and treated stone surfaces were investigated by an Environmental Scanning Electron Microscope (ESEM, Mod. Philips XL30, FEI Company, Eindhoven, The Netherlands). The observations were carried out in low-vacuum mode (0.6 Torr, 25 kV). Both secondary (GSE) and backscattered (BSE) electron detectors were used. Magnifications not over $1500\times$ were set, because surface charging occurred at higher values. The observations through ESEM were performed mainly to search for features of the coatings (such as cracks, bubbles, or other defects) able to influence the behaviour of the stone-coating system in the presence of vapour or liquid water.

Energy-Dispersive X-ray Spectroscopy (EDS) coupled to the ESEM microscope, was applied to detect the presence of Si on the stone surface where the coating was not clearly visible. Qualitative/quantitative analyses were carried out acquiring EDS spectra on spots (live time 60 s).

2.3.3. Water Vapour Permeability Test

The water vapour transport properties of the stone material (untreated or treated) were evaluated at $20\text{ }^{\circ}\text{C}$ by vapour transmission test on the specimens with demensions of $5 \times 5 \times 1\text{ cm}^3$. Each sample was employed to cover a chamber containing 10 mL of deionised water. PVC containers (Figure 1), properly sealed to force water vapour to diffuse through a central circular surface, were used. The filled containers were placed into desiccators with silica gel and stored in a climatic chamber (Mod. UY 600, ACS Angelantoni Climatic Systems, Massa Martana, Perugia, Italy) at $20\text{ }^{\circ}\text{C}$.

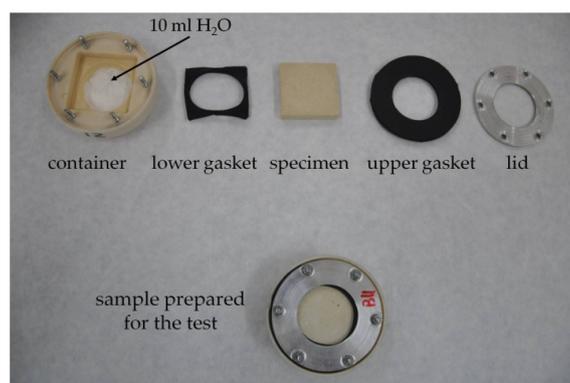


Figure 1. Set-up for water vapour permeability test.

Weight measurements were carried out every 24 h in order to determine the rate of vapour transport through the sample from the water (in the container the R.H. is close to 100%) to the controlled atmosphere of the desiccator (R.H. 15%, 1 atm).

The water vapour flow rate (G) was calculated as the slope of the curve showing the cumulative mass decrease versus time.

The water vapour transmission rate (WVTR) was evaluated as the mass of water vapour passing through the surface unit in the unit time (24 h). This parameter is referred to as permeability in [33]. The following equation was used:

$$\text{WVTR} = \Delta M / (t \times A) \quad (2)$$

where ΔM is weight change in the steady state (expressed in g), A is the exposed area to water vapour (in m^2) and t is the unit time (24 h). The exposed area was 0.001611 m^2 .

Finally, the reduction of the vapour permeability (RVP) was quantified as follows [34]:

$$\text{RVP}\% = [(\Delta M_u - \Delta M_x) / \Delta M_u] \times 100 \quad (3)$$

where ΔM_u is the weight change in the steady state for the untreated sample, and ΔM_x is the same parameter calculated for the treated sample.

In all these cases, the ΔM used was the average of three consecutive values of the daily difference in weight.

2.3.4. Capillary Water Absorption Test

The capillarity water absorption test [35] was performed on the stone specimens measuring $5 \times 5 \times 2 \text{ cm}^3$. The weight measurements during the absorption were taken at 2.5 min, 5 min, 7.5 min, 10 min, 20 min, 30 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, and 24 h.

The amount of absorbed water (Q) was calculated as follows:

$$Q_i = (w_i - w_0) / A \quad (4)$$

where w_i and w_0 are the weight of the sample at time t_i and t_0 , respectively, and A is the area exposed to water.

Q_i values were plotted versus the square root of time, and the capillarity water absorption coefficient (AC), representing the slope of the straight part of the absorption curve, was calculated by linear regression.

