Surface Topography:
Metrology and
Properties

PAPER

Fabrication of bunny ear cactus- mimicking superhydrophobic silica coatings on marble to protect architectural heritage

To cite this article: Akshay R Jundle *et al* 2025 *Surf. Topogr.: Metrol. Prop.* **13** 035017

Surface Topography: Metrology and Properties

RECEIVED
12 May 2025

REVISED
24 August 2025

ACCEPTED FOR PUBLICATION
1 September 2025

PUBLISHED
10 September 2025

PAPER

Fabrication of bunny ear cactus- mimicking superhydrophobic silica coatings on marble to protect architectural heritage

Akshay R Jundle[1], **Sagar S Ingole**[1], **Pradip P Gaikwad**[1], **Rutuja A Ekunde**[1], **Rajaram S Sutar**[2], **Shanhu Liu**[2] and **Sanjay S Latthe**[1,*]

[1] Self-cleaning Research Laboratory, Department of Physics, Vivekanand College, Kolhapur (An Empowered Autonomous Institute), Kolhapur–416003, (Affiliated to Shivaji University, Kolhapur), Maharashtra, India
[2] School of Chemistry and Molecular Sciences, Henan University, Kaifeng, People's Republic of China
[*] Author to whom any correspondence should be addressed.

E-mail: latthes@gmail.com

Keywords: superhydrophobic, marble, protective coating, self-cleaning, bunny ear cactus

Supplementary material for this article is available online

Abstract

The TEOS–PDMS-based superhydrophobic silica coatings for Carrara marble presented in this work is intended to improve the protection of historic buildings against water and pollution-induced damage. This method effectively preserves marble-built cultural heritage by optimizing TEOS:PDMS ratios and processing conditions to provide superhydrophobicity and durability. In this study, a marble was coated with a homogeneous mixture of polystyrene and polydimethylsiloxane-modified silica particles through spray coating. Surface analysis of the coated marble demonstrated a uniform layer of coatings, resulting in a hierarchical surface structure that mimics the Bunny Ear Cactus leaf surface. The coated marble exhibited a water contact angle (WCA) of 168.5 ± 2.5°, underscoring its exceptional water repellency, alongside a water sliding angle (WSA) of 4 ± 1°, which indicates quick droplet runoff. In investigating the mechanical durability, the as-prepared superhydrophobic coating has demonstrated high robustness when subjected to rigorous tests such as adhesive tape tests, sandpaper abrasion, water droplet impact, and sand grain impact. Moreover, the developed superhydrophobic coating exhibited chemical resistance and thermal stability in harsh conditions. The potential applications of such formulation could effectively enhance conservation efforts aimed at preserving the integrity and aesthetic value of architectural heritage.

1. Introduction

The preservation of architectural heritage sites holds global significance, as these monuments reflect the cultural, historical, and artistic achievements of civilizations. Marble, renowned for its aesthetic qualities and structural strength, is frequently employed in heritage architecture. However, marble surfaces face several threats, including erosion from acid rain, water infiltration may cause internal damage, and water ingress that encourages biological growth. Mechanical contact can cause discoloration and weaken the material, while freeze–thaw cycles lead to breakdowns due to expanding water in cracks. Temperature fluctuations can result in surface flaking, and polluted water particularly harms limestone and marble. Salts crystallizing in the pores of the stone contribute to disintegration. Timely maintenance and sealing are vital, as aggressive cleaning methods can harm softer stones. Various approaches for stone conservation have been explored, from traditional to modern techniques. Chemical consolidants like ethyl silicate and acrylic resins are used to strengthen porous stones, but they often cause yellowing and reduce structural integrity [1]. Polymeric coatings, such as epoxy and polyurethane, create impermeable layers that trap moisture and may damage the stone [2, 3]. The Fuller's earth method uses natural bentonite clay for a non-toxic cleaning of marble, absorbing dirt without harsh chemicals [4]. Biocidal treatments help in preventing biological growth but can harm the stone and raise environmental concerns. Laser cleaning provides precision and avoids chemical residues, but it is costly and impractical for large areas [5–7].

Additionally, Atanassova *et al* [8] have developed a hybrid laser-solvent cleaning technique for sensitive artworks, and Gomes *et al* [9] compared graffiti removal methods on granite, highlighting the need for minimally invasive preservation strategies.

To overcome the challenges from traditional and modern methods, superhydrophobic (SHP) coatings have emerged as a promising approach for protecting heritage stones. These coatings repel water and contaminants by creating low surface energy and hierarchical surface roughness. Among the various synthesis techniques, the sol–gel method is particularly attractive for fabricating SHP surfaces due to its low processing temperatures, compositional tunability, and ability to form uniform nanostructured coatings. The sol–gel process involves the hydrolysis and condensation of metal or organosilicon alkoxides to form a porous inorganic–organic hybrid network. While tetraethyl orthosilicate (TEOS) is frequently employed because of its well-understood reactivity, other silane precursors such as methyltrimethoxysilane (MTMS) and isobutyltrimethoxysilane (IBTMS) have also been used, depending on the desired coating properties. The incorporation of polydimethylsiloxane (PDMS) into the silica matrix has proven especially beneficial for lowering surface energy and enhancing mechanical flexibility and water repellency. The spray coating method has gained attention in the conservation field for its scalability, simplicity, and compatibility with delicate and uneven stone surfaces. When combined with sol–gel formulations, spray coating facilitates the formation of crack-free films with hierarchical roughness-critical for achieving long-lasting superhydrophobicity on complex substrates.

Several recent studies have demonstrated the potential of sol–gel-derived SHP coatings on heritage stone. Pinho *et al* [10] developed a mesoporous titania-silica nanocomposite coating on limestone using ethoxysilane oligomers, titanium dioxide nanoparticles, and a nonionic surfactant. This material exhibited both hydrophobic properties and photocatalytic activity. The surfactant played a crucial role in reducing particle aggregation and increasing pore size during the sol–gel transition. A layer of UCATiO (TES40/P25/n-octylamine) coating yielded homogeneous and crack-free surfaces. P25 dispersions and UCATiP (TES40/P25/H_3PO_4) coatings showed minimal color change ($\Delta E^* < 3$), whereas UCATiO coatings exhibited more significant color variation, which decreased as the concentration of TiO_2 increased. The UCATiO coatings also demonstrated improved self-cleaning capabilities. Similarly, Adamopoulos *et al* [11] have applied a superhydrophobic coating of 1H,1H,2H,2H-perfluorooctyl-triethoxysilane (FAS) and TEOS composite on marble through the sol–gel process. This coated marble demonstrated exceptional superhydrophobicity with a WCA of 171.5° and a sliding angle as low as 3°. The TEOS-FAS coating effectively protects against moisture, reducing capillary water absorption by 74.3% ± 3.4% and vapor permeability by 15.6% ± 3.9%. However, the addition of fluorine compounds brings up risks to their safety towards the environment and human health. However, achieving superhydrophobicity on marble surfaces poses challenges due to complex synthesis processes and the use of toxic chemicals, which can harm the environment and health. There is an urgent need for easy-to-apply, cost-effective, and eco-friendly coatings that are durable for large-scale use. Developing simpler, non-toxic methods for creating these surfaces could significantly improve their application in cultural heritage and architecture, where marble is commonly used.

Therefore, a polydimethylsiloxane (PDMS) is promisingly used to enhance the durability and mechanical strength of marble coatings [12]. Illescas *et al* developed a sol–gel process incorporating PDMS into a silica oligomer framework, which improved the mechanical strength, water resistance, and stain protection of pure limestone [13]. This integration increased water repellency by decreasing surface energy and creating dual-scale roughness, with higher PDMS content (up to 56%) further enhancing these properties. Their refined sol–gel mixture yielded crack-free hybrid PDMS-silica coatings, improving the durability of carbonate stones. However, they noted that while more PDMS enhanced hydrophobicity, it also delayed gelation and reduced network density. In another study, Luo *et al* created a tetraethyl orthosilicate-polydimethylsiloxane-hydroxyapatite (TEOS-PDMS-HA) composite coating on sandstone, which improved surface roughness and hydrophobicity, achieving a contact angle over 135° [14].

Based on this literature review, it is evident that while sol–gel derived TEOS–PDMS coatings offer a promising route toward transparent, fluorine-free, and mechanically robust superhydrophobic surfaces, several critical challenges persist. These include optimizing the sol–gel composition for reduced cracking and enhanced durability, improving environmental resistance (e.g., UV, humidity), and scaling up the application process for large and irregular surfaces without compromising coating uniformity or adhesion. Furthermore, there remains a need to design biomimetic micro/nanoarchitectures that can retain functionality over prolonged outdoor exposure. Addressing these gaps is essential to transition sol–gel-based coatings from laboratory-scale experiments to real-world conservation applications. The present work seeks to bridge these gaps by developing an environmentally benign, optically clear, fluorine-free superhydrophobic coating using a TEOS–PDMS hybrid sol–gel system applied via spray coating.

