

On the Oil Repellency of Nanotextured Aluminum Surface

G. Momen, R. Jafari, and M. Farzaneh

Abstract—Two different superhydrophobic surfaces were elaborated and their oil repellency behavior was evaluated using several liquid with different surface tension. A silicone rubber/SiO₂ nanocomposite coated (A) on aluminum substrate by “spin-coating” and the sample B was an anodized aluminum surface covered by Teflon-like coating. A high static contact angle about $\sim 162^\circ$ was measured for two prepared surfaces on which the water droplet roll-off. Scanning electron microscopy (SEM) showed the presence of micro/nanostructures for both sample A and B similar to that of lotus leaf.

However the sample A presented significantly different behaviour of wettability against the low surface tension liquid. Sample A has been wetted totally by oil (dodecan) droplet while sample B showed oleophobic behaviour. Oleophobic property of Teflon like coating can be contributed to the presence of CF₂ and CF₃ functional group which was shown by XPS analysis.

Keywords—Oleophobic, Superhydrophobic, Aluminum surface, Nano-texture.

I. INTRODUCTION

SUPERHYDROPHOBIC surfaces (SH) with high water contact angle ($>150^\circ$) and low hysteresis contact angle ($<5^\circ$) find tremendous importance because of its growth potential across many key industries and it's beneficial. Superhydrophobic surfaces can be developed by a combination of low surface energy materials and surface micro and nanostructures [1]. The most widely known example of a natural superhydrophobic surface is the surface of the lotus leaf (*Nelumbo nucifera*), in which the combination of surface chemistry and roughness (see the inset of Fig. 1 (a)) allows the air (or gas) pockets are trapped in the rough surface cavities. This trapped air imbues the leaf with its characteristic superhydrophobicity.

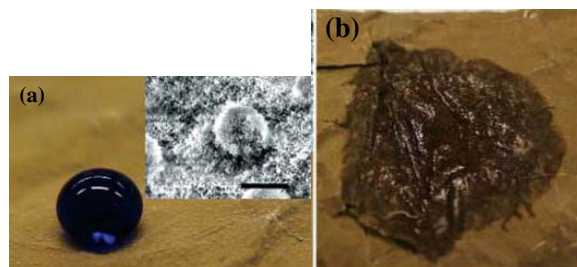


Fig. 1 (a) Image of water droplet (colored with methylene blue) on a lotus leaf surface, the inset shows a scanning electron microscopy (SEM) image of the lotus leaf surface (b) Wetted surface of the lotus leaf after contact with a droplet of hexadecane (oil) [2].

To date, several approaches have been applied to prepare the superhydrophobic surfaces [3]-[7] such as: Wet chemical reaction, electrochemical deposition, self-assembly, layer-by-layer methods, plasma treatments, chemical vapor deposition, sol-gel methods, polymerization reaction, templates, electrospray and sandblasting. Two distinct models of Wenzel and Cassie-Baxter, are commonly used to describe superhydrophobic surfaces which correspond to the homogeneous and heterogeneous wetting as shown in Fig. 2. In Wenzel's model (homogeneous interface), a wetting liquid will be completely absorbed by the rough surface cavities. However in the Cassie-Baxter model (composite interface), air pockets are trapped in the rough surface cavities, leading to a composite solid-liquid-air interface, as opposed to the homogeneous solid-liquid interface [8].

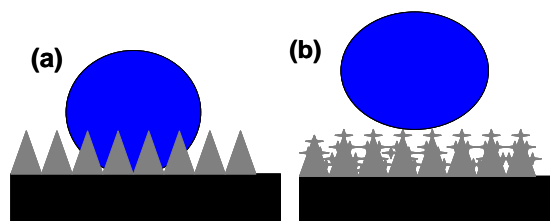


Fig. 2 Schematic representations of wetting models, (a) Homogeneous interface and (b) Heterogeneous interface [3]

G. Momen is Professor-researcher at the University of Quebec at Chicoutimi, Qc, Canada (e-mail: gmomen@uqac.ca).

R. Jafari is Professor-researcher at the University of Quebec at Chicoutimi, Qc, Canada (e-mail: rrjafari@uqac.ca).

M. Farzaneh is Director of the International Center on Icing and Power Network Engineering (CENGIVRE), as well as Chair Holder of the NSERC/Hydro-Quebec Industrial Chair on Atmospheric Icing of Power Network Equipment (CIGELE) and of the Canada Research Chair on Engineering of Power Network Atmospheric Icing (INGIVRE) at Université du Québec à Chicoutimi (UQAC), Canada. (e-mail: Masoud_Farzaneh@uqac.ca).

