Sol-gel derived icephobic coatings for large outdoor structures

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NANYANG
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**SOL-GEL DERIVED ICEPHOBIC COATINGS FOR
LARGE OUTDOOR STRUCTURES**

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School of Materials Science and Engineering

2016

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University in partial fulfilment of the requirement for
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List of Abbreviations

DI	Deionized
FAS	1H,1H,2H,2H-Perfluorodecyltriethoxysilane
MTEOS	Methyl triethoxysilane
GLYMO	3-glycidyloxypropyl trimethoxysilane
POSS	Polyhedral oligomeric silsesquioxanes
FPOSS	Trifluoropropyl POSS
FESEM	Field emission scanning electron microscope
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared spectroscopy
OWRK	Owens, Wendt, Rabel and Kalble

Abstract

Ice accretion possesses serious challenges for maintaining the operation and performance of large outdoor structures in cold climate. Icephobic materials have attracted much attention recently because they have demonstrated good promise in mitigating the problems. Superhydrophobic materials provide a viable option for the development of icephobic materials, as they have several advantages including slower heat transfer and lower sliding angle, which could potentially be exploited for decreasing the icing temperature, increasing the icing lag time, and reducing the ice adhesion strength, etc. However, based on the literatures, not all superhydrophobic materials show icephobic properties. The effect of surface energy, roughness, morphology and condensation should be carefully considered.

In this report, investigation of ice nucleation behaviour and ice adhesion has been presented. The commonly adopted anti-icing tests and materials system for anti-icing applications were summarized based on existing literatures. In order to investigate the effect of surface properties on icephobicity, several series of samples were prepared by mechanical grinding and spraying sol-gel coating. The surface energy, roughness, wettability at different temperatures, ice adhesion and icing temperatures were measured. It was found out that the intrinsic surface energy and surface morphology of the coatings play important roles together in terms of anti-icing performance. Not all superhydrophobic surfaces, as indicated by the water contact angle at room temperatures, could remain water repellent with reduced ice adhesion at low temperatures. The anti-icing performance are closely correlated with the surface properties at lower temperatures instead of that at room temperature. The two aspects of the anti-icing performance, i.e., ice adhesion and icing temperature, are not

necessarily correlated on rough surfaces because of the different mechanism for them. It depends on the size and surface energy of the added particles in the coatings. An optimized icephobic coating was achieved by a fluorinated sample F-16 which can maintain superhydrophobic at sub-zero temperatures.

The effect of different test environments on the icing behaviour of droplets on different samples was also investigated. It was found out that low humidity would lead to higher contact angle especially on hydrophobic or superhydrophobic surfaces that has a hydrophilic component. This would also lead to a decrease of icing temperature on these surfaces because of restrained condensation at the adjacent of the three-phase contact line. For those samples which are hydrophilic or intrinsically hydrophobic, the influence of humidity is not so much when cooling from the bottom of the water droplets. However, all the icing temperatures are lowered to a great extent by isothermal cooling without airflow in the environmental chamber because of humidity was lowered even further. When the droplets are exposed to shear airflow, the icing temperatures would be greatly increased because of the turbulence it causes. The trend of icing temperatures with airflow is that the higher the contact angle, the higher the icing temperature. When it comes to icing lag time, the repeatability and reliability of the measurement is strongly dependent on individual samples and the icing temperatures, and thus render it unsuitable for measurement in current study.

The icing temperatures of 10 μ L droplets on selected series of sol-gel coatings which cover a wide range of roughness, apparent surface energy, and different wetting modes at low temperatures were statistically investigated. The results are in good agreement with the wetting behaviour of the samples at low temperatures. Through analysis based on classical nucleation theory, the geometric factors were found out to be closely

related to the surface property and wetting mode. The pre-factors for the nucleation on the samples was found to be closely related to the geometric factors. For most samples, the lower the geometric factor, the lower the pre-factor. Our fitting results support the conclusion that the dominant heterogeneous nucleation sites in our study are not on the whole water-substrate interface, but mainly on the water-air-substrate three-phase contact line.

Finally, based on the investigation and conclusion from the study, a future work plan was proposed including a more thorough investigation on the effect of test environments on anti-icing performance, a more direct observation of the contact line nucleation, a field test for the icephobic coating, and the investigation of materials with precisely controlled surface properties.

Chapter 1 Introduction

1.1 Background

Ice accumulation can be a serious problem for the performance of outdoor structures, such as pavements [1], aircrafts [2, 3], ships [4, 5], locks and dams [6], offshore platforms [7], navigation and hydroelectric structures [8], wind turbines [9-14], solar panels [15], power lines [16-18], etc. It can either lower the performance of the devices, or lead to total dysfunction of the whole equipment and system and result in great disasters in some cases. For example, the power loss because of ice accretion on wind turbines can reach up to 50% of the annual power production [9]. The ice accumulation on power lines resulted from icy rain can cause the mechanical failure of the lines or collapse of power transmission towers, and resulted in serious electricity blackouts just like what happened in southern China In early 2008 [19]. The ice accumulation is also responsible for the crash of 135 planes between 1993 and 2004 in the United States as reported by Imse [20].

People have been trying to solve the ice accumulation problems for a long time. A lot of methods have been tried to cope with the ice accretion, including using heating systems, chemicals, flexible materials, special coatings, etc. However, most of them have their limitations. Heating systems such as electrical heating [21] or hot-bleed-air circulation systems [22], although considered to be an effective approach, are usually very energy consuming and may cause other problem such as electromagnetic disturbance in some cases [11, 23]. In some systems, an ice detector is utilized in order to reduce the energy consumption. However, the detection was proven to be not so reliable sometimes [24]. In recently years, microwave heating was also explored [25]

to tackle the ice accretion problem. But it has not been implemented successfully yet [9] given the truth that it requires the surface to be microwave reactive and the efficiency is still a problem.

Chemicals have been used for a long time to prevent ice accretion. One of the approaches is to apply substances such as NaCl to lower the freezing point of water. However, it is reported that 75%-90% added salt run off or splash into the roadside which is a big waste and hazard to the water creatures and plants near the roadside [26]. Besides, it may also cause corrosion problems to the reinforcing steel structures in some cases [27]. The other approach is to apply chemicals such as silicone grease to lower the ice adhesion on surfaces so the formed ice can be easily rip off by gravity. This kind of sacrificial coating is naturally less durable [28] and also has potential environmental problems. Both of the methods needs periodical supplement, has low efficiency, and are not environmental friendly, which render them being unsuitable for long term large scale applications.

In some other cases, flexible materials was adopted in order to shear off the ice by the shear stress between formed ice and substrate during deformation or vibration by external forces. But it is not well verified yet [29, 30] and obviously not applicable or practical for most cases. There are also some other methods developed in the past decades, such as black paint [31], active pitching [32], etc. They generally lack of efficiency, and may damage the underneath substrates sometimes [9].

On the contrary, the special coating method is a very promising way to deal with the ice problem since there is already a lot of progress in the research of this area, and it is easy to apply together with low cost and low maintenance requirement.

1.2 Motivation and problems

There is no surface that can really prevent water from forming ice if the temperature is low enough and the contact time is long enough. However, there is definitely something we can do to ameliorate the icing problem. For the design of an anti-icing coating, there are two main considerations. The first is to remove the water before it freezes on the surface. In this case, a superhydrophobic surface with low sliding angle or low contact angle hysteresis is preferred. It is reported that some such surfaces can efficiently delay the icing process [33-36] or lower the icing probability when water is poured onto the surface [37]. The second is to reduce the ice adhesion [38-41] to the substrate if ice forms on the surface, either shear stress or tensile stress.

A lot of effort has been made to develop anti-icing materials, and some progress has been achieved. However, there are still a lot of issues to be dealt with. The influencing factors of icing has not been well understood till date. There are arguments about the role of superhydrophobic materials since they do not always show better anti-icing performance. The effect of roughness and morphology of surfaces on icing behaviour is still not clearly understood. There have been no well-established standard anti-icing test methods yet, and the relevance between different test methods need further investigation. Finally, the mechanism of icing on different surfaces also needs more profound study. All these aspects are important for the developing of anti-icing materials, and thus is worth a comprehensive research on them.

1.3 Objectives

In my current project, the main focus is to investigate the behaviour and mechanism of icing on different surfaces, and to find, based on the sound understandings, suitable anti-icing coatings for large structure applications. The objectives would include:

1. Investigate the effect of surface properties including surface energy, roughness, morphology, etc. on the anti-icing performance of materials.
2. Investigate the effect of test environment on the icing behaviour on different surfaces, and find out the relevance of different test methods.
3. Investigate the mechanism of icing of water on different surfaces.
4. Develop a sol-gel coating which are economic, robust, and easy to apply on large outdoor structures.

Chapter 2 Literature Review

2.1 Fundamentals about ice formation and adhesion

There are two main aspects about the anti-icing performance of a surface. The first aspect is ice nucleation, and the other one is ice adhesion. A lot of work has been done to reveal the connection between different surfaces and the ice.

2.1.1 Ice nucleation

2.1.1.1 Homogeneous nucleation

Like any other nucleation process, ice formation follows the minimum energy principles. From classic nucleation theory, the free energy barrier for homogeneous nucleation is [42]:

$$\Delta G = \Delta G_V + \Delta G_S \quad (2.1)$$

where ΔG_V is the volume excess free energy, ΔG_S is the surface excess free energy. For homogeneous nucleation, the nucleus is supposed to be sphere since it has the least surface area for a given volume. Then Equation (2.1) becomes [42]

$$\Delta G^{\text{homo}} = \frac{4}{3}\pi r^3 \Delta g + 4\pi r^2 \sigma \quad (2.2)$$

where r is the radius of the nucleus, σ is the interfacial tension between water and ice, and $\Delta g = G_S - G_L = -\frac{\Delta H_m \cdot (T_m - T)}{T_m}$ is the unit volume free energy difference between ice and water by assuming that ΔH_m is invariant between real crystallization temperature T and equilibrium crystallization temperature T_m . The free energy change with the radius of the nucleus is shown in **Figure 2.1**.

Figure 2.1 Free energy diagram of nucleation.

The critical nucleus radius can be obtained by letting $\frac{d\Delta G}{dr} = 0$:

$$\frac{d\Delta G}{dr} = 8\pi r\sigma + 4\pi r^2\Delta g = 0 \quad (2.3)$$

Therefore

$$r_c = \frac{-2\sigma}{\Delta g} \quad (2.4)$$

And the critical free energy change is

$$\Delta G_c = \frac{16\pi\sigma^3}{3(\Delta g)^2} = \frac{4\pi r_c^2\sigma}{3} \quad (2.5)$$

The nucleation rate I , which stands for the number of nuclei formed per unit time and per unit volume, can be expressed in an Arrhenius-type equation as [43, 44]:

$$I = Je^{-\Delta G/kT} \quad (2.6)$$

where k is Boltzmann constant; J is the pre-exponential factor accounting for the rate at which the molecules impinge upon and are incorporated into the critical nuclei, and it can be consider as nearly a constant which is typically $10^{15}\sim 10^{30} \text{ cm}^{-3}\text{s}^{-1}$. The

accuracy of J is not so important as I is greatly influenced by the value of $-\Delta G/kT$ [45].

The change of the nucleation rate with the supersaturation or supercooling is shown in **Figure 2.2**. It can be seen that the nucleation rate I remains negligibly small until the supersaturation or supercooling reaches a critical value, the Ostwald metastable limit, at which point I suddenly and dramatically increases. Hence, the onset crystallization temperature, T_c , can be identified with this metastable limit, and the corresponding nucleation rate can be set, with little loss in accuracy, to a suitable detection limit for the technique monitoring the crystallization [46]. In many experiments, the critical supersaturation is defined as the supersaturation that leads to a nucleation rate J equal to $1 \text{ nucleus cm}^{-3}\text{s}^{-1}$ [47, 48].

Figure 2.2 Schematic graph of nucleation rate showing the Ostwald metastable limit which gives the onset crystallization temperature T_c . Adapted from Ref. [46]. © 2012 Cooper S, Cook O, Loines N. Published in Ref. [46] under CC BY 3.0 license. Available from: <http://dx.doi.org/10.5772/47977>.

2.1.1.2 Heterogeneous nucleation

For heterogeneous nucleation, the free energy barrier is decreased by a geometric factor $f(\theta)$.

$$\Delta G = \Delta G^{\text{homo}} \cdot f(\theta) \quad (2.7)$$

For flat surfaces, it is only related to the ice contact angel θ as shown in **Figure 2.3**.

Figure 2.3 Schematic of contact angel

The geometric factor can be expressed as:

$$f(\theta) = \frac{1}{4} (2 + \cos\theta)(1 - \cos\theta)^2 \quad (2.8)$$

The change of geometric factor with contact angle are shown in **Figure 2.4**.

Figure 2.4 Geometric factor versus contact angle on flat surfaces.

Equation (2.8) is based on the assumption that the surface is perfectly clean and flat, and of course it's usually not the case in real life. In order to investigate the effect of the surface geometry on the free energy barrier of nucleation, the concave and convex

surfaces as shown in **Figure 2.5** are considered and investigated by several authors [48-51].

Figure 2.5 Schematic diagram describing nucleation on (a) convex and (b) concave surfaces of radius R . Reprinted with permission from Ref. [50]. Copyright 2008 by AIP Publishing LLC.

In this case, the critical nuclei radius turned out to be the same as homogeneous nucleation as shown in Equation (2.4), and the free energy barrier for the nucleation is [49]:

$$\Delta G = \Delta G^{\text{homo}} \cdot g(R, \theta) \quad (2.9)$$

$$g(R, \theta) = \frac{1}{2} \left[1 - \cos^3(\phi + \theta) - \frac{3\cos\theta\sin^2(\phi + \theta)}{1 + \cos\phi} + \frac{(2 - 3\cos\phi + \cos^3\phi)\sin^3(\phi + \theta)}{\sin^3\phi} \right] \quad (2.10)$$

$$\phi = \arccot \left(\frac{\frac{R}{r_c} - \cos\theta}{\sin\theta} \right) \quad (2.11)$$

where θ is the contact angle between the nucleus and the spherical substrate, ϕ is the angle between the spherical substrate and the plane connecting the nucleus edge as shown in **Figure 2.5**. Equation (2.9)-(2.11) apply to nucleation on both convex and concave ($R, \phi < 0$) surfaces [50]. Equation (2.10) can also be expressed in another form as shown in Equation (2.12) in order to study the contribution of varying θ with a fixed value of R [49].

$$g(R, \theta) = \frac{1}{2} \left[1 - \cos^3(\phi + \theta) - 3 \left(\frac{R}{r_c} \right)^2 \cos\theta (1 - \cos\phi) + \left(\frac{R}{r_c} \right)^3 (2 - 3\cos\phi + \cos^3\phi) \right] \quad (2.12)$$

The relationship between $g(R, \theta)$, R/r_c and θ is shown in **Figure 2.6**.

Figure 2.6 Relationship between $g(R, \theta)$, R/r_c , and θ . Reprinted with permission from Ref. [49]. Copyright 2005 by American Physical Society.

As can be seen in **Figure 2.6b**, $g(R, \theta)$ always changes from 1 to 0 with a very stiff decrease at the beginning of the curve when R/r_c is small. For a given R/r_c , $g(R, \theta)$ is larger when θ is higher. An interesting result is observed in **Figure 2.6c** that not like nucleation on a planar surface in which the free energy barrier always tends to 0 while θ tends to 0, $g(R, \theta)$ only tends to 0 when $R/r_c \geq 1$, and $g(R, 0) = 1 - 3 \left(\frac{R}{r_c} \right)^2 +$

$2\left(\frac{R}{r_c}\right)^3$ as determined by Equations (2.10) and (2.12). The smaller the ratio R/r_c , the closer $g(R, 0)$ is to 1 which means closer to homogeneous nucleation. When R/r_c is larger than 5, $g(R, \theta)$ does not change much with further increase of R/r_c . The curve is already very close to the curve shown in **Figure 2.4** which is the case when R approaches infinity. In summary, smaller particle size and higher intrinsic contact angle are favourable for larger free energy barrier, and thus lower icing temperature.

Cooper et al. [50] developed the equations applied on curve surfaces by adopting θ_p which is the angle between the corresponding planar critical nucleus and the plane tangential to the curved substrate surface, as shown in **Figure 2.5**, and the free energy barrier can be expressed as:

$$\Delta G = \Delta G^{\text{homo}} \cdot f(\theta_p) \quad (2.13)$$

where $f(\theta_p)$ is the heterogeneous nucleation factor like $g(R, \theta)$ in Equation (2.9). The calculated $f(\theta_p)$ and the onset nucleation temperature are shown in **Figure 2.7**. It is clearly shown that nucleation on a concave surface is easier than on a convex one with the same contact angle, and the difference is greater with a smaller R .

Figure 2.7 The calculated (a) heterogeneous nucleation factor $f(\theta_p)$ and (b) onset nucleation temperature on curve surfaces with different contact angles. Negative and positive R values relate to nucleation on concave and convex substrates, respectively. Reprinted with permission from Ref. [50]. Copyright 2008 by AIP Publishing LLC.

Chakraverty et al. [52] and Sholl et al. [53] investigated the nucleation of liquid from vapour on surface steps as shown in **Figure 2.8**. Although the results are for vapour-liquid cases, they can be easily extended to nucleation of crystal from liquid [54].

Figure 2.8 Nucleus with contact angle α on a step of angle η . Reprinted with permission from Ref. [53]. Copyright 1970 by Elsevier.

In this case, the critical nucleus radius is in the same form as in Equation (2.4). The free energy barrier for nucleation can be expressed as:

$$\Delta G = \frac{16\pi\sigma^3}{3(\Delta g)^2} \cdot F'(\eta, \alpha) = \frac{16\pi\sigma^3}{3(\Delta g)^2} \cdot \frac{1}{4} F(\eta, \alpha) \quad (2.14)$$

where

$$F(\eta, \alpha) = \frac{1}{\pi} \left[\cos \alpha \sin^2 \alpha \sin \psi - \cos \alpha (3 - \cos^2 \alpha) \psi + 4 \sin^{-1} \left(\sin \frac{\psi}{2} \sin \frac{\eta}{2} \right) \right] \quad (2.15)$$

The meaning of symbols of α , η and ψ are shown in **Figure 2.9**.

Figure 2.9 Geometry used in evaluating $F(\eta, \alpha)$. Reprinted with permission from Ref. [53]. Copyright 1970 by Elsevier.

The dependence of geometric factor on the values of η and α are summarized in **Table 2.1** and **Figure 2.10**.

Table 2.1 Summarization of different situations of η and α . Reprinted with permission from Ref. [53]. Copyright 1970 by Elsevier.

Conditions on η and α	Replace $F(\eta, \alpha)$ by	Physical situation
$0 \leq \eta \leq \pi, 2\alpha \leq \pi - \eta$	Unstable	Figure 2.10 (a)
$0 \leq \eta \leq \pi, \pi - \eta \leq 2\alpha \leq \pi + \eta$	$F(\eta, \alpha)$	Figure 2.10 (b)
$0 \leq \eta \leq \pi, \pi + \eta \leq 2\alpha \leq 2\pi$	$4 - 2K(\pi - \alpha)^*$	Figure 2.10 (c)
$\pi \leq \eta \leq 2\pi, 2\alpha \leq 3\pi - \eta$	Unstable	Figure 2.10 (d)
$\pi \leq \eta \leq 2\pi, \eta - \pi \leq 2\alpha \leq 3\pi - \eta$	$4 - F(2\pi - \eta, \pi - \alpha)$	Figure 2.10 (e)
$\pi \leq \eta \leq 2\pi, 2\alpha \leq \eta - \pi$	$K(\alpha)^*$	Figure 2.10 (f)

* $K(\theta) = F(\pi, \theta)$

Figure 2.10 Physical situations corresponding to entries in **Table 2.1**. Reprinted with permission from Ref [53]. Copyright 1970 by Elsevier.

The values of the geometric factor $F(\eta, \alpha)$ with different angles of steps are displayed as in **Figure 2.11**. It is clearly shown that the smaller the value of η and contact angle, the smaller the geometric factor.

