## Wettability Engineered Surfaces for Anti-frosting Applications

ΒY

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## THESIS

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Defense Committee:

Constantine M. Megaridis, Chair and Advisor Jie Xu Pietro Asinari, Politecnico di Torino To the loved ones,

thank you for being there.

To you I dedicate my thesis

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#### FIGURE

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## FIGURE

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## LIST OF ABBREVIATIONS

| CA    | Contact Angle                           |
|-------|---|
| CNF   | Carbon Nanofiber                        |
| CNT   | Carbon Nanotube                         |
| DC    | Direct Current                          |
| PMC   | Perfluoroalkyl Methacrylic Copolymer    |
| RA    | Roll-off Angle                          |
| SC    | Self Cleaning                           |
| SEM   | Scanning Electron Microscope            |
| SHPO  | Superhydrophobic                        |
| SHPI  | Superhydrophilic                        |
| SLIPs | Slippery Liquid Infused Porous surfaces |
| SSR   | Solid State Relay                       |
| TEM   | Transmission Electron Microscopy        |
| UIC   | University of Illinois at Chicago       |

## SUMMARY

Improvements in the resistance of machinery to hostile freezing environments is highly sought after today. With the increase of circumstances in which year round operation is a necessity, (*e.g.*, airborne travel, wind turbine, electric power distribution, and off-shore rigs) the interest on reliable, inexpensive, durable surface coatings able to repel frost and ice has markedly increased in recent years.

In the present study, a carbon based, superhydrophobic coating is presented and its properties analyzed for anti-icing and de-icing applications. Thanks to its skin-heating ability, ease of manufacturing, and predictable behaviour, this composition demonstrates that it is a strong candidate to address the frosting problem. The surfaces are prepared in two variants, one as-is and one oil-infused; a performance comparison is carried out between the two. Firstly, behaviour under freezing conditions is observed and analyzed. Subsequently de-frosting is studied, performed using two different approaches. One is the constant power approach, with varying power densities. The other is a pulsed power approach, with varying pulse period and width. A comparison between the two is outlined, and a cost/benefit analysis is performed.

## CHAPTER 1

### INTRODUCTION

### 1.1 Nanotechnology

By definition, nanotechnology is a science that deals with phenomena at the nanoscale, where the discrete composition of a solid, rather than its continuum properties, plays an important role. At such small scales, materials that possess well understood macroscopic properties behave in unexpected manners. An often cited example is colloidal gold. Gold metal in bulk has a characteristic metallic yellow colour, but it has been shown (1) that when gold nanoparticles are suspended in water, the color varies with varying particle sizes. Applications of these unique properties have been present since the 4th century AD, when colloidal gold was used for the production of red cranberry glass (2). Another example is that of damascus steel, an alloy with exceptional properties used until the 17th century for the production of swords in the middle east. Utilizing a Transmission Electron Microscope (TEM), it has been shown in 2006 (3) that damascus steel contains multi- and single-walled Carbon Nanotubes (CNT) in its metallic structure. But only since the arrival of 20th century have the systematic understanding of nanoparticles, and their importance, begun to be the object of scientific research. The famous speech from Richard Feynman "There's Plenty of Room at the Bottom" (4) in 1960, is commonly regarded as the starting point of this new branch of science, which since then has expanded to comprise countless applications.

Presently, nanotechnology is used, to cite only a few examples, in medicine for drug delivery (5), in electronics for the production of batteries and supercapacitors (6) as well as in chemistry as a catalyst (7).

### 1.1.1 Nanotechnology in coatings

Another very common application, and the one we will deal primarly in this thesis, is surface coatings. Coatings containing nanoparticles have shown improved corrosion resistance; this has been attributed (8) to stronger bonding of metal atoms in nanoscopic clusters when compared to the bulk material, and to the possible lack of nucleation sites for defect-born corrosion patterns (*e.g.*, intergranular and crevice corrosion). In the same reported work, other fundamental advantages of nanostructured coatings were outlined, *e.g.*, tunable chemical reactivity, improved strength and wear resistance.

There is a strong interest for nanocomposite-based coatings with enhanced wettabillity behaviour. It has been heavily reported that artificial coatings can be enginereed to mimic nanostructures found in nature (9; 10; 11). Such mimicry is able to reproduce the so-called *lotus effect*, which has been first reported as characterizing the leaves of the acquatic plant *Nelumbo nucifera*. These leaves possess superhydrophic (SHPO) and self-cleaning (SC) properties. Scanning Electron Microscopy (SEM) (12) has shown that these properties are a byproduct of the hierarchical structure that has nano-scale features placed on top of an underlying microscopic texture. This structure allows water droplets to sit on the surface of the leaves without spreading (*i.e.*, superhydrophobic). Keeping their spherical shapes, such droplets easily fall off the surface picking up dusts along the way (*i.e.*, self-cleaning). Similar structures have been reproduced using polymers (13), carbon nanotubes (14), carbon nanofibers (15), and a great deal of many other techniques (16). Such technologies have provided a great advancement in the design and understanding of superhydrophobic coatings.

The fabrication of SHPO coatings is achievable by combining two physical factors: one is the aforementioned hierarchical structure, and the second is a low surface tension (energy) substance. The latter is provided by adding specific chemicals to the substrate (*e.g.*, fluorinated polymers).

In the field of coatings, another inspirational plant is the *Nepenthes* pitcher plant. First reported by Wong et al. (17) in 2011, it allowed for the creation of durable surfaces capable of repelling water and oils, while retaining a high degree of droplet mobility. Such surfaces, often referred to as slippery lubricant infused porous surfaces (SLIPs), function by entrapping oil within the texture of porous materials. Due to the immiscibility of oil and water, the impregnated substrates are inherently repellent to water, while the entrapping of the oil within the texture itself allows for a durable, self-healing material.

In order to create a SLIP surface, three conditions must be met (17). First, the impregnating fluid must be able to wet the solid and adhere to it. Second, in order to be efficient at repelling, the impregnating fluid must be immiscible with the droplet fluid. Therefore usually apolar oils are used, that are immiscible with water (a polar fluid). Third, the solid substrate must be preferentially wetted by the impregnating fluid, locking it in place, in such a way that the repelled fluid does not deplete the lubricant from the surface during shedding.

