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Superhydrophobic surfaces

Abstract: Superhydrophobicity – also known as water repellency – has recently attracted considerable attention because of its numerous potential applications. However, the fundamental concepts and equations describing the wettability of superhydrophobic surfaces have been known since the 1940s. These concepts are reviewed and discussed in the present feature article in light of the recent developments. Furthermore, the potential use of water-repellent siloxane-nanoparticle composites for surface protection and consolidation of stones and mortars used in outdoor objects of cultural heritage is investigated. Finally, it is shown that the wettability of the composite surfaces can be predicted by the Cassie-Baxter equation.

Keywords: composite; superhydrophobic; surface; water repellency.

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1 Introduction

The wettability of solid surfaces (i.e., the interaction between solids and fluids – usually water) is a property that is involved in numerous applications. In the following, we are concerned with superhydrophobic surfaces, which possess the ability to repel water droplets and remain completely dry after rainfall, i.e., the net interaction between a superhydrophobic surface and a water drop is repulsive. In the last decade, water-repellent surfaces have attracted considerable attention as evidenced by the several recently published review articles [1–8]. Some interesting aspects of superhydrophobicity are discussed in this feature article.

In particular, we begin (section 2) with a brief review of the fundamental concepts and equations related to the wettability of solid surfaces. In section 3, we define and discuss the origin of superhydrophobicity. In the fourth section of the article, we stress that superhydrophobicity, as it is now called, was well known in the 1940s,

particularly by the textile industry. Furthermore, we summarize some of the modern methods that have been recently suggested to produce water-repellent surfaces. In section 5, we describe the key results obtained using a very simple method that can be used to achieve superhydrophobicity: siloxane polymers blended with nanoparticles are sprayed onto various surfaces, which obtain water-repellent properties. We show that the wettability of the composite surfaces can be predicted by the Cassie-Baxter equation. Finally, in section 6, we evaluate the efficacy of the application of siloxane-nanoparticle superhydrophobic films as protective coatings on stones that have been used as building materials in monuments of cultural heritage. Furthermore, we show that our suggested method, which includes the addition of nanoparticles, improves the mechanical behavior of the treated stone substrates.

2 Wettability of solid surfaces

2.1 The Young equation

Consider a drop of water resting on a horizontal, passive, and atomically smooth surface (Figure 1). The drop replaces an area of the solid-air interface by an equal area of solid-liquid, and it is accompanied by the creation of a liquid-air interface. As each interface corresponds to a characteristic energy value, the presence of the drop results in a change of the total surface energy of the system.

Neglecting the effect of gravity, the exact shape of the liquid drop is specified by the Young equation [9]. The Young equation, free energies (energy/area) are manipulated as force concepts (force/length). These interfacial surface tensions are numerically equal to the characteristic interfacial-specific energy values and can be visualized as vector quantities, constant in magnitude and variable in direction. The Young equation thus becomes a force balance equation that includes the interfacial surface tensions and the static/equilibrium/Young contact angle (θ_Y), which is defined in Figure 1:

$$\gamma_{sv} = \gamma_{lv} \cos \theta_Y + \gamma_{sl} \quad (1)$$

where γ_{sv} , γ_{lv} , and γ_{sl} are the solid-vapor (sv), liquid-vapor (lv), and solid-liquid (sl) interfacial surface tensions, respectively.

Figure 1 Definition of the Young contact angle (θ_Y).

Therefore, the Young contact angle is influenced exclusively by the intermolecular interactions, and it is thus fixed by the chemical natures of the solid, liquid, and vapor. Inherent hydrophilic surfaces correspond to $\theta_Y < 90^\circ$, and inherent hydrophobic surfaces are defined by larger contact angles ($\theta_Y > 90^\circ$). It is important to note that the effect of surface roughness in the wettability of the solid surface is not taken into account by the Young equation. The role of surface roughness was introduced in a quantitative manner by Wenzel [10], as will be discussed next.