Figure 2.11 $F(\eta, \alpha)$ as a function of contact angle for representative steps. Reprinted with permission from Ref. [53]. Copyright 1970 by Elsevier.

2.1.1.3 Dynamic nucleation

Dynamic nucleation is an important aspect in anti-icing research as one great advantage of superhydrophobic surfaces is the ability to enable the droplet to slip off the surface before it freezes. It is used as one of the criteria of effective anti-icing performance of tested materials in some papers [55-58]. Bahadur et al. [59] established a model to predict the dynamic ice formation on superhydrophobic surfaces as shown in **Figure 2.12**, **Figure 2.13** and **Figure 2.14**.

Figure 2.12 Images of different stages of a 15 μL water droplet impacting a superhydrophobic surface from a height of 10 cm. r is the radius of the contact area between water droplet and substrate during the spreading and retracting process. The maximum spreading radius before retraction is denoted as r_{max} . The inset images are superhydrophobic surfaces with different microstructures (scale bar = 10 μm). Reprinted with permission from Ref. [59]. Copyright 2011 by American Chemical Society.

Figure 2.13 Model for predicting heat transfer from the droplet to the superhydrophobic surface through the thermal resistance imposed by the posts and the air beneath the droplet. The image is not to scale. Reprinted with permission from Ref. [59]. Copyright 2011 by American Chemical Society.

Figure 2.14 Schematic of the formation and propagation of ice nuclei as hemispherical caps on the posts. Reprinted with permission from Ref. [59]. Copyright 2011 by American Chemical Society.

The fundamental theory of ice nucleation is the same as described earlier. The difference is more factors are needed to be considered, such as the velocity and temperature of the droplet, the surface temperature and the heat transfer between surface and droplet. Based on the heat transfer model shown in **Figure 2.13**, the interface temperature can be expressed as [59]:

$$T_{\text{interface}}(t_c) = T_{\text{droplet}} + (T_{\text{substrate}} - T_{\text{droplet}}) \frac{\text{erfc}\left(\frac{h}{2\sqrt{\alpha_{\text{ns}} t_c}}\right)}{\text{erfc}\left(\frac{h}{2\sqrt{\alpha_w t_c}}\right)} \quad (2.16) \text{ where } t_c \text{ is}$$

the total time of liquid contact at a particular radial position (spreading and retraction); α_{ns} and α_w are the thermal diffusivities of the postair domain (volume-averaged properties of the post material and air) and water, respectively; erfc denotes the complementary error function.

Based on the ice formation model shown in **Figure 2.14**, the relationship between contact line position R (defined as r/r_{max}) and retraction time can be expressed as

$$\frac{d^2 R}{dt^2} + (1 - C\phi_0 e^{f(T_{\text{interface}})} t_c^2) R = 0 \quad (2.17)$$

where

$$t = \frac{t_r}{\sqrt{\frac{m_0}{4\pi\gamma}}} \quad (2.18)$$

$$C = \pi J \left(4\alpha_{\text{ice}} \frac{C_{p_{\text{ice}}}}{2H_{\text{SL}}} (T_{\text{slf}} - T_{\text{sub}}) \left[1 + \frac{k_w}{k_{\text{ice}}} \sqrt{\frac{\alpha_w}{\alpha_{\text{ice}}}} \frac{(T_{\text{slf}} - T_{\text{droplet}})}{(T_{\text{slf}} - T_{\text{sub}})} \right] \right) \quad (2.19)$$

$$\phi_0 = \frac{\pi d^2}{4l^2} \quad (2.20)$$

$$f(T_{\text{interface}}) = -\frac{16s\pi\gamma_{\text{SL}}^3 T_{\text{slf}}^2}{3kH_{\text{SL}}^2 (T_{\text{slf}} - T_{\text{interface}})^2 T_{\text{interface}}} s(\theta_c) \quad (2.21)$$

where t_r is the retraction time; m_0 is the droplet mass; γ is the liquid surface tension; J is the pre-factor for nucleation; $C_{p_{\text{ice}}}$ is the specific heat capacity of ice; k is the Boltzmann's constant; H_{SL} is the latent heat of freezing; T_{slf} is the temperature of the freezing front; k_w and k_{ice} are the thermal conductivities of water and ice respectively; α_w and α_{ice} are the thermal diffusivities of water and ice respectively; d is the diameter of the circular posts; l is the square pitch; γ_{SL} is the ice-water interfacial energy, H_{SL} is the latent heat of freezing, θ_c is the contact angle of ice on a flat surface,

$S(\theta_c)$ is the geometric factor for heterogeneous nucleation, which is as same as $f(\theta)$ in Equation (2.8).

The model predicts the existence of a critical substrate temperature of the substrate below which liquid droplets will freeze upon impact, and fits well with the experiments results. This critical temperature depends on the surface morphology, surface chemistry, and thermal properties of the substrate and the liquid. It is also concluded from Equation (2.16) that the interface temperature is dominated by the substrate temperature and shows a weak dependence on the initial droplet temperature.

2.1.1.4 Other factors

There are some other factors that may affect the ice nucleation behaviour, such as the electric field [60], agitation [42], flow of surrounding gas (both its velocity and humidity) [61], droplet size and cooling speed [62], other different modes of ice nucleation [63, 64] and nucleation from vapour [54, 65]. But they are either not practically useful, or mainly for the investigation of ice nucleation in clouds. Thus they are not a main concern in this work.

2.1.2 Ice adhesion

Ice adhesion is an important aspect with respect to the anti-icing performance of a material since no material can actually prevent the ice formation on its surface if the temperature is low enough. Adhesion is a complicated matter since it's related to several aspects, such as electrostatic forces, hydrogen bonding, van der Waals forces, mechanical forces, liquid-like layer at the ice-substrate interface and microstructure of ice etc. A summary was given by Menini [66].

Electrostatic force theory is based on Coulomb's law. It occurs between two materials which are charged. Petrenko et al. [67] investigated the electrostatic interaction between ice and dielectric materials based on Jacard theory. The ice surface may be charged because of the protonic defects on the surface, and thus form a surface electric field and it will cause an image charge on the contacting material. The image charge caused on an insulator surface would be smaller than on a metal surface. The corresponding force or image force is described as follow:

$$F = \frac{q^2}{16\pi\epsilon_0\epsilon r^2} \frac{\epsilon_{ice}-\epsilon}{\epsilon_{ice}+\epsilon} \quad (2.22)$$

where q is the charge of ice; r is the distance to the interface; ϵ_{ice} , ϵ and ϵ_0 are the dielectric constant of ice, substrate and the free space, respectively. The lower the value of ϵ , the lower the electrostatic force. This may be related to the surface tension as well since lower surface tension leads to lower ice adhesion. The surface tension has a good correlation with dielectric constants as demonstrated by Papazian [68] and Holmes [69] although their results only apply to dielectric liquids.

Van der Waals force is a universal phenomenon and it's related to the molecules weight of the substrate. It plays certain role in the ice adhesion. However, as reported by Wilen et al. [70] and Vanoss et al. [71], the van de Waals forces between ice and several metals and insulators are less than the force caused by hydrogen bonding. Petrenko et al. [72] found a great correlation between the degree of hydrogen bonding and the ice adhesion.

Mechanical force exists mainly on those rough surfaces as there will be a kind of anchor effect between the ice and the rough surface [39, 73-82]. As discussed earlier, superhydrophobic surfaces has a rough microstructure, and the surface cannot always maintain superhydrophobic at low temperature because of vapour condensation or

impinging of droplet into the microstructure. Besides, water expands on freezing. Consequently, the mechanical force is significant. In contrast, if the surface can prevent the water from penetrate into the microstructure, the expansion of water would be an advantage for removing the ice because the pressure of the entrapped air would be higher than the atmosphere. However, the robustness of such surface is essential to maintain the icephobic performance. As reported by Kulinich et al [83], the ice adhesion on superhydrophobic surfaces increases after each icing/de-icing circle because the microstructure which enable the surface to be superhydrophobic is damaged, and eventually the ice adhesion on the damaged surface can be even higher than untreated ones because of the anchor effect.

The mechanical force is also related to the liquid-like layer in the interface. The liquid-like layer is well accepted and proven by several authors [67, 70, 84-94]. The thickness of the layer can be up to hundreds of nanometers. It plays an important role in ice adhesion in a practical view, and it has been proven that the nanoscale interfacial water has a much higher viscosity than bulk water especially between hydrophilic surfaces [95]. However, there is no clear clue about how much it will change the wetting behaviour of the surface, or how much contribution it has to the ice adhesion [91].

In contrast, the effect of microstructure of ice on ice adhesion is clearer. It was found that the ice adhesion is lower with a bigger crystal size, and there will usually be a thin film left after the ice is removed because the crystal size of ice which directly contacts the surface is smaller.

2.2 Test methods

Currently there is no standard test method established for anti-icing performance. However, several test procedures have been developed by different authors according to different anti-icing properties, including ice adhesion, icing probability, icing delay and ice accumulation tests.

2.2.1 Ice adhesion test

Ice adhesion tests are one of the mostly adopted test methods to characterize the anti-icing performance of materials. Either shear force or tensile force strength between ice and substrate have been reported. Various equipment and devices are developed by different authors, and most of them are about shear stress measurement because of its relative convenience to set up.

For the shear stress test, the mechanical force needed to remove the ice from the surface is usually generated by relative linear displacement between the force gauge and the ice block [38-41, 81, 96-100]. It is the easiest and most effective way to carry out the measurement. Another relatively well accepted method is to use the centrifugal force to detach ice pre-formed in the end of a rotating beam [83, 97, 101-107]. In addition, there are some other rarely reported methods developed by several groups, such as the torque test [72], modified pendulum impact test [107], bending vibration test [80, 108-110], and the nano-scale ice adhesion test conducted in a scanning probe microscope [111, 112].

There are not many reports about the tensile stress test between ice and the substrate because it is not as convenient as the shear stress test. The most obvious way to measure the tensile stress is to utilize a similar device as for metals tensile testing as done by Yang et al. [39] and Zhu et al. [113]. Another procedure is established by

Andrews et al. [114, 115] to utilize the gas pressure to measure the ice adhesion on a flexible surface. It is not suitable for most materials because it needs to dig a hole in the center of the sample. Unlike applying direct mechanical force or pressure, Somlo et al. [116] and Archer et al. [74] utilized laser-generated stress wave as the source of force, and successfully measured the tensile stress between aluminum alloy and ice. It requires special devices for the measurement and thus it is not widely adopted.

2.2.2 Icing probability test

Icing probability test is another useful way to judge the anti-icing performance of the surface. However, it is not commonly used mainly because of the more stringent requirement for the anti-icing performance of the samples.

The concept of ice probability test was first proposed by Cao et al. [37]. In their experiment, super cooled water was poured onto tilted samples. Observation was made on whether or not ice forms on the sample. The experiment was repeated 20 times on each sample and the icing probability for each sample was determined by dividing the number of experiments when icing occurred by the total number of experiments.

Some other authors [56, 58] used a similar test procedure to investigate the anti-icing performance of superhydrophobic surfaces. The difference is that instead of large amount of water, small water droplets were dropped to the sub-zero surfaces. By contacting the surface, the droplets may bounce off the surface and thus no ice would form on the surface.

Another kind of freezing probability test was conducted by Li et al. [117]. In his experiment, a large number of water micro droplets were formed on the sample surface and became ice when the temperature continually decreased at a certain speed.

The number of nucleation events in each temperature bin were different for different surfaces, and so is the freezing probability distribution.

2.2.3 Icing delay test

Icing delay is one of the important properties of an anti-icing surface as it gives a good indication of the time allowed for the water droplet to slide away before it freezes on the surface in practical situations.

In this kind of tests, the surface temperatures are usually maintained below zero degree. But the water droplets that are in contact with the surface can have a diverse form. It can be either of room temperature [33, 118, 119] or super cooled [120], either big droplets [33, 34, 118, 119, 121, 122], even bulk water [123-125] or micro droplets [120], either formed by deposition [33, 34] or condensation of vapour [36, 126]. Most of the procedures adopted have too many uncontrolled degree of freedom, such as the droplet size, contact condition, humidity, impurities etc. This makes the comparison of the results from different authors difficult. And as reported by Barlow [127], the delayed time of freezing could be more than a few days under a sub-zero degree condition, while most other authors obtained a narrower range of delay time. So this kind of experiment needs further investigation.

2.2.4 Icing temperature test

It has been proven that the icing temperature of water is different on different surfaces. It would be a great advantage for anti-icing performance if a surface can hinder the nucleation of ice to certain extent, although no surface can completely prevent the ice formation when the temperature is low enough. In this kind of test, water is usually dropped onto the surface first, then the temperature would be decreased at certain

speed till the water freezes. Usually the cooling stage from room temperature to zero degree is considered to be unimportant for the test. The detection of ice formation can be done by eye inspection [34, 128], DSC [48], infrared thermometer [119] or laser [127, 129-131].

In order to investigate the nucleation rate of ice, usually a lot of crystallization events are recorded in an experiment either by repeated cooling of a single droplet or bulk water, or by cooling a group of micro droplets and recording the fraction of frozen droplets at different temperatures. For the comparison purpose between different samples, either the average crystallization temperature can be used like in Ref. [129], or the normalized distribution of the nucleation temperature are used as in Ref. [117]. It should be noted that the crystallization temperature is related to the volume (size) and the purity of the droplet [132]. The smaller the volume and the purer the water, the lower the crystallization temperature.

2.2.5 Ice accumulation test

Ice accumulation test is a test method which is closer to what occurs in a natural environment. It usually involves an artificial climate chamber [34, 39, 133] or wind tunnel [57, 134, 135] to simulate the natural situation. The temperature, humidity, liquid composition, flow rate, tilting angle of the sample, and the sputtering distance, etc. can all be adjusted according to specific requirements.

2.3 Materials property requirement and coating systems

2.3.1 Does superhydrophobicity promise icephobicity?

Varieties of coatings, ranging from superhydrophilic to superhydrophobic ones, have been tested and compared for the anti-icing performance. Some [33, 36, 39, 72, 81, 97,

119, 136, 137] showed good correlation between superhydrophobicity and icephobicity, while others [37, 77, 138-141] did not. This may be resulted from different test procedures some of which lack consideration of vapour condensation at low temperature and thus did not reveal the underlying principle.

Some authors [37, 142] tried to correlate the water contact angle obtained at room temperature directly with the anti-icing performance. This is not proper because of several reasons. Firstly, it was reported that high water contact angle may not maintain at lower temperatures because of vapour condensation and thus may change the surface wettability [138-141]. Secondly, receding angle or contact angle hysteresis is a more important parameter for anti-icing performance as proved by Kulinich [83, 102, 103] and Meuler [41]. Receding angle and contact angle hysteresis are also closely related to the wetting mode of the surface. Low sliding angle or contact angle hysteresis means it is a Cassie-Baxter state in which air gaps exist between the water droplets and the surface to reduce the real contact area, while higher sliding angles are indicative of the Wenzel state in which the water droplets penetrate into the asperities and stick to the surface. Obviously the Wenzel state would lead to a much larger real ice-surface contact area and have a kind of anchor effect for the rough surface. Therefore, the ice adhesion on such surface would be much larger than that on the Cassie-Baxter state surface, and sometimes it is even larger than on an untreated smooth surface. It has been proven that vapour condensation may change the wetting mode of the superhydrophobic surface from Cassie-Baxter to Wenzel or mixed mode [34, 139, 140]. Moreover, good correlation between superhydrophobicity and icephobicity was obtained by a procedure in which the vapour condensation was somehow avoided [33, 41, 56, 119]. Therefore, it's not proper to judge the icephobic property of a surface purely by the water repellent property at room temperature.

Instead, their surface water repellent property and the receding or hysteresis angle at lower temperature should be considered and investigated.

However, it seems that not all surfaces would be affected by water vapour condensation at low temperatures. With proper roughness, the surface may maintain the superhydrophobicity when the surface temperature approaches the dew-point [36, 143] or below zero degree [57, 134]. Besides, superhydrophobic surfaces have a big advantage for anti-icing purpose, because an impact droplet may bounce off from the surface, as reported by Mishchenko [56] and Zheng [58]. With this property, the water droplets can easily jump away from the surface before they freeze. A superhydrophobic surface is also supposed to decrease the heat transfer and affect the nucleation of the ice between the water droplets because of the air trapped between them [33, 36, 56, 61].

For hydrophilic surfaces, there is no advantage for preventing heat transfer because the water is closely contained on the surface. And a superhydrophilic surface, which is characterized by a rough surface and high surface energy, was proven to have the least icing delay property [34]. Thus it is not suitable for icephobic application. However, a surface with roughness close to or smaller than the critical nucleus radius of ice seems to delay the freezing significantly because the heterogeneous nucleation is more difficult on smooth and clean surfaces [34, 120, 144]. But its effect on the nucleation seems not as big as the trapped air because some rough superhydrophobic surfaces are proven to have better anti-icing performance than smooth raw materials. Besides, water mobility on hydrophilic surfaces is low, and once the ice is formed on the smooth surface, the ice adhesion is supposed to be much higher than that formed on superhydrophobic surfaces because the contact area is much larger.

In summary, a superhydrophobic surface with Cassie-Baxter wetting state is supposed to have the best anti-icing performance, while in many cases, the vapour condensation would change its wetting state. Therefore, a more comprehensive investigation at lower temperature for superhydrophobic surface needs to be conducted in terms of its icephobic properties.

2.3.2 Effects of surface energy on the icephobicity of surfaces

Based on the above analysis, it is clear that surface energy and morphology play an important role in the icephobicity of a surface. Many experiments have been carried out by different authors to investigate their effects on the icephobicity of surfaces, and surface energy has a relatively simple influence on the anti-icing performance.

Meuler et al. [41] tested the ice adhesion strength on smooth surfaces (Wenzel roughness ratio $r < 1.01$) coated with a thin film (200~300 nm) with different surface energy. A good correlation was found between ice adhesion and the practical work of adhesion scaling parameter $[1 + \cos\theta_{\text{rec}}]$, in which θ_{rec} is the receding angle of the water droplet and only related to the surface energy in this case. Zou et al. [38] reported similar results that for similar rough surfaces, the lower the surface energy, the lower ice adhesion to the surface. Somlo et al. [116] coated polished aluminium alloy with a self-assembled monolayer of dimethyl-n-octadecylchlorosilane and found that ice adhesion was greatly decreased compared to the uncoated one. Petrenko et al. [72] prepared samples with different surface energy via deposition of self-assembled monolayers with varying degree of hydrophobicity/hydrophilicity by mixing the hydrophobic and hydrophilic components. The results showed that the ice adhesion on surfaces with lower contact angle was higher. Na et al. [144] investigated the formation of frost on samples with different surface energy, and proved that a low

energy surface requires 10 times higher degree of supersaturation for frost nucleation than a high energy surface. Li et al. [117] investigated the icing probability on smooth silicon wafer and FAS modified silicon wafer, and found the maximum freezing probability density on coated sample is 0.4 °C lower than uncoated one.

There are some other authors [104, 145] who investigated the anti-icing performance on surfaces with different surface energy. But the experiments did not specifically consider the effect of roughness, and thus the results need further investigation. However, it is clearly demonstrated by those authentic reports that lower surface energy is preferred for icephobicity no matter whether the surface is smooth or rough.

2.3.3 Effect of surface roughness/morphology on icephobicity of surfaces

The effect of surface roughness on the anti-icing performance is complicated since it is related to the wetting mode of the surface and the nucleation of the ice as discussed earlier.

As for the wetting mode, it is hard to directly correlate the roughness with wetting behaviour because of the complexity of the surface morphology, and it's also related to the velocity of water droplet when contacting the surface. Usually most of the superhydrophobic surfaces would lose its hydrophobicity because of vapour condensation when the temperature decreases [139, 140, 146-152]. Only a few papers reported by He et al. [36, 143] showed some samples remaining superhydrophobic even with the condensation of vapour. In ref. [143], it was found that surfaces with area fractions equal to or smaller than 0.068 maintain the superhydrophobicity when the surface temperature approaches the dew-point. In Ref. [36], the contact angle of condensed water was found to be larger than 150°. However, no sliding angle or the wetting mode was revealed in these two papers, and thus their anti-icing performance

is still questionable. Wang et al. [134] claimed to have prepared an aluminium sample which can retain superhydrophobic even at $-10\text{ }^{\circ}\text{C}$ in the chamber. But no humidity data were provided and the condensation can be actually avoided to some extent in a chamber. So its superhydrophobicity in natural environment needs further investigation.

