Development of anti-icing coatings for sports application

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2019

Wu, X. (2019). Development of anti-icing coatings for sports application. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/81282>

<https://doi.org/10.32657/10220/47508>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**DEVELOPMENT OF ANTI-ICING COATINGS FOR
SPORTS APPLICATION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

DEVELOPMENT OF ANTI-ICING COATINGS FOR SPORTS APPLICATION

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

.... 03 January 2019

Date

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Wu Xinghua

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

3rd January 2019

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Date

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Chen Zhong

Authorship Attribution Statement

This thesis contains material from (a) paper(s) published in a/the following peer-reviewed journal(s) where I was the first author.

Chapter 3 is published as X. Wu, V. V. Silberschmidt, Z. T. Hu, Z. Chen. When superhydrophobic coatings are icephobic: role of surface topology, *Surface and Coatings Technology* (2019) Vol. 358, pp. 207-214.

The contributions of the co-authors are as follows:

- Prof Chen provided the initial project direction and edited the manuscript drafts.
- I co-designed the study with Prof. Chen and Prof. Hu, and performed all the laboratory work at the School of Materials Science and Engineering, Nanyang Technological University, Singapore. I also analyzed the data.
- Prof. Silberschmidt helped revised the manuscript.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.

Chapter 4 is published as X. Wu, Z. Chen. A mechanically robust transparent anti-icing coating for anti-icing and self-cleaning applications. *Journal of Materials Chemistry A*. (2018), Vol. 6, pp. 16043-16052.

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Chapter 5 is accepted as X. Wu, X. Zhao, J. W. C. Ho, Z. Chen. Design and durability study of environmental-friendly room-temperature processable icephobic coatings, *Chemical Engineering Journal* (2019) Vol. 355, pp. 901-909.

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- I prepared the manuscript drafts and performed most of the laboratory work at the School of Materials Science and Engineering, Nanyang Technological University, Singapore. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr. Zhao assisted in collecting field emission scanning electron microscopy (FESEM) images of coatings after sand erosion.
- Mr. Ho assisted in parts of mechanical properties test.

3rd January 2019

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Date

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Wu Xinghua

Abstract

Undesired ice accumulation on outdoor sports facilities leads to severe economic issues and even loss of lives. Great efforts have been made to fabricate ice prevention surfaces or facilities since 1800s. The utilized methods can be categorized into four types: mechanical methods, chemical methods, thermal methods and combined methods (combining two or three former referred methods). Considering the economic impact and additional labour burdens, chemical methods are commonly adopted and widely studied. To avoid numerous environmental effect of drain-off chemicals, icephobic coatings, as effective passive anti-icing methods, have attracted much attention in recent decades. However, less attention has been paid on development of the anti-icing coatings for sports facilities and other related applications that requires additional properties including mechanical durability, transparency, easy processability and so on. With expectation to repel incoming water before ice formation, superhydrophobic coatings that exhibit superior water repellency and bouncy effect, have been widely studied since 1997. However, not all superhydrophobic coatings present anti-icing behaviours due to water condensation. This study begins with the investigation of the effect of water condensation on superhydrophobic coatings with different microstructures. To design superhydrophobic coatings with different microstructures, a sol-gel method was employed with adjustment of the weight ratio of nanoparticles with different surface energies. One of the prepared coatings demonstrated robust icephobicity with low ice-adhesion strength of ~ 60 kPa under water condensation conditions; at the same time, it also displayed a low ice-nucleation temperature of ~ -26 °C and low icing probability.

With a strong demand for aesthetics appearance, transparent anti-icing coatings are needed for various applications. However, the well-studied superhydrophobic coatings are usually translucent or opaque because of the micro-nanostructures which greatly affect light transmittance. The state-of-the-art slippery liquid infused porous surface (SLIPS), which presented extremely low ice adhesion, can achieve a high transparency by choosing the substrate and lubricant liquid with matching refractive indices. However, the mechanical property of both kinds of coatings is weak due to the presence of porous microstructures.

To obtain high transmittance and good mechanical properties, a new strategy is designed to fabricate a mechanical durable transparent anti-icing coating by a low cost sol-gel method. The prepared coatings presented a transmittance as high as 99 %, low ice adhesion, good condensation resistance, anti-frost and durable mechanical properties. Besides, this coating demonstrated self-cleaning properties and repellency to various liquids with surface energy ranging from 72.8~22.1 mJ/m². With the demonstrated excellent properties, this coating is promising for anti-icing applications for sports applications and other applications that require good transparency and mechanical durability.

Room-temperature processed anti-icing coatings are highly desirable for large outdoor structures besides the low-cost consideration. In this work, a room-temperature processable, fluorine-free anti-icing coating was designed and investigated. With the design of dual-size nanoparticle fillers, coatings presented denser micro-nanostructure than the ones with single-size fillers. This denser structure of the dual-size coatings enabled better water repellency and anti-icing performance in terms of low ice adhesion and less ice accumulation than the single-size coatings and a commercially obtained polyurethane (PU) coating. To ensure the robustness and durability of the developed coatings, comprehensive mechanical and durability studies including tape adhesion, pencil hardness, dolly-pull tests, nano-indentation, ultraviolet (UV) irradiation, water condensation and sand erosion were carried out according to available ISO or ASTM standard methods. The dual-size coating presented better mechanical properties and UV resistance than the single-size and the PU coatings. Comparable sand erosion resistance were obtained on the dual-size particle coatings.

To sum up, robust and durable anti-icing coatings which can satisfy different application requirements have been designed and developed successfully. The preparation method of these coatings follows some general principles of being simple, scalable, and low cost. Specially, the design of robust transparent coatings is a relatively new territory for passive anti-icing applications. Comprehensive mechanical and durability tests in these studies are novel, and can serve as a foundation for future evaluation of the practically applicable anti-icing coatings. The use of different surface energy nanoparticles, duals-size nanoparticles

and mechanical-force induced deagglomeration are very enlightening methods for future design of functional coatings.

Lay Summary

Ice accretion on sports facilities such as artificial turf structures, ski kits, snowmobiles or skidoos, windows, and roofs may lead to compromised performance or failure of the facilities, and in some cases even loss of lives. To prevent ice formation, various methods have been developed, such as electrical or chemical heating, mechanical actions, and applying chemicals that can reduce icing temperature or present low affinity to ice. The chemical method has certain advantages such as low cost and high efficiency. However, one key problem with the chemical method is the environmental pollution induced by the drain-off chemicals. To obtain a stable chemical layer and lock chemicals in the targeted area, anti-icing coatings have been widely investigated, from a viscous layer, multi-layer system to structured surfaces. Since ice is formed by water, a simple assumption has been that surfaces that exhibit low affinity to water should also display low affinity to ice. A superhydrophobic surface which is defined by the water contact angle larger than 150° and the roll-off angle less than 10° have been studied for anti-icing applications in the last two decades.

In this research, superhydrophobic coatings were prepared with a sol-gel method. With adding different weight ratio of low surface energy and high surface energy nanoparticles (keeping the amount of nanoparticles the same), five superhydrophobic coatings with distinct anti-icing performance were obtained. Very different anti-icing performances have been observe, and the reason for the observed high ice adhesion of some superhydrophobic coatings was analyzed. Scientifically, this research supports the caution realized by scientist that not all superhydrophobic coatings can display good anti-icing performance. In terms of technology advancement, one of the coatings developed in this work has demonstrated easy ice removal properties even after water condensation at -20°C for 24 h with relative humidity (RH) of 80%. In addition, the icing events on this coating took place at the temperature of -26°C with a low icing probability. With low icing temperature and robust low ice adhesion, this anti-icing coating is promising for future practical application on sports facilities.

Most of the reported anti-icing coatings are translucent or opaque because the micro-nanostructures significantly scatter visible light. Although the well-known SLIPS and several polymer coatings presented high transmittance; they are restrained for practical application due to poor mechanical properties. Transparency is a key requirement in many applications, for example, windows, windshields of snow mobiles and photovoltaic devices, especially applications that require aesthetics appearance. To develop low cost and mechanically robust transparent anti-icing coatings, a sol-gel method was employed with addition of nanoparticles. However, agglomeration of nanoparticles will decrease the transmittance. In order to increase transmittance, nanoparticles should be uniform dispersed in the sols. Herein, a simple magnetic stirring was utilized to disperse the nanoparticles. In addition, surface modification of half of the nanoparticles was used to assist the dispersion. At the end of stirring, a transparent water repellent coating was fabricated. This coating demonstrated a significantly reduced ice adhesion, longer icing-delay time, lower icing temperature and better frost resistance than the uncoated substrate. Besides, the coating presented self-cleaning properties and good mechanical properties.

The above obtained superhydrophobic and transparent anti-icing coatings require heating in their processing. To lower the processing cost and make anti-icing coatings applicable to offline products, a room-temperature processable anti-icing coating was designed. With the concern of the adverse impact by long-chain fluorine-carbon molecules, a low cost and scalable silicone-epoxy resin is chosen. Two different size nanoparticles (diameter: 200 nm and 10~20 nm) with weight ratio of 1:2 were mixed with the epoxy resins to fabricate anti-icing coatings. With the design of dual-size nanoparticle fillers, coatings presented denser micro-nanostructure than coatings with single-size fillers. This dual-size coatings enable a better water repellency and anti-icing performance in terms of low ice adhesion and less ice accumulation than the single-size coatings and a commercial PU coating. Comprehensive mechanical and durability studies verified the high hardness, good adhesion to a substrate and scratch resistance, as well as excellent resistance to UV & water condensation and sand erosion.

Acknowledgements

First and foremost I am extremely grateful to my supervisor Prof. Chen Zhong for sharing his superior knowledge and experience, and continuous support of my research, for his patience, motivation and enthusiasm. I benefit a lot from his valuable guidance and positive attitude towards research. I also appreciate my co-supervisors Prof. Vadim Sillberschmidt for sharing his insights on anti-icing coatings with me, and offering selfless help on my research.

I would like to express our sincere thanks towards all my group members, Dr. Tang Yuxin, Dr. Zhang Yanyan, Dr. Fu Qitao, Dr. Divya Kumar, Dr. Wang Chen, Dr. Zheng Shunli and Dr. Shen Yizhou for their help in experiments, discussion and social life. Besides, many thanks to my group members, Dr. Zhao Xin, Dr. Kanhere pushkar, Dr. Wang Danping *etc.* on their social discussions and support in group activities.

In addition, I wish to acknowledge Prof. Peter Wilson in University of Tasmania, who provided valuable comments in my research, as well as my TAC members: Prof. Dong Zhili, Prof. Oh Joo Tien and Prof. Alfred Tok. Your perceptive insights and comments greatly help me through, to focus on the tiny details.

My sincere thanks also go to Mr. Patrick Lai Chee Hoong, Ms. Swee Kuan, Ms. Sharon Tan, Mr. Yong Kwong Tan, Dr. Ang Derrick, Mr. Tan Kek Koon, Mr. Gan Zi Li, Mr. Lim Kian Boon and Ms. Poh Tin Tay for helping me with all the necessary facilities for the research. In special, Mr. Lim Yan Koon, Wilson helps me a lot when I was a teaching assistant of Semester 1 AY2017 MS2081 Laboratory.

I gratefully acknowledge the financial support from the Institute of Sports Research (ISR) Nanyang Technological University in the form of research scholarship.

Finally, I would like to thank selfless support from my parents, my husband and parents-in-law, who takes care of my little son during the past years. I thank all my family members for the unceasing encouragement, support and caring.

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Abbreviations

AFM	Atomic Force Microscope
AIRS II	The Second Alliance Icing Research Study
CAH	Contact Angle Hysteresis
CCN	Cloud Condensation Nucleus
CPI	Cloud Particle Imager
DI	Deionized
ESEM	Environmental Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscopy
GFRE	Glass Fiber Reinforced Epoxy
GLYMO	3-Glycidoxypentyltrimethoxysilane
iCVD	Initiated Chemical Vapor Deposition
PFOTES	1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane
PTFE	Poly (tetrafluoroethylene)
PU	Polyurethane
RH	Relative Humidity
SLIPS	Slippery Liquid Infused Porous Surface
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl Orthosilicate
THRC	Transparent Hydrophobic Repellent Coatings
UV	Ultraviolet
WORK	Owens, Wendt, Rabel and Kalble

List of Publications

1. X. Wu, V. V. Silberschmidt, Z.T. Hu, Z. Chen “When superhydrophobic coatings are icephobic: role of surface topology”, *Surface and Coatings Technology*, 2019, Vol. 358, pp. 207-214.
2. X. Wu, X. Zhao, J. W. C. Ho, Z. Chen “Design and durability study of environmental-friendly room-temperature processable icephobic coatings”, *Chemical Engineering Journal*, 2019, Vol. 355, pp. 901-909.
3. X. Wu, Z. Chen “A mechanically robust transparent anti-icing coating for anti-icing and self-cleaning applications”, *Journal of Materials Chemistry A*, 2018, Vol. 6, pp. 16043-16052
4. X. Wu, Y. Tang, V. V. Silberschmidt, P. Wilson, Z. Chen “Mechanically robust transparent anti-icing coatings: roles of dispersion status of titanate nanotubes”, *Advanced Materials Interfaces*, 2018, Vol. 5, Art. No. 1800773.
5. X. Wu, S. L. Zheng, D. A. Bellido-Aguilar, V. V. Silberschmidt, Z. Chen “Transparent icephobic coatings using bio-based epoxy resin”, *Materials and Design*, 2018, Vol. 140, pp. 516-523.
6. X. Wu, Q. T. Fu, D. Kumar, J. W. C. Ho, P. Kanhere, H. F. Zhou, Z. Chen “Mechanically robust superhydrophobic and superoleophobic coatings derived by sol-gel method”, *Materials & Design*, 2016, Vol. 86, pp. 1302-1309.
7. X. Wu, Z. Chen “Comprehensive investigation of the effect of coatings’ surface characteristics on ice adhesion”, *Cold Regions Science and Technology*, to be submitted.

Conference Presentations

1. X. Wu, Z. Chen “Transparent icephobic coatings based on bio-epoxy resin”, paper presented at 3rd Edition Smart Materials and Surfaces Paris, France, Apr 2017.
2. X. Wu, Y.X. Tang, Z. Chen “Icephobic performance of transparent sol-gel coatings with TiO₂ nanotube fillers”, paper presented at 2nd International Conference in Sports Science & Technology (ICSST2), Singapore, Dec 2016.

3. X. Wu, Q. T. Fu, D. Kumar, J. W. C. Ho, P. Kanhere, H. F. Zhou, Z. Chen
“Mechanically robust superhydrophobic and superoleophobic coatings derived by sol-gel
method”, paper presented at 1st International Conference in Sports Science & Technology
(ICSST), Singapore, Dec 2014.

Chapter 1 Introduction

Introduction

This chapter summarized research background and problems to be solved in this thesis. First, problems of icing on sports facilities were stated. Progress in anti-icing materials were listed and categorized. Advantage and disadvantage of these materials were compared and analyzed. A more promising anti-icing coating was proposed based on the analysis, followed by methods used, objectives and scopes of this study, as well as the outline of this thesis. The work in this thesis covers key aspects of anti-icing coatings:

- 1. Technology development of anti-icing coatings that can satisfy the requirements of various applications;*
- 2. Investigate the factors that will influence the anti-icing performance of coatings;*
- 3. Theoretically study ice nucleation behaviors that happen on different microstructures;*
- 4. Summarize main achievements and outstanding findings of this work;*
- 5. Outlook and suggestions for future works.*

1.1 Problem Statement

1.1.1 Background

Undesired ice accumulation on outdoor sports facilities leads to severe damage and even loss of lives. For example, artificial turf structure will freeze at temperatures lower than minus five degrees centigrade, which causes inconvenience to professional and amateur athletes. The formation and accumulation of ice directly affect a skier's equipment performance and personal safety. A persistent problem of icing occurs on the carburetor, tunnel, air filter and the suspension system components of snowmobiles or skidoos. A significant build-up of ice sheet occurs on the engine of snowmobile or skidoo during a cooling down process when it is parked. Besides winter sports equipment, atmospheric ice accretion can also be a serious problem to power lines, telecommunication networks, pavements, windows, roofs and solar panels used in the sports field, leading to damage, lowered performance and in some cases increased risk towards big disasters. The largest icing accretion ever recorded on power lines was observed in Norway in April 1961. The weight of one-meter length of ice loading was 305kg, and the elliptic cross-section diameter could reach as high as 1.4 m. Even the smallest elliptic cross-section diameter was around 0.95 m. Similar phenomenon was also observed in Iceland [1]. Furthermore, ice storm which is the combination of wind and ice could cause serious damages to power lines, telecommunications and other outdoor structures. The March 1991 ice storm in New York led to economic loss of more than 300 million dollars. The most devastating January 1998 ice storm in North of America caused over 3 million people to live without power for more than one month. The February 2008 freezing rain in southern and central China led to intensive damage to power lines, telecommunications, roofs, water pipes and pavements, and the economic loss was about CNY 150 billion. In December 2010, the freezing rain damaged two power lines in an airport in Moscow. The growing markets of solar panels worldwide have attracted much attention on preventing ice and snow accumulation on solar cells in many cold climates areas, since ice formation greatly reduce the efficiency or even complete stoppage to the clean energy production.

To prevent or alleviate the adverse consequences of ice accretion, two different strategies have been adopted. One is the “active” method, which is based on heating to melt the ice, chemically decrease icing temperature (e.g. salt) to prevent ice nucleation, or mechanical inflation to remove the ice. However, use of heating or chemicals is economically costly, and introduces environmental pollution. Mechanical inflation is limited to working conditions. Sometimes these methods are not applicable to, for example, inaccessible areas. The other is “passive” method to suppress ice formation or weaken ice adhesion by various special surface coatings such as wax, lubricants and other specific chemicals. This method is of low cost and brings no or less harm to the environment. Depending on texture and physical properties of snow, the quality of formed snow on the texture changes over time (e.g. powder-like, wet snow, slush and frozen snow). Therefore, different wax or lubricant materials need to be chosen according to snow quality, and obviously, these are not suitable for all cases. Furthermore, these chemicals will gradually deplete or degrade over time during application.

The anti-icing performance of superhydrophobic coatings has been studied since 1997 [2]. Later, many efforts have been devoted to study the ice-adhesion strength and icing-delay time [3-5]. The advantage of superhydrophobic coatings over hydrophobic coatings was also investigated [6, 7]. The unique properties of robust superhydrophobic coatings including: (i) excellent water repellency and bouncing effect even at low temperatures, (ii) air-trapping induced low ice adhesion and reduced heat transfer index. Recent studies proposed the potential anti-icing applications of superhydrophobic coatings and also pointed out limitations such as water condensation in cavities and poor mechanical properties.

Recently, the SLIPS have gained considerable attentions [8-12]. SLIPS coating was first reported by Wong et al. in 2011 [8]. This surface was created by infusing a micro / nanostructured porous material with a lubricating liquid, thus replacing the trapped air. The liquid should be immiscible with the fluid that it wants to repel. Since lubricating fluid exhibited low surface energy, water and certain kind of oils (immiscible with the used lubricating fluid) can slide down easily. In 2013, Vogel et al. created a nanostructured

surface with polystyrene particles half submerged in liquid glass [13]. When the liquid glass solidified, it could burn away the polymer particles, leaving a network like a honeycomb. The developed SLIPS coating repelled a variety of liquids, including water, octane, wine, olive oil and ketchup. In addition, according to the group's report the coating reduced the adhesion of ice to a glass slide by 99 % due to its slippery properties although the water contact angle is low. Inspired by this, some researchers also tried to trap water in the micro / nanostructures to form liquid-like layer, so that ice adhesion can be reduced [14]. Although researchers carefully designed the micro / nanostructure to trap low surface energy liquids, the liquids will inevitably be depleted with everyday wear and tear. Moreover, they are intrinsically weak against harsh mechanical conditions that are commonly encountered in many applications such as wear, scratch, fretting, erosion, etc.

1.1.2 Summary of problems to be solved

Considerable attention has been given to the problem of icing prevention. However, no surface could completely repel ice or wet snow. Attention has been paid to fabricate easy ice-removal or icing-delay surface. In summary, this thesis aims to solve the following problems:

1. Design of coatings with specific structured to prevent ice formation and to weaken ice adhesion when ice is inevitably formed at very low temperatures.
2. Improve mechanical properties and durability of anti-icing coatings.
3. Currently, most of the proposed anti-icing coatings are not transparent which hinder their practical application where the original color of protected objects should not be altered either for esthetic reason or due to functional requirement. Therefore, development of a transparent anti-icing coating is another important consideration.
4. It is well known that heterogeneous ice nucleation occurs more easily on rough surfaces than on flat surfaces, because the site adsorption and clustering mechanism is rendered less effective when the surface is flat [15]. Considering that high humidity will trigger the water condensation nucleation, condensation resistant of coatings will be testified and optimized.

5. Other considerations of anti-icing coatings include easy processability and environmental friendliness. Due to the side effect of fluorine chemicals, silicone-based polymers with comparable surface energy have received increasing attention from industries and scholars. Furthermore, room-temperature processable coatings are preferred for various applications. Continuous efforts are expected in this research area.

1.2 Objectives and Scopes

This thesis focuses on the design and development of practically applicable anti-icing coatings for sports applications. The coatings should be of low cost, scalable, and highly effective, aiming for protection of winter sports equipment and outdoor structures in cold regions against harsh environment. To evaluate the anti-icing performance of coatings, ice adhesion and ice nucleation were investigated. To overcome the limitations of current anti-icing coatings, extensive mechanical test has been carried out to verify the mechanical robustness and durability of the anti-icing coatings according to ISO or ASTM standard methods. This work not only develops new coatings, but also lays foundation for their practical applications in sports and other related fields.

The sol-gel method is one of the well-known and low cost techniques to fabricate highly homogeneous organic-inorganic composite coatings. The method is first reported by Kistler in 1932 to produce aerogels [16]. The most important advantage of this method is that the properties of coatings can be tuned and precisely controlled by adding different fillers. This offers a wide range of options to incorporate fillers with different properties and functionalities into a system. Furthermore, the microstructure of the prepared coatings can be adjusted with tuning the process parameters during the procedure of hydrolysis and condensation. All these advantages make it one of the simplest and most cost-effective methods of producing wide ranges of coatings. To design a low cost anti-icing coating, silane based precursors were employed as a sol-gel matrix. Tetraethyl orthosilicate (TEOS) is a popular precursor to form silicate based coatings. 3-glycidoxypyltrimethoxysilane (GLYMO), which is an epoxy silane compound, is often employed as a co-precursor to modify the mechanical properties of the silicate coatings. Many researches show that epoxy

silane significantly improve the durability, adhesion to the substrate and scratch resistance in the past decades [17-21]. In this study, SiO₂ nanoparticle, which is one of the most commonly used additives, will be added as fillers to form special surface microstructures. With finely controlling surface energy of the SiO₂ nanoparticles, superhydrophobic coatings with different surface microstructures will be developed. These coatings will be used to analyze the condensation effect on ice adhesion. In addition, the icing probability, ice-nucleation temperature and nucleation rate will be investigated and analyzed. This will serve as a foundation to understand the effect of surface energy and surface topology on anti-icing performance for the development of future coatings.

As discussed above, transparent anti-icing coatings are highly demanded (e.g. windows, solar cells, goggles, billboard and sports facilities). To develop a mechanically robust transparent coating, nanoparticles which can enhance mechanical properties will be employed. However, nanoparticles tend to agglomeration which will greatly reduce transmittance of coatings, thus unique methods need to be used to obtain uniform dispersion of nanoparticles in a sol-gel solution.

Epoxy resin is room-temperature processable, cost-effective and presents excellent mechanical strength, higher adhesive performance, good chemical stability, stable weather-resistance, and large-area process ability. It is a powerful scalable method for preparing coatings on various substrates, and it could be easily introduced into existing industrial systems and directly applied to offline products. Considering a majority of industry applications prefer room-temperature processable and fluorine-free coatings, silicone modified epoxy resin has been utilized to fabricate mechanically robust anti-icing coatings with the help of nanoparticles.

Existing anti-icing coatings reported so far are generally limited in the mechanical reliability and durability. This poses a great hindrance to lots of practical applications. How to further reduce the ice adhesion and suppress ice formation while maintaining the mechanical robustness remains a great challenge. This issue will be addressed in the current thesis work.

Generally, a practically applicable anti-icing coating should satisfy the following requirements:

- Operational requirements such as safety and reliability
- Considering the environmental and climatic conditions
- Simple and cost-effectiveness
- Easy maintenance
- Mechanical and environmental durability

The objectives of this thesis include:

1. Design of anti-icing coatings based on superhydrophobicity. Ice adhesion and ice nucleation of these coatings will be discussed in correlation with the surface energy and surface topology.
2. Enable transparency to the anti-icing coatings with improved mechanical properties.
3. Design and develop mechanically robust and durable anti-icing coatings to be used in harsh environment.
4. Investigate the effect of surface energy, dispersion status and size of nanoparticles on the surface morphology of coatings and the resulted anti-icing properties.
5. Identifying the relationships between water repellency and icephobicity.
6. Experimental and theoretical analysis of the mechanism of ice adhesion and ice-nucleation process.
7. Investigation the ice-nucleation site on a surface.

To sum up, in this study, the main focus is to develop low cost and mechanically robust anti-icing coatings for sports applications. To understand the relationships between water repellency and icephobicity, coatings with various microstructures will be fabricated and analyzed. The effect of dispersion status of nanoparticles on surface microstructure will be developed after the baseline development. Theoretical analysis of icing properties such as ice nucleation, ice adhesion will be carried out. Extensive mechanical tests will be utilized to verify the robustness of the developed coatings. Furthermore, the size effect of nanoparticles on the anti-icing properties and mechanical properties of coatings will be designed and investigated.

1.3 Dissertation Overview

The overall design and development of anti-icing coatings for sports facilities can be divided into three parts. Topics and brief summaries of each chapter are addressed as below:

Chapter 1 provides the background and introduction to the problems under study. First, the economic impact and general requirements of the topic are stated. Then the objectives and scopes of the whole thesis are presented, followed by the outlines of the thesis. Finally, the novelty and main achievements of this study are pointed out.

Chapter 2 summarises the physics and thermodynamic theory of ice formation, followed by the history of anti-icing techniques. Recent progress and research gaps of anti-icing coatings are addressed. In addition, factors influence anti-icing performances are also reviewed.

Chapter 3 studies the anti-icing performance of superhydrophobic coatings with distinct surface morphology. The relationships between water repellency and icephobicity are discussed with emphasis on the underlining mechanism. Factors toward ice adhesion and ice nucleation are identified.

Chapter 4 describes the development of transparent anti-icing coatings with good mechanical properties. Besides anti-icing performance, self-cleaning properties and mechanical properties are investigated.

Chapter 5 designs environmentally friendly room-temperature processable anti-icing coatings. In particular, the effect of dual-size and single-size nanoparticles on anti-icing performance and mechanical properties are extensively studied.

Chapter 6 addresses main achievements and findings of the whole thesis and marks limitations of this work as well as suggestions for future research.

1.4 Findings and Outcomes / Originality

This thesis leads to following novel outcomes:

1. Nanoparticles with different surface energies have been firstly utilized to fabricate superhydrophobic coatings with different micro-nanostructures.
2. Diffusion induced condensation greatly influence the icephobicity of superhydrophobic coatings. To study the effect of water condensation on superhydrophobic coatings, five superhydrophobic coatings with decreased surface energy have been studied. It has revealed that surface geometry plays an important role in ice adhesion rather than surface roughness. Low ice adhesion does not guarantee suppressed ice nucleation due to their distinct mechanisms.
3. Mechanically robust transparent anti-icing coatings are rare. In this study, mechanical agitation has been for the first time used to uniformly disperse nanoparticles in a sol-gel system. It is revealed that mechanical agitation and surface modification accelerated the deagglomeration of nanoparticles. When the nanoparticles are uniformly dispersed, a transparent coating can be achieved as verified by TEM analysis. In addition, this study opens a new avenue for smooth solid coatings. By adjusting dispersion status of nanoparticles, a smooth inorganic solid surface with low surface energy was obtained. The coating presented robust low ice adhesion, delayed ice nucleation, and excellent frost inhibition. In addition, the coating also displayed repellency to various liquids with surface energy ranging from 72.8 to 22.1 mJ/m². The smooth solid coating outperforms reported coatings in terms of hardness, adhesion, and scratch resistance.
4. To overcome the poor mechanical properties of porous microstructure, the size effect of nanoparticles on anti-icing performance, mechanical properties and durability has been studied. Comprehensive mechanical property tests, UV irradiation and water condensation verified superior performance of the coatings with dual-size nanoparticles over the coatings with single-size nanoparticles. Moreover, the sand erosion test confirmed the durability of the coatings with dual-size nanoparticles.

References

- [1]. M. Farzaneh, C. Volat and A. Leblond, *Anti-icing and de-icing techniques for overhead lines*, in *Atmospheric icing of power networks*. 2008, Springer. p. 229-268.
- [2]. H. Saito, K. Takai and G. Yamauchi. *Surface Coatings International Part B: Coatings Transactions*. **1997**, 80, 168-171.
- [3]. D.K. Sarkar, M. Farzaneh. *J. Adhes. Sci. Technol.* **2009**, 23, 1215.
- [4]. M.A. Sarshar, C. Swartz, S. Hunter, J. Simpson and C.-H. Choi. *Colloid and Polymer Science*. **2013**, 291, 427-435.
- [5]. P. Roach, N.J. Shirtcliffe and M.I. Newton. *Soft Matter*. **2008**, 4, 224.
- [6]. B.J. Basu, J. Manasa. *Journal of Colloid and Interface Science*. **2011**, 363, 655-662.
- [7]. Q. Fu, X. Wu, D. Kumar, J.W. Ho, P.D. Kanhere, N. Srikanth, E. Liu, P. Wilson and Z. Chen. *ACS Applied Materials & Interfaces*. **2014**, 6, 20685-20692.
- [8]. T.S. Wong, S.H. Kang, S.K. Tang, E.J. Smythe, B.D. Hatton, A. Grinthal and J. Aizenberg. *Nature*. **2011**, 477, 443-447.
- [9]. P. Kim, Wong, T. S., Alvarenga, J., Kreder, M. J., Adorno-Martinez, W. E., & Aizenberg, J. . *ACS nano*. **2012**, 6, 6569-6577.
- [10]. J. Chen, R. Dou, D. Cui, Q. Zhang, Y. Zhang, F. Xu, X. Zhou, J. Wang, Y. Song and L. Jiang. *ACS Applied Materials & Interfaces*. **2013**, 5, 4026-4030.
- [11]. L. Zhu, J. Xue, Y. Wang, Q. Chen, J. Ding and Q. Wang. *ACS Appl Mater Interfaces*. **2013**, 5, 4053-4062.
- [12]. S.B. Subramanyam, K. Rykaczewski and K.K. Varanasi. *Langmuir*. **2013**, 29, 13414-13418.
- [13]. N. Vogel, R.A. Belisle, B. Hatton, T.-S. Wong and J. Aizenberg. *Nature communications*. **2013**, 4, 2176.
- [14]. J. Lv, Y. Song, L. Jiang and J. Wang. *ACS Nano*. **2014**, 8, 3152-3169.
- [15]. D. Bassett, E. Boucher and A. Zettlemoyer. *Journal of Colloid and Interface Science*. **1970**, 34, 436-446.
- [16]. S. Kistler. *The Journal of Physical Chemistry*. **1932**, 36, 52-64.
- [17]. W.A. Daoud, J.H. Xin and X. Tao. *Journal of American ceramic society*. **2004**, 87, 1782-1784.

- [18]. J.H. Hwang, B.I. Lee, V. Klep and I. Luzinov. *Materials Research Bulletin*. **2008**, 43, 2652-2657.
- [19]. S. Zheng, J. Li. *Journal of Sol-Gel Science and Technology*. **2010**, 54, 174-187.
- [20]. L.Y.L. Wu, E. Chwa, Z. Chen and X.T. Zeng. *Thin Solid Films*. **2008**, 516, 1056-1062.
- [21]. W.A. Daoud, J.H. Xin and X. Tao. *Applied Surface Science*. **2006**, 252, 5368-5371.

Chapter 2 Literature Review

Literature Review

In this chapter, physics of atmospheric ice accretion on outdoor sports facilities is presented and analyzed. Thermodynamic theory of ice nucleation and the mechanism of ice adhesion are reviewed. A brief history of de-icing and anti-icing techniques available in the literature is summarized. Among all the methods, passive anti-icing coating is overwhelming due to its low cost and easy applicability / maintenance. Detailed analysis and comparison were made on this technique. In addition, key factors affecting anti-icing properties of coatings are systematically presented, and major research gaps are revealed based on the literature review.

