Effect of experimental parameters on icephobic measurements

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Abstract— **The evaluation of icephobic properties of the surfaces suffers from a lack of regulations: there is a huge number of measurement systems that are, however, definitively not comparable to one another, such as the measure of adhesion force between a surface and ice and the measure of the delaying time in the ice nucleation process. Even among the same kind of measures, the experimental data are scarcely comparable to each other if collected with a different system as, for instance, centrifugal adhesion test and the shear stress test on static-ice. Also, the adoption of a relative indicator such as adhesion reduction factor (ARF) can be in some cases misleading.**

In particular, for ice adhesion analysis, reliability and repeatability of tests are also cause of concern as ice shedding measures involve setting numerous experimental parameters that can influence the final results. Moreover, it is not yet clear whether there is a dependence between some properties of the tested samples, such as roughness and wettability, and the optimal experimental parameters setting.

To provide a wider sight on this topic, we performed a deep study to find the optimized parameters for our instrumental setup seeking a set of common parameters to be used as a stepping-stone for a further standardization. We studied the icephobic behavior of several samples measuring the shear stress force between ice and surfaces by varying some experimental conditions and the roughness of the samples. The measurements were carried out with a homemade mechanical testing equipment, by measuring the shear stress force between ice and surface in each of the applied conditions.

The samples have been immersed in water and frozen at temperatures ranging from -8 °C to -18 °C with freezing times up to 96 hours to evaluate how ice growth can influence adhesion.

The tested samples were aluminum alloy specimens with different surface finish: smooth samples, micro-roughed samples, and micro-nano roughed samples. The smooth sample was obtained by a wet tumbling process. The micro-roughed specimens were obtained by a sandblasting treatment. The micro-nano roughed samples were obtained with a hydrothermal treatment on the sandblasted specimens: a grass-like nanostructure of boehmite grew on the surface. Lastly, the samples were coated with a thin film of hydrophobic fluoroalkyl silane and with a hydrophilic commercial primer to assess relationship between coating effect and experimental parameters.

To better understand the effect of freezing temperature and time on specimens, all the samples were characterized in terms of morphology, wettability, before and after the icing process. Some differences have been found both in terms of shear stress values and repeatability and correlations were found among testing parameters and sample properties

Keywords— **icephobic surface, shear stress tests, measure reliability, icing, optimized parameters**

I. Introduction

Ice accretion on surfaces is a problem that concerns many aspects of daily life. One of the main issues is related to the icing of the power line components, especially conductors and ground wires: due to the very heavy weight of the snow or ice accretion, the cables can be torn off or dropped and the trellis can collapse. This causes long blackouts and expensive maintenance. Insulators are also subjected to icing phenomena: the surface of insulators can be completely covered by snow or ice causing current leakages giving rise to flashover phenomena.

One of the methods to prevent or, at least, hurdle these icing phenomena is to impart anti-icing properties to the surfaces, which basically consists in modifying the chemical and physical of the surfaces in order to: i) delay the ice- nucleation time, ii) decrease the ice-nucleation temperature and iii) diminish the adhesion between surface and ice or snow. In particular, delaying ice nucleation times and decreasing ice nucleation temperatures make the icing process more and more difficult while diminishing the adhesion between surface and ice facilitates the detachment of the accreted ice on the structure. Despite its crucial role, the definition of icephobicity is not unique. Icephobicity can be defined both as 1) the ability of a solid surface to repel ice and 2) the ability of a solid surface to prevent ice formation [1].

Even the assessment of the icephobic properties of a surface is still a not well-defined topic. A huge number of measurement systems can be adopted to evaluate the anti-icing properties, for instance: freezing time and freezing temperature of a subcooled water droplet [2], wind tunnel icing [3], detachment of the ice with a centrifugal method [4], detachment of the ice applying a normal force [5] or applying a shear force on sample iced in bulk ice [6]. All the mentioned methods give only a partial view of the anti-icing properties and are more or less significant, depending on the application of the icephobic surface. For instance, the wind tunnel methods can be very useful for aircraft application, while the shear stress tests are meaningful for overhead lines' application, in order to evaluate how easy is the shedding of the snow-sleeve. Obviously, a direct comparison among these methods is difficult if not impossible.

