Hydrophobicity of Fluoroalkylsilane- and Alkylsilane-Grafted Surfaces

M. Farzaneh, S.A. Kulinich, and C. Volat
NSERC / Hydro-Quebec / UQAC Industrial Chair on Atmospheric Icing of Power Network Equipment (CIGELE) and Canada Research Chair on Engineering of Power Network Atmospheric Icing (INGIVRE) at Université du Québec à Chicoutimi, Québec, Canada, G7H 2B1 (http://cigele.ca)

Abstract—This work aims at theoretical evaluation of hydrophobic properties of surfaces coated with certain self-assembling organic monolayers (SAMs). Being coatings with low surface energy, such SAMs are potentially useful for snow- and/or ice-repellent applications. In this paper, in a framework of search for snow- and ice-repellent coatings, we analyze wetting behavior of most common and commercially available SAMs. A comparative analysis of hydrophobicity of fluoroalkylsiloxane and alkylsiloxane monolayers, on smooth and rough surfaces, is based on a simple model that considers various self-assembly degrees of organic molecules and various area fractions of air inclusion. Sliding behavior of water on rough “composite” needle-like surfaces is also evaluated. On flat surfaces, regardless of assembly degree of coatings, contact angles of fluoroalkylsiloxane monolayers are always ~10° larger. The difference, however, decreases on rough “composite” substrates with air inclusion. It is shown that assembly order of organic molecules and reduced water-solid contact area are the key factors leading to both high contact angles and low sliding angles.

Keywords: Fluoroalkylsiloxanes; Alkylsiloxanes; Low surface energy; Roughness; Contact angle; Sliding angle; Water repellency; Super-hydrophobicity

I. INTRODUCTION

In cold climate regions, there is always a critical problem of decreasing the adhesion of snow and ice to constructions under low-temperature environment. In recent years, various water-repellent coatings have been proposed for this purpose [1-5]. To reduce the adhesion of ice (an adhesive whose liquid form is water), requires reducing substrate wettability, making it more hydrophobic. This implies reducing its reactivity and surface forces, making it more inert, more incompatible with water [5-11]. The resulting higher contact angle makes it more likely to occlude air at the interface [5-8].

Production of self-assembled monolayer (SAM) coatings is one of the most successful approaches to chemical modification and hydrophobization of many hydrophilic surfaces [6-8,12-16]. A perspective use of various SAM coatings as snow- and ice-repellent materials with low surface energy has been recently reported by a few groups [1-3]. However, there is still a lack of systematic knowledge on how the microstructure and surface chemistry of SAMs influence the hydrophobic and, in particular, snow and ice-repellent properties of the coatings. As SAMs of fluoroalkylsilanes are expected to demonstrate even lower surface energy compared to that of alkylsilanes, it is interesting to compare their hydrophobicity. The latter has been demonstrated to have a direct correlation with interfacial strength between SAM-grafted surfaces and ice [1].

This paper presents a comparative analysis of wetting behavior of both flat and rough surfaces covered with the most common fluoroalkylsiloxane (FAS-17 and FAS-13) and octadeylsiloxane (ODS) monolayers. Such SAMs can be formed from commercially available silanes, such as: 1H,1H,2H,2H-perfluorodecyltrimethoxysilane [6,13,14,17-19] or 1H,1H,2H,2H-perfluorodecyltrichlorosilane [7,20] (FAS-17); 1H,1H,2H,2H-perfluorooctyltrichlorosilane [20] (FAS-13); and octadeyltrichlorosilane [12,15,21-23] (ODS). Another intention of the present study was to show the importance of the self-assembly order as an important factor governing hydrophobicity of SAM-coated surfaces. Both static (defined by the contact angle of water droplet) and dynamic (defined by the sliding angle) hydrophobicities are theoretically modeled as functions of self-assembly order/disorder degree and area fraction of air entrapped into rough hydrophobic surfaces.

