Fabrication of superhydrophobic polyvinylidene fluoride membranes with polytetrafluoroethylene nano-film surface coatings

Ali T. Abdulhussein[*], Ganesh K. Kannarpady[*], Raad A. Alawajji[*], Alexandru S. Biris[*]

[*]Center for Integrative Nanotechnology Sciences, University of Arkansas at Little Rock
2801 South University Avenue, Little Rock, AR, atabdulhusse@ualr.edu

ABSTRACT

In this work, we used pulsed laser deposition (PLD) to coat polyvinylidene fluoride (PVDF) substrates with polytetrafluoroethylene (PTFE) thin films at room temperature. Modifying a PVDF membrane with a superhydrophobic nano-coating of PTFE has been shown to enhance the membrane's self-cleaning ability. The PTFE was deposited at different deposition times (15, 30, 45, 60, and 90 min). The surface roughness increased as deposition time increased up to 45 minutes. The highest water contact angle, 155˚ with negligible contact angle hysteresis, was observed for the sample with 45-minute deposition time. This study produced a superhydrophobic PVDF membrane with outstanding self-cleaning properties using a convenient, one-step, non-polluting technique without a wetting step.

Keywords: pulsed laser depostion, superhydrophobic, PVDF, surface roughness, self-cleaning.

1 INTRODUCTION

Superhydrophobic surfaces have generated great interest due to their myriad practical applications, from industrial to household to technological products [1, 2]. A typical superhydrophobic surface has a water contact angle (WCA) above 150˚ and negligible contact angle hysteresis, which allows liquid to roll off the surface with just a small tilt. Nature offers great examples of superhydrophobic surfaces. The lotus leaf is a well-known example, able to protect itself from dirt and microbes via its unique self-cleaning behavior, known as the "lotus effect". In general, superhydrophobic surfaces are determined by two factors. One is surface energy, which is ruled by chemical composition, and the other is surface morphology [3, 4]. Many techniques have been reported for creating superhydrophobic surfaces, including spin coating, electrospinning, plasma etching, chemical vapor deposition, lithography, and sol-gel methods [5].

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer with amorphous and crystalline phases. The amorphous phase gives the material its flexibility, and the crystalline phase endows thermal stability. Due to their outstanding corrosion resistance, wear resistance, thermal stability, and chemical stability [6], PVDF membranes are extensively used for membrane distillation, oil/water separation, and wastewater treatment. However, current methods for producing superhydrophobic PVDF substrates tend to be complicated and require chemical wetting and toxic components. In this study, we present a simple, one-step, dry, easily controlled, and environmentally friendly method to prepare a superhydrophobic PVDF membrane surface with self-cleaning properties using pulsed laser deposition (PLD). Polytetrafluoroethylene (PTFE), popularly known as "Teflon", possesses excellent thermal and chemical stability and was selected as the target material. The hydrophobicity, chemical composition, and topology of the resulting surface were investigated.

2 EXPERMENTAIL DETAILS

Commercial PVDF membranes (47 mm diameter and 0.45 μm pore size) were bought from EMD Millipore, USA. The PVDF substrates were mounted with carbon tape to the stainless steel rotating substrate holder. This holder was situated opposite from the PTFE targets, 75 mm away. Bulk PTFE was the target for all depositions. A pulsed Krf excimer laser with 10-50 ns pulse duration, wavelength of 248 nm, 10 Hz repetition rate, and energy density of 1.3 J/cm^2 per pulse was utilized. The laser passed through a quartz window and was focused via the lens on the PTFE target. During the deposition process, the substrate rotated at 5 rpm. The pulsed laser was focused on the target at 45˚. The PVDF samples were coated with PTFE thin films under deposition times of 15, 30, 45, 60, and 90 min (labeled as PV1, PV2, PV3, PV4, and PV5, respectively). In addition, one uncoated sample was employed to serve as a control sample (PV0). The deposition was done at room temperature in a vacuum chamber that was evacuated to a base pressure of 1.2×10^{-6} mbar by a turbo pump. After deposition, the samples' superhydrophobicity was analyzed by an EasyDrop (DSA1) device (Kruss Co.) contact angle goniometer utilizing sessile drop technique to measure the static contact angles of the samples. The contact angle measurements were found by placing 5-μm deionized water droplets on three random locations for each sample, then the average values were calculated.