2.1 Physics of Atmospheric Ice Accretion

Ice accretion and formation on outdoor sports facilities such as artificial turf structure, components of snowmobiles or skidoos (engine, carburettor, tunnel, air filter and the suspension system, etc.), power lines, pavements, roofs and solar panels used in sports leads to damage, lowered performance and in some cases increased risk towards big disasters. The purpose of the study of ice is to gather data related to chemical and microphysical properties of ice events, and to develop anti-icing coatings for different environments and different practical applications. In order to delay ice accretion or reduce ice-adhesion force, an understanding of the type of formed ice under a certain condition is needed. To draw water molecules into a certain ice lattice structure, a potential energy of vectorised bonding is needed, that is the energy of freezing [1]. Different crystal structures require different freezing energy. Different types of ice crystals present distinct adhesive force to a solid surface; and the physical properties of formed ice varies in density and appearance.

The common ice events related to sports facilities are precipitation, which can be snow, sleet, freezing rain or frost. The accretion rate is much higher than in-cloud icing, and thus causes more damage. When snow is partially melt at the air temperature of 0~3 °C, it sticks to a surface and is difficult to remove once frozen. Sleet is mixtures of rain and snow, and the size is usually smaller than hailstones. Both sleet and freezing rain are from melt frozen precipitations in warm air. The difference is that sleet freezes before reaching a solid surface, while freezing rain freezes after reaching a solid surface. Freezing rain forms high ice adhesion to a surface with temperature below 0 °C. This phenomenon often occurs during inversion, and the density and adhesion of the formed ice are very high when this phenomenon occurs. Frost appears when atmospheric water vapor solidifies directly on a cold surface when wind speed is low. Frost adhesion force to the surface may be strong [2-6].

The atmospheric icing can form different ice structures. Rime results from heat transfer when supercooled water droplets (temperature can be as low as -30 degree in cloud) impact

on cold surface and freeze instantaneously. Depending on liquid water content and droplet size in atmosphere, water can form soft rime and hard rime. Soft rime is accreted under low liquid water content conditions with small droplet size. It is a thin ice with flakes and needles, containing a high volume of trapped air, thus it appears white and presents a low density of about one quarter of that of pure ice and low adhesion to a solid surface. Hard rime is formed under high liquid water content conditions with large droplet size and comparatively dense, thus it is difficult to remove. Its density is between about 0.6 and 0.9 g/cm³. If formed ice is transparent, free of bubble and high density, then it is called glaze, which exhibits strong adhesion to a surface and often associated with precipitation. The density of glaze is around 0.8-0.9 g/cm³. Sometimes, ice accretions are a mixture of glaze and hard rime, the density is around 0.87-0.89 g/cm³.

To understanding the basic crystal structures of formed ice from atmospheric water vapor, extensive efforts have been made since 1889 [7]. A variety of techniques have been employed to carry out the investigation, including polariscopes [7], electron diffraction investigations [8], x-ray crystallography [9], optical scattering instrument [10], single-crystal neutron diffraction [11], and calorimetric studies [12]. Based on previous study, Kikuchi et al. summarized 121 different types of snow crystals [13]. The ice crystals and other solid precipitations as shown in Fig. 2.1, where C, R, P, CP, A, G, I and H refer to column crystal group (C1-C4), rime snow crystal structure (R1-R4), plane crystal group (P1-P8), combination of column and plane crystals group (CP1-CP9), aggregation of snow crystals group (A1-A3), germ of ice crystal group (G1-G3), irregular snow particle group (I1-I3) and other solid precipitation group (H1-H3). Among these categories, rimed snow crystal group is divided into four types based on the leveling of riming. R1 (rimed crystal) refers to soft rime structure, while R2 (densely rimed crystal), R3 (graupel-like snow) and R4 (graupel) refer to hard rime structures. Other solid precipitation group contains sleet particle, ice pellet and hailstone.

In the mid-latitudes, the common crystal types are dendrite-type (diameter: 1-3 mm, the most typical shape of crystals), plane-type (size: several tenths of a micrometer to 100 μ m, the second most common shape of crystals), germ of ice crystal group (minute ice crystals

with size < 0.1 mm) and column-type ice crystal or ice prism (size: ~ 50 μm , a minute snow crystal results in diamond dust conditions). These crystal types are also the main ice structures that formed on sports facilities [13].

Figure 2.1 Schematic illustration of 121 types of snow crystals, ice crystals and other solid precipitations [13].

Figure 2.2 Habit diagram in text (upper) and pictorial format (bellow) for atmospheric ice crystals obtained from laboratory results [14] and images gathered from cloud particle imager (CPI) during the Second Alliance Icing Research Study (AIRS II) and other field studies. Diagonal bars near the middle of the upper diagram indicated the possibility that the bullet rosette habit could extend to temperatures slightly higher than -40 °C [15].

Besides crystal category by shape, size and region, Bailey and Hallett [15] studied the shape of crystal habits of ice and snow crystals as a function of temperatures, and presented a crystal habit diagram (Fig. 2.2) of snow crystals from 0 °C to –70 °C in 2009 combining older diagrams prepared by Pruppacher et al. [16] and Magono and Chung [17]. The crystal shape changes from plates (0 °C to –4 °C), columns (–4 °C to –8 °C), plates (–8 °C to –18 °C), platelike (–20 °C to –40 °C) to columnar (–40 °C to –70 °C). When temperature is lower than –20 °C, the habit is dominated by polycrystals of various shapes based on the platelike and columnar habit regimes. Moreover, researchers investigated the types of accreted ice as a function of temperature and wind speed as shown in Fig. 2.3. It can be seen that an increase in wind speed can dramatically increase the density of formed ice.

Figure 2.3 Type of accreted ice as a function of air temperature and wind speed [18].

Although types of ice crystals and ice-adhesion force have been studied for decades, there is no direct research on the effect of size, shape of ice crystal and the rate of ice crystal nucleation on ice adhesion force to solid surfaces. Moreover, till now, anti-icing coatings with different surface morphologies have been widely investigated. However, shapes of ice crystals as a function of different surface structure have been rarely discussed. Future studies are needed on these aspects.

2.2 Thermodynamic Theory of Ice Nucleation

Ice nucleation is a natural phenomenon and formation of ice nucleus is the first step of ice crystal formation on a solid surface. In general, the process is classified into homogeneous nucleation and heterogeneous nucleation. The thermodynamic theory of these two processes is well known and significantly different from each other, and both have been employed to explain the ice nucleation on anti-icing coatings, depending on the environmental conditions of the ice formation.

2.2.1 Homogeneous Nucleation

In classic nucleation theory, ice formation follows the minimum energy principles. It suggests that the nucleation process is driven by the ice saturation ratio (related to temperature), the ice / solution interface energy, and the diffusion activation energy for a water molecule to cross the water / ice interface (Gibbs free energy change of the ice crystallization). In homogeneous ice nucleation, the excess Gibbs free energy required for the formation of ice nuclei forms inside water system is

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

where ΔG_V is the volume excess Gibbs free energy, ΔG_S is the sum of surface excess Gibbs free energy. By assuming that the ice nucleus is sphere with a radius equal to r , Equation 2.1 can be written as

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

$$\Delta g = G_S - G_L = -\frac{\Delta H_m \cdot (T_m - T)}{T_m}, \quad (2.3)$$

where γ is the interfacial surface free energy between supercooled water and ice, Δg is the unit volume Gibbs free energy change of the ice crystallization. T is the real crystallization temperature. T_m is the equilibrium crystallization temperature. ΔH_m is approximately independent of temperature between T and T_m in a homogeneous process. Figure 2.4 shows the change of free energy as a function of the radius of the nucleus.

Figure 2.4 Schematic illustration of free energy diagram of nucleation. From Ref. [19].

The maximum value ΔG_{crit} is the excess Gibbs free energy change of formation of a critical ice nucleus. r_c is defined as the radius of the critical ice nucleus, it can be obtained by letting $\frac{d\Delta G}{dr} = 0$:

$$\frac{d\Delta G}{dr} = 8\pi r\gamma + 4\pi r^2\Delta g = 0, \quad (2.4)$$

The critical nucleus size is obtained as

$$r_c = \frac{-2\gamma}{\Delta g}, \quad (2.5)$$

And the critical Gibbs free energy change is

$$\Delta G_{crit} = \frac{16\pi\gamma^3}{3(\Delta g)^2} = \frac{4\pi r_c^2\gamma}{3}, \quad (2.6)$$

It is assumed that the energy level is not a constant at different part inside the water system. Fluctuation in energy occurs around the mean value. These fluctuations can be described as statistical distribution of energy or velocity of water molecules. Since ice nucleus is more likely to be generated in the regions where energy levels happen to be higher than the mean value, the ice nuclei size is assumed to follow Boltzmann distribution corresponding to the energy change $\Delta G(n)$ for n water molecules in ice nucleus:

$$N(n) = N_0 e^{-\Delta G_n^0/kT}, \quad (2.7)$$

where k is the Boltzmann constant, $N(n)$ represents the number of ice nuclei and N_0 represents the number of water molecules per unit volume in the supercooled water system. According to Einstein's theory, the probability of states arising by fluctuation is proportional to the negative exponential of the involved entropy change. Thus, the flux of the ice nuclei growing past the critical size γ_c (assume it is made up of n_c water molecules) can be estimated as the number of nuclei with $(n_c - 1)$ molecules multiplied by the net rate of impingement of molecules on a surface to form a sphere of n_c molecules. Then the nucleation rate which stands for the number of nuclei formed per unit volume and per unit time can be expressed with Arrhenius-type equation as:

$$R = A e^{-\Delta G_c/kT}, \quad (2.8)$$

where A is the kinetic pre-factor, and is expressed as:

$$A = \frac{24}{\sqrt{6\pi k}} \frac{\rho D \lambda_c^{1/6}}{l^2} \left(\frac{\Delta g}{T} \right)^{1/2}, \quad (2.9)$$

where ρ is the density of liquid, D is the diffusion coefficient, λ_c is the size of critical nucleus, and l is the atomic jump distance in liquid. Since a minor change in Δg or γ results in orders of magnitude change in ΔG_c and I , but A remains linear and exhibits a weak dependence on the temperature, thus it can be treated as a constant during calculation. During undercooling, $(T_m - T)$ provides the driving force for nucleation. Substituting $\Delta g = G_S - G_L = -\frac{\Delta H_m \cdot (T_m - T)}{T_m}$ into Equation 2.8, and assuming the critical nucleus to be spherical, the nucleation rate can be written as:

$$I = A \exp \left(-\frac{16\pi\gamma^3}{3kT(\Delta H_m)^2} \left(1 - \frac{T}{T_m} \right)^2 \right) = A \exp(C(1 - T/T_m)^2), \quad (2.10)$$

Thus, homogeneous nucleation rates for ice can be experimentally measured via the temperature difference.

2.2.2 Heterogeneous Nucleation

According to the definition by the Committee on Nucleation and Atmospheric Aerosols [20], the heterogeneous ice nucleation modes can be divided into two kinds, one is deposition nucleation which refers to the formation of ice in an ice-vapor environment. The other one is freezing nucleation which is the formation of ice in an ice-supercooled liquid environment. Further distinction of freezing nucleation is made according to participation mode of a particle as shown in Fig. 2.5.

- Immersion freezing is defined as a particle immersed in the supercooled water.
- Condensation freezing occurs when a foreign particle serves as cloud condensation nucleus (CCN) and induces freezing of the water molecular immediately.
- Contact freezing takes place when a foreign particle contact with the supercooled water.

Figure 2. 5 Schematic illustration of the formation mechanism of ice nucleation [21].

Although researchers have tried to derive an expression for the nucleation process for these modes, it is a very challenging or even impossible task. Many studies managed to experimentally predict nucleation rate and possibility of deposition mode [22-26] and immersion freezing [27-29]. However, the nucleation rate of condensation freezing is related to both the probabilities of condensation and the probabilities of freezing, thus

analysis will be more complex. For contact freezing, the probability of collision between water droplet and impurities is a key factor.

In the classical theory of heterogeneous nucleation, the free energy barrier ΔG^{heter} is predicted to be the energy needed to overcome the formation of sphere-cap-shaped nucleation seeds, which is lower than the ΔG^{homo} for spherical water droplets in the bulk [30]. It is expressed as:

$$\Delta G^{heter} = \Delta G^{homo} \cdot f(\theta), \quad (2.11)$$

$$f(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2, \quad (2.12)$$

where $f(\theta)$ is a factor between 0 ~ 1, and only depends on the contact angle derived from Yang's Equation. It is noteworthy that this derivation is solely adapted to the very smooth, flat and clean surfaces.

For superhydrophobic surfaces with surface roughness values significantly larger than the critical nucleus radius, the heterogeneous nucleation depends mainly on the contact angle θ , then $f(\theta)$ can be expressed as [31]:

$$f(R, \theta) \approx f(\theta) = \frac{(2 + (\gamma_I - \gamma_W)/\gamma_{IW} \cos\theta)(1 - (\gamma_I - \gamma_W)/\gamma_{IW} \cos\theta)^2}{4}, \quad (2.13)$$

where R is surface roughness, r_c is the critical nucleation radius, γ_I , γ_W and γ_{IW} denote the ice-vapor, water-vapor and ice-water interfacial energies, respectively.

Some researchers investigated the free energy barrier of ice nucleation on concave and convex surfaces and found that for a given water contact angle, θ , the energy barrier ΔG^{heter} of a concave surface is smaller than that of a convex one [32-35], and derived the following:

$$f(R, \theta) = \frac{1}{2} \left[1 - \cos^3(\phi + \theta) - \frac{3\cos\theta \sin^2(\phi + \theta)}{1 + \cos\phi} + \frac{(2 - 3\cos\phi + \cos^3\phi) \sin^3(\phi + \theta)}{\sin^3\phi} \right], \quad (2.14)$$

where θ is the water contact angle between the nuclei and the concave surface, R is the radius of a sphere substrate, r_c is the critical nucleation radius, $\phi = \arccot \left(\frac{R}{r_c} \cot \theta \right)$ is the angle between the concave surface and its tangent line at the inflection point [24]. Equation 2.14 can also be written as [33]:

$$f(R, \theta) = \frac{1}{2} \left[1 - \cos^3(\phi + \theta) - 3 \left(\frac{R}{r_c} \right)^2 \cos\theta(1 - \cos\phi) + \left(\frac{R}{r_c} \right)^3 (2 - 3\cos\phi + \cos^3\phi) \right], \quad (2.15)$$

Several researchers studied condensation nucleation [22, 36] and deposition nucleation on surface steps [37] and set up the relationship of the factor f with the special geometry angles. It is noteworthy that researchers have tried to predict ice-nucleation process on superhydrophobic [38, 39], hydrophobic [30, 36], hydrophilic surfaces [40] and SLIPS [41]. However, till now, no general rule has been established to predict all the heterogeneous nucleation processes. Thus, more comprehensive study is needed.

2.3 Theory of Ice Adhesion

Theoretically predicting and / or experimentally measuring ice adhesion are important aspects for anti-icing research, because ice will inevitably form when the ambient temperature is low enough. Ice adhesion on a surface is generally related to temperature, electrostatic forces, hydrogen bonding, ice salinity, van-der-Waals forces, and properties of the adhesion surfaces [42, 43].

On ice / metal and ice / dielectric interfaces, electrostatic attraction induces surface charge to build up. This is known as an image force. When the solid in contact with ice has effective dielectric constant ε larger than that for ice, ε_i , the image force can be described as [44]:

$$F = \frac{q^2}{16\pi\varepsilon_0\varepsilon r^2} \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + \varepsilon}, \quad (2.16)$$

where q is the electric charge of ice, r is the distance to the interface of ice and adhesion surface, ε_i , ε and ε_0 are the dielectric constant of ice, adhesion surface and air, respectively. It is reported that the van-der-Waals force contributes less to ice adhesion than the hydrogen bonding [31, 45, 46].

Makkonen established a model between ice adhesion and water contact angle by combining Young's Equation with thermodynamic work of adhesion [47]:

$$W_a = \gamma_i + \gamma_w \cos\theta + (\gamma_{ws} - \gamma_{is}), \quad (2.17)$$

where W_a is thermodynamic work of adhesion, γ_i , γ_w is the surface energy of ice and water, and γ_{ws} and γ_{is} are interfacial energy of water-solid and ice-solid, respectively. By assuming that the surface energies of water and ice and their interfacial energies at the solid interface are approximately the same, Equation 2.16 can be expressed as:

$$W_a \approx \gamma_w(1 + \cos\theta), \quad (2.18)$$

Figure 2.6 shows the relationship between water contact angle and thermodynamic ice adhesion scaled by surface energy of water. In this model, the ice adhesion decreases as water contact angle decreases.

Figure 2.6 Thermodynamic work of ice adhesion scaled by the surface tension of water as a function of water contact angle θ [47].

However, this model is derivated from the Young's Equation, which are not suitable for rough surfaces due to complex or incomplete ice–solid contact. Besides, in some cases, the adhesive forces required to separate surfaces connected by a capillary bridge of water are dominated by the receding contact angles θ_{rec} , which is defined during sliding behaviors of a water droplet. Thus the work of adhesion could be expressed as [48, 49]:

$$W_a = \gamma_w(1 + \cos\theta_{rec}), \quad (2.19)$$

Furthermore, numerous experimental and theoretical studies on the contact angle hysteresis arouse researcher's interest in its relationships with ice adhesion. It is explained that contact

angle hysteresis is originating from surface roughness and heterogeneities, liquid absorption and retention, surface deformation, molecular rearrangement upon wetting, viscous dissipation and diffusion [50, 51]. Kulinich and Farzaneh measured ice adhesion of superhydrophobic surfaces with different roughness and found that ice adhesion presented a linear relationship with water contact angle hysteresis [52, 53]. This shed a new insight into dynamics wetting related ice adhesion with respect to a rough surface.

Although efforts have been dedicated to study the mechanisms of ice adhesion, experiments studies on different surfaces revealed that waterproofness of a surface is influenced by the size of the pores on a rough surface. Water will readily penetrate into the openings if the pressure behind it is sufficient to break the surface film across the pores. This leads to a complex and inconsistent of ice adhesion results obtained from different surfaces. More fundamental research is needed to establish a model for ice adhesion.

2.4 History of Anti-icing Techniques

To inhibit ice formation and reduce adhesion of ice on exposed surfaces, considerable research work has been carried out, including mechanical, thermal and chemical techniques. Since most of the deicing methods can also achieve anti-icing performance, deicing related methods are also reviewed.

2.4.1 Notions Used to Describe Ice Prevention Properties

It is noted that anti-icing, antiice, deicing, de-ice, icephobic, ice releasing / release, anti-freeze and antifrost were used to explain ice prevention properties. The word “deicing” is firstly used to describe ice removal of electrical heating windows [54]. The notion “anti-icing” is firstly referred by Knapton and Emery in the sentence: “in North America urea is used as a pavement anti-icing agent and glycol is used for aircraft de-icing purposes” [55]. Tabrizi and Keshock described the concept of anti-icing and deicing: anti-icing refers to methods of preventing ice formation and deicing is the periodic removal of ice that is already formed [56]. Anti-icing and anti-ice share the same meaning, so as deicing and de-

ice. The word “icephobic” were first used to describe low ice-adhesion coating materials for aircrafts [57]. “Ice releasing / release” usually describes of releasing ice from a mold [58-60]. A first ice release coating composition was patented in 1959 by Rolle and Barnes to readily remove ice on naval aircraft planes [61]. In this manner, ice releasing is similar to anti-icing. Anti-freeze means providing a method for preventing freezing of surfaces, proteins or liquids [62-64]. Currently, it mostly refer to anti-freeze proteins. Anti-frost is aiming to minimize growth of frost on cold surfaces exposed to humid air. Although frost is a kind of atmospheric ice accretion, anti-frost is a specialized application under certain conditions.

2.4.2 Mechanical Methods

The first anti-icing report that can be found from the literature is a patent filed in 1884, dealing with mechanical devices that could remove ice effectively [65]. It aimed to construct a snow and track clearer to remove snow and ice on streets and tracks without noise. Similar ideas like sweep [66], scraping wiper [67], blades [68] were also developed to remove formed ice. Another mechanical method was introduced by Geer and scoot [69]. They took advantage of the flexibility of rubber, which can be induced a pulsating movement during a plane fly, to break up formed ice, similar to the function of the covering shoe for airplane [70]. To save energy and enhance the efficiency of deicing device, Levin et al. described an electromagnetic field pulse-induced elastic deformation of thin sheets to remove ice [71]. Cattaneo disclosed a flexible and porous membrane to break up the formed ice on the contoured surface of airplanes [72]. If formed ice closes up the pores of the membrane, an inflation of hot air will cause a deformation of the membrane. Methods involving compressed air induced inflation of a covering layer are normally itemed as pneumatic boots. Later developments are mainly focused on the source of air and types of deformable layers [73-75]. Currently, pneumatic boots with continuous development and optimization are still used as deicing boots of wing and stabilizer leading edges of airplanes due to low power requirements, low cost, low weight and retrofit ability. The development of shape memory alloys or polymers introduces a new deicing technology. The actuating properties of shape memory materials enable effective removal of formed ice on a surface

by expanding or contracting. Ingram and Gerardi disclosed a shape memory alloy with transformation temperatures between -100°C . and $+100^{\circ}\text{C}$. The material remembers even if it is severely deformed and the recovery rate is related to how fast heat can be applied [76]. Recently, Dixon et al. reported an icephobic coating utilizing organophosphorous phase change materials [77]. If ice forms on the phase change materials (PCM), the PCM absorb parts of latent heat of freezing process and cause solid-solid phase changes. The phase change induces local strain in the ice-coating interface and results in ice detachment. An inflatable apparatus can distort the exposed surfaces and finally loose and break up ice deposits. This kind of apparatus has been employed to inhibit excessive accumulation of ice. Although good results were obtained for most types of ice using an inflation pressure of about 6~8 psi, it has been found that such pressure could not effectively break up rapidly formed glaze ice. The problem would not be satisfactorily solved simply with an increase in the air pressure that was used in continuous operation. The reason lies in two aspect: firstly, the higher pressure requires bulkier and heavier apparatus for continuous operation; secondly, the conditions of heavy glaze ice is infrequent [78].

2.4.3 Thermal Methods

2.4.3.1 Heating

Besides the mechanical methods, researchers found that thermal methods are more effective, thus heating devices or elements [79-82], heating transition systems [83] and thermal ice-prevention equipment [84] were developed. Researches also combined compressed air and heating elements to obtain an anti-icing system [85, 86]. A flexible electric heating protective coating was disclosed by Ely and Ketcham to obtain mechanical strength and dielectric protection. The heater fabric which consisting of flexible resistor wires was embedded in rubber, silicone, resin or other flexible binds [87]. One problem of the electrical heating systems is high cost and maintenance burdens. In 1970s, Lazarus developed a self-heating mixture, wherein partially reacted droplets of two dissimilar chemical compositions react chemically to generate heat and melt ice formed on a windshield [88]. Shah reported a closed-loop liquid anti-icing system to prevent ice

accretion on wings and engine air inlet of airplanes [89]. The liquid was heated by passing the hot high pressure bleed air from the turbine compressor. Other concepts of heating including electric infrared lamps [90], laser [91], earth heat pipes / geothermal fluids [92, 93], halogen lamps [94], solar heaters [95], conductive fibers embedded composite structures [96], and plasma-based de-icing [97]. These methods overcome the conventional electronic heating system in mechanical simplifications, and possess good reliability and less energy requirement. Another interesting anti-icing technique employs microwave system to remove ice from surfaces [98]. Hansman used the transmission of microwave electromagnetic energy to heat impinging atmospheric supercooled water droplets, so that the temperature of supercooled droplets presented a temperature above the freezing point, and would not freeze upon impact with aircraft structures [99]. He pointed out that the frequency of the microwave electromagnetic energy was more preferably absorbed by the water droplets than ambient air, ice or aircraft structures. Therefore, the electromagnetic energy can effectively heat supercooled droplets to prevent ice accretion. López and Peralta described a de-icing system for windows by nebulized and precipitates hot droplets on windows to eliminate ice [100]. The system consists of a reservoir, a heating element and a pump. The de-icing liquid is pumped from the reservoir through the heating element to outlets, forming nebulized hot droplets. Although a lot of techniques have been reported and discussed, till now, the electro-thermal systems, fabricated by burring resistive circuits into the airframe structure to generate heat, are still most widely used methods in aerospace, windows and engine applications. Both anti-icing and deicing modes are available by generating heat continuously or intermittently.

2.4.3.2 Air bubble

The use of air bubblers for anti-icing applications has been reported abundantly in the literature to maintain ice-free areas in lakes and in the sea [101]. Gross utilized a high rotating speed propeller to generate reduced pressure due to the high velocity of moving water [102]. The reduced pressure drew air down and kept warm air down in the water. Hibburd induced air bubble in seas by mechanical method of generating turbulence [103]. Warm air bubble with appropriate size was produced in cold water to make water surfaces

free of ice. Hoddinott et al. injected air bubbles into water by a land based compressor with perforated hoses or lines [104]. To prevent ice formation, the operation of the air bubbler must begin before freeze-up. The size of air bubble is important. The bubbles should be finely enough to stay in suspension and do not rise to the water surface rapidly. The size of bubbles depends on air-water surface tension, temperature, pressure, purity, etc. In 1999, based on the ice electrolysis, Courville and Petrenko developed interdigitated microelectrode layers to eliminate ice [105]. When ice formed on the microelectrodes layers, a DC current through the ice could be generated by applying a DC bias of 5 V to 30 V. The ice adjacent to the microelectrodes underwent electrolysis and decomposed into oxygen (on the anode) and hydrogen (on the cathode). Therefore, the bonding between the ice and the metal was weakened. In addition, the rapidly growing gas bubbles on the ice-electrode interface could serve as interfacial cracks to reduce ice adhesion.

2.4.4 Chemical Methods

The first chemical materials used to reduce the freezing point of water was urea and salt. However, these two materials have been proved to have a damaging effect on concrete outdoor structures and metal facilities [106, 107]. Phillip® disclosed a frost and obscuring condensation preventive composition consisting of a mixture of mineral oil, such as coal oil, calcium chloride, vinegar and water [108]. Knight and clay found distinct difference between water soluble and insoluble compounds in preventing ice formation [109]. Water soluble compounds were effective anti-icing agents, while the tested water insoluble compounds were ineffective in anti-icing applications. Collins claimed an anti-freeze composition in 1930 (US1776181A), consisting of water, sodium chloride and glucose [110]. One limitation of this type of compositions is high viscosity which results in non-uniform layers when applied. Considering the viscosity of applied liquids, Graves developed an anti-freeze composite with less viscosity, thus liquids spread uniformly on the applied surface [111]. Ideally, these anti-icing liquids sufficiently weaken the bond strength of the ice-surface interface, therefore, ice accretion is not significant. However, these liquids were successfully developed for static conditions only. They didn't perform well in a high-speed air stream. To improve the adhesive force, Zimmer and Morway

developed an antifreeze lubricating grease including lubricating oils and / or fatty oils [112]. Kormann reported an anti-freeze mixture containing gelatine, glycerol, casein, sodium benzoate, and glue [113]. Sydney and King found that a foamable composition containing alkylene polyol, a tertiary amine, etc. It was more stable than liquid ethylene glycol which drained away quickly [114]. Jenkins et al. prepared an anti-icing glycol-based fluid thickened with an associative polymer to improve the adhesive of glycol to aircraft surfaces [115]. Besides, crosslinked acrylic polymers and surfactants were also used as the thickeners [116]. A simple and low cost method to increase the viscosity of an aqueous fluid was to add a small portion of starch to elongate the effectiveness of ice prevention [117]. Moreover, a more stable sol–gel system was also used to slowly release tripropylene glycol and glycerol, which suppresses the freezing point of water [118, 119]. Glycol-based anti-icing or deicing liquids played an important role in ice prevention operations of airplane and airports. However, the run-off of these materials resulted in serious pollution problems. To develop environmental benign anti-icing agents, Mackenzie prepared two parts anti-icing composite with the first part consisting of mineral oil dissolved ester or partial ester, and the second part containing mainly lithium chloride and cellulose [120]. Other environmental benign chemicals like polyhydroxy sugar [121], various monolayers [122], biological glycoproteins [123, 124], and various industrial waste streams [125] were also reported as the antifreeze / anti-icing agents. In 1950s, Fain and Hewitt found a low volatility composition termed as radiator liquid [126]. It consisted of ethylene glycol, potassium thiocyanate and sodium nitrite. Inspired by these anti-freeze compositions, anti-icing additives were added to lower freezing point of gasoline and fuels [127, 128]. Further developments were carried out on lubricants with a cationic or non-ionic surface active agent [129], and organic dyestuff containing sulfonic acid groups [130].

To develop a composition which could withstand the rinsing effect of water and high-speed wind, Kimball first designed surface structures with a series of small holes that allowed the escape of deicing liquids when required to improve durability of liquid layers [131]. Later, molten wax infused anodized surface of aluminum or aluminum alloy were developed to facilitate easy separation of formed ice [132]. Nichols prepared a porous metal panel (40 micro porosity) to distribute deicing fluid to prevent ice accretion on the leading edge of a

plane or other vehicles [133]. Besides trapping or infusing anti-icing liquids, researches continued to develop a durable layer system. Driscoll disclosed a three-layer anti-icing system, consisting of a flexible base layer of water-proof material, an flexible outer layer permeable to atmospheric moisture and an intermediate supporting moisture absorbent layer [134]. The intermediate layer was electrically insulating when dry and electrically conductive when wet. Moreover, an organic-inorganic anti-icing composition [135] and acrylic copolymer latex [136] were also reported.

In 1946, Raymond and Lewis proved that a liquid layer between ice and a blade reduced the adhesion force between the ice and the blade surface [137]. Gradually, researchers realized the existence of a liquid-like layer between the ice and the solid surfaces [138, 139] and produced ice-melting liquid layers by overcurrent [140], short-circuit current [141] and direct current [142]. Longhurst and Robert reported a jelly based composition that reacted with the accreted ice [143]. One component of the composite was gelatinous cryoscopic substance. When the ice was contact with this substance, it melted at the same time and formed a liquid layer. Of course, the effective life of the coating would vary with the severity of the icing conditions and the amount of cryoscopic liquid which would be used up in melting and dissolved out by the water present.

Low surface energy silicone was first used by Haas [144]. He utilized liquid polymeric silicones to form a rubbery surface which could reduce the adhesion of ice. After that, silanes were used to treat non-porous substrates, for example, metal, glass, plastics and ceramics [145]. The United States Army Aviation Engineering Flight Activity evaluated the ice-shedding effect of two commercial available silicone-based polymers (General Electric G697: polydimethylsiloxane (PDMS) compound; Dow Corning E2460-40-1: cationic silicone oil) on the main rotor blades of the UH-1H Helicopter [146]. In 1997, Saito et al. dispersed 1 μ m polytetrafluoroethylene into polyvinylidene fluoride resin using a ball milling for anti-icing applications [147]. However, Maier found that some silicone materials and fluorinated hydrocarbons had no effect on concrete due to the rough concrete pavement [148]. The rough concrete surface presented a strong mechanical interlocking to ice.

The first superhydrophobic layer was reported by Reick [149, 150]. The superhydrophobic layer was prepared with silane modified fumed silicon dioxide which formed a micro-roughness surface. A new icephobic paint based on superhydrophobicity was developed for preventing icing on the airfoils of aircrafts [151]. Compared with all paints available, the ice adhesion strength of the new paint displayed the lowest value. In 2008, Liu et al. found that superhydrophobic surface had a strong ability to restrain frost growth. The superhydrophobic surface demonstrated 55 min delay in frost formation compared with a plain copper surface under the same tested conditions [152]. After that, great efforts were made to develop anti-icing coatings with superhydrophobicity [153-155]. However, superhydrophobic coatings are limited for anti-icing applications due to the water condensations under high humidities and weak porous structures [156-159].

The SLIPS were developed with impregnating a low surface energy lubricant into a textured solid. The smooth liquid over layer could lower ice adhesion and minimize ice nucleation. Later, many similar surfaces were fabricated for the same objective with various low surface energy liquids like perfluorinated chemicals, silicone oil and hydrocarbon. Such surfaces were also termed as ‘liquid-impregnated surfaces’ [160-162]. The key limitations of SLIPS include: i) the liquid will be drained away gradually, ii) weak mechanical property due to porous microstructures [163, 164].

Based on the literature survey, new coatings with improved mechanical properties and durability are needed for various applications such as outdoor facilities, aerospace and marine structures, etc. The coating should withstand supercooled rain impacting, sand erosion and high humidity environments.

