

Elastic Superhydrophobic Nanocomposites with Enhanced Mechanical Durability

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ABSTRACT

Here, we report on the development of mechanically durable, superhydrophobic, nanocomposite coatings based on a combination of acrylonitrile butadiene styrene (ABS), hydrophobically modified fumed silica (HMFS) and a commercial rubber product. The coatings are fabricated via spray coating and exhibit superhydrophobic performance with static apparent contact angle (APCA) 153° and roll-off angle (ROA) 8° . The durability of the coatings is evaluated by linear abrasion and tape peeling tests. The samples are able to maintain superhydrophobic performance (ROA $< 10^\circ$) for 160 abrasion cycles under 20.5 kPa applied pressure while they still exhibit good water repellency (ROA $< 40^\circ$) even after 1400 abrasion cycles. Moreover, free-standing and flexible surfaces can be fabricated out of the same components. This technique is simple, efficient and capable of producing low-cost and large surface area, mechanically durable, water-repellent surfaces, and therefore can find many potential applications.

Keywords: ABS, silicon dioxide, superhydrophobic, durability, spray

1 INTRODUCTION

Superhydrophobic surfaces, inspired by the well-known “lotus-effect” where water drops bead up and roll-off on the natural leafs of the plant *Nelumbo nucifera*, are generally characterized by apparent contact angle (APCA) of water greater than 150° and roll-off angles (ROA) lower than 10° . During the past years they have attracted great attention owing to the vast number of applications that are envisioned such as microfluidic devices [1], anti-icing [2] and anti-fouling [3] coatings, sensors [4], oil-water separation [5], droplet manipulation [6], etc. Although it is evident that the potential commercial applications of superhydrophobic surfaces are numerous, their inherent fragile nature and lack of mechanical durability is the major factor that prevents them from being used extensively thus hindering the financial impact of this research field on the market.

During the last years, intensive research has been conducted by several groups towards improving the mechanical performance of superhydrophobic surfaces [7]. Different approaches have been followed for maintaining superhydrophobic performance after mechanical damage of the surfaces. The most common strategy for improving the mechanical durability is to employ materials that can

withstand structural forces while retaining the micro and nano-scale features associated with the surface topology and the hydrophobic composition associated with the surface chemistry.

Two other alternative strategies to maintain liquid repellency include self-healing surfaces [8] and easily repairable surfaces [9]. In particular, self-healing surfaces are able to recover their liquid repellency upon damage by mainly two approaches. The first approach is based on encapsulation of the liquid repellent component in the pores of rough nano-porous materials. When damaged, this component quickly migrates to the damaged surface and recovers its surface properties [10]. The second approach is based on spontaneous self-organization of liquid repellent colloidal particles at interfaces [11]. On the other hand, easily repairable surfaces are materials whose liquid repellent properties can easily be repaired by deposition of a new material. This strategy is suitable for applications that require long-term functionality of the surfaces, yet continuous maintenance is required. However, the self-healing and easily repairable strategies can both be problematic. Specifically, self-healing surfaces once slightly damaged need some recovery time to self-heal which is an issue for applications that demand to retain the liquid repellency continuously. Furthermore, if the damage is significant (e.g. at the micro-scale), self-repair may not be possible since this strategy tends to be focused on the first few nanometers of the surface. The strategy of easily repairable coatings can compensate for micro-scale wear but requires accessibility for maintenance. For many applications where the object to be coated is not easily reachable by workers (wind turbine blades, for instance) or the area to be coated is very large, recoating would be prohibitive due to these technical issues.

In this work, it is demonstrated a facile method for obtaining superhydrophobic surfaces with enhanced mechanical robustness. A spray coating method was followed because it is fast, introduces surface roughness and can be applied on large surface areas. Although many different spray coating methods have been reported, it is hard to find a method that satisfies simultaneously all the criteria that will render superhydrophobic coatings attractive for commercial applications in terms of superhydrophobicity, mechanical durability, low-cost and simple fabrication steps without sophisticated experimental procedures like in the present case.

