

SUPERHYDROPHOBIC NANOCOATING AND THEIR MECHANICAL STABILITY FOR BUILDINGS MATERIALS APPLICATION

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Abstract

Superhydrophobic durability or robustness refers to the ability of a superhydrophobic coating to maintain its structure and resist external mechanical damage over time since it depends on this ability to be marketable. We developed a superhydrophobic coating surface based on a composite of SiO2-nanoparticles, polystyrene (GPPS), and a non-solvent. The SiO₂/GPPS superhydrophobic composite coating has an apparent static contact angle (ASCA) with water of ~156.72 \pm 0.53° and a water slip angle of ~3.5 \pm 0.32°, these values are similar when the superhydrophobic coating are applied on different substrates surfaces. The durability of the superhydrophobic coating was investigated by applying different tests both in laboratory conditions and in natural environments. After each test, changes in the topography (mechanical wear) of the coating surface were examined by scanning electron microscopy. The superhydrophobic coating on quarry table tile substrate showed outstanding resistance against mechanical damage, including sticking, tangential abrasion, sharp scratching, thermal stability, and chemical corrosion while retaining its superhydrophobicity. The coated quarry table tile also showed excellent durability against the impact of water drops, but poor stability to ultraviolet (UV) radiation, and more importantly, the ceramic essentially showed high repellency to different liquids and, moreover, showed remarkable self-cleaning effect, highlighting its potential use in various practical applications.

Keywords: Superhydrophobicity, Polystyrene Nanocomposite, Self-cleaning Surface, Mechanical Durability, Spray Coating, Sol-Gel Method, Robust Coating.

1. Introduction

The ability of superhydrophobic surfaces to stay dry [1], self-cleaning [2], and anti-corrosion [3] is one of the most discussed topics at the present due to several practical applications across a wide range of areas, including buildings [4], textiles [5], medicine [6], drag reduction during fluid transportation [7, 8] and many others. It is well known that when water droplets get into contact with these surfaces, they must have high apparent static contact angles (> 150°) and low rolling-off angles (< 10°). This is possible for surfaces that have low-surface-energy chemistry and micro- or nanoscale surface roughness, which minimizes contact between the liquid and the solid surface [9 – 11]. Nevertheless, rough surfaces, where only a small fraction of the total area is in contact with the liquid, are very fragile and can be easily destroyed by light friction on the surface.

Up to date, most superhydrophobic surfaces have poor durability and tend to lose their anti-wetting properties even a slight friction or mechanical contact on the surface. The problem of durability or stability refers to wear by exploiting the hierarchical roughness or wear of the low surface energy coating or damage of both. However, mechanical contact not only causes damage to roughness topography but also surface contamination, which shortens the lifetime of superhydrophobic surfaces despite the self-cleaning effect. Thus, durability knowledge of a water-repellent surface is extremely important for applications in practical life, which determines whether superhydrophobic surfaces can be used in the area, and the performance of the devices in the long-term operation [12].

Nowadays, studies have begun to address the mechanical durability and a lot of characterization technique have been proposed, probing different aspects of durability on such surfaces (i.e., mechanical abrasion, dynamic impact, chemicals, severe environmental conditions, etc.) [13]. This in turn has led to the invention of new and more durable superhydrophobic surfaces. A few recent reviews exist which cover some aspects of characterization, enhancing the robustness of the hierarchical structure, and fabricating with hydrophobic materials. Several new strategies have been developed to address and solve this issue, for example, the use of a bonding layer [14, 15] strengthens the bond between the coating and the substrate, the random introduction of discrete microstructures [16 – 18] withstands the force of abrasion allowing the abrasion to wear away the top layers of the self-similar structure, these strategies have resulted in only modest improvements in robustness. To date, new strategic designs continue to be implemented to improve the mechanical

robustness of superhydrophobic coatings. Therefore, more efforts are still required to develop a highly robust superhydrophobic surface for industrial applications.

In this research, we successfully developed a semi-transparent, and mechanically stable superhydrophobic coating by Sol-Gel method. The product can be easily applied by Spray-coating technique on different kinds of solid substrates to create superhydrophobic surfaces with extremely high-water contact angles and low roll-off angles. The fabricated superhydrophobic surfaces were applied on different substrates, their repellency with different liquids was treated, and their self-cleaning effect was tested with water drops. The developed coatings were tested under adverse conditions such as tangential abrasion, temperature, tape peeling, sharp scratching, chemical corrosion, water droplet impact, and the severe environment.