It is highly desirable for superhydrophobic surfaces to also be oil repellent i.e., to exhibit oleophobicity or superoleophobicity; however, this is not always the case since oils have smaller surface tension (surface tension, $\gamma = 72.1 \text{ mN}\cdot\text{m}^{-1}$ for water, and $20\text{--}50 \text{ mN}\cdot\text{m}^{-1}$ for oils). A liquid with a markedly lower surface tension such as hexadecane ($\gamma_{lv} = 27.5 \text{ mN/m}$) rapidly wets the lotus surface, leading to a

contact angle of $\sim 0^\circ$ (see Fig. 1 (b)), clearly demonstrating the leaf's oleophilicity [2]. Indeed, a poor oil repellent surface can be easily contaminated and thus lose its superhydrophobicity. The creation of superoleophobicity is more difficult than that of superhydrophobicity because the surface tension of oil or other organic liquids is lower than that of water.

In this work, we prepared two nanostructured superhydrophobic coatings with different chemistry and topography and we studied their oleophobic properties.

The first coating corresponds to the silicone rubber superhydrophobic film containing CH_3 group as hydrophobic function and the latter is RF-sputtered polytetrafluoroethylene (PTFE or Teflon-like coating) film deposited on aluminum surface with functional group of CF_2/CF_3 as hydrophobic function. Here, we studied the wettability of two developed coatings against three solutions: water (72.1mN.m^{-1}) for their hydrophobic properties and ethylene glycol (48mN.m^{-1}) and Dodecan (24.5mN.m^{-1}) for their oleophobic properties.

II. EXPERIMENTAL

Polished 6061 aluminum alloy coupons ($2.54\text{cm} \times 2.54\text{cm} \times 0.15\text{cm}$) from Rio Tinto Alcan: Mg 1.0, Si 0.6, Cu 0.28, Cr 0.05, Zn 0.1, Fe 0.25 and Mn 0.15 (all in wt.%) were used as the substrate. Two type of sample (**A** & **B**) were prepared by two different methods as described below:

Sample **A** was made by spin coating of room-temperature-vulcanized silicone rubber (RTV SR, from Dow Corning) in Hexane, doped with SiO_2 nanoparticles and dried in oven at 100°C for 3h to remove any volatile components. The spinning speed was set at 3000rpm (20s) and 2500rpm (15s) for the first and second stages, respectively.

Sample **B** was developed by plasma sputtering of Teflon on an anodized aluminum surface. The anodizing process was carried out in 10% w/w solution of H_3PO_4 at $T=18^\circ\text{C}$ at 50V during 90min. The RF plasma sputtering process was carried out in a HICP-600SB PECVD system, manufactured by Plasmionique Inc. The procedure has been described in greater detail elsewhere [4].

The wettability results were collected by using a DSA-100 contact angle goniometer from Krüss (water drop volume $\sim 4\mu\text{L}$). Surface topographies were analyzed with a scanning electron microscopy (SEM, LEO Gemini instrument). The FTIR spectra were obtained for sample A by using the Fourier transformation infrared spectrometer (Perkin-Elmer, Spectrum One). The reflected beam was collected for 24 scans at a resolution of 4cm^{-1} .

The surface chemical composition of sample B was examined using X-ray photoelectron spectroscopy (XPS) at three different spots for each sample (PHI 5600-ci spectrometer, Physical Electronics). Survey and high-resolution spectra were acquired at a detection angle of 45° with respect to the normal of the surface, using the $\text{K}\alpha$ line of standard aluminum ($\text{K}\alpha = 1486.6\text{eV}$) and magnesium ($\text{K}\alpha = 1253.6\text{eV}$) X-ray sources, respectively.

III. RESULTS AND DISCUSSIONS

FESEM investigations of coating A and B showed the evolution of various morphological features as shown in Figs. 3 (a)–(d). The images shown in Figs. 3 (c), (d) (corresponding to coating A and B) were obtained at higher magnification.

Fig. 3 (a) exhibits highly rough “coral-like” structure consisting of micro and nanostructure. Microstructure is basically come from the aluminum hydrate micro-particles ($1\text{--}2\mu\text{m}$) already present in silicone rubber composition. The image obtained at higher resolution (Fig. 3 (c)) showed the presence of SiO_2 nanoparticles ($10\text{--}20\text{nm}$ diameter).

The morphological structure of RF-sputtered PTFE coating has been presented in Figs. 3 (b) and (d). Typically an anodized aluminium surface prepared in phosphoric acid contains large nanopores having thin walls (See Fig. 3 (d)). Fig. 3 (d) shows that the anodized surface is covered very well by the Teflon-like coating and the presence of some nanopores with a diameter of about 100nm surrounded by a bird's nest structure has been observed. The micro/nano scale structure has been observed for two samples A and B that fulfill the superhydrophobic requirement.