In addition, contact angle hysteresis (CAH) was measured by determining the difference between the

advancing and receding contact angles when water was added/removed from the sample surface. The morphology of the uncoated and coated samples was analyzed by scanning electron microscopy (SEM, JEOL SEM7000FE) with 15 KV accelerating voltage and current of 75 µA. To determine the surface roughness and topography of the uncoated and coated samples, the 3D profiles of the samples were found by a Bruker Nanoscope III D3000 atomic force microscope. NanoScope Analysis software (Ver. 1.5) optimized the image quality and analyzed the images. Thermo Scientific K-Alpha x-ray photoelectron spectroscopy was used to obtain widescan and high-resolution spectra for analyzing the chemical nature of the PTFE target and the thin PTFE films on the PVDF surfaces.

3 RESULT AND DISCUSSION

Figure 1 shows the different wettability of the coated and uncoated membranes. The PTFE-coated PVDF sample (PV3) had the highest WCA, 155˚, as shown in Figure 2a; in contrast, the uncoated PVDF membrane was completely wetted by water and had a ~0˚ WCA.
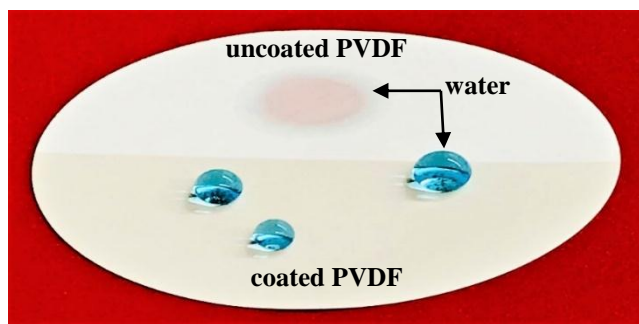

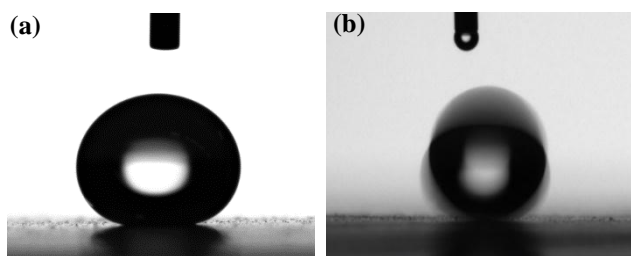Figure 1. Image of water droplets (blue) as quasi spheres on the coated PVDF and a water trace on the uncoated PVDF.

Figure 2. Optical images of (a) water droplet on PV3, and (b) droplet rolling off PV3 when inclined (<2˚).

A surface is considered superhydrophobic when its static contact angle is larger than 150˚, but this is not enough to evaluate a surface's water-solid adhesion. When a water droplet rests on a superhydrophobic surface, it could be in either the Wenzel or Cassie-Baxter state. In the Wenzel state, the water penetrates the asperities of a rough surface, causing the droplet to have full contact with the surface; this state is called the "sticky state". However, in the Cassie-Baxter or slippery state, the water doesn't completely fill the rough asperities of the surface, as those asperities are covered by air pockets.

