Hydrophobe VII *7th International Conference on*
Water Repellent Treatment and Protective Surface Technology for Building Materials
A.Elena Charola and J. Delgado Rodrigues, Editors
LNEC (Laboratório Nacional de Engenharia Civil), Lisbon: 2014 (171-177)

Effectiveness of a novel surfactant-synthesized hydrophobic nanomaterial: laboratory and in situ results

Farid Elhaddad
University of Cadiz, Cadiz, Spain, farid.elhaddad@uca.es

Maria J. Mosquera
University of Cadiz, Cadiz, Spain, mariajesus.mosquera@uca.es

SUMMARY: A novel surfactant-synthesized nanomaterial with hydrophobic properties was applied on stone samples from three archaeological sites located in the south of Spain. For comparison purposes, two commercial products were also evaluated. The study consists of an initial phase in the laboratory to evaluate the product effectiveness. Next, the samples treated with the products were maintained in the archaeological sites and properties were evaluated after one year of exposure. The results obtained showed that the novel product showed higher effectiveness and durability than the commercial products under study.

KEY-WORDS: Effectiveness; Hydrophobic; Nanomaterial; Archaeological sites

INTRODUCTION

The treatment with hydrophobic products of stone monuments in outdoor environment provides a protection against weathering since water is one of the main factors accelerating the deterioration rate of stone. This decay is caused through freeze-thaw cycles or by crystallization of the salts introduced into the monument by water transport from the environment [1,2]. Different hydrophobic coatings, such as fluorinated acrylic polymers and organic siloxanes have been developed recently to reduce the surface energy [3,4]. Our research group has previously designed a simple and low-cost procedure for obtaining crack-free materials for the restoration and protection of building materials. Specifically, we have prepared consolidant products [5] and hydrophobic and superhydrophobic materials [6,7]. The starting sol exclusively contains an aqueous surfactant solution and a silica oligomer. The surfactant provides an efficient means of preventing cracking of the gel, as the result of two factors: (1) increasing the pore size of the gel network; and, (2) decreasing surface tension, both of which reduce capillary pressure. In addition, we have developed a simple modification of this process, adding an organic component to the starting sol. The organic component confers toughness and flexibility and gives hydrophobic properties to the product by reducing surface energy [8].

This study aims to evaluate the effectiveness and durability of the product previously developed when applied to stones from three important archaeological sites in Andalusia.

MATERIALS AND METHODS

The study has an initial laboratory phase to evaluate the effectiveness of the product synthesized applied to stone samples. For comparison purposes, two commercial products were also evaluated. Next, the treated samples treated were kept in an outdoor archaeological site. After one year, various properties were evaluated. For comparison purposes, stones treated with two commercial products, such as a consolidant and a hydrophobic product were also subjected to the durability study.

The organic-inorganic hybrid nanomaterial was prepared from a starting sol containing a commercial silica oligomer (Dynasylan-40 from Evonik) and a hydroxyl-terminated polydimethylsiloxane (PDMS from ABCR) in the presence of a surfactant (n-octylamine, from Aldrich). The PDMS was used in the proportion of 10 %v/v. A 1.57 M aqueous solution of n-octylamine was employed. The proportion of n-octylamine solution in the sol was 0.075 %v/v. The sol was homogenized by high-power ultrasonic agitation (60 $W \cdot cm^{-3}$) for 10 minutes. This hybrid material is denoted by their PDMS and n-octylamine contents. The product was named UCAD (UCA after University of Cadiz and D for Dynasylan).

The products under study were sprayed onto stone samples from three Andalusian archaeological sites using a pressure of ($1.5 \cdot 10^5$Pa) for 25 s. The sites selected were (see Fig. 1):

- Acinipo (Málaga) was founded by the Romans in the first century BC. The city is located in an area of low pollution, being the decay caused by temperature variations.
- Baelo Claudia (Cádiz) was founded by the Romans in the late second century. Since it is not an industrial area, the stone decay is only caused by soluble salts from marine aerosols.
- Carteia (Cadiz) was founded by the Phoenicians in the seventh century BC. This city is located near to a petrochemical company. Thus, stone decay is produced by marine aerosols and by pollution resulting from industrial activities.

