Superhydrophobic 3D Printed Surfaces by Dip-Coating

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ABSTRACT

Here we decribe two different approaches for rendering 3D printed acrylonitrile butadiene styrene (ABS) structures superhydrophobic by using dip-coating based techniques. In the first approach, the ABS structures are sputter-coated with a thin metallic layer and subsequently a dispersion of acrylic fluoropolymer with hydrophobically modified fumed silica (HMFS) is used to dip-coat and render them superhydrophobic. In the second approach, dip-coating with modified superhydrophilic rubber is performed prior to the second dip-coating step with the same fluoropolymer/fumed silica dispersion. The surface modification that each technique induces to the patterns is characterized with contact angle goniometry and scanning electron microscopy. The two approaches are then applied for coating 3D heat exchange elements and their water retaining performance, after immersing them in water baths, is evaluated. Such dip-coating approaches can be proven useful in order to alter the wetting properties of 3D plastic patterns.

Keywords: superhydrophobic, 3D printing, ABS, dip-coating, heat exchanger

1 INTRODUCTION

Three-dimensional (3D) printing is gathering significant interest nowdays since it is a manufacturing technology that allows the engineering of large-scale sophisticated devices that traditionally used to be fabricated with complicated procedures and facilities. In particular, the fused deposition modeling technology is interesting because it uses low-cost thermoplastic materials such as acrylonitrile butadiene styrene (ABS), polylactic acid and polycarbonate [1]. The low cost and fast processing of this technology make it very attractive for industrial applications. Specifically, ABS due to its light weight and good mechanical properties, it is used for the fabrication of toys, musical instruments, pipe systems, mechanical parts, etc.

Developing a dip-coating method that can alter the surface properties of these 3D printed plastic materials could greatly expand their range of applications. Like this, one could take advantage of the bulk properties of the printed structutes and the surface functionality. In fact, 3D printed structural materials with functionalized surfaces have been addressed rarely to date, while the techniques that have been employed (such as surface initiated polymerization) are more complex than the dip-coating approach [2].

Herein, we present a dip-coating approach in order to convert the surface of 3D printed ABS structures to superhydrophobic. To demonstrate a potential application of this technique to 3D structures of higher complexity, we investigate the water retention in 3D heat transfer networks that are used for energy storage by liquid piston-driven isothermal air compression. The superhydrophobic coatings are able to reduce significantly the uptake of liquid on these heat exchangers and consequently improve their functionality.

2 MATERIALS AND METHODS

For the 3D printing, a uPrint 3D printer from Stratasys, USA was used. A linear printing algorithm was followed for the construction of the structures. The processing material was ABS-P430 (Red) from Stratasys, USA. The printed materials had the form of cubes and heat exchange elements. After the printing process, the 3D structures were coated with either an ultrathin metallic coating or a rubber material in order to improve the adhesion of the dip-coated construct.

The first approach was to sputter-coat the ABS structures with Au/Pd by using a Precision Etching Coating System (PECS), Model 682 (Gatan, USA). The samples were left for 4 min under continuous rotation inside the chamber, while tilted at 15° in order to ensure that the inner parts of the 3D printed heat exchangers were covered with Au/Pd. A final coating layer of approximately 20 nm was obtained.

The second approach was to perform a dip-coating step of a material that would act as a primer in order to improve the adhesion of the final superhydrophobic coating. The material that was selected was a superhydrophilic rubber coating. In particular 20 gr of the Plasti Dip® rubber (Performix, USA) were diluted in a mixture of toluene (3.5 ml) and xylene (3.5 ml). As such it was possible to coat more fine feautures since the as received material is highly viscous. Subsequently, 2 wt % of poly(dimethylsiloxane-b-ethylene oxide), methyl terminated (Polysciences, USA) was added in the mixture that was stirred for about 1 min in order to obtain a homogeneous solution. The ABS structures were then immersed in the solution, left inside for 5 sec and subsequently dried in ambient conditions for 4 hours.

