Extended Evaluation of icephobic coating regarding their field of application

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Abstract— **Atmospheric ice that adheres to structures and accumulates is a critical issue in numerous northern areas. Even the availability of different de-icing methods, they consume a great quantity of energy or necessitate elaborate infrastructure. However, using coatings with icephobic properties could be the "ideal" solution. This paper proposes a definition of icephobicity in line with the ice adhesion test methods used. The general way to assess this property is described using a global approach, the first step of which is a screening test campaign with many different candidate coatings evaluated in terms of their adhesion reduction factor (ARF). Further tests are recommended, after the best candidate coatings are identified, in an extensive test campaign performed under simulated icing, and outdoor conditions prevailing in the real environment of the targeted application. Finally, a specific example of a test campaign in which the icephobic coatings are used to Arctic offshore conditions is described.**

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I. INTRODUCTION

Atmospheric ice adhering to structures causes numerous problems in the telecommunications, electrical distribution, road, marine, and aviation transportation networks. The need for reliable transportation in the most severe icing conditions highlights the importance of ice adhesion studies. It is well known that ice accumulation on aircraft causes loss of lift, increase in drag, faults in gauge readings, and greater risk of stalling and potentially fatal crashes.

Despite the fact that the requirements and protocol about de-icing and anti-icing fluid utilization are tightly regulated and well documented, these fluids are useless if they are not used properly, or if they fail to accomplish their work [1],[2]. Consequently, efforts to improve the efficiency of de-icing and anti-icing methods, is still a very active field of multidisciplinary research. Many efficient de-icing methods have been developed, although they consume a great deal of energy and/or necessitate elaborate infrastructure and maintenance [3]. At present, various methods are proposed to remove or even prevent and mitigate the formation of ice on structures and vehicles. These techniques are categorized in three main groups: thermal, chemical and mechanical.

Thermal methods are the most used in both automotive and aerospace applications, where the iced elements have relatively small areas. The most common methods use thermal heating elements, and fluids applied at high temperature. Today, these methods are commonly used for de-icing and anti-icing aircraft protection before take-off. The most common chemical methods use commercial fluids that are aqueous propylene and ethylene glycol solutions, which allow reducing the freezing point of water, thereby preventing the formation of ice. Likewise, other liquids and solids that lower the melting point are also commonly used to de-ice airport runways and taxiways [4, 5]. Mechanical methods using pneumatic boots, electro-expulsive sheaths and piezoelectric cells have also been developed. They are all based on the same principle, as they deform the ice enough to break the adhesive bonding with the interface [6].

A. *Passive Anti-Icing Methods*

Passive methods do not require energy other than from natural forces, such as gravity, wind, or surface tension, to induce ice detachments, or mitigate its formation. Passive methods include surface treatments and coatings that have been developed specifically by the industries and academia to decrease the accumulation and/or adhesion of ice. Ideally, icephobic materials would be solid, durable, easy to apply, inexpensive, and efficient in a wide range of icing conditions.

Today, protective materials applied to ice-exposed surfaces appear to be an interesting solution to prevent ice build-up. Since the early 1960s, several research projects attempting to identify those materials have been published [7]. Over the last decade, the development of efficient icephobic coatings and investigations of their effects have multiplied. Actually more than 120 scientific papers have been published since 2017. Many materials have been developed using polymers and, more recently, nanotechnology-based research involving the "lotus effect" has been done [8-10]. A mixture of micro- and nano-scale roughness combined with a low surface energy induces a superficial superhydrophobic effect with air entrapment, which lowers the contact of ice with the solid [11]-[14]. The latter has been partially validated under specific testing conditions. Moreover, with the development of superhydrophobic coatings, researchers began to combine these coatings with existing de-icing methods in order to improve their efficiency [15],[16].

Despite the considerable number of studies on icephobic materials, knowledge regarding the widely anticipated anti-adhesion properties is still lacking, even at times controversial. It follows that no material has yet been identified as efficient enough to ensure full and safe protection against ice accumulation.