The developed coating exhibits excellent stability for various wear tests and its self-cleaning effect promotes great potential for practical outdoor applications. In brief, the design and fabrication of durable and chemically stable superhydrophobic surfaces has become increasingly significant and practical.

2. Experimental Section

2.1. Materials

General Purpose Polystyrene granules (GPPS grade HF 777), melt flow index (MFI)=8 g/10 min obtained from Resirene S.A. of C.V. (CDMX, Mexico). Hydrophobic Fumed Silica (HFS, AEROSIL R972) (Silica, SiO₂) purchased from First Quality Chemicals, S.A. of C.V. (State of Mexico, Mexico) and used as received. AEROSIL R972 is a fumed silica after-treated with DDS (Dimethyldichlorosilane), it has a specific surface area of 90-130 m2/g and primary particle size of 16 nm. Tetrahydrofuran (THF) and Absolute Ethyl Alcohol (Ethanol, EtOH) were supplied from Merck (Darmstadt, Mexico) and used as received.

2.2. Methods

2.2.1. Preparation of the coating solution

The precursor coating solution was prepared as follows. GPPS solution at 2 wt% was prepared by dissolving GPPS granules into the solvent (THF) at

room temperature for 30 minutes, then, EtOH was slowly added to complete a solvent-nonsolvent ratio of 75:25 (THF/EtOH) and stirring for 15 minutes. Finally, a known amount of SiO_2 -nanoparticles (36 wt%) were dispersed with the master solution while magnetically stirring for 1 hour until a homogeneous mixture was obtained.

The variables conditions for the superhydrophobic coating were content of SiO_2 -nanoparticles at 36 wt%, substrate temperature at 150 °C, and substrate drying time at 50 min. Under these conditions, the surface is extremely rough, inducing non-wetting properties that are virtually unaffected by the underlaying substrate.

2.2.2. Deposition of the coating solution



Figure 1. Image of the experimental spray coating set-up (airbrush + hot plate).

The coating solution were deposited by using the configuration in our previous paper. A simple commercial airbrush (Trupper Aero-35) system supplied by air compressor and fixed on a mechanic arm over a hot plate was used for the spray-coating. The spray distance from the substrate was held constant at 25 cm and air pressure at 45 psi. The solutions were sprayed onto clean substrates for 5 s. This procedure was repeated for 5 times with a time interval of 2 min. The airbrush was slowly moved laterally to make a uniform coating on the substrates. All films were made by this configuration technique. The representative image of the airbrush spray-coating setup is shown in Figure 1. For all substrates, the substrate temperature at 150 °C and the substrate drying time at 50 min. These precursor coating preparation conditions induce non-wetting properties that are virtually unaffected by the underlying substrate.

2.3. Characterizations

2.3.1. Superhydrophobic properties measurements

The surface roughness parameter (average roughness, Ra) was obtained by Dektak3 Surface Profilometer. The arithmetic average roughness value Ra reacts to hills and valleys, the measured length (ln) was $2000 \,\mu\text{m}$ at a speed of $2\,\mu\text{m/s}$. Apparent Static Contact Angle (ASCA) measurements of the superhydrophobic films were performed by the sessile drop method using a micro-pipette and tap water. The reported ASCAs are the mean values of measurements on a 10 μL water droplet at five different positions on each sample. Roll-off /Sliding Angles (SA) were determined by slowly tilting the sample stage until the 10 μL water droplet started to move. This measurement was performed 5 times for each sample, and all reported ASCA and SA are averages of the five measurements.

2.3.2. Superhydrophobic robustness tests

2.3.2.1. Adhesion test

Tape-peeling test was conducted to assess the adhesion stability of the hybrid superhydrophobic coating. The tape-peeling test was carried out using a 3M duct tape, based on the ASTM D3359-02 standard. The tape has a thickness of 0.19 mm and width of 46 mm which is just enough to cover the surface of the substrate. The pressure was laid by using a cylindrical aluminum block (5.0 kg) as a roller (Figure 2) across the coated surface to ensure a good contact with the coating, then slowly pulled away from the sample surface, and this process was repeated for 10 times at the sample place using a new tape. The non-wetting properties, i.e., apparent static contact angle (ASCA) and sliding angle (SA) are evaluated after each peeling cycle.



Figure 2. Photograph showing the tape-peeling test.

