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Silicone nanofilaments grown on aircraft alloys for low ice adhesion

Alexandre Laroche\textsuperscript{a,1}, Davide Bottone\textsuperscript{b,1}, Stefan Seeger\textsuperscript{b,*}, Elmar Bonaccurso\textsuperscript{a,*}

\textsuperscript{a} Airbus Central Research & Technology, Materials X, Willy-Messerschmitt-Str. 1, 82024 Taufkirchen, Germany
\textsuperscript{b} University of Zurich, Department of Chemistry, Winterthurerstrasse 190, 8057 Zurich, Switzerland

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Many novel icephobic coatings have been shown to exhibit low adhesion strength to ice grown at null or low velocity. Of these, few have been shown to also exhibit low adhesion strength to ice grown by impacting high velocity supercooled water droplets. Even fewer of these have been shown to exhibit low adhesion strength to ice grown over a range of environmental conditions. Those that have shown such behavior have been held back by their susceptibility to certain bands of UV-exposure. Here, icephobic coatings made from Silicone Nanofilament (SNF) networks grown on anodic metal oxide surfaces are presented. They show low ice adhesion strength for a range of impact icing conditions and exhibit good durability against the tested conditions. Additionally, their nano-porous structure provides enhanced lubricant retention when infused with oil. The described coatings are a promising candidate for supporting hybrid ice protection systems on aircraft, thereby reducing the energy needed for anti-/de-icing.

\section{1. Introduction}

Aircraft surfaces are optimized for aerodynamic performance in a single-phase flow of air. Liquid contaminants like supercooled water droplets and solid contaminants such as dust, sand, or insects entering the airflow can have detrimental effects to the performance of aerodynamic surfaces. In severe cases, the accumulation of contaminants can quickly lead to an aircraft stall or to loss of control.

Ice is one of the more focused-on of these contaminants due to the rate and stealth with which it grows. Water droplets in close proximity to each other form clouds at high altitude. The air temperature at high altitude is below freezing, but due to the purity of the water droplets, they remain in a liquid state unless perturbed \cite{1-3}. An aircraft flying through the clouds is a sufficient perturbation to initiate a phase change of the supercooled water droplets \cite{4}. Droplets impacting the surface of an aircraft quickly freeze, forming an ice layer which grows forwards as more and more droplets impact \cite{5}.

To protect an aircraft and its passengers from the effects of ice accretion on crucial aerodynamic surfaces, ice protection systems are in place. An ice protection system either prevents any ice from forming on a surface, known as an anti-icing system, or acts to remove accreted ice from a surface, known as a de-icing system \cite{6}. Some types of systems, such as electrothermal, are capable of both modes of protection against icing. Thermal ice protection systems are the most commonly used in commercial aircraft. Air is extracted from the hot section of turbofan engines and passed through pipes in proximity to critical aerodynamic surfaces \cite{6}. The circulation of the hot air is enough to fully evaporate water droplets as they impact the outer face of the heated surface. This method is robust, yet energy intensive \cite{7}.

Small aircrafts for general aviation typically do not have the excess power needed for thermal ice protection systems, and neither will future all-electric aircraft. Ideally, the problem could be solved by a surface to which ice cannot accrete, even below freezing temperature. Superhydrophobic surfaces, for example, are able to repel impacting water droplets. However, surface features which promote hydrophobicity, the tendency of a surface to repel water, have not been able to repel all droplets with the speed, size, and temperature of those encountered in-flight \cite{8}. Some high speed microscopic supercooled water droplets can...
Attention must therefore be turned to the interaction of surfaces and ice. If ice accretion cannot be prevented, then perhaps, at least, the ice which accretes can be easily removed. A number of recent review papers [10–12] give detailed overviews on the state of the art of icephobic surfaces, that is, surfaces designed to minimize their interaction with ice, with some focusing on integrated systems for aircraft icing protection [8].

To assess the performance of icephobic coatings, ice adhesion tests allowing to quantify how strongly ice clings onto surfaces are required. There exist lists of different types of tests for different types of ice and loading conditions [13,14]. Each test is motivated by particular target applications, expertise of the institute performing the test, and available resources. The authors of this paper use a vibrating cantilever test for measuring the ice adhesion strength (IAS) [15].

Since the description of the working principles of the Lotus effect [16], the ability of superhydrophobic surfaces (SHS) to efficiently shed away impacting water droplets has made them a promising target in the search for an ideal icephobic surface. Ice shedding is usually referred to as Cassie ice, by analogy with the Cassie-Baxter state of a water droplet on a rough surface [22]. If the trapped air cushion were to be displaced by water, the surface would undergo a transition from Cassie-Baxter to Wenzel state, with a consequent loss of its properties and a high degree of mechanical interlocking with the accreted ice. Environmental conditions commonly encountered during flight are known to be especially detrimental to the stability of SHS in icing conditions, such as high relative humidity [23] or high Weber number of impacting droplets. Therefore, low wettability alone is not enough to guarantee low ice adhesion arising from a Cassie ice state, and the stability of the trapped air cushion must be guaranteed by an appropriate surface texture [22,24,25]. Vercillo et al. have proposed design rules for hierarchically structured surfaces of relatively high hardness on aircraft alloys [24]. They argued that nanostructures will prevent micron-sized impacting droplets from entering the Wenzel state, and microstructures provide stress concentration zones at the ice-substrate interface once water has frozen. IAS may be lowered using either one of these levels of surface structures and is lowered even further when they are combined. Using laser-patterned surfaces with a perfluoropolyether (PFPE) surface chemistry, they obtained IAS as low as 10 kPa in several atmospheric icing conditions simulating a flight environment. However, a hydrogenated polymeric coating, such as perfluoropolyether, applied on a photoactive oxide, such as TiO2, can be degraded by exposure to UV-radiation [26], to which surfaces are subjected during the cruise phase of commercial flights. Laser structuring is a line-of-sight surface modification technique, making it difficult to treat inner-features of certain components. Additionally, although there have been many advancements in scaling up the surface technology, there are still high costs associated with it, as well as potential thermal stress damage to the substrate material itself.