The final superhydrophobic dip-coating solution was prepared by fist dispersing 1 gr hydrophobically modified fumed silica (HMFS), Evonik Industries, Germany in 17 ml butyl acetate by sonication for 16 min. Subsequently 3 ml of acrylic fluoropolymer (Dupont Capstone ST-200, USA) were added in the solution. This mixture was used to immerse the 3D printed structures. The immersion time was approximately 2 sec and after this the samples were heated at 100° C on a hotplate in order to speed up the solvent evaporation.

The water contact angles (WCAs) and droplet roll-off angles (RAs) of the samples were measured by video based optical contact angle measuring instrument ramé-hart, USA. Ten (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. The standard deviation was ±4° for the WCA measurements and ±1° for the RA measurements. All measurements were performed in ambient conditions. Additionally, water retention measurements were performed by immersing the ABS heat exchangers in deionized water for 2 sec and then measuring their weight. The morphology of the patterned surfaces was characterized by scanning electron microscopy (SEM), FEI Quanta 650, USA.

3 RESULTS AND DISCUSSION

Figures 1a,b depict low (Figure 1a) and high (Figure 1b) magnification SEM images of the surface of the 3D printed ABS. As it is shown in Figure 1a the linear 3D printing algorithm leads to the fabrication of patterned lines. Higher magnification image (Figure 1b) shows that the ABS surface is relatively smooth in the microscale, with some small microroughness arising from the polybutadiene spheres that are embedded in the acrylonitrile and styrene phase. This kind of patterning induces an anisotropic wetting effect on the printed surfaces. In particular, the WCA measured when the camera of the contact angle goniometer was facing perpendicular to the direction of the printed lines was hydrophobic (110.9°, Figure 1a caption). However, when the surface was rotated 90°, so that the printed lines were facing paralell to the camera, the measured WCA was hydrophilic (55.8°, Figure 1a caption). However, in both cases the water adhesion was high, not allowing the water droplets to slide on the ABS surface even at 90° tilt angle.

The pure ABS surface could not be coated with the superhydrophobic dispersion that was prepared. After the printed structures were immersed in the acrylic fluoropolymer/HMFS dispersion and left to dry, several cracks were observed on the surface, unveiling the ABS substrate, while the coating did not adhere well to the surface and could be removed very easily. Such type of fluoropolymer/HMFS dispersions have been used in the literature to coat metallic surfaces but are not so succesful when it comes to plastics [3]. Consequently, in order to improve the binding of the superhydrophobic composite to the ABS surface, a very thin sputter coated layer of Au/Pd was used as a primer.. The WCAs after the sputtering were found to be slightly higher, though maintaining the anisotropy. In particular, the WCA was measured 120° when the camera was facing perpendicular to the printed lines and 70.3° when the camera was in parallel. The water adhesion was still high enough to not allow sliding of the droplets at any tilt angle. However, this time it was possible to deposit the acrylic fluoropolymer/HMFS dispersion, since the presence of the metallic coating significantly improved the coating deposition, while at the same time acted as a protective barrier to the butyl acetate solvent which is an aggressive solvent for ABS. Figure 2a depicts a cube which has been rendered superhydrophobic by combining sputter-coating and successive dip-coating. The WCA on its surface was measured 159°, while the RA was