As for the effect of surface morphology on the nucleation of ice, there are several aspects that need to be considered. First of all, heterogeneous nucleation is more difficult on smooth and clean surfaces. Thus smooth surfaces tend to have longer icing delay time or lower icing temperature than rough surfaces [34, 120, 144]. Secondly, it is much easier for liquid to crystallize on a concave surface than a convex one. The ice formation process on a rough surface is affected by the nano-scale asperity. And it is reported that some rough surfaces can affect the structure or strength of the formed ice so that the ice can be detached very easily from the surface. Thirdly, for a superhydrophobic surface with Cassie-Baxter wetting state, the trapped air between the water and surface is a barrier for heat transfer, thus it is an advantage to delay the freezing process. The final anti-icing performance of the surface is a result of competition of these factors. It is notable that many authors [38, 80, 120] did not consider the wetting mode at low temperature and stated that superhydrophobic surfaces have adverse effect on anti-icing performance, and therefore their results need further investigation. It has been proven that some superhydrophobic surfaces would lead to favourable anti-icing performance [33, 36, 39, 81].

The morphology of surface has significant effect on the anti-icing performance when the water droplet impinge the surface. As reported by Mishchenko et al. [56], superhydrophobic surfaces with structure of narrowly-spaced nanoposts and closed-

cell geometries would remain superhydrophobic and repel the droplets, while widely spaced nanoposts would fail to prevent the ice accumulation on the surface although they could maintain a higher contact angle. The anti-icing performance of blades structure would depend on its orientation. Deng et al. [55] investigated the non-wetting surfaces to impacting droplets by calculation of effective water hammer pressure, and pointed out that surface textures with sub-100-nm structures is essential to avoid possible wetting or partial wetting of the droplets after impingement. Although the theory is investigated under room temperature, it does shed some light on the future study on icephobic surfaces.

In summary, surface roughness and morphology has a complicated effect on the anti-icing performance of materials. For hydrophilic surfaces, the smoother the surface is, the smaller the ice adhesion. For hydrophobic surfaces, the wetting mode at low temperatures and the morphology needs to be considered when it comes to the investigation of icephobicity of the surfaces.

2.3.4 Hydrophilic icephobic coatings

Recently, a new type of icephobic coating was developed by Chen [153, 154] and Dou [155]. Instead of making a hydrophobic or superhydrophobic coating, they prepared smooth hydrophilic coatings which possess the ability to absorb the moisture from humid environments or melt the formed ice or snow on it. Then the hydrophilic pendant groups in the coatings ionize in the water and generate an aqueous lubricating layer between the ice and substrate. This thin water layer can stand till around -25 °C. This kind of coatings were reported to have outstanding low ice adhesion, good durability and promising application on different substrates. However, there is no field test report about the coatings yet. Their practical applications needs further

investigation due to the hydrophilic nature of the coatings which may compromise the icephobicity upon contamination in natural environment.

2.4 Icephobic coatings

Generally, the materials system for icephobic purpose does not have much difference from that for superhydrophobic surfaces. Free surface energy and roughness are always the two key considerations in the design of an icephobic surface. And a lot of icephobic surfaces have been fabricated in different ways.

According to the literatures, one of the most common ways to obtain an icephobic surface is to decorate a rough surface with low surface energy materials, and rough surface can be gained by varieties of ways. Mishchenko et al. [56] fabricated a rough surface with different patterns and then change the surface energy with a hydrophobic silane coating. The surfaces can delay the freezing process and enable the water slide off the surface before it freezes. Wang et al. [134] produced a rough surface on the aluminium samples by chemical etching and then treated the etched sample with stearic acid. He found that the coated superhydrophobic surface retained its water repellent property at $-10\text{ }^{\circ}\text{C}$ and have a much better icephobic performance than hydrophobic RTVSR coated surface. Antonini et al. [57] coated the etched aluminium with Teflon to achieve a very good icephobic surface, which greatly reduced the ice adhesion and changed the ice structure to facilitate the ice breaking. Menini et al. [105, 106] prepared porous aluminium surface by anodization followed by a strong adhesive PTFE coating. The resulting surface is not superhydrophobic, but it reduced the ice adhesion by almost 2.5 times compared to uncoated ones. Jafari et al. [101] used similar procedure to produce the porous structure, but decorated the surface with Teflon via a RF plasma-sputtering process. The resulting surface was

superhydrophobic, and showed 3.5 times lower ice adhesion strength than the uncoated surface. He et al. [36] made an icephobic coating on glass substrate via low-temperature chemical bath deposition of ZnO nanorods followed by surface modification of heptadecafluoro-1,1,2,2-tetradecyl trimethoxysilane. The surface maintained superhydrophobic state at temperatures below 0 °C, which has retarded the freezing process significantly. Ge et al. [156] prepared a superhydrophobic surface by further roughen the octadecyltrichlorosilane film deposited on the sample surface with phase separation procedure, and it led to less ice adhesion and retarded icing process.

There are some other ways reported to successfully prepare an icephobic surface. Cao et al. [37] obtained anti-icing superhydrophobic coatings on Al plates by spraying nanoparticle / polymer binder composites. The coatings with particles size of 20 nm and 50 nm could inhibit the ice formation on the surface when super cooled water was poured to the tilted samples. Zhao et al. [133] fabricated an icephobic hierarchical coating by simply spraying PDMS/nano-silica hybrid onto the surface and the coated sample passed the ice accumulation test. Momen et al. [35] prepared a superhydrophobic coating in one step by spray-coating a silicone rubber / stearic acid mixture on a flat surface, and the surface was proven to retard water freezing greatly. Zheng et al. [58] presented an superhydrophobic coating by depositing acetone-treated single-walled nanotubes on glass substrates, and the coating showed a strong ability to mitigate ice accretion from super cooled water droplets when the droplets were found to bounce off the films tilted at 30°. Fluorinated polyhedral oligomeric silsesquioxane (POSS) was also used by several authors [41, 136] to develop icephobic coatings due to its extraordinary low surface energy.

In addition to the recipes and procedures published in journals, there are also a lot of patents related to anti-icing coating. However, most of them just utilize low surface energy materials to achieve lower ice adhesion and there is no consideration about the morphology and wetting mode of the surface. These kinds of coatings are mainly polysiloxane or silicone with different function groups [157-160]. There are also some patents about superhydrophobic coatings stating that the coatings can be used for anti-icing application, but no evidence or evaluation has been provided [161-167]. Therefore their anti-icing performance needs further study. As for icephobic coatings with superhydrophobic property and proven anti-icing performance, there are only a few patents available. He et al. [168] filed a patent application about an anti-frost coating which have a hydrophilic and hydrophobic composite structure applied on a substrate. The coating contains a hydrophilic inner layer (50-80 wt.%) and a hydrophobic / superhydrophobic surface layer (20-50 wt.%). The hydrophilic polymer is preferably selected from copolymer of two or more of sodium acrylate, acrylic acid, methacrylic acid, 2-hydroxypropyl methacrylate, glycidyl methacrylate, acrylamide and 2-hydroxyethyl methacrylate. The hydrophobic polymer is selected from polyacrylate, fluorine containing polyacrylate and polyolefin, or from copolymer of acrylate and fluorine containing acrylate. The hydrophilic polymer and the hydrophobic polymer are dissolved in a solvent to form a homogeneous solution and then coated on the substrate by conventional methods, dried under reduced pressure and cured between 20-60 °C. The function of the outer hydrophobic / superhydrophobic layer is to slow the heat transfer and make the droplets slip off the surface before they freeze. The inner hydrophilic layer can absorb the condensed water drips that penetrate into the inside of material. The absorbed water will exist in a form of gel so as to stop the formation of frost crystal. The examples shown in the patent

application illustrate high water contact angle and greatly delayed frost formation. In their patent application, Gao et al. [169] described a procedure for anti-icing superhydrophobic coatings which comprise surface modified hydrophobic nanoparticles between 5-100 nm in size (20-40 wt.%) and a polymeric binder (60-80 wt.%). The particle size is preferred to be between 20-50 nm to deter the ice nucleation in the process. The binder can be any suitable polymer as long as it has the ability to react with the surface to be coated. The test procedure and results given in the patent application are similar to the ones in Ref. [37].

2.5 Summary

Anti-icing materials have been a hot topic in recent years with the development of nano technology and superhydrophobic coatings as they shows very strong water repellence. However, not all superhydrophobic coatings were proven to be icephobic. The mechanism of icephobicity needs further investigation. As far as the coating surface is concerned, there are mainly two factors that are related to its icephobic performance, which are the roughness and surface energy. Their roles in the anti-icing performance are still unclear, especially at below dew temperatures and thus need more investigation.

There have been some icephobic coatings developed by different ways such as lithography, etching, anodization, etc. However, most of them either require special equipment with high cost, have potential mechanical problems, or possess limitations in the choice of substrate, rendering them unsuitable for mechanically robust, large scale applications. A new icephobic coating is needed for the large outdoor applications. Among all the techniques available, sol-gel coating, with the ability of easily adjusting surface energy and roughness/morphology through different

precursors, fillers, surface modification and processing methods, is a promising way to develop large scale, durable, easy to apply and low cost icephobic coatings which can be applied in a wide range of substrates.

Currently there is no standard test methods for the anti-icing performance. There were usually only one or two aspects of the anti-icing aspects involved in most of the reports, and the test conditions are usually different even for the same aspect in different reports. Thus it is difficult to compare the anti-icing performance between different reports. It is necessary to investigate the coherency of different aspects of the anti-icing performance in different environment.

Chapter 3 Effect of Surface Energy and Roughness on the Anti-Icing Performance of Surfaces

3.1 Introduction

There are mainly two factors that affects the freezing behaviour of the water droplets on a substrate. One is the surface energy, and the other is surface morphology of the substrate. Although there were investigations about their role in the icing process, there is lack of comprehensive studies about their role especially at lower temperatures.

3.2 Experimental work

To preliminarily investigate the effect of these two factors on the freezing behaviour of water droplet, two series of samples are prepared. The first series of samples compose of a smooth glass slide and four other glass slides mechanically ground with different grit size of sandpapers (P120, P320, P800 and P1200). Hence, the roughness of each sample is different. Each sample, named after the sand paper grade, were ultrasonically washed in acetone, ethanol, and water in sequence for 10 minutes, respectively. Then the samples were dried with air blower. The second series of samples were firstly prepared with the same procedure for series one samples, and then treated with 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (FAS) by immersing the glass slides in 1 vol.% hydrolysed FAS methanol solution for 12 hours. Then the samples were heated at 120 °C for 1 hour, followed by the same cleaning and drying process as mentioned above. This group of sample would have lower surface energy, while the roughness would be similar with that in the first group. They are denoted as F180, F320, F800, F1200 and F-Glass, respectively.

3.3 Materials characterization

The contact angle of each sample was measured with OCA20 contact angle measuring system from Dataphysics, Germany. The capillary length for clean water at room temperature is around 2.7 mm. So a 4 μL of deionized water which has a diameter of 2 mm was used for the measurement of contact angle in order to avoid the effect of gravity on the shape of the droplet. The contact angles under different temperatures were also measured.

The advancing and receding angles under different temperatures were measured by dynamically increasing/decreasing the volume of the droplet as shown in **Figure 3.1**. The tilting stage method was not used here because it is hard for the droplet to slide off the surface when it comes to hydrophilic samples or when the temperature is low, even if the tilting angle reaches to 90° . In the procedure of the measurement, 0.5 μL water was firstly put on the surface, and the tip of the needle was immersed into it and positioned in the middle in order to minimize its effect on the symmetry of contact angle on both sides. Then 10 μL water was released/retracted at a very slow speed of 0.05 $\mu\text{L/s}$ in order to eliminate the effect of dynamic movement on the measurement. The continuous change of contact angle during releasing / retracting circle was recorded and calculated by computer to get the advancing and receding angles.

Figure 3.1 Schematic of measurement of advancing and receding angles

The roughness of the samples was measured by a Surface Profiler (Alpha-Step IQ Surface Profiler, KLA Tencor). The morphology of the surfaces were investigated with a PLμ Non-contact Confocal Imaging Profiler. A 20X lens was used in the measurement, and only the area at or close to the centre of the sample where the droplet would be placed was measure. Usually 4 to 5 spots were measured for each sample, and the measured area for each spot is $694 \times 510 \mu\text{m}^2$. The mean value was used for the evaluation of the samples.

The icing behaviour of the droplet was studied with the cooling component of the contact angle measurement system. It comprises a small chamber with an embedded peltier stage at the bottom, circular cooling water, and integrated temperature detection and control component. In order to maximize the isolation of heat from atmosphere and decrease the temperature gradient, the inside walls of the chamber was filled with adiabatic foam except for the two sides that are for observation. A K-type thermocouple was placed on the sample surface in order to accurately measure the surface temperature. Such additional temperature measurement is necessary as there is a temperature gradient from the peltier stage to the top of the sample. The tip of the thermocouple was wrapped with thermal grease for better thermal conductivity across the interface. The schematic is shown in **Figure 3.2**. There is also an embedded thermocouple in the peltier stage to measure the core temperature of the cooler.

Figure 3.2 Schematic of the measurement device.

The Peltier stage is controlled by the computer. The cooling rate can be accurately set by the program. However, because of the nature of Peltier stage and the loop control based on the feedback from the embedded thermocouple in the Peltier stage, there will be a short fluctuation (± 1 °C) near the set point before it gets stable as can be seen in **Figure 3.3**. Besides, the temperature controlled here is the core temperature of the Peltier stage, and the surface temperature of the Peltier stage and the sample would differ slightly because of the temperature gradient as can be seen in **Figure 3.3**.

Figure 3.3 Temperature change profile and the temperature gradient between the cooling stage and glass surface. (a) The temperature was decreased at 5 °C/min from 22 °C to a set point (-20 °C). (b) The temperature was decreased at 1 °C/min from 0 °C.

The observation of ice formation is by eye inspection on the monitor. And thus the temperature recorded is the temperature at the beginning of macroscopic freezing

instead of the nucleation even per se [129]. However, the water droplet for test is small, and it is usually supercooled to $-15\text{ }^{\circ}\text{C}$ or lower. The lag between nucleation and macroscopic freezing should be insignificant.

Several anti-icing test procedures were tested and evaluated, including icing lag time and icing temperature. As for lag time test, two different procedures were evaluated. The first one is to place the droplet onto the surface before it is cooled. The second one is to cool the droplet and the sample together. In either case, the samples were cooled to a sub-zero temperature at the speed of $5\text{ }^{\circ}\text{C}/\text{min}$. As for the icing temperature test, water was always placed on samples first, and then the samples were cooled at the speed of $1\text{ }^{\circ}\text{C}/\text{min}$ from around $0\text{ }^{\circ}\text{C}$ till the water freezes. The cooling speed between room temperature and $0\text{ }^{\circ}\text{C}$ is as fast as possible to save time, and it is irrelevant to the nucleation of ice.

The ice adhesion was measured with a self-designed adhesion tester which consists of an environmental chamber, an air compressor, an air cylinder combined with a force gauge on the tip of the pole, and a customized sample stage, as shown in **Figure 3.4**.

Figure 3.4 Schematic of ice adhesion tester.

The moving speed of the piston was around 1.3 mm/s before it touched the mould, and the increasing speed for the push force driven by the compressed air was around 12.5

N/s after the piston contacted the mould. The data recording of the force gauge was conducted at 1000 records per second. The ice was formed in a customized Teflon mould which has an inner diameter of 18 mm, and a slope opening to minimize the adhesion between Teflon itself and the coatings. The mould was first filled with DI water, covered by the coatings, turned upside down, and then left in the environmental chamber at -10 °C for at least three hours to ensure the ice formation. The force F needed to push the mould off the coatings was recorded. The stand-off height was 0.5 mm during the shear test. The ice adhesion strength in shear can be calculated by:

$$\tau = \frac{F}{A} \quad (3.1)$$

where $A = \pi \times 9^2 \text{ mm}^2$ is the contact area between ice and the coatings in current study. The ice adhesion on bare glass and FAS decorated glass was also tested for comparison. The ice adhesion was measured at least 8 times on the same spot for each sample to get authentic results as well as to test the durability of the coatings.

3.4 Results and Discussion

3.4.1 Surface morphology and roughness

The surface morphology of uncoated surfaces are shown in **Figure 3.5**. The difference of the roughness between samples are very obvious. The surface morphology of FAS coated samples are not shown here because it is basically the same as the uncoated ones. The detailed roughness for both group of samples are shown in **Figure 3.6**.

It is clearly shown in **Figure 3.6** that the roughness of the sample are affected by the grit size of the sand papers. The error bar is large for some samples because of the way they were prepared. However, statistically significant difference exists among all samples, and the trend for the series of samples is clear.

Figure 3.5 Surface morphology of the uncoated samples by Confocal Imaging Profiler: (a) P180 (b) P320 (c) 800 (d) P1200 (e) Glass.

Figure 3.6 Roughness of the samples by Surface Profiler: (a) uncoated samples, (b) coated samples with FAS.

3.4.2 Wetting status at different temperatures

The contact angle of the samples at different temperatures are shown in **Figure 3.7**.

Figure 3.7 Contact angle of the samples at different temperatures: (a) uncoated samples, (b) coated samples with FAS.

As can be seen from **Figure 3.7**, the contact angle of ground glass slides are relatively low, and they do not change much at lower temperatures, which is different from an unground glass slide. The lower contact angle and the lack of correlation between the roughness and the contact angle for ground glasses may be because of the capillary effect caused by the micro concave tracks arising from grinding. Besides, raw glass is easily contaminated at atmosphere, which may also contribute to the irregular results. However the general trend is clear that roughened glass surface has lower contact angle than the smooth surface, a trend that agrees with the theory that hydrophilic surface becomes more hydrophilic with increased roughness. On the contrary, for the FAS-coated glass slides, the contact angles are larger for the ground ones than the

smooth one as shown in **Figure 3.7b**. And the values are in good correlation with the roughness although the difference between different samples is very small. Again this trend is well predicated by the Cassie-Baxter model.

The advancing angle and receding angle of each samples are shown in **Figure 3.8**. The advancing and receding angle of uncoated samples were not reported here as water was easily stuck to the surface during the retracting process and the contact angle was too small to be measured accurately. As can be seen in **Figure 3.8**, the difference of contact angle, advancing angle and receding angle between the FAS decorated samples are not very much. The trends is consistent though that the advancing and receding angles decrease as temperature is lower, while it's the opposite for the contact angle hysteresis.

The receding angle and contact angle hysteresis are considered to be more related to the ice adhesion in some papers [41, 59, 148]. Here the difference between the samples may be too small to be valid for comparison. Their correlation with the ice adhesion needs further investigation.

Figure 3.8 Advancing and receding angle of coated samples: (a) F180; (b) F320; (c) F800; (d) F1200; (e) F-Glass.

3.4.3 Ice adhesion

The ice adhesion of the samples are shown in **Figure 3.9**. It can be seen that the difference between ground samples in each group are not so much. This might be related to the morphology of the scratches. However, the overall trend is clear that the larger the roughness, the larger the ice adhesion. Comparing the two groups of samples, it is clear that the fluorinated samples always have lower ice adhesion than the non-fluorinated counterparts. This means that lower surface energy is favourable for lower ice adhesion despite of the roughness. This is in agreement with other reports [38, 41, 72, 116].

Figure 3.9 Ice adhesion on the samples

3.4.4 Icing temperature

The icing temperature of water on uncoated and coated glass slides are shown in **Figure 3.10**.

Figure 3.10 Icing temperature on the samples.