2.3.2.2. Tangential abrasion test

Wear abrasion test was conducted as illustrated in Figure 3. In this test, the sample is positioned on a 600-grit size sandpaper with the coated surface in contact with the sandpaper and on top of samples surface placed 320 g of weight is placed. In the first step, the sample travels a distance of 10 cm on the sandpaper, and then the sample is rotated 90°. In the second step, the sample returns to its original position with a travel distance of 10 cm. These two steps are considered as one abrasion cycle. A total of 10 abrasion test cycles are carry out that correspond to a total travel distance of 200 cm. The pressure applied on the surface during the test was approximately 2.33 kPa, according to the size of the piece of quarry table tile of 45 x 30 mm and 320 g of weight on it. After each abrasion, the superhydrophobic surfaces were cleaned by blown with air. The values of the ASCA and SA measurements were taken after every abrasion linear cycle on the material.



Figure 3. Photograph of the abrasion test of superhydrophobic surface.

2.3.2.3. Sharp scratch test

The sharp object scratch test was conducted by using a steel blade as the indenter. The coated samples were placed on a flat smooth stage. The flat steel blade was then dragged by hand in two directions perpendicular to the sample dimensions. In this test, the pressure applied to the top surface of the superhydrophobic film is sufficient to severe damage it.

2.3.2.4. Dynamic impact test

Water-droplet impact experiment was performed and the impingement process of water droplets on the surface was captured by a high-speed camera fitted with a macro lens. The continuous water drops apparatus was homebuilt as shown in Figure 4. The test was carried out following some steps as reported [19 - 21]. The superhydrophobic sample was mounted on a lab tripod stage and place at 35 cm below the shower head water drops exit. The water-droplet impact experiment is supplied with a laboratory peristaltic pump with a velocity of 10 rpm to create a water mass flow rate of 1.8 L/min. Droplets were impacted onto the superhydrophobic sample during 10 min. After drops impact interval, the samples are shaken by hand for 2 minutes to remove embedded drops on the surface, then the tested surface is blown with compressed air 1 minute from approximately 10 cm to remove the drops remaining, all this process was repeated 6 times for a same sample. After 6-time intervals, equaling a total of 60 minutes, the sample was heated at 100 °C for 40 min to evaporate any water trapped inside the surface asperities.



Figure 4. Photo of the water droplets impact test set-up.

2.3.2.5. Environmental test

In order to test the practical performance and durability of the superhydrophobic samples, outdoor weathering test was carried out for a testing period of 2 months (60 days) on the roof of a tall building in Mexico City. Samples were placed horizontally.

Under outdoor weathering, the superhydrophobic coating is exposed against harsh environmental ageing, i.e., heat, moisture, acidic rainfall, and UV radiation. The performance analysis of the superhydrophobic sample was caried out by analysis the ASCA and SA every 10 days till 60 days. ASCA and SA measurements were measured using the same set-up mentioned early at room temperature. The values to be reported are the average of five measurements made on different areas of the sample.

2.3.2.6. Thermal stability test

The effect of thermal stability was performed by heating the superhydrophobic coating into a muffle at a constant temperature. The superhydrophobic samples were exposed to temperatures of 100 °C for 20 days. ASCA and SA values were measured after cooling to room temperature every 5 days.

2.3.2.7. Chemical corrosion test

In this research, we evaluated the acid- and alkali-resistant ability of superhydrophobic of as-prepared material. The ASCAs of acidic and basic aqueous solutions with pH ranging from 1 to 14 were measured. For a pH value, five droplets were placed in different positions for each sample and the ASCA average value was taken as its ASCA value, all measurements were carried out at room temperature.

3. Finding and Discussion

3.1. Wettability of the surfaces: Application on different substrates surfaces a)



Figure 5. Photo of water droplets deposited on different substrates: a) quarry table tile, b) glass coverslip, c) galvanized steel sheet, d) copper sheet, and e) tile.

The methodology development presented has the advantage that it can be easily used to treat surfaces of several kinds of substrate. The evidence for this statement is provided in Figure 5 and Table 1, which show the experimental and observed results of ASCA, SR, and SA measurements, respectively, carry out treated surfaces of tile, galvanized steel sheet, and cooper sheet. For comparison, superhydrophobic properties on glass coverslip and quarry table tile, discussed previously reported, are also included.