2 MATERIALS AND METHODS

2.1 Materials

Acrylonitrile Butadiene Styrene (ABS), manufactured as ABS-P430 (Red) in the form of wires, was purchased from Stratasy, USA. Hydrophobically Modified Fumed Silica (HMFS), manufactured as Aerosil R-812 (particle size of 5-50 nm) was obtained from Evonik Industries, Germany. The multi-purpose rubber Plasti Dip™ was obtained from Performix, USA. 1 mm thick multipurpose aluminum alloy 6061 substrate was purchased from McMaster-Carr, USA and was cut in pieces 2.5 cm wide and 5 cm long in order to be used as substrates for the coatings. Before the coating application the substrates were rubbed with P400 grit size sandpaper and cleaned with isopropyl alcohol. All solvents used were of analytical grade.

2.2 Sample Preparation

For the preparation of the nanocomposite coatings, initially ABS and HMFS were dissolved/dispersed in acetone separately (5 wt %). The ABS solution was left overnight until the copolymer completely dissolved and it was stirred prior to every use in order to avoid the precipitation of the butadiene particles. The HMFS dispersion was sonicated for 16 min in order to improve the dispersion of the particles in acetone. 25 ml of ABS and 10 ml of HMFS were mixed subsequently. In a separate vial a 1:1 mixture of Plasti Dip/toluene was prepared and stirred manually until the rubber dissolved completely in toluene. Subsequently 3.5 ml of the Plasti Dip solution were added in the ABS/HMFS mixture. For the spray coating, a VL double action, internal mix, siphon feed airbrush was used (Paasche, USA). The spray distance was held constant at 15 cm approximately and the air pressure was set at 30 psi. Totally 10 ml of the ABS/HMFS/Plasti Dip dispersions were sprayed on the aluminum substrates. After spraying, the samples were thermally cured at 240 °C, a temperature much higher than the melting point of ABS (105 °C). In order to create free standing elastic substrates the procedure followed is depicted in Figure 1a. First the Plasti Dip solution was drop casted on polytertrafluoroethylene (PTFE) substrates and left to cure in ambient conditions overnight. Subsequently the nanocomposite dispersion was sprayed on top and thermally cured with the aforementioned conditions. Finally, the PTFE substrate due to its low surface energy facilitated the peeling off of the fabricated free standing films. The fabricated free standing films were flexible and superhydrophobic (Figure 1b,c).

2.3 Surface Properties Characterization

The APCAs and ROAs of the samples were measured by video based optical contact angle measuring instrument ramé-hart, USA. 10 μ L of deionized water droplets were gently placed, measured and averaged over three different

spots on each sample. For ROA measurement, the substrate was tilted and the angle that the droplet rolled-off from the surface was recorded. All ROA values were averaged over three different measurements on each sample. All measurements were performed in ambient conditions. The morphology of the patterned surfaces was characterized by SEM, FEI Quanta 650, USA.

1. Drop casting of diluted rubber on PTFE substrate.
2. Curing of the rubber in ambient conditions.
3. Spray coating of rubber/ABS/HMFS dispersion.
4. Thermal curing at 240 °C for 30 min.

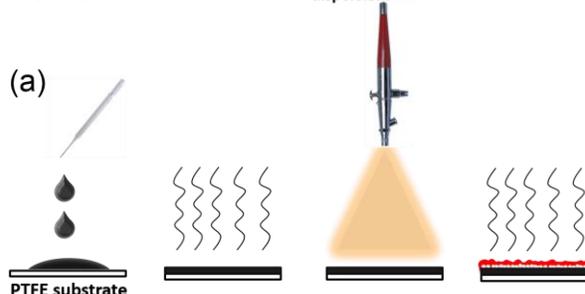


Figure 1: (a) The four main preparation steps for the fabrication of the elastic, free-standing, nanocomposite substrates. (b) The fabricated substrates are elastic and can be folded without losing their properties. (c) Water drops placed on the developed superhydrophobic material.

2.4 Linear Abrasion

To quantify the wear robustness of the coatings, mechanical durability tests were performed with a linear abrader (Taber Industries, USA) under 20.5 kPa applied pressure. WCA and ROA measurements were performed periodically. The abrasant surface of choice was a piece of crocking cloth and the speed used for the mechanical abrasion was held constant at 15 cycles/min.