2.4.5 Combining Methods

Mechanical and chemical anti-icing / deicing methods are simple and low cost; however, they are limited in durability and environment concerns. Heating is an effective ice

prevention method, but it is expensive and high energy consumption. To suppress ice accretion and reduce accumulated ice adhesion on surfaces with a relative low cost, techniques combining mechanical, chemical and electrical methods have been extensively studied. Brammer designed a defroster for aircraft based on the heat exchanger with liquids [165]. This method combined both thermal and chemical method. Jones reported an inflating-heating system that provides electrical heating zones together with a configuration of surface deformation [166]. This system was designed for the purposes of breaking and removing formed ice and preventing ice formation under various icing conditions. Instead of electrical heating, Mueller et al. utilized a mixture of hot water and a thixotropic de-icing fluid to minimize ice formation [167]. Another smart idea was the use of piezoelectric materials [168]. After receiving a current with proper wavelength, amplitude, duration and shape, the piezoelectric material would move or deform to eliminate the formed thick ice. Similarly, a biodegradable, non-flammable, pseudo-plastic composition was developed for aircraft and other surfaces assisted with significant changes in wind shear [169]. Newman and Cunningham described a structural laminate resin including layers of structural fabric [170]. They employed at least one electrically conductive fabric layer, thus the structural composite could be heated by application of an electrical current. Combining mechanical and heating methods, a movable and conductive overlying sheet by means of electrical or hot air heating was reported [171]. The movable sheet could move back and forth to remove the ice. Recently, Wang et al. fabricated a perfluorododecylated graphene nanoribbon layer, which could be switched between the slippery mode and the superhydrophobic mode by the lubricant infusion. The perfluorinated carbons displayed low polarizability, and the graphene nanoribbons presented intrinsic conductive nature. Therefore, this superhydrophobic films exhibited a sheet resistance less than $8 \text{ k}\Omega \cdot \text{sq}^{-1}$ and could prevent ice formation by applying a voltage [172].

- Ice removal device
- Sodium compound
- 1890s
 - Mechanical device and pneumatic boots
 - Heating elements
 - Anti-freeze composite
 - Anodized metal surfaces combined with waxing
 - Solid or semi-solid compositions containing lubricating grease/oil
- 1930s
 - Flexible heating system
 - Heating system with compressed air
 - Low volatility deicing composite
 - Exhaust-gas-thermal
 - Polymeric silicone
 - Deicing wipers/blade
- 1950s
 - Thermal Liquid circulation system
 - Anti-icing additives to gasoline and fuels
 - An electromagnetic field pulses induced elastic deformation of thin sheets
 - Deicing agent
 - Foamable de-icing/defrosting composition monolayers
 - silicone-silicate polymers
- 1970s
 - Laser
 - Electric infrared lamps
 - Earth heat pipes/geothermal fluid
 - Anti-freeze protein from fish
 - Self-heating mixture
 - Introducing air bubbles
 - Organic-inorganic anti-icing composition
 - Microwave deicing method
- 1980s
 - Acrylic polymers with surfactants
 - Calcium/magnesium mixtures with surface modified sands
 - Electrically conductive structural composite
 - A flexible and porous membrane
 - Piezoelectric material
 - A thixotropic de-icing fluid
 - Solar heater
 - Conducting fibers
- 1990s
 - Shape memory alloys
 - Movable, conductive substrate for deicing
 - Starch-containing compositions
 - Associative polymer
 - Pseudo-plastic deicing composition
 - Plasma-based de-icing
 - Icephobic paint
- 2000s
 - Superhydrophobic coating
- 2010s
 - Slippery liquid infused porous surface (SLIPs)
 - Self-lubricating liquid water layer (SLWL)

Figure 2.7 The history diagram of the development of anti-icing coatings.

Figure 2.7 shows the history diagram of development of anti-icing coatings. Literature studied so far indicate that no solid surface can be truly ice inhibiting if placed under extremely adverse conditions. Many aspects of icing behavior remain poorly understood. Thermodynamically, ice formation is a multiphase complex process associated with different nucleation and growth mechanisms, and is highly sensitive to environmental conditions. Besides, the inherent limits on design of icephobic surface such as the surface energy, the intrinsic microstructure defects and inhomogeneities of coatings induce liquid droplet pinning and frost formation. It has posed great challenges to the development of anti-icing coating [173]. More fundamental investigations are needed to fabricate a low cost, high performance, large scale anti-icing surface.

2.5 Factors Affecting Anti-icing Performance

2.5.1 Effect of Non-environmental Factors

To minimize ice formation and accumulation on airplanes, wind turbines, solar cell, sports facilities, pavements, power lines, etc., great efforts have been dedicated in developing effective anti-icing coatings that enable easy ice removal and icing prevention. Identifying key factors that affect anti-icing performance has been an important interest in many studies. Early studies on the ice adhesion of rubber, silicone, stainless steel, polystyrene, and polymethylmethacrylate [139, 174, 175] have confirmed that the ice adhesion increased linearly with decreased temperature. Jellinek declared that the adhesive strength of ice / stainless steel was independent of the cross-sectional area of the specimens and the thickness of the ice [139]. The most common hypothesis is that a surface exhibits poor chemical affinity with water should also present weak bonding strength with ice based on the assumption that the surface free energy of ice and water are comparable. Saito et al. firstly reported a superhydrophobic anti-icing coating and revealed a linear relationship between surface free energy and ice adhesion [147]. Similarly, Petrenko and Peng investigated the ice adhesion of the monolayers coated metals with varying degrees of hydrophobicity / hydrophilicity, and found that the higher hydrophobicity, the lower ice adhesion [176]. These results are reasonable. Since the adhesion force of ice to solid

surfaces depends greatly on van-der-Waals forces and hydrogen bonding [177], thus lower surface energy or a non-polar surface can significantly prevent or delay ice formation on surfaces. Low surface energy is a key requirement in development of anti-icing coatings. Having noticed that the surface energy induced the change of water contact angle, Dotan et al. studied coatings with water contact angles ranging from 20 ° to 160 ° and found that the adhesion of ice decreased with increased contact angles [178]. Similar results were also observed by other researchers [47, 179, 180]. It remains controversial whether there exists a simple correlation between ice adhesion and water contact angle. Loughborough noted that a poor correlation existed between low ice adhesion and water repellency of deicer polymer surfaces [174, 175]. Laforte et al. found no relationship between ice adhesion and hydrophobicity, instead, ice adhesion increased with surface roughness [181]. Kulinich and Farzaneh measured ice adhesion of superhydrophobic surfaces with different roughness and found that ice adhesion presented no correlation between water contact angle but a linear relationship with water contact angle hysteresis (CAH) [52, 53]. Similar results were also obtained by Sarshar et al. [182] They found that delay in ice formation on superhydrophobic coatings exhibited a clear correlation between CAH and surface roughness of coatings: longer icing-delay time was found on coatings with a lower CAH with finer surface roughness. However, Meuler et al. pointed out that water receding angles displayed a stronger effect with the quantity $[1+\cos\theta_{rec}]$ on ice adhesion than CAH after investigating 22 surfaces from hydrophilic to hydrophobic [183].

Among studies on other key factors behind icephobicity, J. Smith et. al studied coatings on aluminum with linear aliphatic dimethylethoxysilanes terminated with methyl or hydroxyl groups, and found that hydroxyl-terminated materials exhibited a greater propensity for ice prevention due to chain mobility [184]. Considering the surface structure, Saito indicated that increasing surface roughness of hydrophilic coatings induced high ice adhesion, and increasing the surface roughness of water repellent coatings decreased the adhesion [147]. The difference was due to the ice anchoring effect on rough surfaces. Fu et al. also found a complicated effect of surface roughness on the ice adhesion [185]. Gohardani and Hammond introduced a non-dimensional parameter of ice-adhesion strength per unit surface roughness to describe the relationship between the surface roughness and the ice

adhesion [186]. Some researchers have investigated the reasons why superhydrophobic coatings did not always display low ice adhesion. Kulinich et al. studied the ice-adhesion strength of three types of superhydrophobic coatings, and confirmed that gradual damage of the surface microstructure and water on the rough structure could lead to greatly increased ice-adhesion strength [187]. Varanasi et al. conducted real-time frost formation on superhydrophobic coatings in an environmental scanning electron microscope (ESEM) and found that unavoidable frost formation increased wetting and increased ice adhesion [188]. They also analyzed the ice-adhesion strength of textured PDMS surfaces and proved that ice adhesion of superhydrophobic coatings was enhanced due to water condensation on their textured surfaces. However, superhydrophobic coatings that could withstand water condensation and frost formation were also reported. Yeong et. al investigated the ice-adhesion strength of hydrophobic and superhydrophobic coatings, and showed a strong relationship between the ice adhesion and the surface topology spatial parameter of autocorrelation length [189]. In summary, although considerable efforts have been made during the past decades, inconsistent findings remain because of the difficulty in controlling surface characteristics of various types of coatings.

Different from the well-studied ice adhesion of anti-icing coatings, ice nucleation on anti-icing coatings has been paid less attention. To date, most of the studies on ice nucleation process have been focused on the analysis of statistical results of occurring nucleation or icing events. As discussed in section 2.2, ice nucleation of water is determined by the free energy barrier. Increasing the free energy barrier of ice nucleation will reduce ice nucleation temperature or time. Besides, the preferred ice nucleation site is another key factor. When the presence of surface roughness at scales larger than that of the size of critical ice nuclei, the surface may be considered unfavorable for ice nucleation. Researchers studied ice-nucleation process of superhydrophobic coatings and SLIPS. They found that these coatings were promising in inhibiting ice nucleation. The low tendency of ice nucleation on superhydrophobic coatings was attributed to the trapped air pockets in the porous micro-nanostructures. The trapped air led to a high temperature gradient [190-192]. Since the trapped air will affect ice nucleation, efforts have been done to establish a relationship between surface contact fraction of a water droplet and ice-nucleation rate [193-

195]. It was found that, in the Cassie-Baxter mode, the ice nucleation rate increased with an increase in surface contact fraction, while in the Wenzel mode, ice-nucleation rate decreased with the reduction of surface contact fraction due to the increased possibility of homogeneous ice nucleation. Another interesting study was reported by Irajizad, *et al.* [196]. They fabricated a new magnetic slippery surface that presented reduced the ice-nucleation temperature, and 2-3 orders of magnitude longer icing-delay time than the reported superhydrophobic and SLIPS coatings. In addition, the ice-delay time for magnetic slippery surface was controllable by the intensity of imposed magnetic field.

In summary, ice nucleation on a non-ideal surface is a complex process, and can be affected by various factors. Therefore, more controlled experiments should be carried out to completely understand the ice nucleation on a coating surface under different conditions.

2.5.2 Environmental Conditions

2.5.2.1 Water Condensation

Condensation on solid surface is initiated by the temperature gradient between the solid surface and the bulk vapor, followed by the latent heat release from the interfacial region in the form of conduction or convection. Generally, condensation is associated with mass transfer due to the vapor molecular migrates from the interface of liquid-vapor. The driving force of molecular transport is pressure reduction at the vapor-liquid phase boundary. Heterogeneous condensation takes place when vapor condenses on a solid surface or spatially distributed nuclei. Homogeneous condensation takes place in the absence of foreign materials in free space. It stochastically occurs as a result of fluctuations of vapor molecules.

It can be clearly seen that condensation occurs when the vapor is cooled or compressed to the point higher than the triple point as shown in Fig. 2.8. After the water is condensed on the surface, ice will form when the surrounding temperature is low enough, combined with the conditions of high humidity and / or high pressure. Subsequently, the spontaneous

growth of formed ice will happen and the ice adhesion between the surface and the frozen condensed water inside the solid surface texture will increase. Therefore, understanding the water condensation process is a key to the design of anti-icing surfaces.

For a solid surface, the nature of condensation depends on the water-solid combination. If a surface is hydrophilic, condensation occurs in the form of continuous water films and spread across the surface. This type of condensation process is termed film condensation. The filmwise condensation can be removed from the solid surface by gravity, viscous forces and acceleration or other body forces in the film. The condensed film builds up a high thermal resistance to heat transfer, resulting in a relatively large temperature gradient.

Figure 2.8 Log-liner pressure-temperature phase diagram of water. The Roman numerals refer to some ice phases. From Ref.[19].

On a hydrophobic surface, condensation takes place in the form of discrete water droplets on the surface and this condensation is termed dropwise condensation. Dropwise

condensation is a heterogeneous and complex process. It involves interactions of several forces presented at the three-phase contact line from molecular level to the body forces of the liquid droplets [197]. It can be described as a quasi-cyclic process as shown in Fig. 2.9.

Figure 2.9 Cycle of dropwise condensation over a cold solid surface [198].

It begins with vapor condenses at preferred atomic-scale nucleation sites, and then the growth of droplets occurs under direct condensation. Beyond this point, coalescence subsequently occurs among neighboring droplets along the growth by combination of direct condensation and coalescence. When the size of condensed water droplet is comparable to the capillary length of water, the gravitational force can exceed the surface tension force and then the droplet departs and slides or rolls off the surface, permitting fresh nucleation to start again. Hence, the dropwise condensation takes place in a wide range of timescales and length scale and is dominated by four factors: (i) the thermophysical properties of water, (ii) microstructures, thermal and physicochemical properties of the solid substrate, (iii) the temperature gradient, and (iv) saturation conditions of vapor [199]. The measurement of heat transfer coefficient during dropwise condensation is challenging due to the small temperature gradient in the process. However, the heat transfer coefficient for drop-wise condensation is nearly an order larger than that

of film-wise condensation and mix mode condensation because of the efficient gravity-driven droplet removal mechanism [200], and thus would be preferred.

Recently, the dropwise condensation on superhydrophobic and SLIPS have gained much attention due to its potential applications in energy production, water collection, self-cleaning, anticorrosion and anti-icing [173, 201-203]. It was observed that water condensation on these surfaces showed enhanced removing mobility than original surfaces due to the reduced pinning force between condensed droplets and the SLIPS. In particular, the coalescence of droplets induces spontaneous motions either in jumping or sweeping at seemingly random directions on ultralow adhesion surface. Generally, it is believed that droplet jumping or sweeping is dominated by the conversion of excess surface energy into kinetic energy during the coalescence of two or more droplets. This process has been proved to follow a simple inertial-capillary scaling [204]. A recent research on superhydrophobic surface demonstrated experimentally and numerically that nearly half of the released surface energy during the jumping droplet coalescence would be converted to kinetic energy. Besides, it was reported that at the beginning, the kinetic energy increased significantly due to the high negative curvature of a liquid bridge [205]. A numerical simulation which replicated the experimental observations clarified the important role of internal fluid dynamics, and proved that the jumping speed depends on droplet size due to internal viscous dissipation [203]. Some subsequent studies tried to explain these results by the energy-balance from viscous dissipation, participating velocity components of jumping droplet and surface adhesion. However, limited success has been achieved. Despite the recent studies on the coalescence-induced jumping or sweeping, the detailed dynamics of the event associated with the energy conversion process have not been fully understood.

2.5.2.2 UV, Dirt and Erosion

UV is presented in sunlight with a wavelength from 10 nm to 400 nm. It can be divided into UVA (320 nm~400 nm), UVB (280 nm~320 nm) and UVC (280 nm~100 nm). All UVC and most of the UVB are absorbed by oxygen or blocked by atmosphere. The UV

radiation that reaches the surface of earth includes UVA and minor parts of UVB. However, it still causes degradation of polymer based anti-icing coatings, resulting in gloss-loss, chalking, cracking, embrittlement, crazing, oxidation or disintegration. Thus UV-stable coatings are preferred and international standards such as ASTM G154, ASTM G53-96 and ISO 11507 are used for UV-resistance assessment. According to the standard, to evaluate aging process of coating surfaces, outdoor weathering are simulated including UV radiations with greater intensity and controlled humidity.

Environmental dirt and dust including powders of organic or mineral matter, soil, bird debris and pollutions may be attached to the surface of anti-icing coatings and led to the malfunction of ice prevention or sometimes increased ice adhesion. These contaminants can also act as ice-nucleation sites and increase ice accumulation. Therefore, an anti-icing coating with self-cleaning properties will significantly improve the anti-icing efficiency.

Figure 2. 10 Erosive wear rate for ductile and brittle materials against the impact angle [206].

Erosion is a common natural phenomenon in earth, and the erosion on anti-icing coatings for outdoor structures is mainly caused by rain, hail, soil and sand. The erosion impact on the anti-icing coatings is affected by the size, shape and type of impingement (including impact angle, speed and frequency) as well as the exposure time. In particularly,

impingement assisted by wind will significantly aggravate the erosion speed of anti-icing coatings. Wind could carry large amounts of sand and water droplets and erode the surface of anti-icing coatings, leading to an increase in surface roughness and ice adhesion. A relationship between wear rate of ductile or brittle materials and impingement angles was depicted as shown in Fig. 2.10. Different materials can be chosen to fabricate low wear rate anti-icing coatings based on the environmental conditions. To date, the environmental erosion of airplanes and wind turbine has been well-documented [206, 207], however, limited studies have been done on outdoor structures and sports facilities.

2.6 Summary

Atmospheric icing on outdoor sports facilities attracted much attention due to the serious economic loss and labor burdens in cold regions. Although extensive studies have been carried out to approach ice free surfaces, there still exists large research gaps, being summarised herein, which need to be further studied.

The first concern is the ice crystal structure and formation conditions of atmospheric ice, since different ice crystals lead to distinct ice adhesion towards a surface. A successful anti-icing coating needs to consider the environmental conditions of proposed applications and the resulted potential structure of ice. Available reports showed that ice formed on sports facilities mainly due to snow, sleet, freezing rain or frost, leading to rime and even glazed ice. The related thermodynamic theory of ice nucleation and mechanism of ice adhesion on a surface also have been reviewed. Regarding the high adhesion and high density of glazed ice, surfaces enabling easy removal of formed ice are preferred, together with low ice nucleation and icing probability. Even though methods enabling low ice adhesion have been well studied, rare attention has been paid the ice nucleation and icing probability, thus further investigations are needed.

To date, active de-icing methods have been systematically studied, and can be categorized into four types: mechanical, heating, chemical and combine methods. Herein, the history of anti-icing techniques was summarized, and advantages / disadvantages of these methods

were discussed. Passive anti-icing coatings are more desirable due to their easy processing, cost efficiency and high performance. Among the studied coatings, superhydrophobic coatings, SLIPS and silicone based polymer coatings are three representative coatings. However, all these coatings are restrained from practical application because of the limitation in durability. Moreover, current studies paid less attention to the transparency of anti-icing coatings. The next step for anti-icing coating development will be focus on transparency and environmental durability.

To enhance environmental durability, factors affect the anti-icing performance should be considered. In this thesis, influence factors of anti-icing surfaces have been clarified and categorized into non-environmental and environmental aspects. Non-environmental factors can be designed and optimized according to the requirements. However, environmental factors such as UV, water condensation and erosion are uncontrollable and inevitable. Design of anti-icing coatings should take into account of these factors and carry out the corresponding simulated evaluations according to ISO or ASTM standards.

To sum up, this chapter summarized the origin of ice, the corresponding crystal structures as well as the thermodynamic theory behind. A history of anti-icing methods was systematically listed from 1800s to nowadays. Advantages and limitations of these methods have been discussed. Moreover, factors that affect anti-icing performance have also been discussed as guidelines for future development.

References

- [1]. C. Olien, M.N. Smith. *Plant Physiology*. **1977**, 60, 499-503.
- [2]. O. Parent, A. Ilinca. *Cold Regions Science and Technology*. **2011**, 65, 88-96.
- [3]. Z.A. Janjua, B. Turnbull, S. Hibberd and K. S. Choi. *Physics of Fluids*. **2018**, 30, 027101.
- [4]. P. Tran, M. Brahimi, I. Paraschivoiu, A. Pueyo and F. Tezok. *Journal of Aircraft*. **1995**, 32, 444-446.

- [5]. N. Bose. *Journal of wind engineering and industrial aerodynamics*. **1992**, 45, 75-85.
- [6]. M. Farzaneh, O. Melo. *Cold Regions Science and Technology*. **1990**, 19, 33-46.
- [7]. J.C. McConnel. *Nature*. **1889**, 39, 367.
- [8]. M. Blackman, N. Lisgarten. *Advances in Physics*. **1958**, 7, 189-198.
- [9]. T.L. Malkin, B.J. Murray, A.V. Brukhno, J. Anwar and C.G. Salzmman. *Proceedings of the National Academy of Sciences*. **2012**, 109, 1041-1045.
- [10]. P.H. Kaye, E. Hirst, R.S. Greenaway, Z. Ulanowski, E. Hesse, P.J. DeMott, C. Saunders and P. Connolly. *Optics Letters*. **2008**, 33, 1545-1547.
- [11]. S. Jackson, V. Nield, R. Whitworth, M. Oguro and C. Wilson. *The Journal of Physical Chemistry B*. **1997**, 101, 6142-6145.
- [12]. C.W. Vertucci. *Biophysical Journal*. **1990**, 58, 1463-1471.
- [13]. K. Kikuchi, T. Kameda, K. Higuchi and A. Yamashita. *Atmospheric Research*. **2013**, 132, 460-472.
- [14]. M. Bailey, J. Hallett. *Journal of the Atmospheric Sciences*. **2004**, 61, 514-544.
- [15]. M.P. Bailey, J. Hallett. *Journal of the Atmospheric Sciences*. **2009**, 66, 2888-2899.
- [16]. H.R. Pruppacher, J.D. Klett. Reprinted 1980. *Springer Science & Business Media*, 2012.
- [17]. C. Magono, W. Chung. *Journal of the Faculty of Science, Hokkaido University. Series 7, Geophysics*. **1966**, 2, 321-335.
- [18]. S.M. Fikke, G. Ronsten, A. Heimo, S. Kunz, M. Ostrozlik, P. Persson, J. Sabata, B. Wareing, B. Wichura and J. Chum, ed. 2006: *Meteo Schweiz*.
- [19]. J.W. Mullin, ed. 2001: *Elsevier*.
- [20]. G. Vali. *Journal of Recherches Atmospheriques*. **1985**, 19, 105-115.
- [21]. N. Miljkovic, R. Enright, Y. Nam, K. Lopez, N. Dou, J. Sack and E.N. Wang. *Nano Lett*. **2013**, 13, 179-187.
- [22]. B.K. Chakraverty, G.M. Pound. *Acta Metallurgica*. **1964**, 12, 851-860.
- [23]. C.A. Sholl, N.H. Fletcher. *Acta Metallurgica*. **1970**, 18, 1083-1086.
- [24]. S. Cooper, O. Cook and N. Loines, *Crystallization in Microemulsions: A Generic Route to Thermodynamic Control and the Estimation of Critical Nucleus Size*, in

- Crystallization - Science and Technology*, M.R.B. Andreeta, Editor. 2012, InTech. p. 121-148.
- [25]. T. Inada, T. Koyama, F. Goto and T. Seto. *Journal of Physical Chemistry B*. **2011**, 115, 7914-7922.
- [26]. C.A. Jeffery, P.H. Austin. *Journal of Geophysical Research-Atmospheres*. **1997**, 102, 25269-25279.
- [27]. A. Heneghan, A.D.J. Haymet, *Nucleation of pure and AgI seeded supercooled water using an automated lag time apparatus*, in *Nucleation and Atmospheric Aerosols 2000*, B.N. Hale and M. Kulmala, Editors. 2000. p. 439-442.
- [28]. A.F. Heneghan, A.D.J. Haymet. *Chemical Physics Letters*. **2003**, 368, 177-182.
- [29]. A.F. Heneghan, P.W. Wilson and A.D.J. Haymet. *Proceedings of the National Academy of Sciences of the United States of America*. **2002**, 99, 9631-9634.
- [30]. G. Mogilevsky, Q. Chen, A. Kleinhammes and Y. Wu. *Chemical Physics Letters*. **2008**, 460, 517-520.
- [31]. J.C. Moreno-Pirajan. *Thermodynamics Approach in the Adsorption of Heavy Metals, In Tech, Croatia, Europe*. **2011**.
- [32]. M.J. Jamieson, C.E. Nicholson and S.J. Cooper. *Crystal Growth & Design*. **2005**, 5, 451-459.
- [33]. D. Xu, W.L. Johnson. *Physical Review B*. **2005**, 72, 052101.
- [34]. S.J. Cooper, C.E. Nicholson and J. Liu. *Journal of Chemical Physics*. **2008**, 129, 124715.
- [35]. N.H. Fletcher. *Journal of Chemical Physics*. **1958**, 29, 572-576.
- [36]. N. Miljkovic, R. Enright, Y. Nam, K. Lopez, N. Dou, J. Sack and E.N. Wang. *Nano Letters*. **2012**, 13, 179-187.
- [37]. H.K. Christenson. *Crystengcomm*. **2013**, 15, 2030-2039.
- [38]. V. Bahadur, L. Mishchenko, B. Hatton, J.A. Taylor, J. Aizenberg and T. Krupenkin. *Langmuir*. **2011**, 27, 14143-14150.
- [39]. Y. Zhang, Z. Jiang, J. Huang, L.Y. Lim, W. Li, J. Deng, D. Gong, Y. Tang, Y. Lai and Z. Chen. *RSC Advances*. **2015**, 5, 79479-79510.
- [40]. W. Stöber, A. Fink and E. Bohn. *Journal of Colloid Interface Science*. **1968**, 26, 62-68.

- [41]. P.W. Wilson, W. Lu, H. Xu, P. Kim, M.J. Kreder, J. Alvarenga and J. Aizenberg. *Physical Chemistry Chemical Physics*. **2013**, 15, 581-585.
- [42]. R. Menini, M. Farzaneh. *Journal of Adhesion Science and Technology*. **2011**, 25, 971-992.
- [43]. Y. Tang, Y. Zhang, J. Deng, J. Wei, H.L. Tam, B.K. Chandran, Z. Dong, Z. Chen and X. Chen. *Advanced Materials*. **2014**, 26, 6111-6118.
- [44]. V.F. Petrenko, I.A. Ryzhkin. *The Journal of Physical Chemistry B*. **1997**, 101, 6285-6289.
- [45]. L.A. Wilen, J.S. Wettlaufer, M. Elbaum and M. Schick. *Physical Review B*. **1995**, 52, 12426-12433.
- [46]. J.A. Zak, ed. 1994: National Aeronautics and Space Administration, Langley Research Center.
- [47]. L. Makkonen. *Journal of Adhesion Science and Technology*. **2012**, 26, 413-445.
- [48]. L. Gao, T.J. McCarthy. *Langmuir*. **2008**, 24, 9183-9188.
- [49]. L. Gao, T.J. McCarthy. *Langmuir*. **2009**, 25, 14105-14115.
- [50]. H. Eral, J. Oh. *Colloid and Polymer Science*. **2013**, 291, 247-260.
- [51]. L. Makkonen. 2015, IWAIS.
- [52]. S. Kulinich, M. Farzaneh. *Applied Surface Science*. **2009**, 255, 8153-8157.
- [53]. S. Kulinich, M. Farzaneh. *Langmuir*. **2009**, 25, 8854-8856.
- [54]. B. H. Goodsell, C. Adamson, and C. O. Hering, U.S. Patent No. 281224A, **1883**
- [55]. J. Knapton, J. Emery, ed. 1898: National Concrete Masonry Association.
- [56]. A. Tabrizi, E. Keshock. *Journal of Aircraft*. **1988**, 25, 343-348.
- [57]. J. Stallabrass, R. Price. 1962, National Research Council Canada.
- [58]. C. L. Riker, inventor; Michael Ebert, assignee. **1976**, U.S. Patent No. 191256A.
- [59]. H.F. Smith, inventor; Motors Liquidation Co, assignee. **1939**, U.S. Patent No. 2,161,321.
- [60]. L.L. Mallard. **1944**, U.S. Patent No. 2,348,014.
- [61]. C.J. Rolle, W.D. Barnes. *Industrial & Engineering Chemistry*. **1956**, 48, 1326-1327.
- [62]. G. Fletcher, D. Slaughter and C. Hew. *Canadian Journal of Zoology*. **1982**, 60, 1851-1854.

- [63]. A.S. Gonzales, inventor; Bozal Gonzalez Jose L, assignee. **1980**, U.S. Patent No. 4,201,219.
- [64]. S. Laplante. **1991**, U.S. Patent No. 5,065,471.
- [65]. L. Sohlze, **1884**, U.S. Patent No. 294084A.
- [66]. F.R. John, inventor, Avery Equipment Ltd., assignee. **1941**, U.S. Patent No. 2,254,997.
- [67]. C.V. Davis. **1927**, U.S. Patent No. 1,640,887.
- [68]. J.R. Oishei, inventor; Trico Products Corp, assignee. **1931**, U.S. Patent No. 1,828,715.
- [69]. W.C. Geer, M. Scott. National Advisory Committee for Aeronautics; Washington, DC, United States, **1930**, NACA-TN-345.
- [70]. T.C. Harper, inventor; Goodrich Corp, assignee. **1947**, U.S. Patent No. 2,653,885.
- [71]. I.A. Levin, A.Y. Levin, N.E. Fedorov, I.A. Rogov and E.E. Afanasov, inventors; Levin Igor A, assignee. **1970**, U.S. Patent No. 3,549,964.
- [72]. C.J. Cattaneo, P.R. Derouet and M.C. Laroche. **1985**, U.S. Patent No. 4,508,295.
- [73]. M.B. Achberger, inventor, Goodrich Corp, assignee. **1971**, U.S. Patent No. 3,604,666.
- [74]. A. Branch, H. Kaatz and C. Small, inventors; Airborne Manufacturing, assignee. **1973**, U. S. Patent No. 3,720,388.
- [75]. S.K. Thomas, R.P. Cassoni and C.D. MacArthur. *Journal of Aircraft*. **1996**, 33, 841-854.
- [76]. R.B. Ingram, J.J. Gerardi, inventors; Innovative Dynamics Inc, assignee. **1997**, U. S. Patent No. 5,686,003.
- [77]. B. Dixon, A. Walsh, B. Gall and M. Goodwin. *Proceedings of the 12th General Assembly of IAMU, Gdynia, Poland*. **2011**.
- [78]. W.C. Geer. **1943**, U.S. Patent No. 2,327,034.
- [79]. A.F. Thompson, inventor; Iceless Air Wing Corp, assignee. **1932**, U.S. Patent No. 1,868,468.
- [80]. L.G. Franzen. **1932**, U.S. Patent No. 1,848,337.
- [81]. R. Zelig. **1939**, U.S. Patent No. 2,142,699.
- [82]. K. Charles. **1929**, U.S. Patent No. 3,178,784.

- [83]. T. Theodorsen, W.C. Clay. National Advisory Committee for Aeronautics. Langley Aeronautical Lab.; Langley Field, VA, United States. **1933**, NACA-TR-403.
- [84]. B.C. Look. National Advisory Committee for Aeronautics. Langley Aeronautical Lab.; Langley Field, VA, United States. **1944**, ARR No. 4B02
- [85]. H.F. Schmidt, inventor; Consolidated Vultee Aircraft Corp, assignee. **1948**, U.S. Patent No. 2,447,095.
- [86]. R.E. Weiler, inventor; Westinghouse Electric Corp, assignee. **1948**, U.S. Patent No. 2,435,990.
- [87]. R.S. Ely, I.M. Ketcham, inventors; Safeway Heat Elements Inc, assignee. **1950**, U.S. Patent No. 2,496,279.
- [88]. S. Lazarus, inventor; Aeroseal Corp, assignee. **1973**, U.S. Patent No. 3,776,775.
- [89]. A.D. Shah, inventor; Boeing Co, assignee. **1976**, U.S. Patent No. 3,981,466.
- [90]. A. Judson, ed. Vol. 187. 1971: Rocky Mountain Forest and Range Experiment Station, Forest Service, US Dept. of Agriculture.
- [91]. J.W. Lane, S.J. Marshall. 1976, Cold Regions Research and Engineering Lab Hanover NH, No. CRREL-76-10.
- [92]. W. Bienert, M. Pravda, H. Suelau and D. Wolf. *NASA STI/Recon Technical Report N*. **1974**, 75.
- [93]. J.W. Lund. *Q. Bull., Geo-Heat Util. Cent.:(United States)*. **1976**, 1.
- [94]. N. Seki, M. Sugawara and S. Fukusako. *Journal of Heat Transfer*. **1979**, 101, 90-95.
- [95]. L. Howe, S.G. Koutavas, inventors; Future Tech Inc, assignee. **1984**, U.S. Patent No. 4,432,341.
- [96]. P. Barbier, A. Cohendy and R. Reynet, inventors, Airbus Group SAS, assignee. **1988**, U.S. Patent No. 4,737,618.
- [97]. V.F. Petrenko, inventor, Dartmouth College, assignee. **2006**, U.S. Patent No. 7,087,876.
- [98]. B. Magenheimer, F. Hains. **1977**, Mechanics Research Inc. Mclean Va Electronics Systems Div.
- [99]. R.J. Hansman Jr, inventor; Hansman Jr Robert J, assignee. **1982**, U.S. Patent No. 4,365,131.

