

Deposition/Characterization of an Ultrathin Film of Polyallylamine/Polytetrafluoroethylene Colloid Coating on Metallic Substrates

Tarek R. Farhat*, Hasan El Rifai, Rana Jisr, Evelyn Patterson, Emily H. Santamaria

Department of Physical Sciences/West Virginia University Institute of Technology, Beckley, WV, USA

Abstract Microparticles of polytetrafluoroethylene (PTFE) were successfully deposited on metal surfaces that are functionalized with a monolayer of polyelectrolyte polyallylamine hydrochloride (PAH). The adherent PTFE colloid created a superhydrophobic ultrathin coating on metal surfaces without using conventional methods of electrostatic/thermal annealing techniques. Deposition of the micron-thin film is at room temperature in aqueous media. The PAH is a diluted polyelectrolyte solution while the PTFE colloid is a 10% colloidal solution. The metallic substrates used are stainless steel plates, SS304 mesh wire, carbon steel, aluminum plates, and aluminum mesh wire. An ultrathin film is deposited starting with PAH to functionalize the metal surface followed by a capping layer of PTFE microparticles to obtain a corrugated surface of low surface energy. The combined effect of the metallic mesh structure, PTFE microparticles, and PTFE low surface energy led to a superhydrophobic coating on the metal surfaces. An instrumental analysis made by infrared spectroscopy, contact angle, and electron microscopy was used to verify the deposition of the ultrathin film coating and the superhydrophobic character. Sessile drops of pure water and solutions exhibited static contact angles up to 160° implying a superhydrophobic character. The PAH/PTFE-coated mesh wires were able to hold a hydrostatic height of 40-50 mm. Our research has applications in the coatings industry that serves corrosion protection, filtration, aqua systems, and others.

Keywords Superhydrophobic, Ultra hydrophobic, Polyallylamine hydrochloride, Polytetrafluoroethylene, Stainless steel plate, Mesh wire, Static contact angle

1. Introduction

Superhydrophobic films or coatings are an extensive area of research where scientists continue to experiment with a combination of chemicals and techniques to expand applications. In corrosion protection, superhydrophobic coating deprives the process of corrosion from water. For filtration and aqua systems, the repelling characteristics of superhydrophobic films initiate precipitation or vaporization of water. The theory of superhydrophobic surfaces is based on having a low surface energy coating on a rough surface [1,2]. From the many techniques that are used to design superhydrophobic coatings, this paper utilizes the sequential deposition of one bilayer and up to three bilayers used in polyelectrolyte multilayer (PEM) techniques to design ultrathin films. Previous work on the PEM technique used polyelectrolytes (PE) with colloidal particles or hydrophobic PEs to create superhydrophobic coatings [3,4,5,6]. When the polyelectrolyte polyallylamine

hydrochloride PAH is used to design hydrophobic coatings, it is usually coupled with an anionic PE (e.g. polystyrene sulfonate PSS, or polyacrylic acid PAA) and silica particles to deposit a PEM film. The film is then capped with a hydrophobic polymer (e.g. perfluorooctyl silane, [7]) to attain superhydrophobic nature. In fact, silica is used extensively in providing the roughness required to design a superhydrophobic coating [8]. The polymer polytetrafluoroethylene PTFE was used as a flexible substrate to support a superhydrophobic coating for biochemical applications, but the PTFE substrate was not part of the hydrophobic ceramic coating [9]. Hydrophobic coating layers with high transmittance were fabricated by optimizing the PTFE colloid content in alumina [10]. Ultra-hydrophobic films were made from titanium dioxide nanoparticles that were fluorinated by the thermal decomposition of polytetrafluoroethylene in a nitrogen atmosphere [11]. Other techniques, roughened the smooth surface of the PTFE substrate by Ar-ion bombardment to design an Ultra-hydrophobic surface [12].

