PROJECT FINAL REPORT

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1 Final publishable summary report

1.1 Executive summary

Ice adhesion and accretion on surfaces such as aircraft presents long recognised problems with respect to safety, efficiency and operational costs. Current active ice removal methods, such as electromechanical de-icers, are often based on melting or breaking already formed ice layers. In addition to their undesired weight and design complexity, these active anti-icing approaches require substantial energy for their operation. Passive solutions such as icephobic coatings have also been evaluated with varying success. Recently, coatings preventing ice accretion have been the subject of more attention stimulated by the remarkable water repellent properties of superhydrophobic surfaces. If superhydrophobic coatings are also not able to fully prevent ice accretion, the development of highly efficient hybrid low power systems combining active electromechanical de-icers and passive icephobic coatings remains highly promising to reduce the ice adhesion. This development and the design optimisation of a hybrid solution require a deeper understanding of the links between superhydrophobicity and anti-icing properties.

To this end, the ICEAGE project aimed at evaluating superhydrophobic coatings regarding ice adhesion reduction and erosion resistance in combination with electromechanical de-icers. Two types of nanostructures (pillars and holes) with two lateral sizes (100 and 500 nm) have been created with selected resins, regarding their elasticity and structurability. These nanostructures have been generated by combining nanosphere lithography, etching, and replication techniques. Holey samples are expected a) to be more erosion resistant than pillared ones, and b) to prevent the formation of strongly adhering 'Wenzel ice' (ice penetrating inside the structures).

Produced samples have been tested regarding the ice adhesion, and the resistance to cracking and erosion. Based on agreed specifications, dedicated set-ups have been designed and fabricated. The samples exhibited all a good cracking resistance (no delamination) along with an exceptionally low ice adhesion (shear strength < 50 kPa), 10 times lower than the ice adhesion of reference surfaces, i.e. aluminium and commercial coatings. Moreover, this ice adhesion of the ICEAGE samples remains low over a large temperature range down to -45°C. Finally, the erosion test demonstrated that the holey samples with a large size (500 nm) exhibit the best erosion resistance of the structured samples. Nevertheless, erosion resistance may be improved by selecting a better resin. In addition to indoor tests, outdoor exposure and bombardment with a snow gun have been performed. Surprisingly, the small pillared sample (100 nm) showed a good resistance to the exposure test. In addition, all the nanostructured samples resisted very well to the snow gun test compared to the reference samples, confirming the ranking of the ice adhesion test.

The low ice adhesion nanostructured layer is foreseen to be coated on the metallic surface of an electromechanical de-icer. Based on experimental conditions proposed by the Topic Manager, vibration modes of a coated aluminium plate have been determined to shed the ice layer.

In order to prepare a more realistic ice wind tunnel test, large samples (A4 sized) have been prepared with two highly promising nanostructures: large holes and small pillars. A step-and-repeat process has been designed to form these large area samples from an elementary 7 x 7 cm^2 sized nanostructured block. After the hydrophobisation step, the produced samples exhibit a similarly high water contact angle as the equivalent small samples. These large area samples are expected to be evaluated in icing wind tunnel to confirm the excellent anti-icing performances measured in the lab.

1.2 Description of project context and objectives

Ice accretion and its adhesion to structured surfaces are detrimental to modern infrastructures including telecommunications, power lines, offshore platform, roads, wind mills and air and ground transportation vehicles. Specifically, the aviation industry has been facing difficulties related to many aspects of flying, such as loss in radar sensitivity, aerodynamic control, and high energy consumption, representing a severe risk for human safety and a significant economic impact on operational costs. When ice builds up on the wings or leading edges of airplanes it may decrease lift force and propulsion efficiency and increase weight and aerodynamic drag, as recently demonstrated by the tragic airplane crash in Buffalo (2009). Ice protection systems are therefore required.

Preventing ice build-up has long been a technological challenge. Ice, with its broad range from snow to glaze, can stick to almost any surface. There have been many attempts to reduce ice adhesion, but fundamental physics of ice adhesion is not yet well understood, requiring in depth modelling.

Many de-icing methods have been developed but none of them is fully satisfactory. In fact none fulfils two major requirements for a true solution: (a) high reduction in ice adhesion, and (b) long service-time in environmental conditions. Traditional approaches rely on mechanical breaking of ice or using chemicals to melt the accreted ice, which are temporary solutions. Moreover, mechanical de-icers may disrupt the laminar flow and consequently increase the drag. So the airliners are not keen on using them. There are some effective methods involving the melting of ice by heating (Joule effect or high frequency current), but they require very high energy. Although de-icing fluids can be applied to ice-covered structures to eliminate such ice build-ups, these substances can have significant negative environmental impacts. Electrolysis is another approach found to be effective for removing ice from certain surfaces, however it is not yet a practical method. All of these de-icing techniques are employed where there is already some ice formed. Several types of anti-icing fluids are used to prevent ice build-up on aircraft surfaces, but the durability of protection depends on precipitation conditions and the properties of fluids. Moreover, anti-icing fluids such as ethylene glycol are toxic and environmentally unfriendly.

An alternative way of preventing ice accretion would be making a durable solid coating which can reduce or even inhibit ice accumulation rather than eliminating it after accretion. Such coatings are called anti-icing materials. Recently, several coatings for icephobic application have been tested and reported. The most promising results have been observed by the application of superhydrophobic coatings, resulting from the combination of surface hydrophobic chemistry and roughening down to the micro-/nano-scale. Both reduced ice adhesion strength and delayed ice accretion on superhydrophobic surfaces have been reported, their anti-icing performance under different conditions has not yet been adequately and systematically examined. Despite the speculations about anti-icing properties of superhydrophobic surfaces, some features of this interface seem to be unanimously accepted:

- The adhesion of ice on solid surfaces is dominated by hydrogen bonding. Therefore, a fluorinated chemistry seems to be the most appropriate for hydrophobic surfaces;
- Recently, a strong and linear relationship between ice adhesion strength and the water wettability parameter $[1+\cos(\theta_{rec})]$ has been established (θ_{rec} stands for the receding angle measured at the interface of a moving water droplet on a hard surface). Further appreciable reductions in ice adhesion strength require surfaces with receding water contact angles θ_{rec} above 120°, corresponding to $[1+\cos(\theta_{rec})] \leq 0.5$. The only known methodology for increasing the receding water contact angle above 120° is to incorporate topographical surface features into/onto a hydrophobic coating, that allow surface-bound water droplets to exist in the composite Cassie-Baxter state before freezing occurs.

