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SUPER-HYDROPHOBIC POLYMER/NANOPARTICLE COMPOSITES FOR THE PROTECTION OF MARBLE MONUMENTS

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ABSTRACT

Water contributes substantially to the degradation of monuments through freezing and thawing cycles and also because it is a carrier of pollutants and salt solutions. Water repellency can be promoted by the application of a thin organic, hydrophobic, film. The efficacy of simple polymer coatings for monument protection is, however, still debated. We demonstrate that a polymer/nanoparticle composite film, composed of a siloxane resin and silica nanoparticles has superior properties. The film was applied on specimens of the Greek marble "Penteliko", which is used for the restoration of the Akropolis of Athens. The equilibrium contact angle and the contact angle hysteresis were found to be 162^o and 6^o respectively, indicating that nanoparticles enhance the hydrophobic nature of the film. We note that the corresponding angles were 108^o and 20^o when pure siloxane resin was applied (no particles). Instead of the traditional film application by brush (or capillary absorption), a simple spraying technique was employed. Water vapour permeability, water capillary absorption and colourimetry measurements of the treated marble specimens were also carried out, to reveal the effect of the nanoparticles on these important parameters. The study was then extended to two more types of Greek marbles, with similar results. SEM and AFM were employed to reveal the micro- and nano-structure of the composite film as a function of the particle concentration. Enhanced hydrophobicity was explained by the Cassie-Baxter model.

INTRODUCTION

Water contributes substantially to the degradation of monuments through freezing and thawing cycles and also because it is a carrier of pollutants and salt solutions. Water repellency can be promoted by the application of a thin organic, hydrophobic, film. The use of simple polymer coatings for monument protection is, however, still debated because of undesirable side effects developed upon ageing. Nevertheless, research on the protection efficacy of such coatings is still carried out, in the light of recent achievements which provide some very promising results.

Several investigations have recently suggested strategies which can impart superhydrophobicity to thin polymer films [1-9]. Many of these strategies however, have some important disadvantages which make them inappropriate for the treatment of large surfaces such as buildings and monuments. For example the use of sophisticated instruments raises the cost of the application method, which therefore cannot be utilized for the treatment of large surfaces. In a previous work, we reported that a simple spraying technique, shown in figure 1, can be used to apply polymer-particle dispersions on large calcium carbonate surfaces [10]. In this study, silica nanoparticles were dispersed in solutions of a functionalized perfluorinated polyether and poly(methyl methacrylate). Dispersions were sprayed on calcium carbonate blocks with the aid of a specific nozzle (figure 1). The resulting films appeared to have an enhanced hydrophobic character [10]. In the present work we apply this strategy using a commercial siloxane resin and silica nanoparticles for the preparation of the dispersions, which are subsequently sprayed on three Greek marbles: Pentelic, Naxos marbles and Thassos. The wettability of these surfaces is discussed in the light of the Cassie-Baxter model. The applicability of the latter is investigated in detail using (instead of marble) glass surfaces as substrates. Water vapour permeability, water capillary absorption and colorimetry measurements of the treated marble specimens are also carried out, to reveal the effect of the nanoparticles on these important parameters, which determine the protective efficacy of a coating for the conservation of monuments of the cultural heritage. An ideal coating must repel rainwater (illustrated in figure 2), must exhibit good permeability for water vapour and must have good optical properties so that it does not alter the aesthetic appearance of the monument.