### 1.2 Fundamentals of wettability

Wettability is an outcome of the interaction of a liquid with varying surfaces. If a droplet of a specific liquid spreads on (*i.e.*, wets) a surface, then that surface is deemed wetting (*i.e.*, hygrophilic). If a droplet of a specific liquid does not spread, the surface is deemed non-wetting (*i.e.*, hygrophobic). In the latter case, what shape will the droplet assume? The answer lies in the energy equilibrium and force balance.

The behaviour of the droplet can be predicted via the surface tensions of the three present interphases: the solid-gas, the liquid-gas and solid-liquid.

Carrying out the appropriate force balance, it is possible to calculate the equilibrium angle, valid only for perfectly smooth surfaces. It is given by the Young's equation (18) as:

$$\cos\theta_E = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \tag{1.1}$$

where  $\theta_E$  is the equilibrium angle, often times referred as the contact angle (CA), and  $\gamma_{sg}$ ,  $\gamma_{sl}$ , and  $\gamma_{lg}$  are the surface tensions of the solid-gas, solid-liquid, and liquid-gas interfaces, respectively.

In 1936, Wenzel (19) expanded Equation 1.1 to account for the role of texture. In his paper, he defined a roughness coefficient r as:

$$r =$$
roughness factor  $= \frac{\text{actual surface}}{\text{geometric surface}}$  (1.2)

Since the surface energy of a solid is proportional to its surface area, a hydrophobic surface with higher surface roughness will need a smaller geometrical area to achieve equilibrium with a drop and therefore the CA will be higher. Then:

$$\cos\theta_W^* = r\cos\theta_E \tag{1.3}$$

For a perfectly smooth surface r will be equal to 1, and the theoretical CA will be measured. But for a surface with different roughness, the apparent CA will be higher (for the hydrophobic case) or lower (for the hydrophilic case) than the theoretical one.

In 1944 another mechanism to modify the wettablity characteristics of a surface was presented by Cassie and Baxter (20), that was applicable to porous surfaces. In their work, the apparent CA was defined as:

$$\cos\theta_{CB}^* = f_1 \cos\theta_E - f_2 \tag{1.4}$$

 $\theta_E$  being the advancing CA at the liquid/solid interface.  $f_1$  and  $f_2$  are to be considered as fractions of the geometrical surface in contact with the drop.  $f_1$  is the droplet base surface fraction in contact with the solid, while  $f_2$  is the fraction of the drop sitting on air bubbles. The concept of the drop not being fully in contact with the solid surfaces is what actually differentiates the Cassie-Baxter *state* from the Wenzel state. Figure 1 explains visually the difference between these states.

In regards to contact angle, superhydrophobicity (SHPO) is a state reached when the water static CA is higher than 150°, a result that can be achieved on either Wenzel or Cassie surfaces.



Figure 1. The contact angle is defined as the angle with the vertex in the triple point, the initial side parallel to the surface, pointing inside the droplet and the terminal side tangential to the droplet in the triple point. In the figure, the left image shows the contact angle on a perfectly smooth surface. In the center, the Wenzel state is depicted. A drop in the Wenzel state is in complete contact with the rough surface, and this causes a strong adhesion between droplet and substrate. Finally, on the right, the Cassie-Baxter state is illustrated. The drop is sitting on air pockets, and is easily displaceable. Typically droplets in the Cassie-Baxter state shows high mobility. (©Vladsinger / Wikimedia Commons / CC-BY-SA-3.0

As far as the roll-off angle (RA) is concerned, different behaviours can be observed. If the drop resting on the surface is in the Wenzel state, the RA will be quite high, a condition called *pinned* droplet. On the other hand, drops in the Cassie state have a much higher mobility, and it has been shown (21) that at angles greater than 8° the drop is already able to shed from the surface.

For SLIP surfaces, we do not have fluid-solid contact anymore, but instead fluid-fluid. This leads to even smaller RA, down to  $2.5^{\circ}$  (22).

#### 1.3 Icing and frosting

The formation of frost and ice is one major cause of failure for countless systems. The main difference between frost and ice lies in the mechanism responsible for their formation. While, chemically, both of them feature water cooled below its freezing point, ice is generally meant as water transformed from liquid phase to solid phase. Frost on the other hand, forms when water vapour in the air, condensating or depositing according to environmental factors, discretely freezes in microscopic crystals that accumulate over time.

Engineering systems negatively affected by ice and frost include airplanes, power lines, wind turbines, and many others. In addition to the risk of failure, icing is also a cause of reduction of productivity for industries that are forced to employ a large quantity of resources for cleaning and servicing machines hit by cold weather.

In this context, the discovery or design of surfaces able to repel frost or, at minimum, delay its formation are seen as a great improvement in current technology.

### 1.3.1 Nucleation theory

The subject of frosting is strictly correlated to that of condensation. The droplets condensing on a surface kept at a temperature below the dew point will eventually freeze if the surface temperature is lower than the freezing point (23). It is also believed that the nucleation of frost of a surface is mainly dependent on the contact angle of the surface itself (24).

The relationship between wettability of a surface and resistance to ice formation led to the understanding that superhydrophobic surfaces might be best for ice repellency (25). This notion has been disputed by Jung *et al.* (26) who concluded that surfaces with a low roughness are better for delaying ice nucleation and therefore, given that high contact angles are usually achieved trough nanoscopic roughness, a trade-off between contact angle and surface roughness must be found to achieve the best possible solution.

### 1.4 Approaches to anti-icing/anti-frosting and de-icing/de-frosting

Deicing, *i.e.*, removal of the accumulated ice or frost from a surface of interest, is the final objective of these researches. The desired result is to have surfaces completely clear of obstructions, in all temperatures and environments. In the following, several methods employed to meet this objective are enumerated.

