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Styliani Katsikoglou, Dimitra Aslanidou, Ioannis Karapanagiotis

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Hydrophobization of limestone using fluorinated and TEOS-based polymers

Styliani Katsikoglou, *Department of Chemistry*, Aristotle University of Thessaloniki, Thessaloniki, Greece

Dimitra Aslanidou. *Department of Chemistry*, Aristotle University of Thessaloniki, Thessaloniki, Greece

Ioannis Karapanagiotis, *Department of Chemistry*, Aristotle University of Thessaloniki, Thessaloniki, Greece
karapana@chem.auth.gr

I. EXTENDED ABSTRACT

Natural stone and stone-built cultural heritage suffer weathering and decay by condensed water. Consecutive freezing and thawing cycles inside the pores of the stone cause the stone deterioration. In addition, air pollutants can also be transferred and cause stone decomposition [1,2]. Hydrophobization of natural stone surfaces is a practical method to impede water induced degradation of buildings of cultural heritage. Silane/siloxane-based products are commonly used for the conservation of natural stone since they possess three important properties: high depth of penetration, stability, and hydrophobicity [3,4]. The inherent hydrophobic character of the silane/ siloxane-based materials originates from the organic groups which are attached to the Si atoms of the backbone chain. Polysiloxane networks originate from small precursor molecules of silanes and siloxanes. These molecules can penetrate deep into the stone network before they become highly viscous gels (i.e., polysiloxanes) through the sol-gel process [5]. This results to higher depths of penetrations by the silane-based consolidants, compared with the high molecular weight organic polymers used in the past for stone consolidation [6,7]. Polysiloxane materials are often considered as hybrid materials because their backbone chains are formed by the siloxane (Si-O) bond which is of "inorganic" nature, while the substituents attached to the Si atom are generally "organic" radicals [7]. This dual nature of polysiloxane compounds offers both stability and hydrophobicity. Stability originates from the high strength of the Si-O bond compared with the C-C bond which forms the backbones of organic polymers. In particular, the strengths of the Si-O and C-C bonds correspond to 108 and 83 kcal/mol, respectively [4]. High Si-O bond strength offers siloxane-based materials with considerable thermal stability as well as good corrosion and UV resistance [4,8-10]. The introduction of fluorine molecules enhances water repellency and resistance by lowering the surface tension of the treated surfaces [11,12].

In the present work two materials were used to treat limestone specimens: Dynasylan F8261 (1H,1H,2H,2H- Perfluorooctyltriethoxysilane, PFOES), purchased from Evonik, and KSE 300 which according to the manufacturer (Remmers) is a stone strengthener on a silicic acid ester base and it is provided for the consolidation of natural stone. In the first set of experiments F8261 was directly sprayed onto the stone samples. Several deposition/spraying cycles were applied resulting in several layers of coating onto the treated stones. In the second set of experiments, stone samples were first immersed in KSE300 baths (dip coating) for 72 h and then F8261 was sprayed on top of treated stones. The latter were purchased from the local market. Static contact angle of water drops (CAs) and colour changes (ΔE*) were measured as a function of deposition cycles i.e. number of deposited layers. ΔE* was calculated using the following equation:

$$\Delta E^* = \sqrt{(L_t^* - L_u^*)^2 + (a_t^* - a_u^*)^2 + (b_t^* - b_u^*)^2}$$

where L*, a* and b* are the brightness, the red–green component, and the yellow–blue component of the CIE 1976 scale, respectively.

The "t" and "u" subscript characters indicate the treated and untreated samples, respectively.

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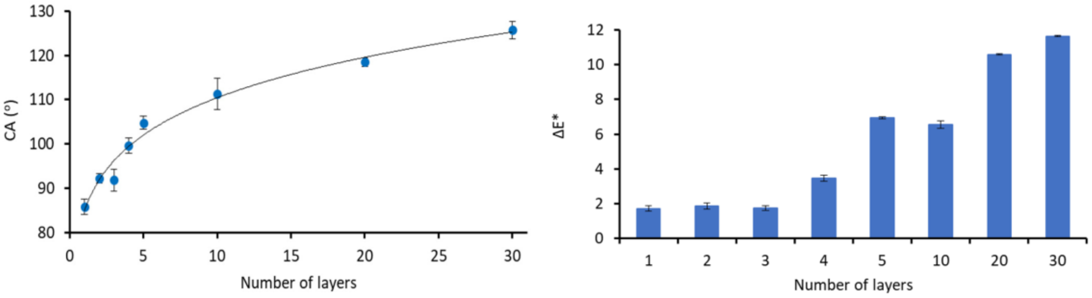

Figure 1. Results obtained after treating limestone samples with F8261. Contact angles of water (CA) drops (left) and colour change (ΔE*) vs the number of coating applications on limestone. A power law fitting is included in the left plot to guide the eye. The results for the limestone samples which were treated only with F8261 (first set of experiments) are included in the plot of Figure 1. Figure 1a shows that CA increases with the number of deposited layers from around 85° (limestone sample coated by 1 layer) to 125° (sample coated by 30 layers). Therefore, the results of Figure 1 suggest that hydrophobization of limestone is promoted with the deposition cycles of the fluorosilane material. According to the results of Figure 1b, the deposition of the first 4 layers of coatings induced an acceptable colour change i.e. ΔE*<5. However, the deposition of more layers (more than 4) resulted in augmented colour changes.

In the second set of experiments, limestone samples were first treated with KSE300, followed by the application of F8261. The CAs, measured after the deposition of one, two and three layers of F8261 were 115°, 121° and 122°, respectively. Notably, 30 layers of F8261 on bare limestone were necessary to achieve a CA of 125° whereas the same degree of hydrophobization was roughly reached with only 3 layers of fluorosilane when it was deposited on limestone which was pretreated with the TEOS-based material. As F8261 is a material of low viscosity, it can easily penetrate into the porous network of limestone. Hence, multiple depositions of F8261 are necessary to form a continuous coating on the surface of limestone and therefore to achieve surface hydrophobization. However, with the pretreatment step the pores of limestone are filled with KSE300 and therefore only few deposition cycles of fluorosilane are necessary to form a continuous coating. However, the second set of experiments resulted in augmented change of the original colour of limestone as ΔE*>10, regardless of the number of the deposited F8261 layers. It should be stressed, that the colour change was induced mainly by the pretreatment step and not by the deposition of the fluorosilane. The colour change induced, in the second step, by the deposition of F8261 was not noticeable. In particular, the total colour difference (ΔE*) between limestone samples treated with both materials (KSE and F8261) and limestone samples treated only with KSE was <3.

The present research is in progress. Scanning Electron Microscopy will be employed to study the surfaces of treated limestone samples and measurements on water absorption by capillarity will be carried out.

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