A livery coating with anti-ice properties for aeronautical components

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Abstract

The aim of this work was to design and characterize multifunctional aeronautical coatings with aesthetical and icephobic properties, as well as high mechanical properties.
Chemical and physical properties of the new surface coating were determined in order to study the behavior of the surface with supercooled water droplets. This was possible through innovative equipment which replicates the flight conditions of pressure and temperature. In particular two performance indexes are taken into account: wettability and surface free energy.
Further tests such as mechanical and corrosive were performed in order to evaluate the performances and durability of the new icephobic coating. It was demonstrated that the new coating has the same or higher performance indexes than the commercial one.

1. Introduction

The icing mitigation systems can be divided in anti-icing systems and de-icing systems. Within the anti-ice systems, the application of icephobic coatings is one of the possible methods for preventing the icing of aeronautical components (leading edges, wings, radomes and so on) [1].
Ice changes the smooth airflow, increasing drag while decreasing the ability of the airfoil to create lift. Ice accumulates on every exposed frontal surface of the airplane not just on the wings, propeller, and windshield, but also on the antennas, vents, intakes, and cowlings [2].
The main function of ice-phobic coatings is to reduce the adhesive forces between the supercooled water or ice and the surface of the component. In particular it is necessary to extent and to retain this ability during long-term operation [3].
The main theoretical prerequisites for the design of icephobic surfaces are usually considered in the context of surface phenomena that occur at the liquid–solid interface, because ice deposits on the surfaces of the components [4].
When water is deposited on the surface in the solid–liquid–gas ternary system, the adhesion between the liquid or solid (upon transformation of water from the liquid state into the solid state) is provided as a result of different intermolecular (van der Waals or chemical) interaction forces [5].
According to the thermodynamic concept of adhesion, the adhesive bonding between the ice and the surface is predominantly governed by the ratio between the surface tensions of the phases (water and substrate material) and wetting [6]. In this case, it is assumed that solidification of water does not lead to a considerable change in the adhesion [7].
Contact angle measurement techniques represent a useful method to characterize the icephobic properties of the surfaces. In fact it is possible to predict the behavior of the water droplets on surface in static state [8]. The term static state is referred to the absence of airflow on the system water droplet-surface [9]. In any case contact angle measurements, using sessile drop method, can be realized in equilibrium state, measuring advancing and receding contact angles and/or evaluating the bounce of the water droplet on the surface.
In any cases at present, in literature [10], these tests are carried out reducing the temperature and keeping the atmospheric pressure. This is true in case of components that work on ground where the temperatures are very low (north and south pole, Nordic countries, etc…) however for aeronautical and aerospace components this type of approach cannot be applicable. In fact these components work at different altitudes and consequently at different static pressure. In addition if we consider the components of an aircraft such as a leading edges, they are under the airflow therefore other than static pressure there will be a dynamic pressure and other important aerodynamic phenomena (i.e. the boundary layer around the wing) [11-13].

It is evident that the modelling of the interaction between the water droplet and surface it is not simple and consequently it is necessary to simplify the problem and study the interaction phenomena step by step.
Therefore it will be necessary to simulate in the same thermodynamic conditions of those present in flight the interaction between supercooled water droplets and surface.
First of all, contact angle measurement technique that takes into account the effect of pressure and temperature in flight is necessary to develop. It will be necessary for designing and developing of the new surfaces with superhydrophobic and ice-phobic properties.
It is clear that other than contact angle measurements, further characterization techniques must be performed in order to evaluate important properties of the icephobic surfaces such as the thermo-mechanical properties. The aim is to estimate the durability and the degradation of the surface during the time as well as due to the impact to dusts, insects, powder and other impurities present in the airflow. In general this type of activity ends performing tests of the new coatings in relevant environment such as Icing Wind Tunnel. Closing this chain, it could be possible to have designed an effective and durable ice-phobic surface.