First, it is also important to differentiate between anti-icing and de-icing. Anti-icing is the passive resistance of a surface to the formation of ice (similar statement can be made for frost) and therefore we designate it, within this thesis, as the *passive approach*. De-icing is the action performed, or system utilized, to remove the ice/frost that has accumulated on the surface. In other words, energy needs to be spent to clear the covered surfaces. For this reason, de-icing (or de-frosting) will be referred to as the *active approach*.

A common active de-icing mechanism is Joule heating, also known as resistive heating. When electric current flows through a conductor, the interaction between the moving electrons and the atoms of the solid results in heat being dissipated. There is a relation between the current and the heat released, known as Joule's first law that is expressed as:

$$Q \propto I^2 R t \tag{1.5}$$

The exact amount of power output by a conductor crossed by direct current (DC) is easily found as  $P = V \cdot I$  where P is the power, V the voltage and I the current. Substituting Ohm's law in this relation we obtain:

$$P = IV = I^2 R = V^2 / R (1.6)$$

the last form being the one utilized in this work to calculate power outputs.

### 1.4.1 De-icing/de-frosting in history

Historically, several techniques have been utilize to fight ice/frost accumulation. The best known example is the de-icing/de-frosting of roads and other structures by means of salts. These salts are strewn to reduce the freezing point of water, melting the snow and avoiding the formation of ice, but are only efficient for temperatures close to 0 °C. Moreover, there is an issue in cleaning these salts off the surfaces at the end of the cold season.

Another example, is the protection of buildings in cold climates. High pitched roofs must be used, but they are usually ineffective at repelling the snow and could fail if exposed to extremely abundant snowfall.

### 1.4.2 Anti-icing/anti-frosting and de-icing/de-frosting today

Nowadays, several more applications, especially in engineering, are sensitive to ice and frost formation. Wind turbines for example can encounter power losses and even catastrophic failure due to ice accretion on the blades surface; thus a mix of passive features like superhydrophobic coatings and active features like electric heating or inflating pneumatic boots must be used to keep those surfaces clean (27). The same techniques can be used for airplanes (28), but the most common one is chemical de-icing. Chemical de-icing provides good performances, but it has the disadvantage of polluting airport runaway waters (29).

#### 1.4.3 Anti-icing/anti-frosting and de-icing/de-frosting under development

Today, the focus for anti-icing is on SHPO surfaces and SLIP surfaces. As already mentioned in (25) and (26), SHPO surfaces reduce the ice nucleation rate and moreover, given the low roll-off angle that these surfaces present, obtain a self cleaning behaviour: the droplets are shed before they can freeze. Frosting presents an additional challenge, since it has been proven (30) that frost nucleation is ubiquitous on micrometric scale features, thus, rendering the inherent benefits of SHPO surfaces nearly useless.

SLIPs are also being studied for their anti-frosting characteristics. They possess extremely low roll-off angles and a molecularly smooth surface that allow the drops of water condensating on the surface to promptly move (or "slip") off them. The lack of pinning sites is what drives this incredibly high mobility. Compared with SHPO surfaces they demonstrated (31) a much lower ice adhesion strength and a better ability to hinder frost formation.

### 1.5 Motivation and scope of work

The primary goal of this thesis is to show the manufacturability of an effective, inexpensive, self-contained de-frosting system. This system is based on a surface coating created by spraying a chemical dispersion. It is, fundamentally, a composite material created by mixing nanoparticles, polymer chains and solvents: it is simple in its composition and working mechanism, and

### TABLE I

## ILLUSTRATION OF ALL POSSIBLE EXPERIMENTAL CONFIGURATIONS PRESENTED IN THIS WORK. FIRST PASSIVE SURFACES (COLUMN 1) ARE CONSIDERED, AND THEN ACTIVE SURFACES. THE ACTIVE SURFACES ARE FURTHER DIFFERENTIATED INTO CONSTANT POWER (COLUMN 2) AND PULSED POWER (COLUMN 3). ALL THE ABOVE CASES ARE REPEATED FOR THE SHPO AND SLIP SURFACES.



this underlines the advantage of its reliability. In the present work we study the use of such coatings under different conditions. They are visually described in Table I.

First, the passive behaviour of the coating is studied under frost-forming conditions. Then, the active approach is taken into consideration, and electric current is applied to the surface. The current is either DC or it is pulsed, forming a square wave. Finally, all the experiments are repeated when the coating is infused with an oil, thus forming a SLIP surface.

In all cases, laboratory scale evaluation of the performances of these systems is performed, and compared. The purpose is to estabilish a cost/effectiveness scale for the different setups, while at the same time presenting the drawbacks of each, in light of possible applications.

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## CHAPTER 2

## EXPERIMENTAL DESIGN AND MATERIALS

## 2.1 Sample preparation

### 2.1.1 Chemical suspension

The suspension, following the procedure (15) outlined in a previous paper from our group, is prepared as follows: 0.3 g of carbon nanofibers (CNF) (PR-24-XT-HHT; Pyrograf III from Applied Sciences Inc., USA) are weighed and introduced in a vial. Then, 14 g of acetic acid (Glacial,  $\geq 99.7\%$  w/w, Fisher Chemical) is added together with 28 g of acetone (ACS reagent,  $\geq 99.5\%$  w/w Sigma-Aldrich). This first vial is sealed with Parafilm<sup>®</sup> M and placed in an ultrasonic bath at 42 kHz (Cole-Parmer, model 8891) for 10 minutes. After the sonication, the suspension is probe sonicated (Vibra-Cell, VCX-750, Sonics & Materials Inc.) for 1.5 minutes at 40% amplitude.

1 g of Capstone<sup>®</sup> ST-100 (20% perfluoroalkyl methacrylic copolymer, PMC, w/w solution in water) is introduced into a second vial, along with 2 g of acetic acid and 4 g of acetone. The contents of the two vials are mixed, and bath sonicated for 10 minutes. The suspension is now ready to be sprayed.

## 2.1.2 Glass substrate

Microscope glass slides (Thermo-Scientific 25x75x1mm) are used as substrate. They are cut at 30 mm in length and have copper tape electrodes applied on both ends, of about 2.5x40mm in size. This results in an active surface of about 25x25mm or 625 mm<sup>2</sup>.

