



A sprayable protective coating for marble with water-repellent and anti-graffiti properties



Dennis Kronlund^a, Mika Lindén^b, Jan-Henrik Smått^{a,*}

^a Laboratory of Physical Chemistry and Center of Excellence for Functional Materials, Åbo Akademi University, Porthansgatan 3-5, 20500 Åbo, Finland

^b Inorganic Chemistry II, University of Ulm, Albert-Einstein-Allee 11, 89031 Ulm, Germany

ARTICLE INFO

Article history:

Received 29 February 2016

Received in revised form 23 June 2016

Accepted 9 July 2016

Keywords:

Marble

Fluorosurfactant

Capstone

Pore hydrophobization

Water absorption

Graffiti

ABSTRACT

A pore-lining coating method for marble stone surfaces based on the fluorosurfactant Capstone FS-63 has been optimized for application through spray coating by tuning the solvent composition. The optimized application conditions showed an effective penetration depth of the hydrophobic properties down to at least 0.5 mm, ensuring a long-term protection against water uptake. Mechanistic studies of the functionalization process revealed that the solution mixtures containing ethylene glycol provide the best pore-lining functionalization, due to the prolonged functionalization time as a consequence of the slow evaporation rate of the solvent combined with the beneficial shift in the surfactant-vesicle equilibrium towards free surfactants. The coatings also display anti-graffiti properties, allowing for graffiti paint to easily be washed away with a standard pressure washer repeatedly 3–4 times. For optimal re-usability of the anti-graffiti coatings, a new coating can be applied when the first coating loses its effectiveness.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Weathering effects and graffiti vandalism are two central problems connected with the damaging of natural stone materials. Weathering creates compositional, structural and morphological alterations to the stone through physical, chemical and biological routes resulting in stone deterioration [1,2]. Particularly calcareous stones are sensitive to the erosive effects related to water (e.g. water vapor condensation, freezing, thawing and (acid) rain dissolution) [3] and the minimization of water contact to calcareous stone surfaces is thus a key aspect in stone conservation. Graffiti is another large problem in our society as it sullies buildings and monuments. Keeping buildings free from graffiti defacing can be laborious and expensive, and it is particularly damaging to our cultural heritage [4,5].

In order to reduce weathering effects, eliminating or at least minimizing the contact of water with the stone surface has been the focus in the development of protective coatings for marble surfaces [6–9]. Current approaches utilize polymers [7,10–15], siloxanes [8,9,16,17] and sol-gel-based hydrophobic coatings [18–20]. One drawback is that after some time in contact with water, some of these coatings display significant water uptake [21] that will

eventually damage the calcareous stones by the above mentioned weathering mechanisms. A more persistent modification is obtained when using a hydrophobizing agent containing functional groups that can bind strongly to marble stone surfaces, like phosphate or phosphonate groups [22–25]. Furthermore, if the hydrophobizing agent is able to diffuse into the porous stone and functionalize the walls of the pores, a more long-term stability can be attained.

Common methods to combat graffiti include mechanical cleaning [26–29], the use of chemical cleaning agents based on organic compounds [26], and sacrificial (often sugar-based) coatings [30,31] which are used to create a layer of a dissolvable coating that can be washed away with for instance warm water. A more permanent solution for keeping stone surfaces clean from graffiti is to use hydrophobic and oleophobic functional coatings [11], which minimize the adhesion of graffiti to the surface. This allows for the soiling color to be washed away with for example organic solvents or pressurized water [11,32].

The main drawbacks of the existing approaches used for graffiti removal are that the mechanical and solvent cleaning methods cannot easily be used for very adhesive soiling agents or if the graffiti paint has penetrated into the porous stone [33]. The drawback of sacrificial coatings is that they have to be reapplied after each graffiti cleaning cycle. For permanent anti-graffiti coatings, a potential problem when using organic solvents to remove graffiti paint is that the color can diffuse into the protective polymer matrix, rendering

* Corresponding author.

E-mail address: jsmatt@abo.fi (J.-H. Smått).

the coating cleaning-resistant over time [34]. Thus graffiti cleaning methods that are based on environmentally friendly water-only systems are preferred [35].

It has previously been demonstrated that a commercial fluorosurfactant (Capstone FS-63) can penetrate into the porous network of Carrara marble and functionalize its pore walls. This provides a complete elimination of water absorption, even when 2 mm of the outermost surface is removed, and without impeding the water vapor permeability [36,37]. Such a deep penetration of the pore-lining fluorosurfactant functionalization was achieved by improving the diffusion of the surfactants into marble pores through solution engineering [36], as this shifted the vesicle-surfactant equilibrium towards free surfactants. However, while providing very well functionalized surfaces, the developed systems in references [36,37] suffer from several practical drawbacks. Chiefly the requirement for the marble material to be immersed for 24 h in the functionalization solution at elevated temperatures (typically 60–80 °C) is problematic for large objects, like a wall of a building.

In this study, a new functionalization method based on the Capstone FS-63 fluorosurfactant system has been developed to eliminate water contact, to minimize weathering effects and to create a semi-permanent anti-graffiti coating for marble surfaces. The previously studied fluorosurfactant system has now been spray-coated in order to reduce material consumption and allow for room temperature processing for optimal results. Furthermore, the anti-graffiti properties of the pore-penetrating fluorosurfactant functionalization were also investigated. The cleanability was tested using a simple pressure washer, thus relying solely on the surface functionalization and creating an anti-graffiti system that only requires water to clean. This new spray coatable solution will be beneficial for hydrophobizing large marble objects, offering environmentally friendly anti-graffiti protection with limited weathering impact.