2.2 The Wenzel equation

Wenzel [10] recognized the significant role of surface roughness in wetting phenomena. He indicated that there is a distinction between the total or actual surface of an interface and what might be called its superficial or geometric surface; the latter is the surface as measured in the plane of the interface. Perfect smoothness is an assumption that can be acceptable for liquid-liquid or liquid-gas interfaces. However, at the surface of any real solid, the actual surface is greater than the geometric surface because of surface roughness. Wenzel defined a “roughness” factor as follows [10]:

$$r = \frac{\text{actual surface}}{\text{geometric surface}} \quad (2)$$

Apparently, the dimensionless roughness factor r is a number larger than unity and equals unity only for ideally flat surfaces.

The Wenzel scenario considers that within a measured unit area of the geometric surface, there is actually more surface induced by the roughness of the surface and suggests that water can fully penetrate and wet the whole surface (Figure 2A). Apparently, surface roughness does not have any effect on specific surface energy values, but it does necessarily involve a change in the wetting characteristics of the solid, which is quantified through the roughness factor. In particular, the apparent contact angle (Wenzel contact angle), θ^* , is related to the Young contact angle (θ_Y) as follows [10]:

Figure 2 (A) The Wenzel scenario where a water drop follows the roughness of the underlying substrate – homogeneous wetting regime. (B) Apparent contact angle, θ^* , as a function of the roughness factor r for an inherent hydrophilic (with $\theta_Y = 60^\circ$) and hydrophobic (with $\theta_Y = 120^\circ$) material, according to the Wenzel equation, Eq. (3).

$$\cos \theta^* = r \cos \theta_Y \quad (3)$$

Considering that for a rough surface r is greater than unity, the Wenzel scenario suggests that roughness enhances the hydrophilic or hydrophobic character of a surface, as shown, for instance, in Figure 2B; therefore, for hydrophilic ($\theta_Y < 90^\circ$) materials, $\theta^* < \theta_Y$, and for hydrophobic ($\theta_Y > 90^\circ$) materials, $\theta^* > \theta_Y$.

2.3 The Cassie-Baxter equation

Some years after the pioneering work of Wenzel on the wettability of rough surfaces, Cassie and Baxter [11] studied the wettability of porous surfaces. The term “porous surfaces” was intentionally used by the two researchers to clearly emphasize that, according to their concept, water cannot fully penetrate and wet the whole surface, as it was the case in Figure 2A (Wenzel scenario). Air is trapped between the drop and the surface pores of the substrate. Therefore, the drop only contacts the solid through the top of the asperities (Figure 3A) on a fraction that is usually denoted as f_s .

Consequently, according to the Cassie-Baxter scenario, the drop is placed on a composite surface of solid (component 1) and air (component 2). The apparent contact angle θ^* is an average between the angles of water on the two components of the composite surface, weighed by the fractions f_s and $1-f_s$, which yields [11]:

$$\cos \theta^* = f_s \cos \theta_Y + (1-f_s) \cos \theta_{\text{air}} \quad (4)$$

where θ_Y is the Young contact angle for water-solid and θ_{air} is the contact angle for water-air. Because $\theta_{\text{air}} = 180^\circ$, Eq. (4) is simplified to:

$$\cos \theta^* = -1 + f_s (\cos \theta_Y + 1) \quad (5)$$

Figure 3 (A) The Cassie-Baxter scenario where a water drop sits on a “composite” surface of air and solid – heterogeneous wetting regime. (B) Apparent contact angle, θ^* , as a function of the solid fraction f_s for an inherent hydrophilic (with $\theta_v = 60^\circ$) and hydrophobic (with $\theta_v = 120^\circ$) material, according to the Cassie-Baxter equation, Eq. (5).

For an atomically smooth surface (i.e., no porosity), $f_s = 1$, and therefore, $\theta^* = \theta_v$. In general, $f_s < 1$, thus suggesting that the water contact angle of any material, either hydrophilic or hydrophobic, increases with surface porosity, as shown for instance in Figure 3B, i.e., in any case, $\theta^* > \theta_v$.

Considering that, in practice, surface roughness and surface porosity are two terms that coincide, as they both describe the topography of the surface, it is important to note that the Wenzel and Cassie-Baxter equations provide opposite predictions regarding the behavior of inherent hydrophilic materials with respect to their surface topography. In the Wenzel model, roughness enhances the hydrophilic character of a surface, i.e., $\theta^* < \theta_v$. In the Cassie-Baxter model, the water contact angle of a hydrophilic material increases with roughness, i.e., $\theta^* > \theta_v$. Both models provide similar predictions regarding the behavior of inherent hydrophobic materials with respect to their surface topography. Both Eqs. (3) and (5) predict that, for $\theta_v > 90^\circ$, the apparent contact angle measured on a rough surface is $\theta^* > \theta_v$.