2. Materials and methods

2.1. Materials

A pure thermoplastic polymer such as Polypropylene acquired by the Goodfellow was used to calibrate the new test room for contact angle measurements.
The new anti-ice coating was obtained starting from the commercial coating used as livery, i.e. a matt grey livery coating.
This is composed of epoxy-modified polyamide primer using VOC exempt solvents (solvent based High Solid coating) which has a function to improve the adhesion of the topcoat, to inhibit the corrosion and to level the surface.
Above the primer, a water-based 3-component, isocyanate cured polyurethane topcoat (in accordance to REACH regulation).
Author modify the formulation of the topcoat in order to give further functionality such as icephobicity without alter the aesthetical properties and the other mechanical and corrosive properties.
At this time the new formulation is under patent protection, therefore no further information can be published.
Both coatings were deposited through spray process on substrate of CFRP (Carbon Fiber Reinforced Polymer). The temperature of the substrate was of 20°C during the spray process. The dimension of the spray nozzle was 1,1 mm, the temperature of air carrier of 20 °C and the air-pressure of 2 bar.
The drying of the coatings was realized using a drying chamber at temperature of 120°C.

2.2. New tool to characterize icephobic surfaces

In order to replicate the same thermodynamic conditions of flight, it is necessary to change both temperature and pressure.
As it is known [14], thermodynamically the surface free energy may be defined as the increase in Gibbs free energy of the whole system per unit increase in interfacial area, carried out under conditions of constant temperature and pressure, that is:

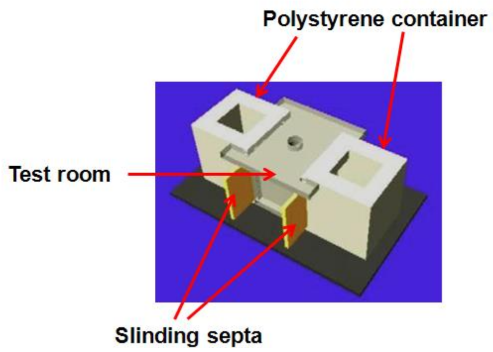
$$\gamma = \left(\frac{\Delta G}{\Delta A}\right)_{T,p} \tag{1}$$

Therefore as described previously, reducing only the temperature, it is not replicated the real thermodynamic condition in flight of the chemical state of the surfaces. The contact angle changes if we consider these three following conditions:

- ambient pressure and temperature;
- temperature in flight and ambient pressure;
- temperature and pressure in flight.

In order to replicate the flight conditions, a test room, to mount on a classical contact angle measurement instrument, was design and developed at CIRA [15]. In particular top, bottom and two lateral and parallel surfaces were realized in insulator material such as Polycarbonate of thickness of 2 mm whereas the other two lateral and parallel surfaces were realized in aluminum Al2024-T6 of thickness of 1 mm.
It was choosen the Polycarbonate because, other than thermal insulating, it is also transparent. This property is needed to capture the liquid drops applied on the surface with camera of contact angle instrument.
The two lateral and parallel surfaces in Aluminum were used for the heat exchange.

The top surface of the test room has a hole with an elastic membrane in order to allow the insertion of the syringe needle to deposit the liquid drop. The syringe employed was Hamilton 600 series – 5 µl.
In order to reduce the temperature, dry ice pellets of 3 mm of diameter were used. As it is known, the dry ice (or carbon dioxide) reach a temperature of -79°C and it could be used to reduce the temperature in the test room. For this reason two Polystyrene containers were realized with a sliding septa and applied on the two sides in contact with the Aluminum faces of the test room. The rendering of test room is reported in figure 1.



(b)

Figure 1 – rendering of the test room complete

Changing the position of septum, different heat exchange surfaces are achieved. In fact opening the septum, an improvement of contact area between dry ice pellets and Aluminum face was reached (Table 1) and consequently the temperature within the chamber decrease. Using this method it is possible to reach temperature of -50°C in the test room. The temperature within the test room was detected using a thermocouple K-type.

Table 1 – correlation between the position of the septum with the heat exchange surface

Septum opening	Heat exchange surface
0 cm: closed septum	0 cm^2
0,5 cm	2,16 cm^2
1,5 cm	5,76 cm^2
2,5 cm	9,36 cm^2
3,5 cm: opened septum	12,96 cm^2