Unlike previous work, our research work succeeded in depositing the PTFE colloid on a metal surface at room temperature under aqueous conditions. Our technique did not use any ceramic powders, thermal annealing,

* Corresponding author:

tarek.farhat@mail.wvu.edu (Tarek R. Farhat)

Received: Jun. 20, 2023; Accepted: Jul. 16, 2023; Published: Jul. 24, 2023

Published online at <http://journal.sapub.org/materials>

ion-bombardment, and specialty fluorinated molecules to attain a superhydrophobic character. Instead, a metal surface was functionalized by a PAH polyelectrolyte layer followed by one layer of PTFE colloid to design the superhydrophobic coating. Sequential deposition of PAH/PTFE ultrathin film on metallic substrates can be achieved if the deposited film is not left to dry. Up to three bilayers of PAH/PTFE were deposited and characterized. Two types of metallic substrates were used to deposit the PAH/PTFE thin films. The first type of substrates used degreased plates of stainless steel SS304, carbon steel, and aluminum. The second type of substrates used mesh substrates of stainless steel 304 (mesh numbers 16, 38, 70, 120), and aluminum mesh#20. Characterization of the deposited PAH/PTFE thin films on the metallic substrates was made using Fourier Transform infrared FTIR, Contact Angle Measurements CAM, and Scanning Electron Microscopy SEM.

2. Experimental Procedure

The per-fluorinated coating did not require any chemical synthesis, thus all chemicals involved were purchased. Instruments used in characterization are available in our department.

2.1. Chemicals and Instrumentation

Polyelectrolyte polyallylamine hydrochloride PAH powder from Alfa Aesar ($M_w \sim 120K$ to $200K$) and Polytetrafluoroethylene PTFE colloid (60%) from Sigma-Aldrich were used without any further processing. Di-ionized pure water was used to prepare the polyelectrolyte solutions and to dilute the PTFE colloid. The PAH solution used has a concentration of 20 mM dosed with 0.1M NaCl salt. The PTFE colloid suspension was diluted to a 10% colloidal solution with pure water. Instrumental analysis was carried out using a NICOLET iS50 FTIR

spectrometer from Thermo-Fisher Scientific, the Contact Angle Measurements (CAM) Goniometer from Ossila Inc., and the PHENOM scanning electron microscope (SEM) analysis from Nanoscience. The metallic mesh substrates from McMaster Carr supplies were of different mesh sizes. The Stainless Steel SS304 has mesh# 120, 70, 38, and 16 while the Aluminum substrate is mesh# 16. The solid plates are SS304 ASTM A240, carbon steel ASTM A216, and aluminum Al-6063. All metallic substrates were rinsed with 95% reagent alcohol, followed by 50/50 peroxide/28% ammonia solution, then plasma etched using a plasma cleaner from Harrick Scientific.

In fact, PAH deposition can work with either wet etching or plasma etching depending on the application. The mesh substrates were machined either to fit the end of a glass pipe (GP) of 1.3 cm diameter (Fig-1(a)), analysis, a round spoon (RS) of 1.5 cm diameter and 0.5-1.0 cm depth (Fig-1(b)), and a mini bucket (MB) of 1.2 cm diameter with a 2.0-2.5 cm height, Fig-1(c)).

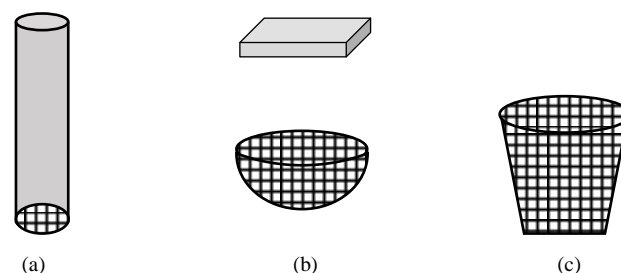


Figure 1. Various substrate geometries, (a) end-of a glass pipe (GP) of 1.3 cm diameter, (b) top: a metallic plate; bottom: a round spoon (RS) of 1.5 cm diameter, 0.5-1.0 cm depth, and (c) a mini bucket (MB) of 1.2 cm diameter with a 2.0-2.5 cm height

2.2. Procedure

A one-bilayer coating of PAH/PTFE, Figure 2, was applied to all plates and mesh substrates as depicted in Figure 2.

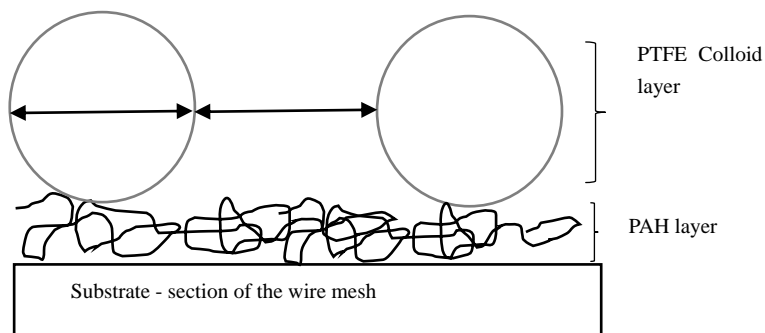


Figure 2. A schematic showing the deposition of polyallylamine hydrochloride (PAH) on a wire mesh substrate followed by a polytetrafluoroethylene (PTFE) colloidal particles layer to form one bilayer