II. MODEL DESCRIPTION

The formation mechanism of fluoroalkylsilane SAMs was not investigated extensively and is likely to be similar to that of alkylsilane monolayers [12,15,21-24]. The analysis of literature shows that self-assembling of alkylsilanes involves the following steps. First, the molecules are hydrolyzed by water and form silanol-containing species. The OH groups of these silanols form hydrogen bonds to each other and to surface OH groups. Interactions between the alkyl chains direct chain ordering to form a well-organized and dense film. Finally, the organized monolayer is covalently grafted by the condensation reaction of the hydroxyl groups to form Si-O-Si linkages within the monolayer and with the surface [12,15,16,21-23]. Depending on reaction conditions, the formation of complete monolayers with a dense, well-organized assembly with aligned alkyl chains, or the creation of a coating with disordered molecules that have not self-assembled to form condensed domains can be observed [12,21-24]. In Fig.1, disordered species (right) and a well-organized domain (left) are shown for a FAS-13 monolayer. The relative proportion of ordered and disordered phases depends on water and silane concentrations, solution age, chain length of silane molecules, temperature, reaction time,
dispersion pH, substrate surface conditions, and steric effects [12,16,21-24]. Moreover, self-assembly is not the only reaction possible between alkylsilanes and surfaces; covalent attachment and vertical polymerization of silane monomers are also possible under certain conditions [24].

On the basis of the above, a model describing the wetting behavior of fluoroalkylsiloxane and alkylsiloxane SAMs with the following assumptions is proposed: (i) The distribution of heterogeneities is assumed to be uniform over the surface, irrespective of their chemical or geometrical character; (ii) The effect of pores in coatings is negligible, and the surfaces are fully grafted by SAM molecules, which expose their topmost CF3 and CF2 (or CH2) groups, respectively. Thus, coatings with high degrees of assembly are characterized by high values of f3 and low values of f2, provided that f3 + f2 = 1; (v) Rough surfaces and air inclusion in the surface structure are modeled by changing fractions of water and air-covered surface domains.

For the simplest cases of smooth and chemically heterogeneous surfaces composed of N phases, the wettability can be evaluated from eqs.(1) and (2), which are generalized cases of the Israelachvili-Gee [25] and Cassie [26] equations for N-phase surfaces with domain sizes of molecular and micrometer dimensions, respectively. Relation (1) is used whenever the size of chemically heterogeneous domains approaches molecular dimensions, while eq.(2) describes surfaces composed of well-separated and distinct patches of micrometer size or larger. Both types of heterogeneity, with patch sizes of below and over 1 µm, have been demonstrated, e.g., for ODS monolayers on Si and mica substrates, and occur depending on process parameters [12,21-23].

\[
(1 + \cos \theta)^2 = \sum_{i=1}^{N} f_i (1 + \cos \theta_i)^2
\]

\[
\cos \theta = \sum_{i=1}^{N} f_i \cos \theta_i
\]

where, θ is the equilibrium contact angle of a chemically heterogeneous and ideally smooth surface; θi contact angle for a pure homogeneous constituent phase with its area fraction fi; θ minimum roughness factor, defined as the ratio of the actual surface area to its geometrically projected area [8,14].

![Fig. 1. 1H,1H,2H,2H-perfluorooctylsiloxane (FAS-13) monolayer on an oxide surface. Well-oriented, or self-assembled, (left) and collapsed (right) molecules are shown, exposing their topmost CF3 and CF2 (or CH2) groups, respectively.](image)

![Fig. 2. (a) Schematic representation of wetting of hydrophobic solid surface at low roughness. (b) Air is entrapped beneath the water droplet on the surface after certain increase in roughness. Schematic illustration of the surface model composed of a series of uniform needles which is used for sliding angle calculations.](image)
experimentally, surfaces with high contact angles do not always show low sliding angles \[6,17,28,30\]. Recently, sliding angles as low as 7° have been experimentally achieved on low-energy surfaces because the intersection of the water droplet with the surface consists of a composite mixture of water-air and heterogeneous surfaces with atomic- or molecular-sized domains. For a 1H,1H,2H,2H-perfluorooctylsilane-grafted surface with completely collapsed monomers (Fig.1, right) eq.(1) is modified into eq.(7):

\[
(1 + \cos \theta_{(\text{FAS-13})})^2 = 0.1(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.7(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.2(1 + \cos \theta_{(\text{CH}_2)})^2
\]

\[
(1 + \cos \theta_{(\text{FAS-17})})^2 = 0.1(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.7(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.2(1 + \cos \theta_{(\text{CH}_2)})^2
\]

From eq.(7) \(\theta_{(\text{FAS-13})} = 105.1^\circ\), which is somewhat lower than the water contact angle of 108° on pure Teflon surface terminated with CF3 groups [10,31]. Similarly, contact angles for completely disordered perfluorodecylsiloxane \(\theta_{(\text{FAS-17})}\) and octadecylsiloxane \(\theta_{(\text{ODS})}\) monolayers are obtained to be equal to 105.7° and 94.8°, respectively. Note that the latter is somewhat higher than 94°, which was previously used for completely disordered alkylsilane SAMs [9,16].