- [100]. M.M. López, J.J.E. Peralta, inventors; Fico Transpar SA, assignee. **2003**, U.S. Patent No. 6,538,235.
- [101]. S. Ince, *A guide to the design of air bubblers for melting ice*, in *Coastal Engineering 1964*. 1965. p. 600-610.
- [102]. G.E. Gross, inventor; Perma Pier Inc, assignee. **1963**, U.S. Patent No. 3,108,146.
- [103]. L.A. Hibburd, inventor; Pneumatic Breakwaters Ltd, **1964**, U.S. Patent No. 3,148,509.
- [104]. W.M. Hoddinott, D.C. Hoddinott. **1967**, U.S. Patent No. 3,318,098.
- [105]. Z. Courville, V. Petrenko. *MRS Online Proceedings Library Archive*. **1999**, 604.
- [106]. D.M. Ramakrishna, T. Viraraghavan. *Water, Air, and Soil Pollution*. **2005**, 166, 49-63.
- [107]. S. Löfgren. *Water, Air, and Soil Pollution*. **2001**, 130, 863-868.
- [108]. S. Phillip. **1922**, U.S. Patent No. 1,410,839.
- [109]. M. Knight, W.C. Clay. National Advisory Committee for Aeronautics. Langley Aeronautical Lab.; Langley Field, VA, United States. **1930**, NACA-TN-339.
- [110]. J.G. Collins, inventor; Perfect Antifreeze Company, assignee. **1930**, U.S. Patent No. 1,776,181.
- [111]. G.D. Graves, inventor; EI du Pont de Nemours and Co, assignee. **1933**, U.S. Patent No. 1,900,014.
- [112]. J.C. Zimmer, A.J. Morway, inventors; Standard Oil Development Co, assignee. **1937**, U.S. Patent No. 2,071,488.
- [113]. F.A. Kormann. **1937**, U.S. Patent No. 2,101,472.
- [114]. D. Sydney, H.C. King, inventors; Shell Oil Co, assignee. **1967**, U.S. Patent No. 3,350,314.
- [115]. R.D. Jenkins, D.R. Bassett, R.H. Lightfoot and M.Y. Boluk, inventors; Union Carbide Chemicals, Plastics Technology LLC, assignee. **1997**, U.S. Patent No. 5,681,882.
- [116]. R. Salvador, J. Kapfinger and E. Leidl, inventors; Hoechst AG, assignee. **1988**, U.S. Patent No. 4,744,913.
- [117]. J. Gambino, M. Janssen and H. J. Pierkes, inventors; Rheox Inc, assignee. **1998**, U.S. Patent No. 5,849,356.

- [118]. W.H. Simendinger III, S.D. Miller, inventors; Microphase Coatings Inc, assignee. **2004**, U.S.Patent No. 6,702,953.
- [119]. J. Ayres, W. Simendinger and C. Balik. *Journal of Coatings Technology and Research*. **2007**, 4, 473-481.
- [120]. W.E. Mackenzie. **1960**, U.S.Patent No. 2,948,625.
- [121]. D.B. Boies, S. Bortz. *NCHRP Report*. **1965**.
- [122]. W. Bascom, R. Cottington and C. Singleterry. **1966**, Naval Research Lab Washington DC.
- [123]. A.L. DeVries, D.E. Wohlschlag. *Science*. **1969**, 163, 1073-1075.
- [124]. A.L. Devries. *Science*. **1971**, 172, 1152-1155.
- [125]. R. Sapienza, inventor; Sapienza, Richard, assignee. **1999**, U.S. Patent No. 5,980,774.
- [126]. J.M. Fain, N.L. Hewitt. **1955**, U.S. Patent No. 2,716,068.
- [127]. J.C. Little, J.P. West, inventors; Dow Chemical Co, assignee. **1969**, U.S. Patent No. 3,440,029.
- [128]. J.A. Shotton, inventor; ConocoPhillips Co, assignee. **1962**, U.S. Patent No. 3,032,971.
- [129]. D. Ayres, D. Greenwood. **1973**, U.S. Patent No. 3,711,409.
- [130]. A.J. Bonnanzio. **1975**, U.S. Patent No. 3,928,654.
- [131]. L.B. Kimball, inventor; Fuel Dev. Corp. assignee. **1937**, U.S. Patent No. 2,097,926.
- [126]. Motors Liquidation Co., **1938**, G.B.130438A.
- [132]. S.R. Prance, H.J. Reindl. 1954, Google Patents.
- [133]. G.L. Nichols, inventor; Ace Filtercraft Inc., assignee. **1971**, U.S. Patent No. 3,614,038.
- [134]. E.A. Driscoll. **1938**, U.S. Patent No. 2,137,394.
- [135]. D. Holley, J. Nika, inventors; Danforth Holley, assignee. **1973**, U.S. Patent No. 3,770,633.
- [136]. X. Jiang, D. Zou, X.Z. Kong, X. Zhu and Z. Zhang. *Journal of Polymer Research*. **2014**, 21, 473.
- [137]. G.T. Raymond, O.J. Lewis, inventors; Honorary Advisory Council Sci., assignee. **1946**, U.S. Patent No. 2,406,367.
- [138]. U. Nakaya, A. Matsumoto. *Journal of colloid science*. **1954**, 9, 41-49.

- [139]. H. Jellinek. **1960**, Snow Ice and Permafrost Research Establishment Wilmette IL.
- [140]. C.H. Graham, inventor; Gra. Tec. Inc., assignee. **1984**, U.S. Patent No. 3,538,940.
- [141]. X. Jiang, S. Fan, J. Hu, Z. Zhang and C. SUN. *Proceedings of the CSEE*. **2010**, 30, 111-116.
- [142]. Z. Wang. *Energy and Buildings*. **2017**, 140, 42-49.
- [143]. W.H. Longhurst, O.A. Robert, inventors; Intava Ltd, assignee. **1945**, U.S. Patent No. 2,373,727.
- [144]. E.G. Haas, inventor; Goodrich Corp, assignee. **1949**, U.S. Patent No. 2,470,772.
- [145]. H.G. Ohlhausen. **1971**, U.S. Patent No. 3,579,540.
- [146]. J.S. Tulloch, R.B. Smith, F.S. Doten and J.A. Bishop. **1978**, Army Aviation Engineering Flight Activity Edwards AFB CA..
- [147]. H. Saito, K. Takai and G. Yamauchi. *Surface Coatings International Part B: Coatings Transactions*. **1997**, 80, 168-171.
- [148]. G. Maier. *Progress in Polymer Science*. **2001**, 26, 3-65.
- [149]. F.G. Reick, inventor; Michael Ebert, assignee. **1980**, U.S. Patent No. 4,224,173.
- [150]. F.G. Reick, inventor; Michael Ebert, assignee. **1976**, U.S. Patent No. 3,931,428.
- [151]. S. Kimura, Y. Yamagishi, A. Sakabe, T. Adachi and M. Shimanuki. 2007, SAE Technical Paper.
- [152]. Z. Liu, Y. Gou, J. Wang and S. Cheng. *International Journal of Heat and Mass Transfer*. **2008**, 51, 5975-5982.
- [153]. L. Cao, A.K. Jones, V.K. Sikka, J. Wu and D. Gao. *Langmuir*. **2009**, 25, 12444-12448.
- [154]. C. Antonini, M. Innocenti, T. Horn, M. Marengo and A. Amirfazli. *Cold Regions Science and Technology*. **2011**, 67, 58-67.
- [155]. A.M. Emelyanenko, L.B. Boinovich, A.A. Bezdomnikov, E.V. Chulkova and K.A. Emelyanenko. *ACS Applied Materials & Interfaces*. **2017**, 9, 24210-24219.
- [156]. T. Furuta, M. Sakai, T. Isobe and A. Nakajima. *Langmuir*. **2010**, 26, 13305-13309.
- [157]. T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala and R.H. Ras. *Advanced Materials*. **2011**, 23, 673-678.
- [158]. R. Karmouch, G.G. Ross. *The Journal of Physical Chemistry C*. **2010**, 114, 4063-4066.

- [159]. L. Yin, Q. Xia, J. Xue, S. Yang, Q. Wang and Q. Chen. *Applied Surface Science*. **2010**, 256, 6764-6769.
- [160]. T.S. Wong, S.H. Kang, S.K. Tang, E.J. Smythe, B.D. Hatton, A. Grinthal and J. Aizenberg. *Nature*. **2011**, 477, 443-447.
- [161]. J. Zhang, C. Gu and J. Tu. *ACS Applied Materials & Interfaces*. **2017**, 9, 11247-11257.
- [162]. M.J. Kreder, J. Alvarenga, P. Kim and J. Aizenberg. *Nature Reviews Materials*. **2016**, 1, 15003.
- [163]. R. Xiao, N. Miljkovic, R. Enright and E.N. Wang. *Scientific Reports*. **2013**, 3.
- [164]. J.D. Smith, R. Dhiman, S. Anand, E. Reza-Garduno, R.E. Cohen, G.H. McKinley and K.K. Varanasi. *Soft Matter*. **2013**, 9, 1772-1780.
- [165]. F.G. Brammer. **1939**, U.S. Patent No. 2,160,397.
- [166]. B.F. Jones, inventor; Goodrich Corp, assignee. **1952**, U.S. Patent No. 2,599,059.
- [167]. W. Mueller, D.M. Inghram and W.B. Walker, inventors, FMC Corp, assignee. **1982**, U.S. Patent No. 4,333,607.
- [168]. L. Bird. **1988**, U.S. Patent No. 4,732,351.
- [169]. F. Fusiak, K. H. Chung and T.C. Bohrer, inventors, ISP Investments LLC, assignee. **1993**, U.S. Patent No. 5,268,116.
- [170]. P.R. Newman, P.H. Cunningham, inventors, Boeing North American Inc, assignee. **1990**, U.S. Patent No. 4,942,078.
- [171]. S. Shatz, inventor; Shatz, Solomon, assignee. **1997**, U.S. Patent No. 5,590,854.
- [172]. T. Wang, Y. Zheng, A. R.O. Raji, Y. Li, W.K. Sikkema and J.M. Tour. *ACS Applied Materials & Interfaces*. **2016**, 8, 14169-14173.
- [173]. P. Kim, T.S. Wong, J. Alvarenga, M.J. Kreder, W.E. Adorno-Martinez and J. Aizenberg. *ACS Nano*. **2012**, 6, 6569-6577.
- [174]. D. Loughborough. *Journal of the Aeronautical Sciences*. **1946**, 13, 126-134.
- [175]. D. Loughborough. *Aeronautical Engineering Review*. **1952**, 11, 29-34.
- [176]. V. Petrenko, S. Peng. *Canadian Journal of Physics*. **2003**, 81, 387-393.
- [177]. J.M. Sayward. 1979, DTIC Document.
- [178]. A. Dotan, H. Dodiuk, C. Laforte and S. Kenig. *Journal of Adhesion Science and Technology*. **2009**, 23, 1907-1915.

- [179]. H. Murase, K. Nanishi, H. Kogure, T. Fujibayashi, K. Tamura and N. Haruta. *Journal of Applied Polymer Science*. **1994**, 54, 2051-2062.
- [180]. V. Croutch, R. Hartley. *JCT, Journal of coatings technology*. **1992**, 64, 41-53.
- [181]. C. Laforte, J. Laforte and J. Carriere. *How a solid coating can reduce the adhesion of ice on a structure*. in *Proceedings of the International Workshop on Atmospheric Icing of Structures (IWAIS)*. 2002.
- [182]. M.A. Sarshar, C. Swartz, S. Hunter, J. Simpson and C.-H. Choi. *Colloid and Polymer Science*. **2013**, 291, 427-435.
- [183]. A.J. Meuler, J.D. Smith, K.K. Varanasi, J.M. Mabry, G.H. McKinley and R.E. Cohen. *ACS Applied Materials & Interfaces*. **2010**, 2, 3100-3110.
- [184]. J.G. Smith, C.J. Wohl, R.E. Kreeger, J. Palacios, T. Knuth and K. Hadley. NASA Langley Research Center; Hampton, VA, United States, **2016**, NF1676L-22412.
- [185]. Q. Fu, X. Wu, D. Kumar, J.W. Ho, P.D. Kanhere, N. Srikanth, E. Liu, P. Wilson and Z. Chen. *ACS Applied Materials & Interfaces*. **2014**, 6, 20685-20692.
- [186]. O. Gohardani, D.W. Hammond. *Cold Regions Science and Technology*. **2013**, 96, 8-16.
- [187]. S. Kulinich, S. Farhadi, K. Nose and X. Du. *Langmuir*. **2010**, 27, 25-29.
- [188]. K.K. Varanasi, T. Deng, J.D. Smith, M. Hsu and N. Bhate. *Applied Physics Letters*. **2010**, 97, 234102.
- [189]. Y.H. Yeong, A. Milionis, E. Loth, J. Sokhey and A. Lambourne. *Langmuir*. **2015**, 31, 13107-13116.
- [190]. A. Michaelides, K. Morgenstern. *Nature Materials*. **2007**, 6, 597.
- [191]. K.A. Koehler, P.J. DeMott, S.M. Kreidenweis, O.B. Popovicheva, M.D. Petters, C.M. Carrico, E.D. Kireeva, T.D. Khokhlova and N.K. Shonija. *Physical Chemistry Chemical Physics*. **2009**, 11, 7906-7920.
- [192]. M. Ghosh. *RSC Advances*. **2014**, 4, 45275-45285.
- [193]. Y. Shen, J. Tao, H. Tao, S. Chen, L. Pan and T. Wang. *Langmuir*. **2015**, 31, 10799-10806.
- [194]. A.K. Metya, J.K. Singh and F. Müller-Plathe. *Physical Chemistry Chemical Physics*. **2016**, 18, 26796-26806.

- [195]. L. Lupi, A. Hudait and V. Molinero. *Journal of the American Chemical Society*. **2014**, 136, 3156-3164.
- [196]. P. Irajizad, M. Hasnain, N. Farokhnia, S.M. Sajadi and H. Ghasemi. *Nature communications*. **2016**, 7, 13395.
- [197]. W. Barthlott, C. Neinhuis. *Planta*. **1997**, 202, 1-8.
- [198]. K. Koch, A. Dommisse and W. Barthlott. *Crystal Growth & Design*. **2006**, 6, 2571-2578.
- [199]. K. Rykaczewski, J.H.J. Scott. *ACS Nano*. **2011**, 5, 5962-5968.
- [200]. C. Lv, P. Hao, Z. Yao and F. Niu. *Langmuir*. **2015**, 31, 2414-2420.
- [201]. S.C. Thickett, C. Neto and A.T. Harris. *Advanced Materials*. **2011**, 23, 3718-3722.
- [202]. W. Zhao, X. Zhang, C.L. Tian and Z. Gao. *Science and Technology of Nuclear Installations*. **2015**.
- [203]. R. Enright, N. Miljkovic, J. Sprittles, K. Nolan, R. Mitchell and E.N. Wang. *ACS Nano*. **2014**, 8, 10352-62.
- [204]. J.B. Boreyko, C. H. Chen. *Physical Review Letters*. **2009**, 103, 184501.
- [205]. Y. Nam, H. Kim and S. Shin. *Applied Physics Letters*. **2013**, 103, 161601.
- [206]. O. Gohardani. *Progress in Aerospace Sciences*. **2011**, 47, 280-303.
- [207]. N. Dalili, A. Edrisy and R. Carriveau. *Renewable and Sustainable Energy Reviews*. **2009**, 13, 428-438.

Chapter 3*

When Superhydrophobic Coatings are Icephobic: Role of Surface Topology

This chapter studied the relationships of water repellency and icephobicity. The superhydrophobic coatings were fabricated with tuning the weight ratio of surface modified to non-modified nanoparticles. Icing behaviour like ice adhesion and ice nucleation of superhydrophobic coatings has been studied. The reasons why superhydrophobic coatings are not always icephobic have been defined. Specially, water condensation which hinders the practical application of superhydrophobic coatings has been investigated. Ice adhesion and ice nucleation of these coatings have been discussed in correlation with the surface energy and surface topology.

*This section published substantially as X. Wu, V. V. Silberschmidt, Z.-T. Hu, Z. Chen, *Surface Coatings and Technology*, 2019, Vol. 358, pp. 207-214.

3.1 Introduction

Ice accretion in cold environment is natural and inevitable. Various studies were carried out focused on delaying ice formation and easy removal of formed ice. Over the past decades, superhydrophobic coatings have shown good promise to repel and shed water [1-3]. Researchers working in various fields mimicked natural superhydrophobic surfaces (plants, insects, bacteria, skin of aquatic animals etc.) and designed numerous synthetic superhydrophobic surfaces. Metals [4-6], copolymers [7, 8], nanoparticles [9, 10], nanotubes [11, 12], nanorods [13] and nanofibers [14, 15] were employed to create air-trapping micro- and nanostructures. The involved methods include atom-transfer radical polymerization, electrodeposition, sol-gel, etching, lithography etc. The first study on anti-icing performance of superhydrophobic coatings was reported by Saito et al. in 1997 [16]. Later, various aspects of anti-icing behavior of superhydrophobic coatings was investigated, including ice inhibition, ice adhesion, ice accumulation and frost formation. Cao et al. [17] observed inhibition of ice formation on superhydrophobic coatings when supercooled water was poured onto a tilted surfaces. Momen et al. [18] found that superhydrophobic coatings greatly retarded water freezing. Jafari [19] and his co-workers showed that the superhydrophobic coating surface presented 3.5 times lower ice-adhesion strength than that of an uncoated surface. Zhao et al. [20] proved that superhydrophobic coatings could significantly restrain ice accumulation on insulator strings. He et al. [21] reported the retardation of frost formation on the superhydrophobic isotactic polypropylene film. Mishchenko et al. [22] designed a highly ordered superhydrophobic coating which can maintain ice-free down to *ca.* -25 to -30°C . Unfortunately, high water mobility and its low adhesion may not always be maintained because of its water condensation in texture [23-25] or drop impact beyond a texture-specific velocity [26]. Boinovich et al. [6] pointed out that the phase transition from supercooled water to ice induced a growth of a frost halo and a metastable iced meniscus near a three-phase contact line, which was responsible for the increased adhesive contact area between the droplet and the substrate.

Because of the outstanding water repellency and reduced heat transfer due to air trapping, robust anti-icing coatings maintaining superhydrophobicity when the temperature

approached the dew-point [27, 28] or below zero degree [29, 30], still attract the interest of many researchers. With fine control of surface microstructures, favorable anti-icing performance can be achieved. For example, Fu et al. [31] designed a robust icephobic coating based on superhydrophobicity via optimizing the coating's surface structure with the help of nanoparticles. Similarly, colloidal surfaces with different content of fluorine polymers were also developed [32]. The optimum coating demonstrated superhydrophobicity under freeze temperatures. Wang et al. [33] reported a flexible superhydrophobic coating which could repel water and ice even at -20°C with a relative humidity (RH) of 90% for more than three months. Shen et al. [34] studied anti-icing properties of single nanostructured and micro-nanostructured superhydrophobic surfaces. They found that the single nanostructure surface demonstrated a reduced icing area and an icing mass than those of the micro-nanostructured surfaces. Emelyanenko et al. [35] verified a durable superhydrophobic coating with snow and ice accumulation in severe outdoor experiments for several months.

Among all the studies, free energy and roughness of surfaces were found to be the main factors for anti-icing coatings. Extensive experiments were conducted to investigate the influence of these two factors on anti-icing performance. It is clear that lower surface energy of a surface results in lower ice adhesion [36-39] and lower icing probability [40, 41]. However, roughness as a key characteristic of a surface could not reflect all the surface properties, especially for rough porous surfaces. Even a relatively small difference on a surface would result in a distinct ice-nucleation process. Therefore, attention is needed to study the effect of surface topology / geometry on anti-icing performance of superhydrophobic coatings.

In this study, five superhydrophobic coatings were created by tuning a weight ratio of surface modified and unmodified SiO_2 nanoparticles in a sol-gel system. By adjusting the surface structure of the coatings, lower ice adhesion and suppressed ice nucleation can be achieved. The series of experiments have allowed identification the key factors behind various indicators of icephobic performance.

3.2 Experimental

3.2.1 Materials

TEOS, GLYMO, 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (PFOTES), SiO₂ nanoparticles with particle size around 10-20 nm, and itaconic acid were obtained from Sigma-Aldrich. Methanol (99%) was obtained from Fisher Scientific. Glycerol and formamide used for surface energy test were obtained from Sigma-Aldrich. Microscope glass slides (25.4 mm × 76.2 mm) and cover glass (diameter: 22 mm and thickness 0.13~0.16 mm), used for ice-nucleation temperature tests, were obtained from Sailboat Lab Co. Ltd. and Marienfeld, respectively.

3.2.2 Preparation Method

3.2.2.1 PFOTES-SiO₂ nanoparticles Preparation

The hydrolysis of PFOTES was implemented by mixing PFOTES, methanol and deionized (DI) water with a volume ratio of 1:96:3 for 24 h. To prepare PFOTES-modified SiO₂ nanoparticles, 0.25 g SiO₂ nanoparticles, 8 ml methanol and 4 ml hydrolyzed PFOTES were mixed at room temperature. Then the mixture was first placed in an ultrasonic bath for 30 min, and then magnetically stirred for 24 h. After stirring, the mixture was centrifuged at 2000 rpm for 5 min (the obtained hydrophobic silica is subsequently denoted as PFOTES-SiO₂). In this step, a total amount of 4.25 g SiO₂ nanoparticles were modified to obtain PFOTES-SiO₂ nanoparticles, which were used as fillers with low surface energy. The as-received SiO₂ nanoparticles obtained from Sigma-Aldrich were used as fillers with high surface energy.

3.2.2.2 Sol-gel preparation

TEOS-GLYMO sol was prepared by mixing 20 ml methanol with 5 ml 1 hydrolyzed PFOTES solution, 0.004 mol TEOS, 0.02 mol GLYMO, 0.076 mol DI water and 0.5 g

itaconic acid for 4 hours under magnetic stirring. Itaconic acid was used to acidify the sol to pH 3~4. The PFOTES-SiO₂ nanoparticles prepared in the first step were added to the TEOS-GLYMO sol. Then, SiO₂ nanoparticles with high surface energy were added to keep the weight of total SiO₂ nanoparticles at 1.5 g for each sample. The detailed weight of SiO₂ nanoparticles with high and low surface energy in each sample is shown in Table 1. After that, the prepared sols were ultrasonically treated for 15 min, and then stirred magnetically for 24 h before they were spray-coated onto the glass slides with an airbrush kit (AS06KB) with a 1.5 mm diameter nozzle using compressed air (pressure at 345 kPa). A distance between the airbrush and the substrate was kept at 10 cm. The coating thickness was fixed at 30 μm (+/-10%). Finally, the prepared samples were cured in an oven at 110°C for 1.5 h and labelled as TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 corresponding to the weight ratio of PFOTES modified and unmodified SiO₂ nanoparticles

Table 3.1 Detailed formulation of sol-gel coatings.

		TGS 1:5	TGS 2:4	TGS 3:3	TGS 5:1	TGS 6:0
Preparation of sol-gel coatings	PFOTES modified SiO ₂ nanoparticles (g)	0.25	0.5	0.75	1.25	1.5
	SiO ₂ nanoparticles (g)	1.25	1	0.75	0.25	0
	TEOS-GLYMO sol	20 ml methanol, 5 ml hydrolyzed PFOTES solution, 0.004 mol TEOS, 0.02 mol GLYMO, 0.076 mol DI water and 0.5 g itaconic acid				

3.2.3 Characterization

The surface morphology of coatings was scanned using a FESEM (JSM-6360, Japan). The water wettability, CAH and receding angles of coatings were measured with a contact angle system (OCA 20, Dataphysics Co., Germany). The measurement results were the average of five measurements obtained at different locations of the coatings. The surface energy was calculated based on the contact angle of glycerol, formamide and water based on the OWRK method [42-44]. Surface roughness was measured with an atomic force microscope

(AFM) with a scanning area of $10\ \mu\text{m} \times 10\ \mu\text{m}$. The roughness value was an average of at least three measurements obtained at different locations of the coatings.

For an ice adhesion test, a PTFE tube (inner diameter: 18 mm) was filled with DI water, and then covered with the sample on the top. The whole set was flipped upside down and placed inside a climate chamber (Cincinnati Sub-Zero environmental chambers, USA) for 24 h at $-15\ ^\circ\text{C}$ and $-20\ ^\circ\text{C}$, respectively. The weight of infilled water is 1.5 g. Measurements of the ice-adhesion strength followed previous reports [31, 39]. The reported ice-adhesion strength is an average value of at least six measurements on the same position of more than three samples. To evaluate the effect of water condensation on the ice-adhesion strength, the coatings were kept in the climate chamber at $-20\ ^\circ\text{C}$ with RH of 80% for 24 h before they were taken out to perform the ice-adhesion test following the procedure described above. The obtained results revealed the resistance of the coatings to water condensation.

The ice-nucleation temperature of coatings was studied following our group's previously report [45]. A $10\ \mu\text{l}$ droplet of DI water was placed on the center of the coating on a thin cover-glass slide. The test chamber was cooled from $\sim 22\ ^\circ\text{C}$ to freezing temperature (target temperature set at $-30\ ^\circ\text{C}$). The ramp rate from room temperature to $0\ ^\circ\text{C}$ was set at $40\ ^\circ\text{C}/\text{min}$, followed by $5\ ^\circ\text{C}/\text{min}$ from $0\ ^\circ\text{C}$ to the set $-30\ ^\circ\text{C}$ to minimize a heat reflux effect. The icing temperature of the coatings was defined as the temperature, at which a detected intensity of a reflected laser beam increased dramatically due to the ice formation. 500 icing-melting cycles were carried out for each water droplet. The results were recorded and statistically analyzed. To make sure that the iced droplet was heated up to ambient temperature and in an equilibrium state, the sample was held for 2 min after it has reached $22\ ^\circ\text{C}$ before the next cycle began.

3.3 Results and Discussion

3.3.1 Surface Characteristics of Coatings

In order to fabricate coatings with different surface microstructures, the low-surface-energy PFOTES-SiO₂ and high-surface-energy SiO₂ nanoparticles with weight ratios of 1:5, 2:4, 3:3, 5:1 and 6:0 were added into the TEOS-GLYMO sol, while keeping the total weight percent of nanoparticles and other components the same. Figure 3.1 shows FESEM images of these coatings. A significantly distinct surface topology of the TGS 1:5 coating compared to other coatings was observed. Large agglomerated clusters (Fig. 3.1a) can be seen on this surface.

Figure 3. 1 Surface morphology of (a) TGS 1:5, (b) TGS 2:4, (c) TGS 3:3, (d) TGS 5:1 and (e) TGS 6:0 coatings with increased weight of PFOTES-SiO₂ nanoparticles.

Increasing the weight ratio of PFOTES-SiO₂ to SiO₂ nanoparticles to 3:3 led to a decrease in the size of agglomerated SiO₂ nanoparticles and an increase in porosity (Fig. 3.1a-c). Generally, both modified and unmodified nanoparticles are prone to agglomerate due to van-der-Waals forces and electrostatic forces [46] as illustrated in Fig. 3.2. According to the tensile strength of agglomerate nanoparticles proposed by Tang et al.[47],

$$\sigma_T = 1.1 \frac{1-\varepsilon_a}{\varepsilon_a} \frac{F_{TOT}}{L_a^2} \quad (3.1)$$

where ε_a is the porosity of the agglomerated clusters and L_a is the size of agglomerated clusters. F_{TOT} is the sum of attraction forces (due to van-der-Waals forces) and electrostatic repulsive forces. The electrostatic repulsive forces is related to surface energy of particles due to surface charge [48]. PFOTES-SiO₂ nanoparticles presented higher electrostatic repulsive forces and lower van-der-Waals force than SiO₂ nanoparticles, therefore, different molar ratio of PFOTES-SiO₂ to SiO₂ nanoparticles lead to distinct degree of agglomeration. In addition, PFOTES-SiO₂ nanoparticles presents lower tensile strength of agglomerate nanoparticles than SiO₂ nanoparticles and can be more easily breaking up. When a portion of the PFOTES-SiO₂ nanoparticles replaces the same portion of SiO₂ nanoparticles, nanoparticles with high surface energy tend to attach to the easily break-up PFOTES-SiO₂ nanoparticles due to the electrostatic force and van-der-Waals force.

Figure 3.2 Schematic illustration of the interactions between surface modified PFOTES-SiO₂ and non-modified SiO₂ nanoparticles.

In such a case, the PFOTES-SiO₂ nanoparticles can serve as spacers to the unmodified SiO₂ nanoparticles and hinder their agglomeration, resulting in an increased porosity in the coatings (Fig. 3.2). Continuously increasing the weight ratio of PFOTES-SiO₂ to SiO₂ nanoparticles from 3:3 to 6:0 caused a progressively increased size of agglomerated PFOTES-SiO₂ nanoparticles (Fig. 3.2). The TGS 5:1 and TGS 6:0 coatings displayed larger

agglomerated clusters than the TGS 3:3 coating (Fig. 3.1c-e). Although all these coatings (TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0) presented micro-nanostructures, smaller agglomerated clusters and more uniform distributions of micro-pores were noticed on the surface of TGS 3:3 coating because of the interaction of the low-surface-energy PFOTES-SiO₂ and high-surface-energy SiO₂ nanoparticles (Fig. 3.1c).

Figure 3.3 (a) Water wettability, (b) surface roughness and apparent surface energy of TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 coatings. (c) The measured ice-adhesion strength of TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 coatings at different temperatures, and (d) ice-adhesion strength of coatings after water condensation for 24 h at -20 °C with RH of 80%.

Water-contact angles and roll-off angles of TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 coatings are shown in Fig. 3.3a. All the coatings demonstrated water-contact angles larger than 150° and roll-off angles smaller than 10°, indicating superhydrophobicity of these coatings. It is well-known that water wettability is controllable by adjusting surface energy

and surface roughness [49, 50]. Intrinsic surface energy of a rough surface is complex and difficult to measure. Herein, the apparent surface energy was measured instead, together with surface roughness (root-mean square, RMS). Although all the five coatings exhibited water repellency, the apparent surface energy decreased with the increasing PFOTES-SiO₂ content (Fig. 3.3b). The TGS 3:3 coating showed the lowest surface roughness –330 nm, while the other four coatings exhibited comparable levels of surface roughness –500 nm. In summary, five superhydrophobic coatings with different surface microstructures were obtained to enable further comparison and analysis the anti-icing performance.

3.3.2 Ice-adhesion strength

Ice-adhesion strength of the obtained coatings at temperature -15°C and -20°C is presented in Fig. 3.3c. Similar to surface morphology, a much higher ice-adhesion strength of the TGS 1:5 coating than the other coatings was observed, and its strength values were in the range of 400-500 kPa. The TGS 3:3 and TGS 5:1 coatings presented comparable ice-adhesion strengths of ~150 kPa at -15°C and ~250 kPa at -20°C, nearly two times lower than those of the TGS 1:5 coating. Only TGS 2:4 and TGS 6:0 coatings exhibited strong icephobic properties with ice-adhesion strength bellow 100 kPa, a key performance indicator for icephobic coatings [51, 52]. The discrepancy of ice-adhesion strengths of the TGS 6:0 coating at different temperatures was the lowest among the five studied coatings. The lower ice–adhesion strength of the TGS 6:0 coating than that of the TGS2:4 coating might be due to its low apparent surface energy. Even though the TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 coatings demonstrated superhydrophobicity, they displayed different ice adhesion.

It should be recalled here that the question whether a superhydrophobic coating is icephobic has been a topic of heated debates for several years and, till now, controversy remains. Some researchers showed low ice-adhesion strength of superhydrophobic surfaces, while others reported very high ice-adhesion strength of such coatings. Here, both cases were observed. The five designed coatings with different surface microstructures had distinct ice-removal properties, and no simple correlation exists between the apparent

surface energy and ice adhesion. There is also no simple correlation between the surface roughness and the ice adhesion strength. When the freezing of a water droplet on a hydrophobic or superhydrophobic surface is not accompanied with a transition from the Cassie-Baxter mode to the Wenzel mode, ice forms on the solid coating surface, while trapped air remains in the surface cavities. In this case, the ice-adhesion strength will be greatly reduced. In the current study, the TGS 2:4 and TGS 6:0 coatings presented the Cassie-Baxter mode thanks to the proper surface geometry, resulting in a low ice adhesion. On the other hand, the highest ice adhesion of the TGS 1:5 coating is attributed to the transition from the Cassie-Baxter mode to the Wenzel mode. Water penetrated into the porous micro-structure of the TGS 1:5 coating during the sample preparation, resulting in the increased ice adhesion thorough mechanical interlocking. The moderate level of ice adhesion of the TGS 3:3 and TGS 5:1 coatings was caused by a partial wetting of the mixed Cassie and Wenzel mode.