It can be seen that although there is a relatively large variation of icing temperature on some samples, the trend is very clear. The icing temperature on both series of samples increase with the roughness. The rougher the surface, the more concave sites exist on the surface which facilitate the nucleation according to the classical nucleation theory as demonstrated in Section 2.1.1. For rough surfaces, it is difficult to calculate the nucleation rate directly due to the lack of information about the geometry of the concave sites. However, for smooth surfaces, such as the unground glass slides, the icing temperature can be determined theoretically. Here the contact angle between ice and substrate is considered to be the same between water and substrate. The direct measurement of contact angle between two solids is impossible [54]. Thus the static water contact angle is usually used instead in the literatures [36, 59, 119]. For nucleation of ice from liquid water, the volumetric free energy difference between ice and water is $\Delta g = \frac{-\Delta H_{m,v} \cdot \Delta T}{T_m}$, where $\Delta H_{m,v} = \frac{6010 \text{ J/mol}}{1.965 \times 10^{-5} \text{ m}^3/\text{mol}} = 3.06 \times 10^8 \text{ J/m}^3$ is the volumetric enthalpy change during ice formation [48, 170], $T_m = 273.15 \text{ K}$ is the equilibrium temperature. So $\Delta g = (-3.06 \times 10^8 + 1.12 \times 10^6 \cdot T) \text{ J/m}^3 =$

$(-1.12 \times 10^6 \cdot \Delta T) J/m^3$. The interfacial energy between ice and water [171] is $\sigma = [28 + 0.25(T - 273.15)] \times 10^{-3} J/m^2$. Substituting these data into Equation (2.5), (2.7) and (2.8), we can obtain the free energy barrier for heterogeneous nucleation of ice on planar surface is:

$$\begin{aligned} \Delta G &= \frac{16\pi\sigma^3}{3(\Delta g)^2} \times \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2 \\ &= \frac{16\pi[28+0.25(T-273.15)]^3 \times (10^{-3})^3}{3 \times (-3.06 \times 10^8 + 1.12 \times 10^6 \times T)^2} \times \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2 \end{aligned} \quad (3.2)$$

According to Equation (2.6),

$$\Delta G = kT \ln \frac{I}{I_0} \quad (3.3)$$

where I can be set to be $1 \text{ cm}^{-3}\text{s}^{-1}$, i.e. $10^6 \text{ m}^{-3}\text{s}^{-1}$ [172]. The value of A is usually between 10^{18} to $10^{35} \text{ cm}^{-3}\text{s}^{-1}$ in the literatures [171, 173, 174]. Here, the value $10^{25} \text{ cm}^{-3}\text{s}^{-1}$, i.e. $10^{31} \text{ m}^{-3}\text{s}^{-1}$ is used. Combining Equations (3.2) and (3.3), the equation showing the relationship between the icing temperature and contact angle can be obtained as shown in **Equation (3.4)** and **Figure 3.11**.

$$\frac{16\pi((28+0.25(T-273.15)) \times 10^{-3})^3}{3 \times (-3.06 \times 10^8 + 1.12 \times 10^6 \times T)^2} \times \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} = 1.38 \times 10^{-23} \ln 10^{31} T \quad (3.4)$$

Figure 3.11 Icing temperature on planar surfaces from calculation (curve) and experiments (bar).

As can be seen in **Figure 3.11**, the calculated icing temperature curve fits well with the data from experiments for FAS-coated glass slide, while it's a relatively big difference for uncoated one. There might be several reasons for this. First of all, the data used for the classic nucleation calculation are all approximate values. The interfacial energy between water and ice and the value of A have a great impact on the slope of the curve. It is very difficult to determine the interfacial energy by experimental techniques, and the value obtained from different authors showed considerable spread (e.g. 24 mN/m to 33 mN/m at 0 °C) and different decreasing slope with decreasing temperature [62, 171, 175]. The difference can be up to 4 °C and 14 °C for uncoated and coated glass slide, respectively. The value of A is usually between 10^{18} to 10^{35} cm⁻³s⁻¹, and will cause a difference of calculated icing temperature of 1.4 °C and 3.5 °C for uncoated and

coated glass slide, respectively. Secondly, the contact angle between ice and the substrate and the shape of the nuclei are impossible to be measured directly. The interaction between ice and substrate is usually assumed to be the same as water and substrate. However, it is notable that the larger surface energy of crystals compared to liquids and the usually large interfacial free energy between two solids means that in general, the effective shape factor will be larger for a solid than for a liquid [54]. Thirdly, as for heterogeneous nucleation without any external gas flow, the freezing of supercooled water is typically initiated at the liquid-solid interface. As for the same volume of water droplet, it will have a larger contact area on the low contact angle substrate than high contact angle ones. Thus, it should have a larger nucleation rate at the uncoated sample than coated one. Finally, it may also be related to the evaluation method. The nucleation rate in classic nucleation theory is based on statistics which usually involves hundreds of icing events, while there are only about 20 events for each sample at present work, which may introduce great deviation.

Nevertheless, the difference of icing temperature on both samples is very clear. Higher contact angle surface is favourable for better anti-icing performance, although the mechanism need further investigation and adjustment.

As for the roughened samples, both the two series showed higher icing temperature than the flat samples. This is reasonable because it has lower energy barrier to form an ice nucleus on a step or concave surface as shown in **Figure 2.7** and **Figure 2.11**, while there are a lot of such sites on a rough surface. It is also notable that the icing temperature increases with the increasing roughness for the samples with same surface energy. It may be because the step angle is smaller on rougher surface. More

experiments needs to be designed to justify this point though because it is impossible to measure the step angle on such mechanically ground surfaces.

3.5 Summary

Preliminary study of icing behaviour on different surfaces revealed strong influences by surface energy and roughness. For both groups of samples, lower surface energy and lower roughness would lead to lower icing temperature and ice adhesion. However, since all the samples are only hydrophilic or hydrophobic, the results cannot reflect as a general mechanism for all situations such as on superhydrophobic surfaces. Further investigation on surfaces with different wetting mode is necessary in order to find out which parameters are favourable for anti-icing performance. Sol-gel coatings, with the ability to easily adjust surface energy, roughness and morphology, are suitable for overcoming the limitations presented by the two groups of samples and further investigating the anti-icing mechanism.

Applying the classical nucleation theory failed to explain the icing temperature on the samples. In order to explain the inconsistency between the classic nucleation model and experiment results, more investigation would be needed. Currently, the water contact angle is used when applying the classic nucleation theory, which has been widely used in the literatures. This method would definitely cause some deviations. Besides, a massive icing temperature for the water droplet on each sample would be needed to have a statistical analysis and provide a more reasonable value when applying the classic nucleation theory to explain the icing behaviour. There are quite limited literatures about the research of this kind of mechanism, especially on rough surfaces. The attempt along this line will be reported later.

Chapter 4 Development of Sol-gel Icephobic Coatings

4.1 Introduction

Currently, most of the techniques used to develop the ice-phobic coatings such as lithography [56, 153, 176, 177], chemical etching [101, 105, 134], liquid-infused porous surface [129], laser irradiation [99], chemical or physical vapour deposition [178] either require special equipment with high cost, or possess limitations in the choice of substrates, rendering them unsuitable for large scale applications. In contrast, sol-gel coatings, with the ability of easily adjusting surface energy and roughness through different precursors, surface decoration with self-assembled layers, addition of fillers of different sizes, etc., are a more promising way to develop large scale, durable, easy to apply and low cost icephobic coatings which can be applied in a wide range of substrates [179-181]. There are quite a few of sol-gel coatings which are developed to achieve self-cleaning property or superhydrophobicity. However there are quite limited investigation on icephobicity by sol-gel coatings.

The choice of precursors has a great impact on the final properties of the formed sol-gel coatings. The precursors are usually metal metal chlorides or alkoxides, which undergo a series of reactions including hydrolysis and polycondensation to form a colloid. The functional group of the precursors decides the final performance of the coatings. In this chapter, methyl triethoxysilane (MTEOS), 3-glycidyloxypropyl trimethoxysilane (GLYMO) and 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane (FAS) were chosen to develop a series of sol-gel coatings with different roughness and surface energy. MTEOS was used as the cross linker and the CH₃ group makes it more suitable for developing a superhydrophobic surface [182]. GLYMO was used as the coupling agent and the epoxy group makes the coatings more adhesive to the substrate.

FAS was added in some of the coatings to introduce lower surface energy to the base gel because of the long fluorocarbon chain. All those three chemicals have a similar core molecular, which enable them to hydrolyse and interact with each other and easy to form a network structure in the end.

In order to introduce different roughness as well as surface energy to the surfaces, different content of particles/fillers were added to the sol. Many types of fillers have been tried to develop functional sol-gel coatings, such as titanium oxide [183, 184], silica [185, 186], zinc hydroxide [187], zinc oxide [188], carbon nanotubes [189], alumina [190], etc. The particles can be reactive or non-reactive depending on the needs. Here we chose two types of particles which are hydrophobically treated silica and Fluorinated polyhedral oligomeric silsesquioxanes (POSS) to modify the sol-gel coatings. Hydrophobic silica is a common filler which has been widely used to fabricate hierarchical superhydrophobic surfaces. Fluorinated POSS, on the contrary, is not so often mentioned in the reports.

Fluorinated POSS has been developed as a new material a few years ago and found to be of extremely low surface energy [191-193]. The POSS itself is a cage like structure of 1.2 nm in size and intrinsically nanostructured material [194]. It has been mainly prepared as superhydrophobic or oleophobic coatings either by itself alone [193] or mixed with other substances such as nano particles [194] or organic compounds [192, 195-197]. The procedure for manufacture of the fluorinated POSS coatings can be in different ways, including dip coating [198], spin coating [196, 197], electrospinning [199], etc. As for anti-icing, there are only a few reports about the application of fluorinated POSS in this area. Meuler et al. [41] reported the anti-icing performance of spin coated fluorodecyl POSS and its blends with poly(ethyl methacrylate) (PEMA)

and poly-(methyl methacrylate) (PMMA). Although the coatings are only hydrophobic (not superhydrophobic), they lowered the ice adhesion to one fourth of that on the uncoated steel substrate. Dodiuk et al. [136] reported one-layer or two-layer fluorinated POSS coatings with or without hydrophilic silica. The two-layer coating with silica as the first layer showed great superhydrophobicity and icephobicity. However, the ice adhesion test was conducted without any repetition on the samples. So it is hard to say the durability of the samples are good enough for applications. Besides, to the best of our knowledge, there is no ice delay investigation on fluorinated POSS coatings yet which is also an important part of icephobicity. Thus it is necessary to further explore the potentials of fluorinated POSS and have a more comprehensive study on its anti-icing performance.

In this chapter, different coatings with different content of silica / fluorinated POSS, and thus different surface energy and roughness were prepared. Surface morphologies and properties of the coatings were reported and correlated with the anti-icing performance.

4.2 Experimental work

Two series of coatings with different roughness and surface energy were prepared. The first series are coatings containing fluorinated POSS, and the other series are coatings with silica only as the fillers. The common sol for both series were prepared as follows. 9.961 mL MTEOS (99%, Sigma Aldrich, USA) and 33.132 mL GLYMO ($\geq 98\%$, Sigma Aldrich, USA) were mixed in 3.91 mL Ethanol (absolute for analysis, EMD Millipore Corporation, Germany) under stirring, and then 5.406 mL deionised (DI) water was added to the solution dropwise. After one hour stirring, 3.55 g itaconic acid ($\geq 99\%$, Sigma Aldrich, USA) was added to the solution to catalyse the hydrolysis

process. The molar ratio of MTEOS, GLYMO, ethanol and water is 1 : 3 : 1.34 : 6. The common sol was stirred for 24 hours before the fillers were added.

4.2.1 Coatings containing fluorinated POSS

Three groups of solutions containing different content of fluorinated POSS were prepared. The first group of solutions were prepared as follows. Trifluoropropyl POSS (FPOSS, Hybrid Plastics, USA) was firstly dispersed in ethanol (each gram of FPOSS in 15 mL ethanol), and ultrasonically treated for half an hour to disperse the nanoparticles. The common sol was then added to the FPOSS-containing ethanol to make solutions with a different weight percentage of FPOSS. The final coatings contain 5%, 10%, 15% and 20 wt.% FPOSS respectively. These samples are denoted as P-x where x stands for the weight percentage of FPOSS in the coatings. The second group of solutions with FAS were prepared similarly, except that part of the ethanol for dispersing silica particles was replaced by FAS (97%, Sigma Aldrich, USA) and DI water. This replacing solution was added to the common sol and stirred for 24 hours before mixing with the FPOSS. The molar ratio of added FAS, DI water and MTEOS in the common sol was kept at 1:3:2 in all solutions of this group in order to make sure the base gel have the same surface energy. However, due to the difference in the amount of added FPOSS, the intrinsic surface energy of the final coatings may differ. This group of samples are named as PF-x where x is the percentage of added FPOSS in the final coatings. Assuming all the FAS remains in the coating after calcination, the same amount of FPOSS per unit of sprayed solution will lead to slightly decreased FPOSS percentage in the FAS-containing coatings. However, by keeping the same amount of FPOSS in the (unit volume) coating solution was found to keep similar roughness of the coatings. The third group of samples were prepared similarly as group two except that the added FPOSS was replaced with half weight

FPOSS and half weight hydrophobic fumed silica particles (AEROSIL R972, 16 nm, Nippon AEROSIL Co. Ltd, Japan). This group was denoted as PFS-x, where x is the percentage of added FPOSS in the final coatings. The composition of the coatings are shown in **Table 4.1**.

The finally mixed solutions were stirred for another 24 hours for better hydrolysis before they were spray-coated onto glass slides. The glass substrate were cleaned with acetone, ethanol and DI water in sequence, and dried with hot air. After the spray coating, the samples were dried at room temperature for one hour, followed by curing at 100 °C for another hour.

4.2.2 Coatings with only hydrophobic silica as fillers

This series of coatings contain two groups which are denoted as the 4th and 5th group respectively in **Table 4.1**. These two groups of coatings only have the hydrophobic silica as the fillers. They were prepared the same way as group one and two respectively except all the FPOSS was replaced with silica and the curing temperature was 120 °C. The samples in these two groups are denoted as M-x and F-x, respectively, where x stands for the weight percentage of silica in the coatings. The composition of the coatings are also shown in **Table 4.1**.

For comparison, a FAS monolayer decorated glass slide (without the sol-gel coating) was prepared as well by heating the sealed bottle which contained the cleaned glass slide and 0.3 mL 1.5 vol. % FAS methanol solution for 1 hour at 120 °C.

Table 4.1 Coatings compositions

Groups	Sample ID	Content of silica in the final coatings (wt. %)	Content of fluorinated POSS in the final coatings (wt. %)	FAS content in the sol ($\mu\text{mol/g}$)
1	P-5	0	5	0
	P-10	0	10	0
	P-15	0	15	0
	P-20	0	20	0
2	PF-4	0	4	0.31-0.35
	PF-8	0	8	0.31-0.35
	PF-12	0	12	0.31-0.35
	PF-16	0	16	0.31-0.35
3	PFS-2	2	2	0.31-0.35
	PFS-4	4	4	0.31-0.35
	PFS-6	6	6	0.31-0.35
	PFS-8	8	8	0.31-0.35
4	M-5	5	0	0
	M-10	10	0	0
	M-15	15	0	0
	M-20	20	0	0
5	F-4	4	0	0.31 - 0.35
	F-8	8	0	0.31 - 0.35
	F-12	12	0	0.31 - 0.35
	F-16	16	0	0.31 - 0.35

4.3 Materials characterization

The roughness of the surfaces were measured by a Surface Profiler (Alpha-Step IQ Surface Profiler, KLA Tencor). The measurement length was 1 mm each time. The surface morphology and elemental analysis were examined using a field emission

scanning electron microscope (FESEM, JEOL JSM-6340F, Japan) and attached energy dispersive X-ray (EDX) spectroscopy. FTIR spectra were measured on a Frontier FTIR spectrometer (PerkinElmer Inc.). The contact angle and sliding angle at different temperatures, and the apparent surface energy of the samples at room temperature were measured with an OCA20 contact angle device (Dataphysics, Germany). In order to avoid a deformed shape of the water droplet during the contact angle measurement, 4 μL of DI water was used to make sure its dimension is smaller than the capillary length which is around 2.7 mm for water at room temperature. The sliding angles were measured with 4 μL and 10 μL droplets respectively. All the measurements were conducted at least 5 times for each sample. As for the surface energy measurement, DI water, glycerol and diethylene glycol were used, and the Owens, Wendt, Rabel and Kalble (OWRK) [200] method was utilized for the calculation. The ice adhesion was investigated as described in Section 3.3.

4.4 Results and discussion

4.4.1 Coatings containing fluorinated POSS

4.4.1.1 Surface morphology and roughness

The surface morphology of the samples containing FPOSS are shown in **Figure 4.1**, **Figure 4.2** and **Figure 4.3**.

Figure 4.1 Surface morphology of P- series coatings: (a) P-5, (b) P-10, (c) P-15, (d) P-20.

As can be seen in **Figure 4.1**, the FPOSS fillers appear mainly as particles of around 30 to 50 nm when the concentration is low (P-5). Then they start to aggregate at higher concentration while the particle size remains the same (P-10). When the FPOSS content reaches 15%, the aggregated sites did not change much comparing to P-10, but the distribution of the particles becomes much denser and the particle size also slightly increases a bit (P-15). At higher concentration, there are more agglomerated sites, and the particles also becomes elliptic with a length of 50 to 100 nm instead of circular.

Figure 4.2 Surface morphology of PF- series coatings: (a) PF-4, (b) PF-8, (c) PF-12, (d) PF-16.

The surface morphologies for PF- series is different from the P- series as can be seen in **Figure 4.2**. The aggregated sites seem smaller and less in number. It might be because of some interaction between FAS and FPOSS. Nevertheless, the surface does look rougher with increased FPOSS content.

Figure 4.3 Surface morphology of PFS- series coatings: (a) PFS-2, (b) PFS-4, (c) PFS-6, (d) PFS-8.

With the addition of hydrophobic nano silica particles, the surfaces show a much different morphology as can be seen in **Figure 4.3**. With the increase of silica content, the coatings have rougher and rougher surfaces, and starts to form a hierarchical microstructure when the silica/FPOSS concentration reaches up to 8 wt.%.

The roughness of the FPOSS-containing coatings are shown in **Figure 4.4**. It is clear that all the coatings roughness increases with the concentration of FPOSS. It is notable that the P- and PF- series has a similar roughness range, while the PFS- series have a overall higher roughness than the counterpart samples in the other two groups. This is because the added silica has a much smaller density than FPOSS.

Figure 4.4 Roughness of the coatings: (a) P- series, (b) PF- series, (c) PFS- series.

4.4.1.2 Wettability and surface energy

The contact angle of the FPOSS-containing coatings at different temperatures are shown in **Figure 4.5**. All the coatings in each group have a similar trend which is the higher the roughness and FPOSS concentration, the higher the contact angle. Only PFS-8 is superhydrophobic at room temperature.

All the contact angles decrease with temperature. None can maintain Cassie wetting mode at sub-zero degrees.

Figure 4.5 Contact angle of the FPOSS-containing samples at different temperatures: (a) P- series, (b) PF- series, (c) PFS- series.

The surface energy of the coatings are shown in **Figure 4.6**. It can be seen that the surface energy of the coatings always decrease with increasing concentration of FPOSS. However, the difference between most of the samples are not much as can be seen from the figures. The lowest apparent surface energy was obtained by PFS-8 which is superhydrophobic. It is worth mentioning that the surface energy measured here is just a rough characterization of the surface properties because it is affected by the surface roughness. Although the results may not represent the real surface energy, they show the difference/trend of the samples in each group in terms of surface energy.

Figure 4.6 Surface energy of the coatings: (a) P- series, (b) PF- series, (c) PFS- series.

4.4.1.3 Ice adhesion

The ice adhesion of the coatings were firstly conducted at $-10\text{ }^{\circ}\text{C}$. It was found out that many of the samples would not freeze or only partly frozen even after 24 hours as can be seen in **Table 4.2**. The ice adhesion of the successfully frozen samples are shown in **Figure 4.7**. In order to get a more stable results and rule out the influence of the microstructure of the formed ice, the ice adhesion at $-20\text{ }^{\circ}\text{C}$ was also investigated. The ice blocks were formed by leaving the samples in the environmental chamber at $-20\text{ }^{\circ}\text{C}$ for over 3 hours. Moreover, the ice adhesion at $-10\text{ }^{\circ}\text{C}$ was also conducted after the ice blockes were formed at $-20\text{ }^{\circ}\text{C}$. Each test was repeated for over 8 times on the same spot of the samples. The results are shown in **Figure 4.7**.