Slippery liquid-infused surfaces (SLIPS) are another class of bio-inspired liquid-repellent surfaces that have come to prominence in the field of icephobicity [27,28]. Inspired by the Nepenthes pitcher plant, these surfaces are described as a solid micro- or nano-texture infused with a lubricating oil. This combination ensures that the system shares properties of both liquids and solids. The smooth liquid surface is stabilized against external action, such as shear flow or gravity, by the capillary forces of the underlying solid texture. Here, water shedding is guaranteed by the theoretically defect-free liquid surface, which does not possess triple line pinning points. Since, when compared to SHS, the role of air is effectively taken up by an incompressible fluid, liquid-infused surfaces are much more stable in high humidity environments and against high impact pressures [28–30]. Such properties have led to reports of extremely low ice adhesion for these surfaces [31–33]. In practice, lubricant-infused surfaces tend to attract surface contaminants which may act as defects if not removed. Additionally, liquid-infused surfaces are prone to suffer a loss of lubricant over time, especially when subjected to high shear flow [34,35]. A recent study on the stability of a self-lubricating surface in atmospheric icing conditions relevant for aerospace applications demonstrates their promise [36].

In this work, we employ a facile gas-phase process, known as Droplet Assisted Growth and Shaping (DAGS), to obtain 1-dimensional polysilsesquioxane nanostructures, called Silicone Nanofilaments (SNFs) [37–39]. SNFs, depending on the choice of trichlorosilane precursor, can be naturally superhydrophobic, and are well suited to be used as the solid component of a SLIPS [40,41]. The process makes use of micro- and nano-droplets of water present on a surface as catalytically active confined reaction volumes, whose size and shape control the final nanostructure obtained [39]. Many different structures have been reported on a variety of substrates [38], and the method is well suited for industrial up-scaling [42]. Moreover, SNFs have been shown to resist long-term outdoor weathering and UV exposure [43].

One of the main drawbacks of the DAGS process is that copious amounts of hydrochloric acid (HCl) are produced during the reaction, which limits the applicability of the coating method to acid-resistant materials. Many metal alloys that are of interest in the field of aviation are typically not resistant to acids. Moreover, the presence of HCl cannot be completely eliminated, as it plays an important catalytic function in the reaction [39]. Here we report a method that greatly reduces the evolution of HCl, consisting in the use of a silane mixture comprising a trichlorosilane, whose hydrolysis provides the necessary catalytic amount of HCl, and a trialkoxysilane, that acts as the main precursor of the final polysilsesquioxane without releasing any corrosive product. The ratio of the two silanes has to be carefully balanced to prevent damage to the substrate while allowing for the reaction to take place. Moreover, the modified process produced less hazardous gas than the original process, making it more environmentally friendly.

2. Material and methods

2.1. Anodic oxide surface preparation

Grade V titanium alloy sheets (VSMPO, Verkhnyaya Salda, Russia), also referred to as Ti-6Al-4V, with 1 mm thickness were cut to size (125 mm × 13 mm) using a hydraulic guillotine. The edges were deburred, and substrates were cleaned by scrubbing with acetone followed by propan-2-ol. Substrates were suspended on a titanium rack and anodized in an aqueous solution containing 130 g/L ammonium sulphate and 5 g/L ammonium fluoride, as described in the literature [44,45] to grow a layer of organized TiO2 nanotubes on the surface. Sheets of aluminum alloy 2024 with a thickness of 1.6 mm (AMAG rolling GmbH, Ranshofen, Austria) were prepared in a similar way as titanium, except they were anodized in an electrolytic aqueous solution containing 40 g/L of sulphuric acid and 80 g/L of tartaric acid in a process known as tartaric sulfuric anodization (TSA) previously described in [46]. Reference aluminum substrates were polished before anodizing using an ad-hoc
substrate holder on a mechanical wet polishing device (Struers Tegramin-20, Struers A/S, Denmark).

2.2. Perfluoropolyether coating

A molecular coating of a perfluoropolyether was obtained by dipping freshly anodized substrates in a two-part commercial PFPE compound in a fluorinated solvent (Episurf®, perfluoropolyether compound by Surfactis, Angers, France).

2.3. Silicone nanofilament coating of titanium substrates

Anodized titanium cantilevers were first rinsed with acetone and deionized water; samples were then rinsed for 30 min in an ultrasound bath in a 10% v/v aqueous solution of Deconex 11 Universal (Borer Chemie AG, Switzerland), an alkaline detergent, at 40 °C. After this step, the cantilevers were abundantly rinsed with deionized water and dried using a dry N\textsubscript{2} stream. Samples were introduced into a custom 6.6 L reaction vessel \([37,38]\), and were exposed to a relative humidity RH = (36 ± 2)% at room temperature \(T = (22 ± 1) ^\circ C\) for 1 h, after which a mixture of 2.25 mmol of tri(methoxy)methylsilane (TMMS, 98% purity, Sigma-Aldrich Chemie GmbH, Germany) and 0.75 mmol of tri(chloro)methylsilane (TCMS, 98% purity, Sigma-Aldrich Co., USA) was introduced. The mixture was left to react for 4.5 h following the DAGS mechanism \([39]\). Samples that would not undergo subsequent fluorination were annealed at 200 °C for 16 h.