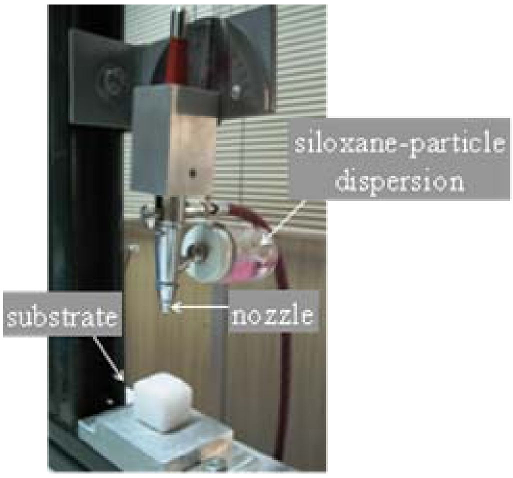


Figure 1. Spraying technique

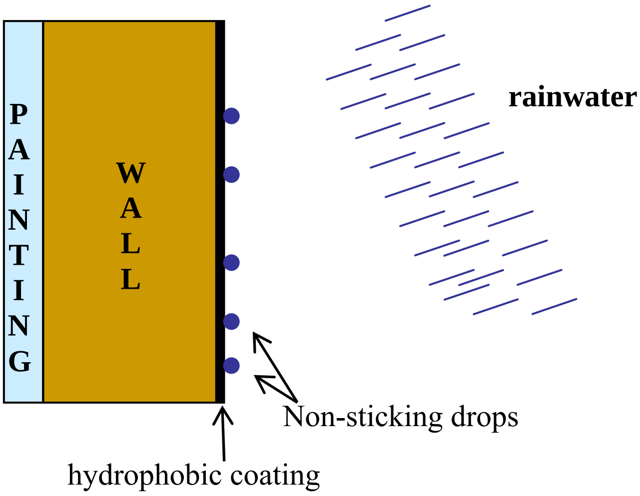


Figure 2. A protective coating applied on the outer surface of a monument must repel rainwater

EXPERIMENTAL

Squared blocks (2.5 x 2.5 x 1.0 cm) of three marbles purchased from local suppliers were used: Pentelic and Naxos marbles (98% calcite, 2% quartz) and marble of Thassos (86% dolomite, 12% calcite and 2% quartz). Silica nanoparticles (Silica, fumed powder, Aldrich) with 7nm mean diameters were mixed with a commercial poly(alkyl siloxane) solution (Rhodorsil Hydrof, Rhodia Silicones). Dispersions of 1 and 2% w/v particle concentrations were prepared, stirred vigorously and sprayed onto the marble substrates. Samples were subsequently annealed in vacuum overnight to remove residual solvent. Another set of siloxane solutions were sprayed onto the marbles as they were received (without particles) by the supplier and annealed to remove residual solvent.

Water contact angle measurements were conducted using distilled water and a Krüss DSA 100 contact angle measuring instrument. Equilibrium contact angles were measured as follows: droplets were delivered to the specimen and from a height sufficiently close to the substrate, so that the needle remained in contact with the liquid droplet. Then, the delivery needle was withdrawn with minimal perturbation to the drop and the image of the drop was captured immediately for contact angle measurement. The contact angle hysteresis was calculated by the dynamic sessile drop method. The advancing/receding contact angle was the maximum/minimum angle measured while the volume of the droplet was increased/decreased without increasing/decreasing the solid-liquid interfacial area.

Water vapour permeability was evaluated by measuring the mass of water vapour passing though the unit surface in 24 h, at 40 ^{o}C, under controlled conditions [11]. Capillary water absorption measurements were performed by the gravimetric sorption technique [11]: the weighted stone block was placed for 1h on a filter paper pad (1cm of Whatman paper, No 4) partially immersed in distilled water and, then, weighted again to calculate the amount of water absorbed by capillary forces. Colour alteration measurements were taken on homogeneous spot areas of 4 mm in diameter, using a portable reflectance spectrophotometer MiniScan® XE Plus (HunterLab Associates Inc.) and evaluated by the use of L*a*b* coordinates of the CIE 1976 scale [12].

The morphology of the films applied on the marble specimens was recorded by Scanning Electron Microscopy (SEM, JSM 840A) mounted with NIH software (National Institutes of Health).

Another set of Rhodorsil-silica dispersions with particle concentrations 0.1, 0.3, 0.5, 1.0, 1.5 and 2.0 % w/v were sprayed on glass surfaces. The latter were cleaned with water and toluene and dried prior to any use. Samples were annealed overnight and contact angles were measured and compared with the Cassie-Baxter (apparent) contact angle which were calculated from the SEM images (NIH software).

RESULTS AND DISCUSSION

Contact Angle Measurements

Figure 3 shows equilibrium water contact angle measurements (θ_e) for composite films prepared from dispersions with 1 and 2% w/v particle concentration. Dispersions were applied on three marble substrates. For comparison θ_e measurements performed on pure (no particles) siloxane films are also included. The results show that nanoparticles enhance the hydrophobic character of the siloxane resin, as the equilibrium contact angle (θ_e) increases from around 110^0 (no particles) to more than 160^0 (1 or 2% w/v particles). Two important conclusions can be drawn from figure 3: (i) θ_e increases rapidly when the particle concentration increases from 0 (no particles) to 1% w/v. Further addition of nanoparticles (from 1 to 2% w/v) does not have any important effect on θ_e. (ii) Contact angles appear to be independent of the type of the substrate. Comparable θ_e were measured for the three types of marbles when these were covered by the same coating i.e. marble substrates were treated with the same polymer-particle dispersion.

