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**Study on Multi-phase Structured Icephobic
Constructions**

By

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Abstract

The accumulation of ice on critical infrastructure, such as aviation, telecommunication, electricity, and transportation systems, can cause severe disruptions to daily life and significant economic losses. While applying icephobic coatings has been proposed as a potential solution, the challenge remains in creating coatings that can effectively withstand adverse environmental conditions, and also demonstrate a long service life and mechanical durability. The motivation of the work is to provide a comprehensive analysis of the fundamental aspects related to icephobicity research, and to explore novel, durable icephobic materials and surfaces, to produce well-rounded research outcomes.

Liquid-infused surfaces (LIS) with self-replenishing properties have been adopted for anti-icing and de-icing applications. However, the mechanical durability of the LIS polymer is limited, rendering them unsuitable for long-term practical use in ice protection. To alleviate the difficulties associated with limited mechanical durability and rapid oil depletion among LIS structures, this study proposes a multi-phase LIS construction based on microporous metallic scaffolds. The proposed approach aims to tackle the problem of icephobicity deterioration in LIS materials. Specifically, the study employed Ni scaffolds and a PDMS-modified silicone oil (NP-SO) system for the LIS construction. The inclusion of Ni scaffolds facilitated stress redistribution during de-icing, thereby safeguarding the LIS material from external loads and impacts. As a result, the ice adhesion strength of the NP-SO samples down to 2.0 ± 0.7 kPa after undergoing 50 cycles of anti-icing/de-icing tests. Conversely, samples without Ni scaffolds demonstrated surface damage after 30 cycles of anti-icing/de-icing tests. The rapid depletion of infused oil due to large polymer deformation was also addressed. The multi-phase construction reduced oil depletion by over three times after 50 cycles of anti-icing/de-icing tests, providing a resolution for the oil depletion concerns in extended service environments.

To achieve enhanced icephobic performance and durability, a novel design concept involving the integration of phase change liquids with Ni scaffolds and polydimethylsiloxane (PDMS) has been introduced in the multi-phase icephobic construction. Incorporating phase change liquids within the LIS construction allows for heat absorption and release during the icing process, which enhances icephobic performance. Differential scanning calorimetry analysis demonstrated that samples with phase change liquids have a phase change enthalpy of 3.2 J/g for groundnut oil and 3.8 J/g for coconut oil, respectively. As a result of the heat release during the phase change process of the incorporated phase change liquids, the surface temperature of the sample increased, resulting in a delayed ice formation of the supercooled water droplet. The observed freezing time of the droplets on the sample surface was 7-8 times longer than that observed on aluminum alloy. Solidification of the phase change liquids occurred at a low temperature, leading to a concurrent reduction in oil depletion during the de-icing process. This effect was confirmed from the weight maintenance ratio of samples, which remained unchanged even after undergoing 50 cycles of anti-icing/de-icing tests.

The introduction of phase change liquids has been demonstrated to be a viable strategy for enhancing the anti-icing performance of icephobic surfaces. A high-quality icephobic surface should encompass multiple facets of icephobicity, such as anti-icing performance, de-icing ability, and mechanical stability. It is noteworthy that achieving all of these requirements simultaneously is a formidable challenge. To address this issue, a potential icephobic structure has been proposed, which incorporates Ni scaffolds with ice depressing liquid and a polydimethylsiloxane (PDMS) matrix. The ice depressing liquid utilized in this study included glycol and glycerol. The incorporation of ice depressing liquid into the surface layer led to an increase in the amount of hydroxyl groups present, resulting in a notable reduction in the freezing point of supercooled droplets at the liquid-solid interfaces. Furthermore, samples containing ice depressing liquid exhibited a considerable delay in the onset of icing, with respective times of 153.7 ± 2.5 s and 209.7 ± 4.5 s. The results of anti-icing tests provided evidence of the efficacy

of ice depressing liquid in reducing the icing point temperature. Upon the sample preparation, the glycol and glycerol in the ice depressing liquid underwent volatilization, leading to the formation of internal porosities within the PDMS. Despite this, the surface morphology of the samples remained smooth and intact. The presence of these internal pores could increase the difference in elastic modulus between the polymer and metallic scaffolds, thus facilitating the initiation of micro-cracks at the ice-solid interfaces and aiding in ice detachment from the sample surface. Consequently, the ice adhesion strength was reduced to below 2 kPa, in contrast to 29.8 ± 2.9 kPa observed for Ni-PDMS samples. Moreover, the results indicated that the de-icing ability of the samples remained stable throughout cyclic icing/de-icing tests.

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List of Abbreviations

Al	– Aluminium
Adv	– Advancing water contact angle
AFM	– Atomic force microscope
ATR	– Attenuated total reflectance
BSE	– Backscattered electron
CAH	– Contact angle hysteresis
CNT	– Carbon nanotube
DI	– Deionised
DSC	– Differential scanning calorimetry
EDX	– Energy dispersive X-ray spectroscopy
ESEM	– Environmental scanning electron microscopy
F	– Fluorine
FE	– Finite element
FTIR	– Fourier transform infrared
GSED	– Gaseous secondary electron detector
ISO	– International Standards Organisation
KE	– Kinetic energy
L	– Length
LIS	– Liquid-infused surfaces
LIT	– Low-interfacial toughness
MACI	– Macro crack initiator
MD	– Molecular dynamic
Ni	– Nickel
OM	– Optical microscopy
PAAO	– Porous anodic aluminum oxide
PDE	– Partial differential equation

PDMS	– Polydimethylsiloxane
PP	– Polypropylene
PS	– Polystyrene
PTFE	– Polytetrafluoroethylene
PU	– Polyurethane
PVC	– Polyvinyl chloride
R	– Thermal resistance
Ra	– Surface roughness
Rec	– Receding water contact angle
RPM	– Revolutions per minute
Si	– Silicon
SA	– Sliding angle
SEM	– Scanning electron microscope
SHS	– Super-hydrophobic surfaces
SLIPS	– Slippery liquid-infused porous surfaces
TIP	– Isopropoxytitanium
TPG	– Tripropylene glycol ether
UV	– Ultraviolet
WCA	– Water contact angle

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Chapter 1 Introduction

1.1 Background and Motivations

The formation of water vapour and ice on surfaces of certain objects may pose unpredictable negative effects to their wide applications [1]. Current industry strategies for combatting icing problems primarily involve active heating, chemical de-icing fluids and mechanical removal [2-4]. But these solutions still have some unavoidable drawbacks in several aspects, including inefficiency, environmentally unfriendly, energy-intensive, high cost and time-consuming. Therefore, it is of great significance to develop a passive anti-icing/de-icing method, which is considered to be more appealing and a universal strategy for mitigating the icing problem.

Passive de-icing normally refers to the construction of surfaces or coatings with anti-icing/de-icing performance. On the one hand, the surface/coating could make it difficult for incoming water droplets to infiltrate the surface of the component and could be easily separated from the surface. The icing duration could be prolonged and the formed ice could be reduced. On the other hand, the formed ice could be shed away from the surface with a minimal applied force due to the low adhesion between the surface and ice. With the two aspects, the aim of passive ice protection is then achieved. In recent years, with more new types of coatings developing, more and more academic and engineering attention has been gained to the ice protection system due to their superior ice protection performance. F. Ibáñez-Ibáñez et al. demonstrated the effectiveness of using surface deformability for reducing ice adhesion by preparing elastic hydrophobic surfaces with ice adhesion strength below 10 kPa [5]. New design strategies such as slippery liquid-impregnated porous metallic structures (LIPMS) with ice adhesion strengths of less than 1 kPa have been proposed for consideration in icephobic and hydrophobic applications [6]. The advantages of being more energy efficient and eco-

friendly than active methods make it a very economical supplementary way for ice protection.

The use of icephobic surfaces is one of the main effective approaches to alleviate the icing hazards in engineering applications [7-10]. Research efforts on developing icephobic surfaces are of great scientific and practical value. It is reported that over 700 accidents and more than 800 deaths took place in aviation history from 1981 to 2009 due to ice accretion issues [11]. Besides, the serious snow disasters led to a direct economic loss of over £17 billion in China in 2008 winter [12]. Various icephobic structures have been developed [13-16], which could mainly be categorized into three strategies:

- 1) To achieve icephobicity by employing superhydrophobic surface [17, 18]. The anti-icing performance could be achieved and strengthened with the formed air cushions between the micro-nano structures of the superhydrophobic surface, which could help with quick slip-away/rebound of the supercooled droplets when they are in contact with the coating surface, thus achieving the anti-icing effect.
- 2) To lower the ice adhesion strength through polymeric elastomer coatings [19-21]. The synergistic effect between the elastomer surfaces with low surface energy decreases the ice adhesion strength, leading to an easy detachment of the accreted ice.
- 3) To minimise the adhesion strength with the slippery liquid-infused porous surfaces (SLIPS) design [22, 23]. The infused liquid inside the surface micro-cavities could seep out under the control of the capillary effect, forming an intact and complete layer coverage and decreasing the ice adhesion strength.

Among the aforementioned methods, the additions of oil/lubricants in SLIPS have demonstrated the great capability of gaining surface icephobicity. Nevertheless, the fast depletion of oil/lubricant from the SLIPS is a great challenge, and the icephobic

performance could deteriorate with possible rapid oil depletion, the impregnated lubricant is often drained out by the shear stress exerted by the external flow. The lubricant could be depleted either via wicking away or evaporation. For example, Zhang et al. reported that the infused lubricating oil (electrolyte hydrogels) lost up to 50% of its initial weight after certain icing/de-icing cycles (during accreted ice removal) [24]. There are few papers reporting this since no paper would highlight the depletion rate of infused oil for relevant applications. Only some papers are published on the understanding for the depletion of lubricant entrapped in confined geometries. For example, the depletion rate of impregnated oil could be affected by the opening ratio of the spherical cavity. And the results revealed that a cavity with a smaller opening ratio (r/R) has better sustainability and less lubricant depletion [25]. To solve this issue, liquid-infused surfaces (LIS) with self-replenishment functions have been proposed and developed for icephobic applications [26-28]. The design of LIS could take advantage of the polymer network and distribute the incorporated oil uniformly inside the polymer matrix. The infused oil could also diffuse out and help to provide a continuous oil layer on the surface, which works for the icephobic purpose. For example, Wang et al. prepared an anti-icing coating using polymers with hydrophilic pendant groups, which could form an aqueous lubricating layer on the as-prepared surfaces [29].

However, the long-term service of LIS could inevitably be limited by the liquidous and soft nature of the infused lubricant, prolonged exposure, high temperature and ultraviolet (UV) rays, which could cause fast degradation and even destructive effect on the lubricant. The icing/de-icing cycles could also result in the loss of lubricant and even complete exhaustion [30, 31]. After the exhaustion of infused liquid, the rough surface structure designed for the prevention of the lubricant wrapping effect would undesirably increase the difficulty of de-icing aspect. Currently, LIS constructions are mainly composed of polymeric materials due to their capability of liquid incorporation and distribution, mainly via the expansion of chain networks. However, the oil infusion into the polymer network would significantly weaken the mechanical properties. The mechanical properties of polymeric material are normally related to the density of

internal crosslinking networks. As depicted in Ma's research, since the silicone oil diffuses easily within the polymer network, they would exist in the crosslinking network gap of the PDMS resin in liquid form and then reduce its crosslinking density which further decreases its strength [32]. Besides, the tensile and flexural properties of the as-prepared samples suffered a slight decrease because of the weakening of interfacial bond strength [33]. The decreased mechanical properties, in turn, would also affect the oil maintenance and release under external force [34, 35]. Overall, the full potential of LIS for ice prevention has yet to be demonstrated, especially for long-term services. Damage or the loss of lubricating layer could occur on the LIS surface [36]. Once the water droplets are shed from the LIS, the impregnated oil could then suffer progressive loss via the entrainment in the water droplets [37]. Considering their low surface energy and smooth surface, the polymer could still maintain low ice adhesion after lubricant loss [38]. Some research results also suggest that the resin-oil layer could also lose after the initial icing/de-icing cycles [39].

To meet the requirements of icephobicity and durability for icephobic surfaces simultaneously, a universal approach has been proposed to introduce microporous metallic scaffolds into the LIS construction. The integration of microporous metallic scaffolds could practically offer mechanical solutions and unfold the potential of LIS. In addition, the difference in elastic modulus between the metallic scaffolds and LIS polymer could result in different distortions locally which could induce the initiation of micro-cracks at the ice/solid interfaces under external loads. Polydimethylsiloxane (PDMS) with silicone oil infusion and modification possesses icephobic properties, but the surface is easy to be damaged after excessive oil addition [32]. To address the issues of oil depletion and limited mechanical durability of the modified PDMS, microporous Ni scaffolds were selected in this study to realise the durability enhancement. The PDMS modified silicone oil (PDMS-SO) system has been selected as the research object of LIS since it works as one of the typical LIS system and possesses icephobic properties.

Since the incorporation of Ni scaffold could ensure the mechanical durability of polymer matrix, the Ni scaffold could act as the armours for filled polymer, against possible mechanical scratch and help to reduce and transfer the local damage, increasing the erosion resistance and avoiding the erosion failure [40]. While for the reason choosing Ni scaffold, first, the porous Ni scaffold has high porosity (the as-received porosity could reach over 90 %), high specific strength, stiffness and good mechanical properties. The nickel scaffold also shows better chemical stability since it is more resistant to corrosion than other metal scaffolds [41]. Moreover, the use of nickel scaffold provides an economic benefit due to its lower cost compared to copper or aluminum scaffolds. With the incorporation of Ni scaffolds, the mechanical properties of LIS system constructed with polymer matrix was guaranteed, it also made some contribution to the icephobicity improvement. Normally, the icephobicity correlated to both anti-icing and de-icing performance. For anti-icing, it can be defined as the ability of a surface to delay or prevent ice nucleation and frost formation, maintaining the liquid phase of water on the surface as long as possible. De-icing ability is defined as the low adhesion strength to ice between surfaces and formed ice [42].

For Ni scaffolds and PDMS modified silicone oil (NP-SO) system, to achieve the ice protection purpose, the de-icing efficiency could be optimized with the role of formed oil layer and the micro-crack initiation mechanism derived from the combination of polymer matrix and metallic scaffolds. However, limited improvement has been made onto the anti-icing performance. In order to address the oil depletion issue fundamentally and further improve the anti-icing ability and icephobicity stability, phase change liquids were selected as the prospective candidates of infused liquid in NP-SO system, which could absorb and release heat over a defined temperature range during the phase change process. It is thought that the absorption and exothermic characteristic of phase change liquids could be applied to introduce delay effect to the ice formation. With the released heat during the phase transition, the temperature at the liquid-solid interfaces increase and the ice formation would be delayed. The infused liquid would change into solid state from liquidous state after the phase transition, which in turn mitigate the oil depletion during the anti/de-icing process.

Another method for enhancing the anti-icing performance without affecting the ice adhesion strength was to introduce ice depressing liquid into the incorporation of Ni scaffolds and polydimethylsiloxane (PDMS) matrix. As reported by Halar et al. [43], for the aim to improve icephobic performance, the concept of imitating lipid droplets in cetaceans' skin was adopted as the icephobic surfaces, while the ice depressing liquid (ice inhibitor) was added to the reinforced composite polymer. It helped to inhibit the formation of ice cores at the solid-ice interface. By taking advantage of the infused ice depressing liquid, the amount of existing hydroxyl groups on the layer surface increased which significantly helped to lower the freezing point of the supercooled droplet at the liquid-solid interfaces. However, the de-icing aspect especially for the ice adhesion strength could deteriorate because of the effusion of large volume of hydroxyl groups [44], which is contrary to the initial ice protection purpose. To solve the problem, the construction of multi-phase structure system has been raised. The icephobic surfaces could be achieved using surface elastoplastic differentiation by incorporating different elastomers having big mismatches in elastic modulus. Silicon-based elastomers with high elastic modulus were used to form the matrix, while Ni scaffolds with relatively low elastic modulus was added to construct the icephobic structure.

It is challenging to achieve all of surface icephobicity requirements including anti-icing performance, de-icing ability and mechanical stability simultaneously. Most of the reported work mainly focus on some of the aspects. In the present work, new icephobic structures were proposed and constructed to provide a solution for such a challenge. Different infused liquids were introduced to incorporate with Ni scaffolds and PDMS matrix, impressive icephobicity and durability enhancement are achieved simultaneously, demonstrating the effectiveness of new icephobic construction.

1.2 Project Aims and Objectives

From the background study, it is believed that the undesirable icing phenomenon often led to severe problems and brings many inconveniences and even hazards to the daily lives and relevant industries. The ice disruption cost up to £25 million only in 2010, as reported by the British Airport Authority [45]. Statistically, the icing-related fatal aircraft accidents could reach 20 to 40 per year in America, especially with the highest incidence in winter season [46]. To mitigate the icing hazards, huge attention has been paid to the relevant area. Great efforts have already been reported, but there are still a number of unsettled challenges: the easy ice accretion on the hierarchical structures under high humidity environment, low anti-icing and de-icing efficiency, limited mechanical durability and icephobic instability. Therefore, the current project focuses on the R&D of durable icephobic coatings with new design concepts.

The main aim of the project is to develop new types of durable and effective icephobic structures for potential ice protection applications in the aerospace. The initial selection of PDMS polymer was based on its favorable hydrophobicity and icephobicity properties. The incorporation of Ni scaffold with the PDMS matrix was subsequently adopted due to the superior mechanical strength it provides, which in turn enhances the overall durability of the system. Furthermore, to meet the diverse requirements of icephobicity such as anti-icing, de-icing, and icephobic stability, various lubricants were also assessed as potential candidates for integration into the system. The detailed mechanisms in mechanical durability and icephobicity will be studied, including the multi-phase layer system and its effect on layer icephobicity.

The objectives of the PhD project are proposed as follows:

- Icephobic structures with excellent icephobic performance and mechanical durability would be designed using the physical concept of multi-phase construction. It is expected that the newly designed coating could be effective in delaying the ice

formation, possessing low ice adhesion and surviving in long-time harsh environments.

- Related fabrication techniques including spin coating, doctor blading and vacuum impregnation will be used to fabricate the icephobic structures with different surface features and properties. The optimised preparation parameters including lubricant addition will also be investigated.
- Various characterisation facilities including optical microscope, scanning electron microscopy, 3D profilometer, fourier transform infrared spectra, differential scanning calorimetry, SAUTER durometer will be adopted to characterise the surface morphologies, shore hardness surface chemistry variation. The relationship between these structural features and material icephobicity will be investigated and discussed. The related simulation on static stress analysis of the de-icing process on as-prepared samples will also be conducted using ANSYS software.
- Surface wettability and icephobicity evaluation including standard and home-made facilities will be conducted to investigate the overall performance of samples. The icephobicity will be assessed from anti-icing (icing delay effect, anti-frost performance, in-situ ice formation) and de-icing aspects (ice adhesion strength, ice diminishing process, cyclic icing/de-icing tests).
- The specific relationship between sample performance and layer structure design will be established based on the mechanical durability and relevant icephobicity results in different layer systems.

1.3 Scope of Thesis

This thesis consists of seven chapters:

Chapter 1 briefly introduces the background and research motivation of this work. The project aims and objectives are identified. The scope of the thesis is also outlined in this chapter.

Chapter 2 provides the literature review of this project, it indicates the developments and challenges and perspectives toward icephobic research, including the significance of ice protection system, principles and basic theories of icephobicity and wettability. This chapter specifically reviews the fundamental knowledge related to icephobic mechanisms and the most up-to-date progress in relevant fields.

Detailed methodologies including substrates, sample preparations, microstructural characterisation, and performance tests such as icephobicity and durability, are presented in Chapter 3. The details of microscopic, spectroscopic and icephobicity tests employed in this work have been described in this chapter.

Chapter 4 reports the fabrication and optimization processes of Ni scaffold/PDMS with silicone oil addition (NP-SO) icephobic layer structure system. Primary investigations and characterisation have been carried out. Good mechanical durability and stability of icephobic performance for as-prepared structured surfaces have also been confirmed. The surface offers a mechanical solution and unfolds the potential of LIS.

In Chapter 5, the mechanisms of phase change liquid modification on altering the surface icephobicity and durability are investigated systematically using liquids with different phase transition substances including silicone oil, groundnut oil and coconut oil. Multiple icephobicity evaluation methods focusing on anti-icing and de-icing aspects as well as the in-situ ESEM observation of water condensation and icing growth

and retardation processes will be applied to evaluate the icephobic performance. The underlying relationship between the changing icephobicity and the phase change liquid introduction are discussed in detail in Chapter 5.

Chapter 6 adapts the design concept and construction of multi-phase layer structure with the combination of Ni scaffold/PDMS with ice depressing liquid incorporations. The multi-phase Ni scaffold/PDMS layer structures with glycol/glycerol modifications have been prepared with the uniformly distributed internal porosities to meet all aspects of the surface icephobicity simultaneously. The mechanical durability and icephobicity stability are significantly improved with the integrated use of Ni scaffolds and glycol and glycerol infusions.

Finally, the key findings of the study are refined and summarised in Chapter 7. New design strategies for icephobic layer structures are proposed based on the investigation of relevant icephobic mechanisms and feasibility in this study. Recommendations for future work are also provided at the end of this chapter.

Chapter 2 Literature Review

2.1 Background of Icephobic Surfaces

Icing is a common phenomenon in nature. However, the unexpected icing phenomenon would often cause economic losses and pose serious safety risks in many areas. Icing would cause problems to the power system, such as the overweight problem of wires and pylons, fracture and collapse to the power transmission system, leaving huge damage to the power system and the national economy. For example, the 2008 snow disaster in southern China seriously damaged the local power system, the power supply in many provinces in China was reduced or cut off because large amounts of primary equipment such as transmission lines and power towers were damaged greatly under the fierce icing environment [12, 47]. Besides, according to the recent statistics data, the economic loss caused by the extreme icing weather has risen by an average of 10 times in the past 40 years [48]. It has also been proved that the total energy loss of a wind generator blade in cold climate lies between 3% to 8% while the ice protection system could consume almost 3 percent of the total energy produced [49].

2.1.1 Hazards of icing phenomena

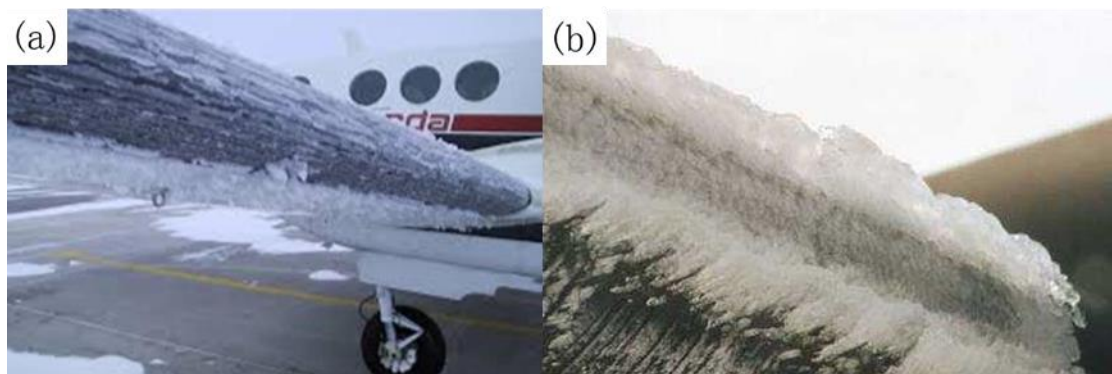


Figure 2.1 Icing phenomenon on engineering surfaces (a) ice accumulation on the wing of aircraft surfaces, (b) undesirable ice accretion (Adapted from Ref [50] and [51]).

Icing poses great threat to aviation equipment and industry. When an aircraft flies at a speed of slower than a critical speed, it could easily encounter supercooled droplets in incoming air flow, they will hit and freeze in the important parts (windward surface) such as the leading edges of the wings and flat tails, resulting in aircraft control failure [52, 53], as shown in Figure 2.1. The serious icing phenomenon on different engineering surfaces including ice accumulation and accretion are illustrated in both Figure 2.1 (a) and (b), respectively. In the aviation industry, icing-related accidents account for more than 15% of aircraft crashes [54], especially in the aircraft industry with high safety standards. For air transportation, accidents in flight safety caused by unexpected icing phenomenon keep happening, and most of them would lead to disasters, resulting in extremely serious life and property loss.

Icing of the aircraft is mainly affected by the shape of the aircraft and meteorological conditions [55, 56]. Ice tends to form on prominent parts of the aircraft, such as the windward surfaces of the wings, tails, windscreen, engine inlets, blades, airspeed tubes and antennas. The shape of the leading edge of the wings and tails could also have significant effect on icing. For temperature ranges from $-20\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$, supercooled water droplets in cumulus and stratus clouds and updraft zones are highly susceptible to forming ice on the flyby aircraft. It could also cause water vapor to freeze when the aircraft flies from zone above zero degrees to zone below zero degree with high-humidity air. Aircraft icing phenomenon could be divided into glaze ice, glaze and rime ice, and rime ice according to the hazard rating from high to low (as shown in Figure 2.2). Glaze ice generally occurs within $-10\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$ environment. Surfaces with formed smooth, transparent and strong ice could be classified as the most harmful icing conditions. Glaze and rime ice are very rough and relatively strong and generally occur from $-20\text{ }^{\circ}\text{C}$ to $-10\text{ }^{\circ}\text{C}$. Rime ice normally appears while aircraft move from a cold zone to a high-temperature area [57]. The specific classifications of ice are discussed in detail in Section 2.2.2.1. The dangers of aircraft icing could be diverse. When ice forms on airplane wings, they would change the shape of the wings, making it difficult to maneuver or even leading to a crash. If the engine air intake is frozen, the airflow would then change, leading to the reduction of engine efficiency and even sudden stop.

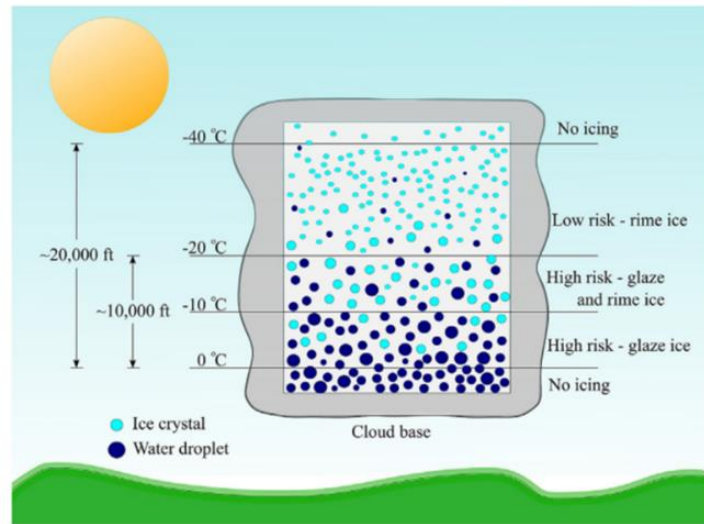


Figure 2.2 Ice formation within a cloud and the resulting probability of aircraft icing [58].