2.4. Silicone nanofilament coating of aluminum substrates

Anodized aluminum cantilevers were rinsed with acetone and deionized water, after which they were immersed for 30 s in a 1 M NaOH aqueous solution to obtain hydrophilic Al(OH)\textsubscript{3} on their surface. Surface pH was then brought below the isoelectric point of Al(OH)\textsubscript{3} (pH = 7.7) \([47]\) by immersing the samples in deionized water for 10 s. Samples were then abundantly rinsed with running deionized water and dried using a dry N\textsubscript{2} stream. Similar to the process for Ti substrates, aluminum samples were introduced into a custom 6.6 L reaction vessel \([37,38]\), and were exposed to a relative humidity RH = (36 ± 2)% at room temperature \(T = (22 ± 1) ^\circ C\) for 1 h, after which a mixture of 2.25 mmol of TMMS and 0.75 mmol of TCMS was introduced. The mixture was used to react for 2 h following the DAGS mechanism \([39]\). Samples that would not undergo subsequent fluorination were annealed at 200 °C for 16 h.

2.5. Fluorination of SNF coatings

SNFs are non-reactive to most chemical functionalizations, and therefore need to be activated to introduce reactive groups on their surfaces. Surface activation was accomplished by introducing OH functionalities through exposure of the samples to O\textsubscript{2} plasma (Femto plasma chamber, Diener Electronics, Germany) at 50 W power for 5 min. Fluorination was then carried out utilizing the same setup and procedure used for SNF growth: samples were exposed to a N\textsubscript{2} atmosphere with RH = (25 ± 3)% and T = (22 ± 1) °C for 1 h, after which the reaction vessel was sealed and an amount of 1H,1H,2H,2H-perfluoro-1-octyl) silane (97% purity, Sigma-Aldrich Co., USA) corresponding to 0.26 mmol per cantilever was introduced and left to react for 16 h. The same procedure was followed for both titanium and aluminum cantilevers.

2.6. Lubricant infusion

Over-filled SLIPS were fabricated by dropwise application of excess lubricant (PDMS oil, 100 CSt at 25 °C, Sigma-Aldrich Co., USA) on the top edge of the vertically held samples, allowing for gravitational spreading, which was facilitated by localized compressed air. A homogeneous layer of lubricating oil was achieved within minutes. Once the lubricated sample was subjected to airflow in the wind tunnel, the excess lubricant would be sheared off by aerodynamic forces \([34]\). This method, while entailing loss of the excess lubricant, was much closer to what might be employed in a real-world scenario compared to other commonly reported infusion methods, such as hemiwickling or dip-coating. Lubricant infusion was performed after the samples were instrumented and placed in the ice adhesion testing setup, since the slipperiness of the surfaces could have prevented an appropriate fastening of the samples and strain gauge attachment. During ice adhesion testing, lubricant replenishment was carried out in the same fashion between each icing condition (every fourth icing/de-icing cycle).

2.7. Wetting characterization

Wetting characterization of samples was carried out with a Krüss DSA25 goniometer (KRÜSS GmbH, Germany), using deionized water as a test liquid. Contact angle (CA) and roll-off angle (RoA) were evaluated using a constant droplet volume of 10 µL and, for RoA, a constant tilting speed of 1 °C s\textsuperscript{-1}. Measurements were carried out on 4 positions, as in the scheme shown in Fig. S6. Wetting behavior of the samples was evaluated before and after the ice adhesion testing routine in order to evaluate the durability of the samples. All wetting measurements took place in air at a controlled relative humidity and temperature of (50 ± 2)% and (22.4 ± 1) °C respectively.

2.8. SEM imaging and EDX spectroscopy

Surface morphology was evaluated with Scanning Electron Microscopy (SEM). Samples were cut to shape (approximately 13 mm by 13 mm square pieces), mounted on aluminum stubs with Leit-C conductive carbon glue (Sigma-Aldrich, USA) and coated with a layer of Pt of nominal thickness 12 nm using a Safeomatic CCU-010 sputter coater (Safeomatic GmbH, Zizers, Switzerland). A rotating planetary stage ensured uniform coating of the nanostructure. SEM micrographs were then captured with a Zeiss GeminiSEM 450 microscope (Carl Zeiss AG, Germany), using an accelerating voltage of 5 kV. Brightness and contrast of images were uniformly adjusted after acquisition. Energy Dispersive X-Ray spectroscopy (EDX) and element mapping were performed with an AZTec Advanced X-MAX80 detector (Oxford Instruments, UK), using a 10 kV voltage.

2.9. Surface profilometry

A stylus profilometer (Bruker Dektak XT, Bruker Corporation, USA) was used with its accompanying software (Bruker Vision 64). At least three independent measurements were taken at distant and random locations on the substrates. The values reported are an average of those three or more measurements and the uncertainty is presented as one standard deviation. Signal filters and length settings were according to ISO 4288:1998 and ISO 3274:1998. Specifically, the stylus tip radius was 2 µm, cut-off length was 0.8 mm, length considered was 4 mm, travel length was 4.8 mm, and the short cut-off length was 2.5 µm. A stylus force of 1 mg was used with the software’s NLite feature for minimizing surface scratches from the stylus. The spatial resolution was 0.05 µm point\textsuperscript{-1}. The measurements were done in a lab with a controlled relative humidity and temperature of (50 ± 2)% and (22.4 ± 1) °C respectively.

2.10. Ice adhesion testing

The iCORE icing wind tunnel (IWT) is a laboratory scale wind tunnel (Fig. S7) equipped with a spray bar for producing droplet clouds and a heat exchanger for cooling the air. Supercooled de-ionized water droplets were produced through three horizontally-aligned air-atomizing nozzles with full-conical spray cross-sections into slow-moving cold air. As the droplet velocities approached the surrounding air velocity, their...
temperature also reached that of the sub-zero air. The droplets remained in liquid form due to their purity, until they impacted the surface of a cantilever substrate in the test section. Further information such as flow uniformity and liquid water content calibration were presented by Hauk et al. [48].