2.5 ASTM D3359 Adhesion Test

The adhesion to the substrate of the coatings was tested by the ASTM D3359 standard. The coatings were cut with a blade in a cross-cut shape (4x4 lines). The distance from one line to the other was 3 mm. Subsequently a 3M 250 masking tape was placed at an angle of 45° with the lines and pressed continuously on the surface (to avoid air pockets formation underneath). The tape was left for 45 s in order for the adhesive to stick to the coating, then was removed and the sample was examined for damages.

3 RESULTS AND DISCUSSION

Plasti Dip is a moisture-cured, protective, rubber coating that it is specifically designed to adhere very well in metallic and plastic substrates (particularly in ABS since it is used to coat ABS 3D printed objects). Since its adhesion is excellent in both the ABS and the aluminum substrate, it is a very good candidate for promoting strong bonding between the coating and the material. Moreover, its rubbery nature provides elasticity to the coating so that it can dissipate better the applied pressure to the coating during the abrasion while it allows the formation of free standing films on elastic substrates. The ABS provides the tough polymeric matrix that is required for the durability while the HMFS attributes a unique surface texture that promotes water repellency. The role of the HMFS is to induce nanoscale roughness that together with the hydrophobic particle functionalization render the coating superhydrophobic. Figure 2 shows an SEM image of the surface nanoroughness of the fumed silica particles.

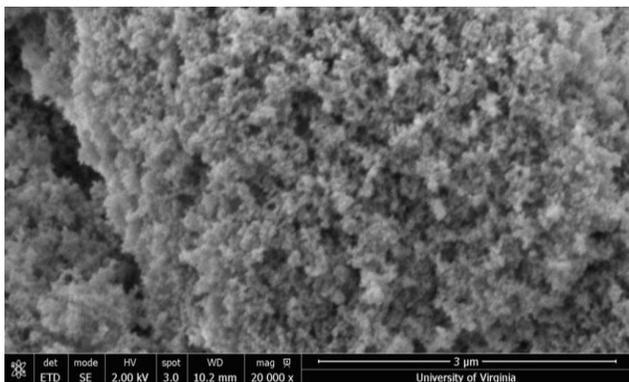


Figure 2: SEM image of the nanoroughness of the HMFS.

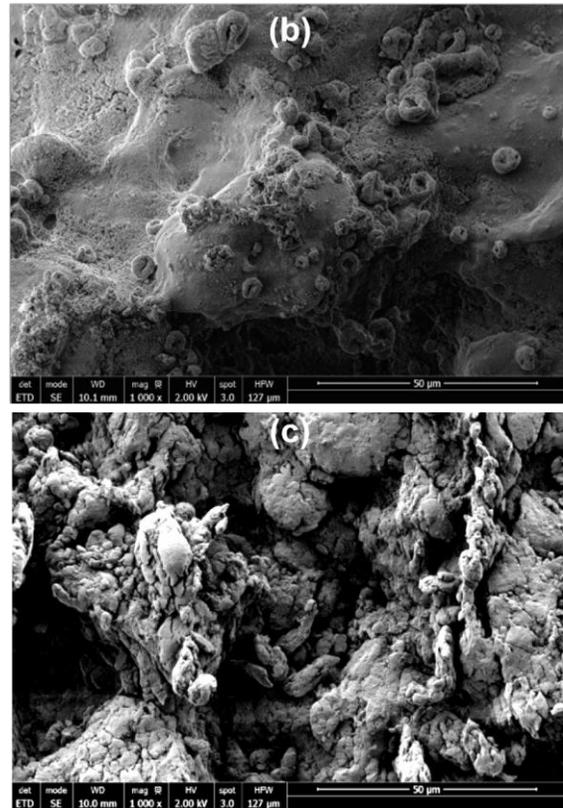
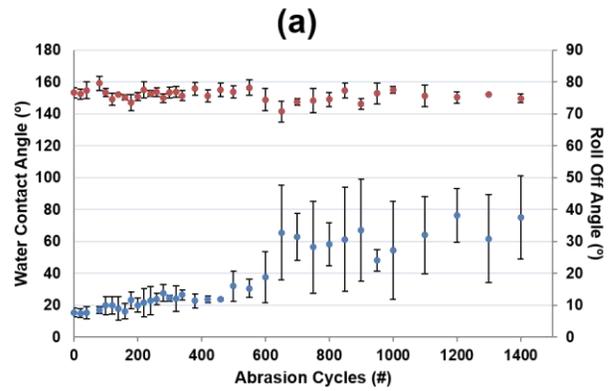