At the same time, engine blade formed ice or impact from fallen ice would also result in engine failure. Icing could be inevitable for many sensors due to their shapes. For example, a crash would easily occur if one of the facilities including the airspeed tube, elevation sensor, temperature sensor, atmospheric data sensor and other detectors and meters fails. The icing on the windshield of the aircraft will obstruct the pilot's vision seriously. Exactly like the icing phenomenon on radome and other parts, such as aircraft shells, turbofan and angle-of-attack vane, it will also increase the weight of the aircraft, causing serious incalculable consequences [57].

Icing brings a lot of danger to safe flying. Therefore, by understanding and studying the reasons and process of icing, then the de-icing technology could be developed, which to a certain extent, could overcome and eliminate the damage caused by unexpected icing. This not only has real world significance but also helps with the deeper understanding of interface interactions and materials.

2.1.2 Current solutions for ice prevention

Ice prevention includes two parts, anti-icing and de-icing: the anti-icing aspect normally exhibits some ubiquitous features: the inhibition of water condensation on the surface

and inhibition of the incoming water's freezing, preventing the ice accrete on the object; while for the de-icing, it is related to the weakening of the adhesion strength of the formed ice, allowing the ice to melt or fall off or be easily removed [9, 59]. At present, there are many anti-icing/de-icing methods, which could be summarized into two methods: active de-icing and passive anti-icing. The active de-icing methods could be divided into three types. One is physical method such as mechanical de-icing with external force, then it is thermal method such as de-icing with heat input. The third one is chemical method including spraying anti-icing agents or de-icing liquids. The most common mechanical de-icing method is pneumatic de-icing, by installing airbags at the icy position such as the leading edge of the wings.

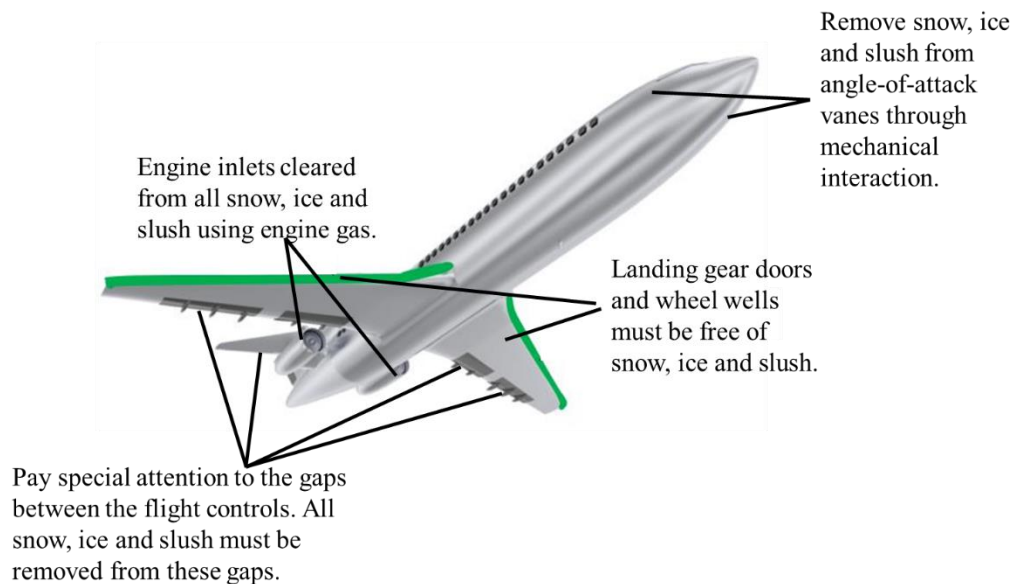


Figure 2.3 Engineering parts on aircraft that require de-icing operations (including Windshield, Probe, Drain mast, Engine air intake, Wing) [60].

Figure 2.3 illustrates some of the engineering parts of aircrafts that require de-icing operations. There are two types of sources for thermal de-icing: hot gas generated by the engines and electrical heating. The exhaust hot air from the engines could be oriented through the internal piping network onto the engine inlets and leading edges, causing the ice to detach and then fall off. However, it also complicates the aircraft architecture severely [61]. Besides, the runback ice or continuous ice accumulation in

the uncovered areas may also pose a dangerous situation because it can drastically affect the aerodynamic loading conditions. Electrothermal de-icing method uses electrical energy to heat the surface of engineering parts to melt and detach the ice. It is usually utilized in windshields, radomes, and other parts of aircraft. But it also has several drawbacks: the electrical heating de-icing device consumes a large amount of energy, resulting in many heater elements leading to weight increase and timer complexity. It is suggested that the good de-icing performance could be achieved with a power input as high as 34 kW/m² using 5 % heater-on/off cycle [62]. And the melted water can easily freeze again. An electrothermal de-icing system is heavy and requires large amounts of power (25 kW) [63]. The heat generated during the process can cause blade damage and delamination [64].

The other method, ultrasonic wave de-icing method is known as a new de-icing method which could achieve de-icing purposes by making relevant parts vibrate and generate heat. The sprayed anti-icing agents and de-icing liquids are still currently the most commonly used de-icing methods because of its easy operation [65]. With liquids possessing a lower freezing point on the surfaces of the engineering parts, the freezing temperature of the frozen parts would be lowered and the prevention or delay of icing phenomenon was then achieved. However, the ice protection effect is limited and ice accretion could take place again. Besides, the usage of de-icing fluid is also not environment friendly the discharge and improper handling of the chemicals could lower the oxygen levels in waterways and prevent fish and other aquatic creatures from breathing, the chemicals that end up in nearby waterways could slowly create waterways that would not support life [66]. This method is simple to operate, but it has limited effect and would do damage to the environment [67].

Although the above active de-icing methods have been widely used, they all have various disadvantages, which have placed huge burden on the structure and maintenance of the aircraft. Therefore, more and more attention has been paid to passive de-icing methods. It also becomes an important research direction in the field of aircraft

anti-icing [68]. Passive de-icing refers to the construction of surfaces or coatings with anti-icing/de-icing capabilities on aircraft which is more prone to icing. On the one hand, this method could make it difficult for water droplets to infiltrate the surface of the component and easily separate from the surface of the component. It could delay the icing time and reduce the amount of icing to achieve ice prevention. On the other hand, due to the low adhesion between the surface and ice, the formed ice would be easy to fall off from the surface, and the aim of passive ice protection is then achieved. There would be little increase in the weight of the aircraft with surface constructions using specific structures. The type of de-icing method also has high reliability and does not consume too much energy or excess manpower.

There are some attempts on icephobic coatings undertaken which have been put into practical applications in the field of aviation [69-71]. For example, black coloured coating (StaClean) was applied onto the blades by Yukon Energy [72], which is abrasion resistant and suitable for high impact. In the aviation field, there remain several specific demands for icephobic coatings, including strong adherence to the substrate, wide temperature range resistance, chemical stability, mechanical durability and corrosion resistance. Among them, mechanical durability and thermal conduction should be emphasized during the design and preparation of icephobic coating. Good mechanical durability can ensure the service life of the coating since good durability could help to sustain the severe water impingement conditions and mitigate and/or resist microstructural damages, fewer cracks would generate on the coating surface under the external de-icing forces [73], good thermal conduction can increase the de-icing efficiency and reduce the overall energy consumption in the active de-icing [74]. The two properties are as important as the low ice adhesion strength in practical applications. Therefore, more systematic studies are needed in the field of icephobic coatings.

2.2 Icephobicity of Solid Surfaces

Some scholars have identified that the design of icephobic surfaces could be motivated from the mechanisms of surface hydrophobicity, for example, the capability to repel water and the freeze delay effect [75, 76]. The assumption behind this is that the mechanisms of icephobicity and hydrophobicity are similar. By designing hydrophobic surface with large water contact angle or low surface energy, one can achieve weak adhesion between the surface and ice, and an icephobic surface could be obtained. Here, the detailed mechanisms from wettability to icephobicity are explained in detail.

2.2.1 Wetting theory of solid surfaces

In order to enable the surfaces with icephobicity, it is necessary to make it difficult for water droplets to infiltrate and remain on the coating surface, thereby preventing the water droplets from freezing and delaying the ice formation. The infiltration of water droplets on the surface is closely related to the water contact angle (WCA). Therefore, the anti-icing performance of different surfaces will be studied combined with the related wetting theory.

2.2.1.1 Wetting on an ideal surface: Young's equation

The wetting phenomenon is a physical phenomenon in which droplets expand along the surface of the solid when the liquid and the solid contact with each other. From the energy perspective, there is cohesion between liquid molecules and also adhesion between liquid and solid. The adhesion between liquid and gas is relatively small. In the case of any molecule in the interstitial space between solid and liquid, if the solid-liquid adhesion is greater than the cohesive force, the resultant force of the molecules would be perpendicular to the contact surface, pointing from the interior of the liquid to the outside. Under this condition, because the internal chemical potential of the liquid is large, the molecules inside the liquid would move to the area where the chemical potential is smaller at the contact surface, and eventually the area of the contact surface

between the liquid and the solid would increase. As the liquid in the contact surface gradually increases, the energy of the entire system becomes lower and lower, and the system tends to remain in a stable state. This would result in the extension of adhesion layer along the surface of the solid and wetting of the solid. It can be seen that the suspended liquid in air would appear as spherical if there is no gravity effect. The vertical tension between any two adjacent positions on the liquid surface and their unit distance critical line is defined as surface tension. Surface energy can be defined as the excess energy at the surface of a material compared to the bulk, or it is the work required to build an area of a particular surface. It can be explained as the required energy change a unit surface area. When a liquid phase comes in contact with solid phase, if the surface energy of solid phase is high, the liquid phase would tend to wet on the solid surface [77].

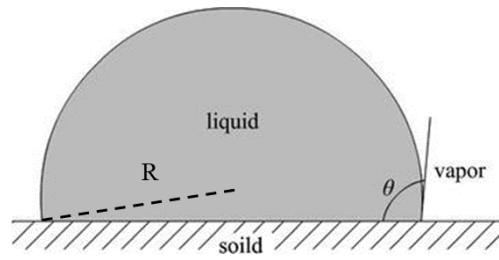


Figure 2.4 Liquid in contact with solid surface [78].

When a water droplet comes in contact with an ideal smooth surface, it shows as a sphere with radius of R . The apparent contact angle between the bottom substrate surface and the ideally smooth surface is θ , as shown in Figure 2.4. According to the geometric relationship, the specific expressions including the volume of the water droplet V , the contacting area of liquid-gas interface S , and the area of liquid-solid contact A can be obtained and the derivation processes are shown in equations (2.1) to (2.3) [79]:

$$V = \frac{\pi}{3} R^3 (2 + \cos\theta)(1 - \cos\theta)^2 \quad (2.1)$$

$$S = 2\pi R^2 (1 - \cos\theta) \quad (2.2)$$

$$A = \pi R^2(1 - \cos^2\theta) \quad (2.3)$$

According to basic thermodynamic theory [80], the Gibbs free energy of a water droplet can be expressed as equation (2.4):

$$G = \gamma_{lg}S + \pi(R\sin\theta)^2(\gamma_{sl} - \gamma_{sg}) = \gamma S - \pi(R\sin\theta)^2R \quad (2.4)$$

where γ_{lg} , γ_{sl} and γ_{sg} represent the surface tension between liquid and gas, liquid and solid and solid and gas interfaces, respectively. Here, the surface is assumed to be an ideally smooth surface. For the convenience of later use, the constant δ is then defined as equation (2.5):

$$\delta = \gamma_{sg} - \gamma_{sl} \quad (2.5)$$

Assuming that the volume of the droplet does not change, V is seen as a constant. Then the equations (2.1) and (2.2) were substituted into equation (2.5), and equation (2.6) could be obtained:

$$G = \left[\frac{9\pi V^2}{(1 - \cos\theta)(2 + \cos\theta)^2} \right]^{\frac{1}{3}} [2\gamma_{lg} - \delta(1 + \cos\theta)] \quad (2.6)$$

From the formula, it can be seen that Gibbs free energy G has only one independent variable at given temperature and pressure, θ represents the intrinsic contact angle.

The derivative of G with respect to θ was shown as equation (2.7):

$$\frac{dG}{d\theta} = 2 \left[\frac{9\pi V^2}{(1 - \cos\theta)^4(2 + \cos\theta)^5} \right]^{\frac{1}{3}} (\delta - \gamma_{lg}\cos\theta)\sin\theta \quad (2.7)$$

When G takes the minimum value, the value of equation (2.7) is zero, then $\delta = \gamma_{lg} \cos \theta_Y$, which can also be written as equation (2.8):

$$\cos \theta_Y = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \quad (2.8)$$

The above formula is Young's equation, which explains why a liquid "stands" stably on an ideal smooth solid surface [81]. It can be seen from the formula that the contact angle could be increased by reducing the solid-liquid surface energy if the droplet and gas environment remains unchanged.

Currently, a surface with a contact angle less than 90° is defined as a hydrophilic surface (good wetting), while a surface with a contact angle greater than 90° is defined as a hydrophobic surface (poor wetting), and surface with angle greater than 150° is always defined as a superhydrophobic surface.

2.2.1.2 Wetting on a non-ideal surface

The Young's equation mentioned in the previous section is applicable for an ideally smooth surface. In fact, the homogeneous solid surface is normally rough, so the apparent contact angle of the same solid surface is different from the intrinsic contact angle calculated by Young's equation. This phenomenon can be explained by the Wenzel's model [82] in this section and the Cassie's model [83] in the next section.

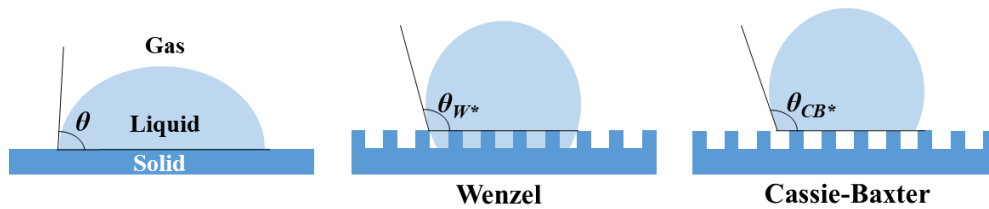


Figure 2.5 Wenzel's Model and Cassie-Baxter's Model [84].

Wenzel's model indicates that when the liquid contacts the rough solid surface, the contacting part of the liquid would completely fill in the asperities of the rough surface

of the solid, as shown in Figure 2.5. Wenzel's model is an equation derived from the free energy change of the system and the principle of zero virtual work under the equilibrium state of constant temperature and constant pressure [85], as indicated in equation (2.9):

$$dE = r(\gamma_{sl} - \gamma_{sg})dx + \gamma_{lg}dx\cos\theta_w \quad (2.9)$$

where dE is the energy required for the contact line to move with an infinitely small amount of dx . If $dE=0$, the system energy is balanced, the relationship between the surface tension and the apparent contact angle θ_w can be obtained [86], that is shown as equation (2.10):

$$\gamma_{lg}\cos\theta_w = r(\gamma_{sg} - \gamma_{sl}) \quad (2.10)$$

where θ_w is the apparent contact angle of the Wenzel's model, r is the roughness of solid surface, which means the ratio of the actual liquid-solid contact area to the horizontal projected area, so $r \geq 1$.

Then equation (2.8) was substituted into equation (2.10), and equation (2.11) was obtained as follow:

$$\cos\theta_w = r\cos\theta_Y \quad (2.11)$$

Since r is no less than 1, when $\theta < 90^\circ$, $\cos\theta_w$ would become larger with the increase in roughness. As θ_w decreases, the hydrophilic surface becomes more hydrophilic as the roughness increases. When $\theta > 90^\circ$, $\cos\theta_w$ would decrease with the increase of roughness. As θ_w increases, the hydrophobic surface would become more hydrophobic with the increase of roughness.

Apart from the aforementioned homogeneous solid surface, heterogeneous solid surface also exists. So, Wenzel's model is not applicable here. On this basis, Cassie and Baxter put forward their ideas. They proposed the concept of "composite contact" and established Cassie's Model to deal with the composite wetting state of solid surface (as shown in Figure 2.5).

Under the equilibrium state of constant temperature and constant pressure, according to the principle that the free energy of the system changes and the zero virtual work, it is concluded as equation (2.12):

$$dE = \sum_{i=1}^n f_i (\gamma_{sl} - \gamma_{sg})_i + \gamma_{lg} dx \cos \theta_c \quad (2.12)$$

At the equilibrium state, dE was put to be 0, and it was substituted into Young's equation:

$$\cos \theta'_c = \sum_{i=1}^n f_i \cos \theta_i \quad (2.13)$$

where f_i represents the area fraction of certain smooth media in all media and $\sum_{i=1}^n f_i = 1$. θ_i represents the intrinsic contact angle between the liquid and the smooth medium i . θ'_c is the apparent contact angle in Cassie's model. For superhydrophobic surfaces, there are only two medias at the bottom of the droplet, the trapped gas between the solid and the surface structure. It is supposed that the area fraction of the solid is f , then the area fraction of the gas is $(1 - f)$, the intrinsic contact angle between the liquid and the solid is θ_Y , and the contact angle between the liquid and the gas is 180° :

$$\cos \theta_c = f \cos \theta_Y - (1 - f) \quad (2.14)$$

$$f = \frac{S_S}{S_B} \quad (2.15)$$

where S_S represents the liquid-solid contact area of the bottom surface, and S_B represents the horizontal projection area of the liquid bottom surface. It can be seen from equations (2.14) and (2.15) that the surface texture structure has a great influence on the apparent contact angle of Cassie's Model.

For solid surfaces with an intrinsic contact angle greater than 90° , both the Wenzel's Model and the Cassie-Baxter's Model could improve the apparent contact angle and hydrophobic performance by increasing the surface roughness. In addition, there is another criterion for hydrophobic performance, namely, contact angle hysteresis (CAH) [87]:

$$CAH = \theta_a - \theta_r \quad (2.16)$$

where θ_a is the forward angle and θ_r is the backward angle, as shown in Figure 2.6. Due to the larger contact area between liquid and solid surface in Wenzel's Model and the anchoring effect between liquid and rough surface, the CAH of liquid in this state becomes larger and its value is much higher than that of smooth surface. In Cassie-Baxter state, the liquid underneath is in the composite contacting state. With both solids and gases, the liquid-solid contact area decreases and the droplets "hover" on the surface. In this way, CAH would be very small, the water droplets are easy to fall off, with a good hydrophobic effect.

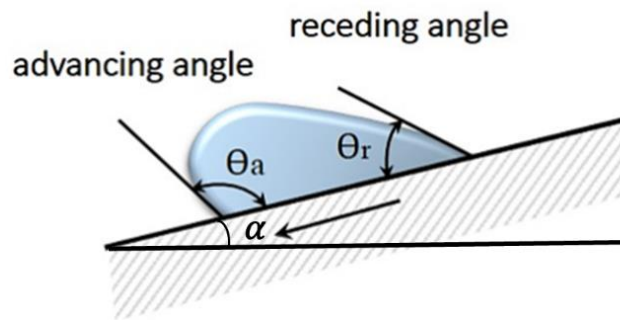


Figure 2.6 Contact angle hysteresis and rolling angle [88].

When the surface of the droplet is tilted, the droplet begins to roll, and the tilt angle of the surface can be considered as the rolling angle α . Furmidge et al. [89] proposed the relationship between the advancing angle and receding angle as well the sliding angle:

$$\frac{mgsin\alpha}{w} = \gamma_{lg}(\cos\theta_r - \cos\theta_a) \quad (2.17)$$

where m is the mass of the droplet, g is the gravitational acceleration, and w is the width of the contact surface between the droplet and the solid surface that is perpendicular to the rolling direction. From this equation, it can be seen that the size of the rolling angle is independent of the absolute value of θ_a and θ_r that are related to CAH, but it also depends on the difference between the advancing angle and receding angle.

2.2.1.3 Relationship between Cassie state and Wenzel state

Under normal circumstances, the droplets would stay on the rough surface in a low-energy contact mode to keep them in a stable state. For droplets with constant volume V , Young's equation (2.8) could be substituted into the Gibbs free energy equation (2.6) to obtain equation (2.18) [90]:

$$G = \gamma_{lg}[9\pi V^2(1 - \cos\theta_Y)^2(2 + \cos\theta_Y)]^{\frac{1}{3}} \quad (2.18)$$

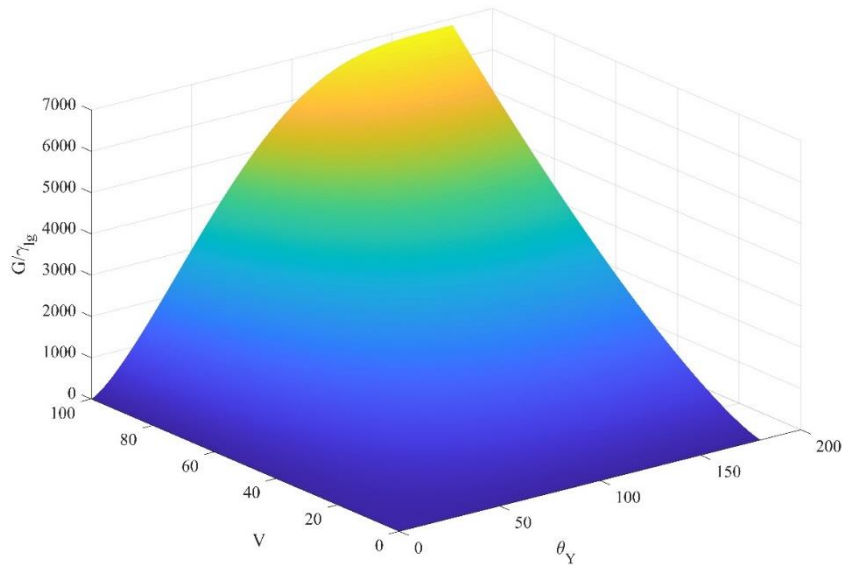


Figure 2.7 Relationships between the Gibbs free energy G , volume V and contact angle θ_Y .

This shows that the Gibbs free energy (G) of the droplet is an increasing function of the contact angle θ_Y , as shown in Figure 2.7. Therefore, smaller apparent contact angle corresponds to lower energy contact state, which also corresponds to the steady state of the droplet. Figure 2.8 indicates the relationship between the Cassie-Baxter state and the Wenzel state. In Figure 2.8, it is necessary to point out that the slope of the curve is r in Wenzel state, and the slope of the curve f is in Cassie state. The intersection point of the two lines should satisfy both equations (2.11) and (2.14), showing that they are equal to each other, for the aim to obtain the threshold value θ_0 . The critical contact angle of Cassie and Wenzel state transition is represented as follows:

$$\cos\theta_0 = \frac{f - 1}{r - f} \quad (2.19)$$

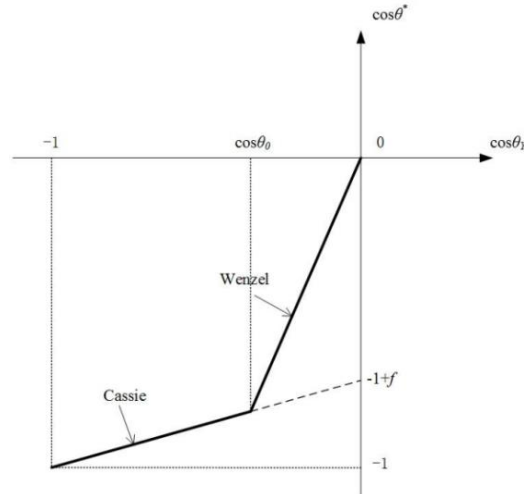


Figure 2.8 Relationship between Cassie-Baxter state and Wenzel state [91].

When $90^\circ < \theta_Y < \theta_0$, the droplet in the Wenzel state would have the lowest energy, which is relatively stable. And when $\theta_Y > \theta_0$, the droplet is in Cassie's state with low energy and is relatively stable. However, as shown in the dotted line in Figure 2.8, under certain conditions, Cassie's state will also exist between the intrinsic contact angle of 90° and the critical contact angle when the surface still has contact between the captured air and water droplets. At this point, although the energy is higher, the droplet could still exist in stable state, which could be defined as a sub-stable state. At this point, if some energy has been provided to the droplet, it is possible for the droplet to change

into the Wenzel's state (droplet is impaled on the surface asperities) from Cassie's state (air remains trapped beneath the droplet), which is represented by the reduced contact angle. Since the trapped air inside the rough structure has been squeezed out, the water droplet then enter and wet the rough structures [92].

In the case of medium hydrophobicity (usually in the presence of water, where Young's contact angle θ_Y does not exceed 120°), it is often observed that the air trapping state in Cassie's state is metastable. By applying pressure to the droplet, it could be induced to another state with an irreversible transformation, which is Wenzel's state. The contact angles in the two states are comparable (Wenzel's apparent contact angle was slightly less than Cassie's apparent contact angle, but both of them were significantly larger than Young's angle), the hysteresis phenomenon is significantly affected by the state change: the CAH values in Wenzel's state is greater than that in the Cassie-Baxter state since the water droplet could stick to the surface, leading to a remarkable adhesive force [93].

One of the weaknesses of superhydrophobic materials is that if the air between the surface textures is squeezed out and filled with water, the material would lose its waterproof properties. There are many methods of invasion, such as droplet condensation, external pressure, condensation of a dew, moisture invasion and drop evaporation [94]. To avoid this phenomenon, θ_0 should be as small as possible, and $\theta_Y > \theta_0$, the droplets on the surface could remain in a stable Cassie state. Since f is a parameter with phenomenological properties, this condition is not easy to create. If $\cos\theta_Y < -1/r$, the r value corresponding to the given hydrophobic material is large, the roughness is also large. In this way, this state could be realized.