No coating exhibiting anti-icing and anti-erosion has been reported. There are still a number of issues that must be understood and addressed before nanotextured surfaces will find widespread use in anti-icing applications, such as systematic studies in environmental conditions:

- Droplet speed: mechanical impact may reduce the long-term anti-icing performances. One of the potential main drawbacks of the micro- and nano-structuration is the low resistance of the morphologies – and subsequently the derived superhydrophobic properties - to mechanical impacts. ;

- Droplet size: depending on humidity, droplets smaller than the surface roughness may condense and freeze within the surface structures, leading to the formation of “Wenzel ice”. If the nucleation is constrained to the top portions of the surface texture, it might be possible to facilitate the formation of weakly adhering “Cassie ice” and prevent the formation of the strongly adhering “Wenzel ice”.
- The development of upscalable and commercially viable fabrication processes.

As the materials for ice protective coatings will be used to a larger extent in the near future, the search for coatings providing icephobic properties with additional erosion resistance are particularly interesting. Based on the above-described context, the innovative approach of the ICEAGE project is articulated on three aspects:

- Design and application of unique ice adhesion measurement equipment and modelling tools for the optimisation of the ice adhesion forces reduction. Specifically designed set-ups will be used to determine the ice adhesion strengths of different surfaces. Moreover, mechanical testing equipment will be built up to evaluate the cracking and erosion resistance of the produced superhydrophobic coatings. These tests will be completed with outdoor exposure and snow gun tests. The ice shedding from coated mechanical de-icer will be modelled in order to predict a complete ice lift off;
- In most of the state-of-the-art coatings, only open structures (pillars, random roughness) have been used to induce icephobicity/superhydrophobicity. Although good results were obtained for icephobicity, a major drawback is the low mechanical resistance of these structures. A remaining challenge is thus to develop a coating being both icephobic and erosion resistant. One approach proposed in ICEAGE is the fabrication of close-cell structures (holes) having similar wetting/icephobic properties but with improved mechanical properties. The project will require low cost surface-structuring processes suitable for large area samples and having a large flexibility in terms of structure dimensions and morphologies. In this purpose, a two-step process chain will be used involving a) the fabrication of a replication master structured as a micro- and nanoscale using state-of-the-art self-assembly techniques and b) the replication of micro- and nanostructures by transfer into the coating;
- Surface fluorination of structured coatings using a MVD™ process, leading to defect-free and highly stable surface coverage, specifically suitable for structured surfaces. Some of the most striking advantages of MVD™ include the low temperature nature of the deposition process, smaller footprint, ultra-low chemical usage and perfectly controlled process at the molecular level. This makes MVD™ particularly relevant for depositing layers onto organic resins and other temperature sensitive materials.

1.3 Main S&T results

1.3.1 Specifications

The ICEAGE project aims at designing and fabricating low ice adhesion coatings to be deposited on the Al surface of an electro-mechanical de-icer in order to reduce its power consumption. The expected performances and the context of the application have led to the definition of a list of specifications, including data on the substrate (size, roughness, thickness) and the icephobic coatings (adhesion strength, mechanical/chemical/thermal resistance, compatibility with structuration processes).

These specifications are used as a frame to perform a benchmarking of relevant commercial solutions (WP1), to select the appropriate raw materials (WP3), and to design the tests (WP2).

1.3.2 Benchmarking of commercial coatings

Information on commercial coatings solutions have been collected from our knowledge accumulated within previous projects on anti-icing coatings development (e.g. EU-AEROMUCO). The survey was completed by searching on internet using relevant keywords. The identified solutions were also finally selected regarding the agreed specifications. More specifically, the applicability on outdoor exposed surfaces and/or the experience with aeronautics surfaces have been taken into account. Specific attention was paid to the potential outdoor resistance and the associated mechanical, chemical, and thermal resistance. These properties are known limitations of the superhydrophobic surface treatments. Most of the listed solutions are applicable by spray, rolling or brushing. The claimed coating adhesion is excellent on a large variety of substrates, including metals, glass, plastics/composites.

Finally, 4 commercial solutions will be tested within ICEAGE and compared to the project nanostructured coatings. One A4 sized coated Aluminium plate has been obtained from Wearlon and NuSil. In addition, one can of paint has been bought by NEI Corporation and Hydrobead.

1.3.3 Manufacture of superhydrophobic coatings

Superhydrophobic or water repellent surfaces are surfaces on which liquid water adhesion is low; defining contact angle as the angle a sessile drop forms when placed on a surface, the term superhydrophobic is usually attributed to surfaces with high contact angles (> 150°). The idea of using superhydrophobic coatings consists in taking advantage of water-repellence and low adhesion of drops in liquid state to such coatings to reduce or eliminate water accumulation on the surface before water freezes. Ice and water adhesion on a solid depends on the intermolecular forces that interact at the ice–solid and water–solid interface. No universal correlation exists between ice adhesion force and water adhesion force on a surface. Nevertheless, some material with superhydrophobic characteristics may also show weak ice-adhesion, and thus have an additional benefit for anti-icing strategies.

Superhydrophobic properties result from the combination of a hydrophobic surface chemistry and a surface roughness. Consequently, water droplets bead up with a contact angle greater than 150° and sometimes also drip off rapidly when the surface is slightly inclined (self-cleaning effect). The published results are contradictory on this point, since they depend on the obtained contact mode with the surface:

- the Wenzel state (complete wetting of the rough surface): the contact area between the water droplet and the surface is maximal. Water droplets thus stick to the surface, increasing the probability of ice nucleation: this configuration is then detrimental and has to be avoided;
- the Cassie-Baxter or ‘fakir’ state (wetting of the asperities top only) the contact area between the water droplet and the surface is minimal. Water droplets are therefore highly mobile and can be removed from the surface before freezing: this state is the best situation to reduce and to delay freezing.

The project will require low cost surface-structuring processes suitable for large area samples and having a large flexibility in terms of structure dimensions and morphologies. In this purpose, a two-step process chain has been used involving:

- The fabrication of a replication master structured as a micro- and nanoscale using state-of-the-art self-assembly techniques
- The replication of micro- and nanostructures by transfer into the coating.

1.3.3.1 Fabrication of structured masters

During the last decade, a new trend has been emerging for surface structuring using self-assembly processes. Depending on the targeted features, various building blocks can be used such as polymers, block-copolymers, nano- or microparticles. The formation of films of such building blocks on surfaces is generally carried out using wet deposition methods. The main advantages of self-assembly techniques are their tuneability and their low cost when compared to conventional photolithography, and their potential for processing large surfaces.

In the ICEAGE project, self-assembly of micro- and nanoparticles has been specifically considered. Monolayers of preformed beads and nanoparticles have then been deposited on surfaces. From commercial suspensions, monolayers of particles are obtained using wet coating techniques such as spin-, dip-, or slot-die coatings. These particle monolayers are then used as etch masks and combined with standard microfabrication processes (dry-etching, electroforming) to create micro-/nano-structured replication masters. In ICEAGE project, the proposed process chains have been used to fabricate open structures and extended to the fabrication of close-cell structures.