2.3.5. "Contact Sponge" Test

The water absorption was also investigated by the contact sponge test [36,37] to simulate a procedure feasible in the field. The test was performed on either the samples of $5 \times 5 \times 2 \text{ cm}^3$ or $5 \times 5 \times 1 \text{ cm}^3$, to control the behaviour of all the specimens.

For the "contact sponge" test, a Petri dish, 3.5 cm in diameter, containing a disc-shaped sponge (area of 9.29 cm^2) was used. All the tests were performed on specimens dried 24 h in oven at $60 \text{ }^\circ\text{C}$ and stored 24 h in laboratory conditions ($23 \pm 2 \text{ }^\circ\text{C}$ and $45 \pm 5\% \text{ R.H.}$).

Preliminary experiments were carried out to establish the volume of water appropriate for the test. The moist sponge was soaked with water and manually pressed against the specimen, which was placed vertically to simulate a small part of a wall. The maximum pressure, restricted by the contact between the dish's borders and the surface, was applied. In this way, the whole surface of the sponge touched the stone, since the wet sponge was only 1 mm thicker than the Petri dish. The test was carried out by using different quantities of water; 2.50, 2.25, 2.00, 1.75, and 1.50 mL. Water dripped from the sponge pressed against the treated surfaces when more than 1.50 mL was used. This volume (i.e., 1.50 mL), thus, was chosen for all the tests.

A further screening carried out on the untreated stone was aimed at selecting the length of the test. The Petri dish and the sponge inside were weighed after the addition of water and after 15 s of contact with the surfaces under investigation. At the end of the test, the stone specimens were dried as previously described (24 h in an oven at $60 \text{ }^\circ\text{C}$ followed by 24 h at $23 \pm 2 \text{ }^\circ\text{C}$ and $45 \pm 5\% \text{ R.H.}$).

The water absorption was calculated as:

$$\text{WA} = (m_i - m_f) / (A \times t) \quad (5)$$

where m_i is the initial weight of the sponge soaked with water, m_f is the weight of the sponge after the contact, A is the area of the sponge, and t is the contact time.

The same procedure was repeated with increasing time of contact; 30, 45, 60, 90, 120 s. As discussed in Section 3.4, the maximum value of WA was achieved in 1 min. Therefore, to compare the behaviour of the untreated and treated stone specimens, only the contact time of 1 min was tested.

3. Results and Discussion

3.1. Preliminary Tests: Colour Variations and Superficial Hydrophobicity

Colour differences and water-stone static contact angle determined on the untreated and treated stone samples are reported in Table 2.

Table 2. Colour difference (ΔE^*_{ab}) and water-stone static contact angle (c.a.), with the related maximum deviation, before and after the treatments.

Samples	ΔE^*_{ab}	c.a. [°]
Untreated	–	Not determinable
T _{2.5}	0.76	145 ± 2
T ₅	1.55	147 ± 3
T ₁₀	2.55	147 ± 2
T ₂₀	2.00	149 ± 2

Colour changes increased as the concentration of the applied solution increased, but always remained acceptable. A lower ΔE^*_{ab} was measured for the T₂₀ samples, in comparison to the T₁₀; this behaviour can be ascribed to the low amount of solution applied on the T₂₀ specimens (see Table 1). High hydrophobicity was obtained after the treatments, irrespective of the solution concentration.

Comparable results were found in a previous study [25], after the application of the same solutions with WR on several stone building materials with porosities from 27% to 45%.

3.2. Morphological Characteristics and Elemental Microanalysis of the Coatings

The morphological appearance of the untreated stone surfaces from the ESEM observation is shown in Figure 2a. The treatment with the solution at 2.5% w/w did not change the characteristics of the stone; in fact, it was not possible to perceive a coating on these surfaces even with high magnification (Figure 2b).