The vibrating cantilever ice adhesion test method consisted of an ice accretion step and an ice delamination step. During ice accretion, the cantilever surface faced an oncoming icing cloud of supercooled droplets, which froze on impact, until sufficient ice thickness had been reached, at which point the water inlet valves to the spray nozzles were closed. During the ice delamination step, the fixed end of the iced cantilever was linearly displaced with increasing amplitude and with a frequency near to or at the first natural frequency of the system until its deflection produced large enough interfacial stresses to initiate and propagate an interfacial crack. A full description of the vibration setup can be found in the literature [49,50], and the version modified for use in the IWT test section was described by Thompson et al. [13]. An illustration of the setup is included as Fig. S8.

The method involved a mixed mode interfacial failure with both peeling and shear stresses. Since no closed-form analytical solution was available for interfacial peel stress of this configuration, only shear stress was reported. The interfacial shear strength was obtained using Eq. (1).

$$\tau_{\text{interface}} = \frac{E_{\text{ice}}(h_{\text{ice}}^2 + 2h_{\text{ice}}e)}{2(x - l)(h_{\text{substrate}} - e)} \varepsilon_{\text{str}},$$  

(1)

where the $\varepsilon_{\text{str}}$ value is the maximum strain measured during vibration before a spike reading was detected (indicative of a change in flexural stiffness of the beam due to interfacial fracture). The strain was measured at the back of the cantilever beam. $E_{\text{ice}}$ is the Young’s modulus of ice (9.0 GPa), $h_{\text{ice}}$ and $h_{\text{substrate}}$ are respectively the thicknesses of the ice and the substrate, $x$ is the position of the strain reading (45 mm from the fixed end), and $l$ is the total length of the cantilever beam (125 mm). The eccentricity $e$, the distance between the ice-substrate interface and the neutral axis of the system, was calculated based on Eq. (2).

$$e = \frac{(h_{\text{substrate}} - nh_{\text{ice}})}{2(h_{\text{substrate}} + nh_{\text{ice}})}$$  

(2)

where $n$ is the ratio of the Young’s modulus of ice and that of the substrate ($n = E_{\text{ice}}/E_{\text{substrate}}$). The values of variables used are listed in Table S2.

Table 1 lists the conditions used to obtain four different ice types, visualized in Fig. S9. On one side of the ice spectrum, pure rime ice is obtained in the coldest conditions with the lowest liquid water content. On the other side, pure glaze ice forms near 0 °C and with relatively high LWC. High impact speed promotes the formation of glaze ice since it increases the rate at which water impacts the surface, creating a warmer surface for the supercooled water to spread over before freezing. Each surface was tested following the sequential order listed in Table 1. Testing started from the mixed/rime icing condition, since its experimental parameters were the most straightforward to achieve with the used equipment and the water catch rate was the highest. If a surface performed poorly in the mixed/rime condition, showing a significantly increasing IAS trend, further testing of that surface was discontinued. This condition was therefore used as a first down-selection test.

3. Results and discussion

An overview of the tested surfaces is summarized in Table 2. The SNF-coated surfaces are first shown along with their wettability and roughness. The surfaces were then characterized by measuring their IAS under four different atmospheric icing conditions. The effect of the icing/de-icing cycles on surface properties was then evaluated by SEM imaging and further wettability measurements.

3.1. Surface fabrication and characterization

SNF were successfully grown onto two aerospace-qualifying metal alloys. Fig. 1 shows SEM micrographs of pristine f-SNF coated titanium and aluminum alloy surfaces imaged at different levels of magnification. It is possible to see from Fig. 1a that the coating process was successful in introducing a SNF coating comprising two components: a relatively loose over-layer of long SNFs on top of a rough under-layer of short SNFs, whose very fine roughness closely follows that of the TiO$_2$ nanotubes (Fig. S1.a-b) on which they were grown [44]. On the other hand, Fig. 1b shows that a maze-like micro-structured layer is present on the aluminum surfaces, on which a uniform layer of short SNFs was grown. It can be seen from Fig. S1.c-d, that the micro-structured layer was introduced on the otherwise featureless anodized aluminum surface by the alkaline etching, to which the aluminum substrates were subjected, to obtain a hydrophilic surface chemistry prior to SNF coating. The micro-structured aluminum oxide layer confers the samples an iridescent appearance. EDX spectra of the substrates and of the pristine coated samples further confirm the presence of SNFs after coating, for both titanium (Fig. S3) and aluminum alloys (Fig. S4.a).

Water contact angle (CA), water roll-off-angle (RoA), average profile roughness (Ra), and average peak-to-peak roughness (Rz) of the surfaces are listed in Table 3. Surfaces T1 and A1 act as reference hydrophilic surfaces of the respective base alloys, as shown by their low CA and complete droplet pinning. After PFPE treatment, samples T2 and A2 showed hydrophobic behavior, with sample T2 exhibiting an almost superhydrophobic character with RoA as low as 15°, thanks to the presence of nanostructured TiO$_2$ nanotubes. On the other hand, sample A2, while having the same surface chemistry as T2, showed a lower CA and complete droplet pinning due to its featureless surface profile. SNF-coated samples T3, T4 and A4 all showed superhydrophobic behavior, owing to their combination of surface texture and surface chemistry, while sample A3, despite being highly hydrophobic, cannot be strictly categorized as superhydrophobic due to its comparatively high RoA. Additionally, in the case of sample T4, it was not possible to reliably record CA and RoA, as water droplet mobility on the surface was too high to allow for the deposition of a sessile droplet. This is, in any case, indicative of the extreme superhydrophobicity of the surface, a result which is supported by supplementary droplet impact tests (Section S2 and Supplementary Movie 1). Sample T5 was infused with silicone oil

