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Hydrophobization of marble pore surfaces using a total immersion treatment method – Influence of co-solvents and temperature on fluorosurfactant vesicle behavior

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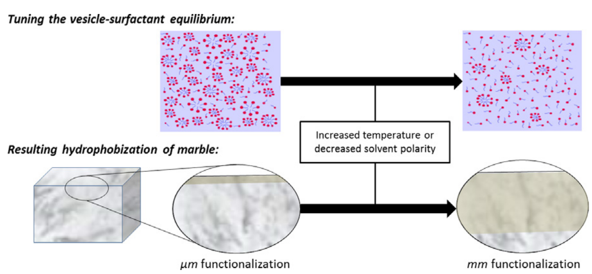
HIGHLIGHTS

- A fluorosurfactant is used to hydrophobize marble stones by total immersion.
- High temperature and addition of a co-solvent improves the protection efficiency.
- The effective functionalization depth increases from the μm to mm scale.
- Dynamic light scattering is used to study the vesicle-surfactant equilibrium.
- Vesicle size distributions and diffusion values correlate well with the efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

A functionalization method for hydrophobization of porous marble networks has been optimized by controlling the vesicle behavior of fluorosurfactants via tuning the solvent polarity and reaction temperature. Total immersion treatments have been used to diffuse and react the investigated fluorosurfactant (Capstone FS-63) deep inside the porous network, which was confirmed through combined mechanical grinding and capillary absorption measurements, showing an increase in effective functionalization depth from μm to mm scale. This was accomplished by exchanging water with less polar co-solvents such as ethylene glycol or ethanol in the fluorosurfactant solution combined with elevated reaction temperatures, driving the vesicle-surfactant equilibrium towards free surfactants, which have been investigated by dynamic light scattering measurements. Quantitative particle size distributions and diffusion values for the different mixtures as a function of temperature can be correlated to the increased functionalization efficiency.

1. Introduction

Weathering is a large problem for natural stones, since structural and morphological alterations occurring via physical,

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chemical and biological processes result in stone deterioration and erosion of the surface [1–4]. In particular calcareous stones are sensitive to several erosive effects related to water, e.g. water vapor condensation, freezing, thawing and (acid) rain dissolution [5]. The elimination of water has thus been a key aspect when protective coatings for marble have been developed [6–10]. Studied approaches include polymers [8,11–17], siloxanes [9,10,17–20] and sol–gel-derived hydrophobic coatings [20–23]. After some time in contact with water, most of these coatings display significant water uptake [24] that will eventually damage the calcareous stones by the weathering mechanisms described above. A more persistent modification is obtained if the hydrophobizing agent contains functional groups that can bind strongly to calcareous stone surfaces, like phosphate or phosphonate groups [25–28]. Furthermore, if the hydrophobizing agent can diffuse into the stone and functionalize the pore channels, a long-term stability can be attained. To improve the stability of natural stones we have earlier developed a surfactant-based coating for marble [29] which displayed essentially no water absorption after removing the outer surface functionalization with strong UV light. Thus, the fluorosurfactant in the optimized protocol in [29] penetrated at least a few microns into the pores of the studied marble, providing a near perfect protective coating without impeding the water vapor regime of the stones. By elucidating the effects of chemical bonding, functionality, concentration and time had on the hydrophobization efficiency, some understanding on the process was gained. The utilized fluorosurfactant (Capstone FS-63 from DuPont) is readily soluble in water, because it is known to spontaneously form supramolecular aggregates (vesicles) in aqueous solutions [29]. These sub-micrometer structures will possibly restrict the diffusion and reaction of the surfactant inside the porous stone. However, by adding a co-solvent or an electrolyte to a surfactant-water system, the vesicle-surfactant equilibrium can be shifted towards free surfactants or other constitutions more suitable to pore penetrations [30–35]. Furthermore, an increase in the solution temperature will change the polarity of the solvent and can thus also affect the vesicle stability [33,36,37]. In the present study, the effects of temperature and solvent composition were investigated with the goal of improving the diffusion into the porous matrix of the stone, studying the protection efficiency down to 2 mm below the surface. We demonstrate that the performance of the different treatment conditions can be linked to the micellar behavior of the fluorosurfactant.