Since the water-condensation effect poses a great threat to superhydrophobic coatings, a condensation test was carried out on five coatings. The measured ice-adhesion strengths are shown in Fig. 3.3d. It is not surprising that TGS 1:5 exhibited nearly no increase in ice adhesion due to the Wenzel mode interaction between water and the coating surface. In contrast, ice adhesion of the TGS 2:4, TGS 3:3 and TGS 5:1 coatings increased significantly due to the condensation-induced transition from the Cassie mode to the mixed Cassie and Wenzel mode. The TGS 6:0 coating demonstrated robust icephobicity with only a slight increase in ice adhesion after the water condensation. Accordingly, it was possible to identify a robust icephobic coating, resistant to moisture condensation before ice formation. Besides surface roughness and apparent surface energy, surface geometry of the sample plays an important role in the ice-removal performance. A lesson learnt from this study is that more attention should be paid to the size of micro-pores on the surface in order to design a robust icephobic coating. Considering only a surface-roughness value may be misleading, particularly when moisture condensation occurs before icing.

3.3.3 Ice-nucleation behavior

In cold-climate regions, ice accretion on outdoor structures is natural and inevitable. However, anti-icing coatings are able to decrease the icing temperature and icing probability of a surface. Thus, icing can be delayed, or even prevented, when the temperature of a surface is higher than the icing temperature. To investigate the icing temperatures of the five developed coatings, 500 cycles of icing and deicing from the temperature of -30 °C to 22 °C were tested for each sample; the obtained results are shown in Fig. 3.4. The distribution of their icing events in the temperature range between -20 °C and -30 °C was analyzed statistically and fitted by the Gauss normalized curve (Fig. 3.5) following our previous studies [45]. The whole icing temperature range of -20 °C – -30 °C was binned with a bin width of 0.2 °C. The temperature of each curve's peak was chosen as the average ice-nucleation temperature of that coating (Table 3.2).

Furthermore, the number of freezing events was used to analyze the freezing probability P , which is defined as [53]:

$$P = \frac{N_i}{N_0}, \quad (3.2)$$

where N_i is the freezing event in the i_{th} bin and N_0 the total number of icing events (500 in this study). To establish a relationship between the temperature and P , the temperature-survival curve $F(t)$ was defined as:

$$F(t) = \frac{N(t)}{N_0}, \quad (3.3)$$

where $N(t)$ is the number of unfrozen events at temperature t . The obtained results are shown in Fig. 3.6. At a certain temperature, the icing probability of the coatings (a portion of frozen events, the opposite to the portion of unfrozen events) from the lowest to the highest was TGS 3:3 < TGS 6:0 < TGS 5:1 < TGS 2:4 < TGS 1:5. The lowest icing probability of the TGS 3:3 coating might be due to its low surface roughness and suitable surface morphology. Some researchers defined the temperature $t_{0.5}$, at which $F(t) = 0.5$ as the average ice-nucleation temperature [54-57]. Herein, these results are also shown in Table 3.2 as a comparison of the Gauss-peak values for the coatings; a perfect agreement between both is noticed.

Figure 3.4 Icing temperatures of (a) TGS 1:5, (b) TGS 2:4, (c) TGS 3:3, (d) TGS 5:1 and (e) TGS 6:0 coatings.

Figure 3.5 Histogram of the icing events on (a) TGS 1:5, (b) TGS 2:4, (c) TGS 3:3, (d) TGS 5:1 and (e) TGS 6:0 coatings with a bin width of 0.2 °C.

Table 3.2 Statistic values of the icing events on the TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 coatings.

Samples	Peak value (°C)	$t_{0.5}$ (°C)	10-90 width (°C)
TGS 1:5	-23.82	-23.96	1.49
TGS 2:4	-24.70	-24.77	0.69
TGS 3:3	-27.08	-27.16	1.27
TGS 5:1	-25.90	-25.96	2.17
TGS 6:0	-26.32	-26.41	1.42

Figure 3.6 Temperature-survival curves of the TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 coatings.

The ice-nucleation temperature of the coatings from the lowest to the highest was TGS 3:3 < TGS 6:0 < TGS 5:1 < TGS 2:4 < TGS 1:5. The TGS 3:3 coating presented the lowest ice-nucleation temperature of around -27°C. It is worth mentioning that the temperature-survival curves were based on 500 cycles, which is 2.5 times more than the threshold of 200 cycles necessary to obtain a stable curve [58]. The 10-90 widths (the range between 10th and 90th percentage of the frozen temperature) for the five coatings as shown in Table 2 are comparable to the data demonstrated in a previous report [59]. Therefore, the analysis of the temperature-survival curves can be considered reliable.

Moreover, the statistical nucleation rate of all five coatings was studied. According to our previous analysis, the statistical nucleation rate $R(T_i)$ at T_i was binned with a width of $\Delta T_i = 0.2$ °C which contains n_i freezing events; then,

$$R(T_i) = \frac{cn_i}{\Delta T_i \left(\frac{n_i}{2} + \sum_{j>i} n_j \right)}, \quad (3.4)$$

where c is the cooling rate (5 °C/min in the current experiment), $\sum_{j>i} n_j$ is the sum of unfrozen icing events. Since ice-nucleation sites at the three-phase contact line on rough surfaces was observed directly in previous studies [60, 61], the corresponding line-nucleation rate can be expressed as

$$R_S^*(T_i) = \frac{R(T_i)}{S}, \quad (3.5)$$

where S is the length of a three-phase contact line between a 10 µl water droplet and a coating surface, calculated as $S = 2\pi r$, and the radius r is given by [62]:

$$r = \left[\frac{3V}{\pi(2-3\cos\theta+\cos^3\theta)} \right]^{1/3} \sin\theta, \quad (3.6)$$

where V is the volume of the water droplet, θ is the static water contact angle. In this equation, the three-phase contact lines of air-trapping sites in the three phase contact line was neglected based on a previously report that this did not markedly change the calculated results [45]. The calculated r and S value is listed in Table 3.3. Consequently, the calculated $R_S^*(T_i)$ of these coatings are shown in Fig. 3.7. Apparently, at a given temperature (marked with a grey line), the lowest line-nucleation rate was obtained for the TGS 3:3 coating, followed by the TGS 6:0 and TGS 5:1 coatings. A line-nucleation rate

higher by two orders of magnitude for the TGS 1:5 and TGS 2:4 coatings indicates a fast icing process at a given temperature.

Table 3.3 The calculated radius and length of the three-phase contact line of five coatings according to the water contact angle.

	TGS 1:5	TGS 2:4	TGS 3:3	TGS 5:1	TGS 6:0
θ (°)	160	168	162	165	169
r (mm)	0.46	0.28	0.41	0.35	0.26
S (mm)	2.87	1.75	2.59	2.17	1.60

Figure 3.7 Calculated line nucleation rates of TGS 1:5, TGS 2:4, TGS 3:3, TGS 5:1 and TGS 6:0 coatings.

Ice nucleation happens randomly, not only at one site. Previous studies found that an ice-nucleation process was influenced by surface energy and surface microstructure. Lower surface energy and convex surfaces were favorable for lowering the icing temperatures [63-68]. Here, all five studied superhydrophobic coatings had a certain portion of convex

structures and nearly no concave pores were observed on the TGS 1:5 coating. A very low line ice-nucleation rate was observed on the TGS 3:3 coating, corresponding to the lowest surface roughness and more uniform distribution of micro-pores. In addition, the TGS 6:0 coating, with a highest portion of PFOTES-SiO₂ nanoparticles and the lowest ice adhesion, demonstrated a line ice-nucleation rate higher than that of the TGS 3:3 coating.

These results imply that the level of surface roughness and the size of micro-pores affect the ice-nucleation process. Moreover, ice adhesion and ice nucleation share distinct underlying mechanisms. Ice adhesion to superhydrophobic coatings is mainly dominated by van-der-Waals forces and mechanical interlocking, while ice nucleation is related to the transformation of disordered water molecules to ordered ones, and the transformation is affected by the ice-water interfacial tension [69], and surface features like pores, steps, cracks, etc. with sizes of the order of the critical nucleus [70]. The ice-nucleation process might be triggered at any suitable sites with a low free energy barrier. The unique surface feature of the TGS 3:3 coating is defined by its more uniform size and distribution of agglomerated nanoparticles than those of the other four coatings. This might contributed to the higher energy barrier of heterogeneous nucleation than for the other coating surfaces. This could explain its observed lowest icing temperature, icing probability and ice-nucleation rate.

Table 3.4 Summary of the relationships between surface characteristics and icephobicity of the five superhydrophobic coatings.

	Ice adhesion	Ice-nucleation temperature	Ice-nucleation rate
Water wettability	✗	✗	✗
Surface roughness	✗	✗	✗
Apparent surface energy	✓	✓	✓
Surface geometry / topology	✓	✓	✓

Table 3.4 summarizes the relationships between surface characteristics and icephobicity of the five superhydrophobic coatings. There is no correlation between water wettability and ice adhesion as well as ice-nucleation temperature / rate. The ice adhesion of the five coatings related to the wetting mode between water and coating surface, whereas the

wetting mode is determined by the surface energy and surface geometry / topology of coatings. Instead, ice-nucleation temperature / rate related to both surface energy and surface geometry. An important revelation by the current work is that there is no simple correlation between the surface roughness and the icephobicity performance such as the ice-nucleation temperature and ice-adhesion strength. This is because a roughness reading does not provide lateral information and cannot differentiate surfaces with different microscopic features between peaks and valleys – surfaces with protruding peaks, cavity, and other irregularities may give the same roughness reading [71]. However, these detailed structures are critical in determining the ice nucleation and ice adhesion behavior. Therefore, detailed topology / geometry has to be considered when designing icephobic coatings, as discussed above.

3.4 Summary

Five superhydrophobic coatings with different surface structures were designed to investigate their anti-icing performance. The surface microscopic features were prepared by varying the ratio of nanoparticles with low and high surface energies while keeping their total amount constant. The ice-adhesion strength and icing temperature of the developed coatings were measured and analysed. The effect of water condensation on ice adhesion of the five coatings verified the robust icephobicity of the TGS 6:0 coating against moisture condensation. It was found that the detailed surface geometry and surface energy of superhydrophobic coatings played important roles in the ice adhesion. The coatings with the ice-nucleation temperature and icing probability ranked from the lowest to the highest were TGS 3:3 < TGS 6:0 < TGS 5:1 < TGS 2:4 < TGS 1:5. The TGS 6:0 coating did not display the most retarded ice nucleation, but it presented an ice-nucleation temperature (-26.4 °C) close to the lowest TGS3:3 coating (-27.16 °C). From the materials-science point of view, it was revealed that reducing the ice adhesion and ice nucleation temperature / rate have different requirements on surface geometry due to their different underlying mechanisms. Therefore, this study supports the view that superhydrophobicity does not automatically leads to icephobicity. Our work has pointed out that the strategy of preparing

superhydrophobic coatings for icephobic applications can be realized when the surface topology is carefully designed.

References

- [1]. Y. Shen, J. Tao, H. Tao, S. Chen, L. Pan and T. Wang. *Langmuir*. **2015**, 31, 10799-10806.
- [2]. X. Wu, Q. Fu, D. Kumar, J.W.C. Ho, P. Kanhere, H. Zhou and Z. Chen. *Materials & Design*. **2016**, 89, 1302-1309.
- [3]. D. Kumar, X. Wu, Q. Fu, J.W.C. Ho, P.D. Kanhere, L. Li and Z. Chen. *Materials & Design*. **2015**, 86, 855-862.
- [4]. Y.Z. Shen, H.J. Tao, S.L. Chen, L.M. Zhu, T. Wang and J. Tao. *RSC Advances*. **2015**, 5, 1666-1672.
- [5]. N. Saleema, M. Farzaneh, R.W. Paynter and D.K. Sarkar. *Journal of Adhesion Science and Technology*. **2011**, 25, 27-40.
- [6]. L. Boinovich, A.M. Emelyanenko. *Langmuir*. **2014**, 30, 12596-12601.
- [7]. K.Q. Zhang, J.Z. Cai, X.H. Li, H. Li, Y.H. Zhao and X.Y. Yuan. *Chinese Journal of Polymer Science*. **2015**, 33, 153-162.
- [8]. H. Li, Y.H. Zhao and X.Y. Yuan. *Soft Matter*. **2013**, 9, 1005-1009.
- [9]. X.L. Zhan, Y.D. Yan, Q.H. Zhang and F.Q. Chen. *Journal of Materials Chemistry A*. **2014**, 2, 9390-9399.
- [10]. X. Wu, X. Zhao, J.W.C. Ho and Z. Chen. *Chemical Engineering Journal*. **2019**, 355, 901-909.
- [11]. F.T. Liu, F.H. Sun and Q.M. Pan. *Journal of Materials Chemistry A*. **2014**, 2, 11365-11371.
- [12]. S.H. Park, E.H. Cho, J. Sohn, P. Theilmann, K. Chu, S. Lee, Y. Sohn, D. Kim and B. Kim. *Nano Research*. **2013**, 6, 389-398.
- [13]. D.P. Singh, J.P. Singh. *Applied Physics a-Materials Science & Processing*. **2014**, 114, 1189-1193.
- [14]. R. Asmatulu, M. Ceylan and N. Nuraje. *Langmuir*. **2011**, 27, 504-507.

- [15]. T. Maitra, S. Jung, M.E. Giger, V. Kandrical, T. Ruesch and D. Poulikakos. *Advanced Materials Interfaces*. **2015**, 2, 1500330.
- [16]. H. Saito, K. Takai and G. Yamauchi. *Surface Coatings International Part B: Coatings Transactions*. **1997**, 80, 168-171.
- [17]. L.L. Cao, A.K. Jones, V.K. Sikka, J.Z. Wu and D. Gao. *Langmuir*. **2009**, 25, 12444-12448.
- [18]. G. Momen, M. Farzaneh. *Micro & Nano Letters*. **2011**, 6, 405-407.
- [19]. R. Jafari, R. Menini and M. Farzaneh. *Applied Surface Science*. **2010**, 257, 1540-1543.
- [20]. Y. Zhao, J. Li, J. Hu and S. Grzybowski. *Icing performances of super-hydrophobic PDMS/Nano-silica hybrid coating on insulators*. in *High Voltage Engineering and Application (ICHVE), 2010 International Conference on*. 2010.
- [21]. M. He, J.X. Wang, H.L. Li, X.L. Jin, J.J. Wang, B.Q. Liu and Y.L. Song. *Soft Matter*. **2010**, 6, 2396.
- [22]. L. Mishchenko, B. Hatton, V. Bahadur, J.A. Taylor, T. Krupenkin and J. Aizenberg. *ACS Nano*. **2010**, 4, 7699-7707.
- [23]. T. Furuta, M. Sakai, T. Isobe and A. Nakajima. *Langmuir*. **2010**, 26, 13305-13309.
- [24]. R. Karmouch, G.G. Ross. *Journal of Physical Chemistry C*. **2010**, 114, 4063-4066.
- [25]. L. Yin, Q. Xia, J.A. Xue, S.Q. Yang, Q.J. Wang and Q.M. Chen. *Applied Surface Science*. **2010**, 256, 6764-6769.
- [26]. K.K. Varanasi, T. Deng, J.D. Smith, M. Hsu and N. Bhate. *Applied Physics Letters*. **2010**, 97, 234102.
- [27]. M. He, H.L. Li, J.J. Wang and Y.L. Song. *Applied Physics Letters*. **2011**, 98, 093118.
- [28]. M. He, J.J. Wang, H.L. Li and Y.L. Song. *Soft Matter*. **2011**, 7, 3993-4000.
- [29]. F. Wang, C. Li, Y. Lv, F. Lv and Y. Du. *Cold Regions Science and Technology*. **2010**, 62, 29-33.
- [30]. C. Antonini, M. Innocenti, T. Horn, M. Marengo and A. Amirfazli. *Cold Regions Science and Technology*. **2011**, 67, 58-67.
- [31]. Q. Fu, X. Wu, D. Kumar, J.W. Ho, P.D. Kanhere, N. Srikanth, E. Liu, P. Wilson, Z. Chen. *ACS Applied Materials & Interfaces*. **2014**, 6, 20685-20692.
- [32]. Y. Tang, Q. Zhang, X. Zhan and F. Chen. *Soft Matter*. **2015**, 11, 4540-4550.

- [33]. L. Wang, Q. Gong, S. Zhan, L. Jiang and Y. Zheng. *Advanced Materials*. **2016**, 28, 7729-7735.
- [34]. Y. Shen, G. Wang, J. Tao, C. Zhu, S. Liu, M. Jin, Y. Xie and Z. Chen. *Advanced Materials Interfaces*. **2017**, 4, 1700836.
- [35]. A.M. Emelyanenko, L.B. Boinovich, A.A. Bezdomnikov, E.V. Chulkova and K.A. Emelyanenko. *ACS Applied Materials & Interfaces*. **2017**, 9, 24210-24219.
- [36]. J.C. Moreno-Pirajan. *Thermodynamics Approach in the Adsorption of Heavy Metals, In Tech, Croatia, Europe*. **2011**.
- [37]. D. Bassett, E. Boucher and A. Zettlemoyer. *Journal of Colloid and Interface Science*. **1970**, 34, 436-446.
- [38]. P. Judeinstein, C. Sanchez. *Journal of Materials Chemistry*. **1996**, 6, 511-525.
- [39]. X. Wu, S. Zheng, D.A. Bellido-Aguilar, V.V. Silberschmidt and Z. Chen. *Materials & Design*. **2018**, 140, 516-523.
- [40]. K.Y. Li, S. Xu, W.X. Shi, M. He, H.L. Li, S.Z. Li, X. Zhou, J.J. Wang and Y.L. Song. *Langmuir*. **2012**, 28, 10749-10754.
- [41]. W. Xinghua, Z. Chen. *Journal of Materials Chemistry A*. **2018**, 6, 16043-16052.
- [42]. D.K. Owens, R. Wendt. *Journal of Applied Polymer Science*. **1969**, 13, 1741-1747.
- [43]. W. Rabel. *Farbe und Lack*. **1971**, 77, 997-1006.
- [44]. D. Kaelble. *The Journal of Adhesion*. **1970**, 2, 66-81.
- [45]. Q.T. Fu, E.J. Liu, P. Wilson and Z. Chen. *Physical Chemistry Chemical Physics*. **2015**, 17, 21492-21500.
- [46]. C. Sauter, M. Emin, H. Schuchmann and S. Tavman. *Ultrasonics Sonochemistry*. **2008**, 15, 517-523.
- [47]. S. Tang, Y. Ma and C. Shiu. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **2001**, 180, 7-16.
- [48]. N.G. Özcan-Taşkin, G. Padron and A. Voelkel. *Chemical Engineering Research and Design*. **2009**, 87, 468-473.
- [49]. D. Öner, T.J. McCarthy. *Langmuir*. **2000**, 16, 7777-7782.
- [50]. D.M. Spori, T. Drobek, S. Zürcher, M. Ochsner, C. Sprecher, A. Mühlebach and N.D. Spencer. *Langmuir*. **2008**, 24, 5411-5417.
- [51]. V. Hejazi, K. Sobolev and M. Nosonovsky. *Scientific Reports*. **2013**, 3, 2194.

- [52]. K. Golovin, S.P. Kobaku, D.H. Lee, E.T. DiLoreto, J.M. Mabry and A. Tuteja. *Science Advances*. **2016**, 2, e1501496.
- [53]. T.F. Whale, B.J. Murray, D. O'Sullivan, T.W. Wilson, N. Umo, K.J. Baustian, J.D. Atkinson, D. Workneh and G. Morris. *Atmospheric Measurement Techniques*. **2015**, 8, 2437-2447.
- [54]. P. Wilson, A. Haymet. *Physical Chemistry Chemical Physics*. **2009**, 11, 2679-2682.
- [55]. P.W. Wilson, K.E. Osterday, A.F. Heneghan and A.D. Haymet. *Journal of Biological Chemistry*. **2010**, 285, 34741-34745.
- [56]. T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala and R.H.A. Ras. *Advanced Materials*. **2011**, 23, 673-678.
- [57]. P.W. Wilson, W. Lu, H. Xu, P. Kim, M.J. Kreder, J. Alvarenga and J. Aizenberg. *Physical Chemistry Chemical Physics*. **2013**, 15, 581-585.
- [58]. P.W. Wilson, A.F. Heneghan and A.D.J. Haymet. *Cryobiology*. **2003**, 46, 88-98.
- [59]. P.W. Wilson, A.D.J. Haymet. *Journal of Physical Chemistry B*. **2012**, 116, 13472-13475.
- [60]. T.J. Athauda, W. Williams, K.P. Roberts and R.R. Ozer. *Journal of Materials Science*. **2013**, 48, 6115-6120.
- [61]. J.L. Carvalho, K. Dalnoki-Veress. *Physical Review Letters*. **2010**, 105, 237801.
- [62]. P. Hao, C. Lv and X. Zhang. *Applied Physics Letters*. **2014**, 104, 161609.
- [63]. M.J. Jamieson, C.E. Nicholson and S.J. Cooper. *Crystal Growth & Design*. **2005**, 5, 451-459.
- [64]. D.H. Xu, W.L. Johnson. *Physical Review B*. **2005**, 72, 05210.
- [65]. S.J. Cooper, C.E. Nicholson and J. Liu. *Journal of Chemical Physics*. **2008**, 129, 124175.
- [66]. N.H. Fletcher. *Journal of Chemical Physics*. **1958**, 29, 572-576.
- [67]. B.K. Chakraverty, G.M. Pound. *Acta Metallurgica*. **1964**, 12, 851-&.
- [68]. C.A. Sholl, N.H. Fletcher. *Acta Metallurgica*. **1970**, 18, 1083-1086.
- [69]. L. Ickes, A. Welte, C. Hoose and U. Lohmann. *Physical Chemistry Chemical Physics*. **2015**, 17, 5514-5537.
- [70]. C. Gurganus, J. Charnawskas, A. Kostinski and R. Shaw. *Physical Review Letters*. **2014**, 113, 235701.

[71]. B. Zheng, L.P. Wong, L.Y. Wu and Z. Chen. *Advances in Materials Science and Engineering*. **2017**, 2017.

Chapter 4* Scalable Mechanically Robust Transparent Coatings with Anti-icing and Self-cleaning Properties

A Mechanically Robust Transparent Coating for Anti-icing and Self-cleaning Applications

This chapter describes a mechanically robust and optically transparent anti-icing coating for sports applications. To achieve high transmittance, mechanical agitation has been firstly employed to obtain uniformly dispersed nanoparticles in a sol-gel system. The liquid repellency and self-cleaning properties of the coating have been investigated. To prevent or delay ice accretion due to natural sleet, freezing rain and frost, ice adhesion, icing delay either in time or temperature and frost resistance have been studied comprehensively. At the end, mechanical properties of the smooth coating have been measured and compared with reported coatings in the literature.

*This section published substantially as X. Wu, Z. Chen, *Journal of Materials Chemistry A*. 2018, Vol. 6, pp. 16043-16052.

4.1 Introduction

Anti-icing coating is a simple and low cost passive method that holds great promise in effectively preventing ice formation and easy ice removal [1-3]. The commonly used evaluation criteria for an anti-icing coating include water repellency, a delay in ice formation either in time or in temperature, and a low ice-adhesion strength no more than 100 kPa [4, 5]. Currently, most of the reported anti-icing coatings are not able to satisfy all these criteria. The widely-reported SLIPS have been proven to be the most promising way to reduce ice-adhesion strength and increase icing-delay time. SLIPS can achieve a high transparency by choosing the substrate and lubricant liquid with matching refractive indices [6]. However, the key limitations of SLIPS are: i) the infused liquid will be drained away eventually by gravity or capillarity force, and ii) the mechanical property is weak due to the porous structures [7, 8]. Another well-discussed anti-icing coating is based on superhydrophobicity. Superhydrophobic coatings have been widely reported for self-cleaning applications, and they also be employed as a candidate for icephobic application since water droplets are able to roll off the coating surface before icing occurs. Superhydrophobic coatings have been fabricated by self-assembly of nanoparticles or embedding surface modified nanoparticles in sols, polymers, resins or foams [9-13]. Agglomeration of nanoparticles facilitates formation of the necessary hierarchal micro/nanostructures to allow air to be trapped in the structures, leading to decreased water-solid interface and increased water contact angle [14]. However, such superhydrophobic coatings may not always be an advantage for anti-icing applications, as some icing conditions may adversely affect the anti-icing performance. For example, if ice formation is caused by moisture condensation and accumulation, the micro/nanoporous structure will result in a larger (than nominal) contact area between the ice and the substrate. Such contact into the micro/nanoscale pores will increase the ice-substrate contact area and the ice-adhesion strength. In addition, the hierarchal surface structure is mechanically fragile and difficult to maintain under a harsh working condition [15-18]. Moreover, the agglomeration of nanoparticles and the trapped air cause light scattering, reducing the light

transmittance of the superhydrophobic coatings. To overcome this problem, researchers found that self-assembly of surface modified with nanoparticles was effective to achieve a high transparency [19-21]. Boal et al. developed a polymer-mediated strategy for the self-assembly of colloidal nanoparticles which can control the agglomeration of nanoparticles [22]. In this regard, Guzman et al. investigated the effect of surface potentials on nanoparticle agglomeration [23]. Hitoshi et al. obtained transparent coatings by trying different types of alcohols used in the suspensions [24]. One major drawback of these coatings is again their poor mechanical property due to the weak structures. Furthermore, increasing the thickness of self-assembled coatings adversely affects the transmittance of coatings with induced porosity [25, 26]. In summary, mechanical properties and transparency are two major limitations for the SLIPS and superhydrophobic coatings due to their porous or rough structures. A new strategy is needed to prepare mechanically robust transparent coatings for icephobic and self-cleaning applications.

4.2 Experimental Methods

4.2.1 Materials

TEOS), GLYMO, PFOTES, SiO₂ nanoparticles with particle size around 10-20 nm, and itaconic acid were obtained from Sigma-Aldrich. Methanol (99%) was obtained from Fisher Scientific. Glycerol, formamide, diiodomethane, α -bromonaphthalene, sunflower oil, hexadecane, dodecane and ethanol used for contact angle tests and silicone oil for self-cleaning test were obtained from Sigma-Aldrich. Acrylic paint was purchased from Tang Art, China. Microscope glass slides (25.4 mm $\times$ 76.2 mm) and cover glass (Diameter: 22 mm and thickness 0.13~0.16 mm, used for ice-nucleation temperature tests) were obtained from Sailboat Lab Co., Ltd. and Marienfeld, respectively. Glass fiber reinforced epoxy (GFRE) substrates used for PosiTect Pull-Off adhesion test were purchased from Thailand. Glass substrates with size of 10 cm $\times$ 10 cm $\times$ 1.1 mm (BBL-001) used for scalability demonstration were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd., China.

4.2.2 Methods

4.2.2.1 PFOTES-SiO₂ nanoparticles preparation

0.5 ml PFOTES was hydrolyzed in 48 ml methanol with 1.5 ml water for 24 h and diluted in methanol with volume ratio of 1:2. After that, 0.75 g SiO₂ nanoparticles were added to the diluted PFOTES solution at room temperature. The mixture was first placed in an ultrasonic bath for 30 min, and then magnetically stirred at speed of 500 rpm for 24 h. After stirring, the mixture was centrifuged at 2000 rpm for 5 min. The obtained hydrophobic silica was subsequently denoted as PFOTES-SiO₂. The above-prepared PFOTES-SiO₂ nanoparticles were used as low-surface-energy fillers. The original SiO₂ nanoparticles obtained from Sigma-Aldrich were used as high-surface-energy fillers.

4.2.2.2 Sol-gel Preparation

The sol matrix was prepared using 20 ml methanol, mixed with 5 ml 1 wt. % PFOTES solution, 0.004 mol TEOS, 0.02 mol GLYMO, 0.076 mol DI water and 0.5 g itaconic acid. The mixture was magnetically stirred for 2 h. The prepared PFOTES-SiO₂ and 0.75 g SiO₂ nanoparticles were added to the sol matrix and placed in an ultrasonic bath for 15 min, and then placed under a magnetic stirrer at speed of 500 rpm for 1 day, 4 days, 6 days, 8 days, 10 days, and 12 days. The obtained sols were spray-coated onto the glass slides and GFRE substrates, separately, through an airbrush kit (AS06KB) with a 1.5 mm diameter nozzle using compressed air (with pressure at 345 kPa). The distance between the airbrush and the substrate was kept at 8 cm. Finally, the prepared samples were cured in an oven at 110 °C for 1.5 h.

4.2.3 Characterization

The surface morphology of the coatings was scanned using a field emission scanning electron microscope (FESEM, JSM-6360, Japan). Atomic force microscopy (AFM, Asylum Research Cypher S, U.S.A.) was used for imaging surface topology of the

coatings. The surface roughness was also obtained from the AFM measurement. The reported roughness data are the average of at least three measurements obtained at different locations of the coatings. The scanned area is $5\ \mu\text{m} \times 5\ \mu\text{m}$. Transmission electron microscopy (TEM, JEOL 2100 HR, Japan) operating at 200 kV was used to observe the distribution of nanoparticles in the coatings. The transmittance of the coatings was examined by UV-VIS spectrophotometer (Shimadzu UV-2501PC, Japan).

The contact angles, sliding angles, receding angles and advancing angles of liquids were measured with a contact angle system (OCA 20, Dataphysics Co., Germany). The water wettability of coatings under low temperature was measured on the cooling stage of Dataphysics OCA 20 system. The temperature was set at 25, 15, 5, -5, -15, and -20 °C. Measurement was carried out when the temperature of samples reached the targeted temperature. The surface energy of coatings was measured according to the Owens, Wendt, Rabel and Kalble (OWRK) [27-29] method, in which water and ethanol were used as polar liquids, while diiodomethane was used as a non-polar liquid.

To investigate the contaminant-removal performance of the coatings, artificial oil contaminant was prepared by blending acrylic paint, soil and silicone oil with weight ratio of 1:1:1.3. Before applying the contaminant, the samples were tilt at an angle of 60° to the horizontal plane.

Measurements of ice-adhesion strength between an ice block and coating surfaces followed the scheme from our group's previous report [30]. A teflon mold with an inner diameter of 18 mm was filled with DI water, and then covered with a coated substrate on top. The whole set was placed upside down in a climate chamber (Cincinnati Sub-Zero environmental chambers, USA) for 24 hours at -15 °C and -20 °C, respectively.

To investigate the icing-delay effect, our transparent hydrophobic repellent coating (THRC) and uncoated glass slides were directly placed on the cooling stage of Dataphysics OCA 20 system first. A 10 μl water droplet was placed on the test surfaces, and then the temperature was decreased from room temperature to -15 °C. The ramp rate was set as 5 °C/min. The time at which the droplet started to freeze was recorded as icing-delay time.

Besides, the ice-nucleation process of the water droplets was recorded by a high speed camera (Phantom Micro 120). The melting process of the frozen droplets was also captured by the built-in camera of Dataphysics OCA 20 system with a ramp rate of 10 °C/min.

The ice-nucleation temperature of coatings was studied by our group's previously reported self-designed automatic measurement system [31]. A 10 μ L DI water droplet was placed on the center of a sample surface, and the test chamber was cooled down from 22 °C down to a set low temperature at -30 °C. The ramp rate from 22 °C to 0 °C was set at 40 °C/min, while the ramp rate from 0 °C to -30 °C was set as 5 °C/min. The temperature at which the droplet was frozen was recorded as icing temperature. Once the whole cycle was completed, the iced droplet was heated up to ambient temperature and held for 2 min to ensure a complete melting of the ice before the next cycle began. Icing temperatures of 500 cycles for each water droplet were recorded and statistically analyzed.

The elastic modulus and hardness of the deposited coatings were investigated using a nano-indenter (Nano-Indentation & Micro-Scratch System, Wrexham, United Kingdom) with indentation depth of 1800 nm. For each sample, 15 points (in 3 lines, 5 points each line) were tested. Pencil scratch test of the coatings was assessed using a commercial pencil scratch tester (Scratch Hardness Tester Model 291, ERICHSEN) according to ASTM D3363 Standard Test Method. The coating adhesion on glass slides and GFRE substrates was assessed by cross-cut tape adhesion test based on ASTM D3359 Standard Test Method. After pencil-scratch and cross-cutting, the coatings were examined under an optical microscope (Olympus BX51). The adhesion strength test was conducted by PosiTest Pull-Off adhesion test according to ISO 4624 Standard Test Method. Aluminum dollies with diameter of 20 mm were used to apply the pull-off load.

