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Multifunctional composite coatings consisting of polymers and zinc oxide nanoparticles for the protection of stone heritage

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I. Extended Abstract

Protection of heritage buildings against the effects of rain and atmospheric humidity is extremely important, as water is a major source of natural stone degradation induced by the freezing-thawing cycles and salt deposition. Biomimetic superhydrophobic coatings can offer enhanced protection to stone, as they have the ability to repel water drops through the famous lotus effect [1]. The first superhydrophobic material designed specifically for the protection of stone heritage was produced by our group about two decades ago [2]. The idea was to tune the wetting properties of products, which were already used in conservation practice (e.g. silane/siloxanes [3]), by adding small amounts of engineered nanoparticles (NPs). The latter affect the morphology of the composite material, which is deposited onto stone, creating a lotus-like, two-length scale hierarchical surface structure. In the last two decades the method has been adopted by numerous scientists using different conservation materials and NPs (usually silicon oxide, SiO_2 NPs) for the protection of limestone, marble and other stones used in heritage buildings, as described in review articles e.g. [4-6]. The suggested composite materials consist mainly of products which are already tested and recommended for stone conservation and a small fraction of NPs. Selecting certified products, used in conservation practice, reduces the danger to induce any undesirable, hazardous side-effect which can be developed through time.

In the present study we produce two composite materials which are applied on marble. The study has two novelties. First, zinc oxide (ZnO) NPs are added to the polymer matrices, instead of the extensively studied SiO_2 NPs, to induce surface roughness which is necessary to achieve superhydrophobicity [7]. The goal is to produce a multi-functional material that can serve simultaneously three purposes: (i) water repulsion, (ii) chemical self-cleaning through photo-degradation and (iii) biocidal activity. It well known that ZnO has photocatalytic [8] and biocidal [9] properties. However, to the best of our knowledge the combined demonstration of the three aforementioned properties by a single composite material, designed for stone protection, has not been achieved yet. Second, to induce enhanced oleophobicity, combined with superhydrophobicity. Oleophobisation of natural stone surfaces is highly desirable to protect heritage buildings which are located in urban areas and are therefore threatened by oil-based urban pollutants [10].

ZnO NPs were added in an aqueous, non-toxic and eco-friendly, silane sol (Dynasylan SIVO 121), in various concentrations and sprayed onto marble specimens. The produced composites are named hereafter as DZn. To enhance the oleophobic character of the resulting composite coating, the above recipe was modified as follows. ZnO NPs were added in an aqueous, mixture consisting of Dynasylan and a water-based fluoropolymer (C6 fluorocarbon polymer, cationic). Dispersions of various NP concentrations were prepared and sprayed onto marble resulting in composites which are named hereafter as DFZn. Prior to deposition, the dispersions were stirred vigorously for 30 min. Spray deposition was carried out using an airbrush system (Paasche Airbrush) with a nozzle diameter of 733 μm. The spray method was employed for the deposition of sols, as it offers flexibility and can be easily used to treat large surfaces. The treated marble specimens were annealed at 60° for 1h to remove residual solvent and accelerate curing. Contact angles of water (WCA) and oil (OCA) drops (8 μL) were measured using the ImageJ software. At least three drops were placed on different areas of coated marble specimens and average values were calculated.

The results are shown in Figure 1. WCAs on coatings which were prepared without NPs (i.e. zero NP concentration in Figure 1) were 115.6±1.7° and 129.5±1.0° for the DZn and DFZn coatings, respectively. A rapid increase of WCAs is shown in Figure 1 when a small amount (1% w/v) of ZnO NPs was added in the coatings, exceeding the threshold of superhydrophobicity (>150°). Further increase of NP concentration in the DFZn coating does not have any effect on WCA

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which is practically constant and large (>150°). However, WCA on the DZn coating decreased when the NP concentration increased from 2 to 3% w/v.

A similar trend is reported for the OCA results of Figure 1. OCA on the DFZn coatings initially increases with NP concentration and becomes large (roughly 140°) and practically stable for coatings which were prepared using elevated NP concentration (>1% w/v). OCA on the DZn coatings initially increases and then drops when the NP concentration increased from 2 to 3% w/v. The results of Figure 1 are in agreement with previously published data which investigated the effect of the concentration of SiO_2 NPs in composite coatings. The increase of WCA and OCA with NP concentration was attributed to the formation of a two-length scale hierarchical structure [1,6] whereas the drop of OCA at elevated NP concentration was attributed to the formation of anomalies (grooves) which are formed [10].

The ongoing research intends to study the surface morphologies of the coatings using Scanning Electron Microscopy (SEM) and, moreover, to subject the coated stone specimens to other important tests, including water absorption by capillarity, vapour permeability and colourimetry. Finally, the chemical self-cleaning through photo-degradation and the biocidal activity of the composite coatings will be accessed.

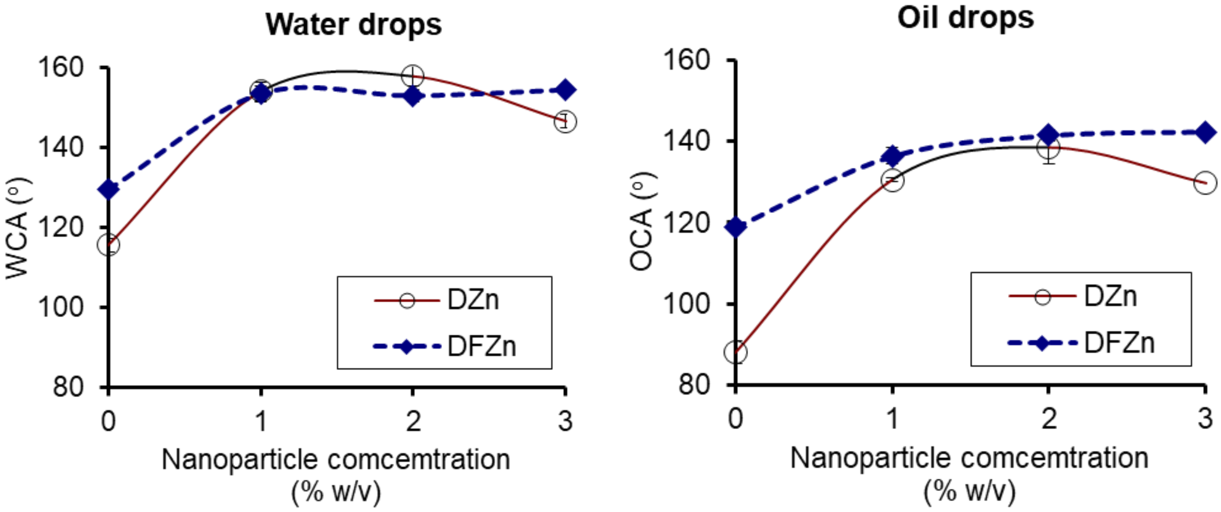

Figure 1. Contact angles of water (WCA) and oil drops on coated marble are shown in the left and right plots, respectively.

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