2.2.2 Formation of ice

2.2.2.1 Physical phenomenon of icing

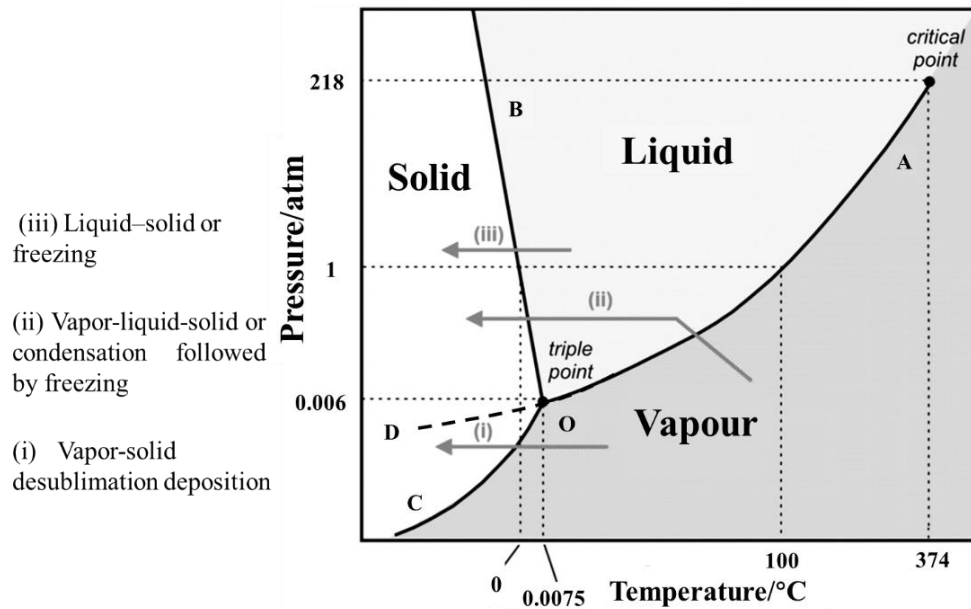


Figure 2.9 Phase diagram of water (Adapted from Ref [95]).

Icing is a complex physical phenomenon with the comprehensive action of multi-factor parameters. It is believed that understanding and mastering the physical process of icing is the premise and foundation for the design of icephobic surface applications. The characteristics of water state are closely related to its pressure and temperature. Figure 2.9 shows the phase diagram of water. O is the triple point (which corresponds to the ambient condition of 0.006 atm and 0.0075 °C), A is the critical point, B & C also indicate the points on the phase changing lines of solid-liquid and solid-vapour, while D shows the point on the extension of OA. OA, OB and OC are the two-phase equilibrium lines of gas-liquid, liquid-solid and gas-solid, respectively [95]. OD is the extension of AO line, which is the metastable equilibrium line of supercooled water and water vapor. Supercooled water is in a metastable state, and it would turn into solid ice as soon as a condensation core is present. It can be seen from Figure 2.9 that there are three main ways to form the solid phase of water: 1) the solidification of liquid water; 2) the condensation and freezing of water vapor; 3) direct condensation of water vapor.

There are many solid forms of water in nature: glaze, rime, frost, snow and ice. The characteristics of ice are closely related to the formation conditions (as shown in Table 2.1) [96]. Among them, the glaze/rime formed by freezing rain on near ground is the most harmful, and it is the main form of freezing problem on many types of equipment.

Table 2.1 Ice-type of different conditions [97]

Ice type	Category	Items	Drop size	Ice density	Adhesion
Glaze	/	Freezing rain	70 μm to a few millimetre	$\geq 0.9\text{g/cm}^3$	Very strong
Rime	Hard rime	Supercooled fog/cold	5-70 μm	0.6~0.9 g/cm^3	Strong
	Soft rime	/	/	0.3~0.6 g/cm^3	Weak
Frost	/	Vapor	/	0.05~0.3 g/cm^3	Weaker
Snow	/	Mixture of ice and water	/	low	Weaker
Ice	/	Liquid water	/	/	Varied

2.2.2.2 Supercooled water

For most of the time, water still remains in stable liquid state and does not freeze even the temperature is much lower than 0 °C. Although from the point of view of thermodynamic, water remains in the metastable state below 0 °C, the formed ice is more stable than liquid water. The state of temperature below freezing point without becoming ice is scientifically acknowledged as supercooled [98]. The degree of supercooling could be expressed as follows in equation (2.20):

$$\Delta T = T_{\text{crystalize}} - T_{\text{current}} \quad (2.20)$$

where $T_{\text{crystalize}}$ represents the theoretical crystallization temperature, T_{current} is the actual crystallization temperature.

The reason for the occurrence of supercooled state is that there are no growable nucleation points for ice growth formed when water try to crystallize to form ice in the system [99]. During the cooling process, the water molecules in liquid phase would keep swaying to produce thermodynamic fluctuations and lead to the spontaneous formation of ice germ microcrystals in the system. However, during this process, most of the microcrystals will dissolve back into the liquid state. The formation process of critical nuclei that can overcome the adverse interaction between the microcrystalline sequence and the environmental liquid molecules and would not be liquefied into water microcrystals could be called as nucleation. Once the critical nucleus is formed, it would grow irreversibly and eventually form ice with large sizes [100, 101]. But it takes some time for the nucleation and growth of the crystals, so that water could stay in supercooled state without freezing.

2.2.2.3 Formation of ice crystal

Ice crystals are formed by the orderly arranged water molecules as well as amorphous ice, which are bonded together by hydrogen bonds to form a loose rigid structure. Ice has more than 20 structural forms, which are usually marked by roman numerals with suffixes. The *h* and *c* behind the Roman numerals normally represent the hexagonal and cubic crystal systems, respectively, such as *Ih* and *Ic*. Among them, the *Ih* type ice is the most common existed. All of the common ice seen in the nature belong to *Ih* structure, while *Ic* structure only exists at very low temperatures. In *Ih* type ice, for every O atom, there would be four O atoms with tetrahedral coordination surrounded by, with bond length of O-O about 0.276 nm and bond angle of O-O-O about 109°, which is very close to the bond angle of ideal tetrahedron [102]. For the distribution of H atoms around O atoms, it can be either disordered or ordered. If the distribution of H atoms is disordered, there will be four H atoms with a space occupying degree of 0.5 distributed around the O atom, the symmetry of the structure is relatively high and the space group is $P6_3/mmc$. If H atoms are orderly distributed, there are two H atoms around every O atom and the space group is $P6_3cm$ (as shown in Figure 2.10) [103].

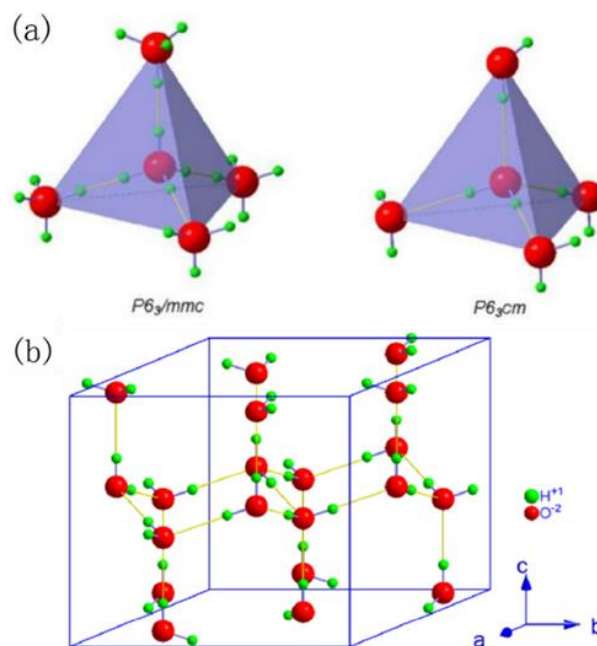


Figure 2.10 (a) The disordered distribution ($P6_3/mmc$) and ordered distribution ($P6_3/cm$) of H atoms around O atoms in Ice-Ih structure; (b) Crystal structure of Ice-Ic ($P6_3/cm$) [103].

2.2.3 Ice nucleation mechanism

2.2.3.1 Homogeneous nucleation and heterogeneous nucleation

An icephobic material should have the ability to delay ice nucleation in terms of temperature (under continuous cooling) or time (under a constant temperature). The ability to prevent or delay ice nucleation on surfaces depends on whether water droplets in supercooled state (below 0 °C) could freeze at the interface and the delay effect it brings to the heterogeneous ice nucleation. The process is governed by ice nucleation and growth, which is consistent with the classical nucleation and crystal growth theories in material science [104].

According to the analysis of the classical nucleation theory, the crystal nucleation for water could be divided into two categories: nucleation theories on homogenous and heterogeneous surfaces.

Homogeneous nucleation indicates the formation of critical crystal nuclei inside a uniform and metastable water phase. It could be categorized into random nucleation

and the nucleation occurs in all parts of the system showing the same probability. The reduction of system Gibbs free energy would occur spontaneously with the icing process. Under the thermodynamic driving force, the ice nucleation could take place once a large amount of relatively long-lived hydrogen bonds at the same location form a compact nucleus [105]. After that, the formed nucleus would keep changing the shape and size until it has reached a stage that allows the rapid expansion and crystallization of the whole system [106]. The three essential conditions of ice nucleation consist of supercooling, structure fluctuation, and energy fluctuation, which have been emphasized by molecular dynamics (MD) simulations. The ice nucleation on homogeneous surfaces could also be regulated by controlling the essential conditions to achieve anti-icing [107]. The critical nucleus radius r_c could be obtained using the classical nucleation theory on a continuum scale, as indicated in equation (2.21):

$$r_c = \frac{2\gamma_{IW}}{\Delta G} \quad (2.21)$$

where γ_{IW} is the water/ice interfacial energy and ΔG is the free energy barrier of bulk ice vs bulk liquid, which conforms to the Gibbs-Helmholtz equation (equation 2.22) [108]:

$$\Delta G = \frac{\Delta H (T_m - T)}{T_m} \quad (2.22)$$

Furthermore, ΔH is the water volumetric enthalpy of fusion, and T_m is the ice melting temperature at 1 atm. Combining equation (2.21) and equation (2.22), the critical ice nucleus radius r_c could be calculated.

It is generally assumed that the ice nucleation is difficult to occur in a completely pure and uniform water without any external changes and disturbances. This is also the reason why water with higher purity normally freezes at a lower temperature. A schematic illustration is given in Figure 2.11 for homogeneous nucleation, heterogeneous nucleation at solid/liquid 2D interface.

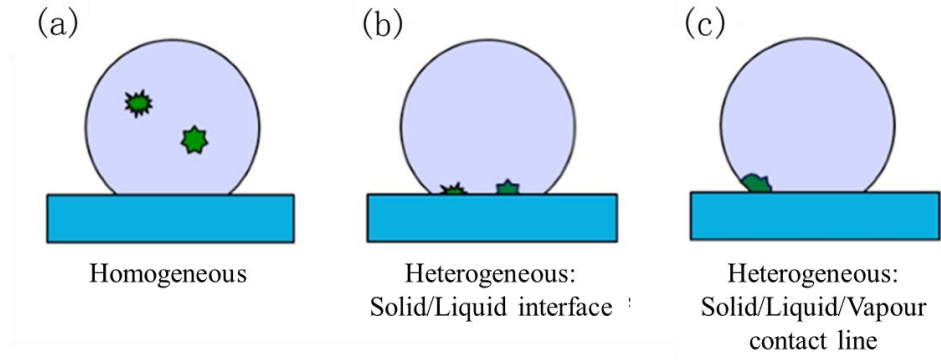


Figure 2.11 A schematic diagram of (a) homogeneous nucleation; (b) heterogeneous nucleation at the 2D solid/liquid interface; (c) heterogeneous nucleation along the 3D solid/liquid/vapor triple-phase contact line(adapted from Ref [109]).

While for heterogeneous nucleation, the ice nuclei often preferentially appear in those inhomogeneous parts of the system, such as defects, special chemical structures and impurity particles, etc. It is more easily triggered with lower nucleation free energy on solid surfaces in a practical situation due to the reduction of the energy barrier. Ice nucleation could also be delayed if the surface roughness is smaller than the critical nucleus size on a very low surface energy surface.

In the heterogeneous nucleation between solid/liquid interface, the free energy barrier $\Delta G_C'$ is reduced by a geometric factor $f(\theta)$ compared with the free energy barrier ΔG_C for homogeneous ice nucleation, and the relationship is well given through the classical nucleation theory, as shown in equation (2.23) [110]:

$$\frac{\Delta G_C'}{\Delta G_C} = f(\theta) = \frac{2-3\cos\theta+\cos^3\theta}{4} \leq 1 \quad (2.23)$$

If the heterogeneous ice nucleation takes place on a perfectly flat surface, it is only related to the contact angle (θ) , and the variation of geometric factor $f(\theta)$ with CA is shown in Figure 2.12.

Alizadeh et al. have investigated the nucleation rates (including homogeneous and heterogeneous) with different icing conditions as a function of surface wettability [111]. The delay effect for ice nucleation derived from the reduced water-solid contact area is more effective at moderate supercooling state. The nucleation effects in both bulk and the air-water interface become equally important. Icephobic surface with a relatively long icing delay effect could be designed upon the aforementioned conditions. It is also suggested that rational design frameworks could be used to develop and design icephobic surfaces focusing on preventing heterogeneous nucleation and prolonging icing delay [112].

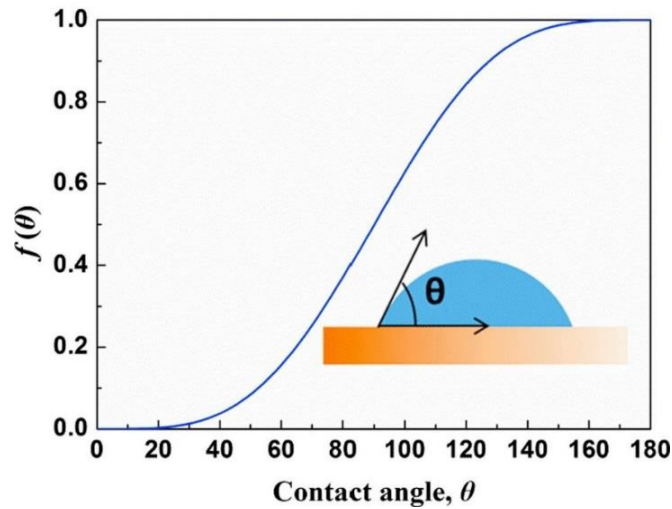


Figure 2.12 Geometric factor $f(\theta)$ for a heterogeneous ice nucleation as a function of contact angle θ on a flat surface [110].

In general, the occurrence of heterogeneous nucleation is easier than that of homogeneous nucleation, thus leading to the higher temperature of heterogeneous nucleation. Therefore, the ice formation is mostly induced by the heterogeneous nucleation of supercooled water. The ice would nucleate preferentially at the "defect" positions on solid substrates when the water build in contact with the substrate, the water molecules around the crystal nucleus would be ordered and arranged by hydrogen bonding and further form ice with macroscopic size.

In consequence, the influence of the properties of solid substrate on icing and thorough understanding of the intrinsic state of the relationship could be one of the core problems in icephobic coating systems.

2.2.3.2 Effect of surface roughness on ice nucleation

Here, the impact of surface roughness on water freezing process needs to be investigated. Some research results claim that there is no obvious difference towards the nominally lowest unfrozen temperature of water on surfaces with different surface roughness within a small range (0.017-0.146 μm) [113]. But for rougher surfaces, the increase of surface roughness in substrates could introduce some difficulties to the supercooling process of the water on the surfaces. For example, Wakomoto et al. [114] studied the effect of roughness on the supercooling and icing processes of the attached water on the substrate by using hydrogen peroxide etching methods on Cu substrate. The results indicate that the supercooled water on the substrate surface could reach its maximum supercooling degree by gradually increasing the etching frequency and lowering the surface roughness under continuous cooling condition, which actually shows an inverse relationship between the surface roughness and supercooling enhancement. Further research reported that the freezing of supercooled water is more likely to take place on surfaces possessing higher surface roughness with respect to surfaces having low surface roughness [115]. Similar to many other studies, surface roughness has a great influence on the supercooling phenomenon. The lower the roughness is, the higher the supercooling degree could reach, and the less likely the solution is to freeze [116].

The reason for the effect of surface roughness on water supercooling and freezing process may be ascribed to the fact that the contacting angle (θ) at the liquid-solid interface is largely related to the roughness. The relationship between the phase transition free energy threshold and the wetting contact angle was proposed by Papon. et al., as shown in equations (2.24) and (2.25) below [117]:

$$\Delta G_n^* = \frac{16\pi\gamma^3 T_{IFP}^2}{3L^2 \Delta T^2} f(\theta) \quad (2.24)$$

$$f(\theta) = \frac{1}{4} (2 + \cos\theta)(1 - \cos\theta)^2 \quad (2.25)$$

where θ is the contact angle (°), ΔT shows the temperature change (°C), L is the latent heat of fusion of ice (J/kg), γ is the radius (m), T_{IFP} shows the temperature of initial freezing point (°C), ΔG_n^* represents the threshold of phase transition free energy (J).

2.2.3.3 Effect of surface free energy on ice nucleation

The surface free energy of the substrate could directly affect the water infiltration on its surface. By changing the substrate surface energy, the contact angle, contact area and adhesion force between water droplets and surfaces will also change. The freezing of supercooled water droplets or condensed water droplets on the substrate surface is accompanied by the mass and heat transfer processes of crystal nucleus formation and ice crystal growth. These processes are associated with the solid-liquid contact state of the water-substrate interfaces. Therefore, the surface free energy of the substrate would also pose certain impacts on the supercooling and freezing processes. Zhang et al. [118] studied the effect of substrate surface energy on supercooling and icing processes of water. By avoiding the effect of contacting area and heat/mass transfer derived from the difference in surface free energy, the influence of surface energy on supercooled water freezing could be investigated independently. Because the rates of surface nucleation and heat transfer could affect the interfacial areas and pose impact on the ice's heterogeneous nucleation ability, which further affect the surface free energy [119]. For drops with volume lower than 10 μL , the supercooling degree of water would increase with the decrease of surface energy and the increase of contact angle. While for large droplets in the case of 300 μL , the surface free energy is independent of the freezing temperature, which is mainly because the increasing volume of water leads to the weakening of surface nucleation compared with bulk nucleation [120].

2.2.4 Ice adhesion on solid surface

Ice adhesion is determined by dividing the maximum breaking force value by the cross-sectional area of the ice–substrate interface [9]. For ice adhesion, it is difficult to explain the principle of ice adhesion with a single model or mechanism, which actually may be caused by a combination of physical and chemical factors. At present, there are four widely recognized mechanisms for ice adhesion, namely chemical bonding, physical adsorption, mechanical interlock and diffusion mechanism. Generally, the ice adhesion is mainly caused by the combination of multiple mechanisms, it cannot be explained by a single mechanism. The importance of different mechanisms is also different according to the physical and chemical characteristics of specific icing surfaces.

2.2.4.1 Chemical bonding mechanism

There are certain chemical bonds between ice and the substrate, which improves the ice adhesion on the substrate surface. It is assumed that the covalent chemical bonding directly associated with the ice surface can also be considered, but it is limited to very short distances (0.1-0.2 nm) and is only a factor for solids with specific chemical and crystal arrangements. Ice consists of polar water molecules that strongly interact with any solid substrate which has dielectric permittivity different from that of ice. There is a great deal of theoretical and experimental evidence for the existence of a surface charge in ice [121]. Furthermore, the surface charge can also interact with the substrate. For example, Ryzhkin et al. [122] studied the correlations between chemical bonding mechanism and electrostatic mechanism. The experimental values of adhesion energy of the ice/metal interfaces of four different metals were measured, as indicated in Figure 2.13. The results are comparable to or higher than experimental results. It indicated that the chemical bonding mechanism plays few role in affecting the adhesion energy, while the electrostatic mechanism is significantly more important than the chemical bonding when the distance is larger than 0.276 nm. They proved that the electrostatic interaction between ice and metals supplies energy that is significantly higher than chemical bonding energy and van der Waals forces at distances greater than intermolecular ones.

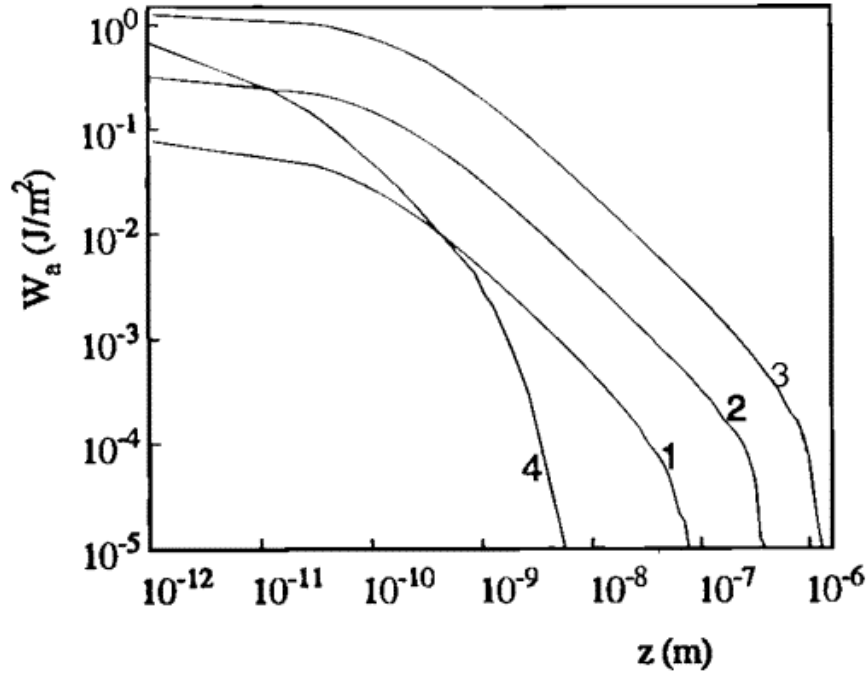


Figure 2.13 Graph illustrating the adhesive energy of the ice/metal interface per surface unit W_a , as a function of distance, z [122].

2.2.4.2 Physical adsorption

Physical adsorption refers to the mutual attraction between ice and substrate through electrostatic interaction or van der Waals forces to improve the bond between the two. Electrostatic interaction is the coulomb force when charge transfer occurs between two material surfaces. Jaccard et al. [123] thought that the charge on ice surface is caused by the defect of proton/hydrogen nucleus, which comes from the deviation of protons from the normal arrangement of ice crystal structure. As shown in Figure 2.14, the proton point defects include D defects (two protons on hydrogen bond) and L defects (no proton on hydrogen bond). Both of these are collectively known as Bjerrum defects, which are caused by the deflection of protons around the oxygen atom. There are also ionic defects in the ice crystals, known as proton transfer: the transfer of a proton from a water molecule to another water molecule, resulting in a positively charged hydronium ion H_3O^+ , and a negatively charged hydroxide ion, OH^- . These point defects are similar to electrons and holes in semiconductors, which could cause the charge on the surface of the ice crystal.

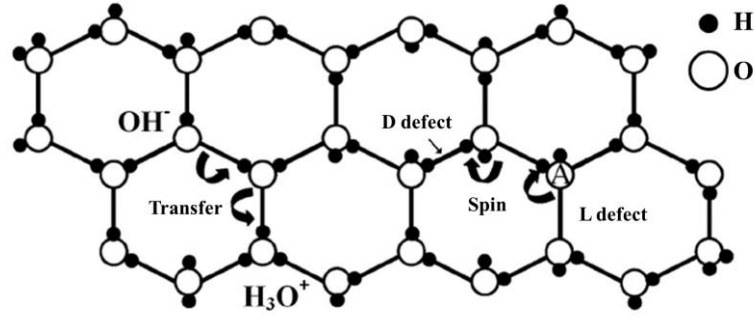


Figure 2.14 Bjerrum and ionic defects in the ice crystal structures [124].

The mirror force F that derives from the charge of point defects near the iced surface to the attached object was inferred as:

$$F = \frac{q^2}{16\pi\epsilon_0\epsilon z^2} \frac{\epsilon_{ice}-\epsilon}{\epsilon_{ice}+\epsilon} \quad (2.26)$$

where q is the content of electric charge, (C); ϵ is the equivalent dielectric constant of attached object, non-dimensional; ϵ_{ice} is the equivalent dielectric constant of ice, non-dimensional; ϵ_0 represents the absolute dielectric constant in vacuum, $C^2/(N \cdot m^2)$; z indicates the distance between the electric charge and interface, (m). Petrenko et al. [124] reported that the adhesion energy range between ice and metal was about $0.08 \sim 1.3 \text{ J/m}^2$. It is also found that the mirrored charge derived from the iced surface onto insulators is smaller than that on metal. Normally, the lower the dielectric constant is, the lower the electrostatic force effect is. For example, polytetrafluoroethylene has a lower dielectric constant ($\sim 2.1 \text{ C}^2/(N \cdot m^2)$), leading to a lower ice adhesion strength [121].

Van der Waals force is also known as the intermolecular force with the action range of $0.3 \sim 0.5 \text{ nm}$, it could pose important effect on the melting point, boiling point, surface tension and other physical and chemical properties. The schematic diagram of Van der Waals force is also displayed in Figure 2.15. Van der Waals force consists of the oriented forces (inherent dipoles), dispersive forces (instantaneous dipoles) and induced forces

(induced dipoles). The bond energies of Van der Waals range from a few to tens of kJ/mol, which is 1-2 orders of magnitude lower than the chemical bond energies. The dispersion force is widely-existed among all molecules, which is also the nonpolar intermolecular interactions. The interaction between the polar and non-polar molecules are the combination of the dispersion force and induced force. For example, Wilen et al. [125] studied the effect of van der Waals force on ice accumulation adhesion strength and found that the influence of electrostatic force on ice accumulation adhesion strength was greater than that of van der Waals force. The sketch map of van der Waals force is also displayed in Figure 2.15.

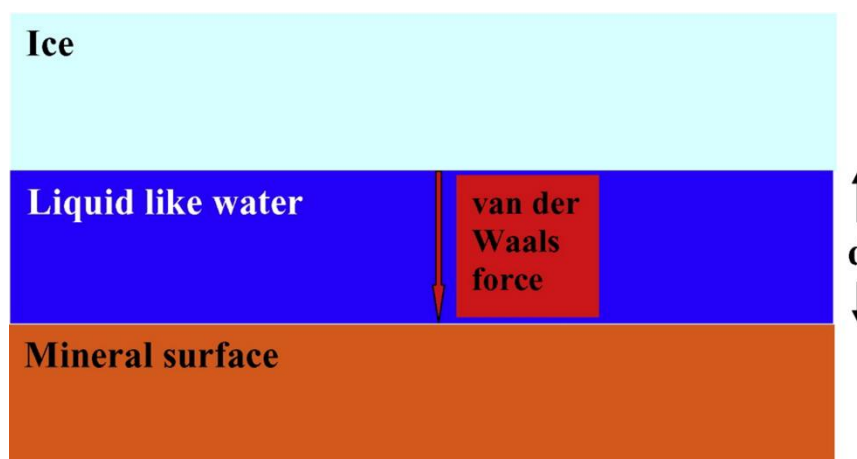


Figure 2.15 Sketch map of van der Waals force in sandwich model of an adsorption water layer between attracting surfaces of ice and adsorbent at temperatures below the freezing point [126].