The deposition process was started by dipping the clean etched substrate in the PAH solution for 30 minutes. The one layer of PAH is to functionalize the surface followed by three times rinsing in pure water. The rinsed surface was dipped in the PTFE colloid solution for 30 minutes followed by three times rinsing in pure water. The PAH/PTFE bilayer coating

was left to cure at a temperature of ~ 50 to 60°C for two hours. After curing, a set of experiments were conducted on the coated substrates. The first set used pure water, the second set used various concentrations of sodium chloride solutions (0.001M to 0.7M with 0.02M increments), and the third set used solutions from pH = 1 to pH = 13 with one pH

unit increment. The liquids were poured on the coated mesh substrates of various geometries i.e. the GP, the RS, and the MB structures to check on their ability to retain pure water, salt solutions, and acid/base solutions of pH range from 1 to 13 imposed by the superhydrophobic effect. The plates (uncoated/coated) were analyzed using CAM and SEM. The mesh wire substrates (uncoated/coated) were analyzed using FTIR, CAM, and SEM.

3. Results and Discussion

Surface analysis on the coated and uncoated metallic plates and mesh substrates was made using Fourier Transform Infrared FTIR, Scanning Electron Microscopy SEM, and Contact Angle Measurements CAM.

3.1. FTIR Analysis

In Figure 3, the FTIR spectrum of the coated SS304 120 mesh substrate shows the two-strong characteristic peaks of the C-F stretch bands at 1150 cm^{-1} and 1200 cm^{-1} that relate to the deposited per-fluorinated PTFE colloid micro-particles [13]. We attempted multiple depositions of two and three bilayers, without curing between layers. Note, at both frequency bands, higher peaks were recorded indicating more deposition of PTFE colloid particles as the number of bilayers increased. The strong trough after the C-F stretch band at 1200 cm^{-1} is not a derivative peak that can be corrected by the Kramers-Kronig algorithm. It might be a diffractive enhancement of the IR beam going through the coated mesh apertures as more layers get deposited.

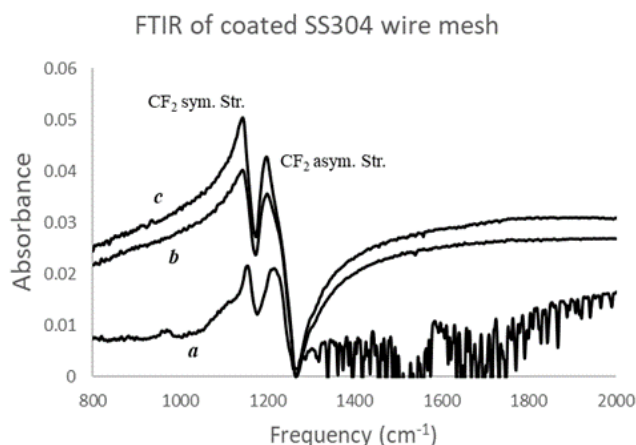


Figure 3. An FTIR spectrum of the coated SS304 120 mesh substrate shows characteristic two-strong peaks of the F-C stretch band at 1150 cm^{-1} and 1200 cm^{-1} . The number of bilayers increased from (a) one bilayer, (b) two bilayers, and (c) three bilayers

The IR spectrum of a wire mesh dipped in PTFE colloid only (i.e. no PAH used) then left to dry on a hot plate yielded a similar spectrum to the 2 or 3 bilayers coating. The only difference, the C-F stretch bands of the thermally deposited PTFE colloid appeared at higher frequencies of 1155 cm^{-1} (*cf* 1150 cm^{-1}) and 1208 cm^{-1} (*cf* 1200 cm^{-1}), that is, a frequency shift of 5 to 8 cm^{-1} . The shift in the two peaks of the C-F

stretch of the PAH/PTFE coating can be attributed to the long-range hydrogen bond interaction between the C-F bond in PTFE and the N-H bond in PAH [14].