Supercooled water droplets were realized using a microliter syringe of Hamilton. Once reached the temperature and pressure in the test room, a small quantity of bi-distilled water was suck up within the capillary of the needle. After, the needle was inserted through the elastic membrane of the test room and leaved within the room for 30 seconds in order to reduce the temperature of the water from ambient temperature to near zero Celsius degree. After this time, the water droplet is deposited very slowly on the surface of the sample presents on the bottom of the test room. During the deposition the water droplet has a further drastically reduction of temperature before to reach the surface of the sample, becoming supercooled. The supercooled property of the water droplet was simulated with a model of the heat exchange surface and phase shift of the water considering the main characteristics of the water droplet.
In order to have also the same pressure of flight altitude, a circuit with a Venturi tube model (ZH-05-DS-06-06-06) was realized. The pneumatic circuit is composed by a main line flow starting from compressor to Venturi tube and a slipstream flow which connect the test room and the throat of Venturi tube as showed in the scheme reported in Figure 2:

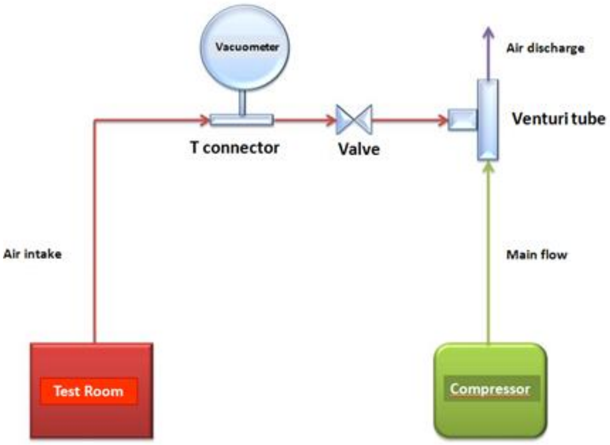
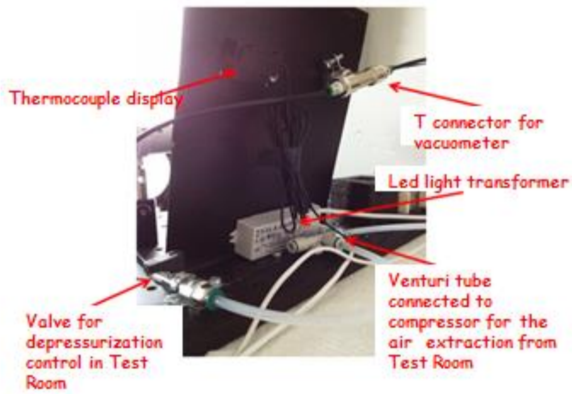


Figure 2 – scheme of pneumatic circuit

Using this method is possible to reach pressure of 0,1 bar in the test room.
Along with this new test room, the contact angle measurement instrument was equipped with a thermocouple display and with a pressure gauge.
Therefore the contact angle instrument with the new test room is completed and it is reported in Figure 3:

(a)



(b)

Figure 3 – (a) frontal image of contact angle measurement instrument. (b) behind image of contact angle measurement instrument

With this new tool it is possible to replicate the pressure and temperature until a flight altitude of about 16.000 meters.
It is necessary to highlight that the highest probability to have icing phenomena according to the standard certification tests realized in the icing wind tunnels is 5.000 meters. At this altitude the temperature is about -12/-15 °C and pressure of about 0,5 bar; therefore using this instrument, it is possible to cover the most risky altitude.
Other than bi-distilled water, diiodomethane and formamide were also used to determine surface free energy and its components of the sample other than work of adhesion and other performance indexes. Ten drops (with volume smaller than 3 µl) of each liquid were deposited on the sample surface.
The surface free energy was calculated according to the Owens-Wendt method [16]. The Owens-Wendt approach is one of the most commonly used methods for calculating the surface free energy of the materials [17]. The principal assumption of the OW method is that the surface free energy is the sum of the two components: dispersion and polar components [18].
The Owens-Wendt model is represented by the geometric mean relationship:

$$\frac{1}{2}\,(1+cos\theta)\gamma_L = (\,\gamma_S^D \cdot\, \gamma_l^D)^{\frac{1}{2}} +\, (\gamma_S^P \cdot \gamma_l^P)^{\frac{1}{2}} \qquad (2)$$

where:

θ = contact angle between the liquid droplet and surface
γ_L = liquid total surface tension
γ_l^D = dispersion component of liquid surface tension
γ_l^P = polar component of liquid surface tension

The unknown terms in the equation (2) are:

γ_S^D= dispersion component of the solid surface free energy
γ_S^P= polar component of the solid surface free energy

The value of total surface free energy of the solid is obtained using the following equation:

$$\gamma_S = \gamma_S^D + \gamma_S^P \tag{3}$$

To solve equation 2, dividing by $\left(\gamma_l^P\right)^{\frac{1}{2}}$, it can be rewritten as:

$$\frac{\frac{1}{2}(1+cos\theta)\gamma_L}{(\gamma_l^P)^{\frac{1}{2}}} = \left(\frac{\gamma_l^D}{\gamma_l^P}\right)^{\frac{1}{2}} \cdot (\gamma_S^D)^{\frac{1}{2}} + (\gamma_S^P)^{\frac{1}{2}} \tag{4}$$

The left-hand side of equation (4) contains quantities which are measured experimentally (θ) or which are available in the literature (γ_l^P, γ_l), so that a plot of the left-hand side of equation (4) versus quantity $\left(\frac{\gamma_l^D}{\gamma_l^P}\right)^{\frac{1}{2}}$ gives a straight line with slope $\left(\gamma_S^D\right)^{\frac{1}{2}}$ and intercept $\left(\gamma_S^P\right)^{\frac{1}{2}}$.
The surface tension of liquids and their components are taken from literature [19]. However these values are referred to standard conditions of ambient temperature and pressure at sea level.
Using the Karbanda's equation, it is possible to rescale the values of surface tension from temperature point of view:

$$\gamma_{T_2} = \gamma_{T_1}\left(\frac{T_c - T_2}{T_c - T_1}\right)^{1,12} \tag{5}$$

where γ_{T_1} represents the surface tension of liquid at 20°C while T_c represents the critical temperature of the liquid. The critical temperature of the three liquids are reported in the table below:

Table 2: Values of the critical temperature of the three liquids employed.

Critical Temperature [°C]		
Water	**Formamide**	**Diiodomethane**
373,94	376,45	474,42

Once rescaled the values from temperature point of view it is necessary to rescale these new value for the new pressure, using the Laplace equation:

$$\gamma_{p_2} = \gamma_{p_1}\left(1 - \frac{K \cdot p_2}{200}\right) \tag{6}$$

where K is a constant value which is function of employed liquids. For the liquids employed in these experiments K=2.

The calculation of all performance indexes of the instrument were determined using a software, designed and developed at CIRA. This software has all main models present in literature other than Owens-Wendt.
It is evident that, in the real condition, the behaviors and dynamics of the interaction between the supercooled liquid dropled and surface are more complex because the supercooled water droplets impact with the speed of the aircraft on components. The dynamics of interaction, happening in a few milliseconds, are in a non-equilibrium condition and there are several phenomena that can occurs (infiltration due to the water hammer pressure, instantaneous freezing or rapid rolling of the droplet, etc….).
In any case the characterization technique developed in this work allows to study the ice-phobic surface in static conditions. This represents a worst condition in fact the supercooled water droplet has a long time to reach into equilibrium state and to freeze on the surface.

2.3. Mechanical characterization

In order to determine the mechanical properties such as hardness and elastic modulus, a nanoidenter NHT, CSM Instrumenets, Peseux, CH was used according to the stanrdard test ISO 14577. The tip employed was a Berkovich. It was preliminary calibrated on silicon.
All tests were performed in load control, with maximum load of 3 mN which is equivalent to the 800 nm of penetration depth. The load speed was 4,50 mN/min and holding time at maximum load of 30 s. On each sample were performed 40 indentations.

2.4. Resistance to aircraft hydraulic fluids

The resistance of hydraulic fluids was performed using Skydrol LD-4 for 30 days at 25°C according to the standard tests (i.e. MIL-PRF-83282, STANAG 4360). Skydrol is the most advanced aviation hydraulic fluid supported by recognized experts in phosphate-ester fluid technology.
The aim of this standard test is to evaluate if at the end of the experiment are occurred delamination, blistering or lack of adhesion.