There are mainly two factors affecting the ice adhesion which are surface energy and roughness. Since all the coatings are wetted at lower temperatures, there is no trapped

air between the formed ice and substrate. Thus it is purely the surface composition that function as the ice inhibitor. It is well proven that lower surface energy and lower roughness lead to lower ice adhesion for a fully wetted surface. When the concentration of FPOSS increases, the surface energy of the coatings decreases, but the roughness increases as demonstrated in **Figure 4.4** and **Figure 4.6**. This explains the fluctuation in **Figure 4.7**.

Table 4.2 Freezing probability after 24 hours at -10 °C

Samples	Unfrozen times out of 9 tries	Partly frozen times out of 9 tries	Successful ice adhesion test out of 9 tries
P-5	2	1	6
P-10	1	2	6
P-15	4	0	5
P-20	4	1	4
PF-4	3	1	5
PF-8	2	0	7
PF-12	2	1	6
PF-16	3	1	5
PSF-2	3	1	5
PSF-4	0	0	9
PSF-6	3	0	6
PSF-8	7	0	2

Figure 4.7 Ice adhesion of the samples at different temperatures: (a) P- series, (b) PF-series, (c) PFS- series.

The lowest ice adhesion is achieved as 0.175 ± 0.050 MPa at -20°C and 0.135 ± 0.029 MPa at -10°C , both on sample PFS-8. The obtained ice adhesion at -10°C is slightly better than the data reported in Ref [41]. For comparison, the ice adhesion on uncoated glass slide was also measured and it turned to be 0.724 ± 0.257 MPa at -10°C and 1.198 ± 0.152 MPa at -20°C . All the coatings showed a much less ice adhesion than the bare glass (0.820 ± 0.096 MPa). The biggest ice adhesion reduction efficiency (ratio of adhesion on bare glass to adhesion on the coatings) is 5.4 at -10°C and 6.8 at -20°C , which shows good potential for applications especially at lower temperatures.

It is noticeable that the ice adhesion at -10°C is always lower than that at -20°C no matter how the ice blocks are prepared. The temperature has an obviously strong effect

on the interaction between ice molecules and the substrate. However, when comparing the ice adhesion at $-10\text{ }^{\circ}\text{C}$ obtained from the direct way (form ice at $-10\text{ }^{\circ}\text{C}$) and detour way (form ice at $-20\text{ }^{\circ}\text{C}$ and then increase temperature to $-10\text{ }^{\circ}\text{C}$), it is interesting to see that they are not always the same. More specifically, the ice adhesion from the detour way is usually higher than that from the direct way. It might be related to the microstructure of the formed ice. Usually the ice mechanical property increases when temperature decreases [201]. Also it will take some time for substrate-ice interface to become rigid and stable at a certain temperature. When freezing at $-10\text{ }^{\circ}\text{C}$, the nucleation and crystal growth take place in a much slower way on some samples depending on the surface composition. Those surfaces which showed such a delay phenomenon are most likely to have a lower icing temperature in theory.

4.4.1.4 Icing temperature

Finally, the icing temperature of the coatings are investigated. The results are shown in **Figure 4.8**. Similar to the affecting factors for ice adhesion, surface energy and roughness are still the main factors influencing the nucleation process. The geometric factor is closely related to surface energy. The lower the surface energy, the lower the geometric factor. For fully wetted surfaces, the roughness usually indicates the available concave sites for nucleation which have a lower free energy barrier.

Figure 4.8 Icing temperature of the coatings: (a) P- series, (b) PF- series, (c) PFS- series.

For the first group, the increase of roughness only have a limited effect on the icing temperature. As can be seen in **Figure 4.1**, the surface morphology does not really change much with the increase of FPOSS. Thus after the initial decrease of icing temperature from P-5 to P-10, the icing temperature remains basically the same for the last three samples.

For the PF- series, it is possible that the surface is already covered by CF_2 or CF_3 groups on the top of the surface, so increasing the content of FPOSS does not change the surface energy much as can be seen in **Figure 4.6**. However, the increased roughness do provides more concave nucleation sites. That's why the icing temperature keep going up with the content of FPOSS.

For the third group, the role of roughness is more dominant because of the addition of silica. As can be seen in **Figure 4.3**, silica totally changes the morphology of the surfaces, and starts to form a hierarchical microstructure at higher concentration. Although the apparent surface energy decreased a lot, the geometric factor plays a dominant role in the nucleation process in this case, and thus lead to the overall increasing icing temperature across the group of samples.

Among all the samples in these three groups, the lowest icing temperature was achieved by PF-4 and PFS-2, which both own a relatively smooth surface. This result is in agreement with the earlier conjecture that the surfaces which tend to delay the icing process at -10 °C are likely to demonstrate lower icing temperatures. However, PF-4 and PFS-2 do not show the lowest ice adhesion as can be seen in **Figure 4.7**. This is understandable because of the different mechanism in the two types of anti-icing performance.

None of the samples can maintain superhydrophobic at sub-zero temperatures, which might be because the microstructures of the surfaces are not rough or hierarchical enough. This led to the investigation of rougher coatings in group four and five which utilize only silica as the fillers. Since silica used here has a much larger particle size (16 nm) than FPOSS (1~2 nm), it will cause a much rougher surface as shown in **Figure 4.3**. Replacing FPOSS with silica would hopefully further roughen the surface and get some improvement of wettability at lower temperatures.

4.4.2 Coatings with only hydrophobic silica as fillers

4.4.2.1 Surface morphology and roughness

The surface morphology of the last two groups of coatings with only silica as the fillers are shown in **Figure 4.9** and **Figure 4.10**. The two groups of samples show similar surface morphology. It is notable that F-8 and F-12 have similar surface morphology as PFS-6 and PFS-8 respectively. This means that FPOSS plays much less important role when it comes to surface roughness because its size is too small. As the content of silica particles reaches 12 wt.%, the surface becomes rougher, and starts to form a hierarchical structure with nano-sized pores. When it reaches to 16 wt.%, the pores are much denser and deeper.

Figure 4.9 Surface morphology of the fourth group of samples without addition of FAS: (a) M-5; (b) M-10; (c) M-15; (d) M-20.

Figure 4.10. Surface morphology of the fifth group of samples with FAS: (a) F-4; (b) F-8; (c) F-12; (d) F-16.

The trend of the roughness increases with silica content is shown in **Figure 4.11**, and detailed data (root mean square, rms) are given in **Table 4.3**. The data for glass and fluorinated glass are also included for comparison.

Figure 4.11. Surface roughness of the coatings: (a) the fourth group of samples without addition of FAS; (b) the fifth group of samples with FAS.

Table 4.3 Surface roughness, apparent surface energy, ice adhesion strength and icing temperatures of the fourth and fifth groups of coatings

Samples	Roughness (rms, μm)	Apparent surface energy (mJ/m^2)	Ice adhesion strength at $-10\text{ }^{\circ}\text{C}$ (MPa)	Icing temperature ($^{\circ}\text{C}$)
Glass	0.001 ± 0.000	61.99	0.820 ± 0.096	-18.80 ± 0.96
M-5	0.078 ± 0.005	30.92	0.421 ± 0.053	-20.69 ± 0.21
M-10	0.741 ± 0.058	24.33	0.550 ± 0.107	-18.09 ± 0.80
M-15	1.183 ± 0.079	11.93	0.659 ± 0.099	-17.71 ± 0.91
M-20	1.730 ± 0.097	1.25	1.144 ± 0.214	-17.85 ± 0.76
F-Glass	0.001 ± 0.000	11.69	0.552 ± 0.062	-20.44 ± 0.56
F-4	0.006 ± 0.001	9.64	0.317 ± 0.082	-21.59 ± 0.36
F-8	0.365 ± 0.038	6.72	0.464 ± 0.073	-20.10 ± 0.76
F-12	1.194 ± 0.100	0.85	0.170 ± 0.066	-21.05 ± 0.59
F-16	1.817 ± 0.140	0.24	0.077 ± 0.023	-22.47 ± 0.40

4.4.2.2 Wettability, surface element analysis and surface energy

The contact angle and sliding angle of the samples, measured from room temperature (RT) down to $-10\text{ }^{\circ}\text{C}$, are shown in **Figure 4.12**.

Figure 4.12. Water contact angle (solid symbol and line) and sliding angle (dashed line if applicable, open symbol for 4 μL droplet or half open symbols for 10 μL droplet) at different temperatures on (a) the fourth group of samples without addition of FAS: only the M-20 sample displays water droplet sliding; (b) the fifth group of samples with FAS: F-12 and F-16 display water droplet sliding, while the others do not.

As seen in **Figure 4.12**, the contact angle of the coatings increases with the roughness. In the first group of samples (M series, without FAS addition), the contact angle at room temperature can reach up to 164.4° , and sliding angle around 8° and 3° for 4 μL and 10 μL droplet respectively, which indicates a Cassie wetting mode. However, when the temperature decreases, all the contact angles would decrease because of the condensation of vapour on the sample surface. And the superhydrophobic sample M-20 immediately loses its superhydrophobicity and becomes fully wetted as the droplets

would not slide off the surface even when the sample is tilted at 90° . The contact angle of the other coated samples also decrease as temperature goes down, but at a much slower rate or even nearly no change for the M-5 sample. This is because these samples (M-15, M-10, M-5) have better wetting at room temperature, and they would not change much when the vapour condenses at lower temperatures.

For FAS containing samples, they show much higher contact angle than their counterparts with similar roughness in the first group because of the introduction of the C-F functional group. As can be seen from the FTIR spectra in **Figure 4.13b**, samples F-4 and F-8 show a strong absorption peak at 1238 cm^{-1} , which corresponds to the stretching mode of the C-F bond [202]. For samples F-12 and F-16, the absorption peak is relatively weak because of the decreased amount of FAS-treated common sol in the solid coating content. However, as can be seen in **Figure 4.14**, the fluorine element can still be detected with EDX even for F-16, while there is no trace of fluorine in the sample M-20. The full elemental analysis for all the coatings is shown in **Table 4.4**.

Figure 4.13 FTIR spectra of the samples: (a) full spectra (b) spectra between 1300 cm^{-1} and 1000 cm^{-1} .

Figure 4.14 Elemental detection of the coatings. (a) M-5; (b) M-10; (c) M-15; (d) M-20; (e) F-4; (f) F-8; (g) F-12; (h) F-16.

Table 4.4 Weight percentage (wt.%) of detected elements in the coatings

Samples	C	O	Si	F
M-5	48.40	38.46	13.14	0
M-10	46.91	41.01	12.08	0
M-15	47.49	40.96	11.55	0
M-20	43.62	45.87	10.50	0
F-4	34.15	32.02	14.90	18.92
F-8	36.45	35.16	11.44	16.95
F-12	36.05	37.51	10.04	16.40
F-16	35.86	38.50	10.23	15.40

The C-F functional groups has a unique chemical structure that exhibits lower surface energy and better anti-wetting property comparing to other functional groups such as C-H groups [203-206]. Firstly, fluorine has the strongest electronegativity, and the great electronegativity different between C and F leads to highly polar C-F bonds, short bond length, and high bond strength. Consequently, there is no chemical bonding can take place. Secondly, the strong electronegativity also leads to low atomic polarizability and small size (van der Waals radius, 1.47 Å) [207]. This contributes to low surface energy and weak cohesive forces between fluorocarbon molecules, as the interaction energy arising from London forces varies as the square of the polarizability [207]. Thirdly, despite of the strong electronegativity, covalently bonded F hardly ever acts as a H-bond acceptor as reported by Dunitz, J. D. et al. [208]. They pointed out that the weak hydrogen bonding capability might be attributed to two factors: low proton affinity (low basicity, low-lying lone pair orbitals, tightness of its electron shell) and inability to modify this by intramolecular electron delocalization or intermolecular cooperative effects although the mechanism still need further investigation [208].

More recently, Dalvi et al. [209] argued that the enhanced hydrophobicity of fluorinated surfaces arises because fluorocarbons pack less densely on surfaces leading to poorer van der Waals interactions with water and the interaction of water with a hydrophobic surface is primarily a function of van der Waals interactions and is substantially independent of electrostatic interactions. And they stated that the independence is primarily due to the strong tendency of water at room temperature to maintain its hydrogen bonding network structure at an interface lacking hydrophilic sites.

Although the mechanism may still need further investigation, there is no doubt that fluorination can help lower the surface energy and wettability of different substrates by either grafting into the substrate structure or by directly decorating on the surface [210-212]. Consequently, the introduction of C-F group in the F- series samples can greatly increases the contact angle of the F- series coatings. More importantly, it also improves the anti-wetting performance at sub-zero temperatures which is more related to the anti-icing performance of coatings. As can be seen in **Figure 4.12b**, the contact angle of FAS containing coatings can reach up to 172.7° at room temperature with sliding angle of 0.8° for a $10\ \mu\text{L}$ droplet and 1.7° for a $4\ \mu\text{L}$ droplet. The contact angle decreases and sliding angle increases as temperature goes down similar to the M series. However, the slope for contact angle change is very small for all samples in this group, and the contact angle remains above 150° even at $-10\ ^\circ\text{C}$ for samples F-12 and F-16. Nevertheless, the increase of sliding angles for these two samples are different. For sample F-12, the sliding angle increases quite a bit as temperature goes down, and reaches up to around 68° at $-10\ ^\circ\text{C}$ for a $10\ \mu\text{L}$ droplet (and no sliding for the $4\ \mu\text{L}$ droplet). This suggests a Cassie-Wenzel mixed wetting mode. For sample F-16, the

sliding angle increases only a little as temperature goes down, and remains below 10° at -10°C , which shows a good Cassie wetting mode.

4.4.2.3 Ice adhesion

The ice adhesion strength for the fourth and fifth groups of samples are tested at -10°C only. All the samples except F-12 were put in the environmental chamber at -10°C for at least 3 hours before the tests. F-12 was put there for over 24 hours before the tests. The results are shown in **Table 4.3** and **Figure 4.15**. Comparing the two groups of samples, it is noticed that for the samples with similar roughness, the lower the surface energy, the lower the ice adhesion. This observation applies to all the samples, and is in agreement with results obtained by other authors.[38, 72]

Figure 4.15. Ice adhesion strength of coatings (a) the fourth group of samples without addition of FAS; (b) the fifth group of samples with FAS.

Inspecting the first group of samples without the FAS addition, the ice adhesion strength increases from 0.44 MPa to above 1 MPa when the silica content increases from 5 to 20 wt.%. Notice that the roughness has increased drastically with the silica addition. The ice adhesion strength of M-20, the one with the highest roughness in the series, is even higher than the one on glass substrate without coating. For a low silica content sample like M-5, the surface is relatively smooth, and its surface energy is

much lower than the bare glass (**Table 4.3**). In such a case the ice adhesion on the coating is lower than on the bare glass, reflecting the effect of intrinsic lower surface energy. For this group of coatings, the intrinsic surface energy, which could probably be best estimated from the relatively flat M-5 sample, is around 31 mJ/m^2 (**Table 4.3**) or lower with more hydrophobic silica addition. Unfortunately we are not able to provide such an estimate when the roughness increases with more silica addition. For such (relatively) high surface energy coatings, the surface morphology plays a dominant role. With increasing silica content, none of the surfaces are able to keep the Cassie wetting mode at sub-zero degrees. This means that the highly roughened coatings were fully wetted and thus when the water freezes, it forms stronger bonding with the substrate due to the mechanical interlocking effect between the ice and substrate, leading to higher adhesion strength.[39, 73, 77, 80] Under this circumstance, the rougher the surface, the greater the anchor effect. That is why the ice adhesion on sample M-20 is the highest, even higher than the uncoated bare glass. From this point of view, M-20 is different from PFS-8 although they are both superhydrophobic at room temperature and lose superhydrophobicity immediately at lower temperatures. PFS-8 shows a much less anchor effect comparing to other samples in the PFS- group. Actually PFS-8 has the lowest ice adhesion as can be seen in **Figure 4.7**. This might be because the surface roughness of PFS-8 is much smaller comparing to M-20, and there is not really a big enough pore to act as an effective anchor to ice. Also the addition of FPOSS could lower the surface energy and might help make the surface less rough.

For the second group of samples with addition of FAS into the coating formulation, the surface energy decreases drastically. Based on the smooth sample F-4, the intrinsic surface energy is around 10 mJ/m^2 , much lower than the M-series. Due to the low

surface energy of the coating, the ice adhesion is lower than on the FAS decorated glass substrate. Referring to **Figure 4.11b**, both F-4 and F-glass have very low roughness compared with other samples in the group. As the content of the silica increases, the roughness increases, and the mechanical anchoring effect may start to influence the ice adhesion. This explains the slight increase in ice adhesion of F-8 sample. However, the ice adhesion strengths of all coated samples remain lower than on uncoated bare glass. For F-12 and F-16, the hierarchical porous coating structure with a hydrophobic base gel contributes to greater water repellence even at low temperatures. Although the sliding angle of F-12 rises to around 68 degrees at $-10\text{ }^{\circ}\text{C}$ (10 μL droplet), which likely indicates a Cassie-Wenzel mixed wetting mode with partially wetted surface, the remaining trapped air is still functional and contributes to the relatively lower ice adhesion than F-8 and F-4. The sliding angle of F-16 is 4.4° for the 10 μL droplet and 8.4° for the 4 μL droplet at $-10\text{ }^{\circ}\text{C}$, which shows great superhydrophobicity and stable Cassie wetting mode at sub-zero temperature. This translates into the lowest ice adhesion strength at 0.077 MPa at $-10\text{ }^{\circ}\text{C}$ (**Table 4.3**), which has an ice adhesion reduction efficiency of 10.6 comparing to bare glass slide.

The trapped air in the Cassie wetting mode may contribute in several ways to the good icephobic performance. Firstly, it prevents the droplet to be in contact with the concave part of the asperities of the surface, i.e., the droplet can only lay on the top of the convex particles. According to the classical nucleation theory [48-51], the heterogeneous nucleation is more difficult on a convex surface than on flat or concave surfaces.

Secondly, it reduces the contact area between ice and the coating surface, which minimize the mechanical anchoring effect. According to Cassie's law [213], the

relationship between the apparent contact angle and surface feature can be described as

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (4.1)$$

where θ is the apparent contact angle, f_1 and f_2 the areal fraction of component 1 and 2, θ_1 and θ_2 the corresponding contact angle of component 1 and 2. When air is trapped, $\theta_2=180^\circ$, and $f_2 = 1 - f_1$, the equation reduces to $\cos \theta = f_1 (\cos \theta_1 + 1) - 1$. For sample F-16, the apparent contact angle $\theta=163.5^\circ$ at -10°C , and assuming the contact angle for a pure flat coating θ_1 is around 110° , then the fraction of the area contacting water is $f_1=6.26\%$. Such low contact fraction, together with the minimized interlock effect, would decrease the ice adhesion dramatically. At the same time, it also minimizes the damage to the coating surface during ice removal, and thus helps maintain the coating durability.

Thirdly, as the volume of water expands upon freezing, the trapped air in enclosure would be compressed and exert a counter-force on the ice block. This will reduce the ice adhesion to certain extent, as well as make the structure of the formed ice at the interface less dense. As can be seen in **Figure 4.16b**, the residual ice crystals left after the adhesion test on sample F-16 are not many and very small, which indicates a loose ice structure at the interface between the ice block and the substrate. In contrast, there is usually a large fraction or full coverage of solid ice left on the Wenzel wetting mode rough surfaces because of the interlock effect (**Figure 4.16a**).

Figure 4.16. Residual ice after the adhesion test on sample (a) M-20, and (b) F-16.