3.2. SEM Analysis

In Figure 4, the SEM image of the uncoated SS304 wire mesh, Fig-4(a), and the coated wire mesh substrate starting with one bilayer Fig-4(b), two bilayers Fig-4(c), then three bilayers Fig-4(d) are taken at a magnification range from 900X to 1400X. The white grid-like structure represents the uncoated SS304 which is conducting with a high Z value to reflect the BSE, while the dark-grey granulated films are those of the nonconducting low Z PTFE colloid coating allowing greater penetration depth of BSE. Note the intensity of the grey PTFE deposition increases with more bilayers deposited. The three bilayers show that the metal surface is nearly covered by the PAH-PTFE coating. The wire mesh adhered to an aluminum stub using graphite paste tape.

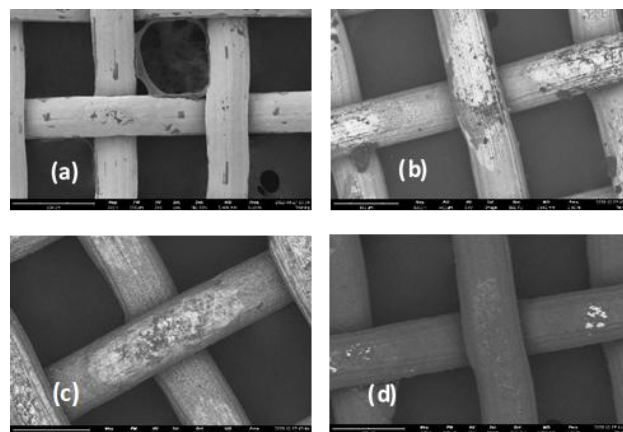


Figure 4. Scanning Electron Microscopy images of (a) uncoated SS304 wire mesh, (b) One bilayer, (c) two bilayers, (d) three bilayers, PTFE/PAH coated SS304 wire mesh Magnification: 900 to 1400, HV = 5KV at a vacuum pressure of 0.1 Pa, Detector: BSD Full

For this study, no attempt was made to deposit beyond three bilayers because the objective is to transform the hydrophilic metal surface to a superhydrophobic surface with little emphasis on the contribution of film thickness that ranged from 0.5 to $1.0\text{ }\mu\text{m}$ thickness for a three-bilayer coating. SEM reveals that a superhydrophobic surface does not necessarily require a uniform hydrophobic coating, but the pinning of scattered hydrophobic patches that is enhanced by the grid-like structure of the wire mesh substrates. SEM images taken at higher magnification of 19000 and 55000 shows the PAH-PTFE film is a porous structure with cavities $< 0.5\text{ }\mu\text{m}$. A porous hydrophobic surface is a condition required to obtain a superhydrophobic effect per the Cassie-Baxter theory [15].

3.3. CAM Analysis

The wire mesh substrate is a wave-like structure, thus another key structural feature that contributes to the superhydrophobic character is the hydrophobic crests of the wavy wire mesh, Figure 5.

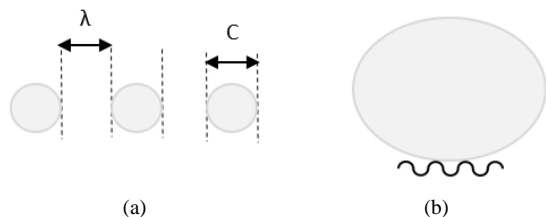


Figure 5. A simplified schematic of (a) line up of 1 μm size colloidal particles that sets $C \sim \lambda$, (b) a liquid drop on a wire mesh

In this regard, a theoretical model that fits a powder-coated substrate is the re-entrant fractal geometry [15] where the Cassie-Baxter contact angle β of a sessile drop is defined as:

$$\cos\beta = -1 + (C/(C + \lambda))[\sin\theta + (\pi - \theta)\cos\theta] \quad (1)$$

The angle $\theta = 105^\circ$ to 115° is the intrinsic contact angle of a smooth clean PTFE hydrophobic surface (i.e. PTFE plate) [16]. According to equation (1), a higher θ value indicates a higher Cassie-Baxter contact angle β . For example, a coating of PAH/PTFE on the SS304 plate exhibits adjacent colloidal microparticles with a ratio of $C/(C+\lambda) = 0.5$. When $\theta = 115^\circ$, would yield a static contact angle $\beta = 141^\circ$, which is within the range of experimental values of metallic plates, Table 1.

