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Salt Weathering on Buildings and Stone Sculptures

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Resistance to salt crystallization provided by a new surfactant-synthesized ormosil applied in monumental stone restoration

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ABSTRACT

Most commercial stone restoration products contain tetraethoxysilane (TEOS). A well-known drawback of these materials is their tendency to form gels susceptible to cracking, which is generated by the high capillary pressures supported during drying. We have synthesized a new nanomaterial by adding a hydroxyl-terminated polydimethylsiloxane (PDMS) to TEOS in the presence of the surfactant, n-octylamine. The surfactant acts to direct the gel network pore structure; the coarsening of the gel network then reduces the capillary pressure responsible for cracking. In addition, methyl groups from the PDMS give hydrophobic properties to the product. In the study reported, we evaluate the durability of a biocalcareous sandstone and a granite treated with the new material by applying a sodium chloride crystallization test. Results obtained show that our product increases the resistance of the stone to the sodium chloride crystallization cycles as a consequence of the combined action of the consolidating and hydrophobic properties of the new nanomaterial.

Keywords: ormosil, nanomaterial, granite, sandstone, salt mist test

1 INTRODUCTION

Commercial products containing alkoxysilanes, such as tetraethoxysilane (TEOS), are commonly applied in the protection of stones. These products polymerize, through a classic sol-gel process, in situ inside the pore structure of the disintegrating stone, and significantly increase the cohesion of the material (Wheeler 2005). A well-known drawback of these conservation products is their tendency to form brittle gels susceptible to cracking (Scherer & Wheeler 1997; Mosquera et al. 2003). Cracking is generated by the high capillary pressures supported by the gel network during drying (Scherer 1990). Our research group has designed an innovative synthesis strategy in which the sol-gel transition occurs in the presence of a surfactant. The surfactant acts to direct the pore structure of the gel network, creating a nanomaterial with uniform pore radius (Mosquera et al. 2008a). This provides an efficient means of preventing the gel from cracking while it is drying inside the stone, and is the result of two factors: (1) the surfactant creates a coarsening of the gel network that reduces the capillary pressure; and (2) the decrease of surface tension provided by the surfactant also reduces the capillary pressure.

The synthesis of organically modified silicates, which have been named ORMOSILs by Schmidt et al. (1985), has been described extensively in the literature, since they constitute a class of materials with potentially high performance, intermediate between “pure ceramics” and “pure polymers” (Kasemann & Schmidt, 1994). Specifically, ormosils present original optical, electrical and mechanical properties. Concerning their mechanical behavior, (Mackenzie et al. 1992; Hu & Mackenzie, 1992) demonstrated that hybrids made from PDMS and TEOS could be rubbery even when the inorganic component is in excess of 70 % by wt. Recently, we have synthesized a new “ormosil” by adding an organosiloxane, hydroxyl-terminated polydimethylsiloxane (PDMS), to tetraethoxysilane (TEOS) in the presence of the surfactant, n-octylamine. An organic-inorganic hybrid mesoporous framework is thus obtained by co-condensation of TEOS and PDMS (Mosquera et al. 2008b; Mosquera et al. 2010). PDMS gives toughness and flexibility to the silica, and contributes to preventing gel cracking during drying. In addition, methyl groups from the PDMS are integrated in the silica polymer, and this gives the product useful hydrophobic properties. A complete characterization of this material, denoted as UCA-1, is reported in a previous paper of our research group (Mosquera et al. 2010). Some significant details of the results obtained are included here. Textural properties of the new ormosil were characterized by the Nitrogen Physisorption test. This showed a type IV isotherm, which is typical of mesoporous materials. This material presented a narrow pore size distribution, which is a clear indication of a uniform pore size network. The same material prepared without PDMS showed a larger pore radius than the gel containing PDMS. We think that this differenceis due to the addition of PDMS to the TEOS sol. PDMS increases the flexibility of silica chains, and so the shrinkage of the material during drying is significantly higher for the gel containing PDMS (UCA-1) than for that prepared without the organic component (UCA-2). This view is corroborated by the degree of shrinkage exhibited by each material, which is significantly higher for the xerogel containing PDMS than for that synthesized without PDMS. Scanning Electron Microscopy studies provided support for the evidence obtained from the nitrogen adsorption tests. N-octylamine produced a gel network composed of uniform polymeric balls. The presence of the surfactant promotes the coarsening of the gel network, increasing the size and uniformity of the pore network, as can be appreciated in the SEM micrographs and corroborated by nitrogen adsorption test data. We have also demonstrated that the new nanomaterial synthesized in our laboratory increases the mechanical resistance of stones treated, and creates a hydrophobic coating (Mosquera et al. 2010).