2. Materials and methods

2.1. Materials and materials characterization

Marble samples from Carrara, Italy, with the dimensions $2 \times 2 \times 1\,cm^3$ were used throughout this study. Italian Carrara marble was chosen since it is known to be a chemically pure marble, consisting almost entirely of calcite, $CaCO_3$, with some minor traces of dolomite, $CaMg(CO_3)_2$, which was confirmed by XRD [29]. Mercury intrusion porosimetry has previously been used to study the porosity of the Carrara marble. It was found that the marble contained a large fraction of pores in the 0.02–0.3 μm range, as well as a presence of pores in the 0.10–100 μm range that could be due to micro-cracking during sample processing. An open porosity of 0.65% was also recorded [29]. The hydrophobization agent Capstone FS-63 (DuPont), containing a fluorosurfactant with phosphate binding groups, was used in the optimizations since it had proven to be a suitable functionalization agent for marble in our previous study [29].

2.2. Dilution of the Capstone FS-63 compound

Co-solvents from the lower part of the log P_{OW} scale were expected to affect the vesicular constitution of the investigated fluorosurfactant without compromising the solubility. First, ethylene glycol (EG) was selected for investigating the co-solvent to water ratio, due to its excellent mixability with the investigated fluorosurfactant. 10 vol-% Capstone FS-63 solutions were produced by dilution in different solvent ratios of ethylene glycol and water (0:100, 25:75, 50:50, 75:25 and 100:0) and these samples are denoted 0% EG, 25% EG, 50% EG, 75% EG, and 100% EG, respectively. Note that all solutions still contain 10 vol-% Capstone FS-63 and the naming only reflect their co-solvent properties. After the initial optimization, other co-solvents with low log P_{OW} values (including propylene glycol, methanol, and ethanol) were also tested under similar conditions. The solutions were analyzed visually as well as with dynamic light scattering (DLS, Malvern Zetasizer Nano ZS) to evaluate the effects the co-solvents had on micellar constitution and stability.

2.3. Characterization of co-solvent effects

The used co-solvent mixtures were characterized using a variety of methods in conjunction with heating apparatus. A KSV Sigma 70 surface tensiometer equipped with a Du Nouy ring was used to determine the surface tension as a function of temperature for the solutions. A Bohlin CS rheometer was used to measure the changes in viscosity as a function of temperature for the analyzed solutions. DLS analysis was conducted on the effect heating had on the micellar aggregates by multiplying the size distribution with the derived count rate, a parameter linked to the concentration of micellar aggregates [38–42], allowing for semi-quantitative analysis of the changes in both concentration and size distribution.

2.4. Hydrophobization of the marble samples

Three marble pieces per treatment were put into beakers containing 40 ml of the selected hydrophobization liquids. Reaction vessels were sealed and put into a temperature-controlled room (20 °C) or into ovens at T = 40, 60 and 80 °C for 24 h. The samples were subsequently washed with water and dried at 60 °C in an oven for another 24 h, after which the samples were kept at room temperature for 24 h before any measurements were performed.

2.5. Intentional removal of outermost functionalization by UV degradation and mechanical grinding

A VZero 085 UV-light from Integration Technology Ltd., with an arc length of 85 mm and a power output of 200 W/cm was used to irradiate the samples for 30 min to intentionally remove the outer surface hydrophobization layer of the samples treated under different conditions, which was subsequently confirmed by contact angle measurements. The 30 min UV irradiation time have previously been found to efficiently degrade coatings that do not penetrate into the porous network [29]. These samples were tested using capillary absorption to evaluate the success of the pore hydrophobization. Furthermore, a belt and disk sander was used to remove 0.5, 1.0 and 2.0 mm of the outermost marble surface, permitting a new surface to be investigated by the capillary absorption method, allowing for a more factual evaluation of the functionalization performance at depth compared to for instance cross-sectional scanning electron microscopy (SEM) [17].