In this study, we developed a novel superhydrophobic coating that mimics the bunny ear cactus, utilizing a composite of TEOS and PDMS. The coating features finely tuned micro- and nano-structures that enhance mechanical durability and water repellency. By optimizing the TEOS to PDMS ratio and sol–gel processing parameters, we have attained a robust, homogeneous superhydrophobic coating on marble surfaces. The applied TEOS–PDMS-based nanocomposite was carefully engineered to form a thin, semi-transparent layer that does not significantly alter the visual characteristics of the marble. While the surface exhibits a slight change in gloss due to the formation of micro/nano-structures, no noticeable discoloration or opacity was observed upon visual inspection. This coating also offers strong resistance to abrasion, chemicals, and heat, making it ideal for conservation applications. Overall, this innovative approach aids in heritage conservation, protecting Carrara marble while preserving its aesthetics for future generations.

2. Experimental section

2.1. Materials

Tetraethylorthosilicate (TEOS, 98%), polydimethylsiloxane (PDMS, 5 cSt viscosity), and Polystyrene (PS, with an average molecular weight of around 280,000) were purchased from Sigma-Aldrich, USA. Oxalic acid was purchased from Thomas Baker Co., Ltd, Ambarnath, India. N, N-Dimethylformamide was obtained from Spectrochem Pvt. Ltd, Mumbai, India, and ethanol (99.9%) from Changshu Hongsheng Fine Chemical Co., Ltd, China. The synthesis process utilized distilled water, while Carrara marble samples (2×2 cm^2) were obtained from the local market.

2.2. Fabrication of superhydrophobic marble

The coating fabrication involved the following steps. Initially, 0.1 mg of polystyrene (PS) was dissolved in 10 ml of dimethylformamide (DMF) while stirring at 600 rpm at 40 °C overnight to ensure a homogeneous solution. Meanwhile, in another beaker, tetraethyl orthosilicate (TEOS) (0.6 ml) was hydrolyzed with oxalic acid (0.2 g) as a catalyst, stirred for 3 h to prevent gelation, then polydimethylsiloxane (PDMS) was added dropwise. The PDMS volume varied (0.4 ml, 0.6 ml, and 0.8 ml) to optimize the surface properties, as shown in figures 1(a), (b). To prepare the coatings, 0.5 ml of PS solution was sprayed on cleaned marble and left to dry for 5 min; subsequently, 1 ml of the TEOS–PDMS nanocomposite was applied through spray coating. Thereafter, the coated samples underwent thermal curing at 120 °C for 2 h to promote solvent evaporation. The samples prepared with variations of 0.4 ml, 0.6 ml, and 0.8 ml of PDMS are labeled as A1, A2, and A3, respectively. The fabrication process of the superhydrophobic coating is shown in figure 1(c).

2.3. Characterizations

The surface and chemical structure of the prepared coatings were analyzed using Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM, JEOL, JSM-IT200), respectively. The wetting properties of the samples were investigated by contact angle meter (HO-IAD-CAM-01, Holmarc Opto-Mechatronics Pvt. Ltd India). The chemical composition of the samples was analyzed using x-ray photoelectron spectroscopy (XPS, Escalab 250Xi, USA) and Fourier-transform infrared spectroscopy (FT-IR, Magna-IR 560, Nicolet). The coating's mechanical endurance was tested using adhesive tape peeling, sandpaper abrasion, and water droplet impact testing. To evaluate the adhesion strength and durability of the superhydrophobic coating, Premier[38] adhesive tape (sourced from India) was firmly applied to the coated marble surface. A 100 g load was placed over the tape to ensure uniform contact. The tape was then repeatedly peeled off from the same location, simulating mechanical stress. This tape peel test helped assess the coating's ability to retain its superhydrophobic properties under repeated abrasion. Additionally, the mechanical wear resistance of the coating was tested using a sandpaper abrasion method. The coated marble sample was placed face-down on 2000-grit sandpaper under a 100 g weight, and then moved horizontally over a 20 cm track. This motion was repeated multiple times to simulate surface friction. The purpose of this test was to examine how well the coating maintains its surface integrity and water-repellent behavior under repeated mechanical stress.

For the water droplet impact test, a superhydrophobic marble sample was placed on a 40° inclined platform, and water droplets were continuously dispensed onto the coated surface from a resonating bottle maintained at a height of 20 cm. A 1-litre volume of water droplets was utilized to study the effect of repeated impacts on the marble surface wettability. In the sand grain impact test, a superhydrophobic marble sample was positioned on a 40° inclined platform, constantly releasing 5 g of sand from a resonating bottle placed 20 cm above the coated surface. The influence of repeated hits on the surface's wettability was assessed using 20 g of sand.

3. Results and discussion

3.1. Surface morphology and chemical analysis

Understanding the surface structural characteristics is essential for a comprehensive assessment of the superhydrophobic properties exhibited by coated marble surfaces. SEM images of the pristine marble reveal a smooth surface with natural grain texture and minimal roughness (figures 2(a) and (e)). SEM images of the coated marbles reveal a distinctive Bunny Ear Cactus leaf-like morphology, which plays a critical role in enhancing the surface roughness of the coating. The marble surfaces are uniformly coated with a spine-like structure, indicating a well-distributed coating conducive to superhydrophobic behavior.

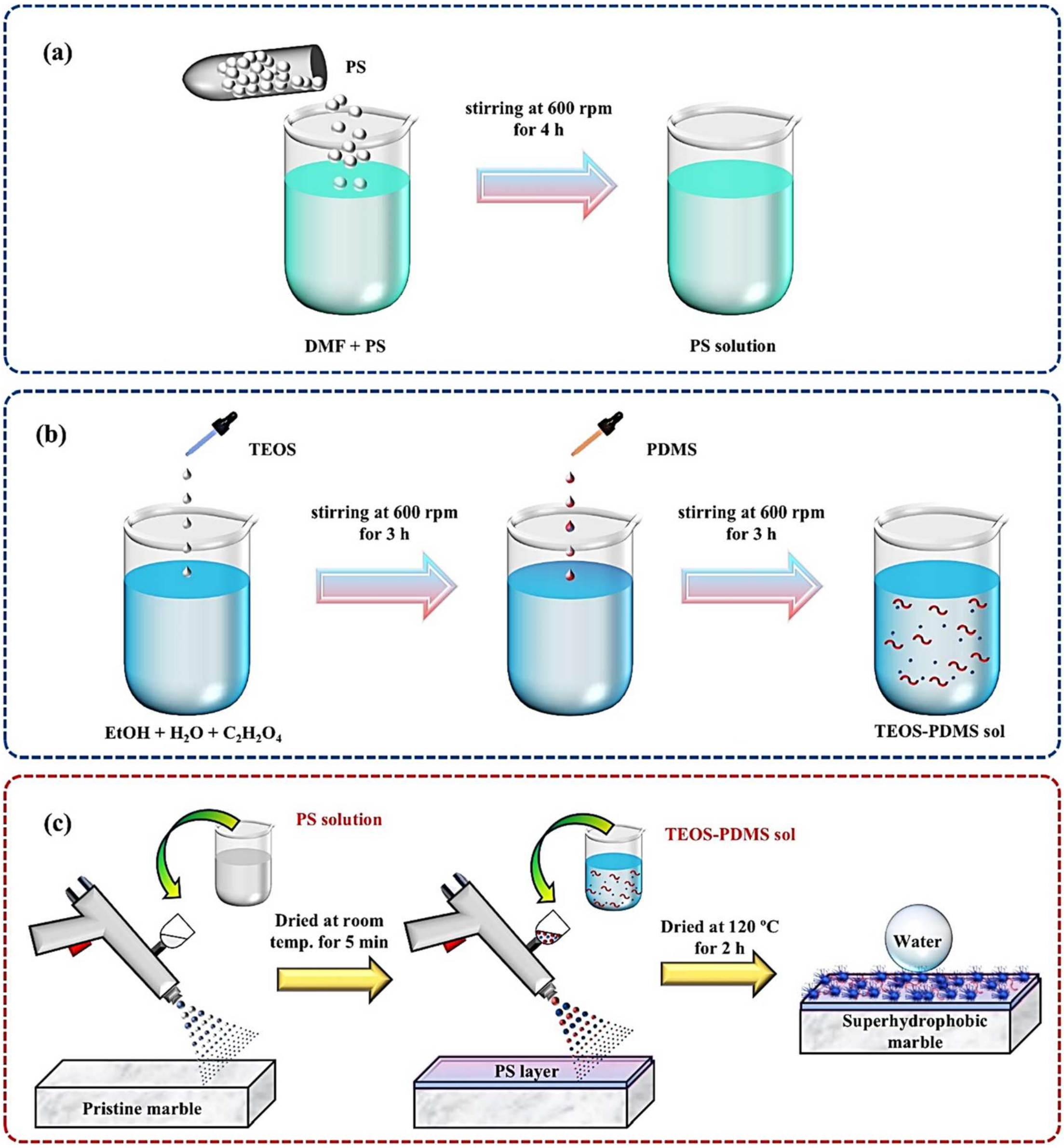

Figure 1. Schematic illustration of the (a) preparation of PS solution, (b) preparation of TEOS-PDMS sol, (c) spraying PS and TEOS-PDMS solutions for fabricating superhydrophobic coating on the marble surface.