Even among the same kind of measures, the experimental data are scarcely comparable to each other if collected with a different system. For instance, in the shear stress measurements, it is possible to carry out the analysis on cylindrical samples or flat samples, varying many experimental parameters such as ice temperature or the speed of the probe.

The complexity of those analyses, together with the lack of regulations, means that the results obtained by different laboratories, even with similar methods, are hardly comparable. In recent years, the need for standardization has prompted researchers to thoroughly investigate many parameters and propose new solutions [6], [7], [8], however, many studies still have to be done to obtain a full understanding of this matter.

In this work, we present a deep study of the effect of some experimental parameters on shear stress analysis conducted with our equipment. We carried out shear stress measurements by freezing a cylindrical shaped sample into a mold together with water and then extracting the sample from the so-formed ice using a hydraulic tensile testing machine. We varied many experimental parameters such as ice temperature, icing time, ice volume and the speed of the piston displacement and we measured many aluminum-alloy samples, with different surface roughness. Starting from these surfaces, we prepared hydrophobic surfaces by covering them with a fluoroalkilsylane coating obtaining samples characterized by the same roughness and different wettability.

The collected results allowed us to optimize the experimental parameters to improve the reproducibility of the analysis, for all the tested samples, considering both the roughness and the presence of the coating. This work can represent a first step towards the standardization of this method of analysis.

II. Experimental

A. Materials

Flat plates (20 × 70 × 2 mm) and bars (12 mm diameter, 100 mm length) of aluminum alloy (6082) were used as substrates. Dynasylan® SIVO CLEAR EC coating was purchased from EVONIK; the product is composed of a fluoroalkylsilane (FAS) 2%, propan-2-ol 93% and dodecane 5% and was used as received. Acetone (> 99.5%) and isopropanol (> 99%) were purchased from Sigma Aldrich. Barrier Primer White (Aerodur 37045) and Hardener (S66/22R) were purchased by Akzo Nobel.

B. Samples preparation

All the aluminum alloy specimens were cleaned with basic soap, rinsed in an ultrasonic bath for 10 min with acetone and dried under nitrogen flux.

The samples were treated with different mechanical and chemical processes and divided into different groups, according to the different final roughness and chemical surface.

In the first group, named AC, no further treatment was done except the cleaning, and the samples were used as received. In the second group, named WT, the samples were treated with a wet tumbling process. In the third group, named SB, the samples were sandblasted with micro glass beads in 40-70 µm diameter range. In the fourth group, named HR, a hierarchical micro-nano roughness was obtained by sandblasting and then boiling the specimens in ultrapure water for 30 minutes. This hydrothermal treatment leads to the formation of a nanometric aluminum oxide-hydroxide (pseudo-boehmite) on the surface of the sample.

Starting from WT and HR, the samples were dip-coated in the Dynasylan® SIVO solution and thermally treated at 120 °C for 1 hour. The resulting samples, whose surfaces were chemically modified with the FAS molecules, are named WT-C and HR-C, respectively.

For comparison purposes, some specimens were covered with the Primer (Aerodur 37045/ Hardener S66/22R) layer (Pr) which gives rise to a smooth and slightly hydrophilic surface.

In the Table below are summarized the prepared samples.

TABLE 1. PREPARED SAMPLES

Name	mechanical treatment	hydrothermal treatment	coating
AC	none	none	none
WT	wet tumbling	none	none
WT-C	wet tumbling	none	FAS
SB	sand blasting	none	none
HR	sand blasting	30 minutes	none
HR-C	sand blasting	30 minutes	FAS
Pr	none	none	Primer

C. Characterization

Static water contact angle (CA) measurements were carried out at 20 °C with the Kruss DSA 30 Drop Shape Analyzer with sessile drop method, using a volume of water variable from 2 µl to 20 µl, depending on the hydrophobicity of the tested surface. The measurements were replicated at least 5 times for each sample.

The roll-off angles (RO) have been measured with the Kruss DSA 30 Drop Shape Analyzer, accessorized with an automatic tilting table, using a volume of 20 µl. At least 5 measures were done for each sample.