3. Results

Tests were performed on standard material such as Polypropylene; it is known that its wettability is about 90°-110° and surface free energy is about 30-35 mJ/m^2 in standard condition (temperature of 20°C and pressure of 1 bar). These two values were taken as reference data to compare with those obtained in "flight" conditions.
Tests on Polypropylene with new test room were realized simulating most the highest risk of icing that occurs at 5.000 meters. At this altitude the temperature reaches to -15 °C and pressure arrives until to 0,5 bar.
Results regarding the wettability are reported in Figures 4 and 5.

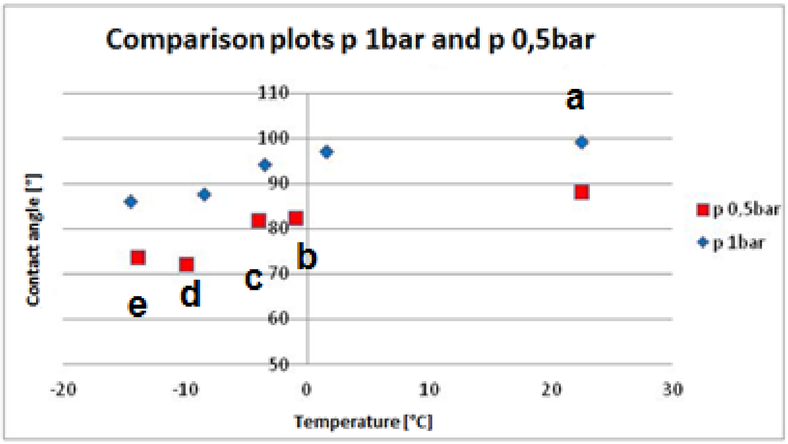


Figure 4 – trend of wettability at 5 different temperature and two values of pressure

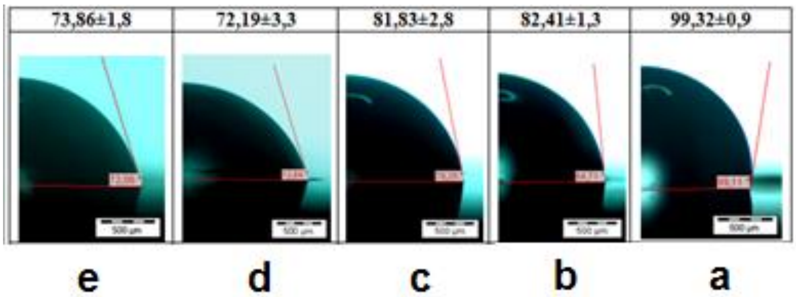


Figure 5 – variation of the behavior of the water droplet on a surface changing pressure and temperature

The blue dots in Figure 4 represent the value at ambient pressure (1 bar); it is evident that the contact angle decreases, reducing the temperature. This means that the surface becomes more hydrophilic respect to the ambient temperature.
The red dots represents the value at pressure of 0,5 bar, reducing the temperature until to -15°C. It is evident that the trend is the same of the experimental data at ambient pressure (blue dots) however they are shift downward. This has a consequence that hydrophilicity is improved.
In Figure 5, the shapes of the drops and the contact angle values of the experimental points from standard condition of pressure and temperature (point A) to the flight conditions at temperature of -15°C and pressure of 0,5 bar (point E) are reported.
Comparing the extreme points A and E the surface has showed an improvement of wettability of 35%.
Analyzing these results, it is highlighted that is important to take into account the thermodynamic properties of the environment in which the surface will work. In fact the risk could be to realize a surface that could seem hydrophobic or super-hydrophobic but in the real condition of utilization, is partially hydrophilic.
A further confirmation of these statements is described in the Figure 6 where the trend of surface free energy is showed.