The sol–gel process, which involves the hydrolysis and condensation of TEOS, leads to the formation of aggregated silica nanoparticles. Although TEOS and PDMS have inherent differences in their affinity for water, this approach was selected because it allows for the controlled development of a hybrid network. Through the fine-tuning of variables such as the ratios of precursors, duration of aging, and choice of catalyst, the compatibility between phases can be effectively regulated. This results in a uniform coating that exhibits exceptional water-repellent characteristics. Upon subsequent heat curing, this phase separation results in the formation of a clustered structure, which substantially enhances the surface roughness [15, 16]. Capillary forces act on the liquid–solid interface during drying (at 120 °C). These forces pull the silica particles into closer proximity, promoting directional agglomeration.

The unique Bunny Ear Cactus leaf-like structure of TEOS-PDMS boosts the surface area and increases the concentration of active sites for molecular interactions. The presence of hierarchical structures greatly enhances hydrophobicity, which is crucial for self-cleaning applications. Similarly, the development of a Bunny Ear cactus-like TEOS-PDMS morphology on marble surfaces promotes superhydrophobicity through micro-scale spines that effectively trap air pockets and reduce liquid adhesion. The formation of these structures occurs in several stages: initially, the aging of the precursor solution encourages the nucleation of nanocrystals, which act as templates for creating well-defined micro-structured spines. The optimized PDMS concentration, along with intermittent heating of the marble substrate, likely plays a vital role in guiding the growth of these micro-scale spines, ultimately resulting in the characteristic Bunny Ear Cactus leaf-like morphology. The

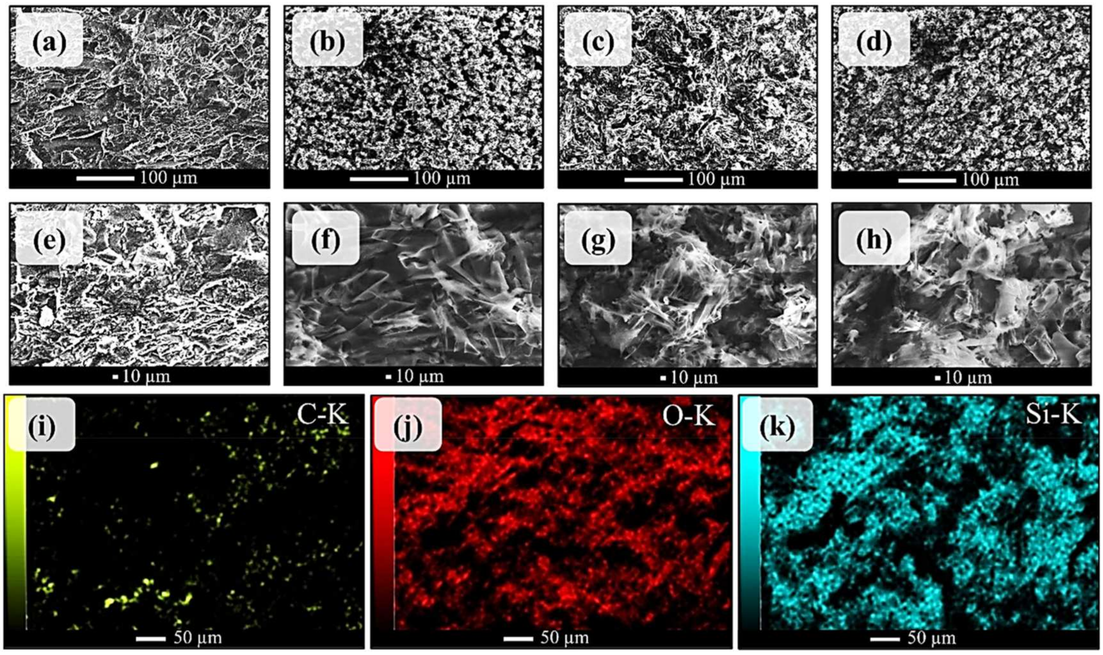

Figure 2. SEM images of (a) and (e) pristine sample, (b) and (f) A1, (c) and (g) A2, and (d) and (h) A3 samples. (i)–(k) The elemental mapping images of the A2 sample.

surface structures of all prepared samples exhibit similarities; nonetheless, minor alterations in surface morphology occur due to differences in the PDMS concentration within the coating solution, as shown in figures 2(b)–(d). Noteworthy differences are observed among the samples: while the A1 and A3 samples present similar roughness values, the A2 sample displays a more compact and irregular arrangement of aggregated structures. This unique arrangement not only enhances the surface roughness but also improves the durability of the coating on the marble substrate.

To quantitatively characterize the roughness of the marble surfaces, a 2D surface profilometer was employed. The 2D surface profilometer study showed that A1 and A3 samples had almost similar surface roughness (Ra) values of 0.765 μm and 0.723 μm, respectively. In contrast, the A2 sample exhibited an average roughness (Ra) of 0.874 μm. The random distribution of the aggregated composite material creates a microstructure akin to that of Bunny Ear Cactus leaf, characterized by randomly arranged papillae that contain low surface energy crystals. This innovative surface architecture traps air pockets, effectively decreasing the contact area that water droplets have with the solid fraction of the surface, thereby facilitating superhydrophobic properties. Importantly, the findings reveal that precise control of the PDMS concentration is imperative in achieving the desired optimal surface structure conducive to superhydrophobicity. In the EDS analysis, the C, O, and Si elements were detected, that attributed to the TEOS and PDMS composite coating on marble surfaces [17]. The elemental mapping images for the A2 sample are shown in figures 2(i)–(k), indicating that both TEOS and PDMS layers were evenly deposited on the marble, with elemental weight percentages of 25.82% (C), 54.89% (O), and 19.29% (Si). The 'C Kα' signal identified at a lower energy (~0.3 keV) confirms the presence of carbon, principally from the PDMS structure, which consists of repeating Si–O–Si units bonded to methyl groups (–CH_3) [18]. The oxygen peak, labeled 'O Kα' and positioned about 0.5 keV, illustrates oxygen's dual involvement in the system: as a structural constituent in the TEOS precursor, producing the silica network during hydrolysis and condensation, and as a siloxane backbone in the PDMS [19]. The 'Si Kα' peak at 1.7 keV verifies the existence of silicon, resulting from the TEOS-derived silica network and the PDMS structure [20]. The silica particles derived from TEOS enhance surface roughness, essential for obtaining superhydrophobicity, but the low-surface-energy PDMS adds to hydrophobicity by limiting water spread over the surface. The high oxygen concentration implies a strong siloxane network, which supports mechanical durability, whereas carbon reveals the organic component of PDMS, which increases flexibility and hydrophobic characteristics.

Figure 3 shows the FT-IR spectrum of the superhydrophobic marble (A2 sample) coated with TEOS-PDMS, highlighting the presence of key functional groups, which confirm the successful formation of the coating. The peak at 2936.8 cm^{-1} is attributable to the C-H stretching vibrations of methyl (-CH_3) groups from PDMS. The peak at 1053.6 cm^{-1} relates to Si–O–Si stretching vibrations, indicating the formation of a siloxane network [21]. The peak at 794.2 cm^{-1} suggests Si-CH_3 bonds, whereas the peak at 1629.6 cm^{-1} denotes

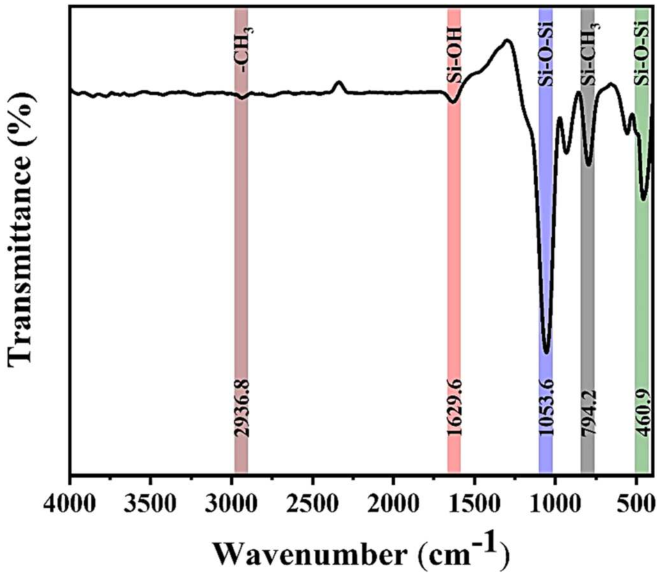

Figure 3. FTIR spectrum of the TEOS-PDMS-coated superhydrophobic coating on the A2 marble sample.

bending vibrations of adsorbed water molecules or remaining silanol groups. Overall, the spectrum indicates the existence of both TEOS and PDMS components and siloxane cross-linking and hydrophobic groups, paving the way for the successful formation of a superhydrophobic coating.