The surface morphologies were examined using a field emission scanning electron microscope (FE-SEM) (Tescan).

A Taylor Hobson mechanical profilometer was used to measure surface roughness, data were averaged over at least 5 runs for each sample.

Ice adhesion properties were evaluated by shear stress analysis performed with a homemade apparatus, applied to a hydraulic testing frame (MTS). Aluminum alloy bars were used as test samples. They were housed in an aluminum alloy mold, and a certain volume of deionized water was added. Further, the mold was wrapped with a Teflon shield and the system was placed in a commercial chest freezer. The shield has a double role: 1) keep the temperature as constant as possible during the assembling of the iced sample in the tensile machine, 2) keep the specimen centered on the mold during the freezing process. After the icing process, the mold was fixed to the tensile machine, and the shield was removed, as represented in Fig. 1.

The sample was then extracted from the ice at constant speed. The Force F needed to pull the sample off the mold was recorded. The ice adhesion strength (τ) in shear can be calculated by:

$$\tau = F/A$$

Where A is the surface of the bar in contact with the ice.

Fig. 1 shear stress equipment: a) tensile machine; b) sample holder before the icing process; c) iced specimen and mold fixed in the tensile machine immediately before the test.

Shear stress tests were carried out at least on 10 different specimens for each treatment and the average and standard deviation were calculated. Since the testing machine is not located in a cold room, the experiments are conducted in less than 1 minute. Doing this and using the Teflon shield is it possible to assume that the temperature of the samples is constant.

III. Results and Discussion

A. Characterization of the specimens

Profilometry tests were carried out on the mechanically treated samples, evidencing the increase of the surface roughness for all the sandblasted samples, while the tumbled sample WT showed smoother surface than the AC.

TABLE 2. ROUGHNESS OF THE PREPARED SAMPLES

Name	Ra (µm)	Rp (µm)	Rv (µm)
AC	0.30	1.11	2.02
WT	*0.06*	*0.18*	*0.53*
SB	*1.50*	*4.55*	*4.68*

The hydrothermal treatment of the aluminum alloy gives rise to the growth of a flower-like nanostructured aluminum oxide-hydroxide, as presented in a previous work [9], evidenced by SEM images (Fig. 2).

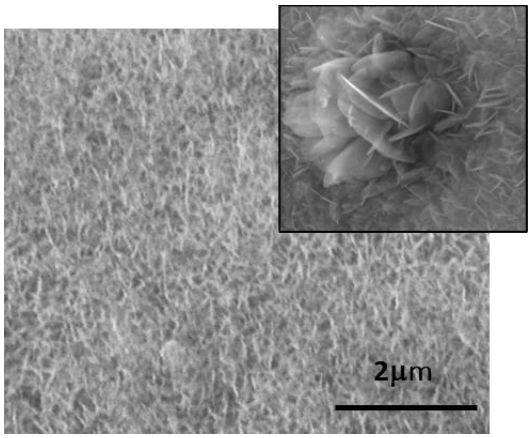

Fig. 2 SEM image of HR sample evidences the nanostructure, 30 kx. In the inset a particular of the structure of the boehmite.

As expected, for the uncoated samples, the rougher the surface, the more hydrophilic the specimen is, as described by Wenzel equation [10]. Due to the presence of the nanoboehmite, the HR sample evidences a superhydrophilic behavior.

The wettability properties were characterized for both the uncoated and coated samples, the results are listed in Table 3.

TABLE 3 WETTABILITY OF THE TESTED SURFACES

Name	CA (°)	RO (°)
AC	91.1 ± 0.5	>90
WT	60.1 ± 3.3	>90
SB	53.2 ± 6.1	>90
HR	7.5 ± 2.1	>90
WT-C	112.6 ± 0.9	>90
HR-C	162.0 ± 2.1	6.0 ± 2.3
Pr	83.2 ± 0.9	>90

The fluorinated molecules on the surface of the coated samples give rise to a high hydrophobic behavior, as for samples WT-C and HR-C. In particular, HR-C has a CA greater than 160° and a RO lower than 10° and can be considered a superhydrophobic surface [10].