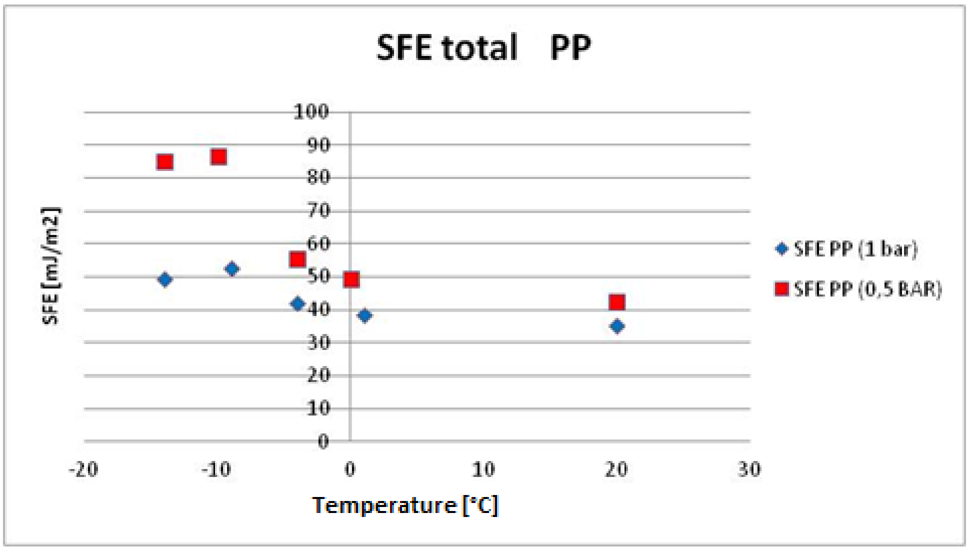


Figure 6 – trend of the Surface Free Energy changing temperature and pressure

The trend is in the opposite respect to those of wettability; in fact, reducing the temperature, the surface free energy increases and reducing the pressure, the trend is the same but shifted upward. This means that respect to the standard conditions in the flight conditions the surface has a highest surface free energy. This means that the surface has potentially more energy to create adhesion respect to the standard conditions. Comparing the extreme points A and E the surface has showed an improvement of surface free energy of 59% (from 34,96 to 84,97 mJ/m^2).
This statement is corroborated, analyzing the graph of work of adhesion between water and surface (Figure 7).

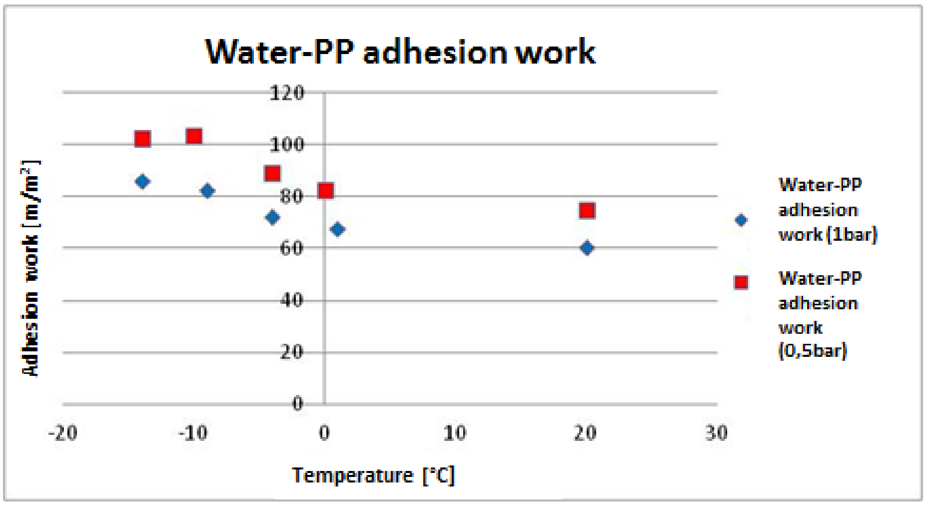


Figure 7 – work of adhesion between water and Polypropylene surface

In fact the work of adhesion between water and the surface of Polypropylene increases, reducing the temperature and pressure. Comparing the extreme points A and E the surface has showed an improvement of surface free energy of 42% (from 60,33 to 102,64 mJ/m^2).
From physical point of view this means that an improvement of the chemical bonds between water and surface is obtained.
Tests with the new tool were performed both on a classical livery coating and on the new icephobic formulation. In particular ten droplets of each liquid: bidistilled water, diiodomethane and formamide were deposited on the surfaces in order to determine surface free energy and its components (polar and dispersion components).
Tests were performed in standard conditions (ambient temperature and pressure at sea level) and in simulated flight conditions (temperature of -12°C and pressure of 0,5 bar).
As showed in Fig. 8, a drastic reduction of these performance indexes is evident; in fact the surface free energy decrease of the 85%, whereas the dispersion component of the 77% and polar component of 99%. Note that the polar component mainly influences the adhesion between water droplet and the surface, therefore the drastic reduction of this component allows to estimate the reduction of the adhesion of water.