The XPS analysis of the TEOS-PDMS-coated SHP A2 sample reveals the surface's chemical composition and bonding states. The survey spectrum in the figure 4(a) displays distinctive peaks for elements like C, O, and Si, indicating the successful application of the TEOS-PDMS coating. Detailed core-level binding energy spectra are shown in figures 4(b)–(d), with decomposed peaks illustrating the chemical bonding environment. The C1s (figure 4(b)) shows two peaks at 284.7 and 285.5 eV corresponding to C–Si associated with PDMS and C-O associated with TEOS, respectively. The O1s spectra (figure 4(c)) show two peaks at 532.9 and 533.6 eV corresponding to O–Si associated with TEOS, and O–C associated with TEOS, contributions from siloxane and organic ($-CH_3$) groups, validating the integration of PDMS into the silica network. The Si2p spectrum (figure 4(d)) exhibits signals attributed to the Si–O–Si bond associated with TEOS at 103.3 eV, demonstrating effective polymerization and surface modification [22]. These observed chemical states indicate that the TEOS-PDMS coating has successfully altered the marble surface, enhancing its superhydrophobic characteristics.

3.2. Wettability and self-cleaning ability

Due to its naturally porous microstructure, pristine marble exhibits hydrophobic behavior, which is quantified by a WCA of 94.1 ± 3° (as shown in figure 5(a)). In contrast, the coated A2 marble sample exhibits a high WCA of 168.5 ± 2.1° and an exceptionally low rolling angle of 4 ± 1° (see figure 5(c)). This allows water droplets to rapidly roll off the surface with minimal surface contact. The significant enhancement in hydrophobicity can be attributed to two key factors: the incorporation of hierarchical roughness due to silica particles and the intrinsically low surface energy of PDMS. The synergistic effect of these factors results in exceptional water repellency, wherein water droplets maintain quasi-spherical morphologies and exhibit minimal adhesion, thus demonstrating the superhydrophobic properties of the coating. In contrast, other samples coated with varying amounts of PDMS, such as A1 and A3, showed WCAs of 161 ± 4.9° and 156.5 ± 1.6°, respectively. Correspondingly, these samples had WSAs of 5 ± 3° and 5 ± 2° (figures 5(b)–(d)).

The concentration of PDMS in the TEOS–PDMS superhydrophobic coating significantly influences surface wettability, morphology, and mechanical durability. At lower PDMS concentrations (0.4 ml), incomplete hydrophobic coverage may result in lower WCA and higher SA, diminishing superhydrophobic performance. An optimal concentration (0.6 ml) ensures a well-balanced hierarchical roughness and hydrophobicity, achieving a high WCA (168.5 ± 2.1°) and a low SA (4 ± 1°), promoting effective water repellency. However, excessive PDMS (0.8 ml) can attenuate surface asperities, decreasing roughness, which affects wettability. Additionally, while increased PDMS content enhances coating adhesion and flexibility. Thus, maintaining an optimal PDMS concentration is crucial for achieving a durable, superhydrophobic coating with excellent self-cleaning properties.

We determined the surface tension (surface energy) of the coated A2 marble sample utilizing equation (2):

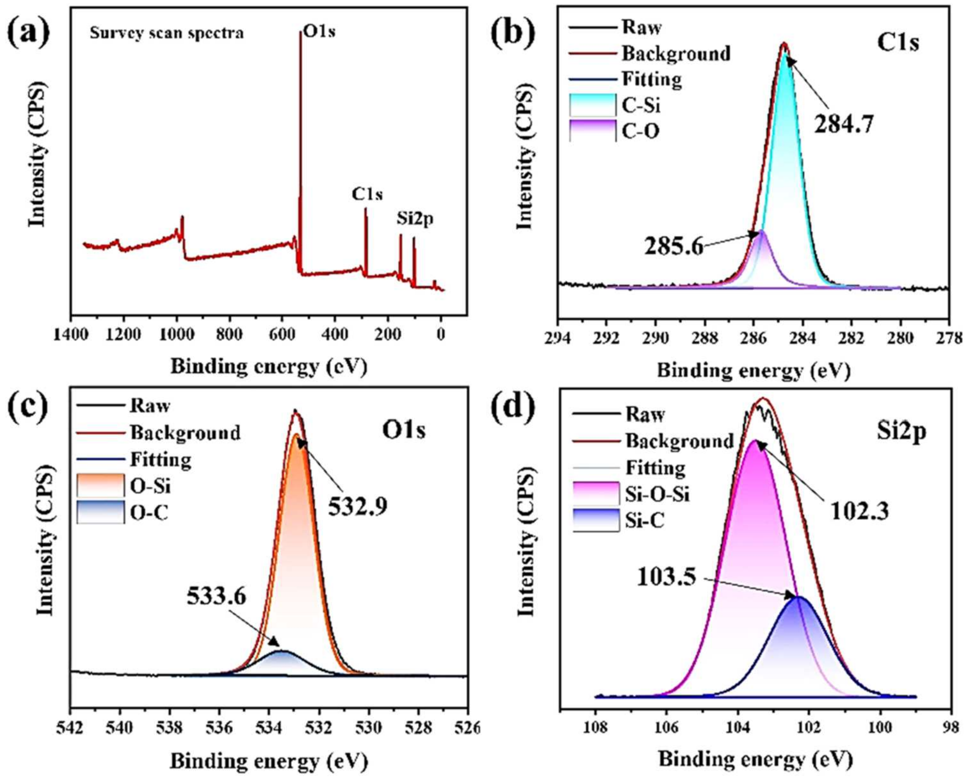

Figure 4. XPS spectra of the TEOS-PDMS-coated superhydrophobic coating on the A2 marble sample: (a) survey scan spectra, (b) C1s, (c) O1s, and (d) Si2p spectrum.

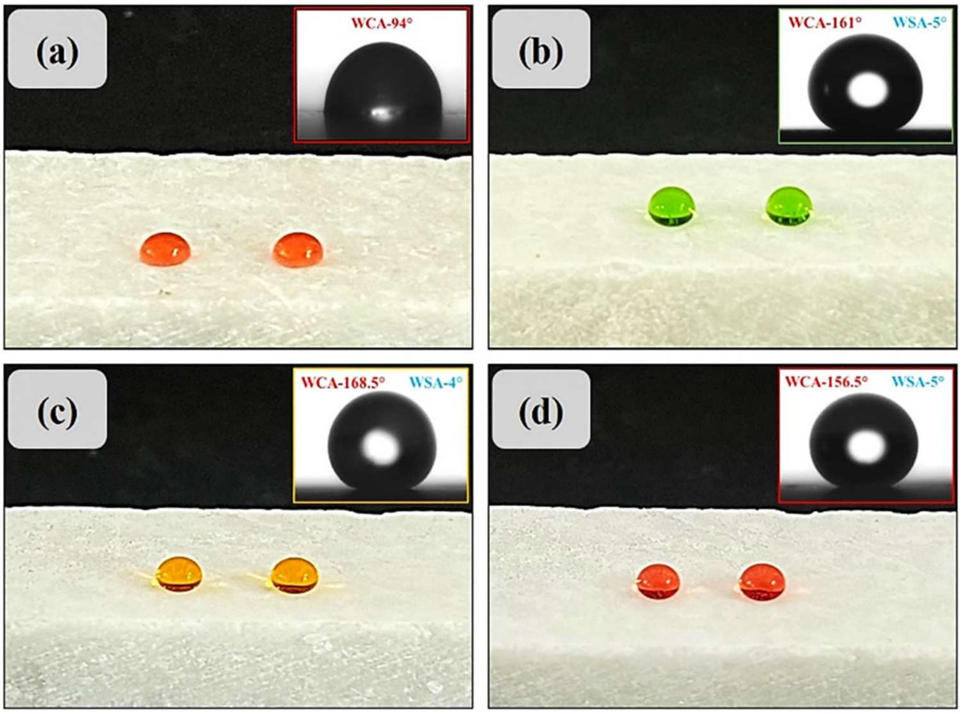

Figure 5. Optical images illustrate water droplets' wetting behavior on the (a) pristine marble sample and (b)–(d) TEOS–PDMS-coated superhydrophobic marble samples (A1, A2, A3), the insets display the corresponding contact angle measurements.

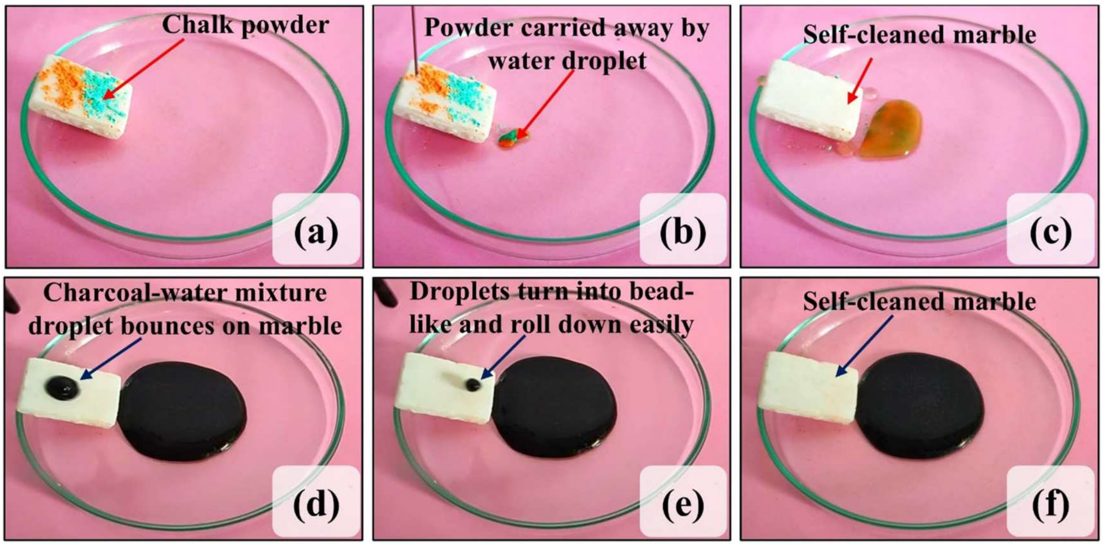

Figure 6. The optical photographs of the self-cleaning process by (a)–(c) fine chalk powders and (d)–(f) charcoal-water mixture.

