Polymer-Silica nanoparticles composite films as protective coatings for stone-based monuments

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Abstract. The decrease of surface energy of mineral substrates similar to those used in many stone monuments of cultural heritage by the application of protective polymer coatings along with the simultaneous increase of their surface roughness can increase their ability to repel water substantially. In this work, the effect of artificially induced roughness on the water repellency of mineral substrates coated with protective polymer films was investigated. Natural marble samples or home made calcium carbonate blocks were tried as the mineral substrates. The roughness increase was achieved by mineral chemical etching or by creation of nanoscale binary composition film on the substrate surface. PMMA and PFPE were the polymers used, while different-sized silica nanoparticles were employed for the production of the nanocomposite films. Examination of the coated and uncoated surfaces with profilometry and AFM and measurements of water contact angles reveal a pronounced effect of the surface roughness on water repellency. Especially in the case of nanocomposite coatings, the surfaces become super-hydrophobic. This result indicates that the nanoscale binary composition film scheme, which is characterized by its simplicity and low cost, is a suitable candidate for the water protection of stone-based monuments on large scale.

1. Introduction

Degradation and deterioration of stone-based monuments is caused by many factors among which water action is of predominant importance. Rain water can cause stone degradation by multiple actions comprising stone disintegration by freeze-thaw cycling inside the stone pores or mineral dissolution, especially by environmentally acidified water. It can also be a carrier of pollutants which have their own contribution to the whole phenomenon [1-2]. The protection of stone-based monuments from natural weathering and/or environmentally-induced accelerated disintegration can be achieved by the application of water-repellent polymer films on the stone surface. Water repellent polymer films have been used extensively during the past decades for the protection of stone monuments, but their protective efficiency strongly depends on the characteristics of the substrate such as roughness and

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porosity [3]. Consequently, developing strategies to enhance the hydrophobicity of these films is important for the effective protection and conservation of monuments of the cultural heritage.

As previous studies have pointed out [4-5], hydrophobicity is governed by two parameters: i) the interfacial tension between the solid and the liquid and ii) the geometrical characteristics of the surface. A liquid either follows the surface (Wenzel scenario) or it leaves air inside the texture (Cassie – Baxter) [6]. In the first case, surface roughness \( r \) (the ratio between the true surface area over the apparent one) is the key factor that controls \( \theta \ast \) contact angle:

\[
\cos \theta^* = r \cos \theta
\]

\( \theta \): Young’s contact angle

In the Cassie – Baxter scenario, a liquid is sitting upon a patchwork of air and solid surface. In this case, the contact angle \( \theta^* \) is an average between the angle on the solid (\( \cos \theta \)) and the one on the air (\( \cos 180^\circ = -1 \)):

\[
\cos \theta^* = -1 + \phi_s (\cos \theta + 1)
\]

\( \phi_s \): fraction of the liquid that contacts the solid

In this study, we investigated the effect of artificially induced roughness on the water repellency of mineral substrates treated with protective polymer coatings. Natural marble samples or home made calcium carbonate blocks were tried as mineral substrates. The roughness increase was achieved by mineral chemical etching or by creation of nanoscale binary composition film on the substrate surface.

2. Experimental part

Initially, blocks of marble of Drama were treated with hydrochloric acid (12.3\% w/v) for various times ranging between 0 – 240 s. Rinsing with water and drying followed and then the marble specimens were immersed in Akeogard P (Syremont, Italy) – a 10\%(v/v) functionalized perfluorinated polyether (PFPE) in 33\%(v/v) isopropanol and 57\%(v/v) water for 1h. A low vacuum (0.5 bar) was subsequently applied to the stone blocks at 35°C for 18 hours. After the evaporation of the solvents, contact angle measurements of the coated marble substrates with deionized water were carried out using a “Kruss” contact angle measuring instrument. Five droplets of water were delivered to different points of each specimen and from a height sufficiently close to the substrate, so that the needle remained in contact with the water droplet. Then, the delivery needle was withdrawn with minimal perturbation to the drop [7]. The volume of each droplet was 8-10 \( \mu l \). Prior to the contact angle measurements, surface roughness measurements of the coated marble specimens before and after their treatment with the acid were conducted using a profilometer (XP-2, Ambios Technology).

As a second approach for the increase of the hydrophobicity of the polymer coating used, hydrophilic silica nanoparticles (Silica, fumed powder, Aldrich) with 7nm and 14nm mean diameters were used. They were mixed with two different protective polymer materials: acrylic and Akeogard P. The acrylic coating (Poly(methyl methacrylate), (PMMA), average M.W. 120000, Aldrich) was applied using toluene as solvent. Different percentages of SiO\(_2\) nanoparticles (0-2\% w/v) were used for mixing with the above polymeric materials. The mixture was stirred vigorously in order a homogeneous dispersion to be prepared. Tablets of calcium carbonate (Purum p.a., precipitated, \( \geq 99.0\% \) (KT) Fluka) were prepared using a pressure of 300 bar. These tablets were used as model, marble-like material. The as-prepared silica/polymer dispersions were sprayed with the aid of a specific nozzle onto the calcium carbonate substrates. Evaporation of the solvent and the measurements of the water contact angles were conducted as described before. Finally, the morphology and the roughness of the surfaces created on the calcium carbonate substrates were evaluated by Scanning Probe Microscopy (SPM) using a CP-II microscope (Veeco Inc.).

3. Results and discussion
3.1. Acidic treatment of the Drama marble blocks

The treatment of the Drama marble blocks with hydrochloric acid resulted in a substantial increase of their measured surface roughness. In addition, the measured contact angles between the polymer-covered roughened marbles and water were increased by about 25% as compared with values of contact angles obtained with the acid-untreated but coated Drama marbles. Figure 1 presents the measured values of surface roughness and contact angle for the acid-untreated but polymer-coated marble blocks and those for the acid-treated and coated marbles.