To study the durability of the coatings, the coatings were eroded by sand using a micro-sand blaster (Comco Inc.). The size of silica (SiO_2) sand particles ranges from 10 μm to 40 μm . The distance between the blaster nozzle and a sample surface was kept at 15 cm. The pressure was set as 100 kPa and 200 kPa, and the erosion time lasted for 15 s, 30 s, and 60 s. The eroded area on the samples was fixed at 1.13 cm^2 (corresponding to a circle 1.5 cm

in diameter). The weight loss of eroded coatings was recorded under the different erosion conditions. After the sand erosion, the roughness of the eroded surfaces was measured by a surface profiler (Alpha-Step IQ Surface Profiler, KLa Tencor, USA) with a scan length of 5 mm. The ice-adhesion strength after the sand erosion was also recorded at -20 °C.

4.3 Results and Discussions

4.3.1 A Smart and Low Cost Strategy to Obtain Water Repellent Coatings

The coating developed in this study provides: i) a solid, transparent water repellent coating without conventional hierarchical micro / nanostructures; ii) mechanically robust with uniformly distributed nanoparticles through the ceramics-based coating thickness. In addition, we aim to ensure that iii) the preparation method is simple, scalable, and of low cost. To satisfy these requirements, we have prepared a series of coatings derived from a sol-gel system. By varying the stirring time of the sol, the dispersion of nanoparticles in the final coatings changes significantly. To assist uniform dispersion of the nanoparticles, prior surface modification by PFOTES was adopted on half of the added SiO₂ nanoparticles. The surface modified nanoparticles were termed as PFOTES-SiO₂ and used as low surface energy additives. Another half of the SiO₂ nanoparticles were used without any surface treatment to serve as high surface energy nanoparticles. In our experiment, the sol contained TEOS, GLYMO, PFOTES, SiO₂ nanoparticles (10-20 nm), DI water and itaconic acid. Transparent glass slides were used as the substrate. To obtain good mechanical properties, the weight percentage of nanoparticles in the final coatings was fixed at 30 wt%.

Figure 4.1 shows FESEM images of the coatings with different stirring times (a) 1 day, (b) 4 days, (c) 6 days, (d) 8 days, (e) 10 days and (f) 12 days. After the 1 day's stirring, the coating surface presented large agglomerated nanoparticles with micro-scale cavities. The continuous application of shear stress drove the nanoparticles to flow and align in a certain direction. This process accelerated the detachment of

agglomerated nanoparticles, and led to a decreased agglomeration size or even complete elimination of agglomerated nanoparticles in the coatings. Figure 4.2 shows the corresponding AFM images of the coatings varying the stirring time. Surface roughness (RMS) of the coatings changes dramatically due to the mechanical dispersion of nanoparticles. After 12 days' stirring, a very flat and smooth surface with surface roughness around 14.0 nm was obtained. Both the AFM and FESEM images verified the surface morphology and surface roughness change with increasing stirring time of the precursors.

Figure 4.1 FESEM images of the coatings with different stirring times of (a) 1 day, (b) 4 days, (c) 6 days, (d) 8 days, (e) 10 days, and (f) 12 days. Insets are schematic illustration of water / coating interfaces.

Figure 4.3 presents the effect of surface roughness on water wettability. The coating with 1 day's stirring time exhibited superhydrophobicity with a contact angle $>160^\circ$ (inset in Fig. 4.3) and a roll-off angle $<10^\circ$, owing to the micro / nanostructures formed by agglomeration of SiO_2 nanoparticles (Fig. 4.1a and inset). After 4 days' stirring, the size of pores formed on the coating gradually decreased due to the good

dispersion of SiO₂ nanoparticles (Fig. 4.1b), forming new water-solid interfaces with a reduced contact angle. As the stirring time further increased, decreased surface roughness allows water to infuse into the grooves or valleys of coatings, presenting significantly decreased contact angles (Fig. 4.1c and inset). Coatings with surface roughness less than 50 nm were obtained with 8 days' stirring or longer. Meanwhile, comparable contact angles $\sim 110^\circ$ were obtained, and water droplets were in contact with the entire solid surface without trapped air (insets of Fig. 4.1d-f). To sum up, a clear relationship between surface roughness and the water contact angle can be observed: the water contact angle decreased with decreasing surface roughness. This is consistent with the general understanding that a rougher hydrophobic surface possesses a higher contact angle. In contrast, a distinct difference was observed on the water sliding behavior. The water sliding angle of coatings increased first, and then decreased after 6 days' stirring. This change indicates that the water affinity with the coatings increased with stirring time initially, and then decreased.

Figure 4.2 AFM images of our coatings with different stirring time (a) 1 day (305.1 ± 12.7 nm), (b) 4 days (235.0 ± 8.2 nm), (c) 6 days (174.2 ± 6.8 nm), (d) 8 days (43.8 ± 5.0 nm), (e) 10 days (22.4 ± 3.6 nm), (f) 12 days (14.0 ± 1.2 nm). The scale bar of the AFM images is 400 nm.

Figure 4.3 Water contact angles and sliding angles of the prepared coatings at different stirring times versus surface roughness (RMS) Inset shows the water droplet profile on the coating with 1 day's stirring.

Conventionally, a surface is termed as hydrophobic when the water contact angle is larger than 90° . Researchers define a surface superhydrophobic when the contact angle is larger than 150° and roll-off angle is less than 10° following the well-known lotus leaf effect. However, there is another wetting state where the contact angle is larger than 150° but a water droplet does not roll off even when the surface is turned upside down (the rose petal effect) [32–34]. The former is a clear indication that water adhesion with the coating surface is very low (repellent), while the latter is high (attractive). Similarly, hydrophobic surfaces with a contact angle $<150^\circ$ can also display different water affinity. Some researchers termed the hydrophobic repellent state as hydrophobic slippage and attempted to explain the water movement on hydrophobic coatings by the viscosity change of water near the hydrophobic surface and concentration of gas-filled tiny cavities close to it [35, 36]. However, their descriptions also included the superhydrophobic states which rely

greatly on the gas-filled tiny cavities. Here, we use the notion of hydrophobic repellent state, to distinguish it from the superhydrophobic state or the hydrophobic attractive state. As described above, a reduced surface roughness allows water to infuse into the grooves or valleys on coating surfaces with 4 and 6 days' stirring (Fig. 4.1b-c), introducing some degree of mechanical interlocking and capillary forces between water and coating surfaces. Therefore, the coatings presented increased sliding angles. The obtained coatings gradually became flat with further stirring beyond 6 days' stirring. The mechanical interlocking is reduced as the water-solid interface of coatings decreases (Fig. 4.1d-f). Coatings with 8 days' stirring or longer exhibited comparable water contact angles around 110° and water sliding angle of $40 \sim 50^\circ$ (Fig. 4.3), displaying hydrophobic repellent behavior.

4.3.2 Scalable Transparency of Water Repellent Coatings and Mechanism Behind

It is noted that existing literatures are mainly focused on increasing the surface roughness to turn hydrophobic coatings to superhydrophobic coatings [13, 30, 37, 38]. However, as discussed earlier, increasing the surface roughness by creating rough or porous surfaces would greatly reduce light transmittance of the coatings. In this work, we take a new strategy to resolve the contradicting requirements by reducing the surface roughness of hydrophobic coatings. This has successfully led to a ceramics-based transparent hydrophobic water-repellent coating, which has not been demonstrated before. Figure 4.4a displays the transition of a superhydrophobic coating to a hydrophobic repellent coating, accompanied with the change of transmittance of the coatings (Fig. 4.4b). Due to partial reflections between the interface and various surfaces, precise calculation of two-layer transmittance is complicated and transfer matrix is needed for the modelling. To simplify the calculation, a first approximation is assumed. The resultant transmittance T of the coated glass slide is given by

$$T = T_g \cdot T_c, \quad (4.1)$$

where T , T_g and T_c are transmittance of glass with the applied coating, the glass slide and the applied coating, respectively. The transmittance index at wavelength of 550 nm was

chosen for this calculation. Table 4.1 shows the calculated transmittance of coatings with different stirring times at the wavelength of 550 nm.

Figure 4.4 (a) Transmittance of coatings with different stirring times. (b) A relationship between surface roughness and transmittance at the wavelength of 550 nm. (c) Optical transmission of the coating with 12 days' stirring and uncoated glass (size: 10 cm×10 cm), and high resolution TEM images of coatings with (d) 6 days', (e) 10 days' and (f) 12 days' stirring (the size of agglomerated nanoparticles are scaled in white lines). Scale bar, 20 nm.

Table 4.1 The calculated transmittance of the coatings with different stirring times at the wavelength of 550 nm.

	T	T_g	T_c
1 day	1.2%		1.3%
4 days	6.1%		6.7%
6 days	29.2%	91.4%	32.0%
8 days	79.9%		87.4%
10 days	84.7%		92.7%
12 days	89.4%		97.8%

The corresponding coatings' transmittance relative to glass substrates shows basically the same trend of increased transmittance over decreased surface roughness. The coating (12 days' stirring) exhibited visible-light transmittance as high as 97.8 %. This coating, spray-coated on glass substrates (10 cm $\times$ 10 cm), has a uniform transparent layer with a thickness of ~ 30 μm and displays visually comparable transmittance to uncoated glass (Fig. 4.4c).

To investigate the reasons behind the transmittance change, we examined the coatings with 6, 10 and 12 days' stirring by TEM (Fig. 4.4d-f). Stirring time-dependent agglomeration of nanoparticles is clearly observed. The size of agglomerated nanoparticles in the coating with 6 days' stirring was as large as ~ 200 nm. With continuously applied shear stress during the stirring, the size of agglomerated nanoparticles gradually decreased to around 50 nm in the coating with 10 days' stirring. Uniform distribution of nanoparticles with the size of 10-20 nm was observed in the coating with 12 days' stirring. The continuous shear action produced by the applied torque of a magnetic stirrer drives the nanoparticles to flow and align in certain direction. This process accelerated the detachment of agglomerated SiO_2 nanoparticles and re-arrangement of the SiO_2 nanoparticles as shown in Fig. 4.5.

Figure 4.5 Schematic illustration of detachment of agglomerated SiO₂ nanoparticles.

Assume a shear stress τ is acting on the agglomerated nanoparticles, which is related to the shear rate γ and viscosity μ for Newtonian fluids:

$$\tau = \gamma\mu, \quad (4.2)$$

where μ is a constant. According to a previous report [39], for turbulent flows

$$\gamma = C \cdot \omega^{3/2}, \quad (4.3)$$

where ω is defined as agitation speed which equals to $\left(\frac{2\pi}{60}N\right)$, and N is set as 500 rpm in our experiment and thus, the shear stress can be expressed as

$$\tau = C_1 \cdot \omega^{3/2}, \quad (4.4)$$

where $C_1 = \mu C$.

For large agglomerated nanoparticles, the shear stress-affected area A is large, thus, they are driven by a relative large force F in the solution. The applied driving force not only supports rotation of agglomerated nanoparticles, but also provides a direct external counter force against the tensile strength (as shown in Equation 3.1, relates to van-der-Waals force and steric hindrance) of agglomerated SiO₂ nanoparticles [40, 41]. The unbalanced force acting on single nanoparticle will push them moving towards various directions at different speeds; and thus the dispersion status of nanoparticles will be statistically different from each other, leading to detachment of agglomerated nanoparticles as illustrated in Fig. 4.5.

It is well known that the silanol groups on the SiO₂ nanoparticle surface react with PFOTES to impart the hydrophobicity. Before the detached SiO₂ nanoparticles approach the thermodynamic stability, PFOTES-SiO₂ nanoparticles will serve as spacers and graft to the hydrophilic SiO₂ nanoparticles by Si-OH groups. Therefore, besides shear stress, the low surface energy PFOTES also plays an important role in the dispersion of nanoparticles. It can graft on nanoparticles in the sol solutions, keeping the nanoparticles from agglomeration by introducing electronegativity and resistance to the van-der-Waals forces [41-43]. The viscosity of the sol solution could be another factor which can withstand the segregation of nanoparticles due to sedimentation [44]. At the end of stirring, all the nanoparticles were uniformly distributed in the sol solution.

As observed, agglomeration of nanoparticles gives rise to the surface roughness of the coatings. Continuous stirring minimizes the agglomeration size, and at the same time, releases the trapped air. Therefore, the scattering of visible light is eliminated. When the size of agglomerated nanoparticles and air bubbles become smaller than one-tenth of the wavelength of the visible light, the particles will no longer be able to scatter the light [45], thus a transparent coating is obtained. The size of nanoparticles in the coating after 12 days' stirring was significantly lower than this critical size (1/10 of 400~700 nm), which explains the high transparency of this coating.

4.3.3 Liquid Repellency and Self-cleaning Properties of THRC

On the basis of the above findings, we have successfully fabricated a transparent hydrophobic repellent coating (THRC) with 12 days' stirring. The surface roughness and surface energy of the THRC were measured to be 14.0 ± 1.2 nm and 15.5 ± 1.0 mJ/m², respectively. The surface energy of the THRC was comparable with 3M[®] Fluorinert[™] and Krytox[®] DuPont[™] liquids that have been used as infused liquids in SLIPS [6, 46]. Moreover, the THRC exhibited repellency to liquids with surface energy ranging from 72.8 to 22.1 mJ/m² (Fig. 4.6). It noticed that the overall tendency of the liquid contact angles decreased with decreasing liquid surface energies (Fig. 4.6a). This is explainable by the classical Young's contact theory. Same phenomenon was also observed on our previously

reported superhydrophobic coatings [13]. Besides the static contact angle, the sliding angles of a 10 μl liquid droplet on the THRC were also measured (Fig. 4.6a). All the tested liquids exhibited sliding behavior on the THRC with a sliding angle no greater than 25° , indicating reasonably good repellency against these liquids (Supplementary Video S1). We noticed that the liquid mobility on the coating surface behaved differently with SLIPS. SLIPS present no dependence on the surface energy of liquids [6], the sliding behavior of liquids is due to the interfacial slip of two immiscible liquids, and the capillary forces are balanced by viscous stresses of the tested liquids. On the contrary, the liquid repellency of the THRC is related to both surface energy and shape of the tested liquids. Generally, a droplet will change shape and become nonaxisymmetric at a tilted angle, α , resulting in CAH which would give rise to a capillary retention force. This force can overcome the gravity, leading to movement of a droplet.

Here, the motion of liquid droplets on THRC greatly depends on the CAH (Fig. 4.6a) with the exception of DI water, glycerol, and formamide. The difference might be due to their high receding angles (Fig. 4.6a, between $90^\circ \sim 110^\circ$) which induces strong curvature of the free liquid surface counteracting with the viscous force along the direction of liquid motion [47]. As explained by Gao et al.[48], a droplet may move by sliding at some points of the contact line and rolling at other points or may advance by rolling and recede by sliding. The shape change of a droplet can serve as an activation barrier to movement that is quantified by increasing liquid-vapor interface area. Therefore, the sliding behavior of DI water, glycerol, and formamide is not only determined by the CAH but also the shape of the liquids. Figure 4.6b shows droplet profiles captured during the sliding motion of liquids. A decrease in curvature at the back of the droplets was observed with decreased surface energy of liquids. This complies with the observed receding angles of the liquids.

To verify the self-cleaning effect of the THRC, contaminant removal tests were carried out on THRC coated and uncoated glass substrate with artificial oily contaminant consisting of acrylic paint, soil and silicone oil. Figure 4.6c compares the self-cleaning performance of THRC coated glass with uncoated glass. The contaminant easily slid down the THRC

in 7 s with only a small amount of residue, demonstrating the self-cleaning ability of THRC. On the other hand, the contaminant stayed firmly on an uncoated glass.

Figure 4.6 The liquid repellency and self-cleaning performance of the THRC. (a) Liquid contact angles, receding angles, advancing angles, sliding angles and CAH on the THRC, and (b) droplet profiles captured during the sliding motion of liquids on the THRC. Scale bar, 1 mm. (c) Captured images of the contaminant movement on THRC coated (right) and uncoated glass (left). Scale bar, 1 cm.

4.3.4 Robust Anti-icing Properties of THRC

Figure 4.7 Comparison of (a) ice-adhesion strength and (b) icing-delay time (scale bar, 10 mm) of THRC coated and uncoated glass.

In addition to high transparency and self-cleanliness, the THRC exhibited ice-adhesion strength as low as 58.2 ± 1.5 kPa and 69.5 ± 2.1 kPa at -15 °C and -20 °C, respectively (Fig. 4.7a). Compared to the uncoated glass, the THRC coating has a reduced ice-adhesion strength to less than 1/4 of the uncoated one (266.8 ± 5.2 kPa and 314.3 ± 8.7 kPa at -15 °C and -20 °C, respectively). This is attributed to its low surface energy. The icing-delay time of the THRC coated and uncoated glass is compared in Fig. 4.7b. The droplet on the uncoated glass slide (Fig. 4.7b left) started to freeze after 54.0 ± 2.6 s, whereas the THRC coated one (Fig. 4.7b right) started icing after 292 ± 4.1 s (delayed 238 s compared with that of an uncoated glass slide) (Supplementary Video S2, note that the time starts count only after the substrate surface temperature has reached the pre-set temperature of -15 °C).

To comprehensively study the ice nucleation behaviors of the THRC coated and uncoated glass, 500 cycles of icing and deicing events were recorded and statistically analyzed. The measured icing temperature of the THRC coated and uncoated glass is shown in Fig. 4.8a. The icing temperature represents the beginning of heterogeneous ice nucleation. To

comprehensively study the ice nucleation behaviors, 500 cycles of icing and deicing were tested for each sample. Both samples displayed slight increase in the icing temperatures after 300 cycles. This is probably due to a slight spreading of the droplets on surfaces caused by water condensation, which has resulted in a lower water contact angle and a larger water-solid contact area [31].

Figure 4.8 (a) Ice-nucleation temperature, and (b) histogram of the freezing events on the THRC coated and uncoated glass with a bin width of 0.2 °C. (c) The survival curves and (d) the calculated line ice-nucleation rate of the THRC coated and uncoated glass, insets are sequential images of the nucleation process on the THRC surface. Scale bar, 1mm.

The THRC sample was less severe in the spreading, which is consistent with the less water condensation (to be further discussed later). The icing temperatures were analyzed by the Gauss normalized distribution curve shown in Fig. 4.8b. The whole icing temperature range was binned with a bin width of 0.2 °C. The Gauss peak temperatures for the maximum freezing events for each sample are shown in Table 4.2. In addition, the number of freezing events is converted to freezing probability defined as Equation 3.2 Then the obtained

temperature-survival curve $F(t)$ according to Equation 3.3 are shown in Fig. 4.8c. The temperature $t_{0.5}$, at which $F(t) = 0.5$, is also shown in Table 4.2 for comparison. A perfect agreement between the Gauss peak values and $t_{0.5}$ was observed. The mean icing temperature of the THRC glass was $\sim 5^{\circ}\text{C}$ lower than the uncoated glass substrate.

Furthermore, the icing temperatures have been studied statistically to calculate the nucleation rate of the THRC coated and uncoated samples. According to our previous report [31] and Equation 3.4, the nucleation rate $R(T_i)$ can be calculated. Regarding the hot debate about the initiation site of ice nucleation, it is observed directly that ice nucleation initiated at the three-phase contact line on the THRC coated and uncoated glass with the help of a high-speed camera system (Supplementary Video S3), which is in agreement with some recent reports.[49-51] Insets in Fig. 4.8d show the sequential images of the nucleation process on the THRC surface. The corresponding line nucleation rate can be obtained according to Equation 3.5 and 3.6. Since the surface roughness of THRC is less than 15 nm, the measured contact angle can be directly used as θ , and the corresponding S value is listed in Table 4.3. Accordingly, the calculated $R_S^*(T_i)$ of these coatings are shown in Fig. 4.8d. It can be seen that the ice nucleation rate on the THRC is significantly lower than that on the uncoated glass at the same temperature.

Table 4.2 Statistical values of the ice-nucleation temperature of THRC coated and uncoated glass.

	Uncoated	coated
Gauss peak value ($^{\circ}\text{C}$)	-21.85	-26.47
$t_{0.5}$ ($^{\circ}\text{C}$)	-21.96	-26.55

Table 4.3 The calculated radius and length of three-phase contact line between water droplet and solid surface.

	θ	r (mm)	S (mm)
Uncoated	20	3.294	20.70
Coated	107	1.431	8.99

Further investigation of the statistical nucleation rate on the three-phase contact line verified the low nucleation rate of the THRC coated glass (Fig. 4.8d). For any given temperature in the range, the nucleation rate for the THRC coated glass is always much lower than the uncoated glass, which perfectly explains the lower icing temperature.

Figure 4.9 (a) Time-lapse images of frost-formation experiments at -15 °C in still air (80% RH) on the THRC coated and uncoated glass slides, and (b) images of melted ice formed on the THRC coated and uncoated glass slides as shown in (a). Scale bar, 10 mm. (c) Water wettability of THRC under low temperatures (from 25 °C to -20 °C).

To understand the frost formation behavior on the THRC coated glass at freezing conditions, samples were placed on a cooling stage without water droplets (Supplementary Video S4). Water vapor was first cooled down to fog up the sample surface and then visible water droplets were formed. The dew drops started to freeze when the temperature is cooled below the freezing point. Figure 4.9a compares the resistance to frost formation of the THRC glass in comparison with the uncoated one at -15 °C and 80 % RH. It was observed that the icing of dew droplets on the bottom of the uncoated glass (circled region on the left hand side sample) took place after 231 ± 2.0 s. At 419 ± 2.4 s, the whole uncoated glass surface was covered with ice. While icing started from the uncoated edge of the THRC coated glass at 524 ± 3.9 s (circled region on the right hand side sample), and then ice

gradually spread to the center of the surface until full coverage at 752 ± 4.5 s. The THRC coated glass presented significant delay in frost formation.

A significant resistance to water condensation of the THRC coated glass slide was observed during the melting cycles of the frost-formation experiment. When being heated from -15 to 25 °C at 10 °C/min, the THRC coated glass slide demonstrated better repellency against water condensation as shown in Fig. 4.9b. Tiny water mists were observed on the coated glass. In contrast, large and continuous water droplets were formed on the uncoated glass. Besides, the water contact angles and sliding angles of THRC at low temperatures also verified its good resistance to water condensation (Fig. 4.9c). A decrease in the water contact angle of THRC was observed when the temperature was reduced from 25 °C to -20 °C due to the condensation effect. However, it is noteworthy that the contact angle of all the tested coatings approached a steady-state value of around 90° when the temperature falls below zero degree. Moreover, a 10 μ l water droplet could slide down the THRC even when the temperature was -20 °C, and there was only a slight increase in the sliding angle at different temperatures, indicating a reasonably good condensation resistance of THRC. The water repellent nature of the THRC helps protect the surface from incoming moisture / water and also ensure low ice adhesion, making it capable of delaying ice formation and easily removing formed ice.

4.3.5 Mechanical Robustness and Durability of THRC

The THRC layer, comprising ceramic sol and a high weight percentage of nanoparticles, possess a much higher hardness compared to superhydrophobic coatings and polymer-based water repellent coatings. An increase in stirring time has significantly increased the hardness and modulus of our coatings (Fig. 4.10a). This is reasonable due to the gradually reduced porosity of our coatings. The THRC presented the highest hardness and modulus of 270 ± 10 MPa and 2.07 ± 0.08 GPa, respectively. Although the modulus and hardness is lower than that of iCVD film [52], they are comparable to the aeronautical livery coating [53] as shown in Table 4.4.

Figure 4.10 (a) The hardness and modulus of coatings with different stirring time measured by nanoindentation, (b) the measured pencil-scratch resistance of the THRC and microscope images of the scratched area, and (c) rate of weight loss, surface roughness (RMS) of the THRC under different sandblasting conditions, and the corresponding ice-adhesion strength of coatings after sandblasting.

In addition, other mechanical properties such as pencil scratch test, cross-cut adhesion and pull-off adhesion were carried out on the THRC to further investigate the extent of coating adhesion to the substrate surface. The pencil hardness was 4 H according to ASTM D3363 standard test method as shown in Fig. 4.10b. The 4 H pencil scratch resistance of the THRC coating is higher than available reports (Table 1). [54-56] The coating also exhibited good adhesion to substrates: the cross-cut adhesion of 5 B (based on ASTM D 3359) was obtained for the coating on epoxy substrates and 4 B on glass substrates. The results are comparable to the recently published anti-icing coatings (Table 4.4) [53, 56-59]. A dolly pull-off adhesion strength of 5.12 ± 0.07 MPa was obtained according to ISO 4624 standard

test method. The adhesion strength is more than two times higher than that of the aeronautical livery coating [53] and the silicone elastomer coating (Table 4.4) [60]. Comprehensive mechanical studies have verified the superior mechanical properties of the THRC to the state-of-the-art superhydrophobic coatings, SLIPS and polymer coatings.

To study the mechanical durability of anti-icing coatings, researches employed eraser rubbing [61], sandpaper abrasion [62], and sand erosion tests [63]. In this study, sand erosion test was carried out (size of sands: 10 ~ 40 μm ; pressure: 100 kPa and 200 kPa) to investigate the durability of the THRC. As shown in Fig. 4.10c, the rate of weight loss is approximately 0.025 $\text{g}/(\text{s}\cdot\text{m}^2)$ under the applied pressures. Although the sandblasting test has slightly roughened the surface (Fig. 4.10c), the THRC could still maintain a low ice-adhesion strength in the range 50-60 kPa at -20 $^{\circ}\text{C}$, indicating its robust icephobicity under sand erosion environment.

Table 4.4 The hardness, modulus, scratch resistance and adhesion strength to the substrates of the THRC in comparison with other available reports.

	Nanoindentation		Cross-cut adhesion		PosiTest Pull-Off adhesion test (MPa)	Pencil scratch resistant
	Hardness (MPa)	Modulus (GPa)	On glass slide	On GFRE		
THRC	270 $\pm$ 10	2.07 $\pm$ 0.08	4 B (5 % delaminated areas due to scratch)	5 B (No delamination, smooth cut)	5.12 $\pm$ 0.07 (on GFRE)	4H
Bilayer icephobic film synthesized on steels or silicon wafers via iCVD [52]	479 $\pm$ 7	19.1 $\pm$ 1.2	N/A		N/A	N/A
Aeronautical livery coating on the carbon fiber reinforced polymer (CFRP) [53]	141 $\pm$ 9	4.8 $\pm$ 0.3	5 B on the CFRP		2.41 $\pm$ 0.04 (on CFRP)	N/A
An Icephobic paint [54]	N/A	N/A	N/A		N/A	2 H
A hybrid film (weight ratio: SiO ₂)	N/A	N/A	0 B on glass and Al substrates		N/A	4 B

(sol)/copolymers=0.8) [55]						
Ice Release Coatings [56]		N/A	N/A	5B on aerospace exterior coatings	N/A	2H~3H
Al ₂ O ₃ /PTFE icephobic coatings [57]		N/A	N/A	5 B of PTFE on the anodized Al 6061	N/A	N/A
An icephobic superhydrophobic coating [58]		N/A	N/A	5 B on aluminium alloys	N/A	N/A
Icephobic hierarchically textured coatings [59]		N/A	N/A	5 B on aluminium surfaces	N/A	N/A
Silicone elastomer coatings [60]	Without silane-based intermedia layer	N/A	N/A	N/A	0.431	N/A
	With silane-based intermedia layer	N/A	N/A	N/A	1.494	N/A

4.4 Summary

This chapter demonstrated a simple method to prepare a mechanically robust, transparent, anti-icing coating with self-cleaning property. It is proved that sol-gel coatings with large percentage of nanoparticles could achieve a high level of transparency once the particles are well dispersed through stirring in the sol preparation stage. Benefited from this method, large-scale transparent icephobic coatings with good resistance to water condensation have been fabricated. Furthermore, the transparent, ice/liquids repellent coating demonstrates high hardness, scratch resistance and good adhesion to the substrates. The sol-gel method is simple, low cost, and applicable to complex shapes and large structures. Therefore, this robust and durable anti-icing coating holds great promise for practical anti-icing and self-cleaning applications.

References

- [1]. L. Bocquet, E. Lauga. *Nature materials*. **2011**, 10, 334-337.
- [2]. P. Guo, Y. Zheng, M. Wen, C. Song, Y. Lin and L. Jiang. *Advanced Materials*. **2012**, 24, 2642-2648.

- [3]. M.J. Kreder, J. Alvarenga, P. Kim and J. Aizenberg. *Nature Reviews Materials*. **2016**, 1, 15003.
- [4]. K. Golovin, S.P. Kobaku, D.H. Lee, E.T. DiLoreto, J.M. Mabry and A. Tuteja. *Science Advances*. **2016**, 2, e1501496.
- [5]. V. Hejazi, K. Sobolev and M. Nosonovsky. *Scientific Reports*. **2013**, 3, 2194.
- [6]. T.S. Wong, S.H. Kang, S.K. Tang, E.J. Smythe, B.D. Hatton, A. Grinthal and J. Aizenberg. *Nature*. **2011**, 477, 443-447.
- [7]. R. Xiao, N. Miljkovic, R. Enright and E.N. Wang. *Scientific Reports*. **2013**, 3, 1988.
- [8]. J.D. Smith, R. Dhiman, S. Anand, E. Reza-Garduno, R.E. Cohen, G.H. McKinley and K.K. Varanasi. *Soft Matter*. **2013**, 9, 1772-1780.
- [9]. B.P. Binks, T.S. Horozov. *Angewandte Chemie*. **2005**, 117, 3788-3791.
- [10]. R.G. Karunakaran, C.H. Lu, Z. Zhang and S. Yang. *Langmuir*. **2011**, 27, 4594-4602.
- [11]. H. Zhou, H. Wang, H. Niu, A. Gestos, X. Wang and T. Lin. *Advanced Materials*. **2012**, 24, 2409-2412.
- [12]. S.G. Lee, D.S. Ham, D.Y. Lee, H. Bong and K. Cho. *Langmuir*. **2013**, 29, 15051-15057.
- [13]. X. Wu, Q. Fu, D. Kumar, J.W.C. Ho, P. Kanhere, H. Zhou and Z. Chen. *Materials & Design*. **2016**, 89, 1302-1309.
- [14]. A.B.D. Cassie, S. Baxter. *Transactions of the Faraday Society*. **1944**, 40, 0546-0550.
- [15]. T. Furuta, M. Sakai, T. Isobe and A. Nakajima. *Langmuir*. **2010**, 26, 13305-13309.
- [16]. R. Karmouch, G.G. Ross. *The Journal of Physical Chemistry C*. **2010**, 114, 4063-4066.
- [17]. L. Yin, Q. Xia, J. Xue, S. Yang, Q. Wang and Q. Chen. *Applied Surface Science*. **2010**, 256, 6764-6769.
- [18]. T. Verho, C. Bower, P. Andrew, S. Franssila, O. Ikkala and R.H. Ras. *Advanced Materials*. **2011**, 23, 673-678.
- [19]. J. Bravo, L. Zhai, Z. Wu, R.E. Cohen and M.F. Rubner. *Langmuir*. **2007**, 23, 7293-7298.
- [20]. M. Layani, S. Magdassi. *Journal of Materials Chemistry*. **2011**, 21, 15378-15382.
- [21]. Y. Rahmawan, L. Xu and S. Yang. *Journal of Materials Chemistry A*. **2013**, 1, 2955-2969.

- [22]. A.K. Boal, F. Ilhan, J.E. DeRouchey, T. Thurn-Albrecht, T.P. Russell and V.M. Rotello. *Nature*. **2000**, 404, 746-748.
- [23]. K.A. Dunphy Guzman, M.P. Finnegan and J.F. Banfield. *Environmental Science & Technology*. **2006**, 40, 7688-7693.
- [24]. H. Ogihara, J. Xie, J. Okagaki and T. Saji. *Langmuir*. **2012**, 28, 4605-4608.
- [25]. X. Deng, L. Mammen, H.J. Butt and D. Vollmer. *Science*. **2012**, 335, 67-70.
- [26]. M.I. Dafinone, G. Feng, T. Brugarolas, K.E. Tettey and D. Lee. *ACS Nano*. **2011**, 5, 5078-5087.
- [27]. D.K. Owens, R. Wendt. *Journal of Applied Polymer Science*. **1969**, 13, 1741-1747.
- [28]. D. Kaelble. *The Journal of Adhesion*. **1970**, 2, 66-81.
- [29]. W. Rabel. *Farbe und Lack*. **1971**, 77, 997-1006.
- [30]. Q. Fu, X. Wu, D. Kumar, J.W. Ho, P.D. Kanhere, N. Srikanth, E. Liu, P. Wilson and Z. Chen. *ACS Applied Materials & Interfaces*. **2014**, 6, 20685-20692.
- [31]. Q.T. Fu, E.J. Liu, P. Wilson and Z. Chen. *Physical Chemistry Chemical Physics*. **2015**, 17, 21492-21500.
- [32]. L. Feng, Y. Zhang, J. Xi, Y. Zhu, N. Wang, F. Xia and L. Jiang. *Langmuir*. **2008**, 24, 4114-4119.
- [33]. G. McHale. *Langmuir*. **2009**, 25, 7185-7187.
- [34]. B. Bhushan, M. Nosonovsky. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. **2010**, 368, 4713-4728.
- [35]. O.I. Vinogradova. *International Journal of Mineral Processing*. **1999**, 56, 31-60.
- [36]. C. Sendner, D. Horinek, L. Bocquet and R.R. Netz. *Langmuir*. **2009**, 25, 10768-10781.
- [37]. H.Y. Erbil, A.L. Demirel, Y. Avcı and O. Mert. *Science*. **2003**, 299, 1377-1380.
- [38]. A. Lafuma, D. Quéré. *Nature materials*. **2003**, 2, 457-460.
- [39]. J.S. Pérez, E.R. Porcel, J.C. López, J.F. Sevilla and Y. Chisti. *Chemical Engineering Journal*. **2006**, 124, 1-5.
- [40]. C. Collier, T. Vossmeier and J. Heath. *Annual Review of Physical Chemistry*. **1998**, 49, 371-404.
- [41]. J.N. Israelachvili, *Intermolecular and Surface Forces*. ed. 2011: Academic press.