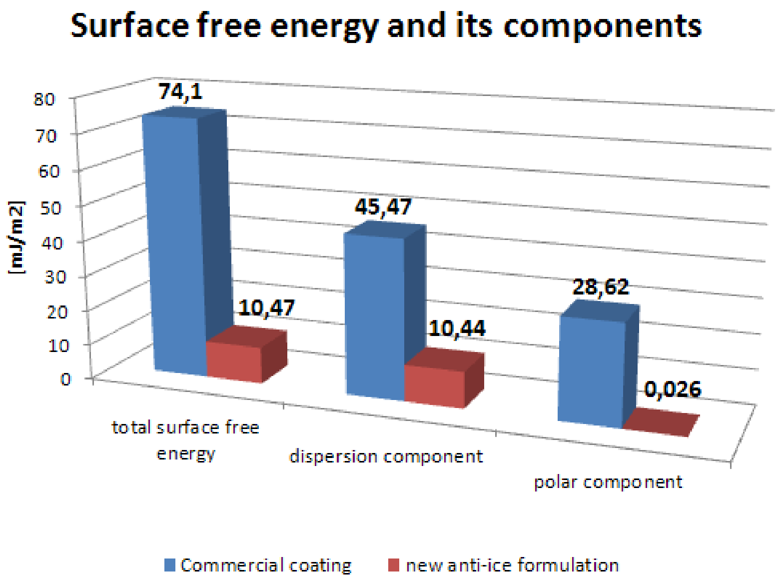


Figure 8 – Comparison of the experimental data of the surface free energy and its components both for classical formulation and for the new anti-ice formulation.

This last statement is also confirmed by the experimental values of work of adhesion. In fact author calculated the work of adhesion of the classical commercial coating and the new icephobic formulation. It is evident from Fig. 9 the reduction of the 92%.

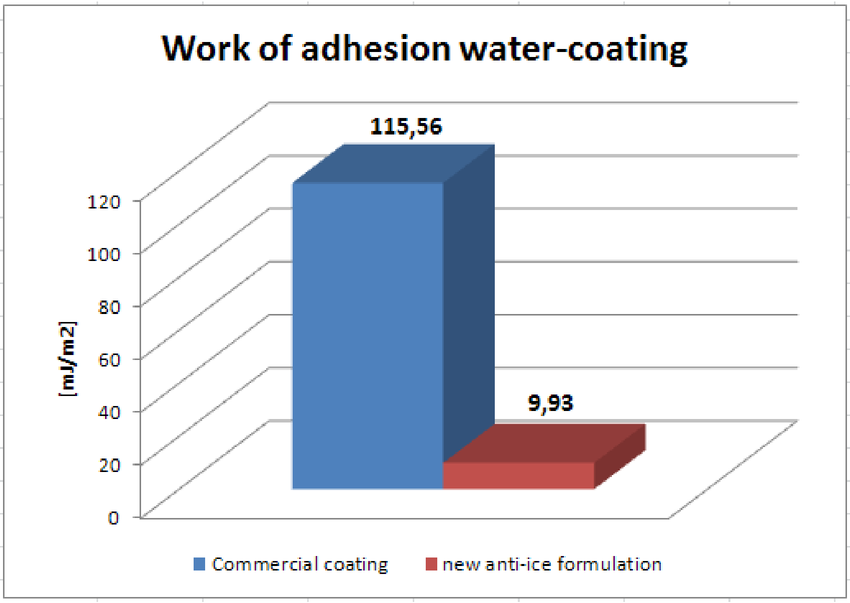


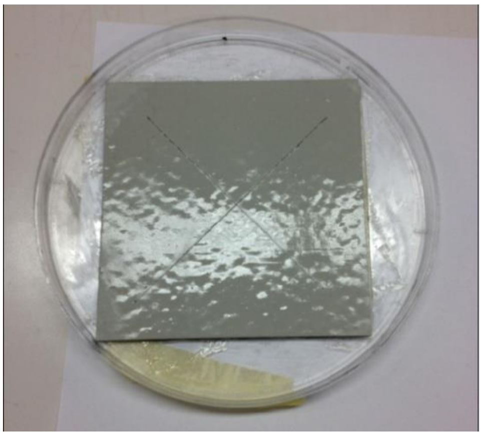
Figure 9 – Comparison of the work of adhesion between the classical commercial coating and the new formulation with anti-ice properties.