It is necessary to measure the contact angle (θ), if one wishes to characterize the surface of a solid in terms of its surface free energy components.

The contact angles of sample A and with different liquid as water (72.1mN.m^{-1}), ethylene glycol (48mN.m^{-1}) and dodecan (24.5mN.m^{-1}) were examined, as illustrated in Figs. 4 (a) to (d) and Table I. A polished aluminum surface showed a water contact angle of about 88° . Fig. 4 (a) shows a superhydrophobic coating of sample A with high water contact angle of about 163° and the roll of properties. This surface exhibits a lower contact angle of ethylene glycol about 137° but stay more than 90° . However, dodecan droplet completely wetted the sample A and it was so difficult to measure the contact angle.

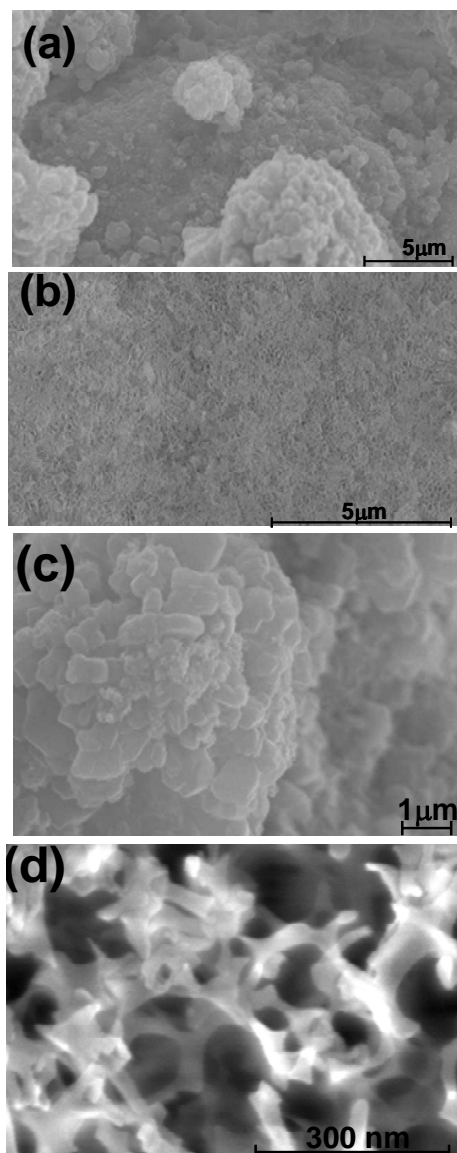


Fig. 3 SEM image of (a) Silicone rubber/SiO₂ coating on aluminum surface (b) RF-sputtered PTFE coating deposited on an anodized aluminum surface

In fact, the final shape of the drop on the solid surface depends on the relative magnitudes of the molecular forces that exist within the liquid (cohesive) and between liquid and solid (adhesive). Thus, the contact angle is a result of the competing tendencies of the liquid drop and solid determining whether it spreads over the solid surface or rounds up to minimize its own area. When a low surface energy liquid wets a solid surface, giving a zero contact angle, the molecular adhesion between solid and liquid is higher than the cohesion between the molecules of the liquid. On the contrary, liquids with high surface tension tend to give a finite (non-zero) contact angle, indicating that the cohesive force is superior than the energy of adhesion between liquid and solid [9], [10].

The RF-sputtered Teflon-like coating on the anodized surface showed the superhydrophobic roll-off property behavior with a water contact of about 162° (Fig. 4 (b)). The contact angle of ethylene glycol decreases slightly and was about 152°. However the contact angle of dodecan on sample B decreased considerably and attains almost 80°. It is apparent from Fig. 4 that the difference between the corresponding contact angles on the two surfaces A and B decrease as the liquid surface tension (γ_{lv}) decreases. However, an oil droplet of n-dodecan wet partially the surface B (Fig. 4 (f)) while the sample A is totally wetted by that as shown in Fig. 4 (e).