Soluble salts are one of the most pernicious agents causing the decay of rocks in monuments and it is well-known that the action of these salts is the main factor responsible for stonework losing its internal cohesion over time. It is therefore essential to evaluate the durability of every proposed new treatment by performing salt crystallization tests. In the work described, a salt crystallization test with sodium chloride was carried out on two stones of very different characteristics: a granite, as a common crystalline rock with low porosity, and a biocalcareous sandstone, as a cemented rock with high porosity. The same salt crystallization test was also carried out on untreated stone samples and on other samples treated with a commercial consolidant and a commercial hydrophobic coating product.

2 EXPERIMENTAL PROCEDURE

2.1 Stones selected

Monte Enxa is a muscovite-rich, medium-coarse grained leucogranite with an evident mineral orientation and low porosity (around 3%). It is currently used in restoration of historic buildings and in construction of new buildings in Galicia (NW Spain).

Puerto de Santa María is a biocalcareous sandstone used in the building of many emblematic monuments in the southwest area of Spain, including the Cathedrals of Seville and Cádiz. It is a yellow-cream stone composed of micritic calcite cement with rounded quartz and feldspar grains as clastic components (more than 50%). Biotite, muscovite and zircon are present as minor minerals. The rock contains many bioclasts and, from this characteristic, its genesis can be attributed to the Miocene. Its porosity is around 20%.

2.2 Nanomaterial synthesis and application to stone samples

The novel nanomaterial, named UCA-1 (after the University of Cadiz), is prepared from TEOS and hydroxyl-terminated PDMS oligomers, in the presence of n-octylamine. The PDMS used presents a degree of polymerization of 12 and an OH percentage ranging between 4 and 6% w/w. The sol is prepared by mixing TEOS and ethanol. Water is then added under high-power ultrasonic agitation (60 $W \cdot cm^{-3}$). Finally, PDMS is added, drop by drop, under the same agitation. The total time of ultrasonic agitation is two minutes. Finally, n-octylamine is added to the mix under vigorous stirring. The mole ratios of the mixture are 1 TEOS/3.7 H_2O/4 ETOH/0.04 PDMS/0.002 n-octylamine.

After completion of the synthesis, the sol UCA-1 was applied by brushing on all the faces of the sample cubes until they were saturated. For comparison, a popular commercial consolidant, Tegovakon V100 (hereafter TV100), supplied by Evonik Goldschmidt GmbH®, has also been applied to other samples of the same stones. TV100 is a solvent-free one-component consolidant consisting of partially pre-polymerized TEOS and dibutyl tin dilaurate (DBTL) catalyst. For comparison of hydrophobic behaviour, other samples were coated with a commercial hydrophobic product, Silres BS290 (hereafter S290), which is a solvent-less silane/siloxane mix marketed by the company Wacker®. Following the specifications of the manufacturer, S290 was diluted in ethanol (dilution: 1/12 v/v) before application to the stone. After the various treatments, all the stone samples were then dried under laboratory conditions to reach constant weight.