II. ICEPHOBICITY

The term icephobic has been chosen by analogy with the word hydrophobic introduced in the 17th century. The adjective hydrophobic describes a substance having only slight or no affinity with water, from a chemistry point of view. Concretely, this no-chemical affinity induces a weak electrostatic bondage of water and a difference between water and surface energies resulting in the formation of water droplets that are more spherical on a hydrophobic surface.

However, in the case of icephobic surface materials, the water is either in a supercooled or solid state, leading to two other aspects: mechanical adhesion and ice accumulation. Therefore, theoretically, an icephobic surface should:

- Reduce the adhesion of ice on a substrate.
- Prevent ice from accumulating on a surface.

Moreover, the hydrophobicity of a surface can be easily assessed by simple methods, such as determining the contact angle of water drops. In the case of icephobicity, its assessment passes through a level of effectiveness in both adhesion and accumulation. So, what is an effective icephobic material? Knowing that the perfect one has not yet been developed, effectiveness must be first determined through targeted applications: energy, transportation, atmospheric, and environmental, in consideration of the economic conditions.

A. Screening Evaluation Tests and Adhesion Reduction Factor (ARF)

Obtaining reliable and precise ice adhesion values is a challenge. Some tests can produce highly variable results, with up to 300% variation. Consequently, it is difficult to compare different icephobic material candidates in order to choose the best ones for further research and development.

To overcome these limitations, accreted ice in the form of freezing precipitation under highly controlled conditions is required. Small ice coupons for a more homogenous ice would also improve repeatability. Any test would also be comparative, where the ice adhesion, or reduction thereof, would be evaluated on coated and uncoated surfaces simultaneously iced, since small variations in the ice cannot be entirely eliminated.

The Centrifuge Ice Adhesion Test (CAT) is a good example of a screening test method meeting these requirements. This method has already been described in the literature [17],[18], and consists of a two-step procedure by which test blades with one extremity either bare or coated with a test sample, are iced on a stand in a cold room. Then they are rotated in a centrifuge until they shed their ice deposits. The adhesion reduction factor (ARF) was first introduced in 2003 by the Anti-Icing Materials International Laboratory, AMIL, in order to normalize ice adhesion reduction values between the different existing methods by incorporating a reference material comparison. The ARF is calculated using the Eq. 1:

$$ARF = \frac{Avg.Ice\ Adhesive\ Stress\ on\ Ref.substrate}{Avg.Ice\ Adhesive\ Stress\ on\ candidate\ surfaces} \qquad \text{Eq.1}$$

The ice adhesion reduction performance of the material surface is evaluated using the following criteria:

ARF > 1: Ice adhesion reduction, icephobic effect, the higher the value, the more icephobic the surface

ARF < 1: An increase in adhesion on the candidate surface with respect to the bare Al

Since 2003, 377 different material surfaces have been evaluated with CAT tests performed under similar icing and experimental conditions, i.e. freezing drizzle at -8°C and centrifuge testing at 10°C. Fig. 1 shows the range of the ARF results, including freshly applied solid coatings, viscous grease, embedded polymeric coupons, and surface treatments. Every coating is compared with either Al 6061 T6 reference or other substrate reference. Note that the standard deviation of ARFs is ± 15% (based on 6 icing test repeats). Most of the candidate coating has an ARF from 1 to 10 over the years.

