Mechanically Durable Superhydrophobic Nanocomposites from Acrylonitrile Butadiene Styrene (ABS)

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ABSTRACT

Here, we report on the development of nanocomposite coatings based on a combination of acrylonitrile butadiene styrene (ABS) with hydrophobically modified fumed silica (HMFS). In particular, one-step and two-step spray approaches are followed. In the one-step approach the two materias are mixed before spraying to form a nanocomposite while in the two-step approach they are sprayed as separate layers. In both cases, the coatings exhibit excellent superhydrophobic performance with static apparent contact angles greater than 160° and roll off angles less than 1°. Moreover, they are able to retain their extreme wetting properties after repeated cycles of mechanical abrasion. Their surface topography is investigated with scanning electron microscopy (SEM) unveiling micron and nanoscale roughness features. Due to the simplicity and efficiency of this technique such coatings can find a wide range of industrial and engineering applications in vehicles, housing, motors, wind turbines, etc.

Keywords: superhydrophobic, ABS, fumed silica, spray, nanocomposite

1 INTRODUCTION

Superhydrophobic surfaces are characterized by apparent contact angle (APCA) of water greater than 150° and roll-off angles (RA) 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, anti-icing and anti-fouling coatings, sensors, oil-water separation, etc [1]. For their fabrication, numerous methods have been suggested including lithography, plasma treatment, self-assembly, electrospinning, spray, immersion, etc [2].

Spray coating has been a common approach in research and industry for the development of coatings with efficient water repellency, mainly because it is fast, introduces surface roughness [3] and can be applied on large surface areas [4]. 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, simple fabrication steps without sophisticated experimental procedures, and use of non-toxic materials and solvents.

In this work we demonstrate simple one-step and two-step spray coating methods for obtaining large area and mechanically durable superhydrophobic coatings composed of a mixture of ABS and HMFS. The ABS component provides the tough polymeric matrix that is required for the durability while the HMFS attributes a unique surface texture to the surface that promotes the water repellency. The combination of these two indgriedients leads to a nanocomposite material that when sprayed and thermally cured leads to the formation of superhydrophobic and mechanically durable coatings. The developed coatings are characterized by means of contact angle goniometry and SEM, while their mechanical durability is evaluated by using a linear abrader.

2 MATERIALS AND METHODS

ABS is a commonly used thermoplastic that has higher WCA compared to the majority of commercial polymers. The WCA for a flat surface was measured approximately 85±3°. However, water adhesion is strong on its surface since the droplets remain adhered on the surface even for 90° tilt angles. Moreover, ABS is known for its strength, rigidity and toughness that make it attractive for different applications including 3D printing, pipe systems, musical instruments, toys, etc. Improving its electrical and mechanical properties by adding nanofillers has been examined [5,6]. However, superhydrophobic ABS nanocomposites, to the best of our knowledge, have not been reported so far.

The type of nanomaterial used in this study was the HMFS. Fumed silica consists of spherical nanoparticles which are fused together forming secondary particles and then agglomerate into tertiary particles. The resulting powder has an extremely low bulk density and high surface area. It serves as thickening agent and viscosity stabilizer in cosmetics, toothpastes, food additives, antiperspirant sprays, medicines, paints, coatings, printing inks, adhesives, etc. Lately, HMFS combined with different organic materials has been used for spray deposition of nanocomposite superhydrophobic coatings on various substrates [7,8]. Their unique surface characteristics provide the desirable hierarchical morphology comprising both micro- and nano-meter scale roughness typically required for superhydrophobic wetting behavior. At the same time, their existance in the organic material increases the robustness of the coating.