The major variation between the superhydrophobicity of Wenzel and Cassie-Baxter states depends on a surface's contact angle hysteresis (CAH). CAH is the difference between the receding and advancing contact angles. It is extremely low for water droplets in the Cassie-Baxter state but high—potentially above 100˚—in the Wenzel state [7]. Therefore, droplets roll easily off a surface in the Cassie-Baxter state but not in the Wenzel state. Figure 2b shows a water droplet rolling easily off the PV3 membrane, indicating the Cassie-Baxter state. The PV3 sample exhibited the lowest CAH of all the PV samples, <2˚. The CAH of the coated PVDF membranes changed based on deposition time. Figure 3 plots the CAH magnitudes of the coated surfaces as a function of deposition time.
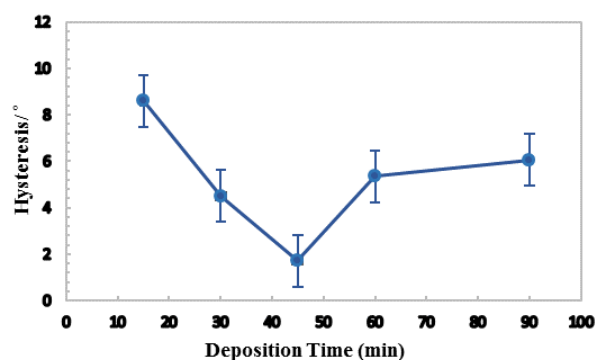

Figure 3. Variation of CAH by deposition time (min) for all PTFE-coated PVDF membranes.
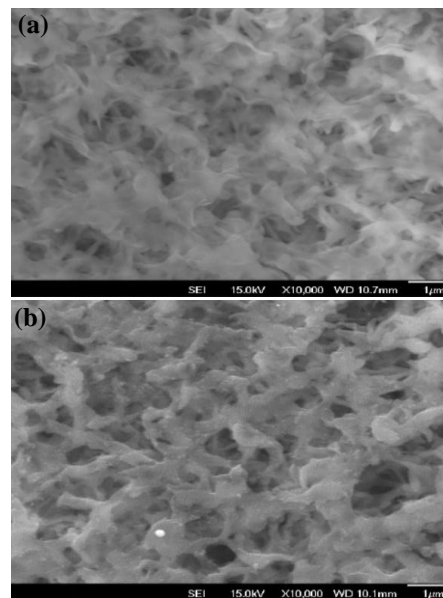

Figure 4. SEM images of (a) PV0 and (b) PV3.

In contrast to the fluffy, smooth texture of the untreated PVDF membrane (PV0) (Fig. 4a), the surface of the Teflon-coated PVDF membrane surface (PV3) was extremely grainy and rough due to the agglomeration of individual,

tiny particulates, created during PLD, that formed nanoscale roughness on the membrane surface (Fig. 4b).

X-ray photoelectron spectroscopy was utilized to investigate the composition and chemistry of the sample surface. The widescan spectra of the PTFE target and PV4 film samples are shown in Figure 5. Fluorine and carbon are the primary elements dominating the widescan spectra. The spectra's main sharp peaks are F1s and C1s for the PTFE target and the PV4 film samples; a small O1s peak appeared only in the PV4 sample. The fluorine concentration was lower and the carbon concentration higher in the PV4 film than in the PTFE target. The pulsed laser used in the deposition process caused this change by breaking the carbon-fluorine bond, which releases a small amount of fluorine from the material [8].