2.4 Advancing and receding contact angles

The aforementioned static contact angles, which describe the contact of a drop at equilibrium with a horizontal surface, do not adequately describe the wettability of a surface [12–18]. To demonstrate this, schematic representations of water drops resting on two different surfaces are provided in Figure 4 [17]. If we focus exclusively on the static situations (Figure 4), then we reach the conclusion that surface A is more hydrophobic than surface B because it corresponds to a larger static contact angle. What if when surface B is tilted 1° from the horizontal, the drop slides off, and when surface A is tilted to any angle,

Figure 4 Which surface is more hydrophobic?

the drop remains pinned to the surface? According to this, we must say that the surface B is more hydrophobic [17].

To clarify the complexity described above, we must recognize that the terms “hydrophobicity” and “water repellency” are not necessarily identical, although quite often, they are used as synonyms. Hydrophobicity (and hydrophilicity) is defined through the static Young contact angle, and therefore, it does correspond to static situations (shown in Figure 4). To describe water repellency, the contact angle hysteresis, defined as the difference of the advancing, θ_A , and receding, θ_R , contact angle (Figure 5) is more relevant [12–18].

The force needed to start a drop moving over a solid surface is given by the following simple formula [16]:

$$F = \gamma_{lv} (\cos \theta_R - \cos \theta_A) \quad (6)$$

where F is the critical line force per unit length and θ_R and θ_A are the receding and advancing contact angles, respectively. According to Eq. (6), as the contact angle hysteresis ($\theta_A - \theta_R$) decreases, the critical force needed to make the drop move decreases. Consequently, surfaces with enhanced water repellency must correspond to small $\theta_A - \theta_R$.

3 Superhydrophobicity: definition and origin

According to the discussion above, a superhydrophobic surface that truly repels water must correspond to a high static contact angle (typically $>150^\circ$) and small contact angle hysteresis (typically $<10^\circ$). Therefore, the water drop has an almost spherical shape when resting on a superhydrophobic surface, as shown for instance in

Figure 5 Advancing θ_A and receding θ_R contact angles of a drop on a tilting surface.

Figure 6. When the drop is left from a height, it bounces and easily rolls off because the necessary force that must be applied to start the drop moving is very small. This is demonstrated in the successive snapshots in Figure 7. Interestingly, as the drop moves, it can remove dust particles and other contaminants, as shown for instance in Figure 8, thus inducing self-cleaning properties to the surface. Figures 6–8 demonstrate, through examples, the interesting wetting properties that define superhydrophobic and water-repellent surfaces: these surfaces correspond to high static contact angles and small forces needed to make the drop to move (i.e., small contact angle hysteresis); furthermore, they exhibit self-cleaning properties. It is noted that the surfaces shown in Figures 6–8 were prepared by our group [19–24], according to the procedures described in section 5.

The origin of superhydrophobicity/water repellency was clearly revealed by the two botanists Barthlott and Neinhuis [25], who showed that the structural features on the plant leaves exhibiting a two-length-scale hierarchical structure together with their waxy surface chemistry render the leaves water-repellent [25]. The leaves of lotus (*Nelumbo nucifera* Gaertn) provides an impressive demonstration of the self-cleaning process that was therefore

Figure 6 Water drops with almost spherical shapes on a superhydrophobic surface. The static contact angle, measured on the right, is clearly higher than 150° .

called the “lotus effect” [25]. Interestingly, specially textured surfaces with hierarchical micrometer- and nanometer-sized structures were observed not only in the plant leaves [25–28], but also in the wings of some insects [29–31] and feathers of birds [32, 33].

A typical structure of a superhydrophobic/water-repellent surface is shown in Figure 9. Micrometer-sized structures are shown in the scanning electron microscopy (SEM) image of Figure 9A. These structures induce an augmented roughness at the micrometer scale. The protruding microstructures consist of further nanostructures, as evidenced by the SEM and atomic force microscopy (AFM) images, shown in Figures 9B and C, respectively. Consequently, overall, a two-length-scale hierarchical structure is formed on the surface, similar to the structure observed in the lotus leaves and in other surfaces of nature.