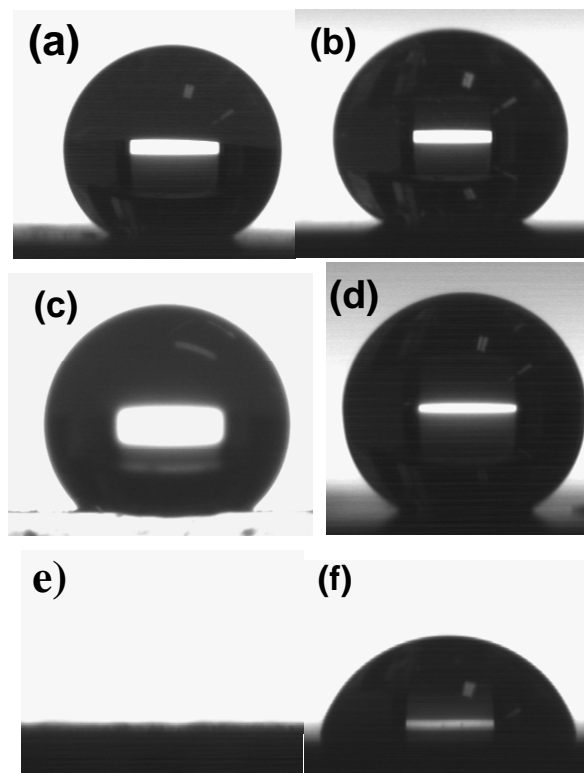


Fig. 4 Images of water (a) (b), ethylene glycol (c) (d) and dodecan (e) (f) droplets on surface of A and B sample, respectively

TABLE I
CONTACT ANGLE OF TWO COATING A AND B FOR THREE LIQUIDS

Sample	Static contact angle (°)		
	Water	Ethylene glycol	n-Dodecan
A(SR/SiO ₂ coating)	163.4±2	137.2±3	2
B (Teflon like coating)	162±3	152.3±4	79.4± 3

To find out how the chemical composition can influence on the hydrophobic and oleophobic properties of the coatings, FTIR spectroscopy has been used in the range of 4000–450cm⁻¹, as shown in Fig. 5. From the obtained spectra, the stronger absorption band at 1270–1255cm⁻¹ can be assigned to the Si-CH₃ bonds. Other typical absorption bands can be attributed to the CH_x symmetric 236 and asymmetric stretching at 2900–2960cm⁻¹. The decrease in the intensity of the band at 1260cm⁻¹ was obtained for the sample A.

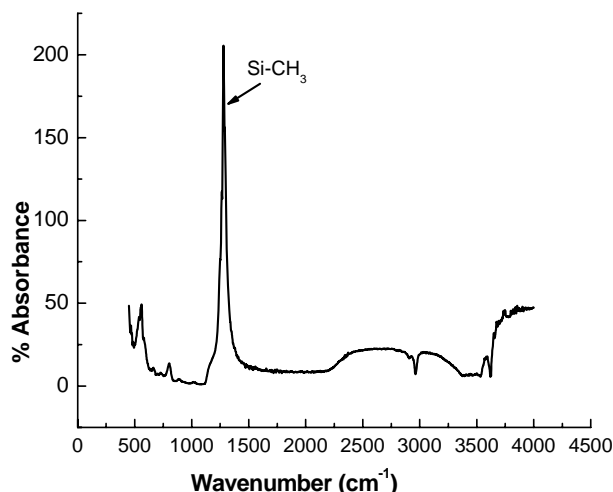


Fig. 5 FTIR spectroscopy of Silicone rubber/SiO₂ coating on aluminum surface

Also, the Teflon-like coatings were analyzed by XPS (see Fig. 6). The spectrum for the C_{1s} core level of a Teflon-like coating can be satisfactorily fitted by a combination of five distinct peaks: the peak at 285.1eV corresponding to C-C moieties, the peak at 287.5eV corresponding to C-F_x species (hydrocarbon adjacent to a fluorocarbon group with x = 1 to 3), the peak at 289.6eV corresponding to CF groups, the peak at 291.8eV corresponding to CF₂ and the peak at 293.9eV being due to CF₃ groups [10]-[11]. The XPS analysis clearly shows the presence of high amounts of -CF₃ and -CF₂ groups on the Teflon-like coating, which contribute to the low surface energy of Teflon coatings [12]. These results show the hydrophobicity and oleophobicity properties of fluorocarbon coating which happens because C-F bond exhibits resistance both to van der Waals forces and polar interactions.