The direct relationship between surface roughness and deposition time is displayed in Figure 6 . Figure 6 (a) shows the 3D surface profiles of PV0, PV2, PV4, and PV6 respectively. Figure 6 (b), shows the surface roughness increased progressively from PV0-PV2 (130-169 nm), after which an abrupt increase in surface roughness to 270 nm occurred for PV3 and, eventually, a reduction to 145 nm for PV5. The roughness increased with deposition time because the Teflon began to form a compact thin film with nano-scale asperities as time went on. As a result, the roughness of the Teflon film increased. The nano-scale asperities helped trap air beneath and in-between the water droplets and the space between the asperities, causing the droplets to rest on them with small water-solid contact area. This yields the Cassie-Baxter state, as demonstrated by the following equation: $\cos \theta_{CB} = f \cos \theta + f - 1$, where f is the area fraction of the water-solid interface and θ is the contact angle on the smooth surface. The Cassie-Baxter equation states that a decrease in water-solid contact area will result in a greater contact angle. In our study, when very compact nano-scale asperities formed on the surface when the deposition time increased to 45 min, the fraction area trapped by air was the greatest, and the contact area between the water droplet and the thin film surface was the lowest. Therefore, the low CAH is attributed to the trapped air beneath the water droplet. The reduction in surface roughness at the later time points is due to the deposition of more Teflon particulates, which led to a decrease in the nano-scale asperities. We can conclude, then, that the low surface energy of Teflon, along with micro/nano surface roughness led to superhydrophobicity.
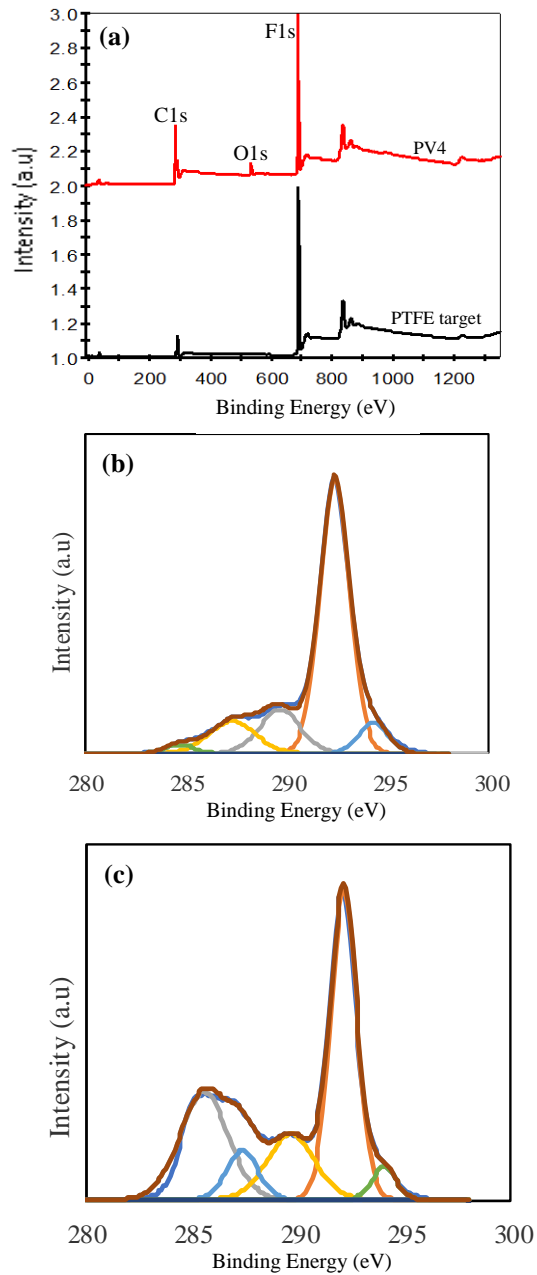

Figure 5. (a) XPS survey spectra for PTFE target, and PV4 sample (b), and (c) XPS narrow spectra of C1s for the PTFE target and C1s for the PV4 sample, respectively

(a)

Ra = 130nm

a1)

Ra = 169nm
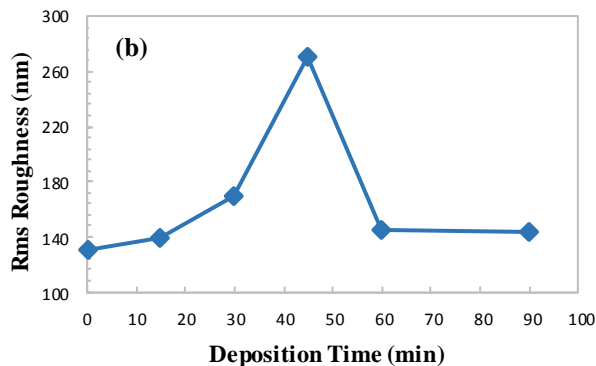
a2)