4 Superhydrophobicity: new methods but old knowledge

As implied in section 2, the origin of superhydrophobicity has been known since the 1940s. Cassie and Baxter [11] were clearly aware of the interdependence between surface roughness and water repellency, as they wrote: “The duck is generally regarded as having attained perfection in water repellency, and it is usually taken for granted that the duck uses an oil or similar coating with larger contact angles than any known to man. In actual fact, the duck obtains its water-repellency from the structure of its feathers.” However, the subject of superhydrophobicity has been recently revisited as the development of new techniques provided the capability to control and manipulate the matter on the nanoscale. Therefore, for

Figure 7 A water drop bouncing on a water-repellent surface. Because the force needed to start the drop moving is very small, the drop rolls off spontaneously. A sequence number is provided in the upper left corner of each photograph.

Figure 8 The self-cleaning process of a water-repellent surface is demonstrated with these successive snapshots. The surface of a concrete segment, covered with a water-repellent film, was intentionally contaminated with black dust particles. Water drops were left to roll off toward the direction shown by the arrow (snapshot 1). Powder particles were gradually removed by the water drops, thus creating a channel of clean surface.

Figure 9 Morphology of a superhydrophobic surface revealed using SEM (A and B) and AFM (C). The hierarchical micrometer-sized structures shown in (A) consist of further nanostructures, as evidenced by the SEM (B) and AFM (C) images. The surface shown in the figure is a composite film that was prepared according to the procedures described in section 5.

instance, the aforementioned argument of Cassie and Baxter was proved accurate only in 2008, when systematic SEM studies revealed a multiscale structure on duck feathers [33].

Apart from the pioneering work of Cassie and Baxter [11], the concept of superhydrophobicity was discussed in other reports in the 1940s [34–38] that were mainly published by scientists and engineers who worked in the textile industry. (Cassie also worked in the textile industry.) This is because superhydrophobicity is apparently extremely useful in textiles, as highlighted in a review article published recently by researchers involved in textile engineering [7].

The development of nanotechnology and advanced instrumentation lead to an increased interest in superhydrophobicity, according to the plot in Figure 10, which shows the annual number of articles that have been published since 2000 and have included the word “superhydrophobic” in their keywords and/or titles. Furthermore, it is noteworthy that innovations on superhydrophobicity were included in the “R&D 100 Award Winners” list by the *R&D Magazine* (Sandia Laboratories & Oak Ridge Laboratory, R&D, 2008).

Several bottom-up or bottom-down strategies have been recently designed and reported to produce well-controlled water-repellent surfaces, such as those shown in Figures 6–9. As these strategies consist in mimicking the hierarchical structured biosurfaces (e.g., lotus leaf), superhydrophobic surfaces are considered as biomimetics materials that have been coming to the fore of science since the turn of the century [39, 40]. Some recently suggested interesting methods to produce superhydrophobic surfaces are summarized in Table 1.

5 Polymer-particle nanocomposite superhydrophobic films

Our group has developed a very simple method that can be used to impart superhydrophobicity to various

Method	References
Wet chemical reaction	[41–45]
Electrochemical deposition	[46–49]
Plasma etching	[50–53]
Sol-gel	[54–59]
Chemical vapor deposition	[60–62]
Polymerization reaction	[63–65]
Composite films	[66–71]

Table 1 Strategies suggested to produce superhydrophobic materials and corresponding references.

surfaces/substrates [19–24]. The method is illustrated in Figure 11 and is summarized as follows: oxide nanoparticles are dispersed in a siloxane polymer solution with an appropriate concentration. The dispersion is then sprayed on a substrate, and the surface of the resulting composite siloxane-nanoparticle film exhibits superhydrophobic properties. This is because a two-length-scale hierarchical structure is formed on the surface of the composite film, which resembles the surface morphology of the lotus leaf. This method was used to produce the surfaces that have been previously presented in Figures 6–9. The composite films, shown in the Figures, were produced using a commercially available poly(alkyl siloxane) solution (Rhodorsil 224, Rhodia Silicones) which was blended with 2% w/v silica (SiO_2 , fumed silica, Sigma-Aldrich) nanoparticles. It is noteworthy that superhydrophobicity can be obtained using different nanoparticles and polymers [19–24]. To simplify the discussion, the results presented herein correspond only to films prepared using the Rhodorsil 224 product, which is an inherently hydrophobic material ($\theta_Y > 102^\circ$), mixed with SiO_2 nanoparticles with a mean diameter of 7 nm.