Substrate	Predicted values		Superhydrophobic properties		
	ASCA (°)	SR (nm)	ASCA (°)	SR (nm)	SA (°)
Quarry table tile	156.51	54.62	157.19±0.33	55.79±0.35	3.2±0.15
Glass coverslip			156.76±0.52	54.32±0.63	3.4±0.45
Galvanized steel sheet			156.19±0.67	54.06±0.73	3.5±0.13
Cooper sheet			156.19±0.74	55.46±0.43	3.4±0.53
Tile			157.27±0.37	55.75±0.84	3.2±0.35

Table 1. Superhydrophobic properties measured on different substrates.

As we can see, the values of ASCA and SR that correspond to the five substrates are in agreement with the expected experimental value. ASCA, SR, and SA reported in Table 1 for various treated substrates show narrow ranges of variations, this could be attributed to the difference on the roughnesses of the substrate materials. We can say that our superhydrophobic coating deposited on these substrates are not affected by the type of substrate surface.

3.2. Wettability of the surfaces: Application with different kinds of liquids

We evaluated some common liquids, such as tea, orange juice, milk, Coca-Cola, and urine. In Figure 6 droplets of different liquids are shown in the shape of a sphere on the superhydrophobic substrate. The superhydrophobic character of the coated substrate was evaluated as performed a water droplet by measuring the ASCA and SA.

The results are shown in Figure 6, the ASCA of the liquids remained above 150° and the SA below 10°. However, we note that for milk, SA showed a slight increase, this may be due to the fact that the surface tension presented by this liquid is very close to the value of the surface tension of the coating.



Figure 6. a) Photo of the different kinds of liquids on the superhydrophobic quarry table tile substrate, b) ASCA and SA of different kinds of liquids.

3.3. Self-cleaning performance

It is well known that the self-cleaning effect is a significant characteristic of superhydrophobic surface in real application. In this study, natural graphite particles were used as a contaminant to investigate the self-cleaning performance of coated surface. The photographs in Figure 7 illustrate the time sequence of self-cleaning ability. The superhydrophobic substrate was set at a $\sim 8^{\circ}$ tilt.

Figure 7a shows the superhydrophobic substrate clean, i.e., without natural graphite particles. While Figure 7b shows the natural graphite particles that were



Figure 7. Time sequence of the self-cleaning test on the coated surface with ~8° tilt.

deliberately spread on the superhydrophobic coating surface. We observed that, as the water droplets were dropped to the coated surface, the droplets began to roll off swiftly taking away the contaminant particles (Figure 7c, 7d). This behavior is attributed to the joint action of the high capillary forces resulting from the water droplet and the weak adhesion of the contaminant particles to the superhydrophobic coated [7]. Therefore, our superhydrophobic film exhibits an excellent self-cleaning effect and expansive potential application prospects.

3.4. Adhesion performance

Testing the adhesion was the first measurement to be conducted in a test series regarding mechanical durability evaluation of the superhydrophobic film. The results are plotted in Figure 8. As we can see, the superhydrophobic of the hybrid coating can maintain until 8 peel cycles (ASCA ~150 \pm 0.30° and SA ~7.50, Figure 8a). Additionally, the inset photographs show remains of tape on the substrate and that when it was removed it stuck to the film or in any case to the substrate causing loss of superhydrophobicity. On the contrary, we noticed 9 and 10 peel-off cycles caused damage or detachment of the film. This negative trend is evidence of the observation that the film was peeling-off the substrate during latest cycles of testing (Figure 8b), indicating that a little hydrophobic SiO₂-nanoparticles were transferred to the tape surface, leading to an antiwetting performance degradation.

This mechanical adhesion stability indicated that the manufactured superhydrophobic layer had a good adhesion property to the quarry table tile substrate up to 8 peel cycles, proving that the coating could be considered as robust.



Figure 8. a) ASCA and SA measured tape-peeling cycles on the superhydrophobic sample. Insets: photographs of tape test and image of scotch tape surface. b) SEM image after peeling off sticky tape. Inset: ASCA of the coating after 10 tape-peeling cycles.

3.5. Wear abrasion performance

In this research work, the superhydrophobic layer was abraded by sandpaper with 10 abrasion cycles. Figure 9a shows the ASCA and SA for different friction cycles and the insets images of the static water droplets for the 1st and 10th abrasion cycles. It can be seen that as the friction cycles increased from 1 to 8 times under 320 g of weight, the ASCA of the material still maintained more than 150° and SA less than 10°. On the other hand, when the abrasion cycles reached 10 times, the surface lost its superhydrophobicity with a travel distance of 200 cm. Further abrasion of superhydrophobic sample makes it superhydrophobic stick and even large water droplets do not roll off at 90° tilt angles. This is due to physical abrasion and resultant polymer/nanoparticle wear and removal from the surface layer. Inspection of SEM images after 10 ties of wear abrasion cycles supports this statement (see Figure 9b).