#### 2.1.3 Spraying and drying of the samples

An airbrush (VL#3L, Paasche Air Brush) featuring a .73 mm nozzle spray head was used (See Figure 2). The pressure was regulated and measured to be about 20 psi static pressure and 18 psi dynamic pressure (while spraying). The sprayer head was kept at 10 cm from the samples, and quickly moved transversely while spraying. After spraying, the samples were placed in a oven at 80  $^{\circ}$ C for 1 hour in order to evaporate the solvents.

## 2.2 Sample measurements

Slides were weighted before and after spraying to calculate the mass deposited using a precision scale (LE26P, Sartorius AG). Using a multimeter (AKTAKOM AMM-3031) and the two points measuring method, resistance was recorded for each sample: immediately after baking them, before frosting took place, and after defrosting was complete.

### 2.2.1 Contact angle measurement

Contact angles images were captured using a digital camera (Mintron MHD-13MG5SH-D) coupled with a high-magnification lens (OPTEM Zoom 100). The images were acquired by a computer software (Kinovea), that allows for real time angle measurements. The angles were measured multiple times and the average was taken to avoid large errors.



Figure 2. Sample preparation procedure. (a) The glass slide are cut to size and copper electrodes are applied. (b) Using an airbrush, the CNF-PMC suspension is applied to the samples. Varying masses of suspension are applied by controlling the number of spray passes the surface is subjected to. For SHPO samples the procedure ends after drying. For the SLIP surfaces (c), the sample is dipped into a Krytox filled container, and allowed to drip the excess oil for a couple minutes before use in experiments.

#### 2.3 Infusing procedure

The SLIP samples were infused with Krytox (DuPont) via dipping and then allowing the excess to drip for about 2 minutes. Krytox is a high perfromace fluorinated oil with superior properties regarding lubrication and high temperature stability. In our case, it was the oil of choice for its low surface tension of  $\approx 20 \text{ mN/m}$ , that allows it to wet the SHPO surface, and its low freezing point, up to  $-55 \,^{\circ}$ C depending on the viscosity.

#### 2.4 Environmental chamber

#### 2.4.1 Frosting

An environmental test chamber was used (Espec SH-641) with both temperature and humidity control. Inside the chamber there is a Peltier cell (TeTech, CP-061), mounted on a stage.

The samples are placed on top of the Peltier cell. To improve thermal contact throughout the experiment, thermal paste (OT-201, Omega Engineering Inc.) was applied underneath the samples. Over the thermal paste and beneath the samples, electrically insulated thermocouples are placed (Type K, OMEGA Engineering Inc.). The thermocouples are connected to a digital acquisition system (OM-DAQ-USB-2400, OMEGA Engineering Inc.). Temperatures at the frequency of 4 Hz are recorded in a computer file.

The electrodes hanging from the samples were connected through crocodile clips to the outside of the chamber and from there to a regulated power supply (Sorensen DCR 40-13B, AMETEK Programmable Power, Inc.) whose voltage varies between 0-40 V (See Figure 3). When the samples are in place inside the chamber, and the electric connection is completed, the

chamber is closed and turned on. Termperature is set to 10 °C and humidity is set to 0% RH. The chamber does not provide dehumidification, if not through the refrigerator cycle. Therefore, the relative humidity never actually reaches 0% but is low enough not to have condensation or deposition on the samples.

When the chamber has reached thermal equilibrium, the Peltier cell is started, set to 100% cooling power. This allows the peltier surface to stabilize around -9 °C. The relative humidity of the chamber is set to 80% in order to allow frost to form on the cold surface of the samples.

#### 2.4.2 Defrosting

For the defrosting experiment, the thermocouples recording was started, as well as the video recording, using a DSLR digital camera (Canon EOS T3i). Subsequentsly, the power generator was turned on and defrosting took place. When the surface was completely devoid of frost, the power supply was stopped, along with the recordings. During the defrosting phase, the Peltier cell was kept on.

### 2.4.3 Pulsing apparatus

A circuit was created to allow the power supply to pulse. A square wave modulation was employed, with variable period and pulse width. The circuit schematic (Figure 4) shows the items needed. A function generator (3011B, B&K Precision Corp.) was used to create and regulate the square wave. It was connected to a solid state relay (SSR) (DC60S5, Crydom Inc.) that bridged the low voltage loop and the high voltage one. On the high voltage loop, the power supply and the samples were present. The SSR was chosen in order to achieve a higher



Figure 3. Stages of the frosting/defrosting experiment. (a) The following samples are placed on top of the Peltier: a control glass slide (on the left), the dry SHPO sample, and the SLIP surface (the Krytox oil is represented in red). (b) After thermal equilibrium is reached, cooling is started and the samples become covered in frost. (c) After one hour, voltage is applied to the active surfaces and defrosting takes place. The Peltier is powered throughout the entire experiment.

precision for the time intervals, due to its fast response. In fact, the slowest response time is given as 0.3 ms on the datasheet.



Figure 4. Circuit used to pulse current through the samples. The function generator is connected to the control side of the relay, and operates it. On the load side, the power supply (here represented as a battery) is wired to the samples. In this example, two equal resistors (each representing one sample) are connected in parallel to the power supply. This configuration was common during the experimentation.

## CHAPTER 3

## RESULTS

There is a plethora of papers reporting the production and implementation of superhydrophobic materials (32). The behavior and performance of our coating stems from the properties of its constituents. We already mentioned that in order to achieve superhydrophobicity two elements are needed: one is low surface energy of the solid, that is supplied by the fluorinated polymer PMC. The other is the texture, that is supplied by the CNFs. Beside the texture, the CNFs play an added role of electrically conducting media.

The novelty of our coating lies in it's intrinsically low electrical resistivity ( $\sim 30 - 200\Omega$ ) that allows for it's use as a self-heating surface. To take full advantage of this phenomenon in every way possible, it is preferential to apply the coating on an originally insulating material. The other characteristics that the substrate must have are low thermal expansion to avoid rupture of the coating's film, resistance to low temperatures and, for laboratory testing, easy availabily and preparation. Thus, the choice to use glass slides as the underlying substrate.