Another type of physical adsorption, the hydrogen bonding also needs to be introduced. Water molecules are easily attracted to electrically positive hydrogen atoms in another water molecule through an oxygen atom with unshared electron pairs. Thus, one water molecule could statically attract four water molecules and form the tetrahedral structure [127]. For hydrogen bonding, the sum of electrostatic attraction between oxygen and hydrogen atoms as well as the van der Waals force is named as hydrogen bonding, the structure is also indicated in Figure 2.16. The figure showed the spatial structure relationship between the two water molecules, where the dashed line represents the formed hydrogen bond between two water molecules.

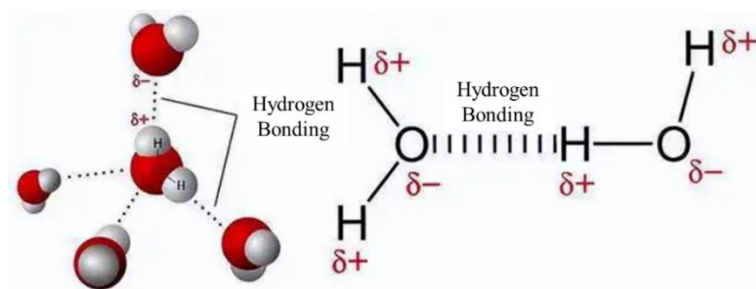


Figure 2.16 Snapshot of the hydrogen bond between water molecules (Adapted from Ref [128]).

Compared with the bond energy of intramolecular covalent bonds (e.g. the bond energy of C-C bonding is about 607 kJ/mol), hydrogen bond energy is relatively weak, about 15~33 kJ/mol [127]. Nevertheless, the intermolecular and intramolecular hydrogen bonding still exist abundantly in water solutions, ice crystals, and protein molecules, and play crucial roles. For example, hydrogen bonding contribute to the transformation liquid water into solid ice and make it exist stably as a crystal structure, the more ordered arrangement of hydrogen bonding which leads to the liquid-solid phase transition [129]. The abnormal changes of water at the melting point and boiling point are also closely related to hydrogen bonds. Water molecules could also form hydrogen bonds with other molecules, which plays an important role in the conformation, function and other properties of biological molecules.

2.2.4.3 Mechanical interlock

Mechanical interlock mainly appears on surfaces with certain rough structures, the formed ice on the surface could join together with the certain position and lead to the increase of adhesion area and adhesion force.

Because material surfaces cannot be ideal surfaces, there would be concave, convex, steps, grooves and fractures existing. Once the surface structure was affected by the water droplet or water vapour condensation, there would be mechanical interlocks taking place at the ice/solid areas after freezing [130]. Therefore, some scholars think the existing mechanical interlock will also affect the adhesion behaviour of ice. Figure

2.17 displayed the interlocked ice formed between the hierarchical structures on coating surfaces. Mechanical interlocks are not the essential factor of ice adhesion, but they can be used to explain the proportional relation between the ice adhesion force and surface roughness.

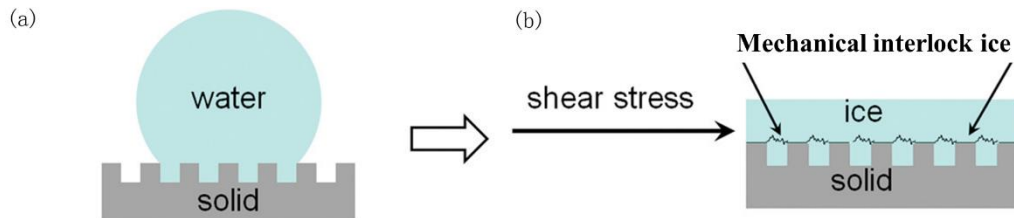


Figure 2.17 (a) Wenzel state of water droplets on a solid surface. (b) Existing mechanical interlocks between the hierarchical structures on a patterned substrate [131].

2.2.4.4 Diffusion mechanism

It is thought that the regular arrangement of water molecules at the boundary of ice crystals could be affected by the interface, resulting in the disordered distribution of water molecules at the interfacial region and the characteristic similar to liquid water. Therefore, an amorphous transition layer (as liquid-like layer, as illustrated in Figure 2.18) exists between the ice and adhered material [132, 133]. Depending on the ambient temperature and adhered material, the thickness of the liquid-like layer ranges from several nanometres to hundreds of nanometres. Wilbert et al. [134] found that the spectral response on iced surface was similar to that of supercooled water when ice was cooled to $-28\text{ }^{\circ}\text{C}$, confirming the existence of a liquid-like layer. Jellinek et al. [135] reported that the tensile adhesion strength at the ice-steel interface is around 15 times higher than that of the shear adhesive strength under the same conditions. The reason here could be ascribed to the additional pressure caused by the surface tension of the liquid layer, which leads to a difference between atmospheric pressure and internal pressure of the liquid layer. In this way, the tensile strength of interfaces is much larger than the interfacial shear strength since the pressure difference needs to be overcome when conducting tensile tests, and shear tests only need to overcome the friction that is much smaller.

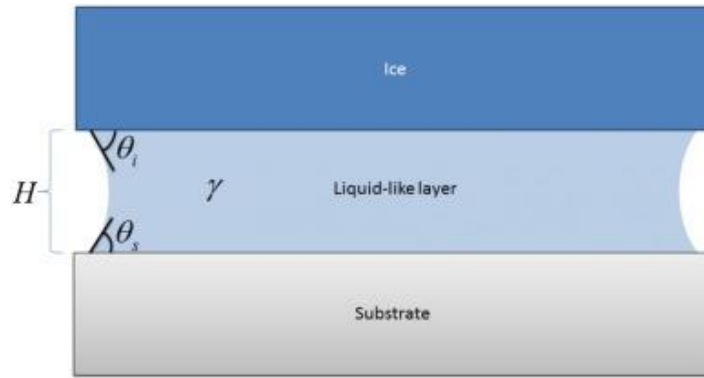


Figure 2.18 Representation of a liquid-like layer between ice and substrate [132].

2.3 Simulation of Surface Icephobicity

With the development of computer technology, computational simulation is being widely used to guide and verify the experiments. Because of the lack of details about icephobic mechanisms at the current stage, there are still much work needed to be done.

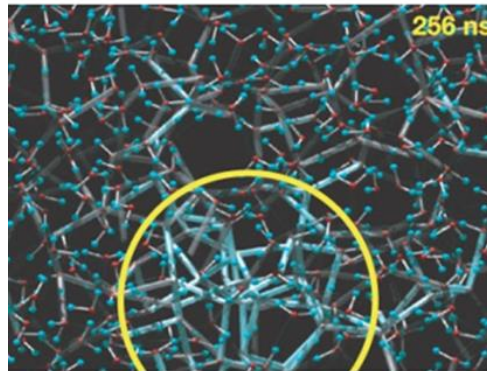


Figure 2.19 The molecularly-simulated hydrogen bond network structures of pure water [136].

The simulation of icephobic coating is mainly divided into the simulation of ice nucleation on the surface and the mechanical analysis of ice detachment. Delaying the freezing process is a significant method for anti-icing. An icephobic material should have the ability to delay ice nucleation or lower the icing temperature (under continuous cooling) [137]. The water freezing process was illustrated by molecular dynamics simulation (MD simulation) in Matsumoto's research [136]. They found that the

formation of long-lived hydrogen bonds is the key to driving homogeneous ice nucleation as shown in the yellow circle region in Figure 2.19. An initial nucleus is formed in the region circled in yellow circle. MD simulation visually exhibits the water freezing process, which further emphasised the three essential conditions of ice nucleation, i.e., supercooling, structure fluctuation and energy fluctuation [107]. Molecular dynamics is a multi-body simulation method. Through the simulation of the motion states of molecules and atoms in a certain period, the behaviour of the system evolution over time is investigated dynamically. Although MD simulation can describe phenomena that cannot be observed experimentally, due to the relatively slow computing speed, especially for large systems (e.g. with tens of thousands of atoms or even more), the time of physical change that can be simulated is very short. The system size that can be simulated by MD is also very small, making it difficult to combine with the specific experiments due to the several orders of magnitude difference between the simulation results and the macro results.

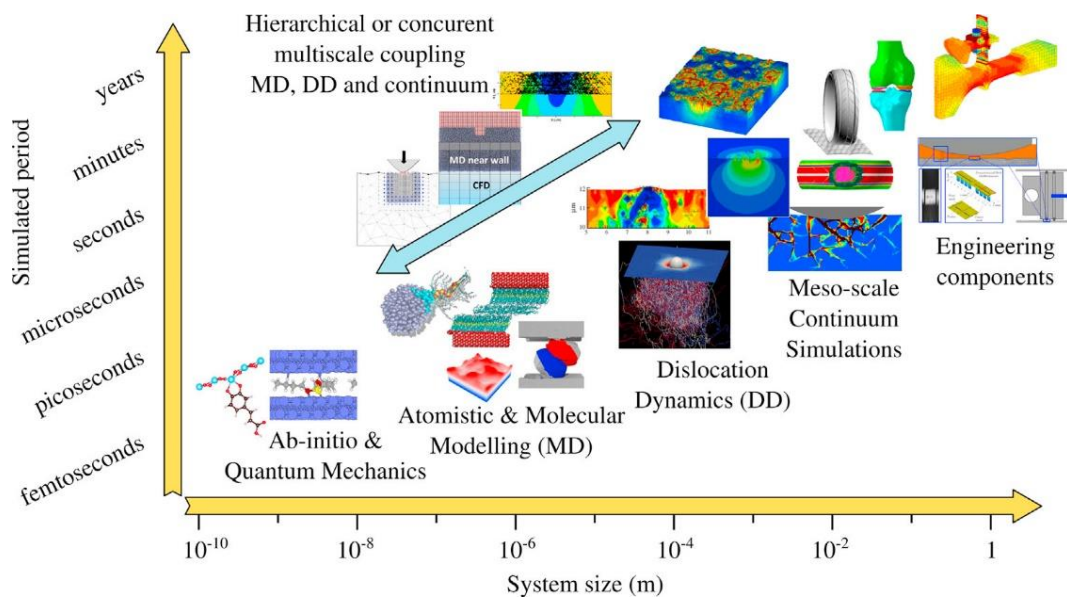


Figure 2.20 A time-vs length-scales map of models developed in engineering science [138].

Comparing to the simulation of anti-icing surface, the mechanical analysis of ice detachment for de-icing surface is on a more macroscopic scale (shown in Figure 2.20 [138]). The experimental results could be in good agreement with the simulation results.

The finite element (FE) method is developed as a kind of approximate numerical method which is based on the rapid development of modern computers, and it could be used to solve mechanics, mathematics with specific boundary conditions of the partial differential equation (PDE) problems. The partial differential equation is common in engineering practice, it is also the basis of solid mechanics and fluid mechanics problems. The FE analysis is suitable for simulation of the loading process and stress distribution at the ice-material interface. Zhang's group used FE simulation to illustrate a concept called macro-crack initiator (MACI) (as shown in Figure 2.21) [139]. This concept introduces stiffness inhomogeneity in both perpendicular and tangential directions to dramatically weaken the ice-solid interface and maximize the crack length underneath the ice.

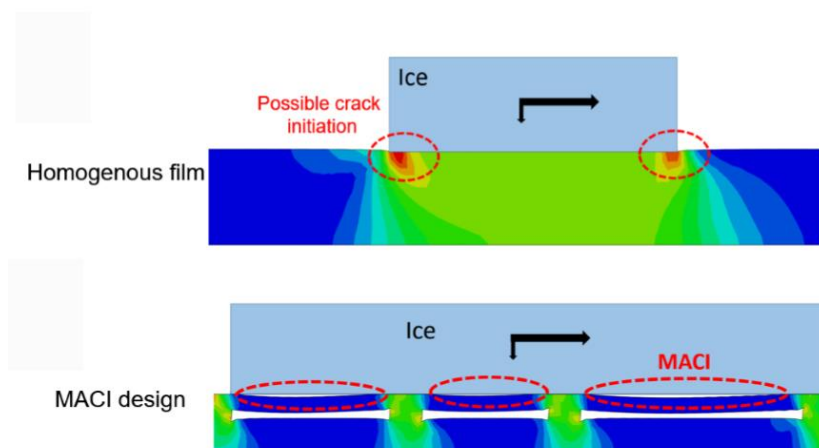


Figure 2.21 2D plane strain FE analysis to illustrate the MACI mechanism [139].

2.3.1 Finite element theory

Finite element theory is an efficient and commonly used numerical analysis method. It is usually necessary to solve a variety of differential equations in the field of scientific computation, and it is also difficult to obtain the analytical solutions of many differential equations. After discretizing the differential equations using finite element theory, some programs can be coded to solve the problem using computer-aided analysis. The finite element theory was developed on the basis of the earlier variational principle. It has been widely applied in various physical fields described by Laplace

and Poisson equations. It is one of the most widely used numerical methods in the engineering area, as well as a numerical simulation and digital simulation technology [140, 141]. The basic idea is to change the problem from obtaining the solution of the given Poisson equation into solving the extreme value problem of solution function.

Because of the application of finite element, a lot of scientific theories have been realized in technological fields, and the development level of human technological ability is constantly being improved. Finite element method is widely used in aerospace, national defense, military and other different fields, as well as in consumer goods, daily necessities and other aspects of daily life. After determining the mathematical models of engineering or physical problems (e.g. basic variables, basic equations, solution domains or boundary conditions, etc.), finite element theory is used as one of the numerical methods for analytical mathematical calculation. The basic idea is mainly simplified into two aspects: the core knowledge of finite element theory is to find approximate solutions and discretization of PDE [142].

(1) To determine the approximate solutions of PDE. All of the partial differential equations in both mechanical and engineering problems could only be solved by simple analytical solutions before the invention of finite element methods. The approach is mathematically demanding and relies heavily on some idealized assumptions. For example, the assumptions of plane section, small strain and ideal plasticity would appear in the calculation of beams and columns in civil engineering. In fact, there are actually quite large differences between the assumptions and actual mechanical/engineering problems. If the problem is slightly more complicated, the analytical solution cannot be obtained directly, or the error of the analytical solution is so large that it could lead to the error in the calculation results. The finite element theory discretizes the overall complex structure into finite elements, and then idealization assumptions and mechanical governing equations could be applied to the elements in the structure. Then the total stiffness equation of the structure could be obtained by element analysis and the total response of the structure is obtained by the boundary

conditions and other constraints. The reactions of each unit in the structure can be mapped from the total reaction one by one, thus directly avoiding the mechanical and mathematical models of complex structures. The whole analysis process could be summarised in Figure 2.22.

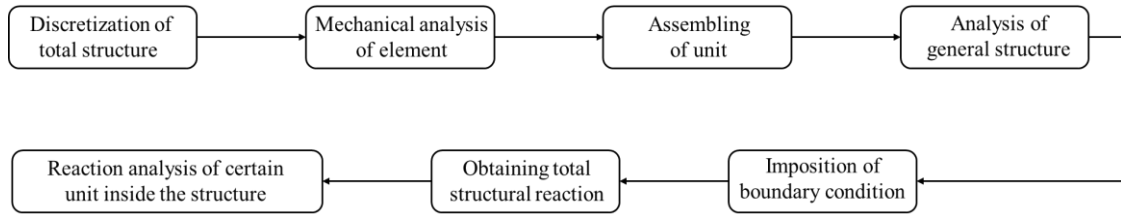


Figure 2.22 Analysis process diagram of finite element simulation.

In the process of finite element analysis and internal reaction analysis, the shape function interpolation and Gaussian quadrature are used to approach the response of any point in the element. This is an important expression form of finite element numerical approximation. In general, the higher the order of the shape function, the higher the approximation accuracy. Besides, the number of unit control points and the number of required Gaussian integration points is also higher. However, the more accurate the finite element accuracy of the above two elements is, the more obvious the unit division will be, and the more accurate the result is, the more rapid increase in the amount of calculation.

(2) The continuum has been divided into several simple basic geometric units (elements) with discretization method. These elements are connected to each other through nodes. The process is often referred to as meshing. For each element, the problem can be solved using the method of the previous section. And then the results of the elements can be integrated into the results of the whole domain through the relationships between the nodes, which are named the combined stiffness matrix [143].

2.3.1.1 Characteristics of finite element theory

Some basic characteristics of finite element theory are mainly reflected in the following four aspects. Firstly, some very complex structures or related structures are often encountered in the daily practical engineering process. And any structure can be discretized into the finite element model expressed by the element assembly. This is because the elements can be multi-dimensional in spatial structure, and each element can have different types and different connected forms. The characteristic is called the adaptability of finite element theory. Secondly, finite element theory is applicable to various physical problems in current disciplines, such as different elastic problems, fluid problems and corresponding mechanical, heat conduction, acoustic problems, as well as various coupling problems in different physical phenomena [144]. The unknown field function in the whole solution domain is expressed piecewise by the approximate function in the element, which neither restricts the form of equation satisfied by the field function nor restricts the same form of corresponding equation of each element. The characteristic is called the applicability of finite element theory. Thirdly, the degree of approximation of the finite element solution could become larger with the increase of the degree of element freedom (i.e. the order of the interpolation function).

If the elements conform to the convergence principle, the approximate solution would eventually converge to the exact solution of the original mathematical model. By using the variational principle or weighted residuals method, due to the finite element equation, it can be mathematically proved that the equivalent integral form of differential equation and boundary conditions are appropriate. So as long as the mathematical model of the original problem is correct, the calculation method of the finite element equation is stable and reliable, the characteristic is then called the reliability of the finite element theory.

Fourthly, with the rapid development of computer hardware technologies and the emergence of new numerical calculation algorithms, the finite element analysis of large-scale complex problems in the actual production process has become an essential

step in the field of engineering technology [145]. Since the steps of finite element analysis could be expressed in a standardized matrix form, the efficiency of the finite element method is very high. And the solved equation can be unified into a standard matrix algebraic problem, especially in the application of computer programming and execution. It can be referred to as the high efficiency of finite element theory.

2.3.1.2 Influencing factors upon the analysis accuracy using finite element method

Using the finite element method to analyze the structure, the smaller the error of the calculation results, the closer it is to the actual working state of the structure. This is also related to the accuracy of finite element analysis method, which is closely related to the following factors:

(1) Solid model. The basis of structural analysis is the correct establishment of the solid model, the 3D solid model established by computer-aided modeling software needs to use the largest restore entity. Meanwhile, some necessary simplifications are needed to meet the corresponding computational requirements.

(2) Unit type. The accuracy and calculation amounts of different unit types are completely different. The more complex the shape of the divided unit type is, the larger the scale of the calculation and the higher the accuracy of the calculation. Also, it could meet more complex structure, and the longer the calculation time is, the higher the requirements for the computer, and vice versa. Therefore, the appropriate cell type should be selected according to the actual demand, so that the accuracy of calculation would not be affected, and the calculation efficiency can be well guaranteed.

(3) Grid division. The finer the grid, the better the accuracy of the calculation. But the requirements for computers are also higher, which could be quite time-consuming, and it will affect the correctness of the calculation results directly.

(4) Boundary conditions. The setting of structural boundary conditions is another key point that affects the finite element analysis. Especially, beginners often make mistakes in the imposition of boundary conditions, resulting in the failure of the final calculation results with large errors [[146](#)].

2.3.2 Application of finite element theory in ice protection areas

Finite element theory is a traditional numerical method. With the development of finite element theory and the practical analysis in the specified application of the mechanical engineering issues, the finite element theory method has gradually upgraded from the initial validation functions to the optimum design with the incorporation of intelligent computer-aided design technology. It also becomes an effective tool to solve the daily practical problems in mechanical engineering aspects. Because of the advantages in solving complex design and problem analysis in engineering aspects, the finite element method is being more widely used in different types of engineering fields, which has also become an important tool in both engineering design and analysis [[147](#), [148](#)]. By simulating the structure with finite element method, it can further provide guidance for solving practical engineering problems. The application of finite element method in mechanical structure analysis mainly includes the following aspects:

(1) Structural statics analysis

The structural statics analysis refers to the analysis of structure under static load. Here, the static load means that the load applied to the structure does not change with time, or the load could change very slowly over time [[149](#)]. The equivalent stress, strain and total deformation of the structure under load can be obtained from the resulting cloud map by carrying out the static analysis of the structure using finite element analysis software. Therefore, the analysis method is the most common method in finite element analysis [[150](#), [151](#)].

(2) Structural dynamics analysis

Apart from the static load, the structure also needs to suffer from the dynamic load during the whole movement. When the external excitation is close to or equal to the natural frequency of the structure, there would be resonance effect generating, and further lead to structural damage with different degrees and even structural failure, so as to affect the normal movement of the structure. Hence, in the design and material selection of the structure, apart from the check on the structure that can meet the requirements of static stiffness, the dynamic stiffness of the key structure needs to be checked again. At present, the mainstream finite element analysis software on the market provides a variety of dynamic analysis tools to users, which could complete the analysis and simulation of various dynamic phenomena [[152](#), [153](#)].

To sum up, the main advantage of finite element theory mainly consists of its wide application range, high efficiency and convenience. It can not only express the physical formulas and mathematical equations visually, but also effectively simplify the difficulty of user operation, which is a relatively rare structural analysis method.

2.4 Developments of Icephobic Surfaces

In the previous sections, the multiplicity of icephobicity definitions and related mechanisms on ice nucleation, icing delay, and ice/solid interaction have been demonstrated. The present part will focus on the discussion of the current progress of mainstream icephobic surfaces.

During the last few decades, studies on preparing icephobic surfaces have caused great interest all over the world [[154](#)]. The wide application of icephobic surface could be the key solution for effectively addressing the undesirable icing problems on engineering surfaces [[155](#), [156](#)]. The design concepts based on the icephobic structure mainly include: 1. for anti-icing, by applying hydrophobic effect to delay or inhibit the nucleation of water droplet [[157](#), [158](#)]; 2. for de-icing, by using the soft-based or

polymeric systems to lower the fracture toughness of ice at the interfaces [159, 160]; 3. for de-icing, by decreasing the ice adhesion strength using the oil layer from the slippery liquid-infused porous surfaces (SLIPS) [161, 162].

2.4.1 Strategies for designing icephobic surface

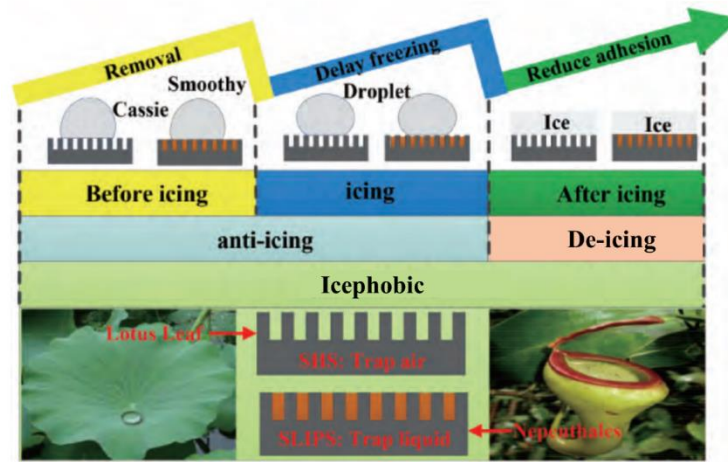


Figure 2.23 Schematics of ice protection systems (anti/de-icing) (Adapted from Ref [163]).

The ideal active icephobic mechanism is reflected in the following three aspects: firstly, it helps the supercooled water droplets to roll off the surface quickly before the ice solidifies; secondly, it could help to delay the crystallization process of supercooled water droplets; thirdly, when supercooled water droplets freeze into ice, the ice adhesion between the interfaces should be small [164]. Icephobic coating is a passive icephobic method based on the above mechanisms, with the advantages of low cost, low energy consumption, simple system structure and easy implementation. It has already attracted wide attention and become a research hotspot in recent years [131, 165, 166]. It is difficult to implement all of the icephobic mechanisms to one surface, so icephobic coatings are mainly divided into the following two categories according to their different icephobic mechanisms (as shown in Figure 2.23): 1) Anti-icing surface, its main purpose is to extend the freezing time of remaining water droplets in supercooled state or to remove the supercooled water droplet out of the surface easily before its solidification using external force [167]. 2) De-icing surface, the main focus is to ensure

low ice adhesion strength (reduction of the ice adhesion) and the formed ice could easily slide off or be removed [23].

Detailed discussions on the icephobic mechanisms are presented below:

1) Direct removal before freezing. Direct removal of water droplets is one of the main features of ice-proof surface, which is embodied in the following three aspects: the direct roll-off of water droplets, self-propelled bounce-off of condensed water droplets and rolling of the liquid lubrication layer. The direct rolling of moving water droplets is mainly aimed at the phenomenon when water droplets or streams on macroscopic scale hit the surface. Since the surface has a low contact angle hysteresis ($CAH < 5^\circ$), the droplets are in Cassie's state or lubricated state which is easy to roll when contacting the surface. This phenomenon causes the moving water droplets to bounce or roll off the surface before freezing. The self-propelled jump of condensed water droplets refers to the self-migration of tiny water droplets formed by microscopic condensation of water vapour under the condensation environment due to the decrease of surface energy during the superhydrophobic surface merging process. Or the droplets on the lubricated surface jump off the surfaces due to the smaller critical rolling radius [168].

2) Nucleation is inhibited during freezing. Once the droplets stick to the surface, preventing them from nucleating becomes the second barrier. Compared with ordinary surfaces, the contact area between droplets and substrates on superhydrophobic surfaces is smaller, the possibility of inhomogeneous nucleation is lower. In addition, the air or other medium captured in the surface structure act as thermal resistance, impeding the energy transfer between the two material and delaying the occurrence of ice [169, 170].

3) Reduces ice adhesion after freezing. Under the meteorological conditions of low temperature, high humidity and high-speed impact, the superhydrophobic surface may easily lose its hydrophobic and anti-icing characteristics, resulting in the loss of the first two stages and the final surface freezing. The ice adhesion also increases with surface

roughness [171]. Water could penetrate the air layer between the solid-liquid interface on the rough surface and increase the ice adhesion after quick freezing. De-icing, which helps to reduce the adhesion between the ice tube and surface, is the only control measure. The mechanism of de-icing on the surface is that the ice could be released from the surface under the action of external forces after ice formation (including wind, gravity and applied force field as well as chemical measurements) by reducing the adhesion between the surface and ice.