B. Optimization of the experimental set-up

-1. Volume of the water in the mold and speed of the mobile traverse

Starting from the AC specimens, the main experimental parameters studied were: *1)* the volume of the water poured into the mold and *2)* the speed of the movable piston.

The volumes tested were 25 ml and 50 ml; the surface of the sample in contact with the ice was about 850 mm^2 and 1700 mm^2 respectively. The specimens were prepared at room temperature, as described above and then pun into the freezer for 17 hours at -18 °C. The speed of the movable piston for these tests was 4.8 mm/min.

TABLE 4 SHEAR STRESS AND STANDARD DEVIATION BY MODIFYING THE VOLUME OF THE WATER

Volume (ml)	Shear stress (kPa)	Relative standard deviation %
25	794	22
50	688	17

As it is shown in Table 4, the obtained results are very similar and can be considered statistically equivalent. Operating with a volume of 50 ml, however, leads to a lower standard deviation, for this reason this volume should be preferred. From here on, the chosen water volume is 50 ml unless otherwise specified.

The study of the piston speed was carried out testing three different speeds: 4.8 mm/min, 18 mm/min and 48 mm/min. To evaluate the effect of the strain rate on different roughed and coated surfaces, both the AC and HR-C samples were studied.

As it is reported in the table below, the speed of the piston does not seem to have a very important effect when a smooth uncoated sample is measured: all the AC specimens are comparable to each other in terms of shear stress and standard deviation. However, it is important to highlight that this parameter is crucial when measuring the HR-C sample. Indeed, the most repeatable results were obtained applying the intermediate speed of 18 mm/min.

It is also important to point out that strain rate has an influence on shear stress values: by moving the piston with the intermediate speed it is possible to obtain the highest values of shear stress both for AC and HR-C samples, however this difference in terms of absolute values is not to be considered negatively if the adhesion reduction factor (ARF) (τAC/) is taken into account. Indeed, the ARFs calculated for 4.8 mm/min and 18 mm/min experiments can be considered alike, while the ARF of 48 mm/min test is considerably higher. From these considerations, the most reliable speed rate is 18 mm/min.

TABLE 5 SHEAR STRESS AND STANDARD DEVIATION BY VARYING THE SPEED OF THE MOBILE TRAVERSE

sample	speed (mm/min)	Shear stress τ (kPa)	Relative standard deviation %	ARF
AC	4.8	688	17	/
	18	844	17	/
	48	699	15	/
HR-C	4.8	168	64	4.1
	18	217	40	3.9
	48	111	70	6.3

-2. Icing time and temperature

Icing conditions are among the most important parameters to be considered. The apparatus used in this work is a commercial freezer that can reach the minimum temperature of -18 °C. The temperature of the freezing water in the mold was first followed by means of a type K thermocouple inserted into a mold, during the icing process of ten samples, simultaneously. The temperature vs time graph of the icing process is reported in Fig. 3.

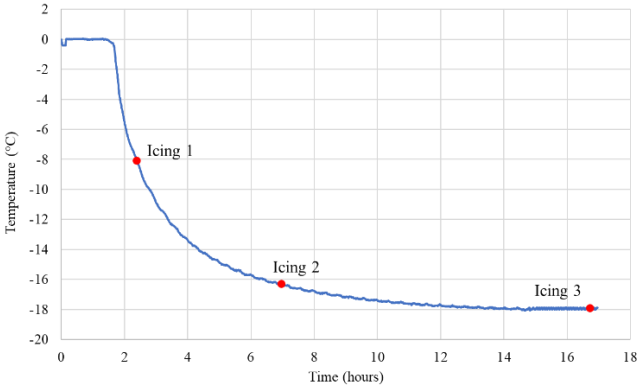

Fig. 3 temperature profile of the freezing process.

We measured the shear stress of samples iced in four different conditions: Icing1, Icing2, Icing3 (see Fig. 3) and Icing 4. We can assume that these icing conditions are representative of one of the strongest atmospheric icing phenomena: the glaze icing. In Icing 1, the sample was tested when the temperature reached -8 °C. In this situation, the water is completely iced but the ice is in a transition state since the temperature is still decreasing steeply. In Icing 2, the sample was tested after 7 hours, when the temperature reached -17 °C and decreasing at a slower rate. In Icing 3, the sample was tested after 17 hours, when the temperature reached the minimum value (-18 °C).