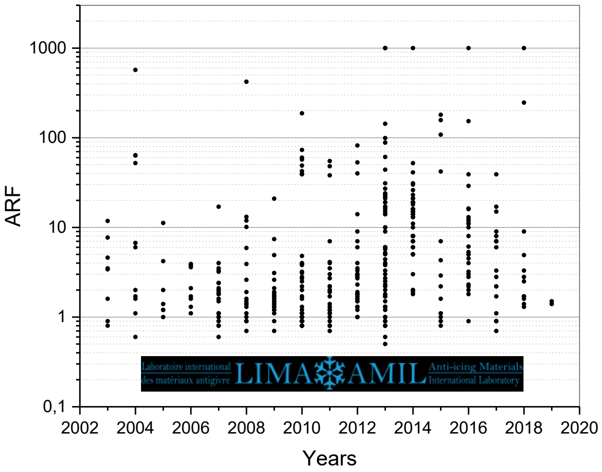

Fig. 1 ARF Results by AMIL over the years

B. *Establishing a Test Campaign to Evaluate the Icephobic Properties/Efficiency*

After establishing the best icephobic candidate material surface with a screening test method like CAT, then further and expanded properties must be considered. Actually, an efficient icephobic surface must not only reduce the adhesion and accumulation of ice, it must be efficient under the targeted application conditions of temperatures, icing, and harsh environment, such as those encountered in actual environments in service use.

The chart presented in Fig. 2 summarizes the main properties that could be taken in consideration for establishing a test campaign to evaluate an icephobic protective surface material.

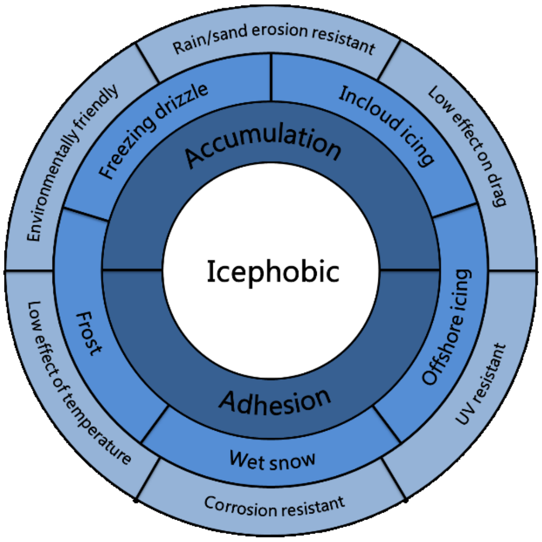

Fig. 2 Icephobic property overview

Obviously, depending on the icephobic application, it can be subjected to different frozen hydrometeors, which do not interact in the same way with the coating. Then, the density of the ice deposit may vary. For example, ice from freezing drizzle has a higher density than frost, and therefore different adhesion properties with the surface material. Moreover, icephobic materials are used under environmental conditions; in some cases they must resist ultraviolet radiation (UV), corrosion, rain and sand erosion at very low or high temperatures, and be environmentally friendly.

Since there is no standard for the evaluation of icephobic material surface, in line with common applications, i.e. aircraft, ground transportation, energy production, or buildings, several tests must be performed to evaluate their true efficiency. The first part of the testing should consider ice adhesion (CAT). In the second part, the coating is put through ice accumulation tests, always depending on its expected use. Lastly, the effect of external conditions, such as temperature, UV, corrosion, rain and/or sand erosion, must be taken into account. However, various other tests could be added to this non-exhaustive list, as needed, following the targeted application. In the next section, an example of an extended test campaign will be described for the application of an icephobic surface material for Arctic offshore applications.

C. Example of Extended Test Campaign: Icephobic Coating for Arctic Offshore Environments

A complete test campaign has been suggested to evaluate 4 different coatings to reduce ice adhesion, and accumulation under Arctic offshore conditions. Firstly, these coatings have been selected from results obtain by CAT. Actually, coatings having substantial ARF results have been selected for further analysis under more specific testing conditions.

Secondly, candidate coatings have been evaluated under simulated icing accumulation. Two types of ice accumulation tests of 15 minutes generated from supercooled water droplets sprayed on the reference cylindrical collector was carried out in a controlled cold room maintained at -20 °C. The setups are presented in Fig. 3 (a-d).