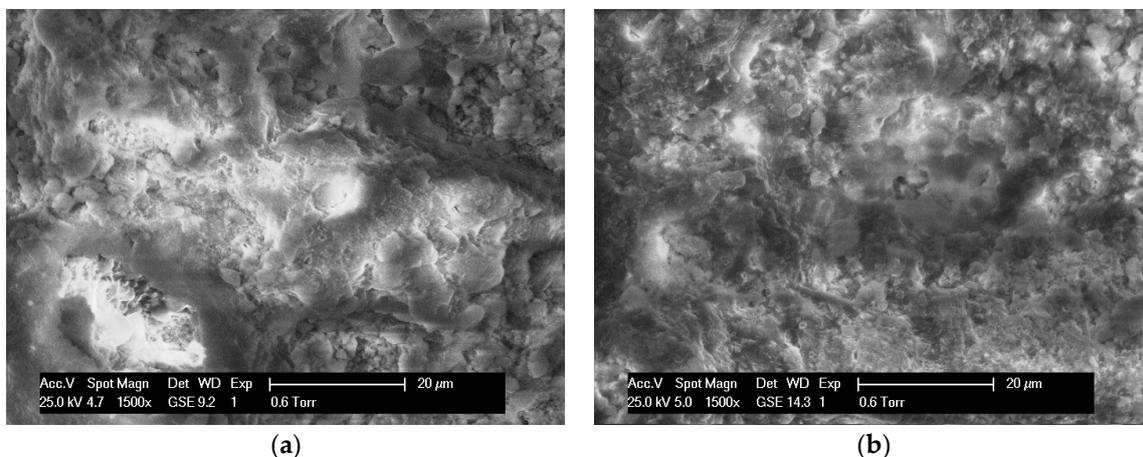


Figure 2. ESEM images: (a) Untreated stone surface; (b) Surface of T_{2.5}.

A similar result was found for the T₅ samples, where the coating was not clearly recognizable (Figure 3a). In this case, however, the surface seemed to be smoother than the untreated stone. This effect was more evident at higher magnifications. In addition, sporadic micro-cracks (highlighted in Figure 3b) occurred in the flat areas.

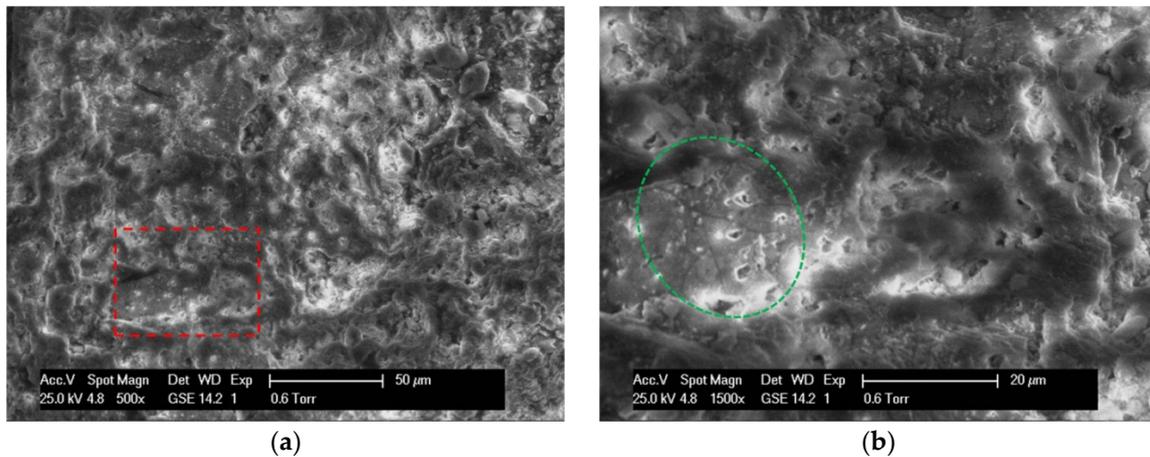


Figure 3. ESEM images: (a) Surface of T₅; (b) Area indicated in (a) at higher magnification.

To prove the occurrence of the coating on these surfaces, Si was searched for using EDS microanalysis. This element can be used as a marker, since WR is a siloxane-based product. Si was already found in very small amounts in untreated Lecce stone (Figure 4a), but increased amounts were expected where the WR was applied. In fact, the higher the concentration of the WR solution, the higher the quantity of Si on the surface (Figure 4b,c). Larger amounts of Si were measured on the T₅ samples. In this case, it is probable that the WR product mainly remained on the surface, producing an extremely thin coating. Conversely, in the T_{2.5} samples, the low concentration of the applied solution enhanced the penetration of WR inside the stone, therefore, lower amounts of Si were found on the surface.