After mechanical abrasion cycles, the tests results demonstrated a slight change in superhydrophobic properties, yet the special hybrid coating could efficiently withstand the abrasion cycles to some extent, maintaining its superhydrophobicity.



Figure 9. a) ASCA and SA measured for the abrasion cycles. Inset: shape of the water droplets on the surface. b) SEM image after 10 cycles of abrasion test.

3.6. Sharp scratched performance

To further study the mechanical durability of superhydrophobic films, a sharp scratch test was performed. As shown in Figure 10a, a series of sharp scratches on the as-prepared hybrid material are noticed, indicating that the superhydrophobic material could not stand for sharp scratch test. However, the water droplets on the scratched superhydrophobic surface can still move freely as long as it does not hit a scratch. We also note that, after sharp scratched tests, severe abrasion scratches are observed at macro-scale on the superhydrophobic surface that even the hybrid material could be removed from the substrate. SEM images of the coating after sharp scratched tests showed significant alteration of superhydrophobic surface morphology (Figure 10b), so the superhydrophobic coating cannot pass the sharp scratch test.

The results demonstrate that superhydrophobic films which have a micro-scale topography is not tolerant to damage. In real application, the high sharp scratch can extend the applied range of the superhydrophobic materials.



Figure 10. a) Image of the superhydrophobic coating after abrasion with sharp scratch. b) SEM micrographs of coated substrate after scratching with a knife.

3.7. Water-droplet impact performance

The durability of the superhydrophobic coating was also assessed by a high-speed droplet impact experiment. Figure 11a illustrates the effect of water on the ASCA and SA of the superhydrophobic film immediately after each spray droplet impact interval. It is evident that the average values of ASCA and SA did not experience significant changes after being sprayed for 20 min. After that exposure time, the sample lost its superhydrophobic performance (ASCA <150° and SA >10°). This indicates that the intense water droplet impact test damages the superhydrophobicity of the coating by either removing SiO₂-nanoparticles from the surface of the composite material or by degrading hydroxyl oxide functional groups or other low surface energy functional groups. Upon heating the samples after the spray droplet impact test, the ASCA of the sample recovered to some degree but did not return to its initial value. This indicates that the loss superhydrophobicity property during droplet spraying was not due to mechanical erosion or change in surface morphology, but rather to saturation of the microstructured surface due to water, as can be seen in the SEM image in Figure 11b. This saturation might effectively change the coating surface from the superhydrophobic Cassie-Baxter state to the wetted Wenzel state [19, 22].



Figure 11. a) ASCA and SA details with respect to exposure time of water droplets impact. b) SEM image of surface after exposure to simulated rain.

Studies reported by Zhang *et al.* [16] conclude that when an external force is applied to the surface either by water jet impact, water drop impact, sand particle impact abrasion or direct shear abrasion, water or sand could impregnate into the grooves od the rough texture if the impact force is large enough and subsequently remove part or all of the coverage of the nanoparticle surface of the coating that does not have chemical bond with the substrate.

3.8. Outdoor weather performance

In order to assess the practical long-term performance of the superhydrophobic substrate, it was exposed to outdoor weathering for a 2-months period. For the outdoor weathering experiment, ASCA values are plotted in Figure 12a as a function of time (days), and the inset images show the surface change and degradation of the superhydrophobic film over the days. From Figure 12a, it is observed that the apparent static contact angles decrease abruptly linearly from $161.58\pm0.78^{\circ}$ to $86.46\pm0.61^{\circ}$ over two months of outdoor weathering.

We believe that the increase deterioration effect of the superhydrophobic film is due to either the accumulation of dust particles on the samples or the sticking of the dust particles after water droplets evaporate from the surface over time. Moreover, it can be clearly observed from Figure 12b that the coating shows some cracks which are the beginning of the deterioration phenomenon.



Figure 12. a) ASCA and SA with respect to exposure time in days. Inset: Photograph of the sample on a certain day. b) SEM image of the coated sample after outdoor exposure. Inset: Shape of the water droplet on the coated surface.