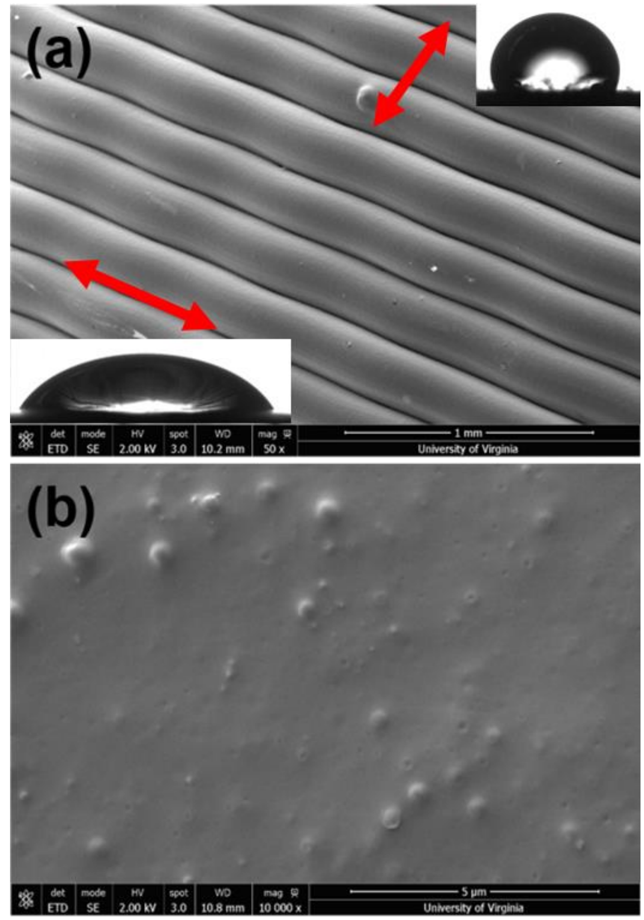

Figure 1: (a) Low and (b) high magnification SEM images depicting the surface of the ABS 3D-printed cubes. Insets (a) Optical images of 10 μl water droplets sitting on the surface of the printed object with the camera facing parallel to the printed lines and perdendicular to the direction of the printed lines.