- [42]. R.J. Plunkett, *The history of polytetrafluoroethylene: discovery and development*, in *High Performance Polymers: Their Origin and Development*. 1986, Springer. p. 261-266.
- [43]. D.Y. Mikhaylov, Y.H. Budnikova. *Russian Chemical Reviews*. **2013**, 82, 835.
- [44]. B.V. Velamakanni, J.C. Chang, F.F. Lange and D.S. Pearson. *Langmuir*. **1990**, 6, 1323-1325.
- [45]. J. Amalvy, M. Percy, S. Armes and H. Wiese. *Langmuir*. **2001**, 17, 4770-4778.
- [46]. P. Kim, T.S. Wong, J. Alvarenga, M.J. Kreder, W.E. Adorno-Martinez and J. Aizenberg. *ACS nano*. **2012**, 6, 6569-6577.
- [47]. E. Rio, A. Daerr, B. Andreotti and L. Limat. *Physical Review Letters*. **2005**, 94, 024503.
- [48]. L. Gao, T.J. McCarthy. *Langmuir*. **2006**, 22, 6234-6237.
- [49]. S. Suzuki, A. Nakajima, N. Yoshida, M. Sakai, A. Hashimoto, Y. Kameshima and K. Okada. *Chemical Physics Letters*. **2007**, 445, 37-41.
- [50]. S. Jung, M. Dorrestijn, D. Raps, A. Das, C.M. Megaridis and D. Poulikakos. *Langmuir*. **2011**, 27, 3059-3066.
- [51]. F. Tavakoli, S.H. Davis and H.P. Kavehpour. *Journal of Coatings Technology and Research*. **2015**, 12, 869-875.
- [52]. H. Sojoudi, G.H. McKinley and K.K. Gleason. *Materials Horizons*. **2015**, 2, 91-99.
- [53]. L. Mazzola. *Surface Engineering*. **2016**, 32, 733-744.
- [54]. S. Kimura, Y. Yamagishi, A. Sakabe, T. Adachi and M. Shimanuki. 2007, SAE Technical Paper.
- [55]. Y. Huang, M. Hu, S. Yi, X. Liu, H. Li, C. Huang, Y. Luo and Y. Li. *Thin Solid Films*. **2012**, 520, 5644-5651.
- [56]. G. Tang, Y.H. Yeong and M. Khudiakov. *Advances in Polymer Science*, Springer, Berlin, Germany, **2017**, 1-17.
- [57]. R. Menini, M. Farzaneh. *Surface and Coatings Technology*. **2009**, 203, 1941-1946.
- [58]. R. Menini, Z. Ghalimi and M. Farzaneh. *Cold Regions Science and Technology*. **2011**, 65, 65-69.
- [59]. G. Momen, M. Farzaneh. *Applied Surface Science*. **2014**, 299, 41-46.
- [60]. M. Esfandeh, S. Mirabedini, S. Pazokifard and M. Tari. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **2007**, 302, 11-16.

- [61]. J. Gao, A. Martin, J. Yatvin, E. White and J. Locklin. *Journal of Materials Chemistry A*. **2016**, 4, 11719-11728.
- [62]. N. Wang, D. Xiong, Y. Deng, Y. Shi and K. Wang. *ACS Applied Materials & Interfaces*. **2015**, 7, 6260-6272.
- [63]. R. Liao, Z. Zuo, C. Guo, Y. Yuan and A. Zhuang. *Applied Surface Science*. **2014**, 317, 701-709.

Chapter 5* Design and Durability Study of Room-Temperature Processable Fluorine-free Icephobic Coatings

Design and Durability Study of Room-Temperature Processable Fluorine-free Icephobic Coatings

This chapter focuses on the mechanical property and durability of icephobic coatings that are fluorine-free and can be processed at ambient temperature. The icephobic coatings were fabricated with a silicone based epoxy resin and nanoparticles with different size. The design of single-size and dual-size nanoparticles led to different surface morphologies. Icephobicity of coatings has been evaluated with the measurement of ice-adhesion strength and ice-accumulation rate. The investigation of the coatings' mechanical properties was following ISO or ASTM standards. The durability of coatings has been evaluated with UV, water condensation and sands erosion. Specially, the mechanical properties and durability of coatings have been compared with available reported anti-icing coatings.

*This section submitted substantially as X. Wu, X. Zhao, J. W. C. Ho, Z. Chen., *Chemical Engineering Journal*, 2019, Vol. 355, pp. 901-909.

5.1 Introduction

To minimize the hazard of ice accretion on facilities, transportation vehicles and buildings, and to reduce the labour cost and downtime associated with removal of accumulated ice, considerable interest on anti-icing coatings has been shown since the 1900s. The first reported anti-icing composition designed for automobile radiator was patented in 1918 [1]. In 1956, Rolle and Barnes claimed that cellulose lacquers could withstand the icing and de-icing test [2]. Jellinek studied the effect of a monolayer on ice adhesion in 1962 [3]. Bascom et al. investigated the ice-adhesion strength and mechanism of failure on hydrophobic and hydrophilic surfaces [4]. Since then, a lot of research work has been carried out, ranging from liquid & grease filled coatings to modified epoxy or urethane paints [5, 6]. Recently available reports show that the adhesion strength between ice and solid surfaces depends greatly on van-der-Waals forces [7]. Thus, low surface energy and textures of solid surface can greatly help in the release of the accumulated ice. In recent years, there has been a growing interest in superhydrophobic coatings consisting of hierarchical micro-nano structures [8-11]. With low surface energy, the trapped air pockets on the coating surface are beneficial in reducing the adhesion of ice, because they are able to decrease the actual contact area between ice and a coating surface. In addition, the presence of air between ice and the coating surface reduces heat transfer, and at the same time provides stress loci to initiate cracks between the substrate and ice during ice removal [7, 12]. However, the existing of micro-nano structures weakens the mechanical durability of superhydrophobic coatings, and in some cases, moisture condensation in the micro / nanoporous surface may lead to a larger (than nominal) contact area between ice and the coating surface, resulting in increased ice-adhesion strength.

SLIPS, inspired by *Nepenthes* pitcher plants, has been explored by some researchers as another strategy to achieve low ice adhesion [13]. Liu et al. prepared anti-icing SLIPs coatings from silicone rubber solution [14]. Zhang et al. reported a double-layered SLIPs coating prepared by hydrothermal reaction followed by perfluoropolyether liquid infusion [15]. An ice releasing coating was manufactured by silicone oil or fluorosilicone fluid embedded within cross-linked silicone resin [16]. The major challenges of SLIPs are

depletion of infused liquids and poor mechanical properties of the porous matrix. Yeong et al. developed an oil-infused icephobic elastomeric coating which showed good durability to abrasion by self-replenish the lost oil [17]. In another effort to avoid depletion of the infused liquid, Coady et al. infused UV-cured siloxane resin into anodized coupons, which were treated with *n*-decyltrichlorosilane and silicone oil [18]. However, after seven de-icing cycles, removal of resin / oil layer was observed.

Among existing reports, epoxy coatings are practically favourable with the advantage of low cost, no limitation on the dimension and shape of targeted substrates, being scalable and easy to process at low temperatures. Li et al. reported a fluorinated coating embedded with surface-modified nano-silica which is promising for anti-icing applications [19]. The coating exhibits superhydrophobicity after 4 weeks of acid/alkali, heat / cool treatment. Atta et al. successfully developed superhydrophobic epoxy coatings with the help of fatty acids modified calcium carbonate nanoparticles [20]. Moreover, magnetic nanoparticles which could be used as heat mediators were introduced into fluorinated epoxy resin by Zhang et al., and they obtained superhydrophobic coating exhibited ice adhesion around 200 kPa [21]. Guo's group demonstrated anti-icing coatings fabricated by spreading $\text{Mg}(\text{OH})_2$ particles treated with stearic acid on the top surface of epoxy resins [22]. Despite these advances, work focusing on the mechanical properties and durability of icephobic coatings remains limited, especially anti-icing properties under UV irradiation and harsh sand erosion environment. Considering that there are different requirements for the mechanical properties and durability for different practical applications (e.g. aeroplane wings vs. wind turbine blades), there is demand for different icephobic materials that can display good resistance under the different application environments.

In terms of the low surface energy materials, fluorocarbons are often used in icephobic coatings because of their low surface energy. For example, Zhang et al. demonstrated a slippery anti-icing coating by trapping perfluoropolyether in the porous AZ31 Mg alloy [15]. Emelyanenko et al. fabricated a fluorooxysilane modified silicone rubber coating with the help of laser treatment, and investigated the anti-icing behaviors of the coating at low temperatures [23]. However, fluorochemicals are bio-accumulative and potentially harmful

to human health. Industries have started to ban the use of long-chain fluorocarbons. As a result, research activity has been in the rise to seek effective replacement for fluorochemicals in hydrophobic and icephobic coatings. In this paper, we fabricated fluorine-free superhydrophobic coatings via a facile method based on silicone-epoxy and dual-scale SiO₂ nanoparticles design. The process is simple and coating can be cured at room temperature. The prepared coatings were tested under simulated harsh environments such as pressurized sand erosion and UV / condensation exposure. The developed superhydrophobic coatings demonstrated excellent durability, and are promising for practical applications.

5.2 Experimental

5.2.1 Materials

SiO₂ nanoparticles with sizes of 10-20 nm and 200 nm, and butyl acetate (99 wt. %) were obtained from Sigma Aldrich. A commercially available silicone-epoxy hybrid resin (SILIKOPON® EF) and PDMS (commercial name Sylgard 184) were obtained from Evonik industries and Dow Corning, respectively. Both are two-part products and were used with weight ratio between the base and hardener at 2 : 1 and 10 : 1, respectively. Tinuvin 292, obtained from BASF, was used as UV stabilizer. Substrates were cut from GFRE plates. For comparison, proprietary polyurethane based composite coating, (denoted as the PU coating thereafter), was acquired and tested.

5.2.2 Preparation Methods

In a typical fabrication process, PDMS grafted SiO₂ nanoparticles was prepared by mixing the elastomer base, its curing agent, and butyl acetate as the solvent for 10 min. The weight ratio of base: curing agent: solvent: silica particles was 1 : 0.1 : 20 : 4. To investigate the effect of dual-sized SiO₂ nanoparticles, comparison was made between the PDMS modified two sized particles (200 nm and 10-20 nm with weight ratio of 1 : 2 mixed) and the 10-20 nm particles only. SILIKOPON® EF (two parts used together) and Tinuvin 292

were added into the prepared SiO₂ particle suspensions and mixed for another 10 min under ambient condition. The detailed weight ratio of the mixtures and sample ID are show in Table 5.1. S20 denotes the coating containing the single-sized 10-20 nm particles, while S200 stands for the coating containing the dual sized silica particles (200 nm and 10-20 nm). A mechanical mixer was used during the mixing process at a speed of 2000 rpm. The obtained particle dispersion solutions were spray-coated onto the GFRE substrates through an airbrush kit (AS06KB) with a distance from the spraying nozzle to the substrate of 10 cm. After 24 h curing at room temperature, superhydrophobic coatings were obtained.

Table 5.1 Sample ID and the corresponding weight ratio of the two types of coatings with different SiO₂ NP sizes.

	SILIKOPON® EF		Sylgard 184		Butyl acetate	SiO ₂ nanoparticles		Tinuvin
	Part A	Part B	Part A	Part B		200 nm	10-20 nm	292
S20	9	4.5	1	0.1	20	0	4	0.08
S200	9	4.5	1	0.1	20	2.67	1.33	0.08

5.2.3 Characterization and Mechanical Testing

The surface morphology of the coatings was observed using a field emission scanning electron microscope (FESEM, JEOL-7600F, Japan). The contact angle and roll-off angle of water were measured with a contact angle system (OCA 20, Dataphysics Co., Germany). The surface roughness of the coatings was evaluated by a surface profiler (Alpha-Step IQ Surface Profiler, KLa Tencor, USA) with a scanning length of 6 mm. The elastic modulus and hardness of the deposited coatings were measured using a nano-indenter (Nano Indenter XP® system, MTS, US) with continuous stiffness measurement (CSM) method [24]. 10 ~ 12 indents were made on each sample. At least three samples of each type of coating were tested. Considering the effect of surface roughness, averaged results were obtained in the depth range of 1500 ~ 2000 nm. For the PU coating, because of its elastomeric nature, continuous stiffness measurement may not be appropriate. Therefore, static loading was used for PU coating. The hardness and Young's modulus values were obtained at the same depth range, 1500 ~ 2000 nm, as in the CSM method. Pencil scratch

test of coatings was assessed using a commercial pencil scratch tester (Scratch Hardness Tester Model 291, ERICHSEN, Germany) according to ISO 15184 standard test method. The brittleness and adhesion properties of coatings were measured by cross-cut adhesion test kit (Cross-Cut Adhesion Test KIT CC1000, TQC, Netherlands) based on ISO 2409 standard test method. After the cross cutting, the surfaces were examined under optical microscope (Olympus BX51, Japan). The bond strength between coatings and GFRE substrates was conducted by an adhesion tester (PosiTest AT-M20, Defescal, USA) according to ISO 4624 standard.

5.2.4 Durability Assessment

UV resistance of the coatings was analyzed by UV accelerated weathering machine (SDL ATLAS, UK) according to ISO 11507 standard. Samples were mounted in the weathering chamber and subjected to a cycle of 4 hours exposure to intense ultraviolet radiation at 60 °C, followed by 4 hours moisture exposure by condensation at 50 °C. The cycle was continued for 288 hours. In addition, a home designed micro-sand blaster was also used to investigate the anti-icing performance of coatings after removal of top surface by sand erosion [25]. Silica particles in size of 63 μm (220 mesh) were used as the test media. The coatings were placed horizontally under the sand spraying nozzle with a distance of 10 cm. The erosion was carried out by impinging the sand particles perpendicular to the coating surface for 30 s at a pressure of 200 kPa over an exposed area of 2.43 cm². The loss in weight was recorded after the sand erosion test. Optical microscope and FESEM were used to observe the eroded regions on the coating surface. The overall depth of the surface damage was scanned by a surface profilometer (Alpha-Step IQ Surface Profiler, KLA Tencor, USA) with a scanning length of 6 mm. Change in water wettability and icephobicity of the coatings were measured after the erosion test.

5.2.5 Ice-adhesion Strength and Ice Accumulation Tests

To prepare for the ice-adhesion strength test, a Teflon tube with an inner diameter of 18 mm was filled with DI water, and then covered with the coated substrate on top. The

substrate was flipped upside down before being placed inside a climate chamber (Cincinnati Sub-Zero environmental chambers, USA) for 24 h at -15 °C. The prepared ice block was sheared off the substrate by a moving piston till failure [26]. The peak force at which the ice block was removed from the substrate was recorded and used for the calculation of ice-adhesion strength. The reported ice-adhesion strength is an average value of at least six measurements on the same position of more than three samples.

Ice accumulation on the sample surface was investigated in the same climate chamber as described before at temperature of -15 °C following our previously reported method [27]. The coated substrate was placed at an angle of 45° to the horizontal plane. Pre-cooled DI water was prepared by storing the container in a refrigerator set at -5 °C until part of the bulk water became ice (the temperature of water was therefore around 0 °C). The water dripping rate was kept at 1 drop every 5 seconds. Each ice accumulation test lasted for 10 min. The dimension of the substrate is 65 mm by 42 mm. At least three samples of each type of coatings were tested, and each sample was repeated for 3 times at the same position. The percentage accumulation with respect to the total weight of the dripped water was recorded.

5.3 Results and Discussion

5.3.1 Design Strategy

SiO₂ nanoparticles have been widely used to prepare superhydrophobic coatings due to their cost-effectiveness, chemical durability and good mechanical properties [28-30]. Athauda et al. [31] investigated dual-size effect of functionalized silica nanoparticles of 7, 12, 20, and 40 nm by layer-by-layer deposition and pointed out that surface roughness can be tuned by employing nanoparticles with different sizes. Raspberry-like SiO₂ particles were prepared by some researchers to fabricate micro-nanostructure surface with superhydrophobicity [32-34]. In this study, dual-sized PDMS modified nanoparticles (10-20 nm SiO₂ and 200 nm SiO₂ nanoparticles) were used to produce dense packing of micro-nanostructure. An in-depth and systematic study of the effect of using dual-sized particles

on icephobicity and mechanically durability was carried out in comparison with the single-size particles. Particularly, to enhance the mechanical durability, nanoparticles were introduced in an epoxy matrix as shown in Fig. 5.1a. nanoparticles have significantly large specific surface areas and tend to agglomerate due to the van-der-Waals forces [35]. The maximally entangled nanoparticles offer a methodical variation of agglomeration size as well as arrangement in surface texture. Smaller nanoparticles have larger specific surface area and greater total surface energy. When small particles are used alone, they tend to show more severe agglomeration and larger porosity as illustrated in Fig. 5.1a.

However, when the two sizes are used together, the small particles are relatively well dispersed between the large ones, effectively reducing the agglomeration and pore size as shown in the schematic illustration. For verification, single-sized and dual-sized superhydrophobic coatings were prepared. Figure 5.1b-c shows the obtained surface morphology of the S20 and S200 coatings, respectively. A micro-nanostructure was observed on both coating surfaces, and such surface feature is critical in introducing superhydrophobicity [28]. The micro-nanostructure enables water droplets to easily roll off the coating surface with contact angle larger than 150° as shown in Fig 5.1d and insets in Fig 5.1b-c. Between the two types of coatings, large protrusions and pores with size around 1-3 μm could be clearly seen in the S20 coatings (Fig 5.1b). In comparison, more densely packed surface with small pores of size less than 500 nm was observed on the S200 coatings (Fig 5.1c). When 33 wt.% of the 10-20 nm SiO_2 nanoparticles were replaced by the same amount of 200 nm SiO_2 particles, a dramatic decrease in the surface porosity and protrusion size was observed. This induced a reduction in the surface roughness of coatings as shown in Fig 5.1e. The S20 coatings presented a surface roughness (root-mean-square roughness, RMS) of $\sim 1.4 \mu\text{m}$, while the S200 exhibited a surface roughness of $\sim 0.9 \mu\text{m}$. Although S20 and S200 coatings exhibited significant difference in surface roughness values, the contact angle of S20 and S200 coatings were very close, and both are larger than 150° due to the micro-nanostructure. However, S200 coatings displayed a slightly higher roll-off angle due to lower surface roughness.

Figure 5.1 (a) Schematic drawing of the surface feature formation mechanisms of S20 and S200, surface morphology of (b) S20 and (c) S200 coatings measured by FESEM, insets are profile of 5 μ l water droplet on the coating surfaces, (d) measured water contact angles and water roll-off angles of S20 and S200 coatings, (e) surface roughness of S20 and S200 coatings.

5.3.2 Anti-icing Performance

Even though the difference in surface features has limited effect on water contact angle and water roll-off angle of the S20 and S200 coatings, it may pose different impact on the icing behavior on the coatings. To better understand the anti-icing properties of S20 and S200 coatings, the PU coatings, which are widely used as a protective layer on outdoor facilities, were measured and compared.

Figure 5.2 (a) Ice-adhesion strength of S20 and S200 coatings, insets are schematics of ice formation mechanisms on these coating surfaces, (b) ice accumulation results of S20 and S200 coatings.

Figure 5.2a shows the measured ice-adhesion strength of PU, S20 and S200 coatings at -15 °C. The obtained ice-adhesion value for PU coatings was larger than 400 kPa and significantly higher than both S20 and S200 coatings. Besides, the lowest ice-adhesion value (64.7 ± 5.4 kPa) was obtained on the S200 coatings, which was about half that of the S20 coatings. It is well accepted that the interaction forces acting at ice–substrate interface include electrostatic forces, van-der-Waals forces, hydrogen bonding, and mechanical interaction.[36] Although both S20 and S200 coatings contain water repellent $-\text{CH}_3$ groups from PDMS and silicone-epoxy hybrid resin which can better prevent or repel frost formation in the air pockets, coatings still absorb water molecules due to electrostatic forces and hydrogen bonding. Due to the high polar nature of water and ice, the directions of water molecules can be controlled by electric fields. When water freezes, the molecules

still keep their polar behavior and tend to adhere to solid surface under electrostatic forces as illustrated in Fig. 5.2a insets (the electrostatic force is marked by the orange dots).

Coatings with larger pores allow access to a greater amount of water adsorption sites than small pores. Therefore, the S20 coating possessing larger pores provides more water absorption site than the S200 coating under high humidity and low temperature condition. Besides, larger pores in the S20 coating are prone to the sagging effect as schematically illustrated in Fig. 5.2a (insets). This leads to greater mechanical interlocking and larger electrostatic forces between water molecular and the S20 coating surface. The less porous S200 coatings promoted and maintained the presence of tiny air pockets at the ice-coating interface to disrupt intimate contact between the ice and the substrate; thus has significantly reduced the ice adhesion. The ice-adhesion strength of the S200 coating is much lower than the reference PU coating and some reported superhydrophobic and hydrophobic coatings [36-38], which reported ice-adhesion strength larger than 400 kPa due to serious mechanical interlocking and hydrogen bonding. The obtained adhesion strength at below 100 kPa means the ice can be easily removed by small centrifuging force, gravity, vibration or even wind flow. Some literatures have set adhesion strength below 100 kPa as a key criterion for defining icephobic coatings [39, 40].

Ice accumulation is another important criterion for icephobicity. In the current work, pre-cooled water ($\sim 0^\circ\text{C}$) was dropwise dripped on to the PU, S20 and S200 coating surfaces at -15°C to evaluate the resistance to ice accumulation. The obtained ice accumulation results of the three separate runs on the same position of each type of samples are shown in Fig. 5.2b. A great reduction in ice accumulation was observed on the S20 and S200 coatings compared to the PU coatings. Besides, there was no apparent difference in ice accumulation on S20 and S200 coatings due to their similar water wettability. The above results are also in line with the recent experimental observations where surface wettability is a key controlling factor for reducing ice accretion and improving water drop shedding effect [41-43]. Although our coatings could not fully prevent ice accumulation, the low adhesion, particularly the one by the S200 coating, enables easy removal of the accumulated ice.

5.3.3 Robust Mechanical Properties

Table 5.2 Summary of measured mechanical properties of the PU, S20, S200 coatings in comparison with literature data for icephobic coatings.

Testing method	Cross-cut test (ISO 2409)	Pencil scratch test (ISO 15184)	Dolly pull-off test (ISO 4624)* (MPa)	Nano-indentation	
				Modulus (GPa)	hardness (MPa)
PU coating	4B (5 % delaminated areas due to scratch)	4B	5.99 ± 0.16 (B, 45%)	0.11 ± 0.01	21 ± 3
S20	5B (Nearly no delaminated areas)	2H	$> 3.50 \pm 0.75$ (Y)	1.28 ± 0.30	37 ± 8
S200	5B (Nearly no delaminated areas)	3H	$> 3.70 \pm 0.52$ (Y)	2.39 ± 0.66	69 ± 14
Hybrid copolymer film [44]	0B	4B	N/A	N/A	N/A
Icephobic hierarchically textured coatings[45]	5B	N/A	N/A	N/A	N/A
Icephobic superhydrophobic coating [46]	5B	N/A	N/A	N/A	N/A
Al ₂ O ₃ /PTFE icephobic coatings [47]	5B	N/A	N/A	N/A	N/A
Ice Release Coatings[48]	5B	2H~3H	N/A	N/A	N/A

Icephobic paint[49]		N/A	2H	N/A	N/A	N/A
Aeronautical livery coating [50]		5B	N/A	2.41 ± 0.04	4.8 ± 0.3	141 ± 9
Silicone elastomer coating [51]	Without silane-based intermediate layer	N/A	N/A	0.431	N/A	N/A
	With silane-based intermediate layer	N/A	N/A	1.494	N/A	N/A
Bilayer icephobic film via iCVD [52]		N/A	N/A	N/A	19.1 ± 1.2	479 ± 7

* For the PU coating, 45% area of the coating is pulled off from the substrate. Following the test standard, “B” denotes adhesion failure between the coating and the substrate. While for S20 and S200 coatings, due to the low adhesion between the applied adhesive and the superhydrophobic surfaces, the coating did not pull off at the coating/substrate interface. In this case, “Y” indicates failure caused by the applied adhesive. The indicated values are the adhesion strength between the applied adhesive and the coating surface, and the actual coating adhesion strength should be greater than the listed values.

Figure 5.3 The surface appearance of (a) S20, (b) S200, and (c) PU coatings after the dolly pull-off test, the inset is a large piece peeled-off piece from the PU coating.

Mechanical properties and durability are primary concerns of anti-icing coatings for many practical applications in harsh environment. To determine the mechanical properties of S20 and S200 coatings, dolly-pull adhesion, cross-cut, pencil-scratch and nano-indentation tests were carried out according to the respective standards. The results are summarized in Table

5.2. Both S20 and S200 coatings demonstrated good adhesion toward the epoxy substrate according to the cross-cut test, and there were no observable coating chipping and peeling. The optical microscope images in Table 5.2 show that the coating edge after cutting was smoother than the reference PU coating, indicating good adhesion and non-brittleness of the coatings. The 5 % delaminated areas of the PU coating is due to the wedge spallation failure which was caused by the applied compressive stress along the scratch groove, as well as ahead of the moving cutter [53]. The cross-cut adhesion test results of S20 and S200 coatings are comparable and are both better than currently literature reported icephobic coatings [44-48] listed in Table 5.2. Besides, the pencil scratch grade of 3H and 4H were obtained on the S20 and S200 coatings, respectively, which is significantly better than the PU coatings (4B) and other reported icephobic coatings [44, 49]. The dolly-pull test on S20 and S200 coatings found that the adhesion strength between coatings and substrates was stronger than that of coatings and the applied adhesive for the test. The failure occurred at the interface of coatings and the applied adhesive as shown in Fig. 5.3a-b. In comparison, the adhesion failure of PU coatings occurred at the interface between the substrates and PU coatings and a large peeling off area as shown in Fig 5.3c. Due to the different failure mechanisms, the reported pull-off data in Table 5.2 should not be used to compare the coating adhesion strength. The results indicate that when assessing the adhesion of hydrophobic coatings, the dolly-pull test may not be as effective as the cross-cut test despite that the former is quantitative while the latter is only quantitative. Because of the adhesive failure of S20 and S200 coatings, the actual adhesion strength of the coating to substrate should be greater than the reported value of 3.5~3.7 MPa, which is higher than the reported aeronautical livery coating [50] and silicone elastomer coating with or without intermediate layer to epoxy undercoat (adhesion strength is around 0.431 to 1.494 MPa) [51]. Further investigation was carried out to study the indentation hardness and Young's modulus of the coatings. S200 coatings presented the highest hardness and Young's modulus when compared with S20 and PU coatings. This is due to the incorporation of the nanoparticles and the reduced pore size as discussed before. Although the measured nano-indentation hardness and modulus of S200 coatings are lower than the reported bilayer icephobic film prepared via iCVD [52] and aeronautical livery coating [50], pencil scratch resistance and

dolly pull-off test verified the good scratch resistance and adhesion of S200 coatings to substrates.

5.3.4 Environmental Durability

In addition to icephobicity and mechanical properties, another key requirement for a practically applicable anti-icing coating is its environmental durability under conditions such as environmental weathering and mechanical erosion. In order to simulate the UV and condensation ageing effect during natural condition, an accelerated UV weathering test was employed to analyze the coating resistance according to ISO 11507 standard test method. The water contact angle, roll-off angle, ice-adhesion strength, percent ice accumulation, and the mechanical performances were measured after the UV weathering test. Comparison with the ones before the UV weathering test is shown in Table 5.3. It was reported that when a superhydrophobic surface begin to degrade, the water roll-off angle would change more rapidly than the water contact angle. It can be seen that after 288 h's UV and water exposure, there is ice-adhesion strength, ice accumulation and mechanical properties of S200 coatings is insignificant, indicating good water condensation and UV resistance. A slight degradation was observed for the S20 coatings. However, the degradation on the PU coatings was more severe than both S20 and S200 coatings. Recently, modern theories of wear pay more attention to the ratio between hardness and modulus (H/E) than hardness alone in measurement of the wear resistance of a coating system [54, 55]. The H/E is calculated to determine the elastic strain to failure in a surface contact. As shown in Table 5.3, PU coatings presented significantly higher H/E values than S20 and S200 coatings, this might due to the good elastic properties of PU coating and higher thickness than S20 and S200 coatings. (Thickness of PU is around 100 μm , while the thickness of S20 and S200 coatings is around 35~40 μm). The H/E value of S20 and S200 coatings are comparable with other reports [56, 57]. All of the measured coatings displayed similar H/E before and after UV and condensation weathering test, indicating their structure stability.

Table 5.3 Summary of results of coatings properties before and after UV and condensation weathering test.

	PU		S20		S200	
	Before weathering	After weathering	Before weathering	After weathering	Before weathering	After weathering
Water contact angle (°)	98 ± 1.3	83 ± 5.4	157 ± 1.2	154 ± 3.6	158 ± 1.8	156 ± 3.7
Water roll-off angle (°)	No	No	10 ± 1.4	30 ± 2.0	15 ± 2.1	20 ± 1.8
Ice adhesion (kPa)	450.0 ± 13.0	474.0 ± 20.0	113.9 ± 8.8	120.1 ± 9.1	64.7 ± 5.4	71.3 ± 6.8
Ice accumulation (wt. %)	24.3 ± 4.0	30.1 ± 4.3	8.2 ± 1.9	13.0 ± 1.7	6.8 ± 1.0	8.8 ± 1.6
Tape adhesion	4B	4B	5B	5B	5B	5B
Pencil scratch	4B	3H	3H	3H	4H	4H
Dolly pull adhesion (MPa)	5.99 ± 0.16 (B, 45%)	3.81 ± 0.12 (B)	>3.50 ± 0.75 (Y)	>3.35 ± 0.76 (Y)	>3.70 ± 0.52 (Y)	>3.64 ± 0.65 (Y)
Nano-indentation modulus (E , GPa)	0.11 ± 0.01	0.12 ± 0.01	1.28 ± 0.30	1.72 ± 0.43	2.39 ± 0.66	2.35 ± 0.68
Nano-indentation hardness (H , MPa)	21 ± 3	23 ± 3	37 ± 8	76 ± 12	69 ± 14	82 ± 16
H/E	0.19	0.19	0.03	0.04	0.03	0.03

Figure 5.4 (a) Weight loss of PU, S20 and S200 coatings after sand erosion. Optical microscope images of (b) S20 and (c) S200 coatings before and after sand erosion and the corresponding FESEM images of sand eroded areas. Insets in (b) and (c) are the corresponding FESEM images under high magnification.

The micro-sand blaster was used to investigate the erosion resistance of the coatings. Mixture of dry air and abrasive particles in micrometer size was propelled out of a nozzle tip at a high velocity, resulting in an abrasive stream vertically above the coatings. Resistance of the tested coatings is determined by weight loss or the coating thickness reduction. The tested samples were weighed before and after 30 s of the sand erosion test to an accuracy of ± 0.001 mg. The result is displayed in Fig. 5.4a. A marked lower weight loss was observed for the S200 and S20 coatings than the commercial product PU coating, indicating better erosion resistance of our coatings. Compared S20 with S200 coating, the latter shows a much better resistance to sand erosion. To further investigate the erosion damage on the S200 and S20 coatings, optical microscope were used to observe the eroded and non-eroded regions on the surface as shown in Fig. 5.4b-c. In the sand-eroded region, micro cutting and ploughing of the relatively soft sol-gel matrix have resulted in exposure of the harder SiO₂ particles. The damaged surface of the S200 coating was smoother than the S20 coating.