Studies conducted by Sakhuja *et al.* [23] report that the degradation effect caused by outdoor weathering on their superhydrophobic films decreases as long as they are mounted at an inclination of either 10° or 20°. They hypothesized that when the dirt particles come into contact with nanostructured substrates, they cannot penetrate the nanosized voids between two adjacent nanostructures, but instead settle on the nanostructures surface of the substrate. Therefore, the contaminant particles flow together with the water off the surface, allowing the coated substrates to exhibit a self-cleaning effect compared to horizontally placed samples where the contaminant particles mix with water and remain adhered to the surface of the nanostructured substrate. Thus, the improvement in the self-cleaning effect may be due to the inclination angle of the substrate. Inclination of the substrate has an important effect on self-cleaning behavior, allowing the water flowing over sample to provide a sheeting effect, removing dirt particles more easily during rains.

3.9. Thermal stability performance

The effect of thermal treatment on the wettability of the superhydrophobic coating was systematically studied. The superhydrophobic substrate was heated

at 100 °C for 20 days, the ASCA and SA values were measured at room temperature every 5 days, and the results are shown in Figure 13.

As can be clearly seen in Figure 13a, the composite coating remained superhydrophobic property till 15 days of exposure time into an oven and water drops rolled on the surface of the coating. However, as the exposure time increases to 20 days, ASCA dramatically decrease to 141.73 \pm 0.56° and SA increased to >10°, this could be attributed to the decomposition of GPPS in the coating composite, and some of the GPPS fragments volatilized leading to the water drops wetting the coating surface. Meanwhile, we believe that silica oxide hydroxyl groups could remain on the surface of hydrophobic SiO₂-nanoparticles reacting with each other, and this reaction might also occur between the substrate and the SiO₂-nanoparticles.



Figure 13. a) Effect of temperature on superhydrophobicity. b) SEM image of superhydrophobic coating after 20 days of heating exposure. Inset: ASCA for the sample.

Nevertheless, with the continuous decomposition of the hybrid nanocomposite and the condensation between hydroxyls, the Si-CH₃ groups lead to decomposition, and a mass of Si-OH generated, could result in the superhydrophobicity of the coating. In addition, we can note that the superhydrophobic coating does not suffer physical damage (Figure 13b) but chemical decomposition as we have just described. These results indicate that the thermal stability of our superhydrophobic film could be stable at least for 15 days.

3.10. Chemical corrosion performance

In our previous tests on mechanical stability, the apparent static contact angle (ASCA) and sliding angle (SA) measurements were evaluated by using pure water. However, in practical applications, the majority of liquids are not pure water only.

Thus, it is recommended to study the wettability properties of different liquids with different pH values on the superhydrophobic films. In this research, we evaluated the acid-and alkali-resistant ability of superhydrophobic GPPS film of different liquids with pH ranging from 1 to 14.

Figure 14a shows the relationship between pH values versus ASCA and SA, and the photograph inset shows the shapes of acidic and basic aqueous droplets on the superhydrophobic quarry table tile substrate. As can be seen, water droplets with pH range from 1 to 12 have no significant effect on the ASCA and SA. That is, the ASCASs are larger than 150° and SAs were still less than 10° for corrosive liquids. In addition, when the aqueous liquid droplets contacted with the porous superhydrophobic GPPS film after a short period of time, no decrease in ASCA was observed, this could be due to the mico/nanostructure of the coating did not deteriorate after being in contact with the aqueous solution droplets. Therefore, the water droplet can be moved easily when the surface is slightly tilted. However, for the pH values of 13 and 14, the ASCAs were 132.34±0.38° and 133.11±0.51°, respectively, and the SAs were not possible to measure it for those pH values. In this case, the less ASCA and the high SA observed in alkaline solution is attributed to the chemical wear degradation of the hybrid nanocomposites being faster than in acid solution. As can be seen in SEM image (Figure 14b), the superhydrophobic coating does not suffer physical damage, but the loss of the superhydrophobic property can be due to the chemical wear of the film, this statement must be corroborated by EDS or FTIR measurements, which are not shown in this study. From an experimental point of view, with respect to these results, our superhydrophobic GPPS is suitable for practical applications in corrosive liquids between the 1-12 pH range.



Figure 14. a) ASCA and SA on the superhydrophobic substrate. Inset: Image of the different pH value liquids on the superhydrophobic material. b) SEM image after chemical corrosion test.