III. RESULTS AND DISCUSSION

A. Flat surface

The contact angle for completely disordered monolayers of fluoroalkylsiloxanes and alkylsiloxanes on smooth surfaces may be calculated from eq.(1), which is for chemically heterogeneous surfaces with atomic- or molecular-sized domains. For a 1H,1H,2H,2H-perfluorooctylsilane-grafted surface with completely collapsed monomers (Fig.1, right) eq.(1) is modified into eq.(7):

\[
(1 + \cos \theta_{(\text{FAS-13})})^2 = 0.1(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.7(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.2(1 + \cos \theta_{(\text{CH}_2)})^2
\]

\[
(1 + \cos \theta_{(\text{FAS-17})})^2 = 0.1(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.7(1 + \cos \theta_{(\text{CF}_3)})^2 + 0.2(1 + \cos \theta_{(\text{CH}_2)})^2
\]

As reported previously [9,25] and as expected from eqs.(1) and (2), for the same values of \(f_3\) the predicted contact angles for surfaces of micro-sized patches are somewhat larger than for those of molecular-size domains; this is also shown in Fig.3a by dashed and solid lines for ODS monolayers.
B. Rough surface and air inclusion

Based on the assumption of uniform surface distribution of CF3 (CH3) and CF2 (CH2)-terminated domains, and assuming air inclusions at micrometer scale or bigger, it is expected that on real SAM-grafted surfaces with air entrapped, the condition of $f_2^w \approx f_3^w$ will be realized. Therefore, hereafter, contact and sliding angles are evaluated only for SAM-grafted needle-like “composite” surfaces with $f_3^w = f_2^w$.

It is well known that water contact angles on smooth hydrophobic surfaces are not over 110-120° [15,31,32]. However, the situation is quite different on roughened surfaces. Fig.3b shows that water contact angles of rough SAM-grafted surfaces in Wenzel’s wetting mode, calculated using eq.(3) for FAS-17 SAMs at $r = 1.1, 1.2, \text{ and } 1.3$, increase constantly compared to those of smooth surfaces (curve marked with $r =1.0$). Thus, rougher substrates allow to raise static water contact angles, and for well-organized fluorosiloxane monolayers the latter can exceed 120°. It is worth noting that surface roughness of hydrophobic SAM-coated substrates can be designed, e.g., by depositing underlayers of SiO2 or Al2O3 with a desirable surface morphology [13], by means of substrate patterning [4,14], or by plasma etching of the substrate before the SAM film is grafted [7].
function of surface water-coverage fraction as \(f_3' = f_2''\) calculated from eq.(5) for FAS-17-grafted “composite” surfaces. Three different cases of SAM assembly degrees with \(f_3 = 0.1\) (1), \(0.5\) (2), and \(0.9\) (3) are shown. It can be observed that higher values of \(\theta'\) are attained at lower, and at increased self-assembly order \((f_3 \approx 1)\).

Fig.4b compares contact angles on FAS-17 and ODS-grafted “composite” surfaces, both with assembly order \(f_3 = 0.5\), as a function of surface water-coverage fraction. It can be noted that contact angles on rough “composite” surfaces coated by perfluorinated SAM (FAS-17) are always higher than those on ODS-grafted surfaces. This can be easily explained by lower energy of fluorine-terminated surfaces [32]. It is clear in Figs.4a,b that water contact angles much higher than 120° (maximum possible for a flat CF₃-terminated surface [32]) can be achieved on rough “composite” surfaces under certain conditions.

Note that the condition of \((f_3' = f_2'')\) for FAS-17 and ODS-covered surfaces in Fig.4b implies their water-coverage fractions to be equal, rather than equal geometrical topologies. We suppose that the ODS-grafted surfaces in Fig.4b should have more “advantageous” topographies compared to those of FAS-17-grafted ones to satisfy the same requirement of, as being higher-energy surfaces. For this reason, it is believed that, on substrates with same topographies, a difference somewhat greater than that between curves 1 and 2 in Fig.4b should be expected, since a higher water-coverage regime for ODS-coated surfaces should be realized (with deeper water penetration into surface troughs) [10].