| Table 1 | List of experimental icing conditions. |
|---------|--------------------------------------|
| **Ice type** | **Total temperature** | **Airspeed** | **LWC** | **Sequential testing order** |
| Rime | –20 | 50 | 0.30 | 2 |
| Mixed/ | –20 | 50 | 0.80 | 1 |
| Rime | –5 | 50 | 0.30 | 3 |
| Mixed/ | –5 | 80 | 1.00 | 4 |

| Table 2 | Overview of tested surfaces. |
|---------|-----------------------------|
| Sample | Description |
| T1 | Bare Ti-6Al-4V, non-anodized |
| T2 | Ti-6Al-4V anodized with TiO$_2$ nanotubes, coated with PFPE |
| T3 | Ti-6Al-4V anodized with TiO$_2$ nanotubes, coated with SNFs |
| T4 | Ti-6Al-4V anodized with TiO$_2$ nanotubes, coated with fluorinated SNFs |
| T5 | Ti-6Al-4V anodized with TiO$_2$ nanotubes, coated with SNFs, infused with silicone oil 100 cSt |
| A1 | Bare Al2024 clad TSA anodized |
| A2 | Al2024 clad TSA anodized, coated with PFPE |
| A3 | Al2024 clad TSA anodized, coated with SNFs |
| A4 | Al2024 clad TSA anodized, coated with fluorinated SNFs |
after being placed in the ice adhesion testing setup, therefore no wetting data on the pristine surface could be recorded.

The Ra and Rz of the reference titanium surfaces were higher than those of the corresponding aluminum surfaces, owing to the different surface finish of the materials. On the untreated Ti-6Al-4V alloy, which was used as received for sample T1, roughness came only from surface grain boundaries. Its Ra increased by 16% due to the anodization process and the introduction of TiO₂ nanotubes, as shown on sample T2. On the other hand, the surfaces of A1 and A2 were mirror-polished prior to anodizing, and the roughness values reported are those of the anodized surfaces. These surfaces were polished to control surface asperities which could otherwise change with successive ice adhesion tests due to wear [25]. The SNF coating process then introduced changes in profile roughness for both Ti and Al alloys, although to different extents. The Ra of T4 was 20% lower than that of T2 due to the smoothing of surface features given by SNFs, that however cannot be resolved individually with the stylus profilometry technique. The Ra of surface T3 was assumed to be identical to that of T4, as the two samples only differ by surface chemistry. On the other hand, SNF coating introduced dramatic changes in roughness to sample A3, with a 30-fold increase in Ra and almost 40-fold increase in Rz compared to A1. This difference was caused by the introduction of the micro-structured oxide layer, shown in Fig. 1, during alkaline etching prior to SNF coating. As sample A4 only differs from sample A3 for its fluorinated surface chemistry, its roughness was assumed to be identical to that of A3. Comparing the SNF-coated Al and Ti alloy surfaces, the Ra of A3 was only 60% that of T4 but it showed a higher Rz, arising, again, from the deeper maze-like microstructure shown in Fig. 1.b. Roughness of sample T5 was not measured, as the presence of infused oil would prevent accurate roughness measurement with stylus profilometry.

### 3.2. Ice adhesion strength

Textured surfaces are expected to show higher IAS in glaze conditions as opposed to rime conditions due to the different timescales for droplet freezing. Glaze ice is characteristically clearer and denser than rime ice. These properties arise from supercooled impacting droplets spending more time in the liquid phase after they impact a surface compared to rime ice conditions, allowing them to fill voids as they accrete [51]. In rime ice, supercooled droplets have less mobility after impact, and typically stack on top of each other forming columnar ice grains with exponentially more pores and potentially more interfacial porosities [52].

Fig. 2 shows the results of the ice adhesion shear strength (IAS) of four types of impact ice with the surfaces on titanium substrates listed in Table 2. Each IAS value shown represents 4 icing/de-icing cycles for each condition, totaling in at least 16 icing/de-icing cycles per surface. T1, the reference surface, showed an IAS above 40 kPa, with the highest at 65 kPa under the glaze ice condition. The T1 surface was tested as received, with only a native oxide layer whose roughness came primarily from grain boundaries, and therefore it had no patterned micro- or nano-structuring. Its relatively high IAS arises from its high Ra and hydrophilic surface chemistry, as unstructured high surface roughness and the presence of sharp micro-features are indicators of high atmospheric IAS [50,53]. A drastic reduction was obtained in IAS of T2 with the introduction of a nano-porous columnar oxide layer with waterrepelling surface chemistry granted by PFPE [44]. The IAS of T2 was found to be below 40 kPa for all conditions, with its highest at 38 kPa under the glaze ice condition, and lowest at 13 kPa under the rime ice condition. Both these surfaces experienced an increase in IAS with

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### Table 3: Wettability and roughness characteristics of the substrates tested for IAS.

| Name | CA | RoA | Ra [µm] | Rz [µm] |
|------|----|-----|---------|---------|
| T1   | 51 ± 1 | Pinned | 0.36 ± 0.28 | 3.97 ± 0.170 |
| T2   | 166 ± 1 | 15 ± 6 | 0.580 ± 0.028 | 4.40 ± 0.174 |
| T3   | 167 ± 1 | 2 ± 1 | 0.02 ± 0.009 | 0.15 ± 0.04 |
| T4   | 50 ± 1 | Pinned | 0.483 ± 0.027 | 3.89 ± 0.261 |
| A1   | 122 ± 1 | Pinned | 0.02 ± 0.000 | 0.15 ± 0.04 |
| A2   | 166 ± 1 | 13 ± 8 | 0.293 ± 0.002 | 5.57 ± 0.741 |
| A3   | 166 ± 1 | 5 ± 3 | 0.84 ± 0.20 | 4.40 ± 0.174 |
| A4   | 166 ± 1 | 5 ± 3 | 0.84 ± 0.20 | 4.40 ± 0.174 |

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Fig. 1. Scanning electron microscope image of SNF grown on (a) anodic oxides of titanium (T4) and (b) aluminum (A4).
increasing LWC.