The corrosion of strong acidic or basic liquids on a solid surface is known to be great. Therefore, the surface micro/nanostructure found on a solid substrate can be destroyed due to the strong corrosive property when suffering strong acidic or basic aqueous solutions, which may lead to the changes of ASCA and SA because the geometric micro/nanostructure of the surface is an important factor for the wettability of a solid [24, 25].

4. Conclusions

The superhydrophobic coating showed exceptional liquid-repellency to some liquids including water, tea, orange juice, milk, coke, and urine. The substrate shown to have almost no effect on the hydrophobic character of the applied coatings, which were produced on quarry tablet tile, glass coverslip, tile, galvanized steel and copper sheet.

The results demonstrated that the superhydrophobic films present a considerable mechanical resistance toward multi-fold, adhesion, wear abrasion, sharp scratch, water-droplet impact, thermal stability, outdoor weathering, and even chemical corrosion. Our design strategy could also be applied to different kinds of heat-resistant materials, brick, aluminum, or concrete, which are needed to retain effective self-cleaning, anti-fouling or anti-corrosion abilities in harsh operating environments.

A proper control of nanoparticles is one of the main challenges to produce a hierarchical rough surface and, moreover, the mechanisms that trigger the Cassie-Baxter and Wenzel regime transitions still need to be further investigated.

The Sol-Gel method and the Spray-Coating technique are simple and cheap, they demonstrate that the development of superhydrophobic surfaces can be obtained in the laboratory for future research and other application areas.

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References

- Wang, D., Sun, Q., Hokkanen, M. J., Zhang, C., Lin, F.-Y., Liu, Q. et al. (2020). Design of robust superhydrophobic surfaces, *Nature*, 582, 55-59. https://doi.org/10.1038/s41586-020-2331-8
- Wang, X.-Y., Zhang, C., Sun, S., Kalulu, M., Chen, L., Zhou, X. et al. (2019). Durable superhydrophobic coating based on inorganic/organic double-network polysiloxane and functionalized nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 578, 123550.

https://doi.org/10.1016/j.colsurfa.2019.06.016

- Figueira, R. B., Sousa, R., & Silva, C. J. R. (2020). Chapter 3. Multifunctional and smart organic–inorganic hybrid sol–gel coatings for corrosion protection applications. In: A.S.H. Makhlouf, N.Y. Abu-Thabit (Eds.). *Advances in smart coatings and thin films for future industrial and biomedical engineering applications*. Elsevier, Amsterdam, 2019, 57-97. https://doi.org/10.1016/B978-0-12-849870-5.00008-2
- Carrascosa, L. A. M., Facio, D. S., & Mosquera, M. J. (2016). Producing superhydrophobic roof tiles. *Nanotechnology*, 27, 095604. https://doi.org/10.1088/0957-4484/27/9/095604
- Zahid, M., Heredia-Guerrero, J. A., Athanassiou, A., & Bayer, I. S. (2017). Robust water repellent treatment for woven cotton fabrics with eco-friendly polymers. *Chemical Engineering Journal*, 319 321-332. https://doi.org/10.1016/j.cej.2017.03.006
- Hou, X., Wang, X., Zhu, Q., Bao, J., Mao, C., Jiang, L. *et al.* (2010). Preparation of polypropylene superhydrophobic surface and its blood compatibility. *Colloids and Surfaces. B: Biointerfaces*, 80, 247-250. https://doi.org/10.1016/j.colsurfb.2010.06.013
- Bake, A., Merah, N., Matin, A., Gondal, M., Qahtan, T., & Abu-Dheir, N. (2018). Preparation of transparent and robust superhydrophobic surfaces for self-cleaning applications. *Progress in Organic Coatings*, 122, 170-179. https://doi.org/10.1016/j.porgcoat.2018.05.018
- Li, K., Zeng, X., Li, H., Lai, X., & Xie, H. (2014). Effects of calcination temperature on the microstructure and wetting behavior of superhydrophobic polydimethylsiloxane/silica coating. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 445, 111-118. https://doi.org/10.1016/j.colsurfa.2014.01.024.
- 9. Quéré, D. (2008). Wetting and Roughness. Annual Review of Materials Research, 38, 71-99. https://doi.org/10.1146/annurev.matsci.38.060407.132434