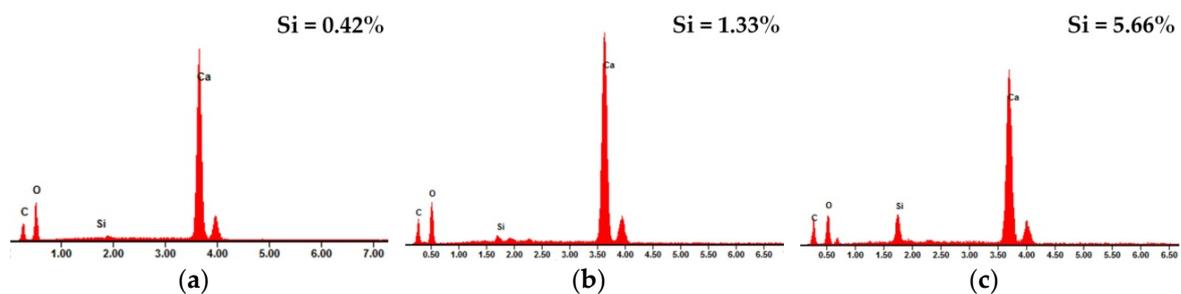


Figure 4. EDS spectra acquired on (a) the untreated stone, (b) the surface of T_{2.5} samples, and (c) the surface of T₅ samples. In each spectrum, the Si quantification (measured as wt %) is indicated.

A thick film was obtained from the application of the solution at 10% and the morphological features of the stone were completely hidden (Figure 5a,b). In this case, an extended network of cracks and fissures, well evidenced by using the BSE detector (Figure 5c,d), affected the coating. The high concentration of the initial solution (i.e., 10% w/w) limited the penetration of the polymer, with accumulation on the stone surface. On the other hand, the WR in solution at 20% w/w (i.e., a more concentrated solution), although used in small amounts, quickly saturated the superficial layer of the stone.