2.4.2 Superhydrophobic surfaces

Since the discovery of "lotus leaf effect" in 1997 [172], the bionic superhydrophobic surface has developed rapidly. Its hydrophobic characteristics have attracted attention of researchers, who designed and studied a series of anti-icing surfaces [173-175].

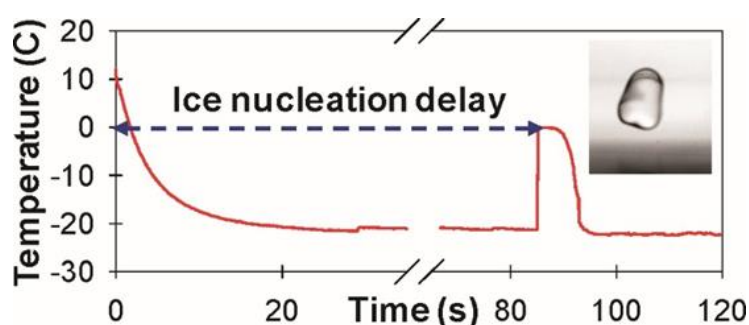


Figure 2.24 Transient temperatures of 4 μL deionised (DI) water droplet freezing on superhydrophobic surface [170].

The superhydrophobic surface can prevent icing phenomenon by slowing down the crystallization process of condensed water droplets. The crystallization process of water could be divided into two stages: nucleation stage and crystal growth stage. Most anti-icing techniques slow down the crystallization of water by inhibiting nucleation. Alizadeh et al. [170] used infrared measurement and high-speed camera technology to track the freezing process of liquid droplets at room temperature after hitting the surface at low temperatures (the volume of the impinging water droplet was maintained at 4 μL with the velocity and the temperature of the substrates was $-20\text{ }^{\circ}\text{C}$) (as shown in Figure

2.24). The contacting area of solid and liquid on the super-hydrophobic surface is very small, which results in the very high nucleation energy barrier of droplets, and it also reduces the possibility of heterogeneous nucleation at the solid-liquid interface. In addition, the air layer between the solid-liquid interfaces greatly reduces the heat exchange between the surface and droplets, making nucleation difficult. The results show that the superhydrophobic surface with a suitable surface structure and chemical modification could effectively delay the freezing process in a low humidity environment.

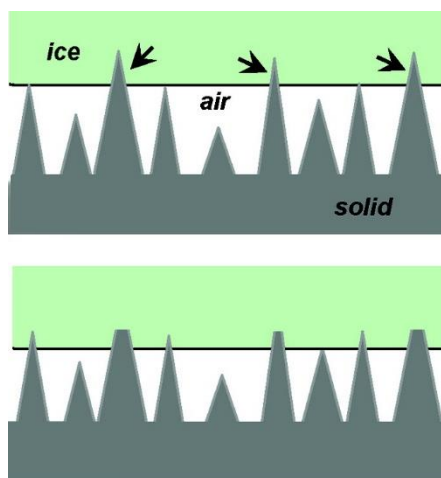


Figure 2.25 Schematic of ice on a superhydrophobic anti-icing surface. The asperities with tips indented into the ice (indicated by arrows) are very likely to be damaged during icing (water solidification) and/or de-icing (ice removal). Ice on the same surface sitting lower on the asperities during the following icing events [176].

Since the performance of super-hydrophobic surfaces (SHS) in low temperature and high humidity condensation environments will be inhibited by condensation droplets, the condensate conditions correspond to temperature lower than $-10\text{ }^{\circ}\text{C}$ and relative humidity higher than 90% [177]. Researchers successively proposed composite two-dimensional and three-dimensional structural surfaces since samples with multiple rough tier exhibit robust Cassie state and it could prevent the surface from being wetted by incoming droplet with a speed over 2 m/s [178, 179]. However, although the surface of this multistage layered structure enhanced the removal behavior of condensed droplets and improved its adaptability, the mechanical strength and stability of the

surface of the structure were damaged. Kulinich et al. conducted 24 freezing/de-icing cycles on the tested samples in the ice wind tunnel with sprayed supercooled microdroplets (with an average size of 80 μm) on the aluminum-based superhydrophobic surface spun in the centrifuge at constantly increasing speed. The as-prepared superhydrophobic surface is not suitable for all working conditions of anti-icing, especially the damage to the superhydrophobic structure caused by low wear resistance (as shown in Figure 2.25) [176].

Based on this, the researchers successively proposed various designs to enhance the mechanical stability of superhydrophobic surface microstructures. For example, the superhydrophobic surface of T-shaped structure proposed by Tuteja et al. [180]. (as shown in Figure 2.26 (a)) and the super-hydrophobic surface with T-shaped double-concave angle structure designed by Liu et al. [181] (as shown in Figure 2.26 (b)). The specific doubly reentrant structure could enable low liquid-solid contact fraction and render surfaces with good repellency. Also, the wettable material with micro- and nanostructure could make it superomniphobic and bounce off all available liquids. Under this structure, the contact area between droplets and solid surface is smaller, and the supporting effect with the suspension force is stronger.

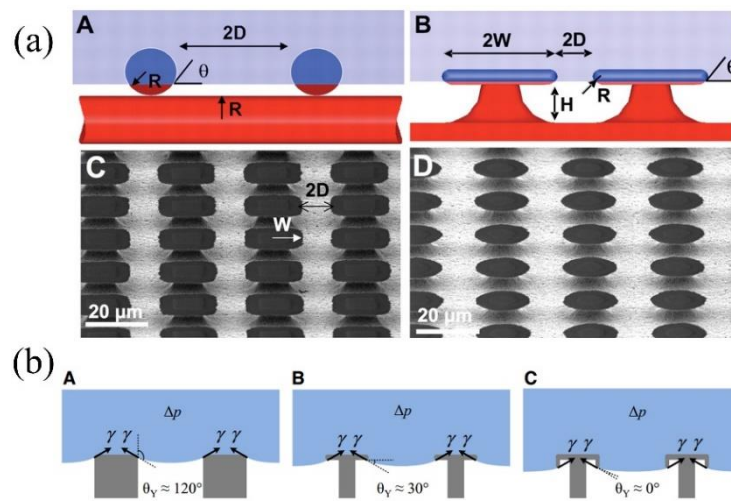


Figure 2.26 (a) Critical role of reentrant curvature (A and B) schematics show the formation of a composite interface on surfaces with re-entrant topography. The geometric parameters R , D ,

H and W characterizing these surfaces are also shown. The blue surface is wetted while the red surface remains nonwetted when in contact with a liquid whose equilibrium contact angle is θ ($< 90^\circ$). (C and D) SEM images for two surfaces having square and circular flat caps, respectively. The samples are viewed from an oblique angle of 30° ;

(b) Liquid suspension on surface structures of three different topologies: (A) Simple structures require $\theta_Y > 90^\circ$ to suspend water. Δp is the pressure difference between the liquid and air. (B) Reentrant structures allow $\theta_Y < 90^\circ$ to suspend oils or solvents. They would fail if $\theta_Y \sim 0^\circ$; as surface tension acts parallel to the horizontal overhangs with little vertical component to suspend the liquid. (C) Doubly reentrant structures allow $\theta_Y \sim 0^\circ$ to suspend any liquid, as surface tension acts on the vertical overhangs with a substantial vertical component. If the liquid-solid contact fraction is small enough, the surfaces would also repel the liquids (Adapted from Ref [180] and [181]).

Inspired by the phenomenon that the external strong impact force could be alleviated by the continuous vibration of lotus leaves, ZnO nanorods with extraction capability were prepared by crystal growth method (sol-gel) on the surface of PDMS flexible micron structure modified with solid-phase micro-extraction fiber [182]. The efficient droplet removal performance (removed easily with high contact angle of 170.2° ; advancing angle of $124.3^\circ \pm 3.1^\circ$ and receding angle of $112.6^\circ \pm 2.8^\circ$) was demonstrated in low-temperature environments ($\sim -5^\circ\text{C}$). However, the general solid surface is in a relatively static state, and its position stability cannot be changed. The change of local structure cannot fundamentally solve the problem of the mechanical structure stability of the superhydrophobic surface with micron and nanometer scales. In addition, the efficiency of surface energy conversion to kinetic energy (KE) is also very low during self-propelled jump of water condensed droplets, the conversion efficiency of coalescence-induced droplet are characteristically smaller than those of a solid disc transitioning to a sphere, which is around 20% [183]. When the droplets hit the superhydrophobic surface at a high speed, the droplets could interpenetrate into the surface microstructure, resulting in the change of droplets from Cassie state to Wenzel state. Therefore the droplets no longer bounce off from the surface and lose their icephobic characteristics.

According to existing literatures [184-186], superhydrophobic surface can only play a role in icing delay, but cannot inhibit icing completely. In view of the disadvantages and shortcomings of superhydrophobic surfaces, the methods to reduce the surface adhesion between the ice cubes are important.

2.4.3 Elastomer coatings

For elastomer based smooth coatings such as polysiloxane based coatings, fluoropolymers based coatings and polyurethane based coatings, they normally possess the virtue of having a very large WCA and exhibiting little sticking to formed ice. A myriad of reports has been published on elastomer smooth coatings which could be classified into the following categories.

2.4.3.1 Soft-based coatings

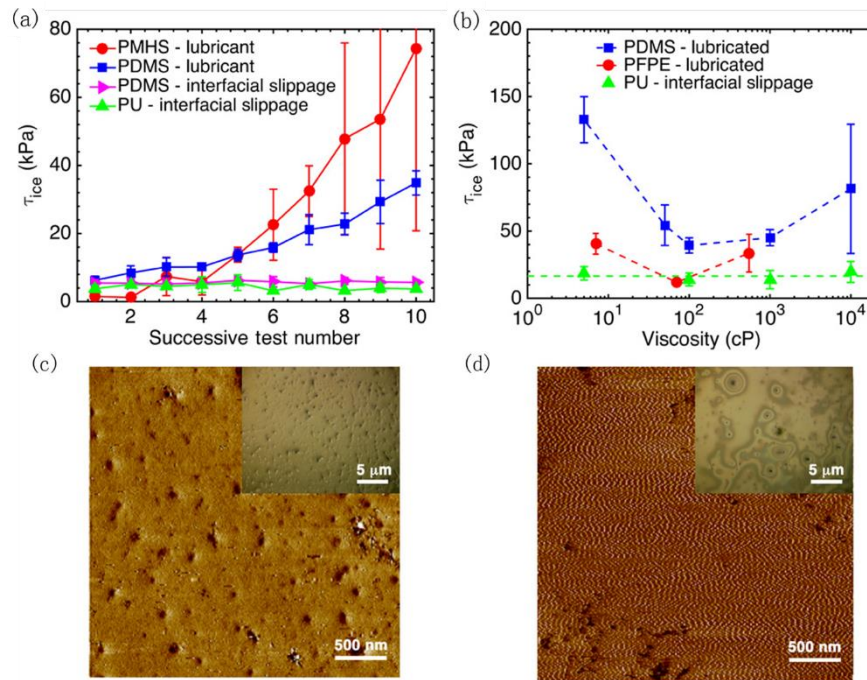


Figure 2.27 Comparison between interfacial slippage and lubrication: (a) Variation of ice adhesion strength with the number of icing/de-icing cycles; (b) Variation of ice adhesion strength with oil viscosity; (c) Atomic Force Microscope (AFM) phase images and optical micrographs of the PU coating with 15 wt % safflower oil; (d) AFM phase images and optical micrographs of the PU coating with 10 % silicone oil [187].

Soft-based coatings (or surfaces with low elastic modulus which is generally lower than 2 MPa) are newly developed icephobic coatings based on mechanical concepts in recent years. The interfacial adhesion energy is reduced by introducing low surface energy materials, while the elastic modulus could be modified using softening agent, plasticizer, swelling method, etc. In this way, the crosslinking density of polymer is also reduced (crosslinking density is the number of moles of crosslinking points per cubic centimetre, representing the degree of crosslinking of polymer chain). For example, Golovin et al. prepared the soft-based icephobic coatings with low crosslinking density and low elastic modulus possessing ice adhesion strength as low as 10 kPa by adding different soluble oil-based polymers into polyurethane (PU), as shown in Figure 2.27 [187]. Jamil et al. [188] prepared the superhydrophobic coating with low elastic modulus by dispersing the candle ash particles into silicone rubber matrix. The low elastic modulus, superhydrophobicity and stress-localization concepts were utilized in the coating with the acquired ice adhesion strength of only 18 kPa.

Due to the low crosslinking density, the mechanical strength of soft based surfaces may be insufficient, so improving mechanical strength and durability is the main focus for current soft coating development.

2.4.3.2 Surfaces with low surface energy

Low surface energy coating is a coating which can reduce the adhesion strength of ice accumulation by introducing low surface energy materials. Its main functional components are polymers containing fluorine (F) and silicon (Si) because polymers containing fluorine and silicon are the two materials known to have the lowest surface energy of all substances in nature. The contact angle of low surface energy materials is greater than 90 °, showing normal hydrophobicity. Previous research results indicate that the order of surface energy of different groups from high to low is: $-\text{CH}_2>-\text{CH}_3>-\text{CF}_2>-\text{CF}_3$ [189]. The surface energy of the surface closely arranged by CF_3 groups could reach as low as 6.7 mN/m with the water contact angle of 119 ° [190]. Therefore, 119 ° is the upper limit of static contact angle for low surface energy smooth materials.

The surface energy of PDMS is about 25 mN/m [191], while the value of typical fluoropolymer polytetrafluoroethylene (PTFE) is about 18 mN/m.

The low surface energy of PDMS mainly comes from the fact that methyl groups (-CH₃) surround and shield the Si-O backbone with high energy, while -CH₃ rotates freely and arranges itself outward on the surface. The symmetrically arranged -CH₃ shows low polarity and has low interaction with other molecules [192]. While for PTFE, the low surface energy is mainly caused by the C-F structure. The bond energy of C-F bond is larger than that of other chemical bonds. Fluorine atoms are densely surrounded by the C-C main chain. Due to the strong binding effect of fluorine nucleus on its external electrons and bonding electron cloud, C-F bond shows low polarization, so PTFE has very low surface energy. Normally, silicone coating has lower ice adhesion strength than fluoride coating, because the electronegativity of fluorine atom is bigger and is easier to form hydrogen bonding with water molecules [193]. Besides, the preparation of fluorinated polymers is difficult, with more complicated molding and preparation parameters (e.g., high temperature melting). Some of the intermediate components may even cause cancer, which makes it difficult to unlock large-scale applications of PTFE. Therefore, the majority of low surface energy icephobic coatings are mainly organosilicon polymers (mainly PDMS). It needs to be known that the ice adhesion strength is generally not less than 150 kPa solely by reducing the surface energy for common low surface energy coatings [194].

2.4.3.3 Low interfacial toughness surface

Recently, Golovin et al. [195] developed a new type of icephobic coating used for large-scale de-icing. Polyvinyl chloride (PVC) with low interfacial toughness, PDMS with low interfacial toughness and polystyrene (PS) with low interfacial toughness were prepared by adding different contents (0%, 5%, 10%, 50%, weight percent) of medium-chain triglyceride oil into different polymers. Considering the low interfacial toughness ($<1 \text{ J/m}^2$, it refers to the ability of an interface between two materials to resist crack propagation under applied loads, low interfacial toughness indicates that the interface

cannot easily withstand crack propagation, the structural integrity can easily lose) at the ice-solid interfaces, there is no relationship between the iced area with required external force for de-icing aim, especially when the icing area reaches a certain extent. So the large-scale de-icing could be realized. Besides, low interfacial toughness also contributes to less snow accumulation and ice accretion, as shown in Figure 2.28 [196].

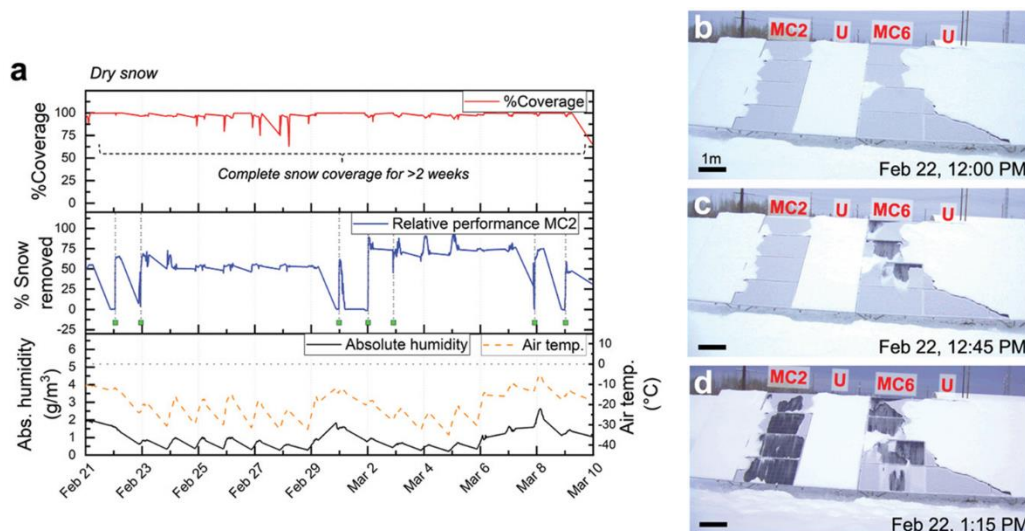


Figure 2.28 Comparison of snow coverage during periods of dry snowfall on an uncoated module, modules coated with MC2 and MC6, over a range of temperatures between -6 and -35 °C. (Green drop points highlight major snow-shedding events as defined in the text. b-d) Images from specific timestamps show thin sheets (thickness < 2 mm) of dry snow coverage and shedding corresponding to data shown in (a). (Adapted from Ref [196]).

PDMS with low interfacial toughness was coated on an aluminum alloy plate with the dimension of 1 m × 1 m. After freezing at -7 °C (thickness of about 1 cm), the aluminum plate was placed at an inclination of 98°. The ice detached and fell off under its own gravity without any external force, demonstrating the large area de-icing ability of the coating with low interfacial toughness. The type of coating could be further applied in large structures such as aircraft, ships, large wind turbines and other equipment.

2.4.4 Slippery liquid-infused porous surfaces and lubricant infused surface

In 2011, Aizenberg et al. [23] first proposed and designed the slippery liquid infused porous surface (SLIPS) based on the principle of catching insects in the colorful labial leaves of pitcher plants (as shown in Figure 2.29). Compared with SHS, SLIPS replace the air layer in the rough structure of SHS with a low surface energy material. The SLIPS replaces the air layer in the rough structure of SHS with a low surface energy material to form a liquid-liquid interface, such as porous Teflon membrane, e.g. 3M Fluorinert FC-70, $\gamma_B = 17.1 \text{ mN m}^{-1}$ or DuPont Krytox oils. The surface has high pressure stability, small CAH ($< 2.5^\circ$), rapid self-repaired damaged structure (0.1~1 s). It can also overcome the influence of SHS microscopic condensation of water and gas on ice suppression performance and the lack of poor structural mechanical stability.

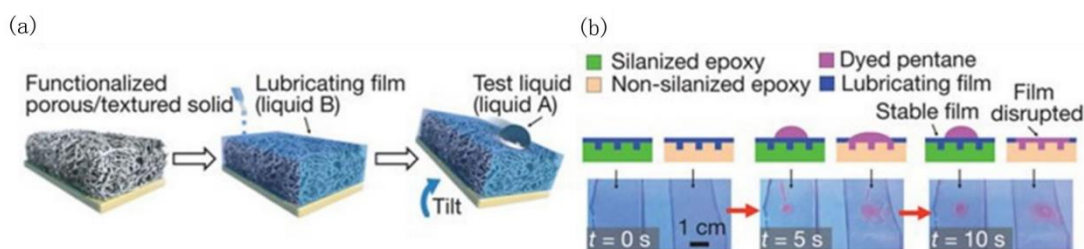


Figure 2.29 (a) Schematics showing the fabrication of SLIPS by infiltrating a functionalized porous/textured solid with a low-surface-energy, chemically inert liquid to form a physically smooth and chemically homogeneous lubricating film on the surface of the substrate; (b) Comparison of the stability and displacement of lubricating films on silanized and non-silanized textured epoxy substrates. Top panels show schematic side views; bottom panels show time-lapse optical images of top views. Dyed pentane was used to enhance visibility [23].

Unlike the superhydrophobic surface, the slippery liquid infused porous surface uses low-surface energy polymer liquids such as lubricating oil to replace the surface micro-nano structure of the air layer. The former gas-liquid-solid three-phase system has also changed into the gas-liquid lubricant-liquid-solid four-phase system, it is not easy to change the infiltration state, since the lubricant layer could tightly adhere to the substrates [197].

The liquid is trapped in the pores of the rough surface by capillary forces, forming a smooth and homogeneous surface on which the CAH is extremely small. In addition to the low CAH value, SLIPS also exhibit anti-wetting behaviour to almost all fluids and show temperature and pressure stability, the stability of SLIPS is largely determined by the thermal stability of the liquid used to prepare the slippery surfaces, For example, SLIPS made using perfluorinated liquids such as perfluorodecalin or perfluoropolyether are stable at low temperatures and can withstand temperatures up to $-196\text{ }^{\circ}\text{C}$ [198]. It demonstrated stability under the environment with pressure ranging from 400 to 1400 Pa). The liquid-like transition layer at the surface could reduce the pinning effect of water droplets (it corresponds to the ability to stop the three-phase contact line at the edges of pillars or holes and increases the contact angle) [199]. The lubricating layer could lower the ice adhesion strength, for example, the ice adhesion strength could be lowered to 30.0 kPa (sample with aqueous lubricating layer) from 800 kPa (aluminum alloy 6061) [29]. At lower temperatures, there would be a change in the molecular configuration of the transition film, which would increase the ice adhesion to a very large scale ($\sim 1192 \pm 195\text{ kPa}$, which is six times as large as that on the substrate (flat neat hydrophilic silicon wafer surface) $\sim 202 \pm 34\text{ kPa}$) [200]. So, keeping a non-frozen liquid-like layer on the surface could help the surface with low ice adhesion strength. Various types of oils have been chosen as lubricants and deposited on substrates with different types of material to fabricate SLIPS. These surfaces are all lubricant-impregnated with a small water droplet sliding angle (normally $< 10^{\circ}$) [201].

For example, Kim et al. [202] reported a new type of SLIPS, where a stable, smooth, low-hysteresis lubricant layer via infusing a water-immiscible liquid into a chemically functionalized nanostructured surface on Al surfaces. They demonstrated that the SLIPS-coated Al surfaces not only suppress ice/frost accretion but also exhibit at least an order of magnitude lower ice adhesion (measured to be 15.6 kPa) than state-of-the-art materials $\sim 165\text{ kPa}$ [203]. Li et al. [204] fabricated a robust SLIPS by infusing silicone oil into the prepared superhydrophobic surface via one-step spraying suspension process which manipulated both the surface roughness and surface energy.

The surfaces also showed good liquid repellency (WCA of as high as $156 \pm 1^\circ$ and SA of as low as $5.5 \pm 0.4^\circ$), anti-corrosion (the I_{corr} of the SLIPS on the Mg substrate decreased by 1 order of magnitude compared with that of the bare Mg substrate), anti-icing performance with intensified durability (the SA of the SLIPS maintained relatively constant at around 106.3° after the anti-icing/de-icing cycles), the schematic of the preparation process and liquid repelling was also indicated in Figure 2.30.

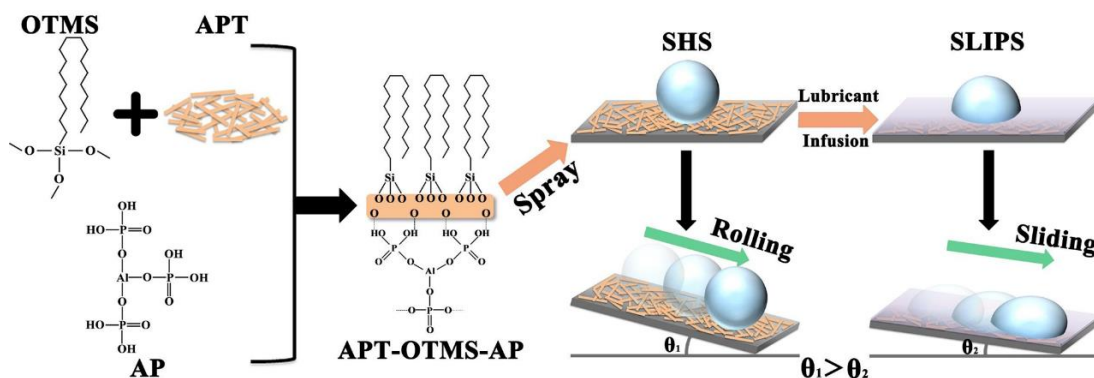


Figure 2.30 Schematic of the preparation process and liquid repelling of SLIPS (APT[Mg₅Si₈O₂₀(OH)₂(OH)₄·4H₂O] with natural micro-nano porous structure was functionalized with octadecyltrimethoxysilane and bonded by aluminum phosphate binder, the SHS was fabricated by spraying APT-OTMS-AP suspension on the AZ31B Mg sheet and cured in the oven. The SLIPS was prepared successfully by infused silicone oil into the as-prepared SHS with a stabilized layer of the lubricant remained on the surface) [204].

Varanasi et al. [205] pointed out that the adhesion strength of the ice on the surface of SLIPS decreased with increasing surface microstructure density, and the ice adhesion strength was inversely proportional to the amount of lubricant on the surface. For example, the ice adhesion strength of the highest-texture-density LIS is about 2 times smaller than that of a smooth surface coated with PEMA-FluoroPOSS. Besides, it is also 4 to 5 times smaller than that of a smooth surface coated with octadecyltrichlorosilane. At present, most researchers usually adopt hydrophobic polymers as liquid lubricants, such as total fluorine oil, silicone oil and hydrocarbon. Erbil et al. [206] used hydrophilic polymer glycol, formamide, glycerol-water and so on as lubricants. By comparing the performance of hydrophobic polymer lubricants

with that of hydrophobic polymer lubricants in ice wind tunnel, the results showed that hydrophilic lubricants, especially water-glycerol, possessed low ice adhesion strength (only 16 ± 3 kPa) under the experimental conditions of temperature of -2 °C and relative humidity of 56-83%.