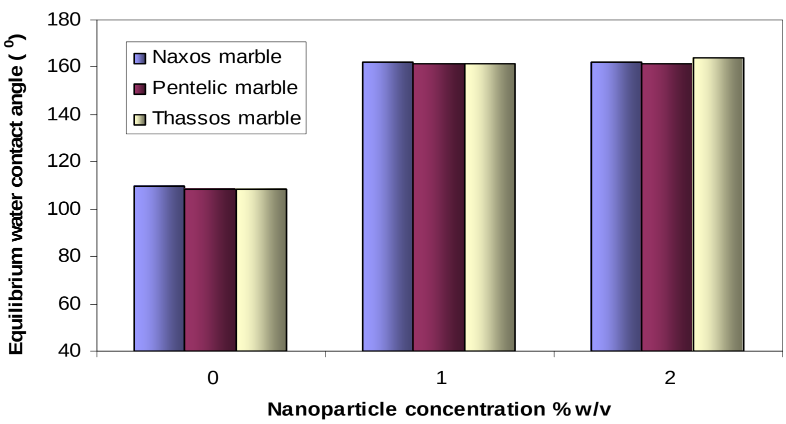


Figure 3: Equilibrium water contact angle (θ_e) as a function of particle concentration

The enhanced θ_e values ($>160^0$) measured for the treated surfaces provide evidence that composite films are superhydrophobic and that they exhibit augmented water repellency. The latter, however, is controlled not only by the equilibrium-static contact angle but also by the contact angle hysteresis which is defined as the difference of the advancing (θ_a) and the receding (θ_r) contact angle. A water repellent surface must exhibit high θ_e and also low hysteresis (θ_a -θ_r). The latter was measured for composite films (2% w/v particles) applied on

Pentelic marble and found to be on the order of 6^0 which is substantially lower that the 20^0 value measured for pure siloxane (no particles) applied on the same type of marble. Cosnequently, the addition of the nanoparticles decreases substantially the contact angle hysteresis and imparts water repellent propertied to the siloxane films. This is confirmed in Figure 4 which shows that a drop bounces off when it impacts a marble surface covered by a siloxane-particle composite film. When a water drop can bounce, the dryness of the substrate is preserved and deserves to be considered as water-repellent [13].

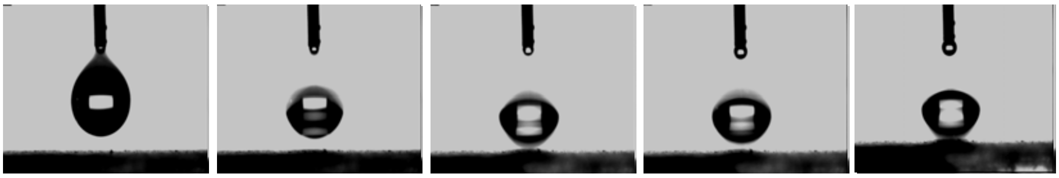
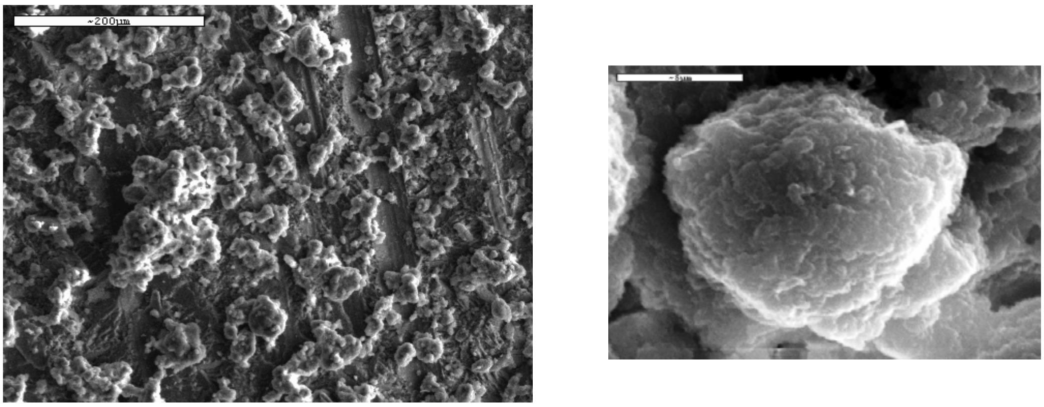