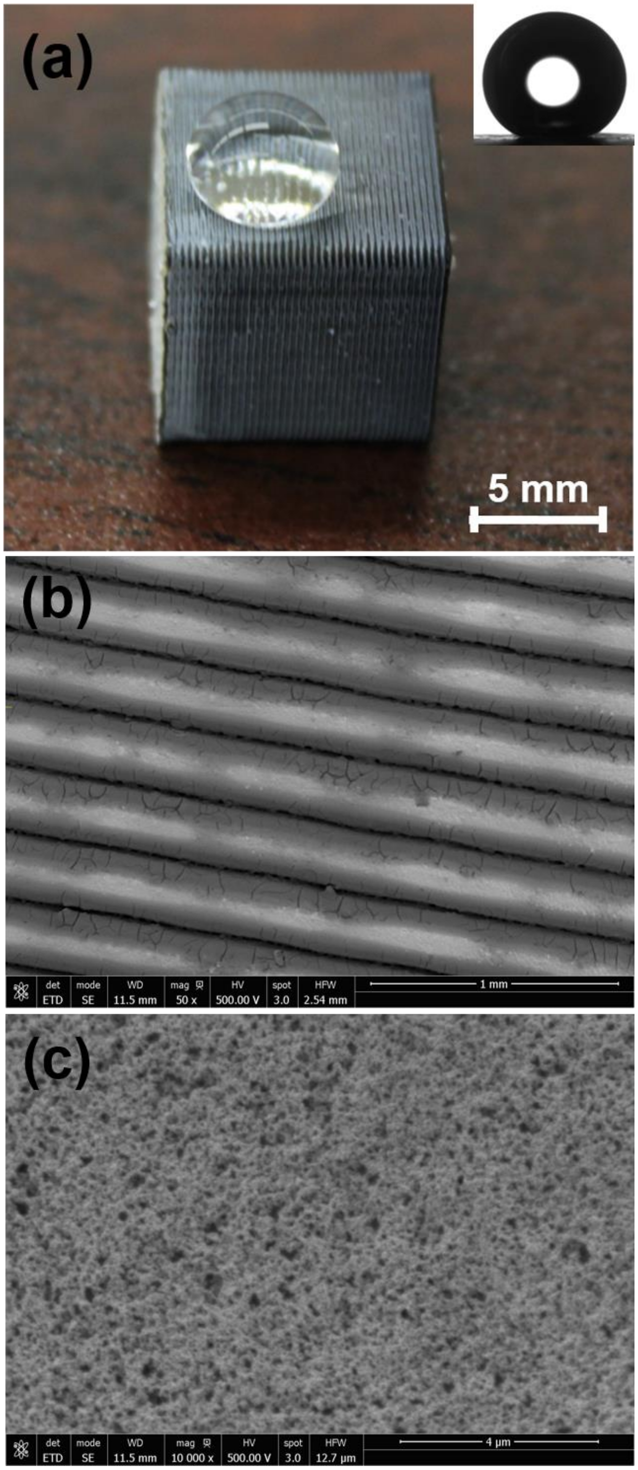

Figure 2: (a) A cube of 1 cm^2 side fabricated with 3D printing and dip-coating. Inset: A water placed on it obtains a spherical shape, characteristic of the superhydrophobic surfaces. (b) Low and (c) high magnification SEM images of the coated ABS surface

5°. Moreover the anisotropic wetting effect was eliminated since the wetting properties were found to be the same when observing the droplet perpendicularly or in parallel with the direction of the printed lines. In Figure 2b, it is clearly shown that the printed lines are coated homogeneously after the dip coating process with some minor cracks in the valleys between them. The higher magnification SEM image shows nano-scale roughness of the coating due to the presence of the HMFS component.

The second approach that was followed was a two-step dip-coating method. First the surface was dip-coated in a solution containing diluted Plasti Dip® rubber with 2 wt % poly(dimethylsiloxane-b-ethylene oxide) surfactant additive that rendered the surface superhydrophilic. An analogous method for hydrophilizing the surface of poly(dimethylsiloxane) has been reported in the literature [4]. After the coatings dried, the rubber coating conformed homogenously on the ABS surface (Figure 3a black coating) and the printed materials showed superhydrophilic behavior. No WCA could be measured since the water droplets were spreading completely on the surface as shown in Figure 3a. Moreover, the line patterning forced the droplet to flow towards the direction of the lines. These enhanced anisotropic wetting effects forced total spreading of a water droplet on the surface of a 2.54 cm side cube only in 7 sec after its deposition. The spreading occured only across the direction of the printed lines.

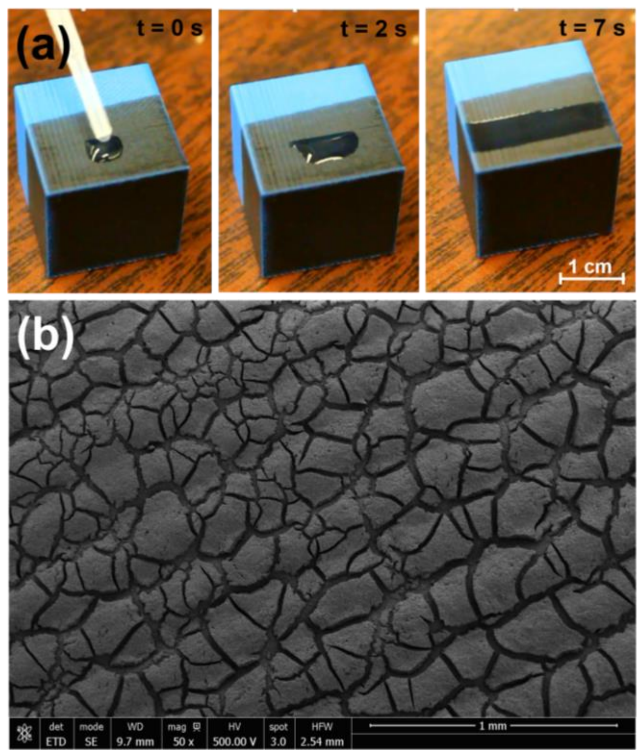

Figure 3: (a) A 3D printed cube dip-coated with modified superhydrophilic Plasti Dip® rubber in different time intervals after the deposition of a water droplet. (b) Low magnification SEM image of the surface after the dip-coating with the acrylic fluoropolymer/HMFS dispersion.

Having a superhydrophilic substrate facilitated the dip-coating with the superhydrophobic coating dispersion that was used before with the only difference that acetone was used as a solvet instead of butyl acetate. Figure 3b shows an SEM image after the second dip coating step. This time, some cracks could be observed on the coating that lead to the formation of small superhydrophobic islands that had dimmensions in the order of a few hundreds of microns. The channels that were surrounding the islands were large enough for inducing some partial Wenzel-type pinning effects that slightly reduced the superhydrophobic performance of the coating compared to the sputtering approach. In fact, the WCA was meadured 154.7° and the RA 30°.