The CNF-PMC solution is sprayed on glass slides to form a superhydrophobic and electrically conductive material. The mass deposited is controlled by limiting, or increasing, the number of spray passes that the substrate is exposed to. This coating provides several advantages over other SHPO surfaces: being applied as a spray, it allows for easy manufacturing of SHPO surfaces, using tools and machinery already present in every manufacturing plants where spray painting is performed, whereas other reported SHPO surfaces require molds and/or photolithography. This translates in reduced costs, and it also implies that this coating is intrinsically more flexible in its potential applications. Specifically, it is possible to apply the CNF-PMC coating also to a curved or complex 3D structure, while photolithography can only be used on flat surfaces.

Another limitation of photolithography, and of mold techniques overall, is the dimension of the surface to be treated. In such cases, the maximum extension of the surface is limited, and requires several hours to be completed. A sprayed coating on the other hand, can be applied on surfaces of every dimension and it only needs several minutes to be applied.

The last and possibly most important advantage of the CNF-PMC surface is its regenerative and repair capabilities. After the surface wears, or suffers damage, it is always possible to restore it to it's previous state simply by spraying an added layer. For conventional SHPO surfaces, after the micro/nanostructure is ruined, it is not possible to regenerate it, only by repeating the entire production process would it be possible to return the surface's original properties.

#### 3.1 Relationship between mass deposited and resistance

Depositing varying masses of the solution by spraying, it is possible to attain varying electrical resistances. By increasing the total mass deposited, there is an increase in the electrical conductance of the material (*i.e.*, lower resistance). By increasing the mass deposited, one is increasing the amount of CNF deposited. Effectively, enhancing the percolation network and allowing for better electrical conductance. Furthermore, there is also an increase in the contact angle of water on the surface (*i.e.*, more phobic). However, after a critical mass of  $0.3 \times 10^{-3}$ g/cm<sup>2</sup>, the contact angle remains relatively constant  $\approx 160^{\circ}$  (See Figure 5(b)). Dif-

ferent behavior is observed for the electrical resistance, which continues to decrease as the mass is increased. Fitting a logarithmic curve to our experimental points (see Figure 5), we are able to obtain the following relationship between specific mass deposited (x in  $[g/cm^2]$ ) and electrical resistance (y in  $[\Omega]$ ):

$$y = -70\ln x - 420 \tag{3.1}$$

We worked with resistances in the order of  $40 - 100\Omega$ . Such values were chosen in order to have a larger choice of output powers when defrosting using our low voltage power supply.

### 3.2 Frosting

The next set of experiments is performed in two sequences. First, the coated surface is allowed to frost for 1 hour, following the procedure outlined in Chapter 2. For the plain SHPO samples, after 1 hour, the samples surface is completely covered in frost (Figure 6(a)). The frost's hazy appearance is due to the crystallization. In fact, no droplet is present on the surface: due to the extremely low temperature, the humidity directly deposits on the surface in the form of frost, similarly to what is shown in (30). A different type of behaviour is observed for the Krytox infused sample: for such a material, the frost cannot directly deposit on the surface due to the smoothness of the oil interface. The lack of texture results in no available pinning sites for the ice crystals to nucleate. Supercooled water droplets condense instead, eventually frosting. These droplets retain their shape after they become solid. Thus, it is possible to see hemisperical frost aggregates (Figure 6(b)) on the frosted SLIP surface. This further delay in frost formation is one of the advantages of SLIP surfaces over the plain SHPO ones.



Figure 5. Relationship between coating mass deposited, electrical resistance and contact angle. For increasing mass deposited (coating level), decreasing values of electrical resistance were obtained. For high mass deposited 5(a), the data was fitted using a logarithmic function (red line). The full table with the numerical values can be found in Appendix A. In 5(b), the critical mass for contact angle improvement is shown by the dashed red line. For coating levels higher than  $0.3 \times 10^{-3}$ g/cm<sup>2</sup> the contact angle no longer increases, but the resistance

continues to decrease.

Both types of observed frost formation due to SHPO and SLIP surfaces present a benefit for the subsequent de-icing. The frost on the SHPO sample totally covers the surface and improves the heat transfer between the heating surface and the frost itself, having a larger contact area between the two. The frost on the SLIP surface on the other hand is a smaller amount to start with, and this of course reduces the quantity of energy needed to melt the solid.

Over prolonged periods of frosting (in excess of 3 hours), the oil-gas interface disappears due to the exceeded accumulation of supercooled water droplets on the surface. Thus, visually there is no difference between the two surfaces, and frost begins to accumulate at the same rate on both specimens.



(a) Plain SHPO sample

(b) Krytox infused SLIP sample

Figure 6. Surface after 1 hour of continuous frosting in the environmental chamber at 10 °C and 80% relative humidity, while the Peltier cell draws full power (samples surface temperature  $\approx -9$  °C). It is important to notice the different frost morphology on their surface. (a) shows porous, crystallized frost while (b) shows frozen droplets alternating with zones of thinner frost.

### 3.3 Constant power defrosting

In the second portion of the experiment, power is supplied to the samples and deicing via joule self-heating is observed. We observe and quantify the time needed to completely clear the surface from frost. The experiment has been repeated for different output powers, and the results are plotted in Figure 7.



Figure 7. Relationship between output power and defrosting time for a standard sized SHPO sample. For higher output powers shorter defrosting times are achieved. We observed that the relationship is not linear, and does not demonstrate constant efficiency due to dissipative losses from convection and conduction directed toward the insulating glass.

Table II shows the energy requirement to defrost these surfaces, per sample or per square meter. It is calculated as a product between power and time. The relationship between power and defrosting time is not linear, and it appears that higher powers are more efficient when defrosting. This behavior can be attributed to dissipative heat transfer. Consider first a system with no losses, with frost on top of the heating layer. In this case, the higher the power, the higher the heat transferred to the frost per unit time, and the lower the defrosting time (with linear proportionality). The energy consumption must be constant. When we consider a real system though, we have convection and conduction through the insulating media (glass in our case). These dissipative components are time dependant and therefore the dispersed energy increase for increasing defrosting times. Moreover, the temperature difference caused macroscopically by the heating layer is so small that they can be considered as constant for our purposes. Therefore, a higher output power, being fed at the frost/surface interface, is able to melt the frost in a short time, reducing the energy losses, where lower powers need to be supplied for a longer time, consequently increasing the losses.