$$\cos\theta_o = \frac{W_{SL}}{\gamma_{LA}} - 1 \quad (1)$$

$$W_{SL} = \gamma_{LA} \quad (1 + \cos\theta_o) \quad (2)$$

where θ_0 represents the static contact angle, W_{SL} denotes the work of adhesion per unit area between two surfaces, and γ_{LA} signifies the surface energy (surface tension) of the liquid against air. The calculated surface energy of the TEOS-PDMS-coated A2 sample was 3.56 mN m^{-1}, whereas for the uncoated marble, it was 79.52 mN m^{-1}. Additionally, we computed the solid–liquid fraction (f_{SL}) using equation (3). The resulting solid–liquid fraction for the A2 sample was 1.8502.

$$\mathrm{Cos}\theta_{CB} = 1 + f_{SL}(\mathrm{Cos}\theta_o - 1) \quad (3)$$

Superhydrophobic coatings are notable for their self-cleaning capabilities, making them valuable across various industrial fields. These materials feature negligible adhesion towards water that causes water droplets to bead and roll off, dislodging dirt and contaminants without manual cleaning. An empirical study was conducted to assess the self-cleaning properties of an A2 sample. During this experiment, both pristine and coated marble surface was contaminated with chalk and ash to simulate real-world dirt accumulation. While water droplets dropped on contaminated marble, the dust particles absorbed water and adhered to pristine marble. On the contrary, A2 marble proved highly effective.

In the experiment, the A2 sample was placed at an approximate 40-degree angle within a petri dish. When water droplets came into contact with marble, they acquired a spherical shape on its surface and were able to roll off with ease, taking along the attached particles and thereby leaving the surface clean, as illustrated in figures 6(a)–(c). The superior performance of the A2 sample can be attributed to its unique microstructural characteristics, which incorporate dual-scale roughness along with low surface energy. A charcoal powder-water mixture was prepared by using charcoal powder (1 g) and water (5 ml) under magnetic stirring for 20 min, form a homogeneous mixture.

The self-cleaning performance of the A2 marble sample is evaluated by this charcoal powder-water mixture. The optical photographs of the self-cleaning process with the charcoal-contaminated water are shown in figures 6(d)–(f). In the experiment, the A2 sample was placed at an approximate 40-degree angle within a petri dish. The A2 sample actively repelled the charcoal-contaminated water, allowing it to form discrete beads that rolled off, similar to the behavior of clean water droplets on superhydrophobic surfaces. Significantly, upon observation, no remnants of dust/charcoal stan were detected on the A2 sample after the test, underscoring the TEOS-PDMS coating's outstanding self-cleaning performance. These compelling results not only demonstrate the remarkable efficacy of superhydrophobic marble in actively maintaining cleanliness but also highlight its promising potential for diverse applications where cleanliness is crucial, especially in architecture.

3.3. Durability tests

3.3.1. Mechanical durability

Superhydrophobic coatings demonstrate outstanding water-repellent properties, but their durability and mechanical robustness pose challenges that hinder their practical application in various fields. This durability depends on several factors, including the compatibility of the substrate for proper adhesion, the thickness of the coating, and the fragility of the surface texture. Superhydrophobic surfaces are exposed to adhesive tape, sandpaper abrasion, water droplet impact, sand grain impact, and UV stability tests. Also, in harsh environments (acidic and basic), and

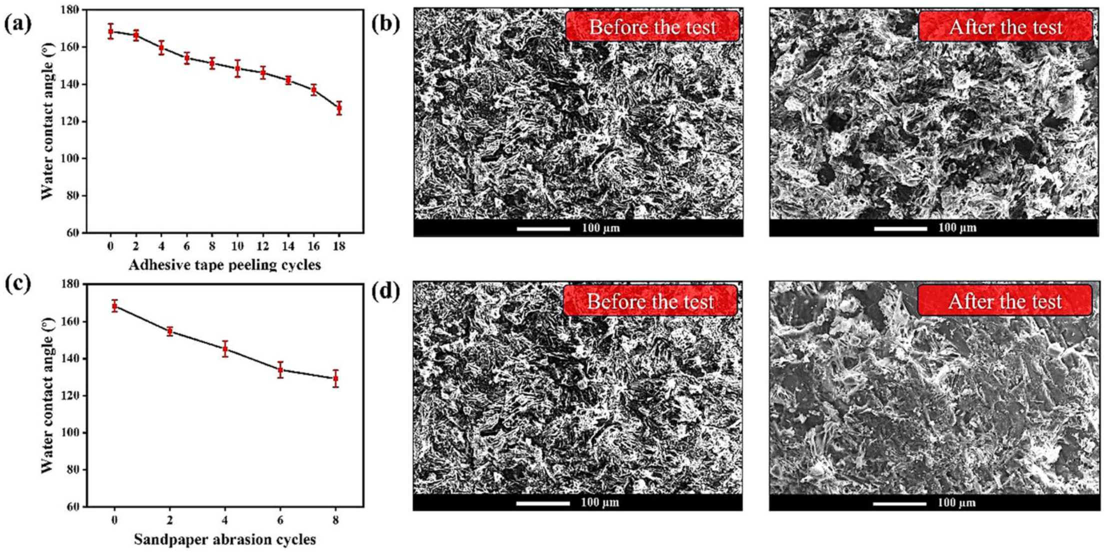

Figure 7. (a) Changes in WCA after every two cycles, (b) SEM image of A2 sample before and after 18 adhesive tape peeling cycles, (c) changes in WCA after every two cycles, (d) SEM image of A2 sample before and after 08 sandpaper abrasion cycles.

thermal degradation. Additionally, organic solvents may weaken the coating, making it more susceptible to damage. Mechanical wear, such as scratching or abrasion, can also diminish superhydrophobic traits by eroding surface texture. Strong adhesion between the coating and substrate is crucial to prevent delamination and detachment. While thinner coatings can improve strength, they may alter surface morphology and affect performance. Therefore, the longevity and mechanical resilience of the as-prepared coatings were investigated by several tests, including adhesive tape peeling, sandpaper abrasion, water drop impact, sand grain impact, UV irradiation, chemical, and thermal stability tests.

The mechanical stability of the coating was assessed through repeated adhesive tape peeling tests using Premier Adhesive Cello tape (23 microns thick, 12 mm wide). We applied adhesive tape to an A2 marble substrate and subsequently rolled a 100 g weight over the tape to ensure proper contact prior to peeling. This process was conducted for 18 cycles to assess the durability of the coating. As depicted in figure 7(a), there was a consistent decrease in the static WCA following each tape peeling cycle. Notably, after 10 cycles, the superhydrophobic properties of the marble surface were compromised, evidenced by a significant reduction in WCA coupled with SEM imagery that revealed the detachment of the composite material from the substrate (see figure 7(b)). Additional optical photographs captured during the adhesive tape testing are presented in figures S1(a)–(d) in the supporting information. The deterioration in surface roughness of the coating corresponded with the observed decrease in WCA. Initially, the WCA measured at 168.5 ± 2.5°, decreased to 148.5° after 10 cycles, and further declined to 127.2° after 18 cycles. Figure S1(d) illustrates the significant amount of coating material adhered to the tape. This trend indicates a substantial loss of coating integrity and a notable decline in superhydrophobic properties. Further, we examined the water droplet bouncing performance on coatings subjected to 5, 10, and 15 cycles of adhesive tape peeling. After 5 cycles, the water droplets were still bouncing freely on the affected area of the coating, indicating the coatings maintained their superhydrophobic characteristics. However, by 10 cycles, we observed significant degradation, with microdroplets beginning to adhere to the surface, reflecting a decline in water repellency. After 15 cycles, adherence worsened considerably may be due to structural damage and the loss of low-energy components critical for superhydrophobicity. Video 1 shows a bouncing water droplet on coated marble after the adhesive tape peeling test. This indicates that repeated mechanical stress from peeling severely compromises the coatings' ability to repel water.