The superhydrophobic coatings were prepared with two-step successive spraying of the two ingridients or one-step spraying of a composite mixture. In the two-step process, ABS-P430 (Red), (Stratasyss, USA) and HMFS (Aerosil R-812, Evonik Industries, Germany) were dissolved/dispersed in acetone separately (1 wt %) and then sprayed on aluminum substrates (5.0×2.5 cm^2). 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. Initially, 6 ml of the ABS solution were sprayed and subsequently 6 ml of the HMFS dipsersion. In the two-step process, the two materials were mixed together in different concentrations prior to spraying. In both processes, after spraying, the samples were thermally cured at 240 °C, a temperature much higher than the melting point of ABS (105 °C). To obtain thicker coatings, which are more resistant to mechanical abrasion, higher concentrations of ABS and HMFS in acetone (5 wt %) were used and 50 ml of the nanocomposite mixture were sprayed. Before spraying, the aluminum subtrates were roughened with P320 sandpaper and washed with isopropanol in order to improve the adhesion of the coating. A schematic represantation of the two processes is depicted in Figure 1.

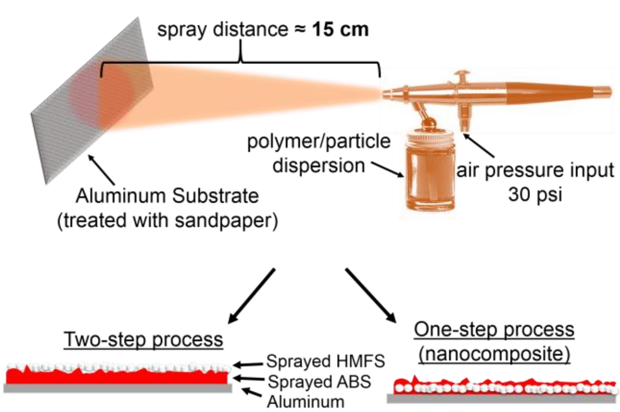

Figure 1: Schematic description of the one- and the two-step spray coating process. In the one-step approach the HMFS remain mainly on top of the coating since it is added as a second layer, while in the two-step process the HMFS is mixed homogeneously with the ABS matrix thoughout the entire volume of the coating.

The APCAs and RAs of the samples were measured by video based optical contact angle measuring instrument ramé-hart, USA. 10 μL of deionized water droplets were gently placed, measured and averaged over three different spots on each sample. For RA measurement, the substrate was tilted and the angle that the droplet rolled-off from the surface was recorded. All RA 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. Surface roughness parameters were calculated by analyzing confocal microscopy images by using a Zeiss 510 meta system, Germany.

To quantify the wear robustness of the coatings, mechanical durability tests were performed with a linear abrader (Taber Industries, USA) under 33 kPa applied pressure. WCA and RA measurements were taken after each 5 cycles of linear abrasion. The abradant surface of choice was a piece of crocking cloth and the speed used for the mechanical abrasion was held constant at 15 cycles/min. The abradant during one cycle covered a distance of 5.08 cm by performing a back and forth linear periodical motion.

3 RESULTS AND DISCUSSION

In the two-step approach the ABS is sprayed first on aluminum substrates as a binder to create a micro-scale roughness. This roughness increases the APCA (113±3°) compared to a flat ABS surface (85±3°). However, even if the hydrophobicity of the material increases statically, the water adhesion is still significantly high, since the water droplet remains pinned on the surface of the coating even for 90° tilt angles. Significant enhancement of the water repellency is achieved when the HMFS suspension is sprayed as a second coating layer to introduce secondary roughness. Subsequently, the coating is thermally cured in order to melt the ABS and entrap inside its matrix the silica particles. The coatings exhibit excellent superhydrophobic performance with static WCA of 163° and RA of 0.5°. This approach takes advantage of the extreme water repellent properties of the HMFS because all the particles are concentrated on the surface. On the other hand this coating is not very resistive in the mechanical wear, since it will loose its superhydrophobic properties when its upper layer that is responsible for the superhydrophobicity is worn off.