In general, with this experiment the surface demonstrates its ability to effectively defrost in a reasonable time, where a traditional passive anti-icing surface in the same condition would have been unable to do so. Moreover, the energy required to perform this operation,  $384 \text{ kJ m}^{-2}$ equivalent to  $0.1 \text{ kW h m}^{-2}$  for the 8 W experiment, is very low and makes this defrosting mechanism a low cost one.

## 3.4 Pulsed defrosting

In order to perform this experiment, the circuit described in the experimental section, pulsed electricity at a constant 8 W power through the self-heating coating. We were able to vary the period of the pulse, as well as the pulse width. After the first trials, we settled for a 2 second

## TABLE II

## ENERGY REQUIREMENT PER UNIT AREA FOR COMPLETE CONSTANT POWER DEFROSTING OF A SHPO SAMPLE AT DIFFERENT POWER DENSITIES. THE SAMPLE SIZE PER SQUARE METER WAS STANDARDIZED.

Power [W] Power Density  $\left[\frac{W}{cm^2}\right]$  Time[s] Energy per sample [kJ] Energy  $\left[\frac{kJ}{m^2}\right]$ 

| 8 | 1.28 | 30  | 0.24 | 384  |
|---|------|-----|------|------|
| 6 | 0.96 | 40  | 0.24 | 384  |
| 5 | 0.8  | 100 | 0.5  | 880  |
| 4 | 0.64 | 140 | 0.56 | 896  |
| 3 | 0.48 | 600 | 1.8  | 2880 |

pulse width. This choice comes from considerations of the thermal inertia of our system. In fact, while a quantitative analysis of this phenomenon is outside the scope of this work, we could qualitatively evaluate that a shorter pulse width would prevent the surface from sensibly changing its temperature. In other words, the temperature of the frost/coating interface would not reach a sufficiently high value, able to initiate de-icing. Pulse periods were varied instead. Varying the period, it was possible to achieve total frost repellency. For our best, *active* SLIP coating, we found by trial and error that the complete repellency could be achieved with a 45 s maximum time period.

The energy consumption for the pulsed runs are reported in Table III.

In Figure 10 we can observe the surface behaviour when the power is not perfectly tuned: the active SHPO surface, while strongly reducing the frost formation compared to the passive

#### TABLE III

ENERGY EXPENDITURE FOR THE PULSED ACTIVE APPROACH. THE POWER IS CONSTANT AT 8 W. DIFFERENT EXPERIMENTS ARE PERFORMED, BOTH FOR SHPO AND SLIP SAMPLES AND FROST-COVERED SURFACE PERCENTAGE IS PRESENTED.

| Coating | Time ON [s] | Time OFF [s] | Energy [kJ] | Specific<br>energy $\left[\frac{kJ}{m^2}\right]$ | Frosted surface<br>after one hour [%] |
|---------|-------------|--------------|-------------|--|---------------------------------------|
| SHPO    | 2           | 45           | 1.28        | 2048   | 12                                    |
| SLIP    | 2           | 45           | 1.28        | 2048   | $\approx 0$                           |
| SHPO    | 2           | 60           | 0.96        | 1536   | 37                                    |
| SLIP    | 2           | 75           | 0.768       | 1229   | 40                                    |

surfaces, it cannot avoid frost accumulation over long time. In this case, a slight increase in output power could lead to the surface being perfectly frost-repellant. The pulse period, and consequently the power to be spent in real life system must be calculated taking into consideration all the environmental factor, *e.g.*, temperature, humidity, wind speed, resulting in a different deposition rate on a case-by-case basis. For this purpose, several ice/frost detection system have been studied (33), relying on variations of reflective properties, mass, thermal conductivity and many others.

We also obsverved the temperature profile of a SLIP sample subject to pulsed defrosting at 8 W power, and compared it to a passive sample (Figure 8). During the ON state, the pulse caused a sensible increase in the sample temperature, of about  $1.5 \,^{\circ}$ C. Nevertheless, the sample never reached the ice melting point, the peak of the pulse being at  $\approx -5.5 \,^{\circ}$ C and fading in  $\approx 10 \, \text{s}$ . The reading thermocouple was placed between the back of the sample and the Peltier cell, and

frost never appeared on the sample top surface (proving that the temperature of the interface went above 0  $^{\circ}$ C). This demonstrates that the heat transfer was mainly directed toward the ice and, at the same time, underlines another advantage of the pulsed approach: it does not cause a permanent temperature increase of the system; the temperature keeps constant between two pulses.



Figure 8. Temperature profiles for a passive SLIP and an active SLIP sample pulsed for 2 second each 45 at 8 W. It's important to note that the pulses do not globally increase the temperature of the samples. Being applied directly at the frost-substrate interface most of the heat is removed by melting the frost itself, and the rest of it cause a small transient of about 1.5 °C lasting less than 10 seconds, as it is recorded by the thermocouples underneath the samples. These 100 seconds are a subset of a 1 hour run, took after the samples reached equilibrium with the Peltier cell.



Figure 9. Growth of frost on the Krytox infused surface, shown at 10 minutes intervals. The images were post-processed in black and white and the pixels of each color were counted. In (f), we show how after one hour the frost covered 93% of the surface. In the same time period, frost covered only 1.5% of the active sample (l). There was already a stark difference after 30 minutes, having 68% of the surface covered in frost for (c) to be compared with again 1.5% in (i). The white pixels in (g) and (h) are due to the light reflection on the oil rather than to frost, and have therefore been ignored.