2. Materials and methods

2.1. Materials used

Italian Carrara marble stones with the dimensions $5 \times 5 \times 1 \text{ cm}^3$ were used for the functionalization penetration depth study, while larger stones with the dimensions of $10 \times 10 \times 1 \text{ cm}^3$ were used for the anti-graffiti experiments and the capillary absorption measurements before and after graffiti cleaning. All experiments were performed in triplicate (i.e. 3 stones per treatment and per test). The purity of the marble has previously been investigated using x-ray diffraction (XRD), and the composition was found to be consisting almost entirely of calcite (CaCO_3) with some minor traces of dolomite ($\text{CaMg}(\text{CO}_3)_2$) [37]. In an earlier study, mercury porosimetry was used to determine that the same Carrara marble contained a large fraction of pores in the 0.02–0.3 μm range, with an open porosity of 0.65% [37]. The fluorosurfactant Capstone FS-63 (Dupont) was used in the optimizations, since it had proven to be the most suitable pore functionalization agent for marble in previous experiments [36,37] and binds very strongly to CaCO_3 through its phosphate linking group [22]. Ethanol (Altia Oyj) and ethylene glycol (Tamro Oyj) were used as co-solvents together with water, since they are able to decrease the fluorosurfactant vesicle size and promote the penetration of Capstone FS-63 into the pore network [36]. The viscosity of the used solutions was measured using a Bohlin CS (Bohlin Reologi AB, Lund, Sweden) rheometer and the vesicle sizes were recorded through dynamic light scattering (DLS) measurements using a Zetasizer Nano ZS (Malvern Instruments, Malvern, United Kingdom).

2.2. Hydrophobization of the marble samples

Functionalization of marble stones was performed by using an optimized concentration of 10 vol.-% solution of Capstone FS-63 [37]. Dilutions were made using solvents, such as water and varying concentrations of two suitable co-solvents for the system [36], ethylene glycol (with EG:water ratios 25:75, 50:50, 100:0) and ethanol (with EtOH:water ratios 25:75, 50:50). The solutions and samples are named according to their solvent component ratio to water, such as 25-EG for the solution (or coated marble sample) consisting of 10 vol.-% Capstone FS-63 diluted in a solvent composed of a 25:75 ratio mixture of EG:water. A volume of 100 mL/m² of all the solutions was applied to the stones using a custom-made spray coater (Arctic IP Investment Ab, Salo, Finland) with variable pressure, flow rate, and pitch. To apply 100 mL/m², a flow rate of 1 mL/min was used with an application speed of 35 mm/s, a pitch of 5 mm, a pressure of 1 bar and a spray-head-to-surface distance of 200 mm. The used sprayhead was a DAGR airbrush (Devilbiss, Dorset, United Kingdom). After coating, the samples were allowed to react for 24 h at room temperature, after which the samples were placed in a 60 °C oven for 24 h. The samples were then kept at room temperature for a week before any experiments were performed.

2.3. Functionality testing

Capillary absorption measurements were performed according to an adapted protocol from the current standard protocol [38]. Measurements were carried out for 48 h, recording any water absorption through capillary forces that occurred during contact with the wet bed. The capillary absorption was calculated according to Eq. (1).

$$Q_{CA} = \frac{\Delta m}{A} \quad (1)$$

where Q_{CA} , the amount of water absorbed per unit area by capillarity (in kg/m²), is calculated by considering the mass difference the sample expresses at time x when compared to the starting mass normalized against the area of the surface in contact with the filter paper bed, A (in m²) as seen in Eq. (2).

$$\%_{Abs} = \frac{Q_{sample}^{48h}}{Q_{STD}^{48h}} \times 100\% \quad (2)$$

The obtained averaged capillary absorption data for the functionalized samples after 48 h on the wet bed, Q_{sample}^{48h} , was normalized against the average value obtained from nine untreated samples of the same dimensions, Q_{STD}^{48h} , thus giving a value in percent absorption, $\%_{Abs}$, compared to the untreated stones at the chosen time point. The time point of 48 h was chosen, since a plateau was reached for the untreated samples within this time frame. The normalized absorption value was then subtracted from 100% resulting in the water protection efficiency of the stone. The contact angle measurements were carried out using a KSV CAM 200 Optical tensiometer from KSV instruments Ltd. Droplets (2 μL) of Milli-Q purified water were applied by a microsyringe and three different measurements were performed for each sample, thus providing the reported standard deviations.

The potential optical effect the functionalizations had on marble was investigated through colorimetric measurements using a Minolta CM3600d spectrophotometer and evaluating the data in the CIELAB color space, where color changes, ΔE^* , as defined in Eq. (3) [39].

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (3)$$

where L_2 is the lightness of the untreated stone sample and L_1 is the lightness of the coated sample. The same annotation also applies

Download English Version:

<https://daneshyari.com/en/article/7106401>

Download Persian Version:

<https://daneshyari.com/article/7106401>

[Daneshyari.com](https://daneshyari.com)