2.3 Static Sessile Drop Test

The effectiveness of the materials in providing hydrophobic protection was characterized by measurement of the contact angle according to the sessile drop method, using a commercial video-based, software-controlled contact angle analyzer, model OCA 15plus, from Dataphysics Instruments. For each treatment evaluated, droplets of distilled water (5 μl) were applied by needle at 5 different points on 3 stone surfaces coated with the product, and from a distance sufficiently close to the substrate so that the needle remained in contact with the applied liquid droplet after delivery. Then, the delivery needle was withdrawn with minimum perturbation to the droplet, and the image of the droplet was captured immediately for measurement of the static contact angle

2.4 Determination of resistance to ageing by salt mist

To evaluate the durability of treatments, an ageing test by exposure to sodium chloride mist was carried out. The salt crystallization test was performed in accordance with the Spanish standard (UNE-EN 14147, 2004). For all the cycles (30 in total), samples were kept inside a climate chamber at 35ºC. Each cycle consisted of two steps: (1) exposure to salt mist for 4 hours; (2) drying inside the climate chamber for 8 hours. After 30 cycles, the samples were repeatedly washed in distilled water to remove the deposited salts inside pores, until the conductivity of the washing water is less than twice that of clean distilled water. Then samples were dried at 70ºC until reaching constant weight, and the weight lost was determined.

The samples corresponding to untreated stone and their treated counterparts were characterized by the procedures described as follows. Characterization was carried out before the salt mist test and after the corresponding 30 cycles of ageing. We evaluated changes in the mechanical resistance of the stones applying the Vicker hardness test, using a Universal Centaur RB-2/200 hardness tester. The loading was 30 Kg during 30 seconds, with a preload time of 15 seconds. 11 measurements were made on the stone specimens. Vicker hardness (VH) was calculated according to the following equation:

$$VH = \frac{1.8544 \cdot W}{d^2} \quad (1)$$

where W is the load over the surface area of the indentation; d is the indentation diagonal.

In order to confirm changes in the hydrophobic behaviour of the materials after the ageing test, the stone samples were subjected to a water absorption by capillarity (WAC) test as recommended in UNE-EN 1925 (2004). Measurements were made for the following periods of time: 1, 3, 5, 10, 15 and 30 minutes, 1, 8 and 24 hours. The results were plotted as the mass of water absorbed per area of sample, versus the square root of time. The first stage of the curve defines water absorption, in which the WAC coefficient was calculated as the slope ($r > 0.99$); the second stage denotes rock saturation. At least 5 points were used for slope calculation.

3 RESULTS AND DISCUSION

In order to confirm the hydrophobic behaviour of the materials under study, we firstly carried out a static contact angle test. Results are shown in Table 1. The samples of the two types of stone treated with UCA-1 presented the highest contact angles, due the presence of PDMS chains integrated in the silica skeleton of the material, creating an organic-inorganic hybrid gel coating. It is well-known that PDMS has a very low surface energy, the water droplet contact angle on a smooth PDMS surface being about 105º (Onda et al. 1996). For the sandstone treated with UCA-1, we found an exceptionally high contact angle value. Since the water contact angle cannot be increased beyond 120º by a purely chemical process on a smooth surface (Wu et al. 2008), we think the high contact angle values obtained is due to the combined effect of PDMS and stone surface roughness. Specifically, a surface with two roughness scales is responsible for high hydrophobicity, known as the Lotus effect (Gao & McCarty, 2006; Manoudis et al. 2009). As we previously reported (Illescas & Mosquera, 2011), PDMS/silica hybrid coatings result in the generation of two distinctive scales of roughness, one corresponding to the silica polymer and the other to the PDMS aggregates.

Finally, we should state that UCA-1 and S290 are the only materials tested on the stone that present values higher than 90º and therefore, theoretically, they would be the only materials capable of preventing the penetration of salt mist inside the stone during the ageing test.

Table 1. Static contact angle values (º) for the treated stones and their untreated counterparts.