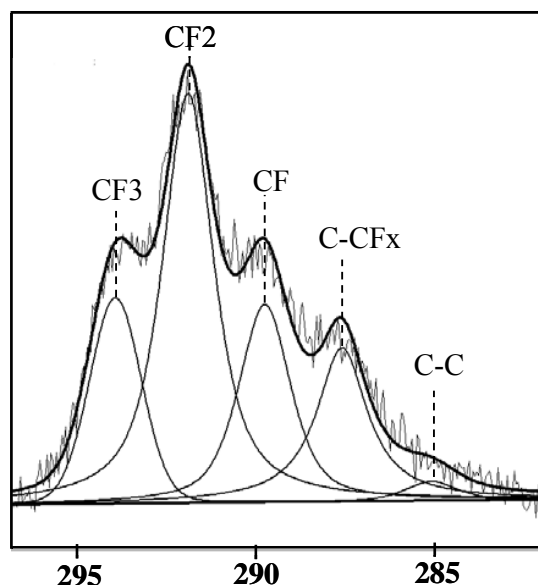


Fig. 6 XPS spectra of RF-sputtered PTFE coating deposited on an anodized surface

IV. CONCLUSION

Two kind of superhydrophobic surfaces were derived using spin coating of a silicone rubber /SiO₂ nanocomposite coated on aluminum substrate (A) and RF-sputtering of PTFE on anodized aluminum surface. A high water contact angle about ~162° was measured for two prepared surfaces on which the water droplet roll-off.

The morphology of these surfaces showed that the presence of micro- nanostructure surface. However these surfaces showed the different contact angles against a low surface tension liquid. Sample A has been wetted totally by oil (dodecan) droplet while sample B showed oleophobic behavior. Oleophobic property of Teflon like coating may be contributed to the presence of CF₂ and CF₃ functional group which was shown by XPS analysis.

ACKNOWLEDGMENT

This work was carried out within the framework of the NSERC/Hydro-Quebec/UQAC Industrial Chair on Atmospheric Icing of Power Network Equipment (CIGELE) and the Canada Research Chair on Engineering of Power Network Atmospheric Icing (INGIVRE) at Université du Québec à Chicoutimi. The authors would like to thank the CIGELE partners (Hydro-Québec, Hydro One, Réseau Transport d'Électricité (RTE) and Électricité de France (EDF), Alcan Cable, K-Line Insulators, Tyco Electronics, Dual-ADE, and FUQAC) whose financial support made this research possible.

REFERENCES

- [1] R. Jafari & M. Farzaneh, "Fabrication of superhydrophobic nanostructured surface on aluminum alloy", Journal of Applied physics A, vol. 102, issue 1, 2011, pp. 195-199.

- [2] A. Tuteja, W. Choi, G.H. McKinley, R. E. Cohen, and M.F. Rubner, MRS BULLETIN • Vol. 33, August 2008 .
- [3] G. Momen & M. Farzaneh, Applied Surface Science Vol. 258, Issue 15, 2012, pp. 5723–5728.
- [4] R. Jafari, R. Menini & M. Farzaneh, " Superhydrophobic and icephobic surfaces prepared by RF-sputtered polytetrafluoroethylene coatings", Journal of Applied surface science, no.257, Nov.2010, pp. 1540-1543.
- [5] G. Momen & M. Farzaneh, "A simple process to fabricate a superhydrophobic Silicone rubber coating", Micro & Nano Letters, Vol. 6, issue 6, 2011, pp. 405-407.
- [6] L. Foroughi mobarakeh, R Jafari & M. Farzaneh, "Superhydrophobic surface elaboration using plasma polymerization of hexamethyldisiloxane (HMDSO)", Advanced Materials Research, Vol. 409, 2012, pp. 783-787.
- [7] G. Momen, M. Farzaneh & R. Jafari, " Wettability behaviour of RTV silicone rubber coated on nanostructured aluminium surface " Applied Surface Science, Vol. 257, issue 15, 2011, pp. 9489-6493.
- [8] B.t Bhushan, Y Chae Jung, "Lotus Effect: Surfaces with RoughnessInduced Superhydrophobicity, Self-Cleaningand Low Adhesion", Ultramicroscopy, Vol. 107, 2007, pp.1033–1041.
- [9] R.-H Yoon, and S. A Ravishankar, "Long-Range Hydrophobic Forces between Mica Surfaces in Alkaline Dodecylammonium Chloride Solutions", J. Colloid Interface Science, Vol. 179, 391, 1996, pp. 403-411.
- [10] Yoon, R.-H. and Pazhianur, R., "Direct Force Measurement between Hydrophobic Glass Sphere and Covellite Electrode in Potassium Ethyl Xanthate Solutions at pH 9.2," Colloids and Surfaces, vol. A144, 1998. pp. 59-69.
- [11] P. Gonon, " Effect of nitrogen addition on the properties of C.F thin films deposited by RF sputtering" Eur. Phys. J. Appl. Phys. 32, 2005, pp. 15-21.
- [12] V. Stelmashuk, H. Biederman, D. Slavinska, M. Trchova, P. Hlídek, "Rf magnetron sputtering of polypropylene", Vacuum 75, 2004, pp. 207-215.