- Butt, H.-J., Roisman, I. V., Brinkmann, M., Papadopoulos, P., Vollmer, D., & Semprebon, C. (2014). Characterization of super liquid-repellent surfaces. *Current Opinion in Colloid* & Interface Science, 19(4), 343-354. https://doi.org/10.1016/j.cocis.2014.04.009
- Liu, T.L., & Kim, C.-J. (2014). Repellent surfaces. Turning a surface superrepellent even to completely wetting liquids. *Science*, 346(6213), 1096-1100. https://doi.org/10.1126/science.1254787
- Verho, T., Bower, C., Andrew, P., Franssila, S., Ikkala, O., & Ras, R. H. A. (2011). Mechanically durable superhydrophobic surfaces. *Advanced Materials*, 23(5), 673-678. https://doi.org/10.1002/adma.201003129
- Milionis, A., Loth, E., & Bayer, I. S. (2016). Recent advances in the mechanical durability of superhydrophobic materials. *Advances in Colloid and Interface Science*, 229, 57-79. https://doi.org/10.1016/j.cis.2015.12.007
- Lu, Y., Sathasivam, S., Song, J., Crick, C., Carmalt, C. J., & Parkin, I. P. (2015). Robust self-cleaning surfaces that function when exposed to either air or oil. *Science*, 347(6226), 1132-1135. https://doi.org/10.1126/science.aaa0946
- Zhang, W., Xiang, T., Liu, F., Zhang, M., Gan, W., Zhai, X. et al. (2017). Facile Design and Fabrication of Superwetting Surfaces with Excellent Wear-Resistanc. ACS Applied Materials & Interfaces, 9(18), 15776-15784. https://doi.org/10.1021/acsami.7b02158
- Zhang, Y., Ge, D., & Yang, S. (2014). Spray-coating of superhydrophobic aluminum alloys with enhanced mechanical robustness. *Journal of Colloid and Interface Science*, 423, 101-107. https://doi.org/10.1016/j.jcis.2014.02.024
- 17. Kondrashov, V., & Rühe, J. (2014). Microcones and nanograss: toward mechanically robust superhydrophobic surfaces. *Langmuir*, 30, 4342-4350.
 - https://doi.org/10.1021/la500395e
- Zimmermann, J., Reifler, F. A., Fortunato, G., Gerhardt, L.-C., & Seeger, S. (2008). A Simple, One-Step Approach to Durable and Robust Superhydrophobic Textiles. *Advanced Functional Materials*, 18(22), 3662-3669. https://doi.org/10.1002/adfm.200800755
- Davis, A., Yeong, Y. H., Steele, A., Loth, E., & Bayer, I. S. (2014). Spray impact resistance of a superhydrophobic nanocomposite coating. *AIChE Journal*, 60(8), 3025-3032. https://doi.org/10.1002/aic.14457

- Sanabria-Mafaile, J., San Martin-Martinez, E., & Cruz-Orea, A. (2020). Thermal properties of superhydrophobic films applied in ceramic tiles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 607, 125524. https://doi.org/10.1016/j.colsurfa.2020.125524
- Bhushan, B., & Jung, Y. C. (2011). Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction. *Progress in Materials Science*, 56(1), 1-108. https://doi.org/10.1016/j.pmatsci.2010.04.003
- Davis, A., Yeong, Y. H., Steele, A., Loth, E., & Bayer, I. S. (2014). Nanocomposite coating superhydrophobicity recovery after prolonged high-impact simulated rain. *RSC Advances*, 88, 47222-47226. https://doi.org/10.1039/C4RA08622H
- Sakhuja, M., Son, J., Yang, H., Bhatia, C. S., & Danner, A. J. (2014). Outdoor performance and durability testing of antireflecting and self-cleaning glass for photovoltaic applications. *Solar Energy*, 110, 231-238. https://doi.org/10.1016/j.solener.2014.07.003
- Sun, X. L., Fan, Z. P., Zhang, L. D., Wang, L., Wei, Z. J., Wang, X. Q. et al. (2011). Superhydrophobicity of silica nanoparticles modified with polystyrene. *Applied Surface Science*, 257(6), 2308-2312. https://doi.org/10.1016/j.apsusc.2010.09.094
- Chen, H., Yuan, Z., Zhang, J., Liu, Y., Li, K., Zhao, D. et al. (2009). Preparation, characterization and wettability of porous superhydrophobic poly (vinyl chloride) surface. *Journal of Porous Materials* 16, 447-451. https://doi.org/10.1007/s10934-008-9217-8