Finally, in Icing 4, the sample was tested after 96 hours, with a completely stable temperature (-18 °C).

The study highlights an important effect of the icing parameters in function of the different tested samples. In general, the lower τ value was recorded for Icing 1 tests.

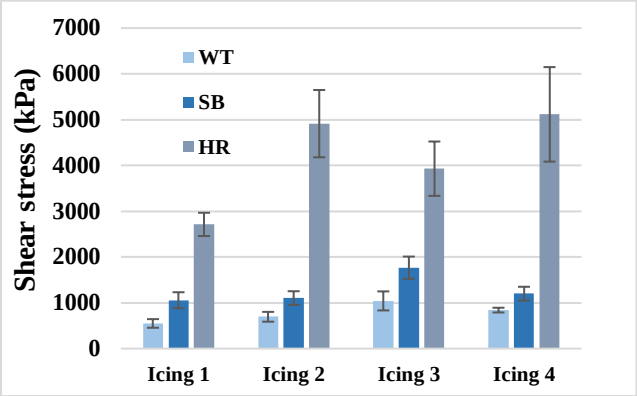

Fig. 4 Shear stress of different roughed samples applying different icing conditions.

TABLE 6 RELATIVE STANDARD DEVIATION OF SHEAR STRESS MEASURES IN FUNCTION OF ICING PARAMETERS AND SAMPLES

Sample	Relative standard deviation (%)			
	Icing 1	Icing 2	Icing 3	Icing 4
WT	17	15	20	6
SB	17	14	14	13
HR	9	15	20	20

As a matter of fact, for the WT and SB specimens, the τ value increases from Icing 1 to Icing 3 and then, decreases in Icing 4. The lowest standard deviation for WT was obtained in the Icing 4 test, for SB the calculated standard deviations can be considered similar. Sample HR, characterized by a micro-nano roughness, showed a significant sensitivity to icing conditions: increasing time and temperature of icing leads to a strong increase of ice adhesion. In the Icing 4 condition, the adhesion of the ice to the substrate is so high that the reported value refers to ice internal cohesive forces. At the same way as τ, standard deviation increases with prolonging icing conditions, while for WT the lowest standard deviation was obtained in the Icing 4 test, and for SB the calculated standard deviations can be considered similar.

To understand icing parameters' effects on coatings, the samples Pr, WT-C and HR-C were tested too. The first one (Pr) represents a smooth hydrophilic surface, the second (WT-C) a smooth hydrophobic surface and the third (HR-C) a roughed superhydrophobic surface.

As for the uncoated samples, a marked increase of the τ values for the Pr, is evidenced by prolonging the icing conditions. The results collected for WT-C and HR-C can be considered statistically equivalent. It is important to underline that the relative standard deviation strongly increases for the roughed sample and better repeatability is obtained by applying the Icing 1 condition. Smoother samples (Pr and WT-C), regardless of their wettability, showed better repeatability for longer icing treatments, however, even in Icing 1 condition, the standard deviation is satisfactory.

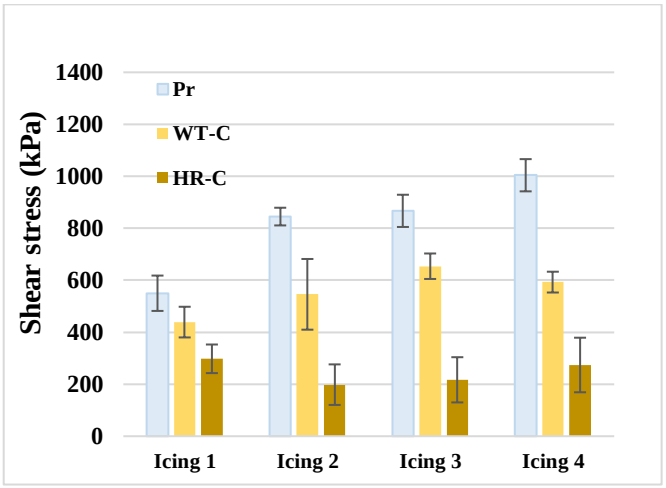

Fig. 5 Shear stress of different coated samples applying different icing conditions