Figure1. Archaeological sites and their corresponding stone samples into the insets: (A) Acinipo. (B) Baelo Claudia. (C) Carteia.

The specific characteristics of the stone under study are given in Table 1. The stone samples are identified as AC (from Acinipo, Málaga), BC (Baelo Claudia, Cádiz) and CA (Carteia, Cádiz). The stone samples were cut as 4 cm cubes and left to dry until constant weight was reached. The sols under study were applied by spraying onto all the faces of the samples. To compare the effectiveness with commercial products, a hydrophobic product (BS290 from Wacker) and a consolidant product (BSOH100 from Wacker) were similarly applied. In the case of BS290, it was diluted in ethanol (12 %w/w.), following the recommendations of the manufacturer. The consolidant product was studied in order to evaluate its hydrophobic properties during the first months after application.

Table 1. Properties of the stones under study.

Stone sample	Type	Mineral components	Porosity (%)
AC	Limestone	Bioclastic calcarenite: fragments of bryozoan and algae. Matrix microsparitic.	11
BC	Sandstone	Calcareous sandstone: texture with heterogeneous fragments of calcite and quartz.	20
CA	Sandstone	Arkose sandstone: composed of quartz grain (50 and 100µm) and feldspar,	6

The samples were then dried in laboratory conditions (20ºC - 60%RH) until constant weight was reached, about one month after application of the product. Uptake of products and their corresponding proportion remaining in the samples after drying, which is referred to as dry matter, were determined in laboratory and after one year of exposure in outdoor conditions. The both parameters were measured by change in the mass specimens.

A JEOLQuanta 200 scanning electron microscope (SEM) was used to visualize changes in the morphology of treated stone specimens and their untreated counterpart. Energy dispersive X-ray spectroscopy (EDX) spectra were recorded in order to elucidate the variations in surface composition after the test.

The effectiveness of the coating materials in providing hydrophobic protection was characterized by the contact angle test according to the sessile drop method, using a commercial video-based, software-controlled contact angle analyzer, model OCA 15plus, from Dataphysics Instruments. Static contact angle values were determined on the stone surface. For each treatment evaluated, droplets of distilled water (10 µl) were applied with needle at 5 different points on each of the 3 stone surfaces.

The changes in color were evaluated by using a solid reflection spectrophotometer, Colorflex model, from Hunterlab. The conditions used were as follows: illuminant C and observer 10º. CIE L*a*b* color space was used and color variations were evaluated using the total color difference parameter (ΔE^*).

To confirm the hydrophobic behaviour of the materials, the stone samples were subjected to a capillary water absorption (WAC) test as recommended in UNE-EN [9] and the absorption coefficients were determined.

RESULTS AND DISCUSSION

The effectiveness of the UCAD product was investigated on the surface of stone samples from three Andalusia archaeological sites. For purposes of comparison, the effectiveness of BSOH100 and BS290 materials were also investigated. Table 2 shows a comparison of dry matter values of the products before and after exposition on archaeological sites for 1 year. The dry matter values obtained after exposition to outdoor conditions for BS290 and BSOH100 products were significantly lower than those obtained for UCAD products.

Moreover, the commercial products showed a higher matter loss after 1 year exposition, excepting AC stone treated with BSOH100.

Table 2. Dry matter values before and after one year of exposition.

Sample	Product	Dry matter (%w/w) Before exposure	Dry matter (%w/w) After exposure	Matter loss (%)
AC	BSOH100	0.61	0.51	16
	BS290	0.21	0.12	42
	UCAD	0.74	0.59	20
BC	BSOH100	2.79	1.04	62
	BS290	0.77	0.67	12
	UCAD	4.33	2.22	48
CA	BSOH100	0.79	0.24	69
	BS290	0.23	0.16	30
	UCAD	0.88	0.32	63

In order to investigate the reasons producing the decrease in dry matter of the products during outdoor exposure, the adhesion of these coatings to the stones was studied by SEM. Fig. 1 shows the micrographs obtained by SEM and the EDX analyses in the case of the AC samples tested in laboratory and outdoor conditions. The UCAD product created a dense and extensively coating on the stone surface. For this product, modifications in the coating morphology after 1-year exposure are hardly visible. In the case of the BS290 and BSOH100 products, a significant loss of the coating was clearly observed after exposure and was confirmed by EDX analysis, where the original high Si peaks were significantly reduced for BS290 and BSOH100 after exposure. On the other hand, a significant reduction of Ca content was also observed for all the stones treated with UCAD after 1 year, which confirms that the coating is maintained on the surface stone. In the case of the samples treated with the commercial products, Ca peak is increased after exposure.