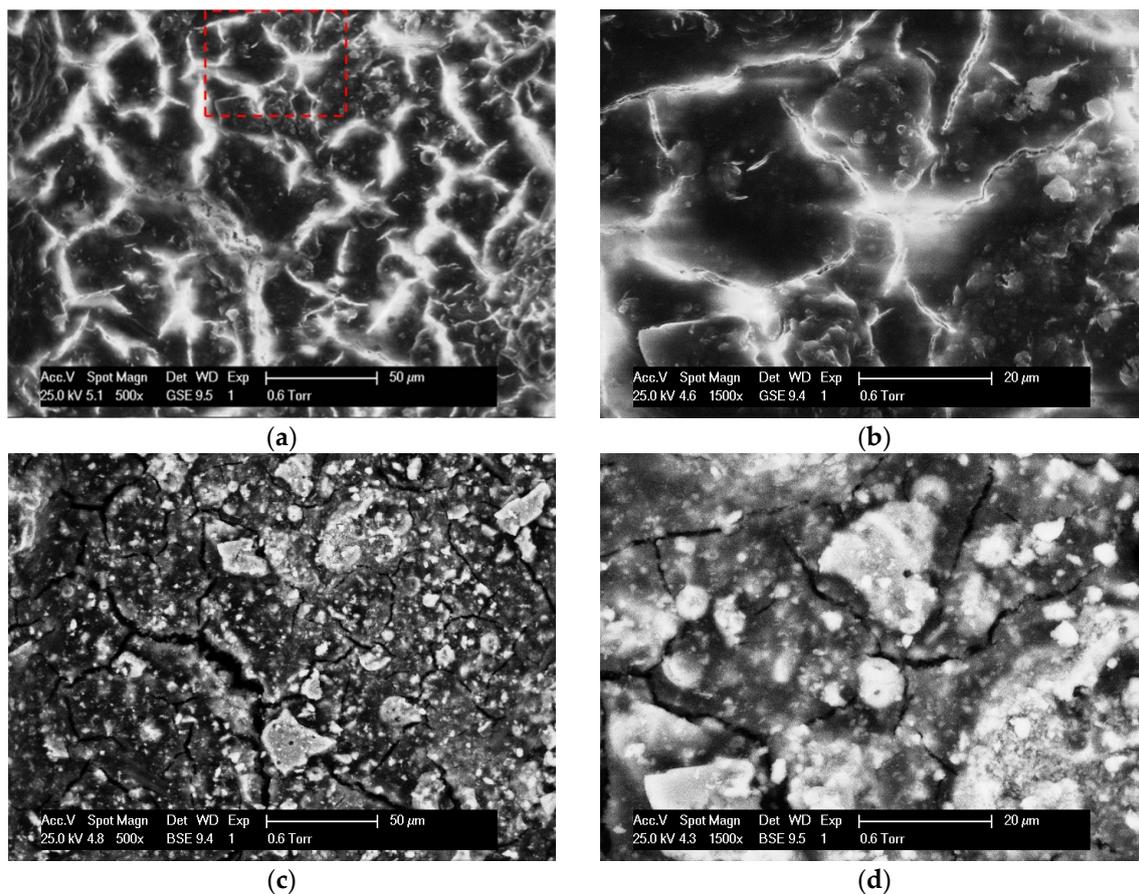


Figure 5. ESEM images: (a) surface of the T₁₀ sample; (b) area indicated in (a) at higher magnification; using the BSE detector, (c) and (d) were taken in exactly the same areas showed in (a) and (b), respectively.

The presence of fractures in the coating was in accordance with other studies concerning siloxane-based products on stone materials [22,38,39]. In fact, products which polymerise by a sol-gel route, such as silanes and siloxanes [5,40], frequently exhibit cracks. These cracks are ascribed to shrinkage phenomena taking place throughout the drying phase [41–43]. In the sol-gel process, shrinking is initiated by evaporation of both solvents and by-products of the condensation step [44]. Then, cracking is generated by the high capillary pressures supported by the gel network during the drying [40]. The amount of water in the ambient atmosphere has been found as a factor influencing the fragmentation of the coating. The lower the amount of water, the more intense the cracking [45]. In our case, the cracking was observed when a smaller amount of water was applied, all other conditions being equal.

3.3. Water Vapour Transport Properties

An important aspect to take into account in evaluating the performance (and compatibility in particular) of treatments for stone materials is the changes in water vapour transport properties. The related parameters should be left unchanged by any treatment because reduced permeability may cause water condensation inside the stone. The accumulation of condensed water at the interface between the treated and untreated stone is able to activate the material's decay [4,46].

The mass changes measured throughout the vapour transmission test are plotted in Figure 6. In each case, a linear trend was observed and the steady state was achieved 48 h after the beginning of the test.

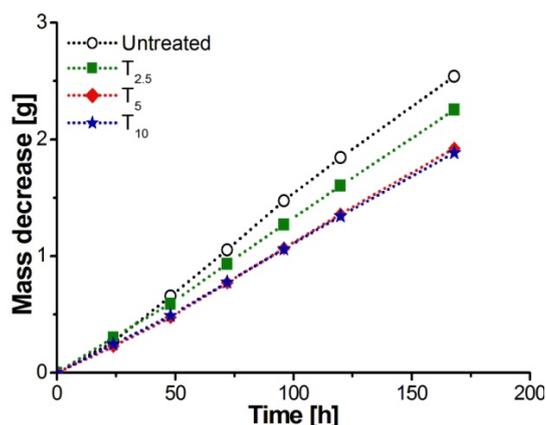


Figure 6. Mass decrease, as a function of time, measured during the water vapour permeability test.

After the application of the WR solutions, reductions were measured for all the water vapour transport parameters (Table 3). The obtained results are comparable to those reported in the literature for siloxane-based coatings on stone materials [15,34,47–49].

Table 3. Water vapour flow rate (G), water vapour transmission rate (WVTR), and reduction of the vapour permeability (RVP). Standard deviations are also reported.

Samples	G [(g/h)·10 ⁻³]	WVTR [g/m ² ·24 h]	RVP [%]
Untreated	15.7 ± 1.1	238 ± 16	–
T _{2.5}	13.5 ± 0.4	188 ± 7	–14
T ₅	11.6 ± 1.2	168 ± 11	–28
T ₁₀	11.3 ± 0.6	166 ± 9	–34

The permeability decrease, RVP, remained below the threshold of 20%, usually accepted as tolerable [50] (p. 540), only for the T_{2.5} samples.