The spray method has the advantage that it can be easily used to induce superhydrophobicity on various surfaces. This is shown by the data of Figure 12 and Table 2. The figure shows the results of static contact (θ_s) measurements performed on treated surfaces of glass, silicon, concrete, aluminum, silk, wood, and stone materials such as three types of marble (Pentelic, Naxos, and Thassos)

Figure 10 Number of published articles per year related to “superhydrophobic,” according to the Scopus database.

Figure 11 A method devised by our group [19–24] that can be used to impart superhydrophobicity to various substrates. A specimen of marble is treated in the photograph. A superhydrophobic polymer-nanoparticle film is deposited on the surface of the marble. A two-length-scale hierarchical structure (at the microlevel and nanolevel) is formed on the surface of the film, as shown in the SEM images, resulting in superhydrophobicity, which is evidenced by the shapes of the resting water drops.

and sandstone (Opuka, Božanovský, and Hořícký) used in Greek and Czech monuments, respectively. To reveal the effect of the SiO_2 nanoparticles on the wettability of the produced films, contact angle measurements that were carried out on pure siloxane films (without particles) are included in Figure 12. Table 2 shows the results of the contact angle hysteresis ($\theta_A - \theta_R$) measurements that were carried out on the composite films of Figure 12. The following conclusions were reached: (i) As described

above, using the spray method of Figure 11, we can induce superhydrophobicity to various surfaces. All composite films applied on the investigated surfaces correspond to high θ_s ($>150^\circ$) and low $\theta_A - \theta_R$ ($<10^\circ$), according to the results of Figure 12 and Table 2, respectively. (ii) Superhydrophobicity is induced by the nanoparticles. When pure siloxane was deposited on the surfaces, low θ_s values were measured (Figure 12). The static contact angle became $>150^\circ$ only when SiO_2 nanoparticles were

Figure 12 Static contact angle (θ_s) measured on pure siloxane (no particles) and siloxane mixed with SiO_2 nanoparticles (composites) films, applied on various substrates. Composites correspond to high contact angles ($>150^\circ$), thus exhibiting superhydrophobic properties. Pure siloxane films are just hydrophobic materials. Films were produced and deposited using the spray method shown in Figure 11.

Substrate	$\theta_A - \theta_R$ (°)	Substrate	$\theta_A - \theta_R$ (°)
Glass	3	Pentelic marble	5
Silicon	4	Naxos marble	5
Concrete	6	Thassos marble	5
Aluminum	6	Opuka sandstone	5
Silk	4	Božanovský sandstone	5
Wood	7	Hořický sandstone	6

Table 2 Contact angle hysteresis ($\theta_A - \theta_R$) measured on various surfaces, which were covered by siloxane-nanoparticle films, according to the method shown in Figure 11.

dispersed in the siloxane solution before film deposition. Furthermore, if we consider the contact angle hysteresis measured on the surfaces of pure siloxanes (not included in Table 2), these were $>14^\circ$ for any of the tested substrates. Hysteresis became $<10^\circ$ only when nanoparticles were used for the preparation of the films (Table 2). Consequently, according to Eq. (6), there must be a considerable difference in the forces required to move the water drops on the pure and composite films. To demonstrate this, we provide the following example. The advancing and receding contact angles measured on pure siloxane deposited on glass were $\theta_A = 107^\circ$ and $\theta_R = 92^\circ$. The corresponding values for the siloxane-nanoparticle film were $\theta_A = 165^\circ$ and $\theta_R = 162^\circ$ (which makes a difference of 3° as shown in Table 2). Using these numbers in Eq. (6), we conclude that it takes about 17 times as much force to move a drop on pure siloxane than on siloxane-nanoparticle composite film deposited on glass. Thus, water drops can roll off the composite siloxane-nanoparticle surface, but they stick on the surface of the pure siloxane.