Stone	Untreated	TV100	S290	UCA-1
Granite	64± 5	66± 5	102± 9	107± 9
Sandstone	72± 4	80±12	98± 9	129±12

Figure 1 shows the weight loss percentage values of the two types of stone under study at the end of the salt mist test. The loss of weight is significantly lower for the granite than for the sandstone. This demonstrates the greater durability of the granite as a consequence of the greater cohesion and lower porosity of this stone. Regarding the different treatments applied on the granite, we observed weight loss of less than 0.4 % w/w for all the samples evaluated including the untreated stone. As expected, the two products with hydrophobic properties showed the lowest weight lost.

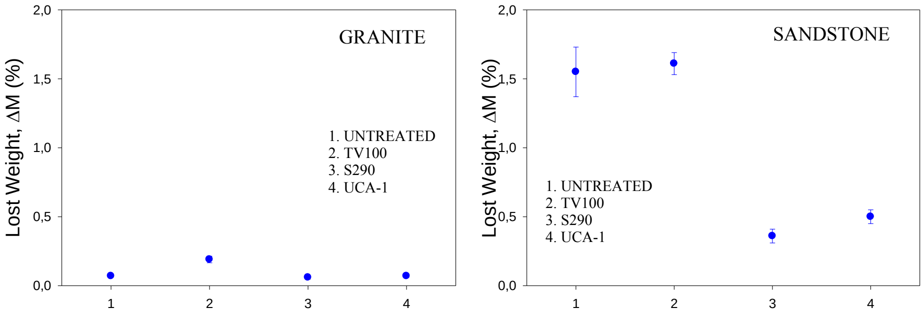

Figure 1. Weight loss of the stone samples after 30 cycles of salt mist test.

Regarding the sandstone, significant differences in weight loss were observed. The untreated stone and samples treated with TV100 showed much higher weight variations than the samples treated with the two products tested that give hydrophobic protection. It is also notable that the weight loss for the two types of stone treated with TV100 was slightly higher than that corresponding to the untreated samples.

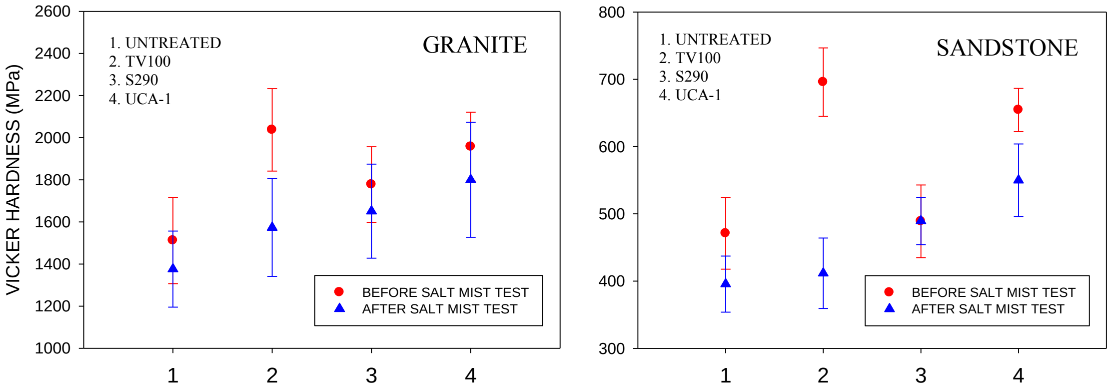

Figure 2. Vicker hardness values of the stone samples before salt mist test and after 30 cycles of test.