Figure 4: Water droplet bouncing on marble which was treated with siloxane and SiO_2 nanoparticles

It is known that superhydrophobic (water-repellent) surfaces exhibit a two-length-scaled hierarchical structure, which resembles the lotus leaf. SEM images revealed that nanoparticles lead to the formation of rough microstructures (figure 5a). On the contrary pure siloxane films applied on marble surfaces appeared to be smooth (not shown). The nanoparticles are not homogeneously dispersed; instead they form aggregates, as shown in figure 5a. These aggregates induce a micro-roughness at the surface of the film. Figure 5b reveals the topography of a single aggregate. It is shown that a nanostructure exists which implies an augmented roughness at the nanoscale. Consequently, figure 5 suggests that the randomly distributed protruded aggregates (fig. 5a) consist of further nanostructures (fig. 5b), implying that a two-length-scaled hierarchical structure is formed in the surface. It is known that such structure exists in the lotus leaf which exhibits water-repellent properties.



(a) (b)

Figure 5. SEM images of Pentelic marble treated with siloxane and 2% w/v nanoparticles.
(a) Aggregates are formed on the surface of the treated marble inducing a microroughness.
(b) Image of a single aggregate (roughness at the nanoscale)

Contact angles of superhydrophobic surfaces can be rationalized by the Cassie-Baxter equation which considers the wettability of porous-rough surfaces and suggests that water cannot fully penetrate and wet the whole surface [14,15]. A detailed investigation on the applicability of the Cassie-Baxter equation on the composite films of our study was performed using glass substrates and it is discussed in detail in the next chapter. Preliminary measurements were performed on the treated Pentelic marble specimens and are discussed in the following. The Cassie-Baxter scenario is illustrated in figure 6 and assumes that air is trapped between a droplet and the rough substrate. The liquid sits upon a patchwork of air and solid surface. The apparent contact angle, θ*, is given by:

$$\cos\theta^* = -1 + \varphi_s(\cos\theta_Y+1) \quad (1)$$

where φ_s is the total area of solid-liquid interface in a plane geometrical area of unity parallel to the rough substrate and θ_Y is the Young contact angle which for the siloxane of our study was measured to be 102°. The calculation of φ_s, defined in equation 1, is necessary in order to compare the experimental points of Figure 3 with the Cassie-Baxter predictions. Values of φ_s were estimated only for treated Pentelic marble samples from SEM images using the NIH Image software. The solid-liquid interface was defined as the area of the SEM micrographs (sets of pixels), which corresponded to the clearly protruded surface sites (particle aggregates of figure 5a). The results were as follows: φ_s = 0.04 and φ_s = 0.05 for the films prepared with 1 and 2% w/v particle concentrations, respectively. According to equation 1 and considering that θ_Y =102°, the apparent contact angle, θ*, is calculated to be 166° and 164° for particle concentrations 1 and 2% w/v, respectively. We note that the experimental equilibrium contact angles (figure 3) for the treated Pentelic marble specimens were 162 ° for both 1 and 2% w/v particle concentrations. Consequently, a relatively good agreement is observed between the experimental results and the apparent contact angles measured by the Cassie-Baxter equation.

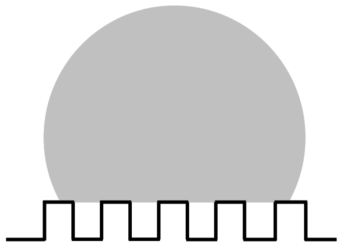


Figure 6. Illustration of the Cassie-Baxter scenario. Air is trapped below the droplet and the solid substrate. The droplet sits upon a patchwork of air and solid surface.

Detailed investigation on the Cassie-Baxter model

As it was mentioned above a detailed investigation of the applicability of the Cassie-Baxter equation on the siloxane-particle composite films was performed using glass substrates. We note that SEM images showed that the topographies of the films applied on glass are similar with the corresponding structures recorded when siloxane-particle dispersions were deposited on marble (figure 5).