As described in section 2, the effect of roughness (or surface porosity) on the wettability of a surface was quantified by Wenzel and by Cassie and Baxter. For inherent hydrophobic materials ($\theta_y > 90^\circ$) such as the siloxane Rhodorsil 224, both states can lead to superhydrophobicity, but the Cassie-Baxter state is the only one that is nonsticking: a Wenzel drop interacts with many defects, so that the associated contact angle hysteresis is very large [18]. Consequently, the wettability of the siloxane-nanoparticle surfaces investigated in the present report must follow the Cassie-Baxter predictions because, according to the results of Table 2, they correspond to a very small hysteresis. The calculation of f_s , which is included in the Cassie-Baxter equation, is necessary to compare the experimentally measured static contact angles on the composite films (θ_s in Figure 12) with the Cassie-Baxter predictions [θ^* in Eq. (5)]. The coefficient f_s was estimated from SEM images using the NIH Image software. It is important to note that this software can be safely applied on patterned

surfaces where f_s can be easily measured, as the area of the solid-liquid interface is essentially specified by the sizes of the well-defined surface protrusions, which can be measured with high accuracy [72], e.g., scheme of Figure 3A. Along this line, we note that the measurement of f_s in the surface structures of our study (e.g., Figure 9) includes a certain degree of uncertainty, as the assessment of the solid-liquid or the liquid-air interface is not obvious. Nevertheless, measurements of f_s were performed, following a carefully devised procedure [21], on films deposited on some selected surfaces. These values of f_s were used in Eq. (5), and θ^* was calculated for films deposited on glass, silicon, aluminum, Pentelic marble, and Opuka sandstone. The results are summarized in Table 3. For comparison, the experimentally measured θ_s values presented in Figure 12 are reproduced in Table 3, which shows that there is a good agreement between the experimentally measured θ_s and the θ^* , which was calculated using the Cassie-Baxter equation. Consequently, the results of Table 3 suggest that the siloxane-nanoparticle films investigated herein correspond to the Cassie-Baxter nonsticking state.

The spray method described above has several important advantages: it is a one-step, low-cost, and very simple method, as it does not include the use of any sophisticated instrumentation and/or expensive materials. Furthermore, it can be easily used to treat various and large surfaces including buildings and monuments.

6 Superhydrophobic films for the protection and conservation of cultural heritage

Water that originates from humidity or rain can cause decay of stone monuments by freezing-thawing cycles, crystallization of salts, and chemical reactions initiated by

Contact angle (°)	Substrate				
	Glass	Silicon	Aluminum	Pentelic marble	Opuka sandstone
θ_s (measured)	164	164	162	162	159
θ^* (calculated)	162	160	164	165	163

Table 3 Contact angles θ^* calculated using the Cassie-Baxter equation, Eq. (5), and static contact angles, θ_s , measured experimentally (reproduced from Figure 12) for superhydrophobic siloxane-nanoparticle films deposited on five substrates.

atmospheric pollutants that are carried by water. For this reason, the application of hydrophobic coatings has been suggested in the past for the surface protection of outdoor cultural heritage assets [73–77]. As shown in the previous section, the spray method of Figure 11 can be easily used to deposit superhydrophobic coatings on various surfaces, including stones used as building materials in monuments of cultural heritage. In particular, according to the results of Table 2 and Figure 12, superhydrophobicity was induced to three types of marble (Naxos, Pentelic, and Thassos) and three types of sandstone (Božanovský, Hořický, and Opuka) used in Greek and Czech monuments, respectively. Our group was the first to introduce superhydrophobicity to the field of conservation science in 2007 [24]. The idea was recently adopted by other research groups that produced superhydrophobic protective coatings and consolidants for monuments [78–80].

Apparently, superhydrophobic materials are advantageous over the traditional hydrophobic coatings suggested in the past because they induce enhanced water repellency. However, water repellency, which is evaluated by contact angle measurements, cannot be the only criterion for the selection of a product used for the protection of outdoor cultural heritage. A good protective material must not affect the aesthetic appearance of the stone substrate, should assure a good permeability for water vapor, and must decrease the amount of water absorbed by capillarity [73–77]. The efficacy of coatings to fulfil the aforementioned properties is evaluated through laboratory tests, as will be described next.