In order to demonstrate a potential application of such approaches for rendering 3D surfaces superhyrophobic, 3D heat exchangers were fabricated. Such type of structures are currently tested for energy storage applications by liquid piston-driven isothermal air compression. Isothermal air compression is achieved by injecting water droplets on the walls of these patterns. However, this type of heat exchangers fails to perform well if there is significant water amount uptaken by their walls during the cooling cycles. Using superhydrophobic coatings to cover entirely these 3D structures could significantly reduce the water retention and consequently improve the functionality of such systems. Figure 4 shows the two dip-coating strategies followed, as described before, for transforming the ABS 3D heat exchanger surfaces to superhydrophobic.

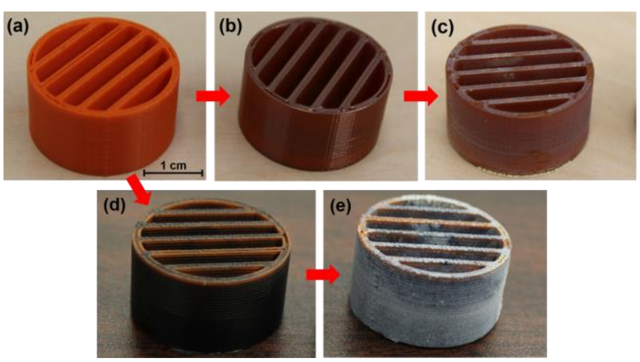

Figure 4: Schematic showing the two different preparation methods followed for the fabrication of superhydrophobic 3D printed heat exchangers: (a) as prepared, (b) after the Au/Pd sputter coating, (c) after dip-coating with the fluoropolymer/HMFS dispersion, (d) dip-coating step with superhydrophilic Plasti Dip® rubber and (e) after the second dip-coating step with the fluoropolymer/HMFS dispersion.

Figure 5 shows a histogram with some preliminary results obtained after immersing the heat exchangers into water. The water uptake compared to the dry mass ratio could be minimized when we used the superhydrophobic dip-coated 3D patterns. In particular the first method described here performed better and reduced the water uptake by 92 %. The second approach also reduced the mass of water retained, but only by 64%. Finally, the superhydrophilic rubber also was tested and the water quantity uptaken in this case was slighlty lower than the pure ABS printed structures.

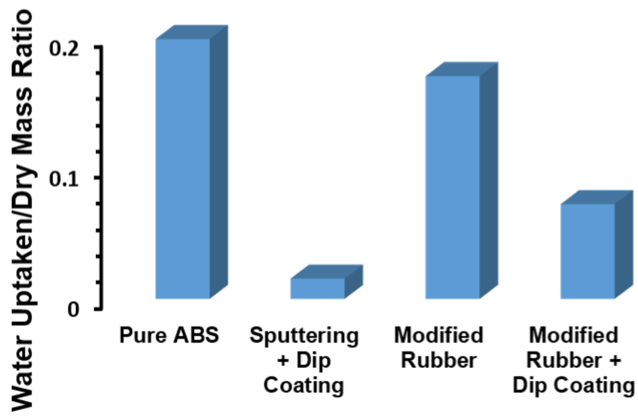

Figure 5: Histogram showing the ratio between the mass of uptaken water to the dry mass of four identical heat exchangers with different coatings.

4 CONCLUSIONS

We have described two different two-step dip-coating approaches for obtaining 3D superhydrophobic patterns and also one method for obtaining 3D superhydrophilic patterns. While the second step is identical in both methods, in the first approach it is required pretreatment with sputter coating and in the second the samples are coated primarily with a modified superhydrophilic rubber. The approaches described here were used to coat heat exchange elements. The coatings were found to improve the performance of the heat exchangers in terms of reduced water retention.

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