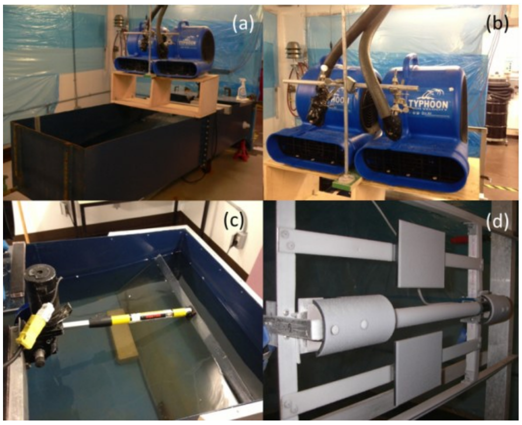

Fig. 3 Sea spray generator: (a) complete setup with the water tank, the fans and sprinklers. (b) White cap spray (WCS) generator with 2 fans that generate 6 m/s wind and 2 sprinklers spraying 70 ± 10 µm supercooled water drops. (c) Wave generators that simulate interaction spray (IS) with 169 to 6097 µm supercooled water drops and (d) accumulation zone with a cylinder as collectors and two control steel plates.

The first accumulation test, presented on Fig. 3, named White Cap Spray (WCS), consists of spraying deionized water droplets of MVD of 70 ± 10 µm at a wind speed of 6 m/s. The selected wind speed is the most common value observed during real sea spray icing events, whereas the 70 µm droplets size is corresponding to the average value determined at 10 m height, the later decreasing with the increased height they collide with the structure [19]. The liquid water content (LWC) was 0.6 g/cm^3. Even if the LWC was approximately 6 times greater than the naturally prevailing value, it yields faster accumulation, thus reducing the accumulation test time to 15 minutes.

The second test, named Interaction Spray (IS), presented on Fig. 3 (c), was performed with 2‰ laboratory seawater drops and droplets cloud, sizes of which were varied from 169 to 6097 µm. The latter were generated from waves produced by a moving plate, at selected intervals, pushing the saline water in a tank, maintained at a temperature of about -0.5 °C. The accumulation zone, presented in Figure 3 (d), consist of a cylindrical aluminum collector of 2.5 cm diameter and 35 cm long. Before and after each accumulation test, the cylinder was weighted while pictures of the iced cylinder taken at the end of each test. Precautions were taken so that the iced collectors were handled carefully during all operations. Two steel plates are also used as control to validate the reproducibility of icing and the reference bare substrate. For each coating evaluation icing of the 2 cylinders is repeated three times.

The Table 1 presents results obtained from ice adhesion test by CAT in terms of adhesion reduction factor compared to bare steel. It is also presented results obtained from ice accumulation tests in terms of accumulated ice weight and the percentage of reduction compared to bare steel. As described in the previous section, ice adhesion test was performed with freezing drizzle ice while accumulation ones with white cap spray WCS and Interaction spray IS.

TABLE 1: ICE ADHESION AND ACCUMULATION TEST RESULTS

	Ice Adhesion CAT	Ice Accumulation Test	
Ice Type	Freezing Drizzle	WCS	IS
Coatings	ARF ± S.D.	Wt.± S.D. (g) % reduction	Wt. ± S.D. (g) % reduction
Steel Ref.	-	26.2 ± 0.6	44 ± 6.0
A	17 ± 3	26.1 ± 0.3 0%	34.4 ± 0.8 22%
B	31 ± 5	26.7 ± 0.5 -2%	42 ± 5 4%
C	44 ± 8	27.1 ± 0.5 3%	40 ± 2 10%
D	1000	11 ± 2 57%	18 ± 5 60%