C. Sliding angle on rough surfaces

Fig.5a qualitatively compares sliding angles of water droplets with \(m = 20\) mg on “composite” FAS-17, FAS-13, and ODS coatings as functions of SAM assembly degree at \(f_3' = f_2'' = 0.5\). The results were obtained by using eq.(6) in combination with eqs.(1) and (5) for surfaces with \(R = 1.15\), in accordance with the surface model of Miwa et al. [6], schematically shown in Fig.2b. For simplicity, the constant \(k\) for FAS-13 and FAS-17 coatings was chosen to be of 12.49 mJ/m² and independent of their assembly degree. This value was reported by Miwa et al. as the experimental constant for flat FAS-17-coated glass [6]. This value is believed to represent the interaction between water and well-assembled FAS-17 siloxane monolayers, although the authors of ref.[6] have not reported any data on the assembly degree of their coatings. For the ODS monolayers in Fig.5a, \(k = 17.8\) mJ/m² is used, which is the experimental constant for the water-polypropylene system [33] and is assumed to be a reliable value for water-alkylsiloxane monolayer interactions (also defined by CH₂ and CH₃ surface groups exposed). It is clear from Fig.5a that sliding angles on perfluorinated-SAM-grafted “composite” surfaces are significantly lower than those on surfaces coated with ODS. The difference between FAS-13 and FAS-17 monolayers is weak and mainly seen only at low assembly degrees of SAMs; and this is because at higher \(f_3\) the interaction water-solid is dictated by CF₃-groups (see Fig.1, left).

Fig.5b shows sliding angles as a function of surface water-coverage fraction. The three dependencies are given for FAS-17-coated “composite” surfaces with different assembly order equal to 0.1 (1), 0.5 (2), and 0.9 (3). It is seen that surfaces indicated by curve 3 (with the highest assembly of organic molecules) provide lower sliding angles. Thus, from Figs.5a,b, one can conclude that lower water sliding angles may be attained on hydrophobic surfaces with low fractions of water coverage for both CF₃ and CF₂ (CH₂) -terminated domains, \(f_3'\) and \(f_2''\). Because of high air ratio at the water-solid interface, sliding resistance of such surfaces is reduced, giving rise to lower sliding angles. It is also seen that increasing \(f_3\) leads to reduced water sliding angles, thus providing enhanced surface dynamic hydrophobicity as well.

Strictly speaking, as being related to the interaction energy between a solid surface and water [6,29,33], the constant \(k\) should be \(f_3\) dependent. Representing the surface energy of a solid, \(k\) is expected to be slightly larger for coatings with low values of \(f_3\) and lower for those with \(f_3\) close to 1. Such a \(f_3\) dependent value of \(k\) is expected to result in somewhat greater sliding angles at low \(f_3\) and lower ones at \(f_3\) close to 1 (see eq.(6)).

It should be mentioned that the approach used in this work does not account for the geometry/topography of the surfaces under consideration. To date, there has been only limited research on how surface shapes and dimensions (roughness topography) influence static and/or dynamic hydrophobicity of rough surfaces [6,14,28,34]. The topological nature of the surface roughness is of prime importance in determining hydrophobicity; a proper interval and height difference in the microstructure are required to provide both high contact angles and low sliding angles on rough hydrophobic surfaces [6,28,34]. According to the recent approach of Chen et al. [28], to decrease water sliding angle, a properly designed surface is expected to not allow a continuous contact of a liquid with the surface and to demonstrate little or no difference in energy between different metastable states. As a result, the liquid droplet would not remain pinned in a metastable state and would move spontaneously on such a surface. Thus, additional work, combining both experimental and theoretical approaches, is needed to further understand the effect of roughness topography on wetting of hydrophobic SAM-coated surfaces.
D. On snow and ice repellency of SAM coatings

It is commonly accepted that finding low-energy surfaces or coatings and introducing air between the ice and substrate stand among the major strategies to reduce ice/surface adhesion that have previously been proposed in the literature [1,3,5,9,10]. As low-surface-energy coatings, certain alkylsilane SAMs have recently attracted the attention of investigators in this field. According to the recent results of Somlo and Gupta [3], ice adhesion decreases when a SAM is formed from dimethyl-n-octadecilchlorosilane on an Al alloy substrate [3]. Furthermore, Petrenko and Peng have found good correlation between the contact angle of water and ice-adhesion strength on surfaces covered with mixtures of SAMs of 11-hydroxyundecane-1-thiol and 1-dodecanethiol with various degrees of hydrophobicity/hydrophilicity [1]. Taking the above into consideration, the following conclusions may be drawn:

(i) The formation of SAMs with high assembly degree [12,16,21-23] appears to be an important factor governing surface hydrophobicity and, probably, snow and ice repellency. As shown above, this improves both static and dynamic water repellency. While this parameter is often ignored in the literature [3,6,7,14], one of the main objectives of this study was to reveal the importance of controlling the assembly degree of SAM coatings, when fluoroalkylsiloxane and alkylsiloxane-grafted surfaces with high hydrophobicity are to be prepared.

(ii) Fluorinated alkylsiloxane monolayers are expected to be more advantageous and efficient compared to alkylsiloxanes, giving rise to surfaces with higher static and dynamic hydrophobicity.

(iii) The use of rough or patterned surfaces [4,7,13,14] as substrates for hydrophobic SAMs, so as to entrap air into the final surface structure, seems to be perspective, too. As was shown in the previous sections, higher contact angles and reduced sliding angles can be attained on such surfaces with an increase in air inclusion. This conclusion is in good agreement with the experimental results of Saito et al. [5], who have reported a linear correlation between the contact angle of water and ice adhesion strength for rough “composite” water-repellent coatings of polytetrafluoroethylene particles dispersed in polyvinylidene fluoride resin binder. Thus, properly designed/patterned rough fluoroalkylsiloxane or alkylsiloxane-coated surfaces are also expected to be good candidates for ice-repellent applications.

IV. CONCLUSIONS

We present a model to describe the wetting behavior of SAM-grafted surfaces as a function of assembly degree of organic molecules and amount of air trapped between water and solid. The model is applied to compare wetting of surfaces fully coated with fluoroalkylsiloxane and alkylsiloxane monolayers, which are formed from certain commercially available fluoroalkylsilanes and alkylsilanes.

The contact angle of a sessile water droplet is shown to be \(\sim 10^\circ\) larger on smooth fluoroalkylsilane-coated surfaces and to gradually increase with the assembly order. The difference, however, decreases when rough substrates with air inclusion are used. The results of modeling predict very close values of contact angles on surfaces coated with perfluorodecylsiloxane and perfluorooctylsiloxane monolayers, however demonstrating little difference at low self-assembly degree, when organic molecules are spread on the surface and their CF\(_2\) and CH\(_2\) groups start interacting with water. At the same time, octadecylsiloxane coatings always show lower values of contact angle, which is due to the higher energy of CH\(_3\) and CH\(_2\)-terminated surfaces compared with that of CF\(_3\) and CF\(_2\)-terminated ones.
It is demonstrated that both static (determined by the contact angle) and dynamic (determined by the sliding angle) hydrophobicity of SAM-coated surfaces are strongly affected by the degree of self-assembly of organic molecules, and by water coverage of a rough “composite” surface, which can trap air. Increasing the assembly order of SAM molecules in combination with properly designed roughness leads to considerably enhanced water repellency of the surface.

Further detailed studies, combining both experimental and theoretical approaches, are needed for further understanding and improvement of hydrophobicity and snow/ice repellency of fluoroalkylsiloxane and alkylsiloxane monolayers on various surfaces.

V. ACKNOWLEDGMENTS

This research was carried out within the framework of the NSERC/Hydro-Quebec Industrial Chair on Atmospheric Icing of Power Network Equipment (CIGELE) and the Canada Research Chair on Atmospheric Icing Engineering of Power Network (INGIVRE) at Université du Québec à Chicoutimi, with the collaboration of Kinetics. The authors would like to thank all the sponsors of the project for their support.

VI. REFERENCES


Author address: Prof. M. Farzaneh, Chairholder, NSERC/Hydro-Quebec/UQAC Industrial Chair on Atmospheric Icing of Power Network Equipment and Canada Research Chair on Engineering of Power Network Atmospheric Icing (INGIVRE), Université du Québec à Chicoutimi 555, Boulevard de l’Université, Chicoutimi, Québec, Canada, G7H 2B1, E-mail: farzaneh@uqac.ca