TABLE 7 RELATIVE STANDARD DEVIATION OF SHEAR STRESS MEASURES IN FUNCTION OF ICING PARAMETERS AND SAMPLES

Sample	Relative Standard deviation (%)			
	Icing 1	Icing 2	Icing 3	Icing 4
Pr	12	4	7	6
WT-C	13	25	7	7
HR-C	18	39	40	38

To better understand the behavior of the coating in contact with ice, samples were iced and de-iced in different conditions and then hydrophobicity was measured. The same measurements were also carried out on the samples after the shear stress tests (*Table 8*).

TABLE 8 WETTABILITY AFTER THE ICING PROCESS

	CA (°) after icing and de-icing process				
Name	**no icing**	**Icing 1**	**Icing 2**	**Icing 3**	**Icing 4**
WT	60.1 ± 3.3	65.2 ± 2.4	63.0 ± 4.1	72.9 ± 2.9	70.7 ± 5.1
HR	7.5 ± 2.1	26.5 ± 3.4	13.9 ± 2.4	19.5 ± 2.9	21.5 ± 6.8
WT-C	112.6 ± 0.9	115.7 ± 3.5	114.4 ± 2.3	115.0 ± 4.9	121.8 ± 1.6
HR-C	162.0 ± 2.1	158.5 ± 1.0	157.1 ± 1.1	161.0 ± 2.4	158.3 ± 2.2
	CA (°) after shear stress tests				
WT-C	112.6 ± 0.9	113.1 ± 3.0	113.7 ± 1.3	125.7 ± 2.7	114.1 ± 1.5
HR-C	162.0 ± 2.1	155.2 ± 3.0	154.7 ± 3.1	152.3 ± 3.0	134.8 ± 3.9

First, it is noteworthy that all the icing processes cause a change in the wettability of all the surfaces. This is more pronounced for HR that loses its superhydrophilic behavior, probably due to a partial deterioration of the nanostructure, caused by ice shrinking and pressing on its surface.

Unexpectedly the coated samples evidenced only a slight change in their wettability. It is important to highlight that the HR-C is maintaining CA>150° even after a prolonged icing process. This means that the coatings are well adhered to the substrate and are not taken away by ice.

Measurements after shear stress tests showed different behavior between WT and HR-C: no degradation of wettability was noticed. For HR-C we can observe a deterioration of its superhydrophobicity during the more stressful conditions applied in Icing 4. This can be attributed to the partial breaking of the nanostructure during the test, as already reported in literature **Errore. L'origine riferimento non è stata trovata.**. However, Icing 1, 2 and 3 just cause a very small degradation of its properties.

IV. Conclusions

This work remarks the importance to standardize some experimental parameters in order to obtain more affordable shear stress measurements and comparable results to better define the icephobic properties.

The study took into account many parameters and different samples, characterized by different roughness and wettability. It was demonstrated that one important parameter is the strain rate: the negative effect of a very high speed is shown on a roughed coated sample and among the tested strain rates, the best one is 18 mm/min.

From these tests it is evident how icing parameters play a decisive role in the definition of icephobicity, even if the effects are not completely clear. First, it is possible to affirm that extending the icing time up to 96 hours (Icing 4) gives rise to a very hard and adhered ice that can damage the morphology of some samples and even degrade the coating. The roughness seems to play a role in terms of repeatability: the rougher the sample, the higher the standard deviation. The best results in testing were obtained with Icing 1: even though the ice is in a temperature transition condition, all the samples evidenced a relative standard deviation lower than 20%. Moreover, in this condition, the adhesion forces between ice and samples are weak and do not damage the surface structure. The intermediate icing conditions (Icing 2 and 3) demonstrated good repeatability for some surfaces (Pr and WT-C) but poor for many other, thus cannot be considered the optimal ones.

In conclusion, by evidencing the importance of a profound attention to the experimental conditions, this work aims to represent a first step to define a guideline for the assessment of icephobic surface properties.

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