For the UCAD product, no significant changes were detected after the EDX test confirming that this product penetrated into the stone pore structure and was capable of adhering firmly to the stone, providing long-term wear resistance. Contrariwise, the BS290 and BSOH100 were removed during outdoor exposure. These results perfectly matched with the dry matter values obtained. In the case of BC stones, similar results were observed. However, CA samples showed a significant loss of the all products under study, as confirmed by the dry matter values obtained.

The effectiveness of the coating materials in providing hydrophobic protection was characterized by the contact angle values. Table 3 shows water droplet static CA values and their corresponding advancing and receding CA values for the surfaces of treated stone samples. All the products tested on the stones, presented receding contact angle values higher than 90°, excepting AC treated with BSOH100. Thus, all these coatings could theoretically be capable of preventing the penetration of water into the stone. It confirms that the commercial consolidant initially presented hydrophobic properties due to the presence of ethoxy groups.

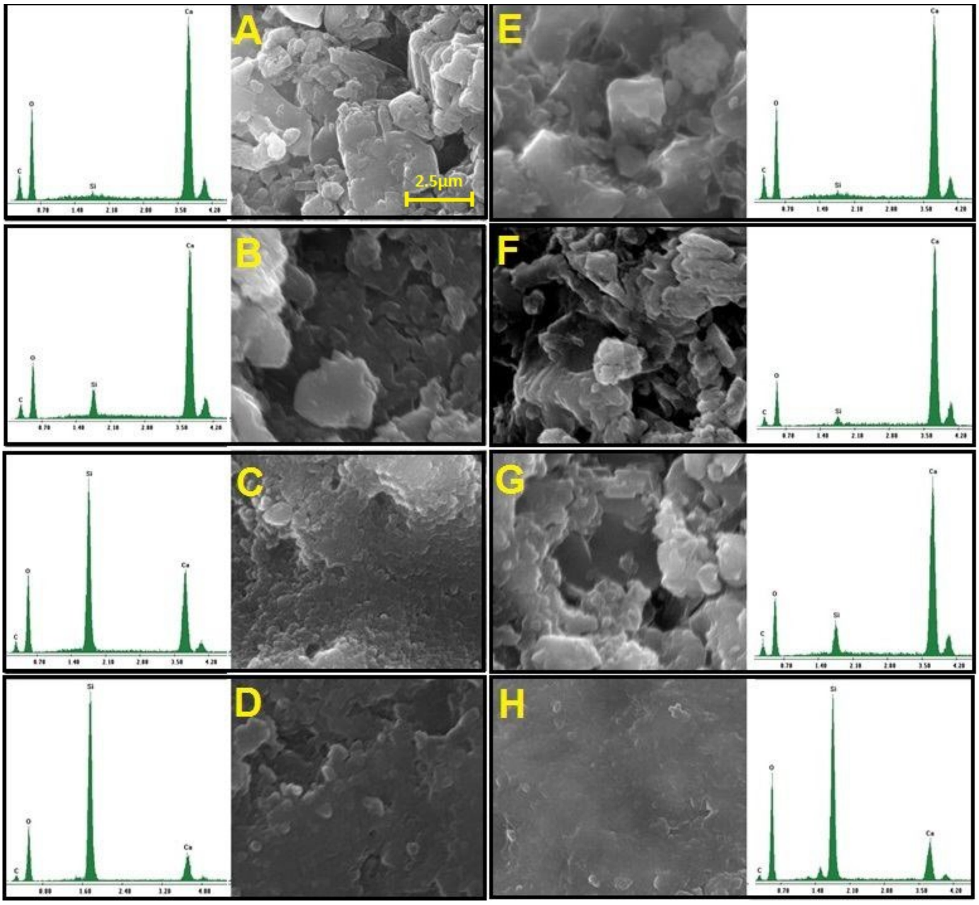

Figure 1. SEM images of the stone surface and their corresponding EDX spectrum: (A) untreated, (B) BSOH100, (C) BS290, (D) UCAD, (E) untreated after 1-year exposure, (F) BSOH100 after 1-year exposure, (G) BS290 after 1-year exposure and (H) UCAD after 1-year exposure.