4.4.2.4 Icing temperature

The icing temperatures of the samples are shown in **Figure 4.17**. It is interesting to notice that the trend of the icing temperature of the samples in these two groups group is basically the same as that of ice adhesion. This is a bit different from the third group. However, the mechanism behind the phenomenon is the same. Surface energy and morphology always play the role together to determine the anti-icing performance. For most surfaces in these two groups except F-12 and F-16, the wetting status at sub-zero temperatures is the same as the first three groups of samples, which is fully Wezel wetting mode. In such a case, lower surface energy and smooth surfaces are favourable for lower icing temperature. Comparing to the third group (PFS- series), the silica particles in the fourth group (M- series) cause a much increase of roughness with the absence of small particles of FPOSS. The decreased geometric factor has a much more impact on the icing temperature than the lowered surface energy. Consequently, the rougher the surfaces, the higher the icing temperature. In contrast, F-12 is semi-Cassie wetting and F-16 is cassie wetting as mentioned earlier. Thus the concave sites are avoided more or less from contacting water, and thus leading to a higher geometric factor for the surfaces. In this case, the higher the roughness, the better anti-wettability, and thus lower icing temperature.

Figure 4.17 Icing temperatures of the samples: (a) the fourth group of samples without addition of FAS; (b) the fifth group of samples with FAS.

4.5 Summary

Two series of sol-gel coatings with different surface energy and roughness have been developed. Their surface properties were investigated including roughness, surface energy, contact angle at different temperatures, ice adhesion and icing temperatures. It was shown that the intrinsic surface energy and surface morphology of the coatings play important roles together in terms of anti-icing performance. Not all superhydrophobic surfaces, as indicated by the water contact angle at room temperatures, could remain water repellent at low temperatures. The anti-icing performance are closely correlated with the surface properties at lower temperatures instead of that at room temperature. The two aspects of the anti-icing performance, i.e., ice adhesion and icing temperature, are not necessarily correlated on rough surfaces because of the different mechanism for them.

For the three groups of samples with addition of FPOSS, none of the surfaces can maintain superhydrophobic at low temperatures. In such cases, lower surface energy and smooth surface are favourable for anti-icing performance. Due to the small particle size of FPOSS, the anchor effect is not much because the lowered surface energy has actually more influence on the final ice adhesion than the increase of

roughness for most samples in these three groups. The lowest ice adhesion was achieved to be 0.175 ± 0.050 MPa at -20 °C and 0.135 ± 0.029 MPa at -10 °C on sample PFS-8. The ice adhesion reduction efficiency (the ratio of ice adhesion on bare glass slide to that on the coatings) reaches to 5.4 at -10 °C and 6.8 at -20 °C. The icing temperature of the samples are strongly related to the surface energy and roughness of the samples. For the first group of samples (P- series), the dominant factor is the surface energy, while surface roughness or geometric factor is dominant for the other two groups (PF- and PFS- series). The lowest icing temperature was achieved by relatively smooth sample PF-4. It is also in agreement with conjecture that those samples which show an icing delay phenomenon are likely to have lower icing temperatures.

For the last two groups of samples with only hydrophobic silica as the fillers, the surface energy and roughness have different influence on the anti-icing performance. The ice adhesion and icing temperatures are on the same trend in each group. For M-series samples, the intrinsic surface energy is around 31 mJ/m^2 , which is about half of the uncoated glass slide. In this series, low surface roughness combined with the reduced surface energy (e.g. M-5) leads to decreased ice adhesion compared with the uncoated bare glass. Increasing surface roughness by adding more silica particles increases the ice adhesion because of the interlocking effect which is not obvious in the first three groups. For the F- series samples, the addition of FAS reduces the intrinsic surface energy of the coating to around 10 mJ/m^2 . Such low surface energy combined with proper microstructures enables the surface to be water repellent even at sub-zero temperatures. Consequently, the trapped air between water and the superhydrophobic substrates can effectively reduce the ice adhesion and lower the icing temperature. The best anti-icing performance was achieved on FAS dosed

coating with 16 wt.% silica, which has a sliding angle as low as 4.4° for a $10\ \mu\text{L}$ droplet at $-10\ ^{\circ}\text{C}$.

Chapter 5 Effect of Test Environment on the Icing Behaviour

5.1 Introduction

Many authors have done a great job to develop icephobic coatings. However, nearly every author has a different test environments and procedures. For ice adhesion test, there are not many variant factors. Most of the tests conducted were shear adhesion measurements which are mainly related to the environment temperature and the rate of the force. Usually the rate of force does not have much influence on the final shear stress on hard substances, and the effect of temperature is obvious. Thus ice adhesion is not included in this chapter. As for the nucleation related tests, there are quite a few factors that can affects the results. Some measured the icing temperature, while some others used the icing delay time at certain temperatures; some utilized nitrogen to avoid the moisture, while others did not; some kept the droplet and sample in the same chamber to achieve an isothermal environment, while others used a peltier stage to cool from the substrate side; some used a constant flow of air, while others did not. It might not be a problem to compare the samples tested with the same procedure. But it is necessary to investigate if they really produce the same results or trend in different situations for two reasons. One is to know if they are comparable between different authors. Another is to know if they produce the same trend in different test environment/procedures.

In this chapter, the icing temperature will be tested on the samples prepared in Section 4.2.2 in these following situation:

1. Cooling with nitrogen protection vs. without nitrogen protection.

2. Peltier stage cooling (with temperature gradient as in Section 3.2) vs. icing chamber cooling (without temperature gradient).
3. Icing with air flow vs. without air flow

At the same time, icing delay time was also investigated with some of the conditions as it was studied before as an icephobic indicator [33, 35, 36, 118, 120, 121, 214]. The purpose is to understand its correlation with icing temperatures. The wettability of the surfaces was also investigated with and without nitrogen protection at different temperatures, and it will be correlated with the results obtained in those different situations.

5.2 Experimental work

The samples used in this study are from the second series of sol-gel coatings introduced in Chapter 4. The contact angle measurement system with a cooling component (OCA20, Dataphysics, Germany) shown in **Figure 3.2** was used for the investigation of contact angle measurement and icing temperature (with temperature gradient). For the test without nitrogen protection, the cooling chamber was simply closed during the measurement. For the test with nitrogen protection, a small pipe was inserted into the back wall of the chamber and reaching the top centre of the chamber. Then pure nitrogen gas (99.9%) was filled into the chamber (about 10 cm x 10 cm x 1 cm) continuously. The measurement was conducted after 1 minute of filling the gas. The contact angle was measured with 4 μL droplets for at least 5 times on each sample. The icing temperature measurement was conducted with 10 μL droplets on the coatings. The temperature was decreased from room temperature to 0 °C as fast as possible, and the temperature ramp was set as 1 °C/min from 0 °C to the freezing temperatures. The temperature was reset to room temperature once the cycle of

freezing was complete. In the next cycle, the temperature was kept at room temperature for 0.5 to 1 minute to ensure the melting of the frozen droplet before cooling down again. The icing temperature was measured at least 10 times on each sample.

For the test without temperature gradient as well as with/without air flow, an environmental chamber (Z-Plus 8, CSZ, USA) was used. During the operation, the chamber was cooled by continuous air flow inside it. Although the speed of the air flow is unknown, it is constant and thus is acceptable for comparison purpose. For the icing temperature measurement, a 10 μ L droplet was always put on the samples first (except superhydrophobic ones), and then the chamber was closed and cooled with a ramp of 1 $^{\circ}$ C/min between 0 $^{\circ}$ C and the freezing point. For superhydrophobic samples M-20 and F-12, they were cooled to 0 $^{\circ}$ C first in the chamber to facilitate the droplet placement since they are superhydrophobic at room temperature and the air flow will easily blow the droplet off the sample surfaces. For F-16, an aluminium substrate with a concave site was used since this coating is superhydrophobic even at sub-zero temperatures. For the measurement without air flow, the samples were covered by a beaker, and a temperature sensor was placed near the sample inside the beaker.

The icing delay time was measured with both apparatus and two droplet placement procedures were investigated. One is to place the droplet before the cooling process; the other is to cool the sample first, and then place the droplet onto the surfaces. 10 μ L droplets were used in all the icing delay tests.

5.3 Results and discussion

5.3.1 Contact angle at different temperatures

The contact angle of the samples in different environments and temperatures are shown in **Figure 5.1**. It can be seen that the contact angle is higher with nitrogen protection than without nitrogen protection especially at lower temperatures. For the samples without fluorination, the nitrogen protection has nearly no influence on the samples with contact angles lower than 90 °C because they did not change much with temperatures even without nitrogen protection. For M-15 and M-20, the influence of nitrogen is obvious, and the higher the contact angle, the bigger the gap between the contact angles in different environments.

Figure 5.1 Contact angle with nitrogen protection (solid line) and without nitrogen protection (dashed line) on samples: (a) non-fluorinated samples (b) fluorinated samples.

For samples with FAS modification, the difference between the contact angles in different environment is not so much although the contact angles are all above 90 °C. This is may be because the surfaces have a better water repellence intrinsically and showed not much change of contact angle even without nitrogen protection just like the hydrophilic samples in the first group.

The reason for the increase of contact angle with nitrogen protection is related to the lack or restraint of condensation on the surfaces. The presence of nitrogen gas in the chamber would decrease the humidity of the internal environment. According to Tavakoli [215], the premature and capillary condensation followed by thin-film formation and propagation around the tri-phase contact line contribute to the spreading of the water droplet. On hydrophobic or superhydrophobic surfaces, the adjacent at the three-phase contact line can be considered to be a confined area which facilitates the capillary condensation. However, this condensation is related to the surface composition. In current study, it seems only the samples which have a contact angle larger than 90° and an intrinsic hydrophilic component are greatly influenced. For hydrophobic samples and superhydrophobic samples with intrinsic hydrophobicity, the spreading will still happen with the decrease of temperature but the extent of the spreading is much less. This can be explained by Kelvin [216] shown in Equation (5.1):

$$\ln \frac{p}{p_0} = \frac{2\gamma V_m}{rRT} \quad (5.1)$$

where p is the actual partial vapour pressure, p_0 the saturated vapour pressure, γ the water-vapour interfacial energy, V_m the molar volume of air, r the radius of the water droplet, R the universal gas constant, and T the temperature. When the surface has an intrinsic hydrophilic component (such as M- series samples), the presumed condensation of water would have a concave meniscus which has a negative radius. Consequently $\ln \frac{p}{p_0}$ becomes negative, which means $p < p_0$. In this case, capillary condensation is easy to occur and facilitate the thin film formation at the adjacent of three-phase contact line. In contrast, if a droplet is formed on an intrinsically hydrophobic surface, the radius of the droplet is positive which leads to $p > p_0$, which

means the droplet will evaporate in order to reach an equilibrium state. Thus the condensation is more difficult to happen on such surfaces.

In terms of forming a continuous thin water film on the rough surfaces, the condensed water must be enough to fill the concave sites in order to coalesce with the adjacent condensed water droplets. The sources of the condensation include the vapour and the bulk water droplet. As demonstrated by Tavakoli [215], the trijunction spreading dynamics are dominated by water liquid itself instead of the vapour surround it because ethylene glycol drops with contact angle of 135° would not spread when temperature decreases. So it is reasonable to say that the condensation from vapour itself is not enough to form a continuous thin film on the surface. Much of the condensation at the trijunction area is from the evaporation of the water droplet. However, the higher humidity does help the thin film formation too because it leads to more condensation from the vapour.

5.3.2 Icing temperature with nitrogen protection versus without nitrogen protection

The results for the icing temperature without and with nitrogen protection are shown in **Figure 5.2**. It is clearly seen that the icing temperatures were lowered to some extent with nitrogen protection on both series of samples. However, the difference for most samples are minor as they basically lie in the range of error bars except M-15 and M-20. This is in agreement with the line nucleation rate theory discussed in 4.5 and the condensation behaviour discussed in Section 5.3.1.

Figure 5.2 Icing temperatures on samples with and without nitrogen protection: (a) non-fluorinated samples (b) fluorinated samples.

During the cooling process, the three phase-contact line is the most unstable area where evaporation of water droplet, vapour condensation on the substrate, coalescence of condensation droplets and spreading of the contact line are happening. As mentioned earlier, the spreading is because of the formation of thin water film on M-15 and M-20. On the one hand, the spreading elongates the contact line which provides more nucleation sites especially concave nucleation sites. On the other hand, the condensed water that was filled concave sites near the contact line may act as a trigger for bulk water nucleation. The formation of thin film at the contact line area is based on the premise that concave sites are fully filled with condensed water so that coalescence of water from adjacent sites can happen. It is possible some of the nearby concave sites are not yet fully filled at some moment, but the temperature is low enough to make it freeze. In this case, the air above the formed ice is oversaturated because ice pressure is always lower than liquid water pressure under 0 °C [217]. Consequently frost starts to grow above the formed ice, and the growth direction is toward the source of the vapour which is the bulk water droplet in current study. The growth speed of frost depends on the temperature and water vapour partial pressure.

When the frost touches the bulk water droplet, it will trigger the nucleation of the whole water droplet because it is a perfect nucleus.

For hydrophilic samples in the first group (Glass, M-5 and M-10), the spreading is not affected much by the humidity because of the well wetting behaviour on the surfaces. There is no confined area at the three-phase contact line in such case, and thus no enhanced condensation and less likely the frost induced nucleation occurs.

For fluorinated samples in the second group (F-glass, F-4, F-8, F-12 and F-16), it is a similar situation although the mechanism (discussion in last chapter) is a bit different. In summary, any factors that facilitate the condensation and spreading of the contact line are favourable for nucleation. Thus the higher the humidity, the higher the icing temperature.

5.3.3 Isothermal cooling with airflow and without airflow

The results for icing temperature under the isothermal cooling with and without airflow are shown in **Figure 5.3**.

Figure 5.3 Icing temperatures on samples with isothermal cooling in environmental chamber: (a) non-fluorinated samples (b) fluorinated samples.

When the samples are isolated from cold airflow, the trend of icing temperatures in each group is basically in agreement with the results obtained by the peltier stage cooling (**Figure 5.2**) although the difference between different samples in each group seems much smaller. Another noticeable fact is that the icing temperature by isothermal cooling in current study is much lower than that by peltier stage cooling for the same samples. This might be related to the humidity change inside the beaker. Since the cooling is from the beaker transferred to the sample and droplet, the beaker would have higher temperature than the samples at all times. Thus the condensation inside the beaker would most likely to happen on the beaker wall instead of on the sample. Moreover, the capillary condensation at the trijunction would also be restrained to some extent in this case. Thus the icing temperature is much lower than that by cooling the bottom of the samples.

For nucleation without cover in the environmental chamber, it can be seen that the airflow has a great influence on the icing temperatures for all samples. The reason for that might involve several factors. To begin with, the airflow may change the way of nucleation. As demonstrated by Jung [61], the temperature at the water-air interface can be lowered by the airflow. When the temperature reduction is large enough, the free energy barrier for the homogeneous nucleation at the water-air interface will be lower than that at the substrate-water interface as can be seen in Equation (5.2) and (5.3) [61]:

$$\Delta T = T_g - T_w \approx - \frac{\Delta H_v \xi \rho_w}{Mr_0 \left(h_g + \frac{k_w}{l} \right)} \quad (5.2)$$

$$\xi = \frac{D \rho_{v,sat}}{\rho_w} (1 - \phi) + C (1 - \phi) \quad (5.3)$$

Where T_g is the temperature of airflow, T_w the temperature of water at the water-air interface, ΔH_v the enthalpy of vapourization, ξ the evaporation rate coefficient, ρ_w the

density of water, M the molecular weight of water, r_0 the radius of the droplet, h_g the convective heat transfer coefficient of air, k_w the thermal conductivity of water, l the height of the droplet, $\rho_{v,sat}$ the density of saturated water vapour, ϕ the humidity. It is easy to conclude that this kind of homogeneous nucleation is more likely to happen on samples with higher contact angle and at lower humidity. Higher contact angle means higher geometric factor according to the classical nucleation theory and thus smaller difference of free energy barrier between heterogeneous nucleation and homogeneous nucleation. Lower humidity means higher evaporation rate coefficient and greater reduction of temperature at the water-air interface according to Equation (5.2) and (5.3), and thus there are chances for homogeneous nucleation at the water-air interface depending on the free energy barrier on both interfaces. In current study, the humidity for all samples are the same. Thus the nucleation is decided by the wettability of the surfaces. The higher the contact angle, the more chances for homogeneous nucleation to happen.

Secondly, the airflow and the vibration of the chamber itself would cause strong turbulence on the droplets especially for those with a higher contact angle or with sliding ability. As reported by Inada [218], the ultrasonic vibration greatly promotes the phases change from supercooled water to ice. Although the vibration or caused by airflow might not be as strong or frequent as ultrasound, it is well accepted that any kind of turbulence will promote the ice formation from supercooled water. The larger the contact angle, the stronger the convection and turbulence on the droplet.

Considering the fact that the icing temperatures with airflow are much lower than without airflow, it is easy to conclude that the turbulence plays the main role in the nucleation process and the effect of vibration from the chamber itself is negligible.

That is why the trend of icing temperatures for both groups are the same: the higher the contact angle, the higher the icing temperature.

5.3.4 Icing lag time

The OCA20 contact angle measurement system was used for the icing lag time investigation. Two procedures of icing lag time were tested. The first procedure is to place the droplet onto the surface after it is cooled and maintained at a fixed temperature. This method was found practically difficult to handle for the purpose of comparison between different samples. For example, if a sample was cooled to a relatively high temperature (e.g. $-5\text{ }^{\circ}\text{C}$), it will take a long time for the water to freeze. And usually at least 10 data is necessary for a convincing comparison. So this type of measurement is too time consuming. If the surface temperature is low (e.g. $-25\text{ }^{\circ}\text{C}$), then it is quite possible to get a reasonable lag time for icing. But the problem is there is also a great chance that water would freeze immediately once it touches the cooled surface. Again this will make the comparison difficult between different samples. It may be possible to find a suitable temperature range for a sample at which it would not take too long for water to freeze, nor freeze immediately at the instant moment of contact. Problems still exist as such appropriate temperature range might not be the same among samples of interest. There are also not many reports utilizing this kind of procedure to characterize the anti-icing performance. Jung et al. [120] investigated the icing delay time by dropping micro droplets onto the surface through a long copper tube in the chamber, so that the temperature of the droplets can reach ambient temperature before it touches the sample surface. The delay time for various samples vary from 2 seconds to around 1100 seconds, and the error bar is big for most of the samples. In summary, this test procedure is not a very good way to compare the ant-

icing performance between different samples as a standard procedure although it is no problem for simple comparison purpose in some cases.

The second procedure for lag time test is to place the water droplet onto the sample surface first, and then it is cooled together with the sample. This procedure have been used in most of the reports which adopt icing delay as a way of characterization. In this way, the time for icing can always be obtained. But another problem arises which is similar as in the first method when it is applied in current study. When the temperature is too low, the water droplet may freeze even before the temperature reaches to the set point. If the set point is closer to the melting point, then it will take a long time for the water to freeze. Generally, lower temperature guarantee a more coherent results. As can be seen in **Figure 5.4**, the icing delay time of an 8 μL water droplet on glass was quite long (> 2400 s) when the cooling temperature was -13.1 $^{\circ}\text{C}$. In this case, the experiment was very time consuming and it would probably take hours or even days for the water to freeze. Thus it is not suitable to adopt this temperature for the measurement. When the temperature decreased to -17.8 $^{\circ}\text{C}$, the icing delay time declined to 581 ± 47 seconds, but the repeatability was gone after 10 tests. This made the results useless for comparison. When the cooling temperature further decreased to -22.5 $^{\circ}\text{C}$, the icing delay time was decreased to 569 ± 51 seconds and repeatable.

Figure 5.4 The icing lag time of an 8 μL water droplet on glass slide at different temperatures. The ramp from room temperature to set point is $-5\text{ }^{\circ}\text{C}/\text{min}$. Those runs with a lag time beyond 2400s were terminated and are shown without markers.

The icing delay time of a 10 μL droplet on other samples was tested at $-17.8\text{ }^{\circ}\text{C}$. The results are shown in **Figure 5.5**.

Figure 5.5 Icing delay time of a 10 μL droplet on samples at $-17.8\text{ }^{\circ}\text{C}$: (a) non-fluorinated samples, (b) fluorinated samples. Those runs with a lag time beyond 2 hours were terminated and are shown without markers.