![Figure 1. Water contact angle vs acid-caused surface roughness (open symbol: acid-untreated & polymer-coated marble blocks; solid symbols: acid-treated & polymer-coated marble blocks)]](image1)

3.2. Polymer-Silica nanoparticles composite films on calcium carbonate surfaces

Contact angle measurements showed a significant enhancement in hydrophobicity for both kind of composite coatings (figures 2 & 3). In particular in the case of PMMA, the contact angle with water increased from 108° to 157±5° and for PFPE from 112° to 162±2° (highest values measured, figure 4).

![Figure 2. Water droplets on CaCO₃ substrate covered by PMMA with 1% (w/v) SiO₂ (7nm)](image2)

![Figure 3. Water droplet on CaCO₃ substrate covered by PFPE with 1% (w/v) SiO₂ (7nm)](image3)

Silica nanoparticles concentration was varied. As it is shown in figure 4, there was a significant enhancement in water contact angle for nanoparticles concentration of 0.5% (w/v). Further addition of nanoparticles did not have a great impact on water repellency. It is clear from figure 4 that a concentration of 1% (w/v) of silica nanoparticles is adequate to maximize the hydrophobicity of the investigated polymer coatings.

For the PMMA coating, the average size of nanoparticles did not affect the enhancement of hydrophobicity, as shown in figure 4. In the case of PFPE, the water contact angle over the polymer–silica composite films containing the 14nm mean size nanoparticles did not increase as much as for the polymeric films with the 7nm sized particles.
Figure 4. Measured water contact angles vs silica nanoparticles concentrations in the composite coating.

Examination of the polymer-silica nanoparticles-coated calcium carbonate surfaces with AFM in intermittent-contact mode ("Tapping Mode") revealed that the nanoparticles significantly changed the morphology of the calcium carbonate surfaces (figure 5). An increase in roughness \( r \) of about 60% for nanoparticles concentration of 1% (w/v) was found, when the measured roughness over the coated substrates was compared to that measured over the uncoated ones. It was also observed that nanoparticles mean size did not have a significant impact on the roughness of the surfaces formed, when PMMA was the polymer used.

Figure 5. 3D AFM topography images of (a) uncoated CaCO\(_3\) substrate, (b) coated with PMMA and 1%(w/v) SiO\(_2\) (14nm). Peak to valley height on the coated with PFPE and 0.5% (w/v) SiO\(_2\) (7nm) surface (c).

The polymers acted as binding media between the nanoparticles and the substrate. High values of contact angles indicate that the nanoparticles were covered by the polymeric coatings rather fully. Whether the nanoparticles are fully or partly covered is a crucial issue, since the silica nanoparticles are hydrophilic. Uncovered areas could cause a decrease in water repellency. To test this hypothesis, AFM phase images were used to examine the areas covered by the hybrid coatings (figure 6).

In the case of PMMA, the AFM phase images demonstrated that the nanoparticles of either mean size i.e. 7nm or 14nm were fully covered by the polymer. For the PFPE hybrid coating, the 14nm
nanoparticles seemed to be partly covered, as the phase images showed an obvious discrimination between the two different phases i.e. PFPE-covered and uncovered particles (figure 6b). In the case of the hybrid PFPE coatings with the 7nm sized silica nanoparticles, the 7nm particles were fully covered by the polymer (figure 6c). These results are in accordance with the observed difference of about 10° to 20° in the values of the measured contact angles for the PFPE hybrid coating at the same nanoparticle concentration, but with different nanoparticle size.

![AFM phase images](image)

**Figure 6.** AFM phase images of (a) PMMA and 0.5% (w/v) SiO₂ (14nm), (b) PFPE and 1% (w/v) SiO₂ (14nm) and (c) PFPE and 1% (w/v) SiO₂ (7nm)

4. Conclusions
Decreasing the surface energy of mineral substrates by the application of protective polymer coatings and simultaneously increasing their surface roughness can increase their ability to repel water substantially. Increase of surface roughness can be achieved by either chemical etching or the insertion of silica nanoparticles in the polymer coating. The increase of roughness by the creation of nanoscale binary composition film composed of SiO₂ nanoparticles and appropriate polymer allowed a substantial increase in water contact angle (from 108° to 157±3° in the case of PMMA-SiO₂ and from 112° to 162±2° in the case of PFPE-SiO₂) and correspondingly made the surface super-hydrophobic. The acquired super-hydrophobic properties can assure maximum protection against water of stone-based monuments.

The simplicity of composition creation by the spraying of the silica/polymer emulsion on the stone surface, the price and the availability of the materials used make the developed approach a very suitable candidate for the protection of stone monuments on a large scale.

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References
[1] Poli T, Toniolo L and Chiantore O 2004 *Appl. Phys. A* **79** 347.
[2] Della Volpe C, Penati A, Peruzzi R, Siboni S, Toniolo L and Colombo C 2000 *J. Adh. Sc. Technol.* **14** 2 273
[3] Tsakalof A, Manoudis P, Karapanagiotis I, Chryssoulakis I and Panayiotou C 2006 *J. Cult. Her.* In press
[4] Feng L, Li S, Li Y, Li H, Zhang L, Zhai L, Song Y, Liu B, Jiang L and Zhu D 2002 *Adv. Mater.* **14** 24 1857
[5] Hsieh C, Chen J M, Kuo R R, Lin T S and Wu C F 2005 *App. Surf. Sc.* **240** 318
[6] Quere D 2002 *Phys. A* **313** 32
[7] Murray M D and Darvell B W 1990 *J. Phys. D: Appl. Phys.* **23** 1150