Figure 2a depicts a scanning electron micrograph of the spray coated surface. It is evident the presence of microstructures that are formed by the evaporation dynamics during the spray procedure. These microstructures are mainly composed of HMFS which attributes to the coating the secondary nanoroughness required for its superhydrophobic behavior. A higher magnification SEM image is depicted in Figure 2c where it is clearly shown the characteristic nanoscale morphology of the fumed silica. The combination of micro- and nano-scale roughness provides a lotus-leaf like dual-scale topography that leads to a self-cleaning surface. By using confocal microscopy images we were able to extract surface roughness parameters. In particular, the surface roughness was measured 2.44 μm, the kurtosis 4.69 and the skewness 0.91.

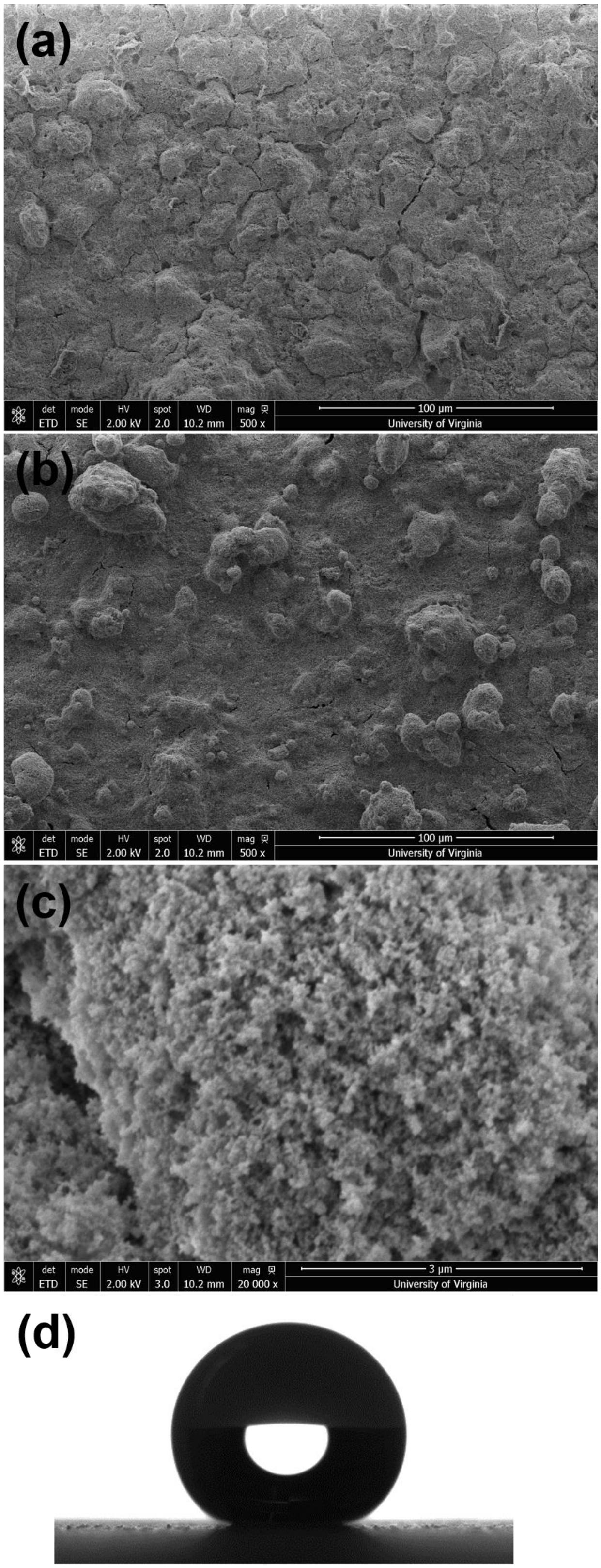

Figure 2: Low magnification SEM images of the coatings prepared with (a) one-step and (b) two-step process. (c) High magnification SEM image unveiling the nanoroughness. (d) Image of a water droplet on the surface.