It is clear that the icing delay time for some samples are quite stable, while there is a great fluctuation for others. Further inspection reveals that those with a stable icing delay time are the rough and wetted ones. The free energy barrier on these surfaces are

the lowest because there are plenty of concave nucleation sites on these surfaces. Besides, the ambient temperature is close to the icing temperatures of these samples as can be seen in **Figure 5.2**. So the nucleation rate on these surfaces are the highest. For other surfaces, the nucleation of the droplets on them is more stochastic since the energy barrier of nucleation is generally higher on them although the surface properties still seem to play a role in the icing delay process. The fluctuation for some samples is so big that it is unsuitable for a quantitative analysis in current study. However, it is noticeable that the overall trend of the delay time seems to be in agreement with the trend of icing temperature although a couple of individual samples are not in a perfect sequence comparing to their corresponding position in icing temperatures.

It is worth mentioning that the big fluctuation of lag time is reported in several literatures [124, 125, 127]. With enough data, it is possible to have a statistic analysis on the unfrozen fracture on samples versus time. However, this kind of test is very time consuming and usually is done with an automatic measurement system. Besides, the comparison between different samples is not purely by lag time but rather by the cooling temperature. In most other related reports [35, 118, 120, 121, 214], the lag time is quantified at a certain temperature and compared by the mean value for each sample.

For comparison purpose, the icing delay time at -20 °C on selected sample was also tested in the environmental chamber without airflow. The results are shown in **Figure 5.6**. The overall lag time on both samples by isothermal cooling in the chamber without airflow is much larger than that with peltier stage cooling although the cooling temperature is actually lower. This is in agreement with the change of icing

temperature in different environment. However, the big fluctuation on some runs makes the tests very time consuming and the artificial interruption makes the results less authentic.

Figure 5.6 Icing delay time of a 10 μL droplet on M-10 and F-8 at $-20\text{ }^{\circ}\text{C}$ in the environmental chamber without airflow. Those runs with a lag time beyond 1 hour were terminated and are shown without markers.

The icing delay time with airflow was also tested in the environmental chamber. The results are shown in **Figure 5.7**. As expected, the icing delay time was shortened extensively especially for those with long delay time shown in **Figure 5.5**. The deviation of lag time for most samples are also reasonably distributed. There are no abrupt increase of lag time during all the runs. However, the difference between different samples are not big enough for an authentic comparison.

Figure 5.7 Icing lag time of a 10 μL droplet on the samples at $-20\text{ }^{\circ}\text{C}$ in the environmental chamber with airflow: (a) non-fluorinated samples, (b) fluorinated samples.

5.4 Summary

The test environment has a great influence on the wetting and icing behaviour of droplets on surfaces. Low humidity would lead to higher contact angle. The change is especially obvious on hydrophobic or superhydrophobic surfaces which has a hydrophilic component. This would also lead to a decrease of icing temperature on these surfaces because of restrained condensation at the adjacent of the three-phase contact line. For those samples which are hydrophilic or intrinsically hydrophobic, the influence of humidity is not so much when cooling from the bottom of the samples. However, all the icing temperatures are lowered to a great extent by isothermal cooling without airflow in the environmental chamber because of humidity was lowered even further. When the droplets are exposed to shear airflow, the icing temperatures would be greatly increased because of the turbulence it causes. The trend of icing temperatures with airflow is that the higher the contact angle, the higher the icing temperature.

When it comes to icing lag time, the repeatability and reliability of the measurement is strongly dependent on individual samples and the test temperature. Lower temperature

means better repeatability for some samples but at the same time it might cause other problems for other samples such as freezing above the set point, or small difference of lag time between other samples. The test environment has a great impact on the results. Lower humidity would lead to longer icing lag time and greater fluctuation. Airflow would shorten the lag time and improve the repeatability but the results are not so valuable due to the tiny difference between different samples.

It can be concluded that icing lag time is not a very reliable characterization method for the anti-icing performance, and therefore it would not be considered in future statistic investigation. Instead, icing temperature will be studied with a higher number of freezing cycles for statistically meaningful results in the next chapter.

Chapter 6 Icing Behaviour of Droplets on Sol-gel Coatings with Different Surface Energy and Roughness

6.1 Introduction

Icing behaviour of droplets on surfaces is a very important aspect of the whole anti-icing investigation. Yet most of the published reports about anti-icing materials lack fundamental investigation except the obvious experimental observations. There were some papers focused on the fundamentals and explored the effect of the surface parameters on the icing nucleation process. However, the involved surfaces were quite limited, and sometimes the results are controversial. Hence, further investigation is needed.

This chapter aims to investigate the ice formation behaviour on the developed sol-gel coatings, which cover a large range of surface roughness and apparent surface energy. Heterogeneous nucleation behaviour of supercooled droplets on different coating surfaces will be investigated statistically, with the aim to reveal of the mechanisms of nucleation, as well as the effect of surface roughness and the apparent surface energy.

6.2 Experimental Work

Two groups of sol-gel coatings with different roughness and surface energy were prepared on glass slides, the detailed procedure was the same as in Section 4.2. The common sol for both groups is made of methyl triethoxysilane (MTEOS, 99%, Sigma Aldrich, USA) and glycidyloxypropyl trimethoxysilane (GLYMO, 98%, Sigma Aldrich, USA). In one group, different amount of silica particles were added to achieve varying degree of surface roughness. In another group, hydrophobic additive, fluoroalkylsilane (FAS, 97%, Sigma Aldrich, USA) was introduced to induce low

surface energy. In addition, bare glass slide and glass slide decorated with FAS (but without the sol-gel coating) were also studied for comparison. The fluorinated glass was prepared by immersing the glass in hydrolysed 1 vol. % FAS methanol solution for 12 hours followed by curing at 120 °C for one hour. The roughness and measured apparent surface energy of the coatings are detailed in **Table 6.1** and also shown in **Figure 6.1**. The wetting status at -10 °C was based on the previous study in Chapter 1. The M-x series of samples are the ones without the addition of the hydrophobic additive FAS, and the number x indicates the weight percentage of silica nanoparticles in the final coating. The F-x series of samples follow the same coating composition and procedure except that they contain the hydrophobic additive, FAS. As a result, the weight percent of the silica particle is slightly lower than their M- series counterpart, but the surface morphology remain similar. In the current study, thin glass substrates of 100 μm thick were used in order to minimize the temperature gradient for a better control of the icing temperature. The coatings thickness is around 20 to 40 μm so that the temperature gradient in the coating can be considered to be negligible.

Figure 6.1 Surface roughness and surface energy of the samples used in the study.

Table 6.1 Sample roughness, apparent surface energy, and wetting status at -10 °C.

Samples	Roughness (rms, μm)	Apparent surface energy (mJ/m^2)	Contact angle at -10 °C (°)	Wetting mode at -10 °C
Glass	0.001 ± 0.000	61.99	28.5 ± 0.3	Wenzel
M-5	0.078 ± 0.005	30.92	70.0 ± 0.4	Wenzel
M-10	0.741 ± 0.058	24.33	75.0 ± 1.1	Wenzel
M-15	1.183 ± 0.079	11.93	81.0 ± 1.2	Wenzel
M-20	1.730 ± 0.097	1.25	115.7 ± 1.9	Wenzel
F-Glass	0.003 ± 0.001	11.69	105.2 ± 0.5	Wenzel
F-4	0.006 ± 0.001	9.64	105.4 ± 0.7	Wenzel
F-8	0.365 ± 0.038	6.72	110.3 ± 0.5	Wenzel
F-12	1.194 ± 0.100	0.85	153.9 ± 3.1	Semi-Cassie to Wenzel
F-16	1.817 ± 0.140	0.24	163.5 ± 2.8	Cassie

The icing behaviour of the droplets on the coatings was investigated by a self-designed automatic measurement system. It consists of two stacked peltier thermoelectric cooling units, an aluminium block with embedded digital temperature sensor, and a loop control system. The schematic is shown in **Figure 6.2**. The function of peltier stage on the bottom is purely for cooling of the peltier stage above it so that it can accomplish repeated cooling and warming cycles effectively. The heat generated by the bottom peltier stage is diffused by the bulk aluminium walls which are also well connected to the heat sink on the back of the device. The system utilizes laser to detect the icing events and the detector was placed normal to the direction of the laser and pointing to the droplet. All the holes for wires and the gap between the lid and

chamber were sealed with silicone to ensure an isolated environment to prevent the moisture outside of the chamber from entering the chamber.

Figure 6.2 Schematic of the automatic measurement system

For each sample, a 10 μL deionised water droplet was placed on the surface and then the sample was cooled from room temperature to a set point which was lower than the suspected supercooling point. After complete freezing, the ice droplet was then warmed up to room temperature and held for 1 - 3 minutes to ensure the complete melting of the ice and equilibrium state before the next cycle begins. The ramp rate from 0 $^{\circ}\text{C}$ to the set low temperature point was set to be 5 $^{\circ}\text{C}/\text{min}$. The ramp rate from room temperature to 0 $^{\circ}\text{C}$ and from set points to room temperature will not affect the nucleation process, and thus was set at 40 $^{\circ}\text{C}/\text{min}$ to save time. A typical cycling record is shown in Figure 6.3.

Figure 6.3 The 170th to 174th cycles on sample M-10.

Upon the onset of freezing process of the droplet, the detected laser intensity would change drastically because of the enhanced refraction and reflection inside the freezing droplet as shown in **Figure 6.4**. Also, there is short time increase of the achieved temperature because of the release of latent heat. This sensitive reaction in turn confirms that the temperature gradient caused by the substrate itself is negligible. The temperature at which a sudden increase of the photodetector reading is observed, i.e. the temperature at the beginning of ice formation, is defined as the supercooling point, nucleation or icing temperature. To study the nucleation behaviour and gather statistical data, each sample was tested with 500 cycles.

Figure 6.4 The icing part of the 170th cycle on sample M-10.

6.3 Results and discussion

The obtained icing temperatures for the samples are shown in **Figure 6.5** and **Figure 6.6** for the M- and F- series of coatings, respectively.

Figure 6.5 The nucleation temperature of 10 μL droplet on (a) glass, (b) M-5, (c) M-10, (d) M-15 and (e) M-20.

Figure 6.6 The nucleation temperature of 10 μL droplet on (a) F-glass, (b) F-4, (c) F-8, (d) F-12 and (e) F-16.

The icing temperatures for most M-series samples have a stationary distribution, i.e. they stay relatively stable with increasing number of cycles. However, M-20 and the F-series tend to show slight increases of the nucleation temperatures in the first a

number of cycles. This may be because of the continuous penetration into the asperities of the surfaces together with slight spreading of the droplets on surfaces which have a higher contact angle. On the contrary, the hydrophilic surfaces with a lower contact angle did not display such phenomenon. Although the spreading was not very significant especially after the first a few cycles, it has led to a larger contact area between the droplet and the surface, thus theoretically would result in more nucleation sites. Consequently, the icing temperature tends to increase slightly. For low contact angle surfaces, the wetting state is relatively stable during the freezing / melting cycles, thus there was little change to the nucleation process.

Despite the mild shift of the nucleation temperatures for some of the samples, there is a good statistical agreement between the first 250 cycles and the next. This kind of phenomenon is actually very common in some other reports [64, 127, 129, 173]. And it would not affect the theoretical analysis that follows. To investigate the distribution of icing temperatures on the samples, we bin the data with a bin width of 0.2 °C across the whole icing temperature range. The distribution of icing event on each bin section with the normalized distribution curve is shown in **Figure 6.7** and **Figure 6.8**. The summarized normalized distribution is shown in **Figure 6.9**. The ordinates here were converted from icing event number to freezing probability which is defined as

$$P = \frac{N_i}{N_0} \quad (6.1)$$

where N_i is the icing event in the i th bin and N_0 the total icing events which is 500 in the current study. The peak temperatures for the maximum freezing probability density for each sample are shown in **Table 6.2**. The difference between the lowest and highest mean icing temperature among all samples is 6.9 °C.

Figure 6.7 Histogram of the icing events on non-fluorinated samples with bin width of 0.2 °C.

Figure 6.8 Histogram of the icing events on fluorinated samples with bin width of 0.2 °C.

Figure 6.9 Freezing probability distribution as a function of temperature on (a) non-fluorinated samples and (b) fluorinated samples.

Table 6.2 Statistic values of the nucleation events on the samples.

Samples	Peak value (°C)	T ₅₀ (°C)	10-90 width (°C)
Glass	-23.95	-24.00	1.63
M-5	-25.23	-25.36	1.94
M-10	-24.26	-24.31	1.63
M-15	-22.76	-22.75	2.06
M-20	-22.42	-22.43	1.69
F-Glass	-25.60	-25.63	1.88
F-4	-27.54	-27.44	1.75
F-8	-24.99	-25.00	1.63
F-12	-24.44	-24.45	2.50
F-16	-29.28	-29.31	1.44

Moreover, the survival curve was also adopted here to give another look at the distribution. The survival curve is defined as[130]

$$F(t) = \frac{N(t)}{N_0} \quad (6.2)$$

where $N(t)$ is the unfrozen events at time t and N_0 the total icing events. Since the temperature decreases linearly with time, **Equation (6.2)** evolves to

$$F(T) = \frac{N(T)}{cN_0} \quad (6.3)$$

where c is the cooling rate. The results are shown in **Figure 6.10**. It is notable that the survival curves have very similar slopes. It shows a clear coherent difference between samples. The T_{50} data (the temperature for 50% unfrozen events), which was used as the icing temperature in some reports [129, 219, 220], are in perfect agreement with the peak values. Notice that the survival curves are based on 500 cycles which is much more than the 200 cycles threshold [130] to make the curve stable, and the slope at the bottom half of the freezing events are nearly zero. Also worthy of note are the 10-90 widths (the range from 10% frozen temperature to 90% frozen temperature) shown in **Table 6.2** which are comparable to the data demonstrated in the reference [221]. Thus we believe that the investigation based on the data is reliable. Such a comparison does suggest however that the nucleation site which is dominant seems not to be changing dramatically in those samples where there is an increasing temperature trend over the 500 runs. That suggests that either; any extra nucleation sites exposed during spreading of the drops are very similar indeed to the sites responsible for the nucleation event say 50 cycles earlier or, that there is simply drift in the temperature measuring – which of course seems not to be the case in most of the 500 runs series carried out.

Figure 6.10 The survival curves on (a) non-fluorinated samples and (b) fluorinated samples.

Nucleation is a stochastic process, yet it is affected by the surface energy and geometry of the surface according to classical nucleation theory. This can be applied to explain why the samples in the current study show different icing behaviour. It has been known that low surface energy and convex surface are preferable for lower icing temperature [48-53].

For the sample group without FAS (hydrophobic) treatment, M-5 has the lowest icing temperature. This is likely because this surface is relatively smooth, and has much lower surface energy than glass (**Table 6.1**). M-10 shows higher icing temperature as it is rougher than M-5 although its apparent surface energy is lower. The other two samples in this group have very similar and high icing temperatures. The two samples are the roughest in the series and can be significantly wetted by water before freezing occurs. It seems that fully wetted rough surfaces provide numerous concave positions for nucleation which have the lowest barrier compared with smooth surfaces.

Similarly, in the second group of samples with FAS (hydrophobic) treatment, F-4 has a relatively lower icing temperature because of its relatively smooth surface and lower surface energy than F-Glass. Samples F-8 and F-12 show higher icing temperature

because of their rough surface and Wenzel wetting status at sub-zero temperature. F-16, on the contrary, has the lowest icing temperature among all the surfaces because it can maintain Cassie state at sub-zero temperatures [222]. This means there is air trapped between the water droplet and the surface. In this case, the contact area between water and the substrate is much less than on flat or fully wetted surface. Although it might not necessarily mean the concave sites for nucleation were totally avoided, the chance for concave surface nucleation was greatly reduced in such a situation.

To further investigate the different nucleation behaviour on the samples, we first employed classical nucleation theory and assumed that heterogeneous nucleation occurs only at the water / coating interface. The nucleation rate can be expressed as [223, 224]:

$$\log_{10}R(T) = \log_{10}(J_A) - \frac{\Delta G_c f_A(\theta)}{2.303kT} \quad (6.4)$$

$$\Delta G_c = \frac{16\pi\gamma^3}{3(\Delta g)^2} = \frac{16\pi\gamma^3 T_m^2}{3\Delta H_{m,v} \cdot (T_m - T)^2} \quad (6.5)$$

where J_A is the pre-factor, k the Boltzmann constant, $T_m = 273.15$ K the melting point of ice, $\gamma = [28 + 0.25(T - 273.15)] \times 10^{-3}$ J/m² the water-ice interfacial energy[171], $\Delta H_{m,v} = \frac{6010 \text{ J/mol}}{1.965 \times 10^{-5} \text{ m}^3/\text{mol}} = 3.06 \times 10^8$ J/m³ the volumetric enthalpy change during ice formation[170], and $f_A(\theta)$ the factor which is dependent on the surface geometry and it is always between 0 (no energy barrier) and 1 (homogeneous nucleation) no matter whether the surface is flat, concave or convex [48-53].

For each data set, the nucleation rate $R(T_i)$ at T_i with bin width of ΔT_i which contains n_i icing events can be expressed as follows [117, 173]

$$R(T_i) = \frac{cn_i}{\Delta T_i \left(\frac{n_i}{2} + \sum_{j>i} n_j \right)} \quad (6.6)$$

where c is the cooling rate, $\sum_{j>i} n_j$ the unfrozen icing events. Since the droplet on each sample has different contact area because of the different contact angle and roughness, the area nucleation rate becomes [117]

$$R_A^*(T_i) = \frac{R(T_i)}{S} \quad (6.7)$$

where S is the actual contact area between the droplet and substrate. For the smooth samples such as the glass slide without sol-gel coating or FAS treated glass (F-Glass), the actual contact area is determined by the nominal area covered by water droplet with a radius of r : [224]

$$r = \left[\frac{3V}{\pi(2-3\cos\theta+\cos^3\theta)} \right]^{1/3} \sin\theta \quad (6.8)$$

where V is the volume of the droplet and θ the apparent contact angle. For rough and fully wetted samples, the actual contact area would be equal to the apparent contact area multiplied by the roughness ratio f_w which is defined by the Wenzel's equation [225]

$$\cos\theta = f_w \cos\theta^* \quad (6.9)$$

where θ^* is the contact angle for ideal smooth surface. However, since the particle and the base gel which constitute the coatings have different surface energy and their fraction in each sample is different, it is impossible to calculate the roughness ratio through this method. According to some reports [226, 227], the roughness ratio for a patterned superhydrophobic surface is between 1.2 and 3.2. For the rough samples M-20 and F-16, their contact angle at room temperature are 162.7° and 172.7° , respectively. Assuming the intrinsic contact angle is between 110° and 120° because the surface is basically fully covered by the hydrophobic nano particles, then the

roughness ratio should be between 1.9 and 2.9 based on the Wenzel's law. This provides a reasonable basis for further analysis. Considering the surfaces roughness is caused by the nanoparticles and it starts to form a kind of porous structure when the roughness gets higher, we assume the roughness ratio changes exponentially with the roughness values. Based on the data we have, the roughness ratio is approximately modelled as

$$f_W = 2^{0.75 r_a} \quad (6.10)$$

where r_a is the roughness of the samples. This makes the roughness ratio for M-20, which is the largest among samples with Wenzel wetting mode, to be 2.458. For superhydrophobic sample F-20, the contact area is decided by the Cassie-Baxter equation [213]

$$\cos \theta = f_C (\cos \theta^* + 1) - 1 \quad (6.11)$$

Since the surface is mainly occupied by the hydrophobic nanoparticles [222], θ^* was assumed to be 110° , which is close to the value for fluorinated flat glass. The calculated contact area of different samples is listed in **Table 6.3**.