In this study, the geometry of the wire mesh, Fig-4(a), renders C and λ nearly equal where the ratio of the aperture size and wire diameter modifies Equation 1 to become Equation 2:

$$\cos\beta = -1 + (A_e/2W_e)[\sin\theta + (\pi - \theta)\cos\theta] \quad (2)$$

For example, for a wire mesh#120, the effective aperture size $A_e = 1.4 \times 10^{-4}$ m and the effective wire diameter $W_e = 4 \times 10^{-5}$ m, the expected static contact angle $\beta \sim 158^\circ$. The measured static contact angles for a wire mesh#120 ranged from 155 to 160°. Contact angle measurements (CAM) are discussed below using pure water, salt solutions, and pH-controlled solution analysis.

A flat metallic plate that is coated with one bilayer of PAH-PTFE film was examined against a reference uncoated clean metallic plate using the three types of solutions i.e. pure water, dilute salt solutions with concentrations ranging from 0.01M to 0.7M, dilute acidic and basic solutions that ranged in pH from 2 to 13. The pure water used is deionized water with ionic conductivity of 3 to 4 μScm^{-1} .

Prior to measuring the static contact angles, the uncoated metallic plates of stainless steel SS304, carbon steel, and aluminum were cleaned with reagent alcohol followed by pure water rinsing. The contact angles measured on the clean metallic surfaces were $65^\circ \pm 4^\circ$, $43^\circ \pm 4^\circ$, and $50^\circ \pm 4^\circ$ respectively. When these metallic plates were etch-cleaned

with peroxide/ammonia solution or plasma, water perfectly wets the metal surface (i.e. contact angle $\sim 0^\circ$). After the deposition of one bilayer of PAH/PTFE/ the contact angles changed to $141^\circ \pm 2^\circ$, $146^\circ \pm 2^\circ$, for SS304 and carbon steel, Figure 6(a), and Aluminum $133^\circ \pm 2^\circ$, Figure 6(b).

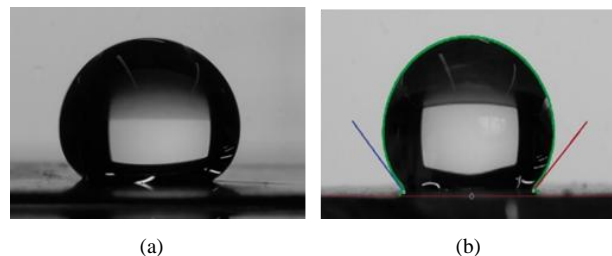


Figure 6. A sessile drop photos of a water droplet on PAH-PTFE coated metallic plates (a) Stainless steel SS304, (b) Aluminium. Droplet size $\sim 20 \mu\text{L}$

Instead of using aggressive methods to create a porous surface on the metal substrates, we opted to use metallic mesh substrates to attain the superhydrophobic character. A high mesh# such as 120 with a characteristic aperture (or sieve opening) of ~ 125 microns is expected to yield the highest contact angle.

For the four SS304 mesh wire geometries i.e. SS304(#16, #38, #70, #120) the contact angles ranged from $146^\circ \pm 4^\circ$ using SS304 wire mesh 16, Figure 7(a) to $160^\circ \pm 2^\circ$ using SS304 wire mesh 120, Figure 7(d). A higher uncertainty in the measurement of contact angle using the SS304 wire mesh 16 is attributed to a bigger mesh hole and wire thickness. There is a correlation between the mesh number and the contact angle. As the mesh number increases (i.e. smaller aperture) the static contact angle increases indicating a higher superhydrophobic character. For example,

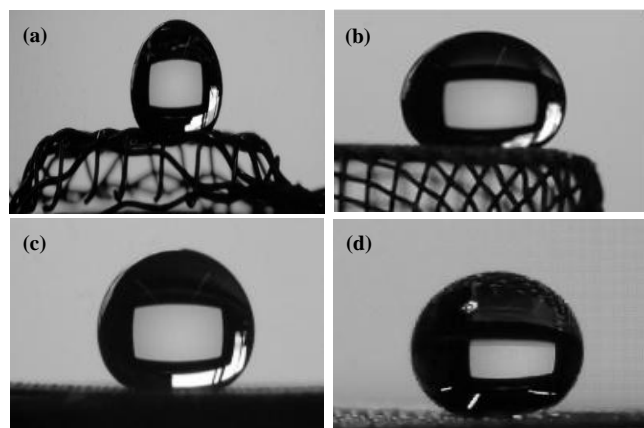


Figure 7. A sessile drop photos of a water droplet on selected SS304 wire mesh samples that are coated with a bilayer of PAH/PTFE. Droplet size $\sim 20 \mu\text{L}$ (a) wire mesh 16, (b) wire mesh 38, (c) wire mesh 70, (d) wire mesh 120