Capillary water absorption measurements are performed by the gravimetric sorption technique. The dried-weighted sample blocks are placed (with the treated/coated sides) on a filter paper pad (1 cm of Whatman paper, No. 4) partially immersed in distilled water. After 1 h, the samples are removed and weighted again to determine the amounts of water absorbed by the capillary forces. The same procedure is applied for untreated samples. Usually, the percentage of reduction of water absorption by capillarity (RC%) is reported as

$$RC\% = \left(\frac{m_{uw} - m_{tw}}{m_{uw}} \right) \times 100 \quad (7)$$

where m_{uw} and m_{tw} are the masses of water absorbed by capillarity by the untreated (bare) and treated substrate, respectively. Apparently, an ideal coating must eliminate the amount of water absorbed by capillarity (RC%=100).

For the vapor permeability tests, sample blocks (coated and uncoated) are fixed on top of cylindrical PVC containers that are partially (half) filled with water. Then, the

sealed containers are placed in a climatic chamber with a relative humidity of 25% and temperature of $40^\circ\text{C} \pm 0.5^\circ\text{C}$. The containers are weighted every 24 h. It is assumed that the vapor flow through the stone has reached a constant value when the difference between two consecutive daily (24 h) weight variations, ΔM_i and ΔM_{i-1} , is <5%:

$$\frac{\Delta M_i - \Delta M_{i-1}}{\Delta M_i} \times 100 < 5\% \quad (8)$$

Under constant vapor flow, the water vapor permeability is evaluated as the mass of water vapor passing through the surface unit (in square centimeters) in 24 h. Three consecutive measurements with intervals of 24 h are carried out. The aforementioned procedures are applied on both treated/coated and untreated/uncoated stone samples. The permeability for water vapor is usually quantified by the percentage of reduction of vapor permeability (RVP%) according to Eq. (9):

$$RVP\% = \left(\frac{m_{uw} - m_{tv}}{m_{uw}} \right) \times 100 \quad (9)$$

where m_{uw} and m_{tv} are the masses of water vapor penetrating the untreated and treated substrate, respectively. Apparently, an ideal coating must have no effect on the water vapor permeability (RVP%=0).

Colorimetric measurements are carried out on both treated and untreated stone specimens using a reflectance spectrophotometer. The results are evaluated by the use of $L^*a^*b^*$ coordinates of the CIE 1976 scale. An ideal protective film should have no effect on the aesthetic appearance of the treated stone. The global color difference (ΔE^*) of the stone surfaces due to treatment is calculated according to Eq. (10):

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (10)$$

where L^* , a^* , and b^* are the brightness (0 for black; 100 for white), the red-green component (positive for red and negative for green), and the yellow-blue component (positive for yellow and negative for blue), respectively.

The measurements of RC%, RVP%, and ΔE^* for the marble and sandstone specimens covered by siloxane-nanoparticle composite superhydrophobic films are summarized in Table 4. For comparison, measurements that were carried out on stone specimens covered by pure (without particles) siloxanes are included. As shown in Figure 12, the addition of the nanoparticles enhances the hydrophobic character of the treated specimens. As a result, higher RC% were recorded for the stones treated with superhydrophobic composites, compared with the

Substrate	Siloxane-nanoparticle film			Siloxane film		
	RC%	RVP%	ΔE^*	RC%	RVP%	ΔE^*
Pentelic marble	95.98	40.3	2.28	75.36	12	1.34
Naxos marble	95.36	36.3	6.94	74.05	11	3.21
Thassos marble	89.48	35	3.75	69.36	10	1.45
Opuka sandstone	94	14.35	4.25	88.5	19.75	1.21
Božanovský sandstone	97.6	19.1	9.37	96.5	13.13	3.33
Hořícký sandstone	98.1	18.3	12.17	97.7	21.7	1.6

Table 4 Results of capillary water absorption, vapor permeability, and colorimetric measurements that were carried out on marble and sandstone specimens covered by superhydrophobic siloxane-nanoparticle and hydrophobic siloxane films. Measurements were carried out using Eqs. (7), (9), and (10).

corresponding RC% values measured on stones that were treated with pure siloxane (Table 4). Furthermore, the use of nanoparticles increased the RVP% measured on marble specimens, but it did not have any obvious or considerable effect on the water vapor permeability tests that were carried out on the sandstone specimens. Finally, the aesthetic appearance of the three stones included in this study was affected by the nanoparticles. Colorimetric measurements showed that ΔE^* measured after treating the stones with siloxane-nanoparticle films was clearly higher than the color change recorded when pure siloxanes were applied on the surfaces of the stones.