## 3.5 A comparison

When comparing active and passive approaches, it is important to take into consideration the operating conditions of our system and their importance. In fact, while there is an interest in reducing as much as possible the energy expenditure, other factors like reliability, fail-proof or continuous operations are often more important to the users. For this reason, we study the feasibility of the pulsed power de-icing technique. There is an assumption that in real-life engineering systems we do not want to wait for frost and ice to form on machines before taking countermeasures. We want our surfaces to be free at all times from frozen materials that are dangerous and also lower the performances of the system. We also want this at a reasonable cost. In fact, while it is possible to address this problem by keeping our self-heating coating on at all times, this would be not only wasteful, but also pose a potential danger, exposing to excessive heating components that are designed to work at lower temperatures.

We believe that this approach holds a greater chance of being employed in real life applications because it is the only one that can guarantee uninterrupted operations of the machinery it is applied to. Even though it is generally less energetically efficient (compare Table III with Table II).

Considering the performance of SLIP surfaces, in the short time period of one hour, there is a large difference between passive (eventually defrosted at constant power) and pulsed power active sample. In Figure 9, a comparison between the two is outlined. For the passive SLIP, after 30 minutes, the forst covers a large portion of the surface. We post processed the images in black and white and counted the white pixels (representing frost). We calculated that 68% of the surface is covered in frost after this short time. Meanwhile, the pulsed active sample displays a mere 1.5% of covered surface. In case *e.g.*, of aerodynamic surfaces, a thin layer of frost can cause a great increase in drag, lift and pitching-moment coefficients (34), up to several orders of magnitude. This and other similar considerations, highlight the importance of the pulsed approach, that can guarantee a frost-devoid surface.



Figure 10. Surface of the samples covered in frost as a percentage of the total surface. It is observed that the untreated surface (glass) demonstrates the worst behaviour. At the other end of the scale, active surfaces remain fundamentally devoid of frost until the end of the experiment. It is interesting to notice the linear increase in frost accumulation (in regards to percentage) on the *Active* SHPO, that hints to an insufficient energy expenditure. In this case, increasing the up-time of the system would guarantee a frost-free surface.

## CHAPTER 4

## CONCLUSION

A novel approach to de-icing is presented: embedded, easily applied and mantained, the self-heating surface coating based on the CNF-PMC dispersion showed a reliable, cost-effective defrosting, thanks to the heat being applied directly at the frost-surface interface. Moreover, we demonstrate how the oil infusion of the coating presents a significant advantage over its dry counterpart, thanks to delayed frost formation and reduced pinning. Finally, two different approaches to active defrosting have been demonstrated. One is the constant energy input approach, that proved having the lowest energy expenditure per unit surface, being suitable for on-demand operations applications. The other is the pulsed approach, which creates a consistently frost-free surface.

We observed that a small amount of energy is sufficient to complete the active defrosting and that the energy output must be optimized according to the environmental factors (*e.g.*, temperature, wind speed, humidity) in order to achieve total defrosting without significantly increase the temperature of the substrate. It is envisioned that this de-frosting system can be applied to an existing apparatus with minimal modifications as well as integrated in the design phase for new ones. In this case, further advantages would arise, concerning weight reduction and system simplicity, due to the absence of additional heating elements. Pulsed power defrosting is deemed more suitable for machinery and systems required to be functional at all times, under a constant operations regime, while constant power defrosting would be the mechanism of choice for system limited in operation to short time or on demand.

Further studies are required to evaluate abrasive wear resistance and natural degradation (e.g., due to ultraviolet exposure).

APPENDICES

Appendix A

Appendix A (continued)

## ADDITIONAL TABLES

## TABLE IV

# EXPERIMENTAL VALUES OF ELECTRICAL RESISTANCE FOR VARYING PMC-CNF COATING LEVELS DEPOSITED ON A STANDARD SIZED SAMPLE

| Mass $\left[\cdot 10^{-} 3 \frac{g}{cm^2}\right]$ | <b>Resistance</b> $[\Omega]$ | Mass $\left[\cdot 10^{-} 3 \frac{g}{cm^2}\right]$ | Resistance $[\Omega]$ |
|---|------------------------------|---|-----------------------|
|   |                              | 0.84608   | 61.4                  |
| 0.4025  | 138.2                        | 0.9888  | 68                    |
| 0.4214  | 132.7                        | 0.99072   | 48.7                  |
| 0.4246  | 122.4                        | 0.99488   | 68.5                  |
| 0.44  | 122.2                        | 1.02112   | 48.2                  |
| 0.46208   | 113.9                        | 1.07008   | 45.6                  |
| 0.47488   | 111.5                        | 1.09952   | 45.4                  |
| 0.4848  | 107.7                        | 1.1904  | 43.8                  |
| 0.4912  | 110.6                        | 1.2208  | 57.2                  |
| 0.49984   | 106.2                        | 1.232   | 40.5                  |
| 0.54176   | 92.6                         | 1.2528  | 46.8                  |
| 0.60288   | 85.5                         | 1.25664   | 45.9                  |
| 0.61024   | 112.6                        | 1.27904   | 54.7                  |
| 0.61024   | 90.3                         | 1.35392   | 52.6                  |
| 0.63712   | 88.5                         | 1.4352  | 39.3                  |
| 0.67904   | 74.7                         | 1.43712   | 40.6                  |
| 0.73664   | 74.4                         |   |                       |