Figure 3: (a) WCA and ROA of the coatings plotted against the number of abrasion cycles. (b) SEM image of a non abraded area of the coating and (c) SEM of an abraded area of the coating after 1400 abrasion cycles.

The as fabricated coatings exhibited APCA 153° and ROA 8°. As shown in the graph of Figure 3a, for increasing number of abrasion cycles there was observed a slight increase of the ROAs as expected, but this occurred gradually and overall the coatings were found to exhibit excellent abrasion resistance behavior. Specifically, the coatings were able to maintain their superhydrophobicity up to 160 cycles (RAs <10°). However, even for further increased number of abrasion cycles the coatings continued to be very resistant and maintained high degree of water repellency. In particular, they were able to maintain ROAs

less than 40° (which is a Teflon-like behavior) for up to 1400 cycles of linear abrasion while the APCAs were always greater than 150° . This is to the best of our knowledge among the best performances that have ever been reported for a superhydrophobic coating excluding the textiles which by their nature are more resistant since they are more flexible and can dissipate the mechanical forces that act on them during wear. It is worth noting that when the coatings lost their water repellency (meaning that no ROA could be measured after 1400 abrasion cycles and the water drops stayed adhered on the surface even at 90° inclination) they were still adhered on the surface. The loss of water repellency was attributed to the gradual removal of the nano-silica particles and to surface deformation for increasing abrasion cycles. This is confirmed by the SEM images before (Figure 3b) and after (Figure 3c) the 1400 abrasion cycles. As it can be observed there is a significant change in the surface morphology which is characterized by a non uniform roughness after the coating failure. Nevertheless, no coating removal was observed after 1400 abrasion cycles, showing that the presence of the rubber component provides good adhesion to the substrate.

This was also evaluated by the ASTM D3359 adhesion test. In Figure 4a and 4b are depicted optical images of cross shaped cuts on the coatings before and after the tape peeling test respectively. As observed the coatings passed the test without any damage after the tape removal confirming the good adhesion of the coating.

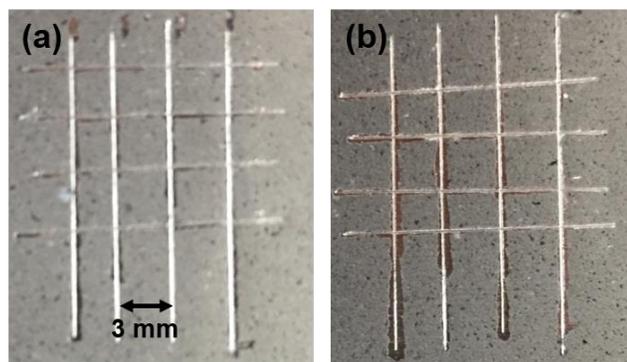


Figure 4: Samples before (a) and after (b) the tape adhesion test.

4 CONCLUSIONS

In conclusion, we have developed a technique that is fast, low-cost, and based on commercially available materials that can successfully produce highly water repellent coatings with stable performance even after several mechanical abrasion cycles. Great abrasion resistance could be achieved with the addition of a commercial rubber on the superhydrophobic nanocomposites. The coatings were able to withstand 160 cycles of linear abrasion under 20.5 kPa pressure without

losing their superhydrophobicity while they retained high levels of water repellency (APCA $> 150^\circ$ and RA $< 40^\circ$) for up to 1400 cycles. Moreover, they were able to withstand the ASTM D3359 adhesion test. Due to the simplicity and efficiency of this technique such coatings can find a wide range of industrial and engineering applications such as in vehicles, housing, motors, wind turbines, etc.

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