Table 1. Table information

Sample	Al plate	SS304 plate	SS304 # 16	SS304 # 38	SS304 # 70	SS304 # 120
Liquid						
H ₂ O	133	141	146	148	151	160
pH= 13	68	140	129	133	139	156
Salt*	92	143	129	132	140	146

* A 0.7 M salt solution

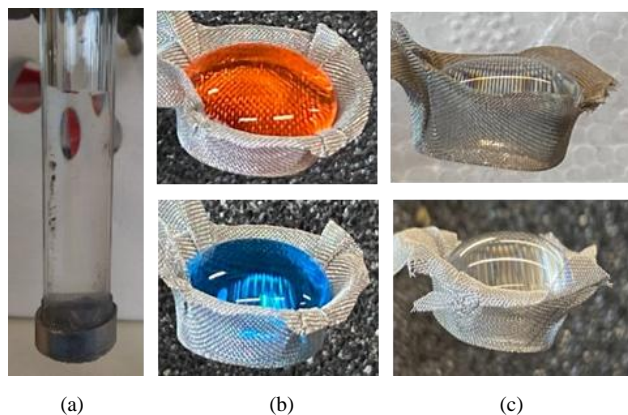


Figure 8. A PAH/PTFE coated SS304 wire mesh 120 (a) capped GP filled with pure water, (b) MB retaining acidic/basic solutions, (c) MB retaining pure water or salt solutions

We have tested the retention of pure water by the various mesh wire buckets by virtue of having superhydrophobic surfaces. For example, a PAH/PTFE coated SS304 wire mesh 120 used to cap a glass pipe GP, Figure 8(a), was able to hold a 5.0 cm column of pure water without leaking.

The mini bucket MB fabricated from a PAH/PTFE coated SS304 wire mesh 120 having a depth of 2.0 cm was able to retain an acid solution of pH = 1 or a base solution of pH = 13 poured into it, Figure 8(b). The same MB was able of retaining salt solutions from 0.001M to 0.7M, Figure 8(c). Using the spoon structures of a 0.5 cm depth, and 1.5 cm diameter of all mesh types i.e. SS304(#16, #38, #70, #120) and Aluminum (mesh # 20) was capable of retaining a 2 mL volume of pure water, solutions of a pH range from 1 to 13 and 0.7 M salt solution. In fact, we tested the PAH/PTFE coating deposited to the mesh wires by incrementing the pH of the acid/base solutions by one pH unit, and for the salt solutions, the NaCl concentration was incremented by 0.02M. Chemical resiliency of the PAH/PTFE coating against concentrated acid/base solutions, salt solutions, and organic solvents shall be conducted in a separate study.

4. Conclusions

A bilayer composed of polyelectrolyte polyallylamine hydrochloride (PAH) and a colloidal solution of polytetrafluoroethylene (PTFE) was successfully deposited on stainless steel SS304 and aluminum substrates. The metallic substrates whether a plate form or a mesh wire form (i.e. mesh#16, 38, 70, and 120) were successfully coated with a PAH/PTFE bilayer and multiple bilayers. Surface analysis instrumentation infrared, contact angle, and scanning electron microscopy verified the deposition of the coating on the metallic surfaces used. Static contact angle measurements of sessile drops were made for pure water, acid/base, and salt solutions and ranged from 130° to 160° implying strongly hydrophobic and superhydrophobic character. The wire mesh substrates were superhydrophobic enough to hold water in mini-buckets and glass pipes up to a 5 cm hydrostatic height.

ACKNOWLEDGEMENTS

The authors would like to thank the West Virginia University Institute of Technology, the Physical Sciences Department, and the NASA West Virginia EPSCoR Consortium for the support of this research.