The sandpaper abrasion test evaluates the mechanical durability of a superhydrophobic surface. In this investigation, an SHP A2 marble sample with a mass of 66.4 g was positioned face down on 2000-grit sandpaper, while a 100 g weight was applied to maintain uniform pressure [23, 24]. The sample underwent horizontal movement along a 20 cm track, completing a single abrasion cycle. After four cycles of testing, the WCA decreased from 168.5 ± 2.5° to 145.3 ± 4.3°, indicating significant damage to the surface nanostructure, as illustrated in figure 7(c). Optical images taken during the sandpaper abrasion process are presented in figures S1(e)–(f) in the supplementary information. Each cycle of abrasion resulted in a measurable loss of material and a compromise in structural integrity. This degradation of the nanoscale structure, evidenced by the flattening and deterioration of the composite material, leads to a reduction in surface roughness and a corresponding decline in superhydrophobic performance, as shown in the SEM image in figure 7(d). The result is a smoother surface

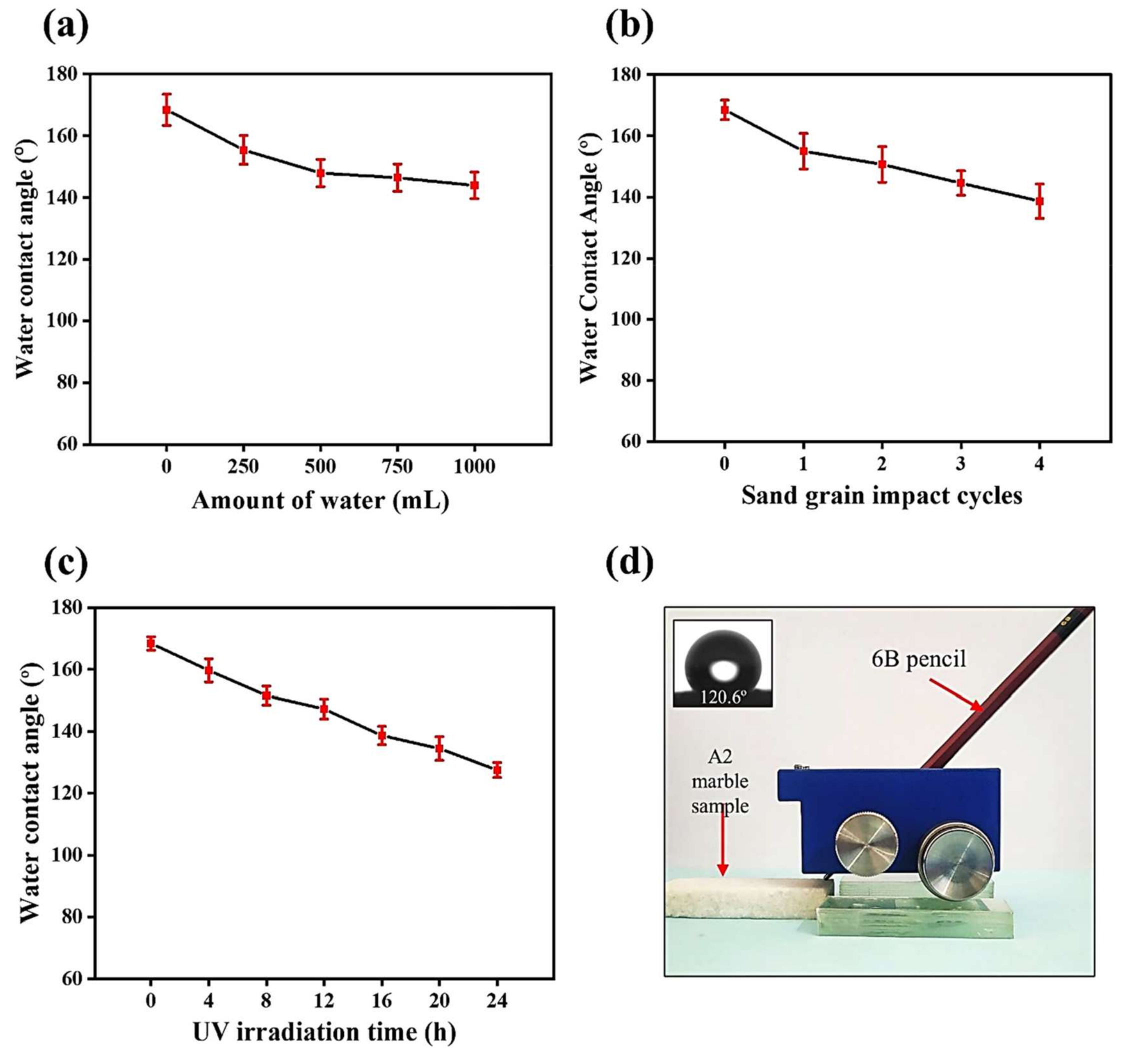

Figure 8. (a) Changes in WCA after each 250 ml of water impacting up to 1000 ml, (b) changes in WCA after each 5 g of sand impacting up to 20 g, (c) changes in WCA after each 4 h UV irradiation up to 24 h, (d) optical photograph during the pencil hardness test, inset image of WCA after the test.

exhibiting diminished superhydrophobicity. After eight abrasion cycles, the WCA further decreased to 129.2°. The detachment of the composite material is attributed to weak hydrogen bonding between the particles within the coating [22]. The coating material detached from the marble surface during the abrasion is shown in figure S1(g). To present more accurate evidence regarding the outcomes of this research, we conducted water droplet bouncing tests to evaluate the superhydrophobic coating's durability under mechanical stress. After two abrasion cycles, the water droplets continued to bounce, suggesting the coating retained its properties. However, after a third cycle, the droplets showed signs of adhesion, indicating a decrease in hydrophobicity. By the end of five cycles, the droplets fully adhered to the surface and failed to bounce. Video 2 visualizes the actual behavior of a bouncing water droplet on coated marble after the abrasion test. These findings reveal that the superhydrophobic coating's integrity significantly degrades with mechanical wear, likely due to structural damage, highlighting the need for developing more durable materials.

The water droplet impact test is an important experimental method for assessing the effectiveness and durability of superhydrophobic coatings during the rainy season. By dropping controlled water droplet impacts on the A2 marble surfaces, we have evaluated their ability to repel water. In this experiment, water droplets were directed onto a marble surface from a controlled height. The setup involved a 20 cm distance between the lower end of a resonating bottle and the A2 marble sample. To ensure stability, the sample was securely attached to an inclined platform at a 40° angle using double-sided tape. We initiated the droplet impacts with a resonating bottle filled with 250 ml of water. As a result of continuous impacts for 1000 ml of water droplets, we observed a decrease in the wettability of the coated surface, indicated by a reduction in the WCA from 168.5 ± 2.5° to 144 ± 4.3° (figure 8(a)). Coating maintained its SHP properties only up to 250 ml of water droplets impacting.

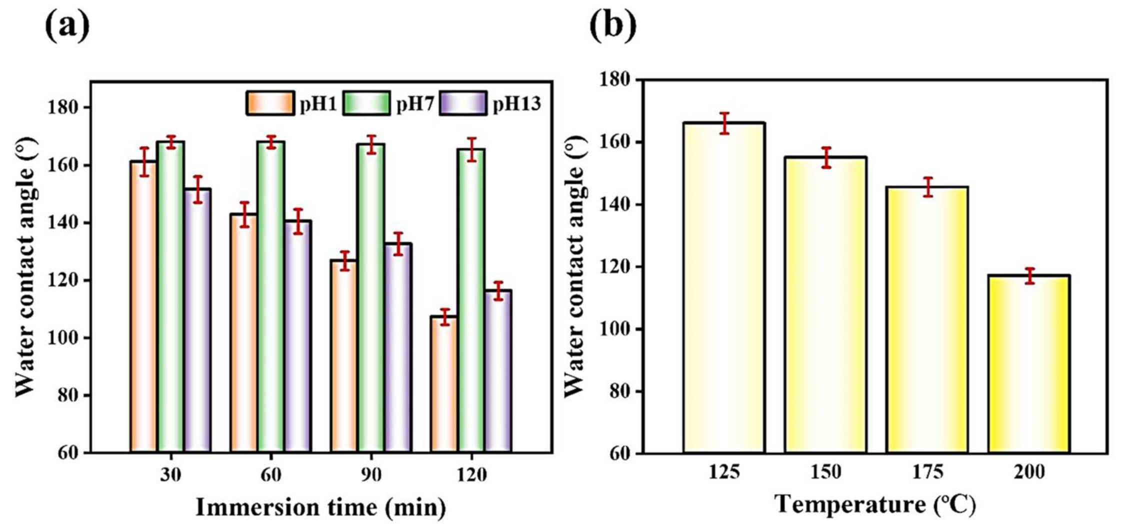

Figure 9. (a) The variation in WCA of the SHP A2 sample was evaluated after immersion in solutions of pH 1, 7, and 13 at 30 min intervals, and (b) variation in WCA after treating marble at 150 °C, 175 °C, and 200 °C for 1 h.

Repeated impingement can dislodge weakly bound surface particles, smooth out micro/nanoscale structure, resulting in the shift from the Cassie–Baxter state to a more wetted Wenzel state. This structural deterioration diminishes air trapping at the interface, reducing the water-repellent characteristics of the coating. Additionally, we tested the non-wetting stability of the coating on the A2 marble using a water jet impact test. A 10 ml syringe (Nozzle Diameter-50 mm) was employed to deliver a precise jet on the coating in a repeated manner. In which the coated A2 marble surface was exposed to a water jet stream at a flow rate of approximately 7.692×10^{-4} ml s^{-1} (7.692×10^{-7} l s^{-1}) for a continuous duration of 13 s. The coating maintained its superhydrophobicity, with minimal reduction in WCA and no visible structural damage, demonstrating its resilience against high-velocity water impact. After the water jet impact test, the water droplets were released on the marble surface from the top. We observed that the water droplet quickly bounced back, indicating that the coating retained its superhydrophobicity even after being hit by the water jet (Video 3). The coating successfully passed the water jet impact test, demonstrating its ability to withstand continuous water exposure.