Even if the coating shows icephobic properties, it is important to preserve these properties during the entire cycle of flight from one maintenance and other of the aircraft. For this reason, it is important to evaluate the mechanical properties of the new coating. In fact the keeping of the icephobic properties of the new coating is correlated with the mechanical properties such as hardness and elastic modulus. In fact, it is necessary to point out that this functionalized coating is undergone to severe operating conditions during the flight. In particular it is subject to the impact due to send, dust, insect, rain which can alter the original morphology; this as a consequence that the icephobic property can be lost during the life time.
In table 3 the main mechanical properties are reported. Hardness and elastic modulus are the same for both samples: the new icephobic formulation and the commercial coating used as reference. This corroborate the high mechanical properties of the new formulation that is the same of the commercial one. It is highlighted that the commercial coating is already certified and therefore can be used as reference sample in term of all performance indexes that are investigated.

Table 3: nanoindentation results regarding the commercial coating and the new formulation.

	Commercial coating	**New icephobic formulation**
HIT [MPa]	157±16	141±9
$HV_{0.003N}$	14.57±1.41	13.06±0.85
EIT [GPa]	4.60±0.63	4.84±0.28

Finally, resistance to hydraulic fluids was performed. In particular according to the standard test, droplets of Skydrol were applied on the two surfaces (commercial coating and new icephobic formulation) for one month.
As reported in Figure 10, the new icephobic formulation as well as the commercial coating had not showed blistering, delamination, color changes. In addition, it is interesting to highlight that the Skydrol applied on commercial coating creates a thin and uniform film on the coating. On the contrary the new icephobic formulation showed a different behavior; in fact the Skydrol did not create a film but remained in macrodroplets on the surface. The different behavior is due to the super-hydrophobic property of the new formulation. It represents a further advantage because the super-hydrophobicity preserves the surface of the new coating.


(a)

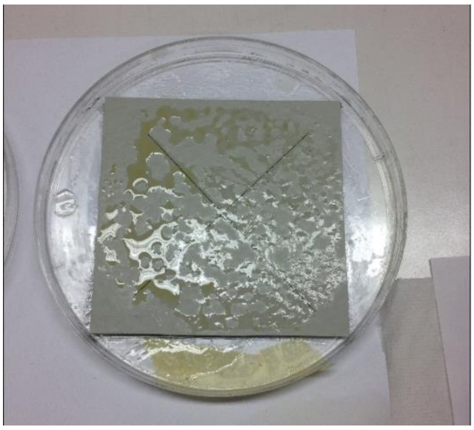

(b)

Figure 10 – (a) behavior of the commercial coating after 30 days. (b) behavior of the new anti-ice formulation after 30 days. It is evident the different behavior of the liquid droplet respect to the commercial coating.

4. Summary and Conclusions

In this work a new icephobic coating for aeronautical application was designed, developed and characterized.
In particular in this work a new tool to use with contact angle measurement instruments was designed and developed. The new tool is a very useful test room in which is possible to modify the thermodynamic condition of pressure and temperature. With this method is possible to perform contact angle measurements in flight conditions. The simulation of an environment closer to the real one allows to have a more truthful behavior of the surface or of the coating to characterize.
Once design and realize the test room, it was validated with standard material such as Polypropylene and it was demonstrated the effectiveness of the new tool for the characterization of the surfaces. In fact the influence of pressure was demonstrate other than those of temperature.
This useful tool is extremely versatile and can be realized and applied for all contact angle measurement instruments. In addition it is possible to reach very low temperature (until -50°C) and low pressure (< 0.1 bar).
This new tool represents an effective improvement of the characterization of ice-phobic surfaces and it will give further information for the right design of the surfaces and coatings with ice-phobic properties. In fact it was used to characterize the new coating. It was demonstrated the icephobicity of the new coating.
Mechanical tests as well as corrosion resistance test were performed to corroborate the effectiveness of the new coating. It was demonstrated that the new icephobic coating has the same aesthetical and mechanical properties of the commercial one other than to have a further extreme property such as icephobicity.

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