However, under the action of capillarity, the liquid layer on the surface of the material is easy to lose along with the cycle of icing/melting during the process of release, resulting in the attenuation of ice inhibition. In addition, the released droplet lubrication layer may also pose a hazard to the environment because the nonsolid phases are sacrificial and they can leak into the surroundings, causing significant environmental problems [35, 207, 208]. Inspired by the ice skating (since the adhesion strength between the skate blades and the ice decreases substantially due to the existence of a self-lubricating liquid water layer between the ice and the blades [209]), Wang's team proposed and designed a water-lubricated layer of ice-repellent coating, which is constructed by the addition of hydrophilic acrylic acid inside a superhydrophobic microstructure and water absorption to form a water-lubricated layer on the surface of the substrate. The ice wind tunnel experiment shows that the adhesion strength of the substrate surface of the water-based lubricating layer is only 60 ± 16 kPa with a probe speed of 0.5 mm/s at -15 °C, while the ice adhesion on an equivalent hydrogel grafted flat surface was 113 ± 21 kPa, and its ice inhibition performance has not been affected basically after 30 ice-freezing/ice-melting cycles [200].

2.4.5 Recent concepts of icephobic surface and design

Research progress on icephobic surfaces has developed rapidly due to the advancement of nanomaterials, coating fabrication methods and biomimetics, and more in-depth understanding of ice nucleation and ice adhesion mechanisms. Many new designs and concepts have also been proposed and promoted the development of icephobic surfaces. For example, Zarasvand et al. [210] introduced the new concept of metallic plate buckling for durable and scalable icephobic surface design (as indicated in Figure 2.31,

the ice was dislodged due to its own weight by tilting the surface), the sparsely confined metallic sheets were used and the surface buckling instability was tailored. Here, the elastomer-like ability indicates the elastic mismatch using elastomers which exhibit low ice adhesion via interfacial cavitation and the surface instability could promote the debonding at the interface [187]. The acquired buckling elastomer-like anti-icing metallic surfaces exhibit low ice adhesion and the mechanical resilience of metals. These newly developed surfaces supply a new paradigm for developing icephobic surfaces.

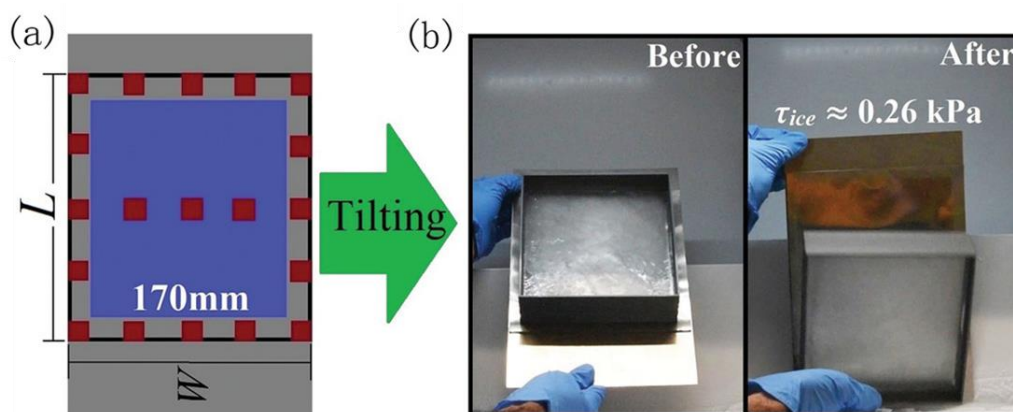


Figure 2.31 (a) A 30 mm thick piece of ice adhered to scaled beams ($L=W=200$ mm and $t=0.05$ mm); (b) The ice dislodgement from the beams under its own gravity by tilting the surface (Adapted from Ref [210]).

Ayres et al. [211] prepared a titanium alkyd sol system that contains tripropylene glycol ether (TPG) and glycerol ligand using TPG, glycerol and isopropoxytitanium (TIP). It was then embedded into a common hydrophobic coating substrate. The TPG and glycerol could then slowly release by the hydrolysis and condensation reaction of titanium alkyd. The two molecules can help to achieve the purpose of icephobicity by reducing the freezing point of water and inhibiting the formation of ice nucleation. There would be some small molecules released from the sacrificial coating and it could further inhibit the crystallization of supercooled water, for example, the addition of specific lubricants (polyampholyte with carboxyl and amino groups) could depress the freezing point of water and the nucleation of ice could also be inhibited, the delay duration could reach up to 7800 s [212]. The lubrication of ice and material surface

would increase and the adhesion strength of ice accumulation would be lowered, leading to the detachment of ice naturally.

2.5 Challenges and Perspectives towards Icephobic Surfaces

2.5.1 Durability of icephobic surfaces

While the main research driving forces focus on preventing ice nucleation and icing delay, as well as lowering the ice adhesion strength, it still cannot make good balancing of the trade-off of the limited durability of icephobic surfaces under various harsh environmental conditions. The constructed surface micro/nano structures might easily be damaged with the exposure to different conditions including mechanical abrasion and wear, sand or droplet impact, chemical contaminants, ambient temperature variation, and long-time sun exposure (for example, the infused liquid would diminish, besides, the black coating after silanization remained superamphiphobic even after its top layer was damaged by sand impingement) [213, 214]. The mechanical, chemical and environmental durability of icephobic surfaces needs to be guaranteed. The ability that the surfaces possess that could keep its surface topography intact and the low surface energy under practical working conditions is defined as durability. It is encouraging to see emerging efforts are devoted to addressing the long-term durability issues of icephobic surfaces as well as the main expected figures of merit in practical use. Even though there are significant progress already made among the theoretical and experimental aspects in icephobic surfaces, it still remains a big challenge to solve the existing problem. Surfaces showing a high extent of icephobicity in certain conditions may not perform well in others. For instance, in aerospace, aeroplane wings and turbine blades can be bombarded by droplets, dust or sand particles and thus can be subjected to excessive shear force [215]. Furthermore, it should be noted that the surfaces that are optimal for one specific requirement may not necessarily be the most effective for another [216]. A bulk of research studies have been focused on this, and the progress is still not satisfactory.

First and foremost, there are concerns about issues of robustness and surface fragility, both thermodynamic and mechanical [217], especially on the polymeric coatings. To achieve low ice adhesion strength, compromises may need to be done for the stiffness of the current polymeric surfaces. Normally, low stiffness leads to low durability, while stiffness refers to the ability to resist elastic deformation when stressed, it can be used to characterize the difficulty of the elastic deformation, and the stiffness of certain material is usually evaluated using the elastic modulus [218]. Many research interests have been drawn onto the non-durability issues, which focus on the design and development of durable icephobic coatings, for example, the recently developed textured solids s impregnated with liquids are able to circumvent these durability issues. Apart from this, by manipulating the aspect ratio of the surface pattern, the shear could be limited for the aim to retain their lubricating properties [208, 219].

To ensure good icephobicity and practicality, the poor mechanical stability of the microscopic surface topography in polymeric surfaces needs to be overcome since the surface icephobicity degrades gradually along with the depletion of lubricant via external mechanical forces, for example, the PDMS layer on Al surfaces suffered breakage after the 30 icing/de-icing cycles [27, 187, 220]. The fragile micro- and nano-hierarchical structures are prone to be destroyed after a slight scratch, abrasion, impacting, and even finger touch [221], to say nothing of peeling with adhesive tape or the abrasion by the sandpaper. For the aim of foreseeing the immediate, worldwide applications of such extremely durable, icephobic coatings across various industrial sectors, academic disciplines and engineering endeavours, consistent efforts are still needed for enhancing the durability of polymeric icephobic surfaces. For instance, designing double networks or energy dissipating networks to enhance the toughness (it maintained a reasonable extensibility and recoverability of the strain, up to 4 megapascals and 9 kilojoules per square meter [222]) of soft coatings against mechanical damage [223, 224]. Meanwhile, the UV-durability and anti-corrosion properties are equally crucial for practical outdoor use, which mainly depends on the surface chemical composition and surface structures [225].

2.5.2 Attempts toward durable icephobic surfaces

Currently, towards the development of icephobic coatings, a number of strategies aiming to solve the durability issues have been proposed and developed in recent years:

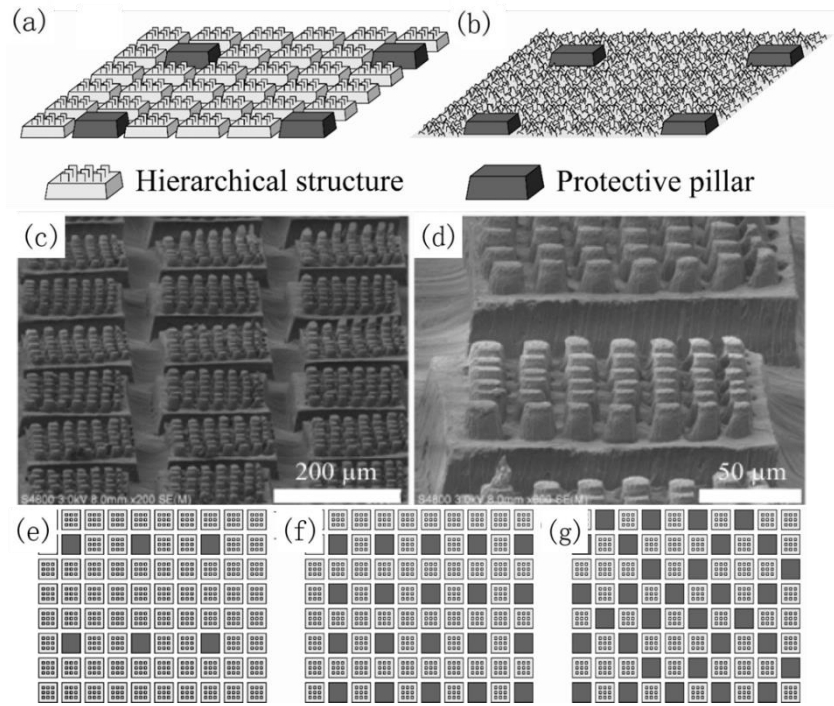


Figure 2.32 (a) and (b) Schematic views of hierarchical micro and nano structures with protective pillars; (c) and (d) SEM images of the fabricated structures on the PP surfaces; (e)-(f) the design schematics of fine-scale surface topographies with positioning of the replacement grids (Adapted from Ref [226]).

1. Icephobic surfaces constructed with protective pillars. The design concept with protective pillars is mainly focusing on the isolation of hierarchical structures and avoid the compression or abrasion forces. For instance, Pakkanen et al. [226] protected the fragile fine-scale surface topographies against wear by superhydrophobic polypropylene (PP) surfaces with larger scale sacrificial micropillars, as illustrated in Figure 2.32. If the protective pillars are made of harder materials such as metals or inorganic oxides, the mechanical performance could be better, the wetting properties of the as-prepared samples (static contact angle $\sim 150^\circ$ and sliding angle $\sim 10^\circ$) remained unchanged after 30 cycles of mechanical compression up to 20 MPa and abrasive wear tests up to 120 kPa.

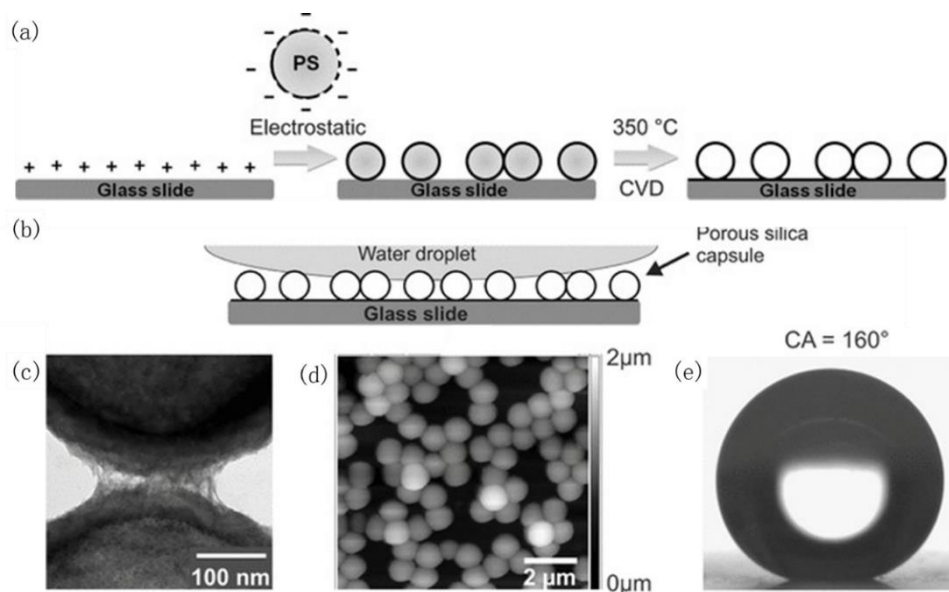


Figure 2.33 (a) Sketch diagram of the preparation procedures of superhydrophobic surfaces using grafting; (b) Sketch of the solid-liquid-air three phase contact line; (c) High resolution TEM image of two neighbouring silica capsules connected by a silica bridge; (d) AFM height image of the superhydrophobic surface; (e) Photograph of static contact angle on the surface (Adapted from Ref [227]).

2. Using grafting and/or crosslinking methods. The mechanical properties of the polymer components could be enhanced through the incorporation of monomers and create cross-linking sites. Cross-linking could either be incorporated homogeneously throughout the thickness of the polymer or graded in concentration. For example, Vollmer et al. [227] prepared transparent and mechanically-durable superhydrophobic surfaces using porous silica capsules by chemical vapor deposition in an environment of ammonia for the aim to chemically crosslink dip-coated polystyrene nanoparticles. Figure 2.33 indicated that the superhydrophobicity could be maintained after the sand impacting tests (sand grains with the size from 100 to 300 μm hit on the surfaces from impact heights up to 30 cm) and tape adhesion tests (pressed with double sided adhesive tape at the pressure of approximately 10 kPa).

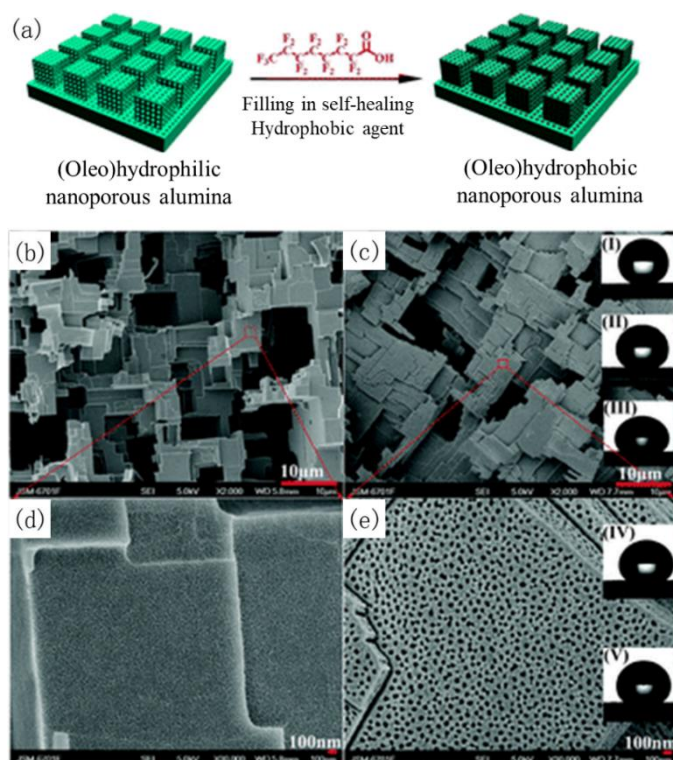


Figure 2.34 (a) schematic depiction of a nanoporous alumina substrate and filling in hydrophobic perfluorooctyl acid; (b)-(d) SEM images of anodized alumina without nanopores; (c)-(e) SEM images of anodized alumina with high density nanopores. (The insets are snapshots of representative liquid droplets on the perfluorooctyl acid loaded nanoporous alumina: (I) water, (II) glycerol, (III) CH_2I_2 , (IV) hexadecane, (V) rapeseed oil.) (Adapted from Ref [228]).

3. Create damage-tolerant, protective icephobic surfaces that are self-repairable upon mechanical damage or other external force. These damage-tolerant superhydrophobic surfaces typically normally have low surface energy and textural features that extend throughout the bulk materials. However, the progressive loss of superhydrophobicity and potential icephobicity upon prolonged wear conditions could also be unavoidable. The main reason here should be ascribed to the physical wear and tear from the surfaces, including abrasion, scratching, or other types of physical damage that can alter the surface morphology and reduce the superhydrophobicity. Besides, the presence of micro- or nanoscale surface features to repel water and other liquids could also be affected by the accumulation of contaminants. In addition, prolonged exposure to harsh environmental conditions such as UV radiation, extreme temperatures, or chemical

exposure can also lead to the progressive loss of superhydrophobicity and icephobicity [229]. So, designing icephobic coatings with self-replenishing capabilities could help a lot with the recovery of potential hydrophobicity and icephobicity loss. Wang et al. [228] prepared the superhydrophobic coatings with chemical perfluorooctyl acid encapsulated by the nanoporous anodized alumina substrate. The release of the perfluorooctyl acid from nanopores and subsequent migration to the surface was the main causing factors to regain the superhydrophobicity, as indicated in Figure 2.34. The main limitations for self-repairable coatings include: 1. the number for self-repair ability is limited, it is often difficult to achieve self-repairing at the same area more than once, and the reason is that once the healing agent is released out, the self-repair ability would lose. 2. If the broken area on the coating surface is too large, it may be difficult for the self-repair ability taken into effect [230].

4. Synergic combinations of mechanically-durable structures and low surface energy materials. Methods with durable structure preparation with low surface energy material incorporation have gained popularity because of their versatility. For example, Park et al. [231] reported the preparation of a dual-hole patterned superhydrophobic surface which is made up of a non-fluorinated composite of PDMS and carbon nanotubes (CNTs) using a pre-structured nickel stamp. The honeycomb-like structure remained its morphology and hydrophobicity even after 600 cycles of rubber tip sliding tests under the load of 1.5 N, showing effective durability against physical damage.

Apart from the above-mentioned durability strategies on increasing the durability of icephobic coatings, surfaces prepared with metallic-based substrate incorporated with low surface energy layer could also be a good option. In recent years, metallic-based coating systems are keeping attracting significant attention considering their mechanical durability and possible multi-functionalities. For example, Tan et al. [232] prepared a Cu-based composite surface using electrodeposition method which exhibited good hydrophobicity (contact angle of around 160° and sliding angles of nearly 1°), environmental adaptability, high anti-corrosion ability, and good mechanical property

(the as-prepared surface morphology maintained after abrasion of 400 mm and no obvious delamination or detachment of the coating was observed within the square lattice). Raeissi et al. [233] reported that with the construction of micro-nano flower-like surface structure, the obtained Ni-Co coatings exhibited durable performance, chemical stability and self-cleaning effect. The superhydrophobic aluminum surface treated with anodisation and surface modification methods displayed a water contact angle of 156 ° and a sliding angle (SA) as low as 2.5 °. The anti-corrosion resistance (highly durable against chemical corrosion in different pH solutions) and icing delay effects (the icing process with 4 µL droplet was 23 s on SHS compared to bare Al surface (2 s)) were also obtained [234].

With the synergic effect of metallic scaffolds strengthen effect and good hydrophobic/icephobic performance from the deposited low surface energy layer, the metallic-based coating systems could ensure the good mechanical and environmental durability. Boinovich et al. [235] reported a multimodal roughness textured SS surface modified with 2D polymer network of fluorooxysilane showing good icephobicity (the contact angles formed by iced drops on as-prepared coatings ranged around 160 °, and the drops demonstrated delayed freezing in comparison to freezing time for drops of supercooled water atop the untreated steel surface) and remaining stable after 100 icing/de-icing cycles accompanied with mechanical stresses. Deng et al. [185] designed and constructed surfaces with interconnected micro-frame structures constructed on Si substrate which have two different length scales for the aim to protect the fractal fluorinated SiO₂ nanoclusters, as shown in Figure 2.35. Relevant research could provide important theoretical and technical guidance for the preparation of polymeric composite coating systems.

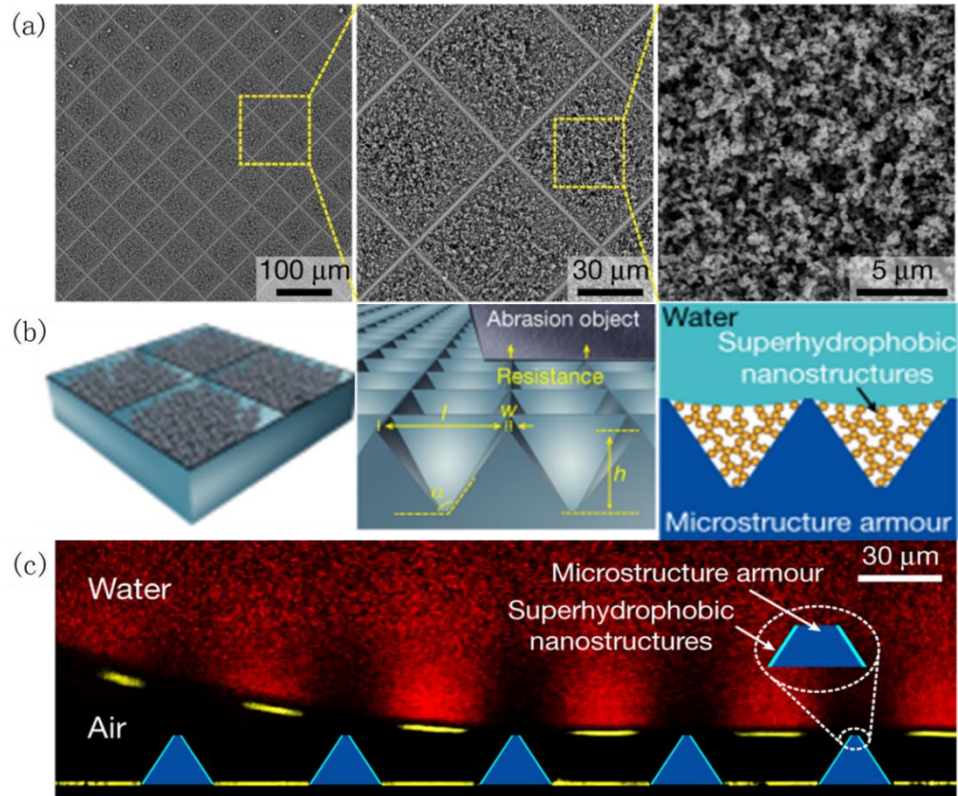


Figure 2.35 Micro-nano superhydrophobic surface structures constructed through micrometer scale frame protective structures and nano-SiO₂ clusters (Adapted from Ref [185]).

For the aim to acquire long-time mechanical, chemical and environmental durability, the metallic-based coating systems could be considered, it is one of the most promising research directions and is of great significance to be widely studied. The new design concepts of non-wetting, liquid-infused and hydrated surfaces have also inspired the large-scale development of icephobic surfaces. For example, Irajizad et al. [236] reported the stress-localization physical concept, minimising the solid adhesion on certain surfaces with the implementation of elastomers. The new form of icephobic surface is composed of a matrix with high shear modulus (it varies, around 80 kPa) as phase I and a highly dispersed phase II with low shear modulus (around 1-2 kPa). The schematics are shown in Figure 2.36. Phase I is a silicon elastomer and phase II is a silicon-based organogel. To ensure the major role of the matrix in long-term mechanical durability, it is very important to choose an elastomer (phase I) with high shear modulus. For the aim to form a homogenous material, compatibility of the matrix and the

dispersed phase II is also very important. Phase II would be responsible for cavitation and crack initiation at the interface. Stress-localization leads to a shear force at the interface. The interfacial cracks could then form at the coordinate of phase II, which easily detaches the ice from the material.

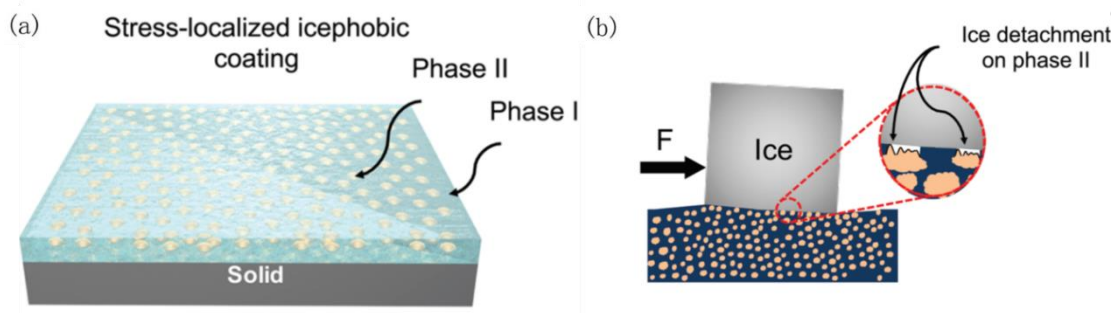


Figure 2.36 (a) Stress-localized icephobic surfaces (b) Schematic of formation of crack at the coordinate of phase II with minimal forces [236].

Low-interfacial toughness materials used for effective large-scale de-icing with good mechanical durability could also be a good research direction. Golovin et al. [195] has verified the concept that the force needed to remove an ice layer reaches an asymptotic value if the interface is long enough. Materials (mainly polymers) that exhibit low-interfacial toughness (LIT) with ice could lead to the low forces that are required to remove large areas of ice from systems and is independent of the iced area. The reasons could be ascribed to: (1) The low bonding energy between the ice and coating, a lower bound on this energy could be 0.1 J/m^2 , corresponding to van der Waals interactions [237]; (2) Another reason could come from the localised losses among the as-prepared coatings, associated with the high-stress region at the crack tip. The research describes a class of materials that are made of such low-interfacial toughness that allows ice to be shed readily from large areas merely by self-weight. Another significant example was proposed by Cheng et al. [238], they combined the hydrophobic PTFE coating with nickel sheet and the frame can effectively protect the brittle and easily worn coating surface and fluoride silane substances, as shown in Figure 2.37. The interconnected metal frames could guarantee that the coating remains hydrophobic even after 1000 times of linear wear at a local pressure of 0.12 MPa.