For comparison, the hydrophobic effectiveness was also evaluated in samples with similar treatments after one year exposure to outdoor conditions (see Table 3). In the case of the samples treated with BS290 and BSOH100 products, an important decrease in the contact angle values was observed. The contact angle values for the AC and BC samples treated with UCAD product was maintained, being even increased in AC. In CA samples, the contact angle was significantly reduced after 1 year exposure.

In order to confirm the results from the contact angle test, the capillary water absorption test (WAC) was carried out on the stone samples treated with these products. A comparison of the capillarity water absorption coefficients obtained is shown in Table 4. Higher water absorption was observed for all the samples treated with BS290 and BSOH100 products. In the case of the UCA product, coherent results between the high measured values of the contact angle and the capillary absorption were found. They confirmed the hydrophobic effectiveness of UCA product on all the stones tested.

Table 3. Static CA values and their corresponding advancing and receding contact angle for the stones treated, where before is the initial evaluation and the after corresponds to 1 year outdoor exposure. Standard deviations are also indicated.

		Static angle (°)		Advancing angle (°)		receding angle (°)		Hysteresis (°)	
Sample	Treatment	Before	After	Before	After	Before	After	Before	After
AC	untreated	19±2	14±1						
	BSOH100	117±1	12±1	119±1		97±1		22±1	
	BS290	149±2	39±2	152±1		133±1		18±1	
	UCAD	115±2	136±1	116±2	139±3	94±1	118±1	22±1	21±1
BC	untreated	31±6	34±4						
	BSOH100	80±6	27±3						
	BS290	108±4	31±3	111±1		92±1		19±1	
	UCAD	98±3	91±4	101±1	93±1	82±1	72±1	19±1	21±1
CA	untreated	21±2	8±3						
	BSOH100	94±3	10±4	95±1		71±2		24±1	
	BS290	146±2	84±3	152±1		143±1		14±1	
	UCAD	149±3	16±2	147±1		133±1		14±1	

The total color difference values (ΔE^*) of the stone before and after 1 year exposure are also listed in Table 4. For the UCAD product, ΔE^* was low and below the visible perceptibility threshold ($\Delta E^* < 3$), excepting for AC stone.

Table 4. Capillary water absorption coefficients (WAC) and color difference (ΔE^*) for each treated stone and their untreated counterpart before and after 1 year outdoor exposure.

		WAC ($kg.m^{-2}.h^{-1/2}$)		ΔE^*	
Sample	Treatment	Before	After	Before	After
AC	untreated	0.17	0.30		
	BSOH100	0.16	0.24	6.5	1.1
	BS290	0.04	0.05	3.9	1.2
	UCAD	0.02	0.01	6.6	10.6
BC	untreated	4.12	4.37		
	BSOH100	3.54	4.10	4.7	4.4
	BS290	0.20	0.59	12.4	6.7
	UCAD	0.30	0.31	16.1	3.1
CA	untreated	0.41	0.52		
	BSOH100	0.33	0.67	2.6	4.7
	BS290	0.05	0.10	12.9	2.9
	UCAD	0.05	0.07	0.7	1.4

CONCLUSION

The results obtained in this study showed that the nanomaterial synthesized in our laboratory produces a hydrophobic coating with higher durability than those produced by the two commercial products under study on the stone samples from Baelo Claudio and Acinipo. We assume that it can be associated to the higher adherence it has to the three substrates than that obtained from the two commercial products tested, and could be attributed to the higher penetration of the UCAD sol promoted by the absence of volatile organic components in the product. In the case of the Carteia samples, a lower durability of our product was found as a consequence of its lower adherence to the substrate.

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