In Figure 7 experimental θ_e values and theoretically measured θ* angles are plotted as a function of particle concentration. Apparent contact angle, θ*, were measured from SEM images according to our previous discussions. Figure 7 shows that the contact angles measured for surfaces which were treated with dispersions with high particle concentrations (2, 1.5, 1 and 0.5 % w/v) are in a relatively good agreement with the Cassie-Baxter predictions. On the contrary, the contact angles of films which correspond to dilute dispersions (particle concentration of 0.1 and 0.3 % w/v) deviate substantially from the values obtained from the Cassie-Baxter equation. This result is supported by the film morphologies which were recorded by SEM. Large smooth areas were visible in the films which were prepared from dilute dispersions (SEM images are not shown). For these surfaces the Cassie-Baxter scenario which suggests that the water drop sits on the spikes and does not fill the grooves (figure 6) is quite unlikely. When dispersions with elevated particle concentrations are spayed on the glass surfaces the produced films exhibit a dense rough surface (figure 3).

The separation distance between the protruded aggregates is small and therefore one can assume that air is trapped between the droplet and the substrate.

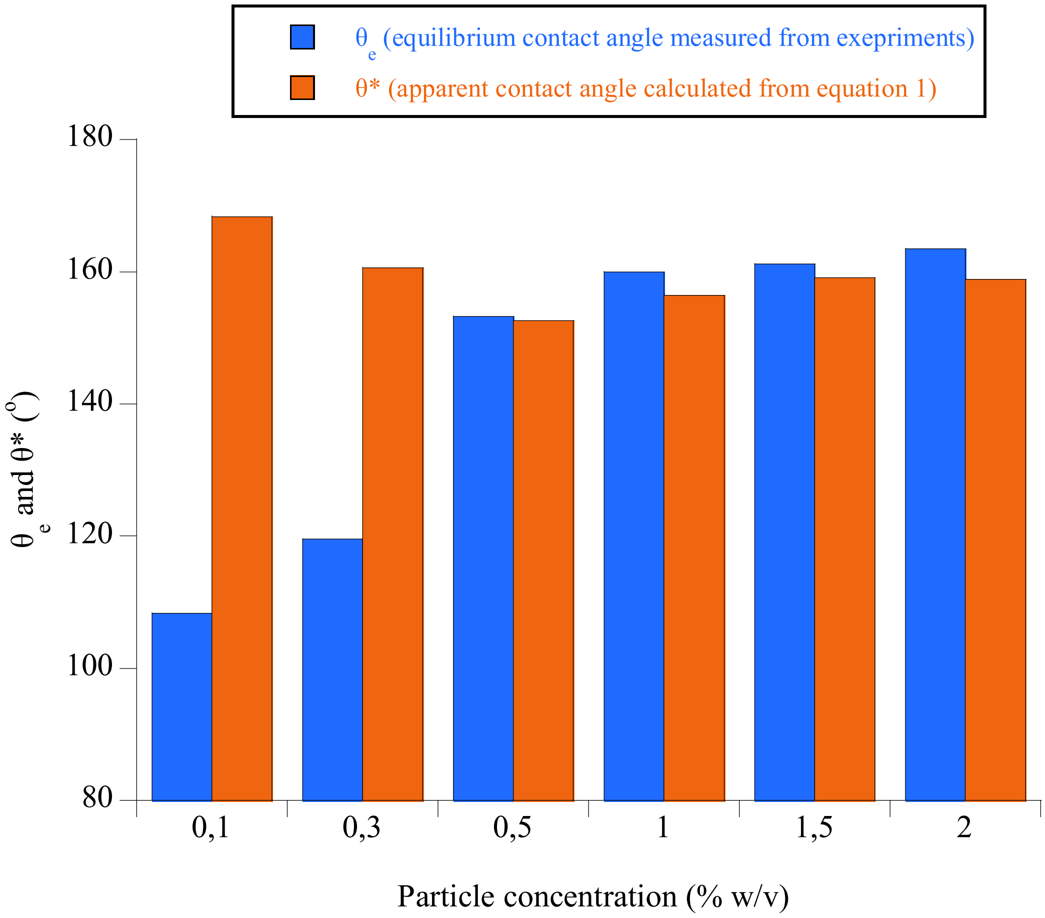
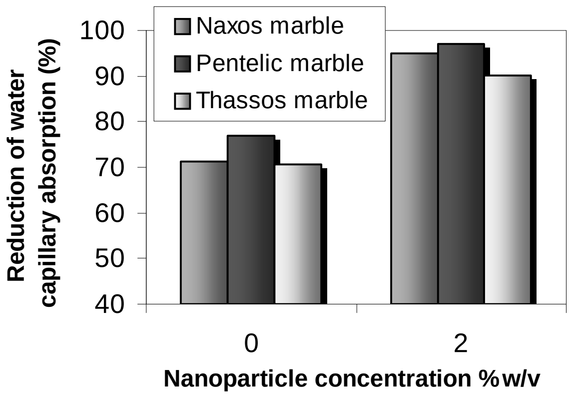