REFERENCES

- [1] Muhammad Zaman Khan, Jiri Militky, Michal Petrub, Blanka Tomková, Azam Ali, Elçin Tören, Sajida Perveen (2022). Recent advances in superhydrophobic surfaces for practical applications: A review, *European Polymer Journal*, Volume 178(5).
- [2] Xiao Wang, Cheng Fu, Chunlai Zhang, Zhengyao Qiu, and Bo Wang, (2022) A Comprehensive Review of Wetting Transition Mechanism on the Surfaces of Microstructures from Theory and Testing Methods, *Materials*, 15, 4747.
- [3] E. Pakdel, J. Wang, S. Kashi, L. Sun, X. Wang, (2020) Advances in photocatalytic self-cleaning, superhydrophobic and electromagnetic interference shielding textile treatments, *Adv. Colloid Interface Sci.*, 277, 102116.
- [4] D.W. Wei, H. Wei, A.C. Gauthier, J. Song, Y. Jin, H. Xiao, (2020), Superhydrophobic modification of cellulose and cotton textiles: Methodologies and applications, *J. Bioresour. Bioprod.*, 5, 1–15.
- [5] X.J. Guo, C.H. Xue, M. Li, X. Li, J.Z. Ma, (2017) Fabrication of robust, superhydrophobic, electrically conductive, and UV-blocking fabrics: via layer-by-layer assembly of carbon nanotubes, *RSC Adv.*, 7, 25560–25565.
- [6] Y. Zhao, Y. Tang, X. Wang, T. Lin, (2010) Superhydrophobic cotton fabric fabricated by electrostatic assembly of silica nanoparticles and its remarkable buoyancy, *Appl. Surf. Sci.* 256, 6736–6742.
- [7] J. Bravo, L.Zhai, Z.Z. Wu, R.E. Cohen, M.F. Rubner, (2007) Transparent superhydrophobic films based on silica nanoparticles, *Langmuir*, 23, 7293.
- [8] Konica Sharma, Amrita Hooda, M.S. Goyat, Radheshyam Rai, Ajay Mittal, (2022) A review on challenges, recent progress and applications of silica nanoparticles based superhydrophobic coatings, *Ceramics International*, 48, 5922–5938.
- [9] Zhiqian Wang, Sumona Paul, Louis H. Stein, Arash Salemi, and Somenath Mitra, (2022) Recent Developments in Blood-Compatible Superhydrophobic Surfaces, *Polymers*, 14, 1075.
- [10] Ik-Soo Kim, Myung-Yeon Cho, Yohan Jeong, Yun-Cheol Shin, Dong-Won Lee, Chulhwan Park, Sang-Mo Koo, Weon Ho Shin, Won-Jik Yang, Yeol Park, Hiesang Sohn, Jong-Min O. (2021) Aerosol-deposited Al₂O₃/PTFE hydrophobic coatings with adjustable transparency, *J Am Ceram Soc.*; 104: 1716–1725.
- [11] Wang, Feng; Zhang, Huapeng; Zhu, Hailin; Guo, Yuhai; (2014) Ultra-hydrophobic modification of TiO₂ nanoparticles via thermal decomposition of polytetrafluoroethylene, *Powder Technology*, Volume 253, Pages 548-552.

- [12] Inoue, Youichi; Yoshimura, Yasuhiro; Ikeda, Yukiko; Kohno, Akiomi; (2000) Ultra-hydrophobic fluorine polymer by Ar-ion bombardment, *Colloids and Surfaces B: Biointerfaces*, Volume 19, Issue 3, 30, Pages 257-261.
- [13] Joanna Piwowarczyk, Roman Jędrzejewski, Dariusz Moszyński, Konrad Kwiatkowski, Agata Niemczyk, Jolanta Baranowska, (2019) XPS and FTIR Studies of Polytetrafluoroethylene Thin Films Obtained by Physical Methods, *Polymers*, 11, 1629.
- [14] Daniel G. Abebe, Tarek R. Farhat* (2010) "Self-assembly of Nafion®/poly(vinyl alcohol) at pH = 1.2 and Nafion®/poly(allyl amine) at pH = 11, *Soft Matter*, vol.6, issue 6, pp. 1325.
- [15] Xiao Wang, Cheng Fu, Chunlai Zhang, Zhengyao Qiu, and Bo Wang,*, A Comprehensive Review of Wetting Transition Mechanism on the Surfaces of Microstructures from Theory and Testing Methods, (2022) *Materials* 15(14): 4747.
- [16] Zhang J, Li J, Han Y. (2004) Superhydrophobic PTFE surfaces by extension. *Macromolecular Rapid Communications*. 1; 25(11): 1105-8.
- [17] Reese, L. C., and Welch, R. C., 1975, Lateral loading of deep foundations in stiff clay., *J. Geotech. Engrg. Div.*, 101(7), 633–649.