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## CITED LITERATURE

- Schmitt, J., Mächtle, P., Eck, D., Möhwald, H., and Helm, C. a.: Preparation and optical properties of colloidal gold monolayers. Langmuir, 15(4):3256–3266, 1999.
- Wagner, F. E., Haslbeck, S., Stievano, L., Calogero, S., Pankhurst, Q. a., and Martinek, K. P.: Before striking gold in gold-ruby glass. Nature, 407(October):691–692, 2000.
- Reibold, M., Paufler, P., Levin, a. a., Kochmann, W., Pätzke, N., and Meyer, D. C.: Materials: carbon nanotubes in an ancient Damascus sabre. <u>Nature</u>, 444(October):286, 2006.
- 4. Feynman, R. P.: There's plenty of room at the bottom. <u>Engineering and science</u>, 23(5):22–36, 1960.
- Farokhzad, O. C. and Langer, R.: Impact of Nanotechnology on Drug Delivery. <u>ACS Nano</u>, 3(1):16–20, 2009.
- Serrano, E., Rus, G., and García-Martínez, J.: Nanotechnology for sustainable energy. Renewable and Sustainable Energy Reviews, 13:2373–2384, 2009.
- 7. Pyun, J.: Graphene oxide as catalyst: Application of carbon materials beyond nanotechnology. Angewandte Chemie - International Edition, 50:46–48, 2011.
- Baer, D. R., Burrows, P. E., and El-Azab, A. A.: Enhancing coating functionality using nanoscience and nanotechnology. <u>Progress in Organic Coatings</u>, 47(3):342–356, 2003.
- Wang, B., Liang, W., Guo, Z., and Liu, W.: Biomimetic super-lyophobic and superlyophilic materials applied for oil/water separation: a new strategy beyond nature. Chemical Society Reviews, 44(1):336–361, 2015.
- 10. Guo, Z., Liu, W., and Su, B.-L.: Superhydrophobic surfaces: from natural to biomimetic to functional. Journal of colloid and interface science, 353(2):335–355, 2011.
- 11. Marmur, A.: The lotus effect: superhydrophobicity and metastability. Langmuir, 20(9):3517–3519, 2004.

### CITED LITERATURE (continued)

- Neinhuis, C. and Barthlott, W.: Characterization and distribution of water-repellent, selfcleaning plant surfaces. Annals of Botany, 79(6):667–677, 1997.
- Sun, M., Luo, C., Xu, L., Ji, H., Ouyang, Q., Yu, D., and Chen, Y.: Artificial lotus leaf by nanocasting. Langmuir, 21(19):8978–8981, 2005.
- Lau, K. K., Bico, J., Teo, K. B., Chhowalla, M., Amaratunga, G. A., Milne, W. I., McKinley, G. H., and Gleason, K. K.: Superhydrophobic carbon nanotube forests. <u>Nano</u> letters, 3(12):1701–1705, 2003.
- Das, A., Schutzius, T. M., Bayer, I. S., and Megaridis, C. M.: Superoleophobic and conductive carbon nanofiber/fluoropolymer composite films. <u>Carbon</u>, 50(3):1346– 1354, 2012.
- 16. Li, X.-M., Reinhoudt, D., and Crego-Calama, M.: What do we need for a superhydrophobic surface? a review on the recent progress in the preparation of superhydrophobic surfaces. Chemical Society Reviews, 36(8):1350–1368, 2007.
- Wong, T.-S., Kang, S. H., Tang, S. K., Smythe, E. J., Hatton, B. D., Grinthal, A., and Aizenberg, J.: Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity. Nature, 477(7365):443–447, 2011.
- De Gennes, P.-G., Brochard-Wyart, F., and Quéré, D.: <u>Capillarity and wetting</u> phenomena: drops, bubbles, pearls, waves. Springer Science & Business Media, 2004.
- 19. Wenzel, R. N.: Resistance of solid surfaces to wetting by water. Industrial & Engineering Chemistry, 28(8):988–994, 1936.
- 20. Cassie, A. and Baxter, S.: Wettability of porous surfaces. <u>Transactions of the Faraday</u> Society, 40:546–551, 1944.
- Boreyko, J. B., Srijanto, B. R., Nguyen, T. D., Vega, C., Fuentes-Cabrera, M., and Collier, C. P.: Dynamic defrosting on nanostructured superhydrophobic surfaces. <u>Langmuir</u>, 29:9516–9524, 2013.
- 22. Kim, P., Kreder, M. J., Alvarenga, J., and Aizenberg, J.: Hierarchical or Not ? Effect of the Length Scale and Hierarchy of the Surface Roughness on Omniphobicity of Lubricant-Infused Substrates USA 2 . School of Engineering and Applied Sciences , Harvard University, Cambridge, MA USA 3 . Department of Chemist. 2008.

#### CITED LITERATURE (continued)

- Piucco, R. O., Hermes, C. J. L., Melo, C., and Barbosa, J. R.: A study of frost nucleation on flat surfaces. Experimental Thermal and Fluid Science, 32:1710–1715, 2008.
- 24. Na, B. and Webb, R. L.: A fundamental understanding of factors affecting frost nucleation. International Journal of Heat and Mass Transfer, 46:3797–3808, 2003.
- 25. He, M., Wang, J., Li, H., and Song, Y.: Super-hydrophobic surfaces to condensed microdroplets at temperatures below the freezing point retard ice/frost formation. <u>Soft</u> Matter, 7:3993, 2011.
- Jung, S., Dorrestijn, M., Raps, D., Das, A., Megaridis, C. M., and Poulikakos, D.: Are superhydrophobic surfaces best for icephobicity? Langmuir, 27(6):3059–3066, 2011.
- Parent, O. and Ilinca, A.: Anti-icing and de-icing techniques for wind turbines: Critical review. Cold Regions Science and Technology, 65(1):88–96, 2011.
- 28. Gent, R. W., Dart, N. P., and Cansdale, J. T.: Aircraft icing, 2000.
- Castro, S., Davis, L. C., and Erickson, L. E.: Plant-enhanced remediation of glycol-based aircraft deicing fluids. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management, 5(3):141–152, 2001.
- Varanasi, K. K., Deng, T., Smith, J. D., Hsu, M., and Bhate, N.: Frost formation and ice adhesion on superhydrophobic surfaces. Applied Physics Letters, 97(2010), 2010.
- 31. Kim, P., Wong, T.-S., Alvarenga, J., Kreder, M. J., Adorno-Martinez, W. E., and Aizenberg, J.: Liquid-infused nanostructured surfaces with extreme anti-ice and anti-frost performance. Acs Nano, 6(8):6569–6577, 2012.
- Roach, P., Shirtcliffe, N. J., and Newton, M. I.: Progess in superhydrophobic surface development. Soft Matter, 4(2):224–240, 2008.
- 33. Sunden, B. and Wu, Z.: On icing and icing mitigation of wind turbine blades in cold climate. Journal of Energy Resources Technology, 2015.
- 34. Gray, V. H. and Von Glahn, U. H.: Aerodynamic effects caused by icing of an unswept NACA 65A004 airfoil. National Advisory Committee for Aeronautics, 1958.

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