To determine the mechanical endurance of the coating under simulated sandstorm circumstances, a series of sand impact tests was performed on the A2 marble sample. Each impact cycle used 5 g of sand, with the sample positioned 20 cm below the lower end of a sand container. A total of four impact cycles were completed. Figure 8(b) shows that the WCA decreases gradually as the number of impact cycles increases. After three cycles, sand impact of 15 g, the coating demonstrated a small decline in superhydrophobicity, with a WCA of around 144.6 ± 4°, showing adequate resistance to mechanical deterioration under simulated sandstorm conditions.

Ultraviolet (UV) resistance of superhydrophobic materials is vital for coatings applied to marble, commonly used outdoors [25]. These coatings protect marble from UV damage while preserving the superhydrophobic properties. The TEOS-PDMS-coated A2 marble can withstand continuous UV irradiation for up to 4 h. However, as seen in figure 8(c), superhydrophobic characteristics degrade gradually up to 24 h, as shown by a reduction in the static WCA (130 ± 2.4°). This reduction is attributed to the UV-induced photodegradation of the PDMS in the coating [26]. This degradation diminishes the coating's hydrophobicity, resulting in a lower WCA. Therefore, developing durable UV-resistant coatings is essential to retain the superhydrophobic qualities of marble in outdoor applications.

The pencil hardness test determined the pencil hardness of the TEOS-PDMS-coated A2 marble surface. For this test, pencils with hardness ratings 6B and 5B were used. A pressure of 1420 g, equal to the weight of the instrument, was applied to the pencil tip, which was positioned at a 45° angle to the coated surface. The setup was moved slowly and steadily along the coating, ensuring the pencil lead remained in continual contact with the surface, as shown in figure 8(d). Observations confirmed that the coated layer was completely removed from the dragged region, leaving no visible coating remnant. The inset image shows that the WCA reached 120° after using a 6B pencil. Also, the coating performed poorly in cross-cut tests, earning a 5 rating, which means the tape peeled >65% coating material from the surface.

3.3.2. Chemical and thermal stability

The chemical stability of TEOS-PDMS-coated superhydrophobic marble surfaces is vital for their effectiveness, especially in harsh environments. The TEOS-PDMS coating enhances hydrophobic properties by combining TEOS's cross-linked silica network with

Table 1. A comparative study of current research on superhydrophobic-coated marble in relation to previously reported findings.

			Mechanical durability tests					
Materials	Method	WCA/WSA (°)	Adhesive tape peeling (cycles)	Sandpaper abrasion (cycles)	Water impact (mL)	Chemical stability (h)	UV Stability (h)	References
Tetraethoxyorthosilicate, polydimethylsiloxane	Spray	168.5/4	16	08	250	0.5	08	Present work
Tetraethoxyorthosilicate, 1H,1H,2H,2H-perfluorooctyl triethoxysilane	Brush, spray, and dip	172.5/2.3	—	—	—	—	—	[29]
Sodium silicate solution, trimethylchlorosilane	Spray	166.5	—	5	—	—	—	[30]
Water-based stone protective reagent (DC-30, containing mainly octyl silane and siloxane)	Spray	158/5	—	1	18	—	—	[31]
ZnO nanoparticles, SiO_2 nanoparticles, fluorocarbon compound	Spray	163.6	—	—	—	—	300	[32]
Protectosil SC 30, Zinc oxide (ZnO) nanoparticles	Pipette	153	25	—	—	—	—	[33]
Dodecyltrimethoxysilane, SiO_2 and TiO_2 nanoparticles,	Pipette	152.1	—	—	—	—	144	[34]
Oigomeric ethoxysilane, polydimethylsiloxane, SiO_2 nanoparticles	Spray	~150–155	70	—	—	—	—	[35]
Tetraethoxyorthosilicate, Polydimethylsiloxane, Hydroxyapatite	Brush	127.5	—	—	—	16	—	[14]
Tetraethoxyorthosilicate, 1H,1H,2H,2H-perfluorooctyl triethoxysilane	—	130	—	—	—	—	—	[36]

PDMS's low-surface-energy characteristics. Its interaction with alkaline and acidic chemical reagents can impact stability and functionality. Superhydrophobic A2 marble samples were immersed in solutions with pH 1, 7, and 13 for 30, 60, 90, and 120 min. The samples' WCAs were recorded at 30 min intervals. The WCA steadily reduced in the acidic solution (pH 1), and the sample lost its superhydrophobicity after 30 min of immersion (figure 9(a)). The optical photograph of the A2 sample after the immersion test in pH 1 is shown in figure S2(a) in the supporting information. The marble sample turns yellowish due to etching. Similarly, the WCA in the basic solution (pH 13) declined over time, and the sample lost its superhydrophobicity after 30 min of immersion.

In contrast, the sample immersed in a neutral solution (pH 7) maintained its superhydrophobicity throughout the test. The chemical deterioration of the TEOS-PDMS-coated A2 marble's coating is responsible for the loss of superhydrophobicity in both acidic (pH 1) and basic (pH 13) solutions. The optical photograph of the A2 sample after the immersion test in pH 7 and pH 13 is shown in figures S2(b) and (c), respectively, in the supporting information. In basic conditions, hydrolysis of the silica network weakens the coating, whereas in basic settings, alkali-induced etching destroys the surface structure, impairing its hierarchical roughness and hydrophobicity. This resistance under neutral conditions demonstrates the TEOS-PDMS coating's efficiency as a protective barrier against chemical degradation, highlighting its potential for use in chemically demanding situations.

The thermal stability of the TEOS-PDMS-coated superhydrophobic A2 marble was evaluated by heating the A2 sample for one hour at temperatures of 150 °C, 175 °C, and 200 °C. Figure 9(b) shows the variation in WCA after treating the marble at these temperatures. The coating maintained its superhydrophobicity up to 150 °C, as indicated by the retention of high WCA values. However, as the temperature increases beyond 150 °C, the superhydrophobic performance decreases, likely due to the degradation of the hydrophobic functional groups necessary for maintaining elevated WCA values. High temperatures can break the siloxane bonds in PDMS, thereby diminishing the coating's low-energy properties and reducing its hydrophobicity. In addition to changes in WCA, heat treatment caused noticeable color changes on the marble surfaces, suggesting that the coating may have undergone chemical changes [27]. This color shift could be attributed to oxidation processes or alterations in the nanocomposite matrix, which would superhydrophobic coating [28]. The optical photograph of the A2 sample after being thermally treated at 150 °C, 175 °C, and 200 °C for 1 h is shown in figures S2(d)–(f) in the supporting information. Therefore, while the TEOS-PDMS coating demonstrates strong water repellency under moderate thermal exposure, its durability decreases at elevated temperatures, limiting its applicability in high-temperature environments. The results of mechanical durability and chemical and thermal stability studies of the as-prepared A2 marble were compared with previous reports, and are summarized in the table 1.

4. Conclusions

In summary, we developed superhydrophobic coatings on marble by applying a layer of PS and PDMS-modified silica particles using a spray coating technique. Surface analysis of the coated marble revealed a Bunny Ear Cactus leaf-like surface structure, resulting in a rough texture and reduced surface energy that significantly enhances hydrophobicity. The coated marble displayed an impressive WCA of 168.5 ± 2.5°, indicating its exceptional water repellency, and a WSA of 4 ± 1°, which reflects efficient droplet runoff. The surface energy of the coated marble was calculated to be 1.44 mN m^{-1}, which is markedly lower than that of the uncoated marble, measured at 66.97 mN m^{-1}. This reduction in surface energy contributes to the enhanced superhydrophobic properties of the coated marble. Additionally, the solid–liquid fraction of the coated surface was determined to be 1.8502, further corroborating its optimized surface characteristics. In terms of long-term durability, the superhydrophobic coating demonstrated high robustness under rigorous testing. It maintained its effectiveness even after 10 adhesive tape cycles, 04 sandpaper abrasion cycles, exposure to 250 ml of water droplet impacts, and assessments of water jet impact. Additionally, the developed coating showed excellent chemical resistance against alkaline, neutral, and acidic solutions, as well as thermal stability. The coated surface exhibits a slight change in gloss due to the formation of micro/nano-structures; no noticeable discoloration or opacity was observed upon visual inspection. These results show great potential for real-world use in protecting marble-based cultural heritage, especially against water damage, weathering, and pollution. The easy-to-scale fabrication process, along with the coating's strong durability, makes it a practical choice for preserving historic stone structures. However, more research is needed to understand how well the coating holds up under long-term UV exposure and varying climates. Future improvements could include adding features like antimicrobial or anti-graffiti properties to better protect monuments in polluted urban areas. While the current coating avoids harmful fluorinated chemicals, further work should aim to make it even more eco-friendly by using biodegradable or bio-based materials.