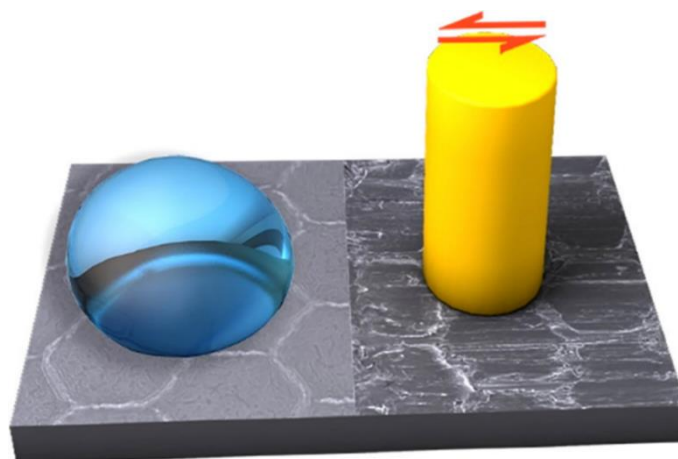


Figure 2.37 Sketch map of the micropatterned composite metal-polymer hydrophobic surface structure (by integrating a mechanically durable nickel skeleton with an interconnected microwall array filled with hydrophobic PTFE) [238].

Compared with the traditional coating design, the developed concepts of combination using flexible and mechanically durable metallic-based skeletons with fragile hydrophobic/superhydrophobic materials incorporation could be implemented in a broad range of material systems to minimize adhesion of any solid, including bio-species, salt, dust and gas hydrates, and on surfaces with no compromise in mechanical properties. New icephobic coating design could be developed towards the inspiration of the demonstrated concepts. It is envisioned that newly designed and developed surfaces could help with a wide range of applications including aviation systems, oceanic sciences, energy systems and bio-sciences.

2.6 Summary

When facing the challenge of ice accumulation, durable icephobic structures have been demonstrated as an effective passive approach. By elucidating the fundamental principles of surface wetting and icephobicity, this chapter presented the design principles and associated limitations of icephobic structure from a theoretical standpoint. Initially, hydrophobic structures were considered as a potential anti-icing approach, especially superhydrophobic structures (SHS, $WCA > 120^\circ$) with high surface

roughness [18, 239]. Surface roughness can enhance water repellency by trapping air in the surface void valley, resulting in an early roll-off of water droplets [240]. However, certain environmental conditions can transform water droplets into the Wenzel state [241, 242], leading to a substantial contact with the surface and increased energy required to break mechanically interlocked ice formed around surface asperities [243], which can pose challenges for hydrophobicity-induced icephobicity applications, particularly in sub-zero temperatures [244]. These performance challenges may lead to a reduction in the effectiveness of hydrophobicity in inducing icephobicity.

Ice nucleation can be significantly delayed or eliminated by utilizing surface roughness patterns that are similar in size to or smaller than critical ice nuclei [245]. Smooth surfaces are preferred over rough surfaces due to their increased durability and reliable icephobic performance in icy conditions [246]. The absence of surface roughness-induced hydrophobicity also eliminates the possibility of damage during ice shearing processes.

Lower surface roughness can enhance ice adhesion due to increased interfacial contact, and therefore, material chemistry and properties are crucial in reducing ice adhesion. Minimizing ice anchoring points alone is insufficient, and a synergistic effect of low surface energy or a softer interface is necessary for inducing low ice adhesion. Smoother and functionalised surfaces can lower the free energy barrier and promote homogeneous ice nucleation, leading to significant delays in freezing [110].

Polymeric surfaces and coatings, including the implementation of liquid infused surfaces (LIS), have gained significant attention among researchers for their potential in passive ice protection. Several studies have reported lower ice adhesion strengths on polymeric coatings and surfaces [13, 247]. Polymer coatings with lower modulus enable easy release of ice, thanks to the large moduli difference that causes mismatch in strain under stress [248]. Additionally, functionalization with low surface energy chemicals or the infusion of lubricating liquids can reduce the probability of

heterogeneous ice nucleation [249]. However, the durability of these coatings, liquid replenishment within the material matrix, and the ability to maintain icephobic performance after microstructural damage require more research. Therefore, considering the long-term service requirements of icephobic materials in the aviation field, the current research focus should be on ensuring the mechanical durability of icephobic structures, while simultaneously improving their anti/de-icing performance and icephobicity stability.

Effective approaches for the research and development of icephobic coatings could involve exploring smoother surface structures, incorporating lubricating liquids/hydrophobic functionalization, utilizing nano- and micro-particles, and employing polymeric coatings with reduced elastic moduli [247, 250]. Once low-adhesion polymers or composite materials are pre-selected, the next step can be carried out to modify them in order to improve the durability and erosion resistance of the coating, while ensuring its sustained icephobic performance. To fundamentally improve the mechanical properties of icephobic materials, this study proposed the concept of a two-phase icephobic structure based on the inspiration of framework-protected surface structure design [40]. The mechanical properties and durability of the filled polymer were enhanced by introducing metal scaffolds. Based on this two-phase structure, new multi-phase icephobic structure system was designed and improved in order to obtain durable icephobic structures.

Chapter 3 Methodologies

3.1 Raw Materials and Chemicals

3.1.1 Raw materials

Two types of metallic samples were used in this project, including: (1) T2024 Aluminium alloy (Aluminium 2024, Smith Metal Centres Ltd, Biggleswade, UK) was purchased from GoodFellow Cambridge Ltd (Huntingdon, UK), and the detailed elemental composition is also supplied and is shown in Table 3.1. Here, the T2024 Al was used as the substrate for the preparation of reference samples. The reason here that T2024 was chosen is due to their high strength (tensile strength: ≥ 390 MPa, yield strength ≥ 245 MPa) and good fatigue strength (long fatigue life [251]) and their wide applications in aircraft structures including the aircraft envelope, propeller components and so on; (2) Nickel (Ni) foam was obtained from TMAX Battery Equipment Ltd (Xiamen, China), with larger specific surface area and higher internal porosity (over 95%), as well as the extensibility of lengthwise $\geq 5\%$, widthwise $\geq 12\%$, tensile strength lengthwise ≥ 1.25 N/mm², widthwise ≥ 1.00 N/mm².

Table 3.1 Detailed elemental compositions of T2024 aluminum alloy substrate.

T2024	Si	Fe	Cu	Mn	Cr	Zn	Ti
Wt (%)	0.5	0.5	3.8-4.9	0.3-0.9	0.1	0.25	0.15

3.1.2 Chemicals

All of the involved chemicals in this study have been displayed in Table 3.2. PDMS was selected as the prepolymer during the whole study. The specified PDMS (Sylgard 184: two-part silicone elastomer dispersed in xylene) was purchased from Dow Corning Technology (High Wycombe, UK). Sylgard 184 would be useful for coating small parts that would fit in and withstand the temperatures in an oven. All of the chemicals were analytical grade reagents and used as received. Xylene was applied to add into the

precursors to adjust the viscosity of the as-prepared PDMS polymer precursor and it was purchased from Fisher Scientific UK Ltd (Loughborough, UK).

Table 3.2 Lists of chemicals.

Items	Features	Origin	Specification	Viscosity (mPa s)	Other Info
Aluminiumoxid C	Powder	AEROXIDE	85-115 m ² /g	/	Aerogel
Silicone oil	Liquid	Merck Life Science	0.967 g/mL	100	Infused oil
Groundnut oil	Liquid	Sainsbury	0.914 g/mL	1000	Infused oil
Coconut oil	Liquid	Sainsbury	0.922 g/cm ³		Infused oil
Glycol	Liquid	Merck Life Science	1.113 g/cm ³	22.13	Anti-freezing liquid
Glycerol	Liquid	Merck Life Science	1.261 g/cm ³	1499	Anti-freezing liquid
PDMS Silicone Sylgard 184	Liquid	Dow Corning Ltd	1.04 g/cm ³	3500	Two parts
Xylene	Liquid	Thermo Fisher Scientific	0.86 g/cm ³	0.75	Washing
Deionised water	Liquid	Produced in Lab Thermo	1.0 g/cm ³	1.01	Solvent
Formamide	Liquid	Fisher Scientific	1.133 g/cm ³	2.93	Free energy measurement
Methylene Iodide	Liquid	Thermo Fisher Scientific	3.238 g/cm ³	3.35	Free energy measurement

For the research work of Chapter 4, several different types of oil were chosen as the infused additive including Silicone oil (Merck Life Science UK Ltd, Gillingham, UK); Groundnut oil (Sainsbury, London, UK); and Coconut oil (Sainsbury, London, UK). Groundnut oil shows a viscous liquid state with clear yellow colour and has a density of 0.91 g/mL at 20 °C. For coconut oil (also purchase from Sainsbury, London, UK), it is low-melting solid with almost white colour, and the melting point is around 20-28 °C. It would remain in solid state during the whole test. For the candidates of anti-freezing liquid, the glycol and glycerol were both chosen as the ice depressing liquids. The melting point of glycol (purchased from Merck Life Science UK Ltd, Gillingham, UK) is around -11.5 °C and it can be mixed with water, ethanol, acetone and other organic solvents in any ratio. But for glycerol (from Sigma-Aldrich), the melting point is 18.17 °C, it would stay in a solid state under the testing condition. It can also be miscible with water and ethanol in infinite proportions. Aluminiumoxid C powder (AEROXIDE, Degussa AG) was used to prepare the aerogel.

To establish a solid foundation for material selection, the choice of Ni scaffold was justified by multiple factors. Initially, the porous Ni scaffold exhibits high porosity (around 95%, as-received), specific strength (around 1 MPa m³/g) and superior mechanical properties (yield strength: 0.3 MPa, tensile strength: 0.65 MPa) [252]. The Ni scaffolds exhibit remarkable ductility, exhibiting an elongation of at least 5% along the longitudinal axis and 12% along the width. The tensile strength along the longitudinal axis is at least 1.25 N/mm², while in the widthwise direction it is at least 1.00 N/mm² [253]. Highly porous Ni scaffold can reduce the impact of the Ni scaffold on the surface properties of PDMS by accommodating a larger volume of the material. The incorporation of the Ni scaffold may enhance the mechanical strength of the multiphase structure due to its specific strength and superior mechanical properties. Additionally, the use of nickel scaffold offers an economic advantage due to its lower cost compared to copper foams (the price per unit of copper foam is over 10 times higher than that of Ni scaffold) [254].

PDMS is often chosen for icephobic applications due to its ability to maintain elastomeric physical properties at extreme temperatures (it can be maintained to as low as $-120\text{ }^{\circ}\text{C}$) [255, 256]. PDMS has also been extensively tested in extreme environmental conditions. For example, PDMS that has been distressed to simulate wear, thermal aging, and humidity and salt spray exposure continues to perform better than Teflon (the industry low-friction material standard) [257]. Silicone-based coatings may be effective in withstanding sand erosion and are resistant to many fuels, lubricants, cleaners, and deicing fluids. Besides, PDMS also shows the good compatibility with different substrate surfaces and does allow ice to break easily from surfaces [258].

Silicone oil could be a good candidate for lubricant and obtain slippery properties and improved icephobic performance, the introduction of silicone oil is safe for biological environments due to its low toxicity [259]. After the pre-experiments, the silicone oil could be completely infused into the porous interconnected network [260, 261]. It is reported that a hydroxyl-terminated silicone oil -PDMS composite surfaces show ice adhesion strength of roughly 12 kPa throughout the 12 icing/de-icing cycles [262]. The silicone oil with low viscosity ($\sim 0.65\text{ cSt}$) [263] is also widely used as a lubricant for LIS for the aim to possess anti-icing/de-icing properties [264].

Groundnut oil exhibits a freezing point ranging from $-5\text{ }^{\circ}\text{C}$ to $-3\text{ }^{\circ}\text{C}$, a melting point within the range of $25\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$, and an enthalpy change of 36 kJ/mol during the solidification process [265, 266]. Coconut oil, on the other hand, has an enthalpy change of approximately 180 kJ/mol and a freezing point of $22\text{ }^{\circ}\text{C}$ to $26\text{ }^{\circ}\text{C}$ (with a melting point of $24\text{ }^{\circ}\text{C}$ to $27\text{ }^{\circ}\text{C}$) [267]. The infusion of lubricants with appropriate enthalpy changes can effectively regulate energy exchange during freezing by releasing heat, thereby reducing the energy requirement for ice melting or removal from surfaces. Additionally, lubricants with low freezing points prevent solidification at low temperatures. For instance, coconut oil remains in a liquid state well below freezing, making it a practical choice for use in cold climates [268].

Groundnut oil and coconut oil have been previously investigated for their ice adhesion reduction and icephobicity enhancement properties, despite being distinct types of natural oils. For example, the coconut oil is solidified and could be locked in the textured structure, which could be used for the infused lubricant in this study [269]. The groundnut oil-infused porous PDMS surfaces reduced the ice adhesion strength (~22 kPa) compared to uncoated surfaces, with the degree of reduction varying depending on the surface type and oil concentration [270]. He et al. reported that groundnut oil can reduce ice adhesion strength by up to 40% on aluminum surfaces, indicating the promising icephobic potential [271]. Because the two oil lubricants are derived from natural sources and are biodegradable. They are non-toxic and do not pose risk to human health or environment. Besides, they are relatively inexpensive compared to synthetic materials like silicone oil, making them a cost-effective option for icephobic applications [272].

Glycol and glycerol are widely employed as anti-icing agents for engineering surfaces in icy conditions due to their low freezing points (glycol: -13 °C, glycerol: -36.6 °C) [273], which facilitate the depression of freezing points and the reduction of ice adhesion [274]. Glycol and glycerol can act as freezing point depressants by reducing the freezing point of water, thereby impeding the formation of ice. Additionally, their relatively high viscosity and thick, adhesive properties enable them to adhere effectively to surfaces and form a protective layer [275]. The hydrophilic nature enables that it has strong affinity for water molecules, which allows them to compete with water molecules on surfaces, preventing them from forming ice crystals [276]. The molecules can absorb onto the surface, forming a thin layer that can help to prevent ice from forming a strong bond with the surface, reducing the amount of ice that forms on a surface in the first place, acting as a barrier to supercooled water droplet and prevent the ice formation. The two liquids also show good chemical stability, they could resist degradation from exposure to sunlight, oxygen, and water, making them reliable and long-lasting icephobic candidates. For example, Pan et al. reported the icephobic construction by integrating a superhydrophobic copper mesh with anti-freezing agent

composing ethylene glycol and water [277]. Memon et al. proposed the glycerol-infused fiber reinforced polyurethane coatings, the inclusion of glycerol delayed water droplet freezing duration by 659 %, demonstrating the icephobic potential [43]. Besides, the two mentioned ice depressing liquids are non-toxic, environmentally friendly and biodegradable without harmful chemicals, which are safer and more environmentally friendly alternative [278]. They are also relatively inexpensive and widely available, making them cost-effective solutions for icephobic constructions.

3.2 Preparation of Ni/PDMS Based Samples

All of the substrates were machined into applicable shapes for later surface/layer preparation according to their as-received form. T2024 Al was processed into 50 mm × 20 mm × 1 mm rectangle plates. The Ni foam was cut into 50 mm × 20 mm × 0.3 mm rectangle plates. To ensure the comparability, all substrates were manually sandblasted to an average roughness using Guyson Formula 1200 cabinet (F220 with alumina, average size 68 μm) with the following parameters: 7.3 bar for gas pressure, 5 cm distance between the nozzle and the specimen and 30 s for sandblasting duration. The sandblasted samples were cleaned with diluted hydrochloric acid for 2 min to remove the surface oxide and oil contamination later, then followed by cleaning using deionized water. They were finally dried using the compressed air and were ready for subsequent experiments. Laboratory-grade II+ deionised water with a resistivity of 18.2 MΩ•cm was used throughout the whole process of coating preparation for the ice block preparation.

The rectangular plates of the substrates were prepared with dimensions of 50 mm × 20 mm × 0.3 mm. The substrates underwent a cleaning process involving three cycles of ultrasonic cleaning using acetone and deionized water, followed by drying with compressed air. Sandblasting is a process that uses high-pressure abrasive material to clean or shape metal surfaces. It serves to remove accumulated rust, paint or surface

coatings, and can roughen the surface, increasing adhesion to subsequent coatings or materials [279]. The Al plate coated with a PDMS layer required sandblasting treatment prior to the coating preparation, whereas the T2024 Al reference sample was utilized in its as-received state without undergoing sandblasting treatment.

Table 3.3 Typical physical properties of Sylgard 184 PDMS [280].

Uncured	
Viscosity	3600 cPs
Work time	> 72 hr
Cured	
Shore hardness, Type A	40
Tensile strength	900 psi
Elongation	100%
Tear strength	15 psi
Thermal conductivity	3.5×10^{-4} cal/($^{\circ}$ C/cm)
Coefficient of linear thermal expansion (-55~150 $^{\circ}$C)	3.0×10^{-2} 1/K
Coefficient of volumetric thermal expansion (-55~150 $^{\circ}$C)	9.6×10^{-2} 1/K

Sylgard 184 is a two-part elastomer that shows low surface adhesion, around 19.18 mN/m [281], when in contact with ice. Part A of the precursor mixture contains the prepolymer component required for curing inside a silicone base and Part B is made up of crosslinker and inhibitor in xylene. The detailed physical properties are shown in Table 3.3. The two individual components would be thoroughly stirred prior to addition to ensure the homogeneity. The two medium viscosity parts would then be blended in a 10:1 ratio (Part A: B).

3.2.1 Ni/PDMS with silicone oil additions

For the preparation of Ni scaffold/PDMS-silicone oil sample system (NP-SO system), the detailed preparation process is shown in Figure 3.1. In the set of experiments, Part A and Part B of PDMS (Sylgard 184) were mixed together using the weight ratio of 10:1 (A: B) applied with magnetic stirring to ensure the solution uniformity, which is named as mixture 1. The resulting mixture of Sylgard 184 was viscous. Then different weight percentages (with respect to the total solution) of silicone oil (0, 10, 20, 30, 40, 50 wt%) were gradually introduced and mixed into the precursor mixture (PDMS-SO) solution during the stirring, respectively. The solutions were magnetically stirred for a further 30 min. The mixture solution was then degassed inside a vacuum oven (vacuum degree: 0.1 bar) at room temperature for a duration of 30 minutes to remove the existing air bubbles among the porous structure. The samples were then conducted with post-baking treatments inside a vacuum oven set at 85 °C for 4h. The as-fabricated NP-SO samples could be obtained after cooling down. Additional PDMS-SO mixture solutions were later applied onto the pre-prepared samples by the spin coater to smoothen the surface morphology. Here, the spinning coating is mainly used to prepare uniform thin films in the thickness range of micrometers to nanometers. It consists of several stages, such as fluid dispense, spin up, stable fluid outflow, spin off, and evaporation, respectively [282].

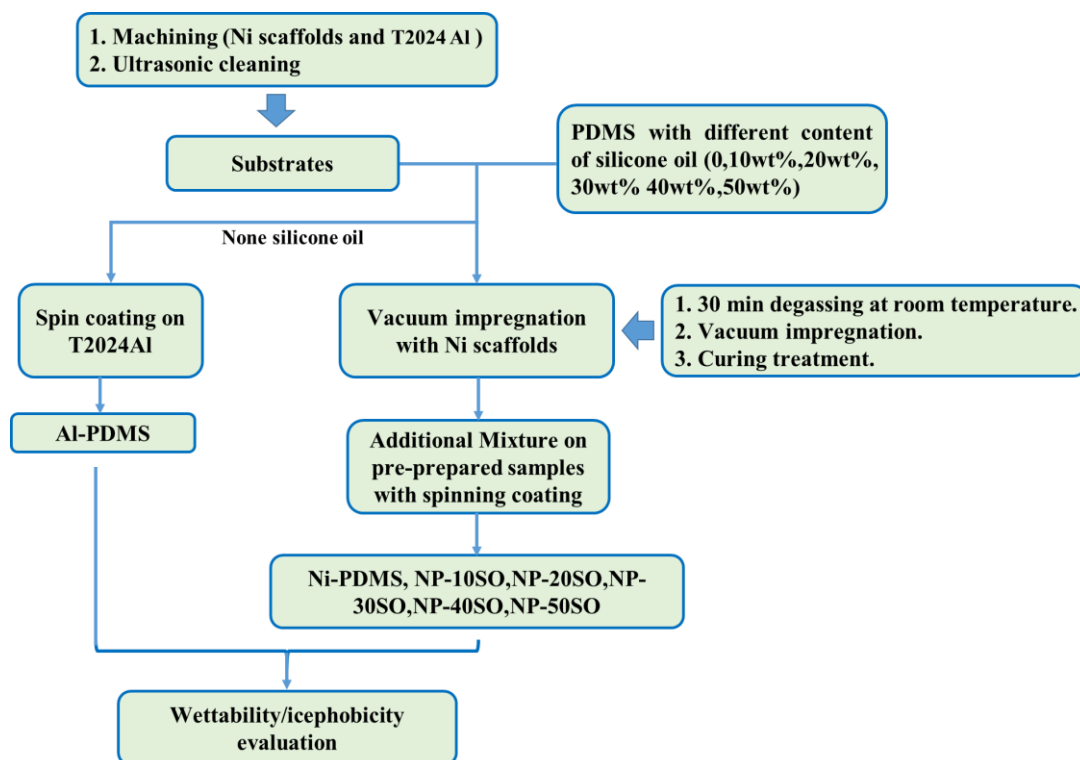


Figure 3.1 Process flow chart of preparation process of NP-SO.

For reference samples, as-received Al plate was selected and ultrasonic cleaned and ready for use. As for Al-PDMS, the pristine Al plate was first undergone the sandblast treatment, and then mixture 1 was also applied onto Al plates using spinning coater at the speed of 1000 rpm (revolutions per minute) for 90 s. While for Ni/PDMS samples, the whole preparation process was similar to that of NP-SO samples. The same vacuum impregnation and followed spinning process were also conducted during the sample preparation. The differences mainly lied in the applied solution and the curing treatment parameters (120 min at 65 °C).

Ni-PDMS samples with 10, 20, 30, 40, 50 wt% silicone oil addition were designated as NP-10SO, NP-20SO, NP-30SO, NP-40SO and NP-50SO, respectively. For reference samples, pristine as-received Al substrate was named as Al, while Al substrates with PDMS coverage were abbreviated as Al-PDMS. Pure PDMS samples with 10, 20, 30, 40, 50 wt% silicone oil addition were designated as PDMS-10SO, PDMS-20SO, PDMS-30SO, PDMS-40SO and PDMS-50SO, respectively. While the sample that is made up of Ni scaffolds and PDMS filling was designated as Ni-PDMS.

3.2.2 Ni/PDMS modified with phase change oils

For Ni/PDMS with different phase-change oil infusions, the detailed preparation process is shown in Figure 3.2. The Aluminiumoxid C aerogel powder was first mixed inside the different types of oils (including silicone oil, coconut oil and groundnut oil, etc) with a weight ratio of 3:20 and magnetically stirred for around 2 h, as mixture 2. Then mixture 2 was put into the low-vacuum oven (Vacutherm, Vacuum Heating and Drying Ovens, ThermoFisher, Waltham, MA USA) overnight for the aim to ensure adequate absorption of the oil content. Then the two parts of the PDMS (Sylgard 184) prepolymer were mixed with a 10:1 ratio and magnetically stirred for 3 h. Two more hours of magnetic stirring were carried out after mixing the two solutions, and the overall weight percentage between mixture 1 and 2 was 23:77, which means that the weight of aerogel accounts for 3 % of the overall mass and 20 % for oil addition. The resulting mixture 3 was viscous. The Ni scaffolds substrates were put into mixture 3 to make it fully immersed. Then it was transferred into the vacuum oven (0.1 bar) for 30 min at the temperature of 40 °C (for the aim to ensure the liquid state of coconut oil) to degas the existing air bubbles among the porous structure, followed by post-baking treatment at 85 °C for 360 min (elevated curing temperature). The degassing process would decrease the number of air bubbles generated during the curing process effectively. Additional mixture 3 solution was later applied onto the pre-prepared samples again by the spin coater (KW-4A, Chemat Group, Northridge, CA, USA) to make the surface morphology soft and smooth. The spinning process was later carried out on the pre-prepared samples again. Same curing treatments were carried out on the samples after the spinning process.

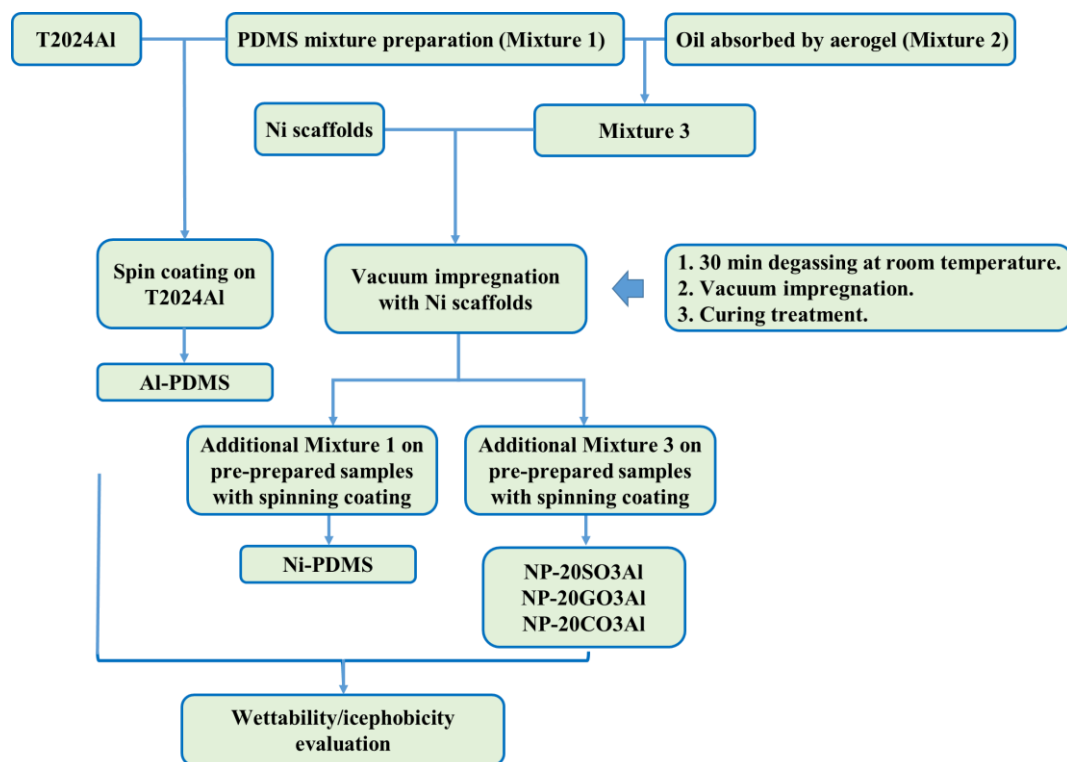


Figure 3.2 Process flow chart of preparation process of Ni/PDMS modified with phase-change oils.