In the single step approach the two materials are mixed together prior to spraying in order to form a nanocomposite. By tuning the weight ratio of the two materials we were able to obtain APCAs greater than 160° and RAs less than 1° after the thermal curing, if the HMFS concentration was held equal or greater than 40 wt %. Specifically, Figure 3 shows the APCA and the RA values of nanocomposite coatings with different ABS/HMFS weight ratios. In particular, the coatings with HMFS concentration 60 wt % and above exhibit extremely water repellent properties both before and after the thermal curing with APCAs always greater than 160° and RAs lower than 2°. The RAs for the samples with 0 and 20 wt % loading in HMFS are not reported since the water droplets stay adhered on the surface even for 90° tilt angles.

The thermal curing step leads to melting of the ABS, thus eliminating its contribution in the surface roughness. Consequently, its role is restricted in entrapping the HMFS and binding it to the aluminum substrate, thus acting like a stable matrix. This is more evident by inspecting the graph in Figure 3. The APCAs are lowered after the thermal curring for the samples in which the ABS is the dominant component (pure ABS and 20 wt % HMFS). On the contrary, when the concentration of HMFS is increased, the APCAs and RAs retain almost the same values or slightly improved in terms of water repellency (increased APCAs and lowered RAs).

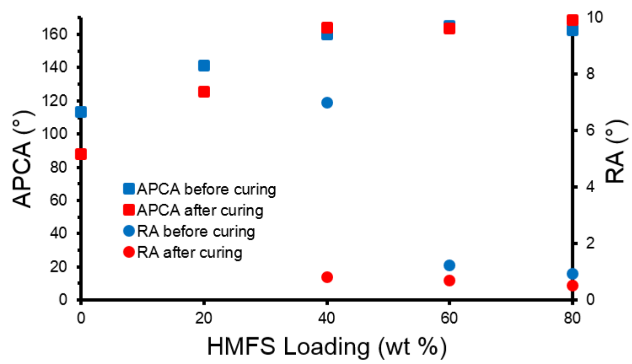

Figure 3: APCA and RA measurements plotted against the HMFS loading before and after the thermal curing.

The surface morphology in this case again exhibits micro- and nano-scale roughness after the thermal curing as it is observed in the SEM image of Figure 2b (sample with 60 wt % loading in HMFS), even if it is slightly different compared to the two-step process. In this case we have bigger microfeatures that are not as closely-packed as in the case of Figure 2a. Higher magnification SEM micrographs unveil the same nanorough characteristics as in the two-step approach (Figure 2c). In the image of the Figure 2d, a superhydrophobic water droplet placed on these coatings is shown. This approach has the advantage that the nanocomposite coatings exhibit the same superhydrophobic chemistry in their entire thickness, since the HMFS is homogeneously dispersed in the ABS matrix. Consequently, even if the coatings are subject to strong wear with material removed, the underlying layers which are subsequently exposed exhibit the same anti-wetting characteristics due to the wear similarity that the material presents. Moreover, the hydrophobic nature of ABS minimizes the possiblity of losing the superhydrophobic properties, due to the formation of hydrophilic defects on the coating as a result of wear [9].