The IAS of the f-SNF, T4, was fairly consistent across the conditions tested, exhibiting remarkably low IAS in the range of 12 kPa to 16 kPa. Its IAS was considerably lower than that of T2 in the glaze ice condition, which can be explained by the combination of higher surface compliance, lower surface free energy, and lower thermal diffusivity of the SNF coating. Sample T3 showed a strongly increasing trend of IAS upon successive cycles during the first mixed/rime testing (shown in Fig. S2), starting at 24 kPa and reaching 66 kPa by the fourth cycle; its testing was therefore discontinued, as per experimental protocol. No significant degradation of IAS as a function of consecutive icing cycles was observed on the other tested surfaces.

The lubricant-infused SNFs, T5, showed IAS close to that of T4 but slightly lower, ranging from 6 kPa to 13 kPa. For mixed/rime and glaze icing the SLIPS surface out-performed the f-SNF surface. Sample T5 also exhibited high durability against aggressive aerodynamic icing conditions. SLIPS have been tested before in atmospheric icing conditions by Niemelä-Anttonen et al. They found that lubricant-infused polymers were durable enough to show low IAS in an icing wind tunnel operating at −10 °C and at an airspeed of 25 m s⁻¹ for 4 cycles. Teethe and Loth have pushed their self-lubricating icephobic coating to an airspeed of 40 m s⁻¹ at −21 °C for 5 cycles. Here, it is shown that SNF networks can retain a relatively low-viscosity lubricant (100 cSt at 25 °C) for speeds of up to 80 m s⁻¹ at −5 °C for 4 icing/de-icing cycles. Only glaze ice conditions are considered in this analysis since lubricant was replenished between each icing condition. Under high aerodynamic shear flow, excess lubricant was visibly blown out of the surface. Despite that, high capillary forces from the nanometric inter-filament spacing helped to retain enough lubricant for low IAS, meaning that the lubricant had an interface with the ice. A more thorough analysis of SLIPS durability is reported in paragraph 3.3.

**Fig. 2.** Interfacial shear strength for titanium substrates; where T1, bare Ti-6Al-4V, is shown as a solid bar, T2, PFPE-coated TiO₂-nanotubes, as a bar with diagonal hatches on a dark background, T4, fSNF on TiO₂-nanotubes, as a bar with cross-hatch, and T5, lubricant infused SNF on TiO₂-nanotubes, as a bar with diagonal hatch on a light background.

A2 as it was on T2 – owing to the different oxide surface morphology. Nevertheless, consistent with the results of the titanium substrates, A3 and A4 both showed lower IAS than their reference counterparts, A1 and A2. The IAS of the SNFs, A3, ranged from 20 kPa to 32 kPa. Differently from its Ti alloy counterpart, T3, A3 did not show any significantly increasing trend of IAS with consecutive icing cycles, which demonstrates its better durability. IAS of the f-SNFS, A4, was below the range observed for A3, with its lowest value at 10 kPa and 27 kPa under the mixed/glaze and glaze conditions respectively. Therefore, as shown for the Ti alloys, fluorination of the SNFs and the consequent decrease of their surface free energy led to a measurable reduction in IAS.

**Fig. 3.** Interfacial shear strength for aluminum substrates; where A1, anodized AA2024, is shown as a solid bar, A2, PFPE-coated anodized aluminum, as a bar with diagonal hatches on a dark background, A3, SNF on anodic aluminum oxide, as a bar with horizontal hatch, and A4, f-SNF on anodic aluminum oxide, as a bar with cross-hatch.

### 3.3. Durability assessment

Results of the durability assessment of the tested surfaces to icing/de-icing cycles, as evaluated by SEM and wettability, are summarized in Fig. 4. Fig. 4a shows the surface morphology change after 16 icing/de-icing cycles by the f-SNF-coated titanium and aluminum alloy samples, T4 and A4. The SEM images were taken at 45 mm from the fixed end of the cantilever (at the strain gauge position) and as such are representative of the area of the samples subjected to the highest interfacial shear stress. A similar microstructural evolution was observed on the non-fluorinated SNFs counterparts, T3 and A3, whose SEM images are shown in Fig. S5.

The over-layer of long SNFs originally present on sample T4’s surface was lost after ice adhesion testing. The finely rough under-layer that was visible on pristine surfaces, composed of stumpy, wool-like SNFs, possibly including the roots of longer abraded SNFs, was exposed. However, comparison with reference surfaces reveals that the base layer of TiO₂ nanotubes had not been exposed. The EDX spectrum of sample T4 (Fig. S3) show strong Si and F peaks even after ice adhesion testing, further confirming the permanence of a fluorinated SNFs layer. The striking uniformity of this coating is a sign of its durability against aggressive atmospheric icing conditions, and a further confirmation of the remarkably strong substrate adhesion of DAGS coatings.