Consequently, the use of nanoparticles as additives in protective coatings of monuments provide positive and negative results. Nanoparticles induce superhydrophobicity and water repellency (high θ_s and RC%), which are very attractive properties because they enhance the resistance of the stone to the negative effects of rainwater. However, nanoparticles affect the aesthetic appearance of the stone, and they can have a negative impact on vapor permeability, as was observed in the marble specimens. Reduction of the negative effects of the nanoparticles can be achieved by tuning crucial parameters such as the particle concentration, as discussed elsewhere [22]. In summary, the use of the superhydrophobic composite films for monument protection is a very promising idea, which, however, must be further examined. For instance, before making the superhydrophobic product(s) available to conservators, the durability of the good properties of the composite materials must be investigated through acceleration of aging and *in situ* pilot-scale experiments. The results of these investigations must be duly taken into account. Furthermore, a reduction of the negative effects raised by the use of

nanoparticles must be carefully considered by tuning crucial parameters involved in the production of superhydrophobic materials [22].

The aforementioned discussion was related to the surface protection of the stone. We turn now our attention to another field of monument conservation, and that is stone consolidation. Polymeric materials are used to strengthen detached parts of monuments. Historically, acrylic polymers were first tested and used as stone consolidants. These materials, however, are disadvantageous because their macromolecular nature prevents their penetration into the pores of the stone. The problem was tackled using organic-silicon-based compounds [81–83]. Siloxane molecules of low molecular weights have the ability to migrate into the pores of the rock because of their small size, whereas under the influence of air humidity, they gradually polymerize spontaneously to macromolecules, therefore creating an effective consolidation network. Consequently, siloxane products such as those investigated above for the protection of the stone surface can be simultaneously used for stone consolidation. However, the effects of the nanoparticles that can be added to the siloxane material to achieve superhydrophobicity (i.e., to enhance surface protection) on the mechanical properties of the stone have not been investigated before. A preliminary study is presented for the first time in the present study.

The efficiency of a material to be used as a consolidant for monuments of cultural heritage can be evaluated through various tests, such as compressive, bending, and tensile strength measurements. However, the output of most of these methods is a value characteristic of the bulk. Indentation/hardness tests, meanwhile, provide results related to the mere surface of the stone. In the last decade, the portable Drilling Resistance Measurement System (DRMS) device, shown in Figure 13, has been recognized as one of the most important methods for both laboratory and on-site testing of stones and mortars used in monuments [84, 85]. DRMS has two important advantages:

Figure 13 The DRMS in the laboratories of the University Ecclesiastical Academy of Thessaloniki.

Figure 14 Average force needed to drill to a depth of 10 mm (i) an untreated mortar, (ii) the same mortar treated with a pure siloxane product (no particles), and (iii) the mortar treated with a composite, siloxane-nanoparticle, superhydrophobic product.

(i) as stated above, it is a portable device, thus providing the opportunity to carry out measurements on site and (ii) it measures the variation of strength with depth

at the millimeter scale, which is the appropriate scale to indicate a decay process or to determine the depth a consolidation has been achieved.

Figure 14 shows the measurements that summarize the average forces needed to drill to a depth of 10 mm (i) an untreated mortar, (ii) the same mortar treated with a pure siloxane product (no particles), and (iii) the mortar treated with a composite, siloxane-nanoparticle, superhydrophobic product. According to the results of the figure, nanoparticles improved the resistance of the treated mortar specimen to the drilling force, thus suggesting that the composite product is a better consolidant than the pure (no particles) siloxane. This preliminary result offers new perspectives in the application of siloxane-nanoparticle products for the conservation of monuments of cultural heritage.

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