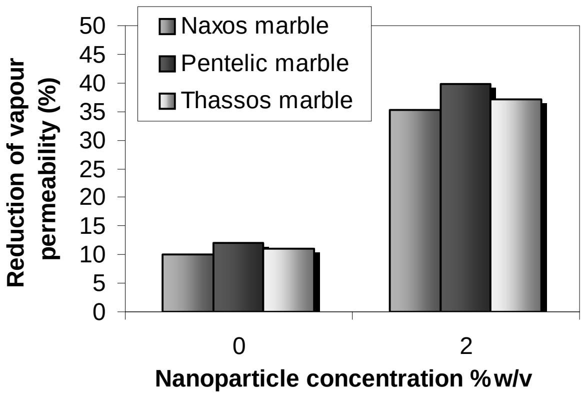
Figure 7. Equilibrium contact angle (θ_e) and apparent contact angle (θ^*) as a function of φ_s for silonaxe-SiO_2 on glass.

Other measurements

Figure 8 summarizes the results obtained from three experiments which were performed to reveal the effect of the nanoparticles on water absorption, water vapour permeability and aesthetic appearance of the marbles. The figure shows that the reduction of water capillary absorption for the marble specimens treated with pure siloxane (no particles) is on the order of 70%. When particles (2%w/v) are added to the polymer solutions the protective efficiency of the applied films against water absorption is improved, as the reduction of water capillary absorption increases to around 90%. The data reported for the vapour permeability follow (qualitatively) the trend of the contact angle measurements, reported in figure 3. Water repellency is enhanced by nanoparticles (figure 3) resulting thus in a substantial reduction of the water vapour permeability (figure 8).

Brightness values (L*) are reported for bare (untreated) stone samples and for samples which were treated with pure (no particles) siloxane and siloxane with 2% w/v silica nanoparticles. As it was expected pure polymer coatings (no particles) darkened the marble surfaces. The addition of the silica particles, however, resulted in a gradual increase of L*. This is explained by the augmented brightness of the silica particles which was found to be L*=88. We finally note that nanoparticles did no have any major effect on the a* and b* coordinates (results are not shown).





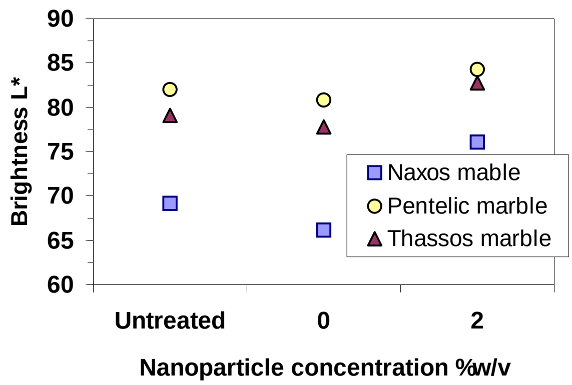


Figure 8. Reduction of water capillary absorption and water vapour permeability for three marbles treated with pure (no particles) siloxane and dispersions of siloxane and particles (2% w/v). Brightness (L) measurements correspond to untreated marbles and marbles treated with pure (no particles) siloxane and dispersions of siloxane and particles (2% w/v).*

CONCLUSIONS

Silica (SiO_2) nanoparticles were dispersed in solutions of a commercial poly(alkyl siloxane) and the suspensions were sprayed on three marble surfaces. The results can be summarized as follows: (i) Equilibrium contact angles (θ_e), measured on surfaces which were treated with siloxane-particle composites are higher than 160^o and appear to be independent of the type of the substrate. (ii) The contact angle hysteresis (θ_a -θ_r) was measured for treated Pentelic marbles and found to be 6^0 which is substantially lower that the 20^0 value measured for pure siloxane (no particles) applied on the same type of marble. (iii) SEM images showed that a two-length-scaled hierarchical structure is formed on the surface of the superhydrophobic films. (iv) The high contact angles measured for the composite films can be rationalized by the Cassie-Baxter model. This was proved through detailed measurements performed on treated glass substrates but it was also shown for marble substrates as well. (v) The use of nanoparticles results in a decrease of the water vapour permeability and the amount of absorbed water. (vi) Finally, it is demonstrated that nanoparticles increase brightness values, recorded for the treated the specimens.

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