Water vapour transport decreased as the concentration of the applied WR solution increased. However, an unexpected behaviour was observed in the T₁₀ samples, where values similar to those of the T₅ samples were found. This behaviour was already observed in similar coatings [51] and attributed not to a higher permeability of the system, but to the formation of small cavities and cracking in the polymer film [9]. The coating on T₁₀ was fractured and it is probable that the cracks facilitated the passage of the vapour through the coating. As a consequence, the reduction in permeability did not further increase, although the applied solution was more concentrated.

3.4. Water Absorption

The capillary water absorption curves and the related parameters (i.e., the maximum amount of water absorbed after 24 h and the capillary absorption coefficient) are reported in Figure 7 and in Table 4, respectively.

Lecce stone is able to absorb large amounts of water by capillary suction [25,52]. In our tests, the untreated samples took approximately 500 mg of water per cm² in 24 h; around 92% of this quantity was already gained after 1 h of exposure. The application of the WR solutions on the stone surfaces strongly affected the capillary water absorption of the stone material, in accordance with the results reported in the literature for similar systems [13,49]. All the treatments yielded a marked effect in terms of both the maximum absorbed water and the rate of absorption. The reduction of water up-take was greater in the T₅ samples, while the lowest ability to limit the water suction was measured in the T₁₀ samples.

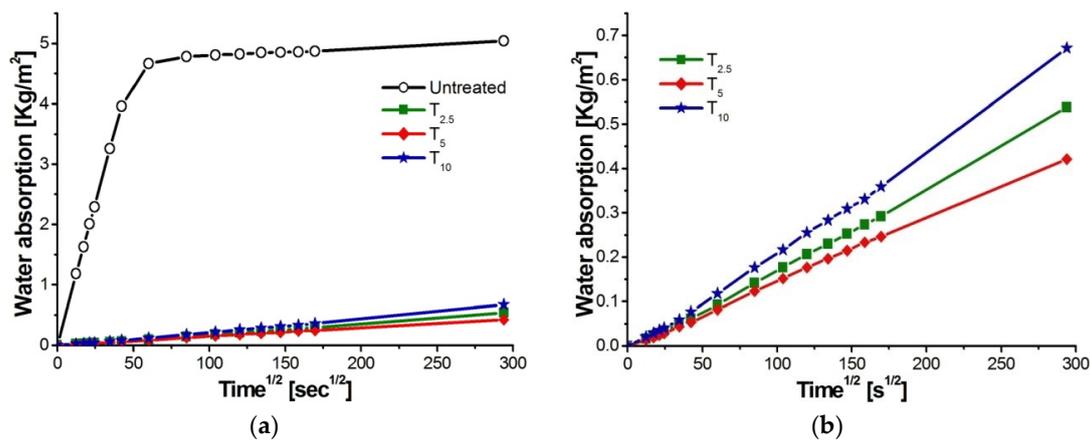


Figure 7. Capillary water absorption curves: in (a) untreated and treated samples are compared; in (b) only the curves related to the treated samples are reported.

Table 4. Water absorption by capillarity: water absorbed at the end of the test ($Q_{24\text{ h}}$) and the capillary absorption coefficient (AC). For each data set the standard deviation is reported.

Samples	$Q_{24\text{ h}}$ [kg/m ²]	AC [(kg/m ² ·s ^{-1/2})·10 ⁻²]
Untreated	5.04 ± 0.04	9.34 ± 1.65
T _{2.5}	0.54 ± 0.01	0.15 ± 0.01
T ₅	0.42 ± 0.06	0.13 ± 0.01
T ₁₀	0.67 ± 0.02	0.19 ± 0.05

As previously discussed for the water vapour transport, the fractured coating on the T₁₀ samples reduced the ability of the applied coating to act as a barrier against water. As a consequence, the capillary absorption in T₁₀ was higher if compared to that of the T_{2.5} samples where the coating was thinner but without cracks.