Table 5.4 Water wettability of coatings before and after the sand erosion test.

	PU		S20		S200	
	Before	After	Before	After	Before	After
Water contact angle (°)	98 ± 1.3	103 ± 2.1	157 ± 1.2	132 ± 2.2	158 ± 1.8	148 ± 1.5
Water roll-off angle (°)	No	No	10 ± 1.4	No	15 ± 2.1	85 ± 2.1

The sand erosion also changed the surface morphology of coatings as shown in FESEM images of Figure 5.4b-c. Large and smooth surface features were observed on the S20 coating surface due to the removal of the porous structure; no air-trap site can be observed (inset in Fig. 5.4b, which explains the decrease in water contact angle and inability to roll off (Table 5.4). In comparison, the S200 coating (Fig. 5.4c) still maintained some cavity structure after the erosion that enables some degree of air trapping. As a result, the roll-off

angle did not increase as much as the one for S20, and water could still roll off though at a much higher angle (Table 5.4). The PU coating surface was initially relatively smooth with a lower hardness. During the sand erosion test, micro-cutting and ploughing actions removed the coating material and increased the surface roughness. Thus, the PU coating exhibited an increased water contact angle but the water droplet still could not roll off from the surface.

Figure 5.5 (a) Ice-adhesion strength and (b) ice accumulation rate of PU, S20 and S200 coatings before and after sand erosion.

Figure 5.5 compares the (a) ice-adhesion strength and (b) percentage ice accumulation of PU, S20 and S200 coatings before and after sand erosion. The ice-adhesion strength and percentage ice accumulation increased substantially after the sand erosion due to the change of surface morphology as discussed before. The induced surface morphology

change caused surface wettability change, which has led to the observed degradation in the icephobic performance. Nevertheless, S200 coatings still exhibited better anti-icing properties among others. The adhesion strength remained lower than 100 kPa, a key performance indicator for icephobic coatings. Furthermore, S200 coatings kept icephobicity after removal of around 5 μm top surface, implying anti-icing properties of the whole coating instead of only top surface which involves post-treatment of micro-nanostructures by low-surface-energy chemicals [23, 58].

Table 5.5 Comparison of durability of reported icephobic coatings with S200 coatings.

Durability	Mechanical resistance		UV irradiation
	Sandpaper abrasion	Sand erosion	ASTM D4587 / ASTM G154 or ISO 4892 standard
S200 (the current work)	N/A	Maintain icephobicity after sand erosion at pressure of 200 kPa for 30s	Maintain icephobicity and good mechanical properties. Ice adhesion increased by ~10% from 64.7 kPa to 71.3 kPa after 288h UV irradiation and condensation condensation.
Liquid infused SiO ₂ -Polyethylene composite coating [13]	Presented superhydrophobicity after abrasion on 200 grid sandpaper (pressure: 2.25 kPa; length: 1080 cm; cycles: 1)	N/A	N/A
Self-lubricating icephobic elastomer coating (SLIC) [17]	The SLIC degraded immediately after abrasion at an applied pressure of 20.5 kPa for 2 cycles, however, the SLIC presented a recovery a few days later	N/A	N/A
Ice release coatings [48]	N/A	N/A	The ice-adhesion strength of the topcoat increased from ~100 kPa before the UVB exposure to ~260 kPa

			after the exposure for 1700 h
Self-lubricating liquid water layer (SLWL) [59]	The ice adhesion around 63 kPa after abrasion test (pressure: 12.5 kPa; cycles: 80)	N/A	N/A
Superhydrophobic aluminum alloy [60]	The roll-off angle increased to $53 \pm 5^\circ$ after 10000 grit sandpaper abrasion (pressure: 10 kPa; cycles: 5)	Roll-off angle increased ($< 30^\circ$) after free-fall sand dropping from a certain distance	N/A
Dual geometric architectures with anti-frost properties [61]	Presented water contact angle larger than 150° after abrasion test on 400 grit sandpaper with a loading of 50 g for 120 cm (sample size: $20 \times 20 \times 1 \text{ mm}^3$), no report of roll-off angle.	N/A	N/A
Durable superliquiphobic coating [62]	Water contact angle larger than 100° after 30 cycles of abrasion	N/A	N/A
Flame-sprayed polymer coatings [63]	N/A	The distance between the abrasive gun and the sample is 30 mm. The sand erosion area is 25 mm in diameter. Sands: Al_2O_3 abrasive ($\sim 340+170 \text{ }\mu\text{m}$) Sample weight increase after sandblasting test at 2.5 bar pressure for 120 s.	N/A
Icephobic fluoropolymer film [64]	N/A	N/A	Water contact angles remained constant at 155° after 120 h of test
Dissimilar SAMs Coatings [65]	N/A	N/A	Water contact angles reduced dramatically after the 20 cycles
Robust icephobic, and anticorrosive plasma polymer coating [66]	N/A	N/A	Water contact angle decreased from 162° to 150° after 300 h of UV exposure according to ASTM G154, no report on water roll-off angle

			and icephobicity after UV irradiation (the original ice adhesion is 83 ± 5 kPa).
Superhydrophobic steel surface [67]	Maintain superhydrophobicity after 10000 grit sandpaper scratching (pressure: 16 kPa; length: 110 cm; cycles: 1)	N/A	Maintain superhydrophobicity after 500W UV irradiation for 50 h at 50 °C

Table 5.5 compares the durability of S200 coatings and literature reported coatings. Most of the reported icephobic coatings can maintain superhydrophobicity after sandpaper scratching under pressure 2~20 kPa [13, 59-62, 68]. or free-fall sand erosion. However, no ice-adhesion strength or other anti-icing tests were reported. Koivuluoto et al. found weight gain of the polymer coatings after sand erosion at pressure of 2.5 bars (= 250 kPa) but they did report other properties [63]. In comparison, the S200 coatings presented water repellency and icephobicity after sand erosion at pressure of 200 kPa, indicating a very good sand erosion resistance.

Some researchers also investigated UV resistance of coatings according to ISO or ASTM standard methods with different irradiation durations [48, 64-68]. With exception of the ice releasing coatings reported by Tang et al.[48], which reported ice-adhesion strength of coatings after UV resistance test, other works only reported the water wettability of coatings. In this study, the ice-adhesion strength of the S200 coating after 144 h UV irradiation and 144 h water condensation displayed a ~10% increase (to 71.3 kPa), but this strength is lower than the ice-adhesion strength of the topcoat ice-releasing agent reported by Tang et al. before UV exposure (~100 kPa).

So far, the reported superhydrophobic coatings are mainly relied on loosely bonded and porous structures. Although they can display high water contact angles and low water roll-off angles, most of them are limited in practical applicability due to their poor mechanical properties or durability. Herein, a simple method has been described to fabricate durable icephobic coatings by designing the “bulk” coating properties with surface morphology

control. The use of silicone-epoxy hybrid resin improves adhesion strength between coatings and the substrates, and at the same time, provides a room-temperature processable water repellent matrix because of the presence of silicone. The addition of PDMS coated dual-sized nanoparticles enables controllable formation of the micro-nanostructured surface, which is mechanically robust yet keeps enough air pockets on the surface. The use of the dual-sized nanoparticles provides the benefits of denser packing while not losing its ability to trap air, and thus is able to maintain the excellent water repellency. Such design principle is easy to adopt, scalable, and applicable to other functional coatings. In particular, extensive mechanical test, UV irradiation with water condensation, and sand erosion test have verified the robustness and durability of the S200 coatings which exhibited ice-adhesion strengths below the well-accepted 100 kPa icephobicity criterion.

5.5 Summary

In summary, fluorine-free icephobic coatings have been prepared using a facile and scalable process. A comprehensive investigation has been carried out on the environmental and mechanical durability of the room-temperature processable coatings. The anti-icing and mechanical properties of superhydrophobic coatings with different surface morphology were analysed. The design of dual-sized nanoparticles has led to better anti-icing properties as well as better sand, UV and condensation resistance than single-sized nanoparticles due to more favourable surface features. In particular, ice-adhesion strength of the dual-size SiO₂ nanoparticles coating was lower than 100 kPa after the UV weathering and sand erosion. The developed icephobic coating can be applied for practical applications on outdoor facilities under a harsh working environment.

References

- [1]. C.A. Lewis. 1918, U.S. Patent 1,282,249.
- [2]. C.J. Rolle, W.D. Barnes. *Industrial & Engineering Chemistry*. **1956**, 48, 1326-1327.
- [3]. H. Jellinek. *Canadian Journal of Physics*. **1962**, 40, 1294-1309.

- [4]. W. Bascom, R. Cottington and C. Singleterry. *Journal of Adhesion*. **1969**, 1, 246-263.
- [5]. J.R. Saroyan. *Ocean Engineering*. **1969**, 1, 435-456.
- [6]. R.J. Anderson, R.C. Miller, J.L. Kassner Jr and D.E. Hagen. *Journal of the Atmospheric Sciences*. **1980**, 37, 2508-2520.
- [7]. J.M. Sayward. 1979, DTIC Document.
- [8]. H.Y. Erbil, A.L. Demirel, Y. Avcı and O. Mert. *Science*. **2003**, 299, 1377-1380.
- [9]. A. Lafuma, D. Quéré. *Nature materials*. **2003**, 2, 457-460.
- [10]. L. Zheng, Z. Li, S. Bourdo, K.R. Khedir, M.P. Asar, C.C. Ryerson and A.S. Biris. *Langmuir*. **2011**, 27, 9936-9943.
- [11]. S. Dierer, R. Oechslein and R. Cattin. *Advances in Science and Research*. **2011**, 6, 245-250.
- [12]. M. Nosonovsky, V. Hejazi. *ACS nano*. **2012**, 6, 8488-8491.
- [13]. N. Wang, D. Xiong, S. Pan, K. Wang, Y. Shi and Y. Deng. *New Journal of Chemistry*. **2017**, 41, 1846-1853.
- [14]. Q. Liu, Y. Yang, M. Huang, Y. Zhou, Y. Liu and X. Liang. *Applied Surface Science*. **2015**, 346, 68-76.
- [15]. J. Zhang, C. Gu and J. Tu. *ACS Applied Materials & Interfaces*. **2017**, 9, 11247-11257.
- [16]. D. Gao, inventor; University of Pittsburgh, assignee..**2017**, U. S. Patent No. 9,688,894.
- [17]. Y.H. Yeong, A. Milionis, E. Loth and J. Sokhey. *Cold Regions Science and Technology*. **2018**, 148, 29-37.
- [18]. M.J. Coady, M. Wood, G.Q. Wallace, K.E. Nielsen, A. M. Kietzig, F. Lagugné-Labarthe and P.J. Ragona. *ACS Applied Materials & Interfaces*. **2018**, 10, 2890-2896.
- [19]. J.H. Li, R. Weng, X.Q. Di and Z.W. Yao. *Journal of Applied Polymer Science*. **2014**, 131, 40955.
- [20]. A.M. Atta, H.A. Al-Lohedan, A.O. Ezzat and S.A. Al-Hussain. *Progress in Organic Coatings*. **2016**, 101, 577-586.
- [21]. T. Cheng, R. He, Q. Zhang, X. Zhan and F. Chen. *Journal of Materials Chemistry A*. **2015**, 3, 21637-21646.

- [22]. Y. Si, Z. Guo and W. Liu. *ACS Applied Materials & Interfaces*. **2016**, 8, 16511-16520.
- [23]. A.M. Emelyanenko, L.B. Boinovich, A.A. Bezdomnikov, E.V. Chulkova and K.A. Emelyanenko. *ACS Applied Materials & Interfaces*. **2017**, 9, 24210-24219.
- [24]. L. Shen, P. Lu, S. Wang and Z. Chen. *Journal of Alloys and Compounds*. **2013**, 574, 98-103.
- [25]. D. Kumar, X. Wu, Q. Fu, J.W.C. Ho, P.D. Kanhere, L. Li and Z. Chen. *Materials & Design*. **2015**, 86, 855-862.
- [26]. Q. Fu, X. Wu, D. Kumar, J.W. Ho, P.D. Kanhere, N. Srikanth, E. Liu, P. Wilson and Z. Chen. *ACS Applied Materials & Interfaces*. **2014**, 6, 20685-20692.
- [27]. X. Wu, S. Zheng, D.A. Bellido-Aguilar, V.V. Silberschmidt and Z. Chen. *Materials & Design*. **2018**, 140, 516-523.
- [28]. X. Wu, Q. Fu, D. Kumar, J.W.C. Ho, P. Kanhere, H. Zhou and Z. Chen. *Materials & Design*. **2016**, 89, 1302-1309.
- [29]. D. Ebert, B. Bhushan. *Langmuir*. **2012**, 28, 11391-11399.
- [30]. B.J. Sparks, E.F. Hoff, L. Xiong, J.T. Goetz and D.L. Patton. *ACS Applied Materials & Interfaces*. **2013**, 5, 1811-1817.
- [31]. T.J. Athauda, W. Williams, K.P. Roberts and R.R. Ozer. *Journal of Materials Science*. **2013**, 48, 6115-6120.
- [32]. C. Xue, S. Jia, J. Zhang, L. Tian, H. Chen and M. Wang. *Science and Technology of Advanced Materials*. **2008**, 9, 035008.
- [33]. H.J. Tsai, Y.L. Lee. *Langmuir*. **2007**, 23, 12687-12692.
- [34]. C.C. Carcouët, A. Esteves, M.M. Hendrix, R.A. van Benthem and G. de With. *Advanced Functional Materials*. **2014**, 24, 5745-5752.
- [35]. T. Tadano, R. Zhu, Y. Muroga, T. Hoshi, D. Sasaki, T. Hagiwara and T. Sawaguchi. *Polymer Journal*. **2015**, 47, 311-319.
- [36]. R. Menini, M. Farzaneh. *Journal of Adhesion Science and Technology*. **2011**, 25, 971-992.
- [37]. A. Davis, Y.H. Yeong, A. Steele, I.S. Bayer and E. Loth. *ACS Applied Materials & Interfaces*. **2014**, 6, 9272-9279.

- [38]. J. Chen, J. Liu, M. He, K. Li, D. Cui, Q. Zhang, X. Zeng, Y. Zhang, J. Wang and Y. Song. *Applied Physics Letters*. **2012**, 101, 111603.
- [39]. V. Hejazi, K. Sobolev and M. Nosonovsky. *Scientific Reports*. **2013**, 3, 2194.
- [40]. K. Golovin, S.P. Kobaku, D.H. Lee, E.T. DiLoreto, J.M. Mabry and A. Tuteja. *Science Advances*. **2016**, 2, e1501496.
- [41]. L. Cao, A.K. Jones, V.K. Sikka, J. Wu and D. Gao. *Langmuir*. **2009**, 25, 12444-12448.
- [42]. S. Farhadi, M. Farzaneh and S. Kulinich. *Applied Surface Science*. **2011**, 257, 6264-6269.
- [43]. C. Antonini, M. Innocenti, T. Horn, M. Marengo and A. Amirfazli. *Cold Regions Science and Technology*. **2011**, 67, 58-67.
- [44]. Y. Huang, M. Hu, S. Yi, X. Liu, H. Li, C. Huang, Y. Luo and Y. Li. *Thin Solid Films*. **2012**, 520, 5644-5651.
- [45]. G. Momen, M. Farzaneh. *Applied Surface Science*. **2014**, 299, 41-46.
- [46]. R. Menini, Z. Ghalimi and M. Farzaneh. *Cold Regions Science and Technology*. **2011**, 65, 65-69.
- [47]. R. Menini, M. Farzaneh. *Surface and Coatings Technology*. **2009**, 203, 1941-1946.
- [48]. G. Tang, Y.H. Yeong and M. Khudiyakov. *Advances in Polymer Science*, Springer, Berlin, Germany, **2017**, 1-17.
- [49]. S. Kimura, Y. Yamagishi, A. Sakabe, T. Adachi and M. Shimanuki. 2007, SAE Technical Paper.
- [50]. L. Mazzola. *Surface Engineering*. **2016**, 32, 733-744.
- [51]. M. Esfandeh, S. Mirabedini, S. Pazokifard and M. Tari. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **2007**, 302, 11-16.
- [52]. H. Sojoudi, G.H. McKinley and K.K. Gleason. *Materials Horizons*. **2015**, 2, 91-99.
- [53]. Z. Chen, L.Y. Wu, E. Chwa and O. Tham. *Materials Science and Engineering: A*. **2008**, 493, 292-298.
- [54]. D. Galvan, Y. Pei and J.T.M. De Hosson. *Surface and Coatings Technology*. **2006**, 200, 6718-6726.
- [55]. A. Leyland, A. Matthews. *Wear*. **2000**, 246, 1-11.

- [56]. C. Rebholz, A. Leyland, J. Schneider, A. Voevodin and A. Matthews. *Surface and Coatings Technology*. **1999**, 120, 412-417.
- [57]. W. Ni, Y.-T. Cheng, M.J. Lukitsch, A.M. Weiner, L.C. Lev and D.S. Grummon. *Applied Physics Letters*. **2004**, 85, 4028-4030.
- [58]. N. Li, L. Wu, C. Yu, H. Dai, T. Wang, Z. Dong and L. Jiang. *Advanced Materials*. **2018**, 30, 1703838.
- [59]. J. Chen, R. Dou, D. Cui, Q. Zhang, Y. Zhang, F. Xu, X. Zhou, J. Wang, Y. Song and L. Jiang. *ACS applied materials & interfaces*. **2013**, 5, 4026-4030.
- [60]. Y. Zhang, D. Ge and S. Yang. *Journal of Colloid and Interface Science*. **2014**, 423, 101-107.
- [61]. Q. Zhang, B. Jin, B. Wang, Y. Fu, X. Zhan and F. Chen. *Industrial and Engineering Chemistry Research*. **2017**, 56, 2754-2763.
- [62]. D. Nanda, P. Varshney, M. Satapathy, S. Mohapatra, B. Bhushan and A. Kumar. *Journal of Colloid and Interface Science*. **2017**, 507, 397-409.
- [63]. H. Koivuluoto, C. Stenroos, M. Kylmälahti, M. Apostol, J. Kiilakoski and P. Vuoristo. *Journal of Thermal Spray Technology*. **2017**, 26, 150-160.
- [64]. R. Jafari, G. Momen and M. Farzaneh. *journal of coatings technology and research*. **2016**, 13, 405-412.
- [65]. S. Farhadi, M. Farzaneh and S. Simard. *Journal ISSN*. **2012**, 1929, 1248.
- [66]. L.F. Mobarakeh, R. Jafari and M. Farzaneh. *Cold Regions Science and Technology*. **2018**, 151, 89-93.
- [67]. F. Wang, S. Yu, J. Ou and W. Li. *Journal of Sol-Gel Science and Technology*. **2015**, 75, 625-634.
- [68]. N. Wang, D. Xiong, Y. Deng, Y. Shi and K. Wang. *ACS Applied Materials & Interfaces*. **2015**, 7, 6260-6272.

Chapter 6 Conclusion and Future Works

Conclusion and Future Works

This chapter summarises main achievements, novelty, findings and conclusions of this thesis. To design practically applicable anti-icing coatings, sol-gel systems and epoxy resins were used as matrixes, and nanoparticles with different surface energy, different dispersion status and different size were added as fillers to design coatings with desired microstructures and properties. Systematically study of these coatings revealed environmental and non-environmental factors that would affect the coatings' anti-icing performance. Experiments conducted in this study not only provide methods to fabricate mechanically robust anti-icing coatings, but also unveil novel insights to fabricate anti-icing coatings with conventional methods. In addition, comprehensive mechanical robustness and durability tests could be used as a guideline for future development of practically applicable anti-icing coatings for sports facilities. Furthermore, limitations of this study, suggestions and opportunities for future development of anti-icing coating were indicated as prospective works.

6.1 Conclusions

The main objective of this thesis is to design and develop anti-icing coatings for sports applications. With careful control of surface characteristics, for example, surface roughness and surface geometry, coatings with desired anti-icing behaviours have been fabricated. Firstly, the effect of water condensation (one of the key factors influence anti-icing performance of superhydrophobic coatings) on ice adhesion of five superhydrophobic coatings with different surface microstructures has been discussed. Secondly, with concern for the needs of durable transparent anti-icing coatings, a novel approach to uniformly disperse nanoparticles has been described. The final transparent coating presented ice-adhesion strength as low as ~60 kPa, icing temperature lower than -27 °C, anti-frost and significantly icing-delay effect. This transparent coating also demonstrated self-cleaning properties and mechanical durability, which were superior over the state-of-the-art superhydrophobic coatings, SLIPS and polymer coatings. Finally, room-temperature processable and fluorine-free coatings have been prepared. Extensive mechanical tests and UV irradiation under humidity verified the durability of the coatings for applications under harsh environment. The detailed novelty and main achievements of this thesis are discussed as follows.

6.1.1 Superhydrophobic Anti-icing Coatings

Superhydrophobic coatings that mimic natural leaves, fishes and insects have aroused great interest for anti-icing applications. However, controversies towards superhydrophobic coatings exist due to their inconsistent anti-icing performance. To identify the failure mechanism of some superhydrophobic coatings, nanoparticles with different surface energy were utilized to prepare superhydrophobic coatings. Five coatings with different surface microstructures corresponding to different weight ratio of surface modified to non-modified nanoparticles have been successfully developed. Only one of the five coatings displayed robust icephobicity. Measurements of ice adhesion at different temperatures and icing temperatures of these superhydrophobic coatings led to a conclusion that ice adhesion and ice nucleation shared different mechanisms and behaviour on the same

superhydrophobic coating. Ice adhesion of superhydrophobic coatings is dominated by surface energy and surface geometry. Minor effect of surface roughness on ice adhesion of superhydrophobic coatings has been noticed. However, ice nucleation is related to a nanoscale structure that enables formation of ordered water molecules, thus surface roughness plays an important role in the ice-nucleation process and the resulted icing probability. Although low ice adhesion doesn't guarantee low ice nucleation process, a compromised anti-icing performance was observed on the TGS 6:0 coatings which presented robust ice adhesion of 50~60 kPa and ice-nucleation temperature lower than -26 °C.

6.1.2 A Robust Transparent Coatings for Anti-icing and Self-cleaning Applications

Transparent coatings are preferred for various applications with and without requirement of visibility because of an increasing demand for aesthetic appurtenance. It can be used in airplanes, wind turbines, windows, windshields of automobiles, instruments, sensors, cameras, satellites, weapon systems, and energy-harvesting devices. In this thesis, a unique and low cost method was developed to fabricate a transparent anti-icing coating. SiO₂ nanoparticles are commonly used fillers to enhance mechanical properties. However, nanoparticles tend to agglomerate, forming large clusters in solutions or coatings. In this manner, the transmittance of coatings will be decreased due to the visible light scattering. Magnetic agitation is usually used to mix nanoparticles in a solution. Herein, magnetic stirring was employed to deagglomerate nanoparticles in a sol-gel system. The sol was magnetically stirred for 12 days till a transparent coating was developed. The transparent coating presented a transmittance as high as 99%. This transparent coating also presented self-cleaning properties and displayed repellency to liquids with surface energy ranging from 72.8 to 22.1 mJ/m². Moreover, this coating presented low ice adhesion of ~60 kPa, icing-delay time of ~300s, ice-nucleation temperature of ~-27 °C, low icing probability and ice-nucleation rate which are superior to an uncoated glass. Mechanical property of coatings as important criteria for practical application was carried out. Comparison of the transparent coating with reported anti-icing coatings verified its good mechanical properties in scratch resistance, hardness and adhesion to substrates.

Furthermore, it is found that an increase in stirring time significantly decrease surface roughness and increase the transmittance of the prepared coatings. FESEM, AFM and TEM studies on the obtained coatings proved the gradually deagglomeration of SiO₂ nanoparticles in a sol-gel system due to the applied mechanical force. A relationship between surface roughness and transmittance were noticed. Investigation on ice adhesion of these coatings indicated that ice adhesion of coatings decreased as surface roughness of coatings decreased. At the first day's stirring, the coating presented superhydrophobicity with contact angle larger than 150 ° and roll-off angle less than 10 °. Increasing stirring time decreased water contact angles of coatings, while sliding angles of coating increased first till pining of a 10μl water droplet and then decreased to ~40 °. However, the movements of superhydrophobic coatings and transparent ones share different mechanisms. Specifically, the ice adhesion of coatings decreased with decreasing surface roughness of coatings. The high ice adhesion of the superhydrophobic coating was due to the water condensation induced mechanical interlocking. In comparison, the transparent coating can withstand the water condensation effect and demonstrated water repellency even at temperature of -20 °C, and thus frost resistance.

Instead of porous structure and smooth liquid layer of the two state-of-the-art superhydrophobic coatings and SLIPS, a smooth solid surface exhibited anti-icing and self-cleaning properties. The mechanical properties of the smooth solid coating were also better than the superhydrophobic coatings and SLIPS.

6.1.3 Durable Room-Temperature Processable Fluorine-free Icephobic Coatings

This study was designed to fill up the research gap of improving mechanical durability of anti-icing coatings based on superhydrophobicity. In addition, the coating was developed at room temperature which could be applied to a vast number of applications. With concern for the bio-accumulative and potentially harmful to human health of fluorine chemicals, the preparation of the coating employed silicone-epoxy resin. To obtain mechanically robust superhydrophobic coatings, nanoparticles with different size were utilized and the

dual-size coatings presented better anti-icing performance, mechanical properties and durability than single-sized coatings due a denser micro-nanostructure.

To comprehensively study the durability of the superhydrophobic coating, water wettability, anti-icing performance and mechanical properties before and after 144 h UV irradiation and 144 h water condensation were compared. Furthermore, sand erosion which usually used to remove top layer of a surface was carried out, and the resulted water wettability and anti-icing behaviour were also compared with those of coatings before sand erosion and available reported coatings in the literature. The test methodologies and results provide guidelines for future design and characterization of anti-icing coatings to achieve environmental durability in sports use.

6.2 Future Works

In this thesis, three anti-icing coatings for different features have been successfully developed together with the analysis of factors affecting anti-icing performance. However, there are still several limitations needing further in-depth study.

Firstly, although the effect of surface characteristics including surface geometry, surface roughness and surface energy on ice adhesion, icing-delay time, ice nucleation and durability of anti-icing coatings has been referred and discussed in previous chapters of this thesis, less attention has been paid on the relationship between surface characteristic and anti-icing performance. In literature, studies also have been carried out to establish relationships between surface characteristic and ice adhesion or ice nucleation. For example, it is well-known that water wettability is controllable by adjusting surface roughness and surface energy [1, 2], and so as the work adhesion of water droplets on a coating surface. Researchers found correlations between water contact angle, water receding angle or CAH and ice adhesion based on the assumption that ice and water exhibits the same surface energy. However, even though one could assume the surface energy of ordered (ice) and disordered (supercooled water) water molecules shared the same surface energy, the contact angles, receding angles and advancing angles used were

not equal to the angles at the temperature which disordered water molecules form ordered water molecules. Therefore, controversies exist towards the effect of water wettability on anti-icing performance due to the limitation in sampling number and design of surface patterns. In the next step, more comprehensive studies on a vast number of samples with precisely controlled surface geometry or pattern are necessary to draw conclusion of correlations between the surface geometry factors or water wettability and anti-icing performances of coatings, thus provide a more specific and optimized guidelines for the design of durable anti-icing coatings.

Secondly, in this thesis, statistical analysis of the coatings' icing temperatures was utilized to verify the ice nucleation and icing probability, in-depth thermodynamic simulation of a heterogeneous ice nucleation process on a coating surface would be recommended to simulate the obtained ice nucleation results in this thesis. Fletcher studied the size effect of nanoparticles on heterogeneous nucleation [3]. Sholl and Fletcher analyzed the nucleation behavior as a function of surface step angles on large flat surfaces [4]. Xu and Johnson constructed a model which considers the size effect of foreign nanoparticles on heterogeneous nucleation [5]. Cooper et al. predict the ice-nucleation temperature of convex and concave surfaces based on classic nucleation theory [6]. Iwamatsu introduce a variable shape factor to study the heterogeneous nucleation on a spherical substrate and a spherical cavity [7]. Considering the random surface morphology / topology of the coatings developed in this study, fractal dimension, which provides a ratio how structure details in a fractal pattern (surface topology) changes with the measured surface roughness, can be used as a quantity to reflect the change in surface topology. In this study, porous structure is a representative of concave surfaces, and rough coating without pores represents convex surface, based on previous study, investigation of the fractal dimension effect on heterogeneous nucleation is suggested. In addition, it remains unclear how microscopic properties of a coating affects the macroscopic ice nucleation. Good crystallographic match between substrate and ice plays an important role in ice nucleation, especially in bulk nucleation. Alternatively, water adsorption properties of the substrate dominate the heterogeneous nucleation from the vapor if no favorable substrate structure exists [8]. Future efforts could be made to correlate the ice crystal structures as shown in Chapter 2 to surface

microstructures under different humidity or temperature. Thus more fundamental and comprehensive understanding of icing behavior can be developed.

Some studies have reported the ice nucleation occurred on the water-solid interface, while some observed ice nucleation took place at the three-phase contact line. In this study, with the assistant of a high-speed camera, It was observed that ice nucleation preferred at the three phase contact line. Future works can be done on the simulation of heterogeneous ice nucleation at the three phase contact line and predict the ice nucleation temperature of the studied coatings based on the classic nucleation theory.

Thirdly, based on the available research reports, more and more testing methods of anti-icing performance have been developed and utilized; one of the outstanding issues is the lack of universally accepted test standards and comparison among reported results from different research groups. For example, literature studies have shown that ice adhesion and ice nucleation would be affected by the water purity level, water droplet size or weight, the cooling rate and humidity. However, meaningful comparison among different reports can only be made if the reported testing conditions are consistent or can be calculated. Looking ahead, standardization of evaluation techniques of anti-icing performance is urgently needed, and this requires joint effort from ISO / ASTM, funding agencies, research institutions, and industries to work together.

Fourthly, a relatively new territory is the smooth solid coatings with low surface energy, especially the ones with good mechanical properties, such as the THRC discussed in Chapter 4. The THRC, with a well-controlled hydrophobic flat surface, presented much-delayed icing time, low ice-nucleation temperature, and weak ice-adhesion strength, which were superior to the ones with the micro-nanotextured superhydrophobic surfaces. An added advantage for THRC, compared with micro-nanoscale rough coatings, is that it is highly transparent since it is free of surface light scattering. More investigation on this new class of anti-icing coatings is certainly necessary.

Lastly, durable anti-icing coatings against mechanical damages and environmental degradation are overwhelmed from the practical point of view. The study of the room temperature processable coating described in Chapter 5 provides perspectives for future effort in the development of anti-icing coatings. In next step, the effect of volumetric ratio or size ratio of dual nanoparticles on hydrophobicity performance is suggested. Anti-icing coatings could be explored to enhance transmittance and self-cleaning properties. In addition, there is an increasing concern on the development of easily repairable or self-healing coatings to reduce the economic loss and labour burden due to the down time. Moreover, a smart coating responding to stimuli from the surrounding will be interesting, for example, a coating that could release anti-freezing liquids once surface icing is detected.[9] In terms of materials used for anti-icing coating fabrication, environmental friendly materials (e.g. bio-based epoxy resin) and coating technologies (e.g. NoSOC - no small organic molecules - coating formulation) will certainly become the next generation techniques because of the daily increased environmental awareness and commercial competition.

Moreover, a field test is suggested to conduct under harsh environmental to find whether the designed anti-icing coatings can withstand the UV light, rain, sleet, frost, wind or other factors in the natural environment like cold wet winter or hot dry summer and maintain their anti-icing performance for a long time.

References

- [1]. M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto and T. Watanabe. *Langmuir*. **2000**, 16, 5754-5760.
- [2]. Q. Fu, X. Wu, D. Kumar, J.W. Ho, P.D. Kanhere, N. Srikanth, E. Liu, P. Wilson and Z. Chen. *ACS Applied Materials & Interfaces*. **2014**, 6, 20685-20692.
- [3]. N. Fletcher. *The Journal of chemical physics*. **1958**, 29, 572-576.
- [4]. C. Sholl, N. Fletcher. *Acta Metallurgica*. **1970**, 18, 1083-1086.
- [5]. D. Xu, W.L. Johnson. *Physical Review B*. **2005**, 72, 052101.

- [6]. S.J. Cooper, C.E. Nicholson and J. Liu. *The Journal of chemical physics*. **2008**, 129, 124715.
- [7]. M. Iwamatsu. *Langmuir*. **2015**, 31, 3861-3868.
- [8]. D. Bassett, E. Boucher and A. Zettlemoyer. *Journal of Colloid and Interface Science*. **1970**, 34, 436-446.
- [9]. X. Sun, V.G. Damle, S. Liu and K. Rykaczewski. *Advanced Materials Interfaces*. **2015**, 2, 1400479.