On the other hand, significant damage to the micro-structured alumina layer was observed on sample A4. Many inter-ridge spaces had been closed and there was an overall flattening of the microstructure. The SNF coating was visibly smoothed over, although comparison of the EDX spectra of sample A4 before and after ice adhesion...
testing (Fig. S4.a) shows that a fluorinated SNFs layer is still present. Even prior to ice adhesion testing, the micro-structured alumina exhibited a partial peeling from the metal substrate in a few circumscribed areas (Fig. 4.b). Following icing/de-icing tests, complete removal of micro-structured aluminum oxide patches was observed, although not uniformly (Fig. 4.c). Macroscopically visible change to the sample surface, observed as a gradual loss of its iridescence with cumulative icing cycles, coincided with SEM images of exposed flat patches of the native oxide layer. No such behavior was observed for sample A3, as shown in Fig. S5, whose anodic oxide layer remained attached to the substrate, but showed an otherwise similar degradation to that of sample A4. Therefore, although the finely rough silicone under-layer showed strong adhesion to the oxide, it was overshadowed by the poor durability of the micro-structured oxide and the loose bond between the oxide and the bulk alloy, weakened during micro-structuring by alkaline etching. The mechanical protection of the superhydrophobic nano-texture granted by the hard microstructure was consequently compromised.

A closer look at the SEM images of sample A4 from Fig. 4.b and Fig. 4.c gives further evidence of a weakened oxide adhesion. For instance, pits were visible in the exposed areas of the samples, evidence that pitting corrosion progressed at the base of the anodic oxide. This phenomenon can be explained by examining the coating fabrication steps. Tartaric sulfuric acid (TSA) anodized aluminum (Fig. S1.c) was etched in an alkaline solution of 1 M NaOH. As a result of this process, a micro-porous texture of valleys and ridges was formed from the anodic oxide (Fig. S1.d). The base passivating oxide layer at the valley floors was likely damaged or largely removed by the etchant. This explanation is supported by the lower concentration of O in the valleys compared to the crests, as shown by EDX elemental maps (Fig. S4.b) and EDX spectra of valleys and ridges (Fig. S4.c), which is evidence of a thinner oxide layer. Then, during DAGS coating, the surface was exposed to an aqueous phase containing Cl\(-\) ions, arising from hydrolysis of TCMS. The Cl\(-\) ions likely caused pitting corrosion of the exposed zones with little or no passivating oxide [56,57]. The introduction of TMMS as a co-precursor to SNFs in a ratio \(r = n_{\text{TMMS}}/n_{\text{TCMS}} = 3\) led to a reduction of the amount of evolved HCl by a factor of \(1 + r\) when compared to a process using an equivalent amount of TCMS alone. However, HCl could not be entirely eliminated due to its catalytic role in the reaction [39]. Moreover, HCl is released during the fluorination step, although the SNF coating should protect the underlying substrate from it [58]. Corrosion of the bulk alloy weakened its bond with the oxide [59]. The fact that oxide delamination was observed only on sample A4 points to the fluorination process or the lack of annealing after SNF coating as the cause of said delamination. However, further investigation is required to conclusively determine the cause.

The aluminum alloy leans on a robust aluminum-oxide layer for enhanced corrosion protection. Anodic oxide growth provides consistent layer thicknesses and is a promoter of strong coating adhesion. The protective oxide was damaged during the SNF coating process, leading to the onset of pitting corrosion, as observed in the aluminum alloy coated with f-SNFs. Nevertheless, the presence of remaining oxide coated with f-SNF was sufficient for the surface to exhibit low IAS. The removal of the anodic-oxide passivation layer is, however, unacceptable.
by aerospace standards for risk of exposure to corrosive environments, since the natural oxide cannot adequately protect the alloy [60]. No oxide delamination was visible on the non-fluorinated SNF surface, but that does not discount the possibility of underlying pitting corrosion. For this reason, the non-fluorinated SNF coating would be preferred over the f-SNF on aluminum 2024, despite its slightly higher IAS. Further work is necessary to optimize the coating parameters to avoid de-passivation of the metal substrate, particularly the alkaline etching time, NaOH concentration, and the ratio of TMMS to TCMS.

As a measure of effective durability, the wettability of the surfaces was tested following 16 cumulative icing/de-icing cycles. Fig. 4.d shows the distribution of water contact angle and roll-off angle measurements over the length of interest of each cantilever substrate. An image below the chart serves to locate the discrete position of each measurement point with its position during the ice adhesion test. Sample T3 is not included in the analysis because it did not complete the whole ice adhesion testing routine; its wetting data is available in the Supporting Information.

Repeated icing/de-icing cycles resulted in decreased contact angle and increased roll-off angle on all non-infused surfaces, showing a loss of their superhydrophobic character. However, the lowest contact angle measured on post-icing SNF coatings was 120°, which confirms that a hydrophobic silicone layer was still present on the whole length of the surface, as the bare substrates were hydrophilic. This result is in agreement with SEM imaging, shown in Fig. 4.a, where a nano-rough ceramic layer was observed after icing.

Moreover, CA was found to be on average lowest near the fixed end of the cantilever and to increase gradually until the free end. This result indicates that damage was most severe near where the interfacial crack with ice was initiated. That observation agrees with the Euler-Bernoulli bi-material cantilever beam model where the interfacial shear stress is highest closest to the fixed-end [49]. As an interfacial crack propagates along the beam, the distance between the crack front and the free end decreases, which would result in an increase of shear stress according to Eq. (1). However, linear strain along the cantilever decreases at a faster rate, resulting in an overall lower shear stress. Therefore, larger shear stresses cause an earlier and more severe degradation of surface properties.