Table 6.3 Calculated contact area of different samples

Samples	Roughness (μ)	Contact radius (mm)	Contact area ratio	Water-substrate contact Area (mm ²)
Glass	0.001 ± 0.000	2.907	1.001	26.548
M-5	0.078 ± 0.005	1.985	1.041	12.889
M-10	0.741 ± 0.058	1.908	1.470	16.802
M-15	1.183 ± 0.079	1.818	1.850	19.188
M-20	1.730 ± 0.097	1.296	2.458	12.960
F-Glass	0.003 ± 0.001	1.459	1.001	6.689
F-4	0.006 ± 0.001	1.456	1.003	6.678
F-8	0.365 ± 0.038	1.381	1.209	7.239
F-12	1.194 ± 0.100	0.591	1.860	2.042
F-16	1.817 ± 0.140	0.382	0.063	0.029

Using the nucleation rate from experiment, the best fits to **Equation (6.4)** is shown in

Figure 6.11. The fitted $\log_{10}(J_A)$ and $f_A(\theta)$ are listed in **Table 6.4**.

Figure 6.11 Area nucleation rate on (a) non-fluorinated samples and (b) fluorinated samples. Hollow symbols are data derived from experiment. Solid lines are the best fits by **Equation (6.4)**.

Table 6.4 Theoretical and fitted nucleation parameters.

Samples	Theoretical $f(\theta)$	Fitted $f_A(\theta)$	$\log_{10}(J_A)$	Fitted $f_L(\theta)$	$\log_{10}(J_L)$
Glass	0.011	0.172	8.860	0.172	6.023
M-5	0.253	0.154	7.914	0.154	4.928
M-10	0.310	0.241	11.039	0.241	8.186
M-15	0.383	0.136	8.452	0.136	5.678
M-20	0.804	0.118	7.953	0.118	5.155
F-Glass	0.692	0.249	10.611	0.249	7.475
F-4	0.694	0.254	9.258	0.254	6.121
F-8	0.749	0.231	10.495	0.231	7.416
F-12	0.992	0.152	9.005	0.152	5.666
F-16	0.999	0.390	13.239	0.390	8.019

In the non-fluorinated group, the area nucleation rate for M-20 and M-15, Glass and M-10 are very close. This is in agreement with the big overlap among these samples as shown in **Figure 6.9**. M-5 has the lowest nucleation rate, so it shows the lowest icing temperature in this group. For the fluorinated samples, they showed a relatively well separated and parallel trend. However, the curve for F-16 indicated an extraordinary nucleation rate (2 orders of magnitude higher than other samples). There might be several factors involved. It may be possible that the surface can withstand the cooling and spreading of the droplet only up until some threshold value. After that, the energy barrier of nucleation on a convex surface is conquered by the super cooling and all the contact area could serve as active nucleation sites. This would explain the observed lower starting icing temperature, but rapid nucleation rate. However, this assumption may not stand statistically. As can be seen in **Figure 6.11**, the fitted curve for F-16 has similar slope as others. It predicts nucleation rate at the order of 10^2 - 10^4 $s^{-1}m^{-2}$ between -24 °C and -26 °C. At such rate, at least some icing events would have occurred with

reference to other samples. However, there was not a single icing event in this range after 500 cycles for F-16. Besides, the lowest and highest nucleation rates are both 2 orders of magnitude larger than other samples. This is contradictory to the observed lowest icing temperature of F-16. Therefore the assumption made earlier that nucleation occurs at the water / coating interface needs to be further examined.

Given that the calculated nucleation rate was based on the actual contact area, a positive shift of the nucleation rate is expected if the actual contact area is only a small fraction of the projected area. This is exactly the case for F-16. To resolve the discrepancy, we suggest that the nucleation process is dominated by another mechanism rather than the heterogeneous nucleation at the water-substrate interface which we began this analysis with. The possible nucleation sites generally include the water-solid interface, the water-air interface and the bulk water. Bulk water nucleation is obviously not dominant in the current case as it is homogeneous nucleation which has the highest free energy barrier. Nucleation initiating at the water-air interface has been reported by several authors [61, 228-231]. However, they were mostly with cases of falling water droplets which lack the substrate-water interface to provide the low energy barrier nucleation site. The droplet size in our study is also not in the micro scale so that the surface-to-volume ratio can never be large enough that the surface nucleation rate would contribute dominantly to the total nucleation rate [231]. Jung [61] reported a case in which the nucleation started at the water-air interface. However, it was because of the air flow which accelerated the evaporation of the droplet and caused increased temperature difference in the water-air interface. Besides, another unmentioned contribution could be the disturbance of the air flow on the droplet surface which would definitely favour the nucleation process. In our case, the droplet

was cooled from the bottom and there was no air flow inside the test chamber. So it is therefore unlikely the surface nucleation could dominant the process.

With regard heterogeneous nucleation process [34, 118, 224], a water droplet always became blurry or non-transparent at the onset of freezing which demonstrated a formed ice shell around the droplet. It was also confirmed by infrared thermography [119, 232] that there was a sudden temperature jump in a very short time at the top of the droplet because of the release of latent heat. However, there has been quite a debate about the initiation site of nucleation. Some authors [120, 233, 234] suggested that the nucleation preferentially starts at the three-phase contact line, while Gurganus [235, 236] claimed that it starts randomly at the whole solid-liquid interface. The controversy might be caused by different test environments or substrate microstructures. Despite the debate, it was confirmed also by Gurganus [237] that a nanotextured surface can greatly promote the chances of contact line nucleation. Given the truth that most of our samples are covered by nanoparticles, Further inspection suggests that the ice shell always started from the contact line (three-phase junction line) of the droplet [120, 238] even if there was a superhydrophilic area at the centre of the water-substrate contact [233]. Thus, we believe the dominant nucleation sites are mainly along the three-phase contact line instead of on the whole contact area assumed earlier. Accordingly, we define a line nucleation rate as

$$R_l(T_i) = \frac{R(T_i)}{2\pi r} \quad (6.12)$$

Such a nucleation rate is plotted in Figure 6.12 and the corresponding fitting parameters $f_L(\theta)$ and $\log_{10}(J_L)$ are shown in **Table 6.4**. It is worth mentioning that there are also three-phase contact lines at the water-substrate interface for F-16 as there is trapped air there. We have ignored this for the convenience of calculation in

the current work. Fortunately, the negligence does not substantially change the fitting results, as the larger the denominator in **Equation (6.12)**, the lower the curve of F-16 in **Figure 10b**. Besides, the reflected nucleation rate is not very sensitive to the contact line length change due to the exponential relationship as shown in **Equation (6.4)**.

Figure 6.12 Corrected nucleation rate on (a) non-fluorinated samples and (b) fluorinated samples. Hollow symbols are data derived from experiment. Solid lines are the best fits by Equation (6.4).

Comparing **Figure 6.11** and **Figure 6.12**, it is clear that the relative position for most samples does not change much except for F-16. With the three-phase contact line nucleation assumption, the nucleation rate for sample F-16 became comparable with that of other samples. Statistically it also makes good sense as the top and bottom icing temperature lay reasonably in the area. For any given temperature in the range, the nucleation rate for F-16 is always the lowest, which explains perfectly the lowest icing temperature.

As can be seen in **Table 6.4**, the change of the fitting mode from contact area to contact line showed no influence on the value of fitting geometric factors in the fitting process because they reflect the slopes of the curves as revealed in **Equation (6.4)**. For most of the samples, the geometric factors are much lower than the theoretical values

(based on the apparent contact angles at $-10\text{ }^{\circ}\text{C}$ and assuming ice contact angle is equal to water contact angle) except for the uncoated glass slide. The roughness of the glass slide is around 1 nm, smaller than the critical nucleus size. According to the simulation conducted by Guo et al.[239], when the nano-pillars spacing on the surface is smaller than 2.22 nm, which is 6 lattice constant based on the gas model of water, the nucleation process is always inhibited comparing to the perfect smooth surface regardless of the height of the pillars. This explains the higher fitted geometric factor than the theoretical one on the uncoated glass sample. For other samples, the roughness is always larger than the critical nucleus. Thus the geometric factors are always affected by the surface morphology. On the one hand, it is often assumed that the interaction between ice and a surface is the same as the one between water molecule and the surface. It is actually also supported by simulation [240] although some of the points raised in the paper are still debatable. However, apparent contact angle on a rough surface is not equal to the intrinsic contact angle as demonstrated in Section 3.4.2. Roughness would enhance the hydrophilicity on hydrophilic surfaces and hydrophobicity on hydrophobic surfaces. Since ice nucleus is in the nano scale, the micro-wetting behaviour of the ice nucleus on the surface is not necessarily the same as a bulk water droplet on a bulk surface. Rather it is related to the surface properties, which are decided by the composition on the surface. This greatly contributes to the higher theoretical geometric factors than the fitted values for hydrophobic and superhydrophobic samples. On the other hand, the roughness changes the shape of the nucleus. For Wenzel wetting mode samples, the nucleus are more likely to form at the concave sites between the particles and base gel or between two particles. The wedge shaped nucleus on these surfaces would lead to lower geometric factor than the crown shaped ones on flat or convex surfaces [52, 53]. This

contributes to the higher theoretical geometric factors for the hydrophilic samples. Finally, the nucleus at the three-phase contact line may be more complicated than the usual nuclei models on two-phase interfaces. To the best of our knowledge, there is no theoretical report on nucleation at the three phase contact line yet although such phenomenon has been observed in experiments [120, 238]. Nevertheless, for most of the samples (except M-5), the fitted values of the geometric factors reflect the change of corresponding icing temperatures in each group, i.e., the lower the geometric factor, the higher the icing temperature. It is also noticed that the samples in the fluorinated group generally have higher geometric factors than their counterparts in the non-fluorinated group. This reflects the effect of decreased intrinsic surface energy of samples with addition of FAS. Among all the samples, F-16 has an extraordinarily high geometric factor. This is because of its non-wetting behaviour at low temperatures. Consequently the concave sites are prevented to certain extent from being in contact with water droplet because of the trapped air.

As for the pre-factors, it is interesting to notice that most of them follow the trend of the corresponding geometric factors in each group (except F-4). Generally, the pre-factor represents the diffusion of water molecules to the ice embryo [241]. It is related at least to the fractional area for nucleation, the number and size of nuclei, and the rate of molecular kinetics at the critical nucleus boundary [173, 241, 242]. Although the exact quantification for the pre-factor has not been resolved satisfactorily [243], it seems that the pre-factor is closely related to the geometric factor in current study. It is probably because the water-ice interfaces are less on a given size nuclei formed on a concave site than on a flat or convex site. Consequently the efficiency for the water molecular to move to the ice embryo is lower on a concave nuclei site. Thus, the lower the geometric factor, the lower the pre-factor.

6.4 Summary

We investigated the icing temperature of 10 μL droplets on a series of sol-gel coatings which cover a wide range of roughness, apparent surface energy, and different wetting modes at low temperatures. The results are in good agreement with the wetting behaviour of the samples at low temperatures. Low surface energy coupled with rough surface and Cassie wetting mode is preferred for delay in icing temperature. The icephobic coating in the fluorinated series can lower the icing temperature by up to 6.9 $^{\circ}\text{C}$.

Through analysis based on classical nucleation theory, we found that the geometric factors are closely related to the surface properties and wetting mode although the influential factors need further investigation. The pre-factors for the nucleation on the samples are closely related to the geometric factors in the current study. For most samples, the lower the geometric factor, the lower the pre-factor. Our fitting results support the conclusion that the dominant heterogeneous nucleation sites in our study are not on the whole water-substrate interface, but mainly on the water-air-substrate contact line.

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Chapter 7 Conclusions and Future Work

7.1 Conclusions

In this work, the correlation of surface properties and anti-icing performance on different substrates covering a large range of surface energy, roughness, morphologies, and wetting modes at different temperatures has been investigated. Two series of sol-gel coatings have been developed and optimized for anti-icing applications. The effect of test environments on the icing behaviour has been explored. The icing behaviour of droplets on the selective sol-gel coatings were also statistically and theoretically analysed. The following summarize the major contribution of the current work.

1. Anti-icing performance on ground glass slides

Glass slides ground with different grit of sand paper and treated with/without FAS were prepared. Icing behaviour was found to be dependent on surface energy and roughness. Lower surface energy is favourable for anti-icing performance despite of the roughness. Lower roughness would lead to lower icing temperature and ice adhesion for glasses, but the difference for ground glasses is small. Although the results cannot reflect as a general mechanism for all situations since all the samples are only hydrophilic to hydrophobic, it shows a direction for the subsequent investigation.

The classical nucleation theory was initially applied to explain the icing temperature on the smooth samples. The nucleation rate and pre-factor were fixed as a constant, and water contact angle was used as the ice contact angle. However, the fitting results cannot explain the different icing temperatures on glass and FAS-treated glass. This has prompted the statistical investigation in Chapter 6 in which the pre-factors and geometric values were fitted out instead of being fixed manually.

2. Development of sol-gel coatings with different surface energy and roughness, and their anti-icing performance

Two series of samples with different surface energy and roughness were prepared. The first series consists of three groups containing FPOSS, and the second series consists of two groups which have hydrophobic silica as the only filler. Their surface properties were investigated including roughness, surface energy, contact angle at different temperatures, ice adhesion and icing temperatures. It is shown that the intrinsic surface energy and surface morphology of the coatings play important roles together in terms of anti-icing performance. Not all superhydrophobic surfaces, as indicated by the water contact angle at room temperatures, could remain water repellent at low temperatures. The anti-icing performance are closely correlated with the surface properties at lower temperatures instead of that at room temperature. The two aspects of the anti-icing performance, i.e., ice adhesion and icing temperature, are not necessarily correlated on rough surfaces because of the different mechanism for them.

For the three groups of samples in the first series with addition of FPOSS, none of the surfaces can maintain superhydrophobic at low temperatures. In such cases, lower surface energy and smooth surface are favourable for anti-icing performance. Due to the small particle size of FPOSS, the anchor effect is low because the lowered surface energy has actually more influence on the final ice adhesion than the increase of roughness for most samples in these three groups. The lowest ice adhesion was achieved to be 0.175 ± 0.050 MPa at -20 °C and 0.135 ± 0.029 MPa at -10 °C on sample PFS-8. The ice adhesion reduction efficiency (the ratio of ice adhesion on bare glass slide to that on the coatings) reaches to 5.4 at -10 °C and 6.8 at -20 °C. The

icing temperature of the samples are strongly related to the surface energy and roughness of the samples. The dominant factor is different for each group, and thus leads to different trend of icing temperatures in each group. The lowest icing temperature was achieved by relatively smooth sample PF-4.

For the last two groups of samples in the second series with only hydrophobic silica as the fillers, the surface energy and roughness have different influence on the anti-icing performance comparing to the samples with FPOSS. The ice adhesion and icing temperatures follow the same trend in each group. Increasing surface roughness by adding more silica particles increases the ice adhesion because of the interlocking effect which is not obvious in the first three series. The addition of FAS reduces the intrinsic surface energy of the coatings and enables the rough surface to be water repellent even at sub-zero temperatures. Consequently, the trapped air between water and the superhydrophobic substrates can effectively reduce the ice adhesion and lower the icing temperature. The developed icephobic coating (F-16) has a sliding angle as low as 4.4° for a 10 μ L droplet at -10 °C.

3. Effect of test environments on the icing behaviour of droplets on surfaces

The test environment has a great influence on the wetting and icing behaviour of droplets on surfaces. Low humidity would lead to higher contact angle. The change is especially obvious on hydrophobic or superhydrophobic surfaces which has a hydrophilic component. This would also lead to a decrease of icing temperature on these surfaces because of restrained condensation at the adjacent of the three-phase contact line. For those samples which are hydrophilic or intrinsically hydrophobic, the influence of humidity is not so much when cooling from the bottom of the samples. However, all the icing temperatures are lowered to a great extent by isothermal

cooling without airflow in the environmental chamber because of humidity was lowered even further. When the droplets are exposed to airflow, the icing temperatures would be greatly increased because of the enhanced cooling and turbulence it causes. The trend of icing temperatures with airflow is that the higher the contact angle, the higher the icing temperature.

When it comes to icing lag time, the repeatability and reliability of the measurement is strongly dependent on individual samples and the icing temperatures. Lower temperature means better repeatability for some samples but at the same time it might cause other problems for other samples such as freeing above the set point, or too small difference of lag time between other samples. The test environment has a great impact on the lag time results. Lower humidity would lead to longer icing lag time and greater fluctuation (larger error bar). Airflow would shorten the lag time and improve the repeatability but the results are not so valuable due to the tiny difference between different samples.

4. Icing behaviour of droplets on selected sol-gel coatings

We investigated the icing temperature of 10 μL droplets on a series of sol-gel coatings which cover a wide range of roughness, apparent surface energy, and different wetting modes at low temperatures. The results are in good agreement with the wetting behaviour of the samples at low temperatures. Low surface energy coupled with rough surface and Cassie wetting mode is preferred for delay in icing temperature. The icephobic coating in the fluorinated series can lower the icing temperature by up to 6.9 $^{\circ}\text{C}$ (5 $^{\circ}\text{C}/\text{min}$ from 0 $^{\circ}\text{C}$ to the freezing point).

Through analysis based on classical nucleation theory, we found that the geometric factors are closely related to the surface property and wetting mode although the influential factors need further investigation. The pre-factors for the nucleation on the samples are closely related to the geometric factors in the current study. For most samples, the lower the geometric factor, the lower the pre-factor. The fitting analysis support the conclusion that the dominant heterogeneous nucleation sites in our study are not on the whole water-substrate interface, but mainly on the water-air-substrate contact line.

7.2 Recommendations for future work

Based on the investigation and conclusions from current study, a series of possible future in-depth work could be conducted in order to have a better understanding of the affecting factors for anti-icing performances on different substrates, and thus provide a more specific and optimised strategy to manufacture icephobic materials.

First of all, a more controllable test environment can be developed to have a comprehensive understanding of the effect of test environments on the icing behaviour on different surfaces. In currently study, the test environment was roughly controlled, and some affecting effect cannot be avoided such as the vibration of the environmental chamber. The humidity control is also very rough although it does not affect the comparison. In an ideal test environment, all the affecting factors such as the humidity, air flow, vibration, cooling method, etc. should be able to be controlled so that a more complete report about the effect of test environments can be formed and provide a fundamental support for applications.

Secondly, a direct observation on the nucleation on the coatings can be conducted. There has been several reports about the optical observation of nucleation on surfaces

by speed cameras. However, none nucleation on a superhydrophobic surface has been reported to the best of my knowledge. Currently, our fitting results support the three-phase contact line nucleation. It would be great to prove it by having a direct observation of such phenomenon.

Thirdly, a field test should be conducted to see if the icephobic coating can maintain good performance at outdoor environments. It is necessary to see if the UV light, rain, air flow, or other factors in the natural environment can affect the anti-icing performance.

Fourthly, precisely controlled surface microstructures need to be developed and analysed for anti-icing performance. All the surface morphology of the samples in current study are not precisely controlled. In another word, the microstructures of the surfaces are quite random in the micro scale. In this case, there is no way to find out how the surface properties (roughness, surface energy, etc) affect the icing behaviour although an overall result can always be obtained. If the morphology of the surface can be precisely controlled in the micro and nano scale, then it is easy to figure out the geometric factor directly, and consequently can get the ice contact angle fitted out though the statistical analysis. With these information, the design for icephobic coatings can be easier and customized, and the understanding of nucleation theory can be promoted.

Finally, a systematic theoretical study on the nucleation at the three phase contact line would be necessary in order to explain the proposed line nucleation theory. The role of air, which contributes to the largest portion of entropy than the liquid and solid, would also need further investigation.

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Publications and Conferences

Publications

Fu, Q., Wu, X., Kumar, D., Ho, J. W. C., Kanhere, P. D., Srikanth, N., Liu, E., Wilson, P., and Chen, Z., Development of Sol–Gel Icephobic Coatings: Effect of Surface Roughness and Surface Energy. ACS Applied Materials & Interfaces, 2014. 6(23): p. 20685-20692.

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Conferences

Fu Qitao, 7th International Conference on Technological Advances of Thin Films & Surface Coatings (THINFILMS2014), 15th to 18th July, 2014, Chongqing, China. (Poster, 3rd Prize of Poster Award)

Fu Qitao, 1st International Conference in Sports Science & Technology (ICSST), 11th to 12th December, 2014, Singapore. (Oral Presentation)