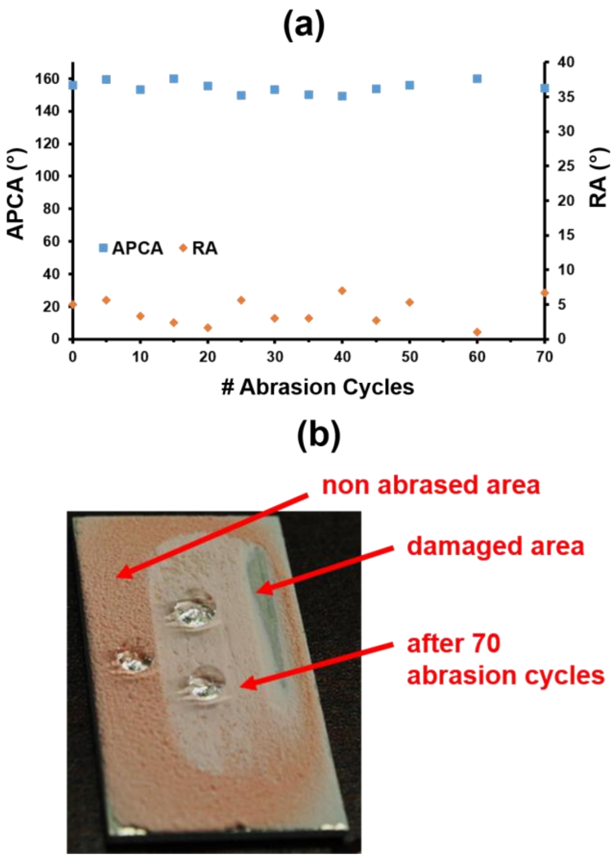

Figure 4: (a) APCA and RA measurements plotted against the number of abrasion cycles. (b) In the image it is shown the non abrased and the abrased part of the coating after 70 abrasion cycles. The droplets maintain a spherical shape (even on the abrased areas) until the surface is completely damaged in some parts of the sample, after 70 abrasion cycles.

To prove this claim and quantify the wear robustness of the nanocomposite coatings, a mechanical durability test was performed on the nanocomposite coatings with 60 wt %, by using a linear abrader. This sample was selected due to its extreme water repellency before and after the thermal curing. The total pressure that was applied on the coatings by the abradant reached 33 kPa which is comparable with other mechanical durability tests that have been performed in the literature [10], while the surface that was chosen as abradant was a common textile.

In Figure 4a the values of the WCAs and the RAs are plotted against the number of abrasion cycles. As it can be observed, the coatings did not lose their water repellency up to 70 abrasion cycles. The WCAs in all the measurements were found to be greater than 150° while the RAs were less than 10°. In fact, as it can be seen in the photograph of Figure 4b, the coatings retained the superhydrophobicity until the coating was completely worn off (depicted as damaged area). Even if a very thin layer of coating still remained on the aluminum substrates after 70 abrasion cycles, the water dropets were still beading up, indicating a wear similarity behavior of the nanocomposite coating.

4 CONCLUSIONS

In conclusion, we have developed a technique that is fast, low-cost, and based on non-toxic commercially available materials that can successfully produce highly water repellent coatings with stable performance even after several mechanical abrasion cycles. 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.

REFERENCES

[1] Y.K. Lai, Z. Chen and C.J. Lin, J. Nanoeng. Nanomanuf. 1, 18, 2011.
[2] P. Roach, N.J. Shirtcliffe and M.I. Newton, Soft Matter 4, 224, 2008.
[3] A. Milionis, D. Fragouli, L. Martiradonna, G.C. Anyfantis, P.D. Cozzoli, I.S. Bayer and A. Athanassiou, ACS Appl. Mater. Interfaces 6, 1036, 2014.
[4] T. Schutzius, I.S. Bayer, J.Qin, D. Waldroup and C.M. Megaridis, ACS Appl. Mater. Interfaces 5, 13419, 2013.
[5] M.H. Al-Saleh, H.K. Al-Anid and Y.A. Hussain, Compos. Part A 46, 53, 2013.
[6] A. Ambre, R. Jagtap and B. Dewangan, J. Reinf. Plast. Comp. 28, 343, 2009.
[7] B.J. Sparks, E.F.T. Hoff, L. Xiong, J.T. Goetz and D. Patton, ACS Appl Mater Interfaces 5, 1811, 2013.
[8] T. Schutzius, I.S. Bayer, G.M. Jursich, A. Das and C.M. Megaridis, Nanoscale 4, 5378, 2012.
[9] T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala and R.H.A. Ras, Adv. Mater. 23, 673, 2011.
[10]Y. Xiu, Y. Liu, D.W. Hess and C.P. Wong, Nanotechnology 21, 155705, 2010.