Acknowledgments

One of the authors, SSL is grateful for financial assistance received through Seed Money Scheme from Vivekanand College, Kolhapur (An Empowered

Autonomous Institute), Ref. No. VCK/3108/2023-24 dated 30/03/2024.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

Akshay R Jundle
Conceptualization (equal), Investigation (equal), Methodology (equal), Writing – original draft (equal)

Sagar S Ingole
Data curation (equal), Methodology (equal)

Pradip P Gaikwad
Data curation (equal), Investigation (equal)

Rutuja A Ekunde
Data curation (equal), Methodology (equal)

Rajaram S Sutar 0000-0002-9184-5038
Investigation (equal), Methodology (equal), Writing – original draft (equal)

Shanhu Liu 0000-0003-1382-7157
Supervision (equal), Validation (equal), Writing – review & editing (equal)

Sanjay S Latthe
Funding acquisition (equal), Supervision (equal), Validation (equal), Writing – original draft (equal)

References

[1] Mariani A and Malucelli G 2023 Consolidation of stone materials by organic and hybrid polymers: an overview *Macromol. Chem. Phys.* **224** 2300053

[2] Sawdy A and Price C 2005 Salt damage at Cleeve Abbey, England: Part I: a comparison of theoretical predictions and practical observations *Journal of cultural heritage* **6** 125–35

[3] Warscheid T and Braams J 2000 Biodeterioration of stone: a review *Int. Biodeterior. Biodegrad.* **46** 343–68

[4] Khallaf M, El-Midany A and El-Mofty S 2011 Influence of acrylic coatings on the interfacial, physical, and mechanical properties of stone-based monuments *Prog. Org. Coat.* **72** 592–8

[5] Brand J, Maximova K, Madden S, Wain A, Rode A V and Rapp L 2023 Femtosecond pulse laser cleaning of Makrana marble *Appl. Surf. Sci.* **641** 158484

[6] Brand J, Wain A, Rode A V, Madden S, King P L, Mohan M, Kaluarachchi W, Ratnayake J and Rapp L 2023 Femtosecond pulse laser cleaning of biofilm and dirt: preserving the Sydney Harbour bridge *Journal of Cultural Heritage* **60** 86–94

[7] Xu Z, Bai Y, Yan J, Liu X and Yang J 2025 An experimental study on laser cleaning of the soot deposition layer on a white marble surface *Surfaces and Interfaces* **56** 105533

[8] Atanassova V, Dinu M, Polizu S-R and Radvan R 2023 Photonic applications for restoration and conservation of 19th century polychrome religious wooden artworks *Coatings* **13** 1235

[9] Gomes V, Dionísio A, Pozo-Antonio J S, Rivas T and Ramil A 2018 Mechanical and laser cleaning of spray graffiti paints on a granite subjected to a SO2-rich atmosphere *Constr. Build. Mater.* **188** 621–32

[10] Pinho L and Mosquera M J 2011 Titania-silica nanocomposite photocatalysts with application in stone self-cleaning *The Journal of Physical Chemistry C* **115** 22851–62

[11] Adamopoulos F G, Vouvoudi E C, Achilias D S and Karapanagiotis I 2021 Fluorosilane water-repellent coating for the protection of marble, wood and other materials *Heritage* **4** 2668–75

[12] Kapridaki C and Maravelaki-Kalaitzaki P 2013 TiO2–SiO2–PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection *Prog. Org. Coat.* **76** 400–10

[13] Illescas J F and Mosquera M J 2011 Surfactant-synthesized PDMS/silica nanomaterials improve robustness and stain resistance of carbonate stone *The Journal of Physical Chemistry C* **115** 14624–34

[14] Luo Y, Xiao L and Zhang X 2015 Characterization of TEOS/PDMS/HA nanocomposites for application as consolidant/hydrophobic products on sandstones *Journal of Cultural Heritage* **16** 470–8

[15] Lee E-J, Deka B J, Guo J, Woo Y C, Shon H K and An A K 2017 Engineering the re-entrant hierarchy and surface energy of PDMS-PVDF membrane for membrane distillation using a facile and benign microsphere coating *Environmental Science & Technology* **51** 10117–26

[16] Liu Y and Liu J 2016 Synthesis of TEOS/PDMS-OH/CTAB composite coating material as a new stone consolidant formulation *Constr. Build. Mater.* **122** 90–4

[17] Liu Y, Lin Q, Chen J, Shao Y, Wang Y and Wang J 2022 PDMS-OH and nano-SiO2 Modified KH570-TEOS silica-sol coating and protective effect on concrete *Colloids Surf., A* **648** 129279

[18] Su X, Li H, Lai X, Zhang L, Wang J, Liao X and Zeng X 2017 Vapor–liquid sol–gel approach to fabricating highly durable and robust superhydrophobic polydimethylsiloxane@ silica surface on polyester textile for oil–water separation *ACS Appl. Mater. Interfaces* **9** 28089–99

[19] Eduok U, Faye O and Szpunar J 2017 Recent developments and applications of protective silicone coatings: a review of PDMS functional materials *Prog. Org. Coat.* **111** 124–63

[20] Almeida J, Castro A, Lancastre J, Salvado I M, Margaça F, Fernandes M, Ferreira L and Casimiro M 2014 Structural characterization of PDMS–TEOS–CaO–TiO2 hybrid materials obtained by sol–gel *Mater. Chem. Phys.* **143** 557–63

[21] Ingole S S, Jundle A R, Gaikwad P P, Ekunde R A, Sutar R S and Latthe S S 2024 *ChemSci Advances* **1** 21–7

[22] Wang T, Lei C H, Liu D, Manea M, Asua J M, Creton C, Dalton A B and Keddie J L 2008 A molecular mechanism for toughening and strengthening waterborne nanocomposites *Adv. Mater.* **20** 90–4

[23] Esmeryan K D, Castano C E, Chaushev T A, Mohammadi R and Vladkova T G 2019 Silver-doped superhydrophobic carbon soot coatings with enhanced wear resistance and anti-microbial performance *Colloids Surf.* A **582** 123880

[24] Qu M, Ma L, Hou L, Yuan M, He J, Xue M, Zhou Y, Liu X and He J 2019 Fabrication and color-gradient control of colorful superhydrophobic materials with mechanical durable, oil/water separation and recyclable properties *Appl. Surf. Sci.* **466** 328–41

[25] Mohamed M, Adel O and Khamis E 2023 Fabrication of biochar-based superhydrophobic coating on steel substrate and its UV resistance, anti-scaling, and corrosion resistance performance *Sci. Rep.* **13** 9453

[26] Han X, Xu Y, Han Y, Wang Y, Wang J, Li X, Wu F, Wang B and Lu C 2024 One-step light-induced hierarchical surface wrinkles on photodegradable polymer films *Polym. Degrad. Stab.* **228** 110924

[27] Toniolo L, Poli T, Castelvetro V, Manariti A, Chiantore O and Lazzari M 2002 Tailoring new fluorinated acrylic copolymers as protective coatings for marble *Journal of cultural Heritage* **3** 309–16

[28] Wang G, Chai Y, Li Y, Luo H, Zhang B and Zhu J 2023 Sandstone protection by using nanocomposite coating of silica *Appl. Surf. Sci.* **615** 156193

[29] Adamopoulos F G, Vouvoudi E C, Pavlidou E, Achilias D S and Karapanagiotis I 2021 TEOS-based superhydrophobic coating for the protection of stone-built cultural heritage *Coatings* **11** 135

[30] Zulfiqar U, Awais M, Hussain S Z, Hussain I, Husain S W and Subhani T 2017 Durable and self-healing superhydrophobic surfaces for building materials *Mater. Lett.* **192** 56–9

[31] Xu K, Ren S, Song J, Liu J, Liu Z, Sun J and Ling S 2021 Colorful superhydrophobic concrete coating *Chem. Eng. J.* **403** 126348

[32] Chai Y, Li Y, Wang W, Shi P, Luo H, Ma T, Zhao X, Zhang B and Zhu J 2023 Sandstone monuments still standing after storms: waterproofing and durability protection *Journal of Cultural Heritage* **62** 242–50

[33] Manoudis P N, Zuburtikudis I, Konstantopoulos G, Khalifeh H A, Kottaridi C and Karapanagiotis I 2024 Superhydrophobicity, photocatalytic self-cleaning and biocidal activity combined in a siloxane-ZnO composite for the protection of limestone *Biomimetics* **9** 573

[34] Peng M, Wang L, Guo L, Guo J, Zheng L, Yang F, Ma Z and Zhao X 2022 A durable nano-SiO2-TiO2/dodecyltrimethoxysilane superhydrophobic coating for stone protection *Coatings* **12** 1397

[35] Carrascosa L A, Zarzuela R, Botana-Galvín M, Botana F J and Mosquera M J 2022 Achieving superhydrophobic surfaces with tunable roughness on building materials via nanosecond laser texturing of silane/siloxane coatings *Journal of Building Engineering* **58** 104979

[36] Sharifzadeh S, Hassanajili S and Rahimpour M 2013 Wettability alteration of gas condensate reservoir rocks to gas wetness by sol–gel process using fluoroalkylsilane *J. Appl. Polym. Sci.* **128** 4077–85