Several types of samples were prepared and further studied in this part of the experiments: the sample prepared with Ni scaffolds, PDMS filling and Aluminiumoxide C aerogel with silicone oil, groundnut oil and coconut oil additions were named as 20SO3Al, 20GO3Al and 20CO3Al, respectively. The reference samples were also prepared using the same preparation parameters mentioned in Section 3.2.1 including Al, Al-PDMS and Ni-PDMS.

3.2.3 Ni/PDMS with ice depressing liquids

For this set of work, the same Ni foam porous substrates were first cleaned using ultrasonic bath in deionised water for 10 min. In this set of experiments: PDMS (Sylgard 184) was applied and mixed together using the weight ratio of 10:1 (A: B) applied with magnetic stirring to make the solution uniform. Then 20 wt% of glycol and glycerol were added into the PDMS precursor mixture, respectively. The mixture solution was then degassed inside the vacuum oven at room temperature for around 30

minutes to drive away the existing air bubbles. Then the Ni foams were immersed in the well-distributed Ni/PDMS-glycol or glycerol mixtures under vacuum conditions (vacuum degree: 0.1 bar) for around 30 minutes with the aim to drive away the existing air inside the porous structures of Ni foam. The post-baking treatments were then carried out on the samples using a vacuum oven set at 40 °C for a duration of 24 h. Followed by air-cooling, the as-fabricated Ni/PDMS-glycol or glycerol samples were then obtained. Same as before, the additional PDMS-glycol or glycerol mixture solutions were further applied onto the pre-prepared samples again by the spin coater to smoothen the surface morphology at the speed of 700 rpm for 90 s. The process flow chart of the whole preparation process was shown in Figure 3.3. In this series of experiments, the reference samples were also prepared using the same preparation parameters mentioned in Section 3.2.1 including Al, Al-PDMS and Ni-PDMS.

Several types of samples were prepared and further studied in this work: Ni foam samples with glycol or glycerol incorporations were designated as NP-glycol and NP-glycerol, respectively.

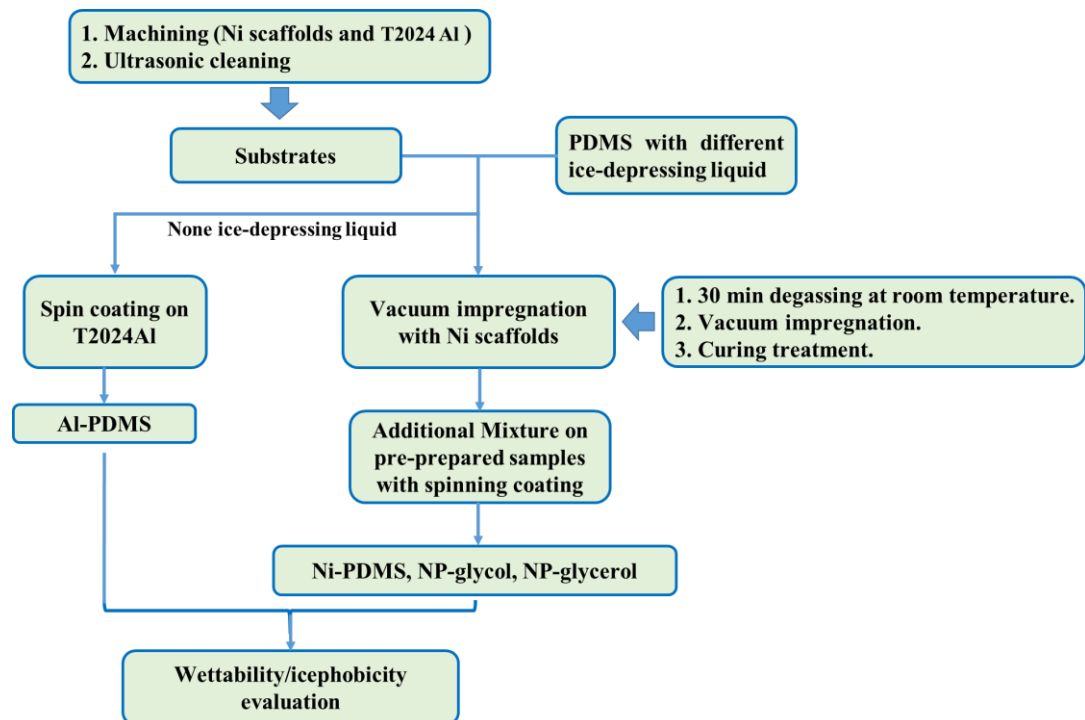


Figure 3.3 Process flow chart of preparation process of Ni/PDMS with ice depressing liquid.

3.3 Microstructural Characterisation

3.3.1 Optical microscope (OM)

Metallography mainly refers to the material discipline branch that analysed, studied and characterised the microscopic structure, low-power structure and fracture structure of materials with the help of optical (metallographic) microscope and stereomicroscope. It includes not only the imaging and qualitative and quantitative characterization of the microscopic structure of materials but also the necessary sample preparation, preparation and sampling methods [283].

In this study, the OM examinations were carried out using an optical OM (ECLIPSE LV100ND, Nikon, Japan), including the microstructure of substrates and as-prepared samples, the dimension of specific surface textures was also calculated using the bundled software. Using the bundled software inside the OM system, the dimension of surface texture could be obtained, for example, the dimension of the remaining cavities in Ni scaffolds.

3.3.2 Scanning electron microscopy (SEM)

The surface morphologies of the involved samples were characterised by a JEOL-6490LV SEM operated with 20 kV voltage. A 10 mm working distance was always kept during the observation. The spot size of the electron beam was adjusted to a proper scale with the aim to reduce the deadtime when conducting energy dispersive X-ray analysis. The backscattered electron (BSE) mode was also utilized to characterize the samples to give better revelation for elements difference and cross-sectional areas of as-prepared samples. For the involved polymeric surfaces, to give better imaging and prevent charging by the electron beam, Pt layer needs to be deposited onto the samples in advance using a Quorum and Polaron Platinum Sputter Coater. The cleaning treatment also needs to be carried out to improve the imaging quality of SEM observation using the Plasma Cleaner (Model 1020, Fischione) to quickly remove the

remaining dust and residue on the sample surfaces with gas mixture of 25 vol% oxygen and 75 vol% argon.

3.3.3 Surface roughness (3D topography)

Surface roughness refers to the quantitative measurement and characterization of irregularities, deviations, or variations present on the surface of a material or object at a micro or nanoscale level. It represents the spatial arrangement and distribution of surface features, such as peaks, valleys, and asperities, which deviate from the ideal or smooth surface [284]. It is commonly quantified using parameters of mean roughness (R_a). The parameter is calculated by measuring the vertical distance between the actual surface profile and a reference line or plane over a specified sampling length. It provides objective and quantitative assessments of the surface irregularities, enabling comparisons between different surfaces and facilitating the characterization of their roughness properties [285]. The mathematical equation (equation 3.1) for R_a is shown as follows:

$$R_a = \frac{\sum |Z_i - Z_{avg}|}{N} \quad (3.1)$$

where N is the number of data points, Z_i represents the height of each data point, and Z_{avg} is the average height of the surface profile. These mathematical formulations provide objective measures to characterize and compare the roughness of different surfaces.

In this study, a non-contact optical profiler (Zeta-20, KLA-Tencor) was applied to measure the sample surface roughness. The measurement system is designed for critical analysis of high precision applications. The limitations also exist and are mainly related to light properties and its behavior at the interface. The maximum detectable slope is rather small, and always limited by the finiteness of the objective lens numerical aperture [286]. It delivers an in-depth understanding of characteristics such as radius,

form, surface smoothness, contour and dominant wavelength, providing important feedback for improvements in design and production [284]. The values of surface roughness would be determined by the average value of several measurements and R_a is measured over an area stretching across the observed surface. Normally smaller R_a leads to smoother surfaces.

3.4 Chemical Composition Characterisation

3.4.1 Fourier transform infrared (FTIR) spectra

The spectrometer is mainly developed based on the principle of Fourier transform of infrared light after interference. As indicated in Figure 3.4, the source light is divided into two beams by a beam splitter (similar to a semi-transparent and semi-reflective mirror). One beam is transmitted to the moving mirror and the other beam is reflected to the fixed mirror. The two beams are both reflected by the fixed mirror and the moving mirror respectively and then back to the beam splitter. The moving mirror moves in a straight line at a constant speed, so the two beams that are separated by the beam splitter could form optical path differences and produce interference. The interference light would pass through the sample pool after the beam splitter is assembled, while the interference light containing the sample information reaches the detector after passing through the sample. Then the signal would be processed by Fourier transform mechanism, and finally, the infrared absorption spectrum of transmittance or absorbance with wave number or wavelength is obtained.

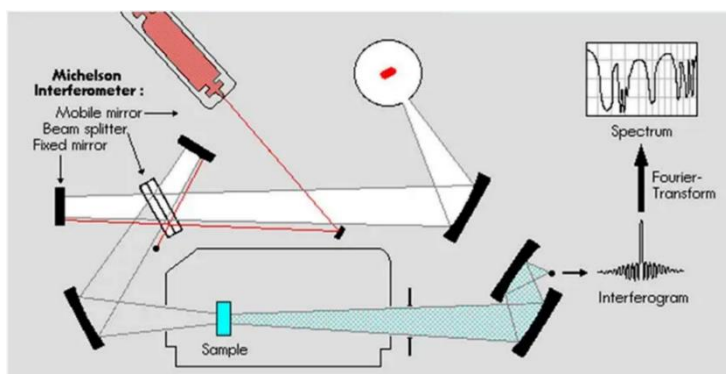


Figure 3.4 Detailed mechanism of FTIR spectrum (Adapted from Ref [287]).

In this study, the variations in the chemical composition of surfaces were qualitatively analysed using a FTIR spectrometer (Spectrum One, Perkin Elmer, Akron, OH, USA). The analysis was carried out using an attenuated total reflectance (ATR) sample holder (GladiATR, PIKE Technologies, United States) with a diamond crystal. Surfaces were directly placed in contact with the crystal for the analysis. The FTIR spectra were measured using attenuated total reflection mode in the wavenumber range of 650 cm^{-1} and 1400 cm^{-1} in the air at room condition, recording 32 scans with a resolution of 0.02 cm/s .

3.4.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a kind of thermal analysis method, which mainly measures the power difference (e.g. in the form of heat) between the input to the sample and reference in relation to temperature at a programmed temperature. The DSC curve corresponds to the recorded curve by the differential scanning calorimeter, the ordinate is the heat flow rate dH/dt (unit millijoule/second), which is also the sample heat absorption or heat release rate. The schematic diagram and images of the DSC facility was also shown in Figure 3.5 (a) and (b), respectively. While the abscissa is temperature (T) or time (t). The method could measure a variety of thermodynamic and kinetic parameters. The method has a wide temperature range ($-175 \sim 725\text{ }^{\circ}\text{C}$), high resolution and less sample consumption, which is suitable for analysis of inorganic matter, organic compounds and medicines [288].

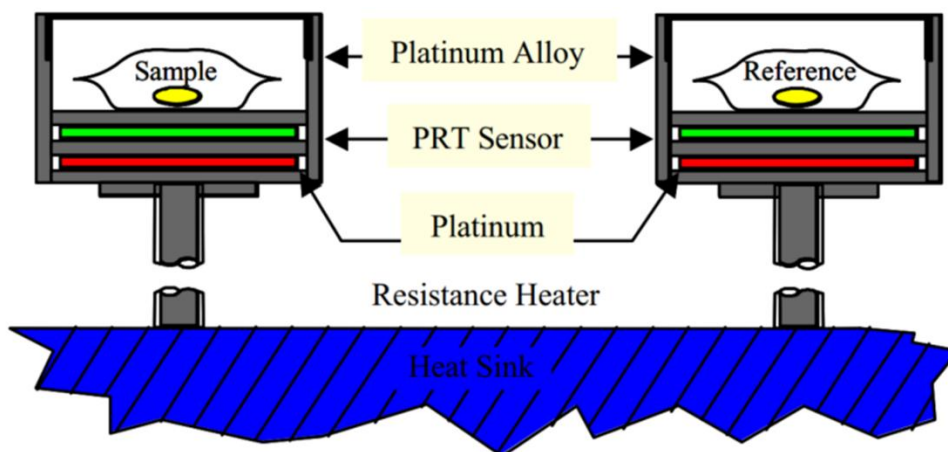


Figure 3.5 Schematic diagram of DSC with power compensation mode [288].

The thermal unfolding of the polymeric components of involved samples was monitored by SETARAM Micro DSCII calorimeter. All experiments were conducted between 0 and 100 °C. The heating rate was 0.3 K/min in all cases. Conventional Hastelloy batch vessels were used during the denaturation experiments with 850 μ L sample volume in average. The sample and reference samples were equilibrated with a precision of ± 0.1 mg. There was no need to do any correction from the point of view of heat capacity between sample and reference samples [289]. The repeated scan of denatured sample was used as baseline reference, which was subtracted from the original DSC curve. Calorimetric enthalpy was calculated from the area under the heat absorption curve by using two-point setting setaram peak integration.

3.5 Evaluation of Surface Performance

3.5.1 Wettability evaluation

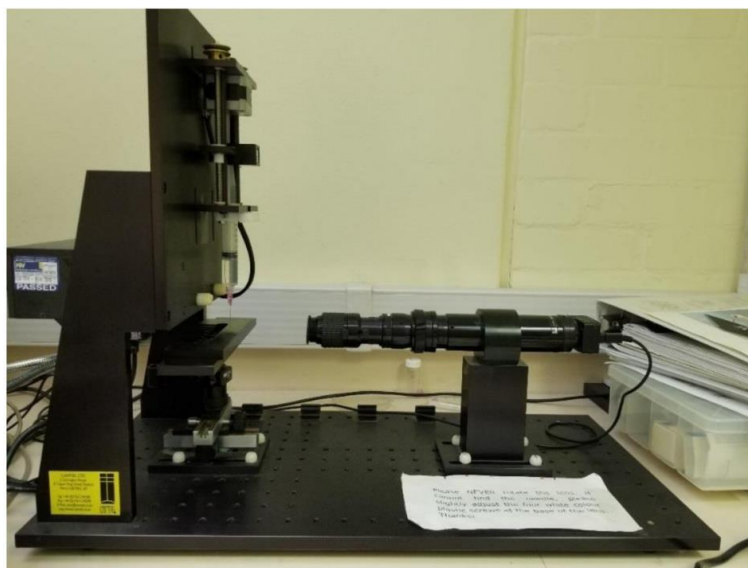


Figure 3.6 Contact angle measurement system (FTA200, First Ten Angstroms).

The wetting behaviour of the as-prepared samples was evaluated using a contact angle goniometer (FTA200, First Ten Angstroms, Inc., Portsmouth, VA, USA) with pumping out rate of 1 μ L/s using micro-pipettor and a fixed droplet volume of 5 μ L, as illustrated

in Figure 3.6. It includes static water contact angle (WCA), advancing WCA (Adv) θ_A and receding WCA (Rec) θ_R and contact angle hysteresis (CAH) ($CAH = \theta_A - \theta_R$). All of the measurements were conducted at room temperature and humidity conditions. To ensure the data accuracy, a minimum of five measurements were performed for every sample at a controlled time point.

The equilibrium contact angle described by the Young-Laplace equation is measured from a static state. A given substrate-liquid-vapour combination yields a continuous range of contact angle values in practice. The typical WCA measurement as well as the detailed spreading situation of liquid staying on common solid substrate are illustrated in Figure 3.7. It also indicates the ability of liquids to form boundaries with solid phases. For the initial step of the WCA measurement, the baseline needs to be determined, which is between the water droplet and the sample surface, showing as yellow. The tangent lines along with the boundary of the water droplet are determined. After confirming the two specific lines, the static contact angle could be acquired.

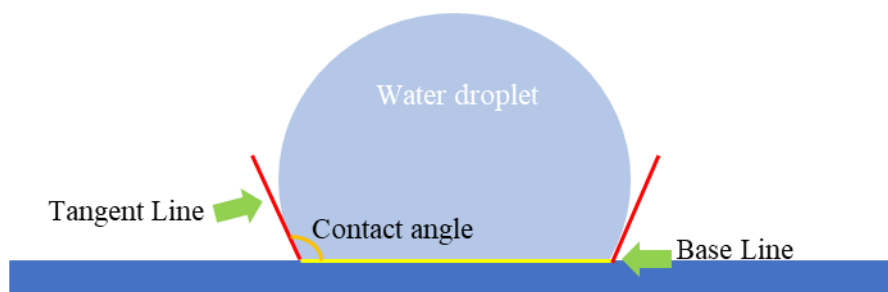


Figure 3.7 Schematic diagram of static water contact angle measurement (including base line, tangent line and contact angle labels).

CAH could be calculated by the subtraction between advancing angle and receding angle. The advancing contact angle can be described as a measurement of the liquid-solid interfacial contacts while the receding contact angle is a measurement of liquid-solid adhesion. The advancing and receding contact angles are measured from the dynamic experiments where droplets or liquid bridges are in movement [290]. The

pumping out rate of the water droplet is 1 $\mu\text{L/s}$. The whole process is monitored by the camera of the goniometer with an image every 0.5 s. The sketches of the advancing angle and receding angle measurement processes were shown in Figure 3.8. With the liquid in movement, the WCA still remains in a steady state. For advancing angle and receding angle, the size of water droplet would keep becoming larger or smaller, while the shapes of the droplet show little change. In this way, the advancing angle or receding angle could then be determined. It could be inferred that the adhesion energy varies locally according to the Young-Dupr   equation. Thus, the liquid needs to overcome the existing local energy barriers to wet the surfaces. One consequence of these barriers corresponds to CAH: the extent of wetting as well as the observed contact angle (averaged along the contact line), depending on the real-time state that the liquid stays, which includes advancing state and receding state.

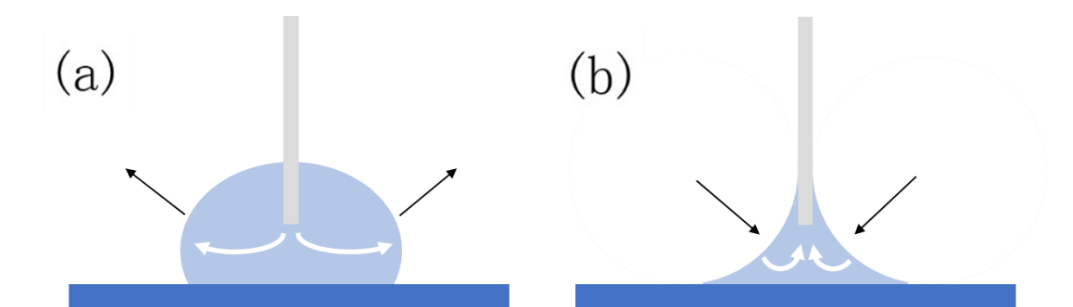


Figure 3.8 Schematic diagrams displaying (a) advancing angle and (b) receding angle measurements.

3.5.2 Measurement of surface free energy

The surface energy of the coating is an important parameter for the icephobic surface. Owens-Wendt approach is one of the most commonly used methods for calculating the surface free energy of the materials. In this work, Owens-Wendt method was applied to measure the surface energy of the coatings [291]. In this method, it is assumed that the total surface free energy is the sum of the two components: dispersion components γ_S^D and polar components γ_S^P , as indicated in equations (3.2) and (3.3) below:

$$\frac{1}{2}(1 + \cos \theta)\gamma_L = (\gamma_S^D \cdot \gamma_L^D)^{1/2} + (\gamma_S^P \cdot \gamma_L^P)^{1/2} \quad (3.2)$$

$$\gamma_S = \gamma_S^D + \gamma_S^P \quad (3.3)$$

where θ is the contact angle between the liquid droplet and coating surface, γ_L is the liquid total surface tension, γ_L^D is the dispersion component of liquid surface tension, and γ_L^P is the polar component of liquid surface tension. γ_S^D is the dispersion component of the solid surface free energy. γ_S^P is the polar component of the solid surface free energy. And γ_S is total surface free energy of the solid surface. All of the values of surface tension of liquids and their two components are referred to standard conditions of ambient temperature and pressure at sea level. (T= 20 °C, P= 1 bar) [292].

Table 3.4 Detailed parameters of liquid surface tension of three different liquids.

Liquids	γ_L (mN/m)	γ_L^D (mN/m)	γ_L^P (mN/m)
Distilled Water	72.8	21.8	51.0
Formamide	58.0	39.0	19.0
Methylene Iodide	50.8	50.8	0

The liquids employed are given in Table 3.4. Three liquids including distilled water, formamide and methylene iodide (analytical reagent) were employed to determine the surface energy. Six droplets of each liquid were deposited on each sample. The volume of each droplet is 5 µL. All of the measurement processes were conducted under atmospheric conditions at temperature of 20 °C and pressure of 1 bar.

3.5.3 Shore hardness tests

The measurement of hardness on elastomers could basically be divided into two types, one is International Standards Organisation (ISO) test, which employs a spherical indenter; the other one is shore hardness test, employing truncated cylinder, containing two hardness tests, Shore A and Shore D, covering different hardness ranges [293].

In the study, the hardness measurement is conducted using shore hardness tests with a SAUTER durometer that is attached to the SAUTER test stands TI-AO and TI-D for Shore hardness A and D scales, respectively. The shore hardness A scales were used in this work, the indenter is a truncated cone with a conical angle of 35° , with the apex plane diameter of 0.79 mm [293]. For every sample, 10 separate measurements were carried out to confirm the average penetration (Shore) value and minimize the existing error.

3.5.4 Tensile test of mechanical characterisation

The tensile tests were conducted using an Instron 5969 Dual Column Tabletop Universal Testing Systems (Instron, High Wycombe, UK) equipped with the utilised clamps (Instron 2710-101). The samples were cut into rectangular bars with dimensions of 20 mm $\times$ 0.3 mm among the cross-sectional area. A Hildebrand rubber thickness gauge with the length of 6 mm was used to measure the thickness and width.

In practice, the process of obtaining the thickness measurement was complicated by the viscoelasticity and high compliance exhibited by the elastomers as the rubber thickness gauge probe applied a small force, causing the material to deform. Therefore, to calculate the thickness in the absence of the probe force, the elastic solution developed by Lebedev and Ufliand was used to correct the deformation [294].

The rectangular specimens were attached to the apparatus with staple-like clips. Strain was then applied to the specimens using the counter-rotation of the drums. To check whether the specimen is straight before the tests, a small torque was applied to the specimens. The tensile tests were then conducted with the applied motion rate 1.0 mm/min at room temperature ($18 \pm 1^\circ\text{C}$) and humidity ($50 \pm 5\%$). The raw data obtained from the tests could be utilized to determine the nominal strain and the nominal load.

3.6 Studies of Icephobicity

Generally, the icephobicity could be reflected from both anti-icing and de-icing aspects. Anti-icing performance refers to the ability to prevent and delay ice nucleation and formation and adherence of supercooled droplets on sample surfaces. While de-icing performance normally means low adhesion strength between formed ice and solid surface, leading to easy detachment of formed ice from certain surfaces.

3.6.1 Evaluation of anti-icing performance

3.6.1.1 Droplet icing delay

The ice formation time is an important parameter for icephobicity evaluation because it reflects the length of time a supercooled water droplet takes to freeze on certain surfaces [15]. The larger the freezing delay time, the lower the probability of the droplet freezing on the specific surfaces as the external forces can expel the droplet away. So the ice formation tests were carried out to better evaluate the anti-icing performance of as-prepared samples.

The cold plate (Para Cooler O, Weinkauf Medizin und Umwelttechnik, Hallerndorf, Germany) with an adjustable temperature was utilized to provide an icing environment with temperature maintained at $-20\text{ }^{\circ}\text{C}$, as shown in Figure 3.9. The insulated and transparent plastic sheets were used to minimize the environmental effect and give intuitive observation of the experiment procedure. The samples were first put inside the cold plate overnight for pre-cooling. Droplet icing tests were carried out by determining the duration of ice formation from water droplets with a volume of $4\text{ }\mu\text{L}$ using micro-pipettor on five different points on the as-prepared samples. The corresponding substrates were also involved for comparison. The whole process was also video recorded to determine the icing duration. The average icing duration was recorded to evaluate the anti-icing performance and the detailed icing process could also help to explain the mechanism.

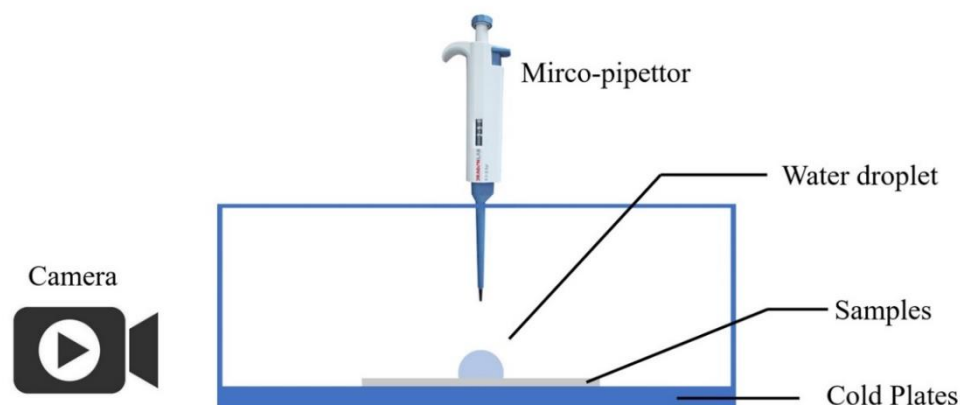


Figure 3.9 Schematic diagram of droplet icing test.

3.6.1.2 Icing test under frost environment

To better evaluate the anti-icing property of coatings under the actual working condition, the rotary dynamic frost formation tests would be carried out. During the test, to guarantee equal icing area, the uncoated parts including the backside and side areas of the samples were completely covered by insulation tape and they were peeled after the tests. To ensure same icing conditions, the tested samples were placed at the same distance from the sprayer output point. A custom-built metal rotor with six seats for samples was used for rotary tests. The samples were fastened by means of a screw, and the rotor was spun at the speed range between 30 to 300 rpm. The cold plate would be set at $-25\text{ }^{\circ}\text{C}$, which can easily obtain glaze. An aerosol generator (Ultrasonic Nebuliser NE-U17, Omron, Inc) with deionized water was utilized to produce moisture. Two electric fans were also applied to ensure the uniform distribution of the moisture. Due to the cold temperature inside the cold plate, the moisture would become glaze during the movement. There would be glaze that keeps forming on the tested samples. The whole experiments last 60 min. The mass difference of the samples before and after the experiment was monitored. The mass of formed glaze per unit area would be calculated. Samples with less glaze formation per unit area could explain the good anti-icing performance. Several experiments would be carried out on one sample to make sure the data's accuracy.