As previously described in Section 2.3.5, a preliminary screening was carried out on the untreated stone in order to select the length of the “contact sponge” test. A progressive increase of WA was measured by up to 1 min of contact (Figure 8). Longer contact times were not able to cause greater absorptions, but the calculated WA decreased. This result can be the effect of both the saturation of the superficial layers of the stone and an intrinsic limit due to the amount of water used to soak the sponge (i.e., 1.5 mL). In fact, after 1 minute about 73% of the added water was absorbed by the stone. Therefore, 1 min of contact was adopted for the subsequent tests on the treated surfaces to compare the results obtained in the same test conditions.

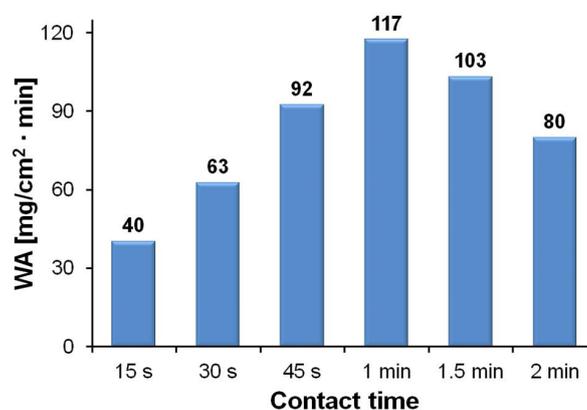


Figure 8. Water absorption measured by the “contact sponge” test on the untreated samples.

The “contact sponge” test verified variations in the water absorption similar to those observed in the test by capillary rise. The WA values found for the untreated stone were very high and comparable to those reported in the literature [17]. A strong reduction in water up-take was measured after the application of WR (Table 5), with slight differences between the treated samples. The T₅ specimens exhibited the lowest WA, while the application of the most concentrated solution (at 10% w/w) did not further reduce the absorption. On the contrary, for these latter samples, WA values greater than those obtained for T_{2.5} and T₅ were calculated.

The same trend was observed when performing the “contact sponge” test on both the specimens 5 × 5 × 2 cm³ and those 5 × 5 × 1 cm³ in dimensions.

Table 5. Water absorption (WA) measured by the “contact sponge” test. For each data set the maximum deviation is reported.

Samples	WA [mg/cm ² ·min]	
	¹ 5 × 5 × 2 cm ³	¹ 5 × 5 × 1 cm ³
Untreated	117.38 ± 4.44	135.02 ± 5.58
T _{2.5}	2.43 ± 0.32	2.50 ± 0.04
T ₅	1.81 ± 0.22	1.90 ± 0.20
T ₁₀	2.69 ± 0.28	2.86 ± 0.05

¹ Samples' dimensions.

4. Conclusions

In this study, a commercial alkyl-siloxane, able to provide hydrophobic coatings, was tested on a highly porous stone. As recommended by the suppliers, the treatments were performed starting from water solutions with different contents of the product. Although the porosity of the stone was elevated, the application of concentrations not higher than 10% w/w was feasible. The treatments provided hydrophobicity to the stone surface and acceptable colour changes. Variations in permeability to water vapour and in absorption of liquid water were found in all the treated samples. Among the applied solutions, the mixture at higher concentration (10%) did not yield the best performance in terms of protection against water, suggesting that smaller quantities of the product can be effective. In fact, a concentration below the minimum level suggested by the manufacturer was still able to provide coatings that acted as a good barrier against water. When the most concentrated solution was used, polymer accumulation on the stone surface and a coating with extended cracks were obtained. The presence of cracks affected, even if to a low extent, all the evaluated properties of the applied product.

The obtained results suggest that the recommendations given by the suppliers are often generic and sometimes not suitable for specific applications. Therefore, the efficacy of any treatment should always be assessed on the particular material which needs protection, balancing the conservation requirements and the sustainability of the interventions.

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Author Contributions: M. Lettieri conceived and designed the experiments; M. Masieri performed the ESEM-EDS experiments; M. Lettieri performed the permeability and “contact sponge” tests; Chem Spec S.r.l. (Peschiera Borromeo, Milano, Italy) supplied the WR product; M. Lettieri and M. Masieri analyzed the data; M. Lettieri wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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