The first step of the process chain for the production of nanostructured coatings was the fabrication of structured masters having surface micro-nanostructures tailored for superhydrophobicity. As aforementioned, a monolayer of nanoparticles was first deposited on a substrate. Fig. 1a shows the results obtained when depositing 500 nm (sub-microstructures) and 100 nm particles (nanostructures). This allowed the variation of the lateral size and densities of the structures.

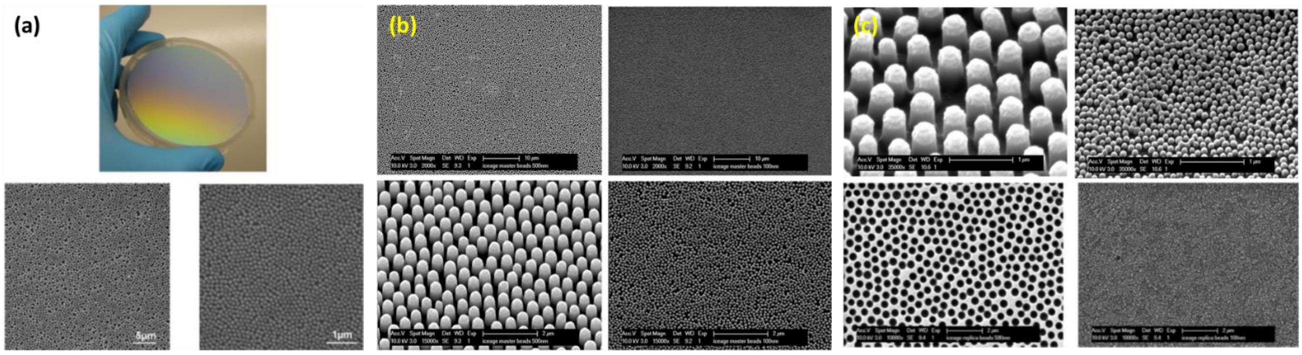

Figure 1: (a) top) photograph of a 100 mm wafer coated with a monolayer of 500 nm particles. Bottom, left) SEM image of a monolayer of 500 nm particles. Bottom, right) SEM image of a monolayer of 100 nm particles. **(b)** SEM images of the masters: (left) master with 500 nm structures. (Right) master with 100 nm structures. **(c)** SEM images of (Top) 1st and (Bottom) 2nd level replica in resin 1.

1.3.3.2 Replication of micro-nanostructures

The structured masters have been used to replicate the structures into coatings applied on standard aeronautic substrates (Al2024) and polyester substrates by means of UV-nanoimprint. Three resins have been selected as coating material to enable an effective replication of high aspect ratio features while keeping good mechanical resistance.

The most critical step was the transfer of the structures into the underlying substrate. The starting substrate was a disc of 100 mm in diameter. This was achieved using dry etching process. The etching conditions were adjusted to tailor the aspect ratio (height/width) and vertical profile of the structures. In Fig. 1b, scanning electron microscopy images of the resulting structures after transfer are presented. The aspect ratio is (2:1) for the sub-micro structure and (1:1) for nanostructures.

The two structured masters produced were then used to fabricate moulds for the replication of the features into a coating made of a UV-curable material (UV-nanoimprint). Two types of replications were made: 1st level replica involve a single replication step using the structured mould to produce pillar structures (like on the masters). 2nd level replica were made by a dual replication for the production of hole/honey comb structures. In both cases, replication was performed at the scale of the master (100 mm diameter), which allowed the fabrication of square 70 x 70 mm^2 samples.

In Fig. 1c, SEM images of the resulting 1st level replica and 2nd replica for each type of structure are presented. An accurate replication has been obtained for both micro and nanostructures in resin 1. In ICEAGE project, additional materials were investigated. Resin 1 is a hybrid, organic/inorganic material, which was selected for its good moulding performances at sub-micro and nanoscale. Another advantage of this material was its high hardness and ease of surface functionalization. Resin 2 was developed to obtain a UV-curable, urethane-based coating. The underlying reason was to get closer to the characteristics of current commercial urethane coatings standard in aircraft manufacturing. One key aspect was the erosion resistance, which is known to be better for polyurethanes. Resin 3 was formulated to obtain a hard coating using organic/inorganic, silicone based precursors. The organic/inorganic precursor ratio was adjusted to obtain a good replication accuracy. Similar structures have been obtained in Resin 2 and 3.

1.3.3.3 Hydrophobisation of structured surfaces

As surface structuring has to be combined with a suitable surface chemistry to obtain optimal results, the samples produced have been post treated by the modification of surface chemistry using the MVD™ process. Typical molecules used for the silanization are composed by fluorinated groups on the carbon chain. Properties of the MVD™ films can be tailored and were found to exhibit superior performance compared the liquid-phase deposited films. The MVD™ films are dense, smooth, and exhibit improved chemical and thermal stability as compared to standard liquid or other vapour deposited coatings.

The deposition from the gas phase allows reaching substrate cavities such as narrow channels and vials, deep holes, and otherwise masked areas which cannot be reached by more directional deposition methods. Therefore MVD™ technology is an excellent versatile tool for the hydrophobisation/fluorination of structured surfaces prepared in the ICEAGE project. The adhesion and stability properties of the hydrophobic layers are a key factor for the mechanical resistance. The surface functionalization with a dense monolayer of self-assembled fluorinated chains by MVD™ has precisely shown to be very hydrophobic and stable.

The density of the fluorinated chains prevents the nucleation of ice from a contact between a water droplet and a cold hydrophilic area on the surface, and therefore is expected to favour wetting Cassie-Baxter states. Second, the important chemical and thermal stability of the fluoro-silane self-assembled monolayer is due to the stable siloxane chemical bonds linking the chain to the hydrophilic surface.

The replica made with the three resins were functionalised using MVD™ process and characterized in terms of wettability prior to ice adhesion tests. A quantitative measurement of dynamic contact angles (advancing and receding contact angles) was performed to fully describe the wetting state of water on the surfaces.

For resin 1, all advancing contact angles were superior to 150° and superior to that obtained on the flat control. Moreover, all receding contact angles were higher than that of the flat control. The superhydrophobic surfaces obtained were self-cleaning and water drop were in a Cassie-Baxter wetting state. For resin 2, advancing contact angles were always higher on structured surfaces than on the flat control but the receding contact angles were equal or smaller. This suggested that water drops were in a Wenzel state, for which a high adhesion of water is obtained due to a very high contact angle hysteresis. A similar result was obtained for resin 3.