Ice accumulation on the bare steel is about 26 g and 44 g for the WCS and the IS respectively. As expected IS is a more severe icing conditions than the WCS caused by its great range of droplet size and amount of water. WCS seems to be the icing conditions the less sensitive of the type of surface. Coatings A to C had nearly accumulated the same mass of ice as steel with a percentage of reduction to-2 % to 3%. Only the icephobic D, with a considerable icephobic effect with an ARF of 1000 produces a reduction of ice accumulation of 57%. Results with IS icing present more variation to one coating to another with mass reduction to 4% to 60%. An important observation from these results is that the percentage of reduction is not directly related to ARF as already observed with static ice accumulation test with freezing drizzle [20]. Candidate A, ARF of 17, reduce the ice mass by 22% while the candidate B, ARF of 31, reduce it by only 4%. IS icing is a more elaborated and stochastic process because of the effect of the variable splashing forces not imply in the WCS accretion. A parametric study including a full physicochemical characterization of the coating would be interesting to move further this research.

Pictures of the accreted ice is presented in Fig. 4. On the bare steel, the half-cylinder surface exposed to ice is covered. However, at the right, with the candidate D, it could be seen that the cylinder is partially covered. At Fig. 5, with accreted ice form IS, the observation is practically the same as one with WCS, but the effect of the coating on the ice is more obvious with different shapes where some accreted ice are a part of the main ice deposit. Depending on where droplets or splashes collide, they accumulate differently. When they strike the upper or lower part of the cylinder, they do not solidify immediately upon contact, as it occurs on the bare steel. When the water splashes split into smaller droplets, it can solidify on the cylinder. After the first drops have solidified, other drops can anchor to them.

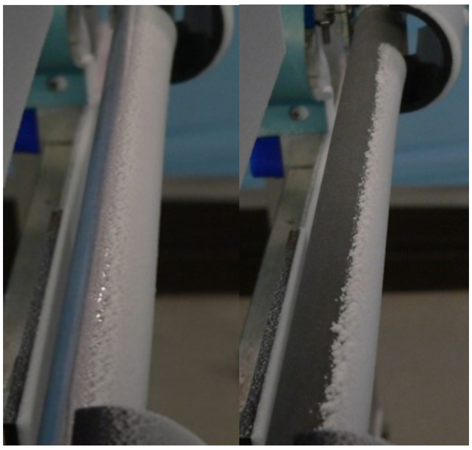

Fig. 4 Cylinder of steel (left) and cylinder covered with D candidate with WCS accreted ice

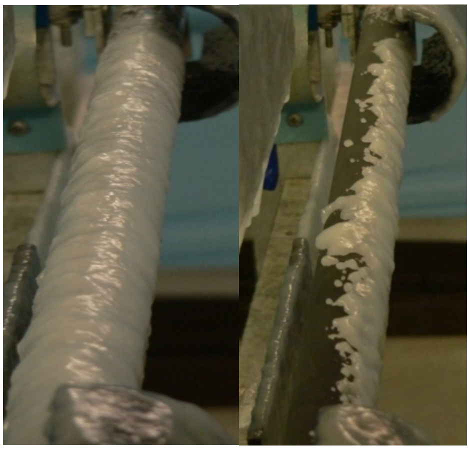

Fig. 5 Cylinder of steel (left) and cylinder covered with D candidate with IS accreted ice

III. CONCLUSIONS

The aim of this paper was to suggest a definition of icephobicity expressed in terms of ARF measured under general testing conditions. Moreover, the coating's efficiency needs to be assessed under the most specific icing conditions representative of harsh environments prevailing in the field. Therefore, the icephobic coating's efficiency is more than a simple measurement of ice adhesion; indeed, many more aspects need to be considered; these being related to targeted applications considering first. Different icing conditions as freezing drizzle, white cap spray and interaction spray, could lead to different results on ice adhesion and on ice accumulation without strong relation between them. Finally, a parametric study including a full physicochemical characterization of the coating would be interesting to move further this research. For application case as oil rigs, which they are submitted to many types of icing, these results could lead to target the best coating for ice protection.

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