Ra = 270nm
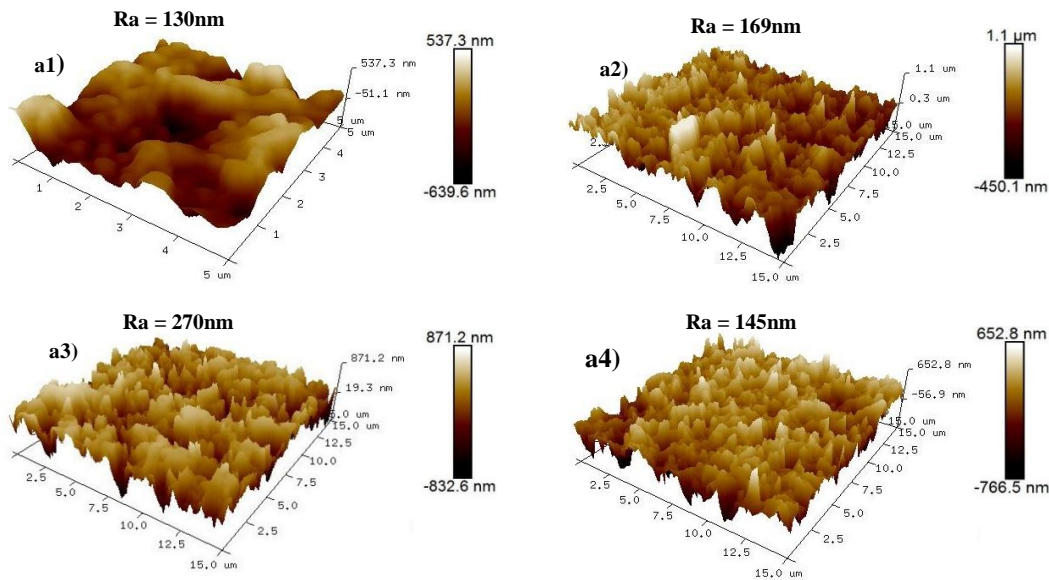
a3)

Ra = 145nm

a4)

(b)

Figure 6. (a) 3D surface roughness profiles for (a1) PV0, (a2) PV2, (a3) PV3 and (a4) PV5. (b) variation of surface roughness vs. deposition time for PTFE-coated PVDF membranes.

4 CONCLUSIONS

In this work, superhydrophobic PTFE thin coatings were successfully fabricated on PVDF membranes by pulsed laser deposition at room temperature. Characterization by SEM and AFM showed that the deposition time of 45 min was optimal, resulting in the highest WCA of 155˚ with negligible hysteresis and the maximum obtainable surface roughness, 270 nm. Therefore, using low surface energy PTFE to create nano-sized roughness on a PVDF sample resulted in a superhydrophobic surface.

5 REFERENCES

[1] B. Bhushan, Y.C. Jung, Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction, Progress in Materials Science, 56 (2011) 1-108.

[2] R. Blossey, Self-cleaning surfaces — virtual realities, Nature Materials, 2 (2003) 301.

[3] L. Jiang, J. Zhao Y Fau - Zhai, J. Zhai, A lotus-leaf-like superhydrophobic surface: a porous microsphere/nanofiber composite film prepared by electrohydrodynamics, DOI.

[4] A.T. Abdulhussein, G.K. Kannarpady, A. Ghosh, B. Barnes, R.C. Steiner, P.Y. Mulon, D.E. Anderson, A.S. Biris, Facile fabrication of a free-standing superhydrophobic and superoleophilic carbon nanofiber-polymer block that effectively absorbs oils and chemical pollutants from water, Vacuum, 149 (2018) 39-47.

[5] A.T. Abdulhussein, G.K. Kannarpady, A.B. Wright, A. Ghosh, A.S. Biris, Current trend in fabrication of complex morphologically tunable superhydrophobic nano scale surfaces, Applied Surface Science, 384 (2016) 311-332.

[6] Z. Zheng, Z. Gu, R. Huo, Y. Ye, Superhydrophobicity of polyvinylidene fluoride membrane fabricated by chemical vapor deposition from solution, Applied Surface Science, 255 (2009) 7263-7267.

[7] A. Lafuma, D. Quéré, Superhydrophobic states, Nature Materials, 2 (2003) 457.

[8] R.K.Y. Fu, Y.F. Mei, G.J. Wan, G.G. Siu, P.K. Chu, Y.X. Huang, X.B. Tian, S.Q. Yang, J.Y. Chen, Surface composition and surface energy of Teflon treated by metal plasma immersion ion implantation, Surface Science, 573 (2004) 426-432.