Figure 2 shows Vicker hardness data for the two types of stone under study. Hardness values for the granite were significantly higher than those for the sandstone. In the case of granite, the highest hardness values before the ageing test corresponded to the sample treated with TV100 followed by the sample treated with UCA-1. However, after the test, the TV100 sample showed the highest reduction in hardness. A similar tendency was observed for the sandstone evaluated. In this case the increase in hardness due TV100 and UCA-1 treatment was significantly greater than comparable increases for the granite. Finally, it should be noted that stones treated with UCA-1 showed higher values of hardness after salt crystallization test than those treated with S290. Regarding the S290 product, it should be noted that it creates only a superficial coating on the stone whereas TV100 and UCA-1 penetrate into the stone pores, thus acting as consolidants. In a previous paper (Illescas & Mosquera, 2011), we confirmed that S290 forms a thin film after the solvent has evaporated completely. Thus, it contributes very little to the mechanical resistance of the stone whereas TV100 and UCA-1 increase significantly the stone's mechanical resistance.

To evaluate the effect of the ageing test on the hydrophobicity of stones, we carried out water absorption by capillarity (WAC) tests on stone samples treated with the materials under study. Coefficients for water absorption by capillarity (WACs) obtained before and after the sodium chloride tests are shown in Figure 3. The results obtained confirm the effective hydrophobic behaviour of UCA-1 and S290, which is maintained for both products after 30 cycles of the test. In the case of TV100, the stones treated showed slightly higher absorption coefficients, as expected for materials with the contact angles below 90º. Also as expected, the untreated samples of the two stones showed the highest WAC values before and after being subjected to the salt mist test.

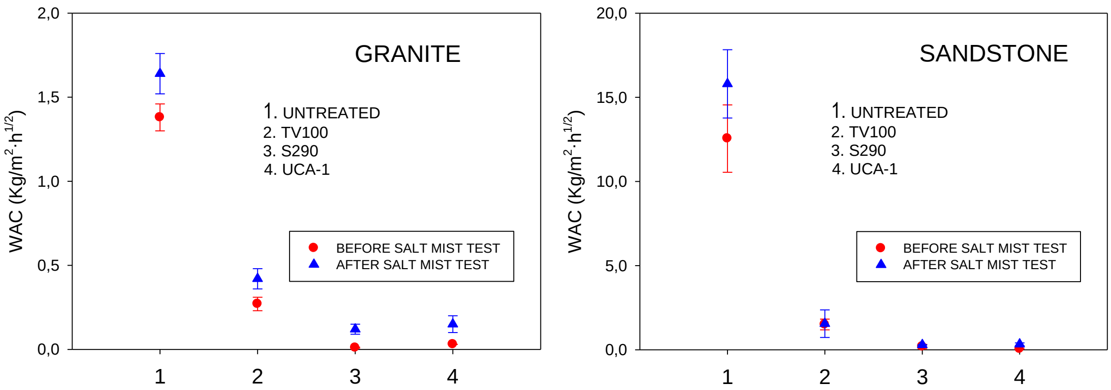

Figure 2. Coefficients for water absorption by capillarity of the stone samples before the salt mist test and after 30 cycles of test.

Finally, we report that we have also evaluated the durability of the treatments by measuring the resistance of these treated stones to sodium sulphate crystallization cycles and to UV light exposure. The results show that the resistance of stone treated with UCA-1 is better than that of stone treated with TV100 (Sanmartín et al. 2008).

4 CONCLUSIONS

We have evaluated the durability of a new nanomaterial synthesized in our laboratory, with both consolidant and hydrophobic properties, in samples of two types of stone subjected to 30 cycles of a standard sodium chloride salt test. For comparison we also evaluated the durability of commercial consolidant and hydrophobic products. The results show that resistance to the salt mist test of the two types of stone treated with UCA-1 is better than that of the same stones treated with the two commercial products. Specifically, our product and S290 are more effective than TV100 since they prevent the salt solution from penetrating into the pore structure. In addition, our product increases the mechanical resistance of the stone whereas S290 has no effect on the hardness of the stone. Thus, we conclude that the durability of the stones treated with the product synthesized in our laboratory, when subjected to the salt crystallization test, is a consequence of the combined action of the consolidating and hydrophobic properties of the new material.

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