Fig. 4.d also shows that, while samples T4 and T3 exhibited complete pinning of water droplets, even at an inclination angle of 90°, surface A4 retained a certain degree of droplet mobility. Indeed, A4 showed complete pinning until after the half-way mark where the RoA started to decrease to approximately 10° at the free end. This result implies that the micro-structured oxide layer offered some mechanical protection to SNFs, and it was able to withstand the less severe stress conditions at the free end of the cantilever, in general agreement with what was observed for CA. The difference in this regard between samples A3 and A4 was due to different surface chemistries. Fluorinated surface chemistry, as in A4, reduced IAS due to weaker Van-der-Waals interactions with water [61], leading to reduced mechanical damage during ice removal. However, the significant damage observed for higher stress zones of sample A4, both from SEM and wettablity measurements, suggests that the hard microstructure failed to offer a long-term protection to the SNFs in icing conditions, and that more favorable surface chemistry was insufficient to compensate this effect entirely, contrary to expectations [62,63]. Microstructures have been used to protect nanostructures against mechanical abrasion [64-66]. Evidence shows that similar microscopic asperities can be damaged or removed by de-icing in ice adhesion tests [25,67]. In the present study, observations near the fixed-end of sample A4 agree with the latter evidence.

An altogether different situation was observed for the liquid-infused sample, T5. Fig. 4.d shows that T5 had a uniform contact angle of 112° and RoA (sliding angle in this case) of 10° over the whole length of the cantilever. Both values are typical for liquid-infused surfaces, although the measured sliding angle is at the upper limit of what can be considered slippery [68]. It should be noted that the presence of a wetting ridge around the water droplet is not appreciated during sessile drop measurements on a conventional goniometer, and, as such, CA measured for such surfaces is only partly indicative of their thermodynamic equilibrium [33]. Moreover, since the lubricant in T5 was replenished every fourth icing/de-icing cycle, the extent of lubricant depletion observed by CA and RoA measurements was only after 4 consecutive glaze icing cycles (as opposed to 16 cycles of mixed conditions).

Nevertheless, the uniform wettability observed on sample T5 is evidence that the lubricant remained uniformly infused in the surface, which was able to maintain its slippery character. Two main pathways of lubricant depletion have been identified when dealing with simulated atmospheric icing laboratory tests: removal by aerodynamic shear flow [34] and capillary wicking into the porous ice structure [29]. Both these mechanisms played a role in lubricant depletion of surface T5, although not concurrently. In the employed ice adhesion testing conditions, excess lubricant was rapidly sheared away as soon as the sample was exposed to the airflow, since no capillary action was exerted on it from the underlying surface texture to oppose shear flow. As soon as the lubricant level reached the surface texture, depletion was limited by capillarity and the rate of lubricant loss was reduced. When ice started to accrete on the sample, the liquid-infused surface was effectively shielded from shear flow-induced depletion but was instead subjected to depletion arising from wicking of lubricant into the porosity of the ice. Lubricant wicked into ice was permanently lost when the accreted ice was removed. This alternation between exposure to airflow and ice accretion efficiently mimicked the depletion modes to which a lubricant-infused surface would be subjected to in flight. It should be noted that the presence of an un-iced region at distances from the fixed end lower than 45 mm (Fig. 4.d) might have partly compensated lubricant depletion, as it could have acted as lubricant reservoir, facilitating redistribution of the infused oil between icing/de-icing cycles. The good durability shown by sample T5 is an important step in testing its viability for real-world application, although long-term evaluation is necessary.

4. Conclusions

The DAGS coating method was selected to produce icephobic surfaces because many of its features are advantageous for aerospace coatings. For instance, it enables the growth of superhydrophobic nanostructures such as Silicone Nanofilaments on virtually any shape, owing to its vapor-phase nature. It is carried out at room temperature, well below any aircraft alloy melting point, thereby conserving an alloy’s mechanical properties. Finally, its industrial scalability has been demonstrated in reaction chambers up to 9 m². Its primary drawback, however, is the evolution of significant amounts of HCl during the coating reaction.

In this work, an adaptation of the DAGS process designed to reduce the amount of corrosive volatile compounds typically produced during the reaction was presented. The proposed method made use of a mixture of trialkoxysilanes and trichlorosilanes, whose amounts were tuned to supply the minimum catalytic amount of HCl required. This modified process maintained the well-established advantages of the DAGS method while protecting metal substrates from excessive corrosion. Silicone Nanofilaments were grown on Ti-6Al-4V, anodized with TiO2 nanotubes, and on TSA-anodized aluminum 2024 alloy, on which a micro-structured oxide layer was introduced by an alkaline etching process.

The fluorinated SNF coating on titanium and aluminum alloys showed low IAS for 16 cycles of icing/de-icing. Even though superficial filaments were removed in the process of de-icing, the base silicone layer had a strong adhesion to the underlying anodic oxide layer, resulting in sustained low ice adhesion properties. Moreover, liquid-infused SNFs on Ti-6Al-4V showed consistently low ice adhesion that even surpassed that of f-SNFs, especially in mixed/rime conditions. Good short-term durability was proven against glaze ice conditions, but further testing is required to assess its long-term stability.
In an effort to reduce the environmental footprint caused by commercial air travel, aircraft manufacturers have turned to hybrid or fully electric aircraft concept designs. The reduced overall energy consumption of those aircraft requires that all the subsystems reduce their energy demand as well, including active ice protection systems. Passive ice protection systems are therefore in high demand but need to pass rigorous aerospace requirements prior to being considered as design options. Before a candidate coating is subjected to durability tests, it must first show its effectiveness as a passive ice protection system either through suppressed ice accretion and/or low ice adhesion; the latter being the more realistic goal. Our findings show that DAGS-grown Sil-icone Nanofilaments are a promising candidate for further investigation as passive de-icing coatings, to increase aircraft energy efficiency and help bring about a cleaner future for air travel.

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CRediT authorship contribution statement

Alexandre Laroche: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. Davide Bottone: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. Stefan Seeger: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. Elmar Bonaccurso: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Alexandre Laroche: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. Davide Bottone: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. Stefan Seeger: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. Elmar Bonaccurso: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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