We observed on untreated aluminium an advancing angle and hysteresis of 94° while the mirror polished aluminium has an advancing angle of 90° with 23° hysteresis. Wenzel wetting is assumed as the roughness of the untreated sample slightly increases the contact angle. At the same time the missing receding angle indicates extremely bad dewetting properties due to the inhomogeneous topography. Polished aluminium has significantly increased dewettability compared to untreated rough aluminium and is the state-of-the-art material used in airborne applications but still at the edge to hydrophilicity. Moderate hydrophobicity was found for the commercial coatings Wearlon, Nusil, and Nanomyte which is attributed to low micro-scale roughness, higher surface energy due to missing fluorination, and macroscopic inhomogeneities. Nusil was observed to have mm-scaled dents at the surface which probably cause the large contact angle hysteresis. Hydrobead performed an advancing angle of 155° and an excellent 9° hysteresis. The outstanding hydrophobicity might be attributed to the high hierarchical nano- and micro-roughness that we observed on SEM images.

1.3.4 Characterisation of the samples and modelling

1.3.4.1 Icephobicity

In the ICEAGE project the adhesive strength of ice is measured in shear with a custom built apparatus illustrated in Fig. 2. The shear device as well as the sample preparation, influence of sample size, shear velocity, sample cylinder, and shear height was studied in detail and available in ”Macroscopic Ice Adhesion Strength and Related Physical Properties Measured in Shear Experiments” which is a supplement to the master thesis of S. Grimm who greatly contributed to the ICEAGE project. We define the adhesion strength of ice as the force causing an adhesive failure in shear divided by the sample area.

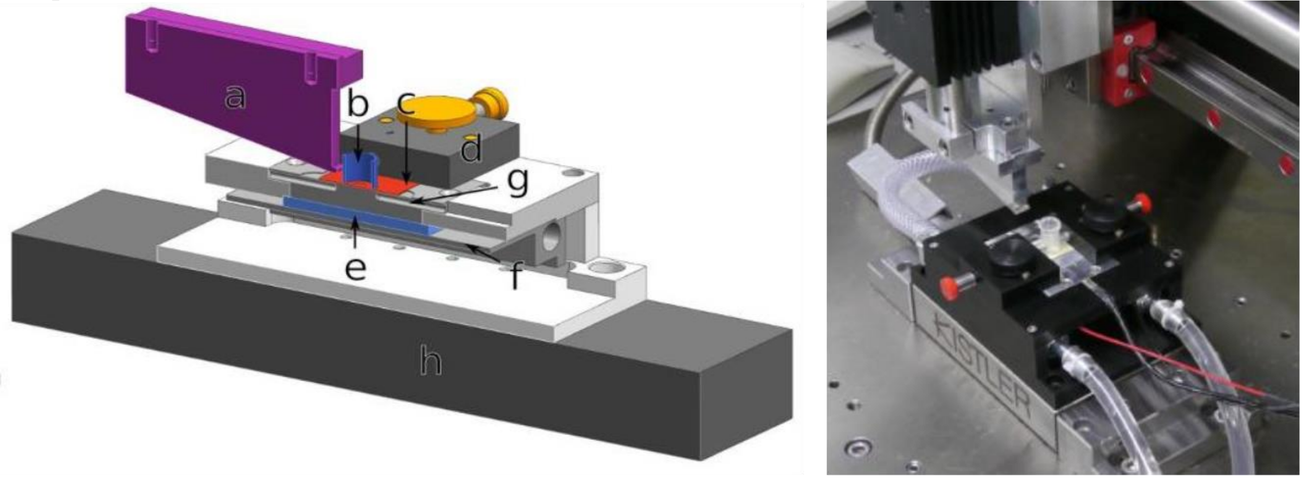

Figure 2: (Left) Lateral cut sketch of the shear apparatus. The cantilever (a) shears the sample (b) off the substrate (c), which is fixed by the mounting clamps (d). The sample temperature is controlled by a Peltier element (e) which is cooled by a liquid cooling circuit (f). An embedded temperature sensor (g) is used as feedback for the Peltier controller. The framework is made of POM and it is rigidly mounted onto a Kistler three axis dynamometer (h). **(Right)** Photograph of the shear apparatus for ice adhesion measurements.

Polycrystalline bulk ice is created on the surface of the specimen in a Teflon coated steel cylinder. Purified 0°C liquid water is injected into the steel cylinder. The temperature of the substrate is then quickly lowered to -20°C. The resulting cylindrical ice sample is then sheared at a constant velocity of 5 mm/s at a shear height of 1 mm by a displacement controlled cantilever. The substrate temperature is controlled by a Peltier element providing the temperature range of 5 to -50°C.

The results of the adhesion strength measurements of ice in shear are plotted in Fig. 3a. All samples maintained the adhesion strength after repeated icing/de-icing cycles, except Hydrobead where shearing off ice caused delamination of the coating. The shear failures occurred adhesively, unless stated differently.

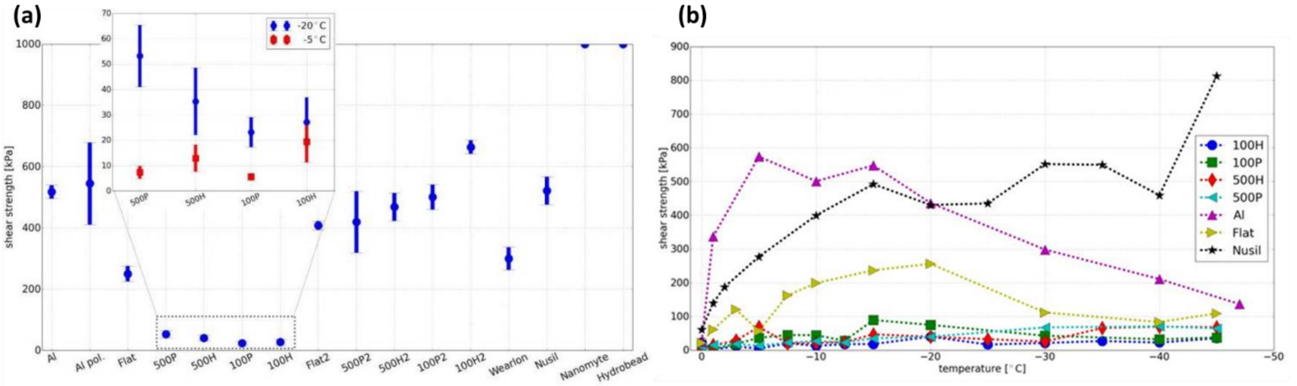

Figure 3: (a) Ice adhesion strength in shear at -20°C. The data points and error bars represent the mean value and standard deviation of at least three measurements. Measurement points at 1 MPa represent fully cohesive failures. The zoomed area of the nanostructured samples contains five measurements per point and additional measurements at -5°C surface

temperature. **(b)** Dependence of adhesion strength on temperature between 0 and -50°C. The data points represent a single measurement, except for data points at -20°C and for Al where the mean of 5 and 3 measurements, respectively, was used.

We observed the same adhesion strength of 500 kPa for both, untreated and polished aluminium. The application of the flat coating resin 1 reduces the adhesive strength by a factor of two compared to aluminium to 250 kPa. When introducing the nanostructures the adhesion strength decreases significantly by one order of magnitude relative to aluminium. The adhesion strength of the hole structures decreased to 40 kPa and 27 kPa for the 500 nm and 100 nm, respectively. These values are comparable to the 100 nm and 500 nm nanopillars with 23 kPa and 53 kPa, respectively. The overall low adhesion is attributed to the Cassie-Baxter state wetting which provides a low effective interfacial contact area. The resin 1 nanostructured samples all show excellent icephobicity which outperforms all other tested materials by at least one order of magnitude.

The defect resin 2 samples are not ice-phobic with values >400 kPa, similar to aluminium. The high nano-roughness combined with the coarse defects observed by SEM cause a rose petal or mixed mode wetting, which was also observed by the large contact angle hysteresis. The mechanical interlocking increases the adhesive resistance to shear stress.

Surprisingly, we measured high ice adhesion strength on all commercial samples. The measured values are much higher than the numbers published by the distributors: For Wearlon, we measured 300 kPa while the published value by Laforte from the Anti-icing Materials International Laboratory of the University of Quebec (AMIL) is 40 kPa. The discrepancy of the measurements might be explained by the sample preparation method. The centrifuge method was used by AMIL to determine the ice adhesion strength on Hydrobead. A value of 20 kPa was reported while we observed cohesive failure in the ice. The published ice adhesion strength for Nusil is 40 kPa in contrast to our result of 521 kPa. The official testing was done at the Cold Regions Research and Engineering Laboratory (CRREL) with a zero-degree cone test. There is no significant difference between the cone test and our shear device method nor the sample preparation. For Nanomyte, the published value is 20 kPa while we measure cohesive failures within the ice > 1 MPa. The used method based on droplets is not comparable to our shear device.

Fig. 3b shows the temperature dependency of the ice adhesion strength in the range between 0 and -45°C for all nanostructured resin 1 coatings, the untreated aluminium substrate, and Nusil. The ice adhesion strength on aluminium reaches the maximum of 550 kPa between -5°C to -20°C, decreases rapidly for warmer temperatures, and decreases linearly to 130 kPa as the substrate is cooled down to -48°C. The flat resin sample follows a similar trend with a maximum adhesion strength of 250 kPa at -20°C while decreasing to almost 0 kPa and 100 kPa for warmer and colder temperatures, respectively. The ice adhesion strength on the nanostructured samples remains extremely low through the hole temperature range and tends to raise with decreasing temperature to 35 kPa and 75 kPa for the feature sizes 100 nm and 500 nm, respectively. On the other hand, the commercial Nusil coating show a strong dependence on temperature as the adhesion strength increases continuously from <100 kPa at 0°C to over 800 kPa at -45°C.

We demonstrated the importance and influence of low energy materials, surface topography, coating elasticity, and temperature on ice adhesion. The new nanostructured resin 1 coatings are extremely icephobic in the temperature range from 0 to -45°C. Pillars and holes have equivalent properties. The aluminium substrates as well as the commercial coatings could not compete by an order of magnitude. But the comparison with literature values might not be straightforward as the test methods and sample preparation might influence the results.

We observed that the adhesive strength strongly depends on the temperature and the evolution is specific to the substrate material. An interesting result is that at low temperatures (below -30°C) the ice adhesion on the best nanostructured coatings has only a factor of two advantages to aluminium, compared to the factor of 20 between -5 and -15°C. As a result, at high altitude flying the icephobic coatings have relatively little advantage in de-icing. The resin 1 100 and 500 nm both the pillar and hole structures all demonstrated superhydrophobicity with a low contact angle hysteresis, as well as extremely low ice adhesion strength that is at least one order of magnitude lower than on aluminium. Based on the wettability and ice adhesion properties any nanostructured resin 1 coating can be recommended for upscaling to the application in an electromechanical de-icer.

1.3.4.2 Mechanical durability tests

Surfaces with exceptional icephobic characteristics usually rely on both surface morphology and surface chemistry. The long term functionality of an icephobic surface requires to maintain both features intact. Therefore such surfaces need to have long term mechanical durability and chemical stability. The delicate nanostructures have to survive the harsh in-flight conditions characterised by high velocity impacts with water droplets and dirt particles, severe temperature cycling and a high amount of UV radiation.

In the ICEAGE project, we proposed closed-cell structures for superhydrophobic coatings. These honey-comb-like nanostructures have the inverse topography of the pillars. The resin matrix is continuously connected which promises an increased mechanical durability while the holes contribute to a low effective interfacial contact area between water/ice and substrate. Each newly developed coating underwent three durability tests. These tests included erosion tests in a wind tunnel, crack resistance tests in the cold laboratory and outdoor exposure tests on a mountaintop. After all three durability tests the wettability and ice adhesion of the samples were measured in order to see if they maintained their hydro- and icephobicity. After the erosion resistance test the samples were imaged by electron microscopy in order to see if the surface structure remained intact.

The erosion resistance of the newly developed icephobic coatings was tested by imitating this harsh erosion process as close as practically possible in a laboratory. To this end a custom designed and built icing wind tunnel was installed in the walk-in cold laboratories at SLF (Fig. 4a).

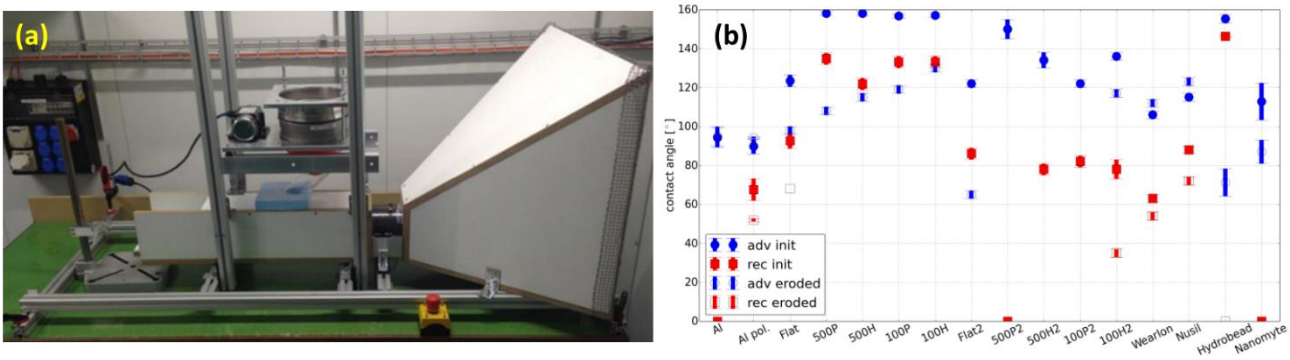

Figure 4: (a) Photograph of the custom built erosion test apparatus. A 4 kW electric wind turbine provides a maximum wind velocity of 80 m/s in a 1 m long tunnel with a 10 x 10 cm^2 cross section. **(b)** Advancing and receding contact angles before and after 1 hour of erosion test. Error bars represent standard deviations.

A 4 kW electric wind turbine generates an air stream. The maximum wind velocity at the 10 x 10 cm^2 output channel is up to 80 m/s. Fine round grained natural ice is sieved into the air stream. The ice particles with an average diameter of 0.5 mm accelerate over a 0.5 m distance and hit the 3 x 3 cm^2 sample, which is placed in front of the output channel. During a test cycle approximately 0.25 m^3 of snow is sieved into the tunnel (T = -8°C). The erosion of the samples is characterised by water contact angle and ice adhesion measurements before and after the tests.

No surface icing occurred on any of the samples during the 1 hour erosion test. The test did not cause any damage visible to the naked eye except to the Hydrobead sample, which eroded completely down to the substrate after only 10 minutes.

As expected, untreated and mirror polished aluminium came through the test with no significant change in wettability and ice adhesion. All the tested coatings were affected to a lesser or greater degree by the erosion test. Only the nanostructured resin 1 samples and NuSil showed lower ice adhesion than aluminium after the erosion test. Every other coating degraded such that the ice breakage occurred cohesively *i.e.* the ice adhesion strength was greater than the tensile strength of polycrystalline ice (2 MPa).

We observed in the SEM imaging that the resin 1 samples eroded. The original pillar structures have been cut to the basis, whereas the hole structures are still visible, providing a certain surface roughness, but the height of the structures is reduced. As intended, the hole structures are less sensitive to mechanical erosion as the equivalently dimensioned pillars evidenced by the higher hydro- as well as icephobicity. However, the erosion rate indicates that the desired long term erosion resistance is still not achieved.

Surprisingly, icephobicity on Nusil increased by a factor of two from 520 kPa to 255 kPa. The eroded surface might have obtained a micro-structure that provides good icephobicity. But the fact that the surface eroded is reason enough to assume, that long term stability is not given, either.

The electromechanical de-icer works by inducing oscillations of the air plane surface. It is important that a coating applied to the surface does not crack or delaminate as the result of these oscillations. The maximum expected bending deformation is around 1 mm. A simple method was developed and implemented in the cold laboratory at SLF to test the crack resistance of the newly developed coatings. It basically consists of a fixed and a moving part that are 10 mm apart. The 30 x 30 mm^2 sample is clamped between these two parts. The moving part oscillates with a frequency and amplitude of 10 Hz and 2 mm, respectively. All tests were performed at a constant temperature of -20ºC. A test run consisted of 20 thousands cycles of oscillation.

The crack resistance of the samples is characterised by water contact angle and ice adhesion measurements before and after the tests. In addition, SEM imaging was used to observe possible damage to the surface such as micro cracking.

The test did not cause any damage to the coatings visible to the naked eye. No delamination occurred and no scratches appeared in any of the tests. Except along the clamping perimeter where clearly visible scratches appeared on all nanostructured coatings. No change in wettability and ice adhesion was found in any of the samples as the result of the crack resistance test.

In the outdoor exposure test, samples were mounted on a long wooden board and installed on Weissfluhjoch in the Swiss Alps facing WNW at an altitude of 2660 meters. The board with the samples was installed inclined 45 degrees to the horizontal to encourage the run-off of water and snow. The samples were left on site for 2 months between 2nd March and 6th May, 2015.

The test site was visited twice during the 2 month test period. Photographs of the samples were taken on both visits. On the first visit (26th March, 2015) temperature was above freezing. The water droplets on the samples are still visible. The amount of water on the surface is a good indication of the hydrophobicity of the samples. The four nano-structured resin 1 samples and the commercial samples (Hydrobead, Nanomyte, and Wearlon) show excellent hydrophobicity, while all the resin 2, resin 3 and the 2 aluminium samples are less hydrophobic. This corresponds qualitatively to the results of the laboratory contact angle measurements. There was no damage visible to the naked eye to any of the samples at this point.

There was a heavy snowfall overnight before the second visit (April 7th, 2015). The temperature was below freezing on this day. Most of the snow was blown away from the samples by the strong westerly wind. Only the 2 uncoated aluminium samples had snow frozen to their surface.

After approximately 2 months of exposure the samples were taken down on the 6th May, 2015. Water contact angle and ice adhesion measurements were performed. Surprisingly, all but three samples were affected by the exposure test. The commercial coatings Wearlon and Nusil remained completely unaffected. They had practically the same contact angle and ice adhesion strength as before the test. Among the most promising nanostructured samples, the resin 1 series, only one remained superhydrophobic. Sample '100p_r1' had an advancing and receding contact angle of 156 and 130°

before, and 151 and 116° after the exposure test. Ice adhesion strength increased from 20 to 80 kPa as a result of the outdoor exposure.

In summary of the mechanical tests, mechanical susceptibility is the biggest drawback of the superhydrophobic and icephobic surfaces today. In the ICEAGE project, we proposed closed-cell honey-comb like nanostructures instead of the common pillar structures to increase mechanical durability. These newly developed structures exhibit the same excellent superhydrophobicity and icephobicity as their pillar counterparts. They have also proven to be mechanically more durable. Unfortunately, this increased durability has still to be improved for aeronautical applications. Then, the 500 nm holey structure was selected for scaled-up demonstrator.

All samples have survived the crack resistance tests intact with no delamination and/or cracking.

The outdoor exposure test showed similar results. Only one of the nanostructures samples (100p_r1) remained superhydrophobic and icephobic as the result of the thermal cycling, rain, snow and wind experienced during the exposure test. This nanostructure has been selected for scaled-up demonstrator.

1.3.4.3 Computer modelling

In-flight ice accretion occurs by the freezing of supercooled water droplets to the fuselage and the appendages of the aircraft. It is inherently a multiphysics and multiscale problem. Although multiscale simulations that try to use the results of nanoscale molecular dynamics simulations as an input for macro-scale continuum computational fluid dynamics simulations exist, they lack predictive capability in terms of icephobicity.

The original idea in the ICEAGE project was to use discrete element simulations to evaluate the surface morphology of nanostructured coatings in terms of ice adhesion by simulating an ice particle impacting the surface. In this model, the coating consists of dozens of thousands of little spheres in the exact topography of the modelled manufactured surface. The adhesion energy between substrate material and ice is an input parameter obtained from real ice adhesion experiments. Some of these simulations were set-up and ran, but they did not provide useful results.

A more practical and useful simulation tool would be the direct modelling of the macroscopic scale electromechanical de-icer. To this end, we developed a downscaled discrete element model simulation of Topic Manager de-icer demonstrator that is capable of predicting whether accreted ice is shed or remains bonded to the surface for a given set of experimental parameters (amplitude and frequency of vibration) and ice adhesion strength. The limitation of these downscaled discrete element simulations is that they are not capable of reproducing the dynamical response of the real de-icer that turned out to be extremely important in the shedding process. Therefore, a direct comparison between experiments and these simulations is not possible.

In order to overcome this limitation, a finite element model of the full size de-icer was developed. This model is the direct digital replica of the real world de-icer demonstrator geometrically, as well as mechanically. The study of the dynamical response of this model revealed several important points in the design and optimal operation of the electromechanical de-icer.

The finite element model was based on the demonstrator of electromechanical de-icer. A 1 mm thick aluminium plate with and area of 30 x 20 cm^2 forms the basis of the de-icer. The ice layer is in contact with the aluminium plate and has the same area with an arbitrary thickness. The edge of the aluminium plate is constrained and has zero displacement. A harmonic oscillation as a prescribed displacement is applied on a circular spot in the centre of the plate corresponding to the electromechanical actuator.

First, a modal analysis of the de-icer with three different ice thicknesses was performed. The presence of ice then considerably changes the stiffness and dynamical properties of the de-icer. For a given frequency an entirely different mode of oscillation is activated when ice is present. The activated mode also depends on the amount of ice on the surface. Therefore, the optimal shedding frequency also changes with the amount of ice. This indicates that in practise a frequency sweep to cover a considerable frequency range is required unless the amount of ice on the surface in known. This model enabled us to study the modal shapes, modal frequencies, effect of ice thickness on the stiffness and dynamic response of the electromechanical de-icer. The results all indicate the sensitivity of the system to the applied frequency and amount of ice accreted on the surface. The displacement of the de-icer, and thus its effectivity in the shedding of ice, varies by a factor of 5 depending on the frequency applied and the thickness of the ice layer.

As a next step, cohesive zone modelling was used to include the adhesion between aluminium and ice in the finite element simulations. With this model the aluminium-ice interface breaks when either the tensile or shear strength of the contact elements is exceeded. Similar to the discrete element case the microscopic contact parameters must be fitted to the macroscopic adhesive strength. This model can predict whether the ice remains attached to the surface or is shed for a given set of design parameters. These design parameters include the geometry of the de-icer, the location of the actuator, the amplitude and frequency of the applied oscillation, the thickness of the accreted ice and the tensile and shear strength of the surface-ice interface. While not perfect this simulation tool is already useful in the optimization of a real world de-icer.

The main drawback of the cohesive zone finite element simulations is the absence of material failure in the model. Both the aluminium plate and the ice sheets are and remain sheets of elastic continuums that either separate or remain bonded in the course of a simulation. Tests performed by Topic Manager with the de-icer showed that the ice always breaks up into small fractions during shedding. Including material failure in the simulations would be a natural extension of the work presented here.

1.3.5 Demonstrator manufacturing

The developed replication process has been scaled up to enable the structuring of much larger samples. Three structuration approaches have been identified. In agreement with the Topic Manager, the preferred approach consisted in producing a standard sized master, and then in preparing a large mould from the master using a step and repeat procedure. Then, the final coating is structured in one step with the large mould.

Based on previous results and in agreement with the Topic Manager, the demonstrator was designed as follows:

- Base substrate: PET foil (thickness of 125 microns)
- Replication: application of a UV-curable coating and UV-nanoimprint replication
- Sample size: 14 x 28 cm^2
- Two types of structures: 100 nm pillars and 500 nm holes
- 2 samples to produce for each structure
- Resin 1 selected
- Surface modification using MVD™ process

The upscale of the replication process is based on a step and repeat process. The standard process uses a master and mould having a size of 70 x 70 mm^2. Each replication step required to bring into contact the mould and the UV-curable coating and cure the coating with UV. A total of eight replications per sample were carried out to reach the targeted sample-size.

A total of four samples was produced, two samples having 500 nm large hole structures (referred as sub-microstructures), the two others 100 nm large pillar structures (referred as nanostructures). In Fig. 5, photographs of the produced samples are shown.

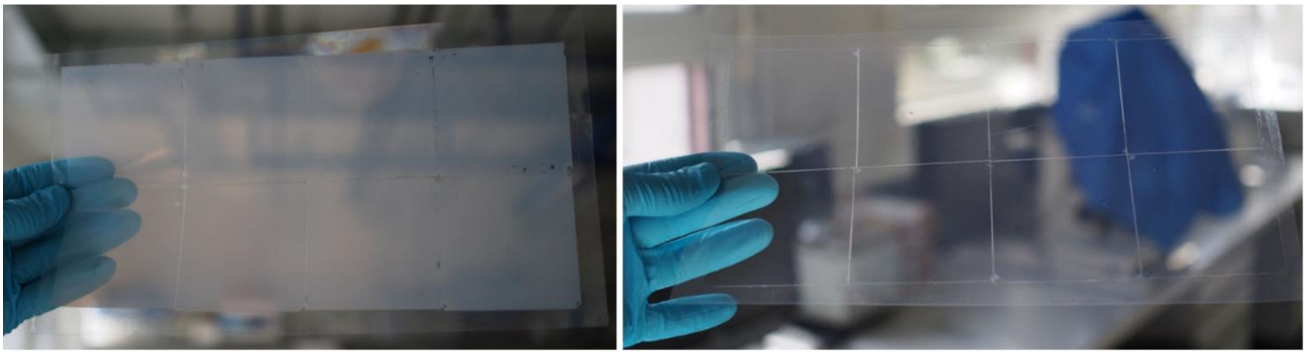

Figure 5: Photograph of the 14 x 28 cm^2 sample with (left) 500 nm and (right) 100 nm structures.

The imprinted area was 140 x 280 mm^2 and the interstitial spaces between each replica smaller than 1 mm. The main source of defects in the process was the quality of the starting masters and moulds, which have been used throughout the all project and the presence of bubbles which was strongly minimized but difficult to totally remove. For all samples, a plasma surface activation combined with the deposition of a primer layer was compulsory to obtain a good adhesion of resin 1 on the PET substrates. In a same manner, series of plasma surface activations (different times and powers) were carried out combined with MVD™ deposition to obtain a similar wettability as for the small samples sent to SLF for ice adhesion measurements.

Dynamic contact angles measured on the up-scaled samples show similar advancing contact angles as observed for small samples, and only a low difference for the receding contact angle. A qualitative test was also done to characterize the self-cleanliness of the samples: water drops were deposited at different locations of the hydrophobic samples and the complete sample was tilted to make the water drops roll off the surface (see timelapse image, Fig. 6). The scaled-up samples will be evaluated in icing wind tunnel in collaboration with the Topic Manager. The ICEAGE project objectives have then be fully achieved.

Figure 6: Timelapse photograph illustrating the self-cleanliness of the upscaled sample with sub-micron holes.

1.4 Potential impact, dissemination activities and exploitation plan

CleanSky objectives, in line with the Vision 2020 goals (ACARE) are:

- 20-40% cut in CO_2 emissions per pass-Km by drastic fuel consumption reduction
- To reduce NO_x emissions by 40% in landing and take-off

ICEAGE will contribute to the Vision 2020 goals in the following way:

- Development of a new concept of coatings able to maintain laminar flow and thus reducing drag, allowing to pursue the target to reduce fuel consumption and hence CO_2 emissions.
- Electromechanical de-icers are more or less effective but they may change the aerodynamic flow of the aircraft. Consequently, to increase their efficiency integrating icephobic coatings will help maintain the laminar flow and consequently pollute less by reducing the fuel consumption.
- The implementation of icephobic coatings on the aircraft structures will ease maintenance activities and hence reduce operational costs.
- Last but not least, ICEAGE coatings have potential applications in fields that go beyond aeronautics. For example, icephobic coatings could be installed on windmill blades and on photovoltaic installations.

The major impact of ICEAGE will be to maintain laminar flow during flight, something key to reduce fuel consumption and consequently reducing CO_2 emissions by 7 to 10%. This correlates to 50 to 70 billion tons of CO_2 reduction based on the annual CO_2 emission of 680 billion tons caused by aircrafts.

Ice accretion is not only a problem for the aeronautics and aerospace industries, but also for the automation, signalling devices, railway systems, buildings, bridges, antennas, windmills blades, freezing systems, and many others. Advanced icephobic solutions developed for aircraft could help develop solutions in many other markets and therefore strongly increase the customer value.

The competitiveness of the European industry on the global market will be increased creating additional benefit for the European citizens and society.

Impact with respect to science and technology

ICEAGE has pursued novel paths to address a key issue of sustained laminar flow aircraft, i.e. the production of erosion stable icephobic surfaces. This project has generated new scientific knowledge, as well as new technologies and thus strengthens the European position on this field.

Steps needed to bring about these impacts

For many years, CSEM has invested in the development of high performance coatings. It has a long track record in the functionalization of smart surfaces.

SLF is an institute active in the domains of snow and ice.

Both partners are complementary and have successfully contributed to the fulfilment of the impacts mentioned before. The support of the Topic Manager was essential to achieve the ICEAGE goals.

The ICEAGE consortium would like the icephobic coatings developed in ICEAGE project to be tested either in the CleanSky ITD Technology Evaluator or in an icing wind tunnel in order to have a better understanding of the behaviour and performance of these coatings in a real environment. The results of such tests will help to develop more performant coatings on other aeronautical structures materials, as well as to improve the coating and ice adhesion forces simulations. For this second option (ice wind tunnel testing), the consortium will negotiate with the Topic Manager the possibility to evaluate the produced icephobic demonstrators in an icing wind tunnel according to the Topic Manager conditions on a model equipped with an electromechanical de-icer.

The ICEAGE consortium expects to raise enough interest in such an important topic in order to continue the research and transfer to industry on this technology after the completion of the project. Discussions have been initiated with resins suppliers (to identify resins combining erosion resistance and structurability) and process partners able to scale up the structuration methods.

Assumptions and external factors to determine the achievements of the impacts

The SGO topic manager has provided us with:

- detailed specifications of the icephobic coating and integration requirements
- further information to define the demonstrator
- regulation and standard documents important for this project

Based on the partners collective technological excellence and experience, proven technology transfer capabilities and experience in the development of Aeronautics solutions, ICEAGE will make a significant contribution to the accessibility for European industry to technology in icephobic coatings that are at least matching the best technologies available elsewhere, thereby enabling European industry either exploiting or using the technology to compete in the world market.

Dissemination of the project results is performed by publication of results to scientific journals and conferences (SLF and CSEM) and by communication of descriptions and/or demonstration of the most promising icephobic coatings to relevant institutions internal to the CleanSky umbrella in order to raise interest towards the exploitation exercise (CSEM).

Therefore, dissemination activities, which are also described under WP4, contain the following main actions:

- SLF and CSEM will publish non-confidential results of the project in scientific journals and conferences.
- CSEM will issue a press release of the project, drafted by the professional PR office of CSEM with the support of the ICEAGE technical team.
- SLF will disseminate among the ice and snow researchers, when relevant, their characterisation methods that could be successfully linked to other markets apart from Aeronautics.
- The partners will participate in national and international conferences and/or exhibitions to present the project (presentation and/or poster).
- Dissemination of the project results will be also performed by communication of descriptions and/or demonstration of the most promising icephobic coatings to relevant institutions internal to the CleanSky umbrella in order to raise interest towards the exploitation exercise.

Planned dissemination activities have been summarised in the table below:

Year	Disseminating partner	Category	Type	Event & Date	Title	Contact point	Dissemination events	Comments
2015	University of Basel	High Education	Master thesis	Publication date to be confirmed	Optimization of nano-structured ice-phobic coatings for aeronautical applications	Martin Schneebeli		
2015	CSEM	Research Centre	Conference	Polymer Replication on Nanoscale 2015	Fabrication of Functional Nanostructured Polymer and Hybrid Components	Emmanuel Scolan	Conference	Done
2015	CSEM	Research Centre	Conference	Swiss Nanoconvention 2015	Fabrication of submicro-/nano-structured surfaces with enhanced performances	Emmanuel Scolan	Conference	Done
2015	CSEM, SLF	Research Centre	Conference	Aerodays 2015	Anti-icing coatings designed to decrease ice adhesion on aeronautics structures	Emmanuel Scolan	Conference	Done
2015	CSEM	Research Centre	Article	By the end of 2015	Ice Phobic Coating to develop Low Power Electromechanical De-icers	Emmanuel Scolan	CSEM scientific reports	Done
2016	CSEM, SLF	Research Centre	Article	Proceedings Aerodays 2015	Anti-icing coatings designed to decrease ice adhesion on aeronautics structures	Emmanuel Scolan	Conference	Done
2016	SLF, CSEM	High Education	Article	Publication date to be confirmed	Optimization of nano-structured ice-phobic coatings for aeronautical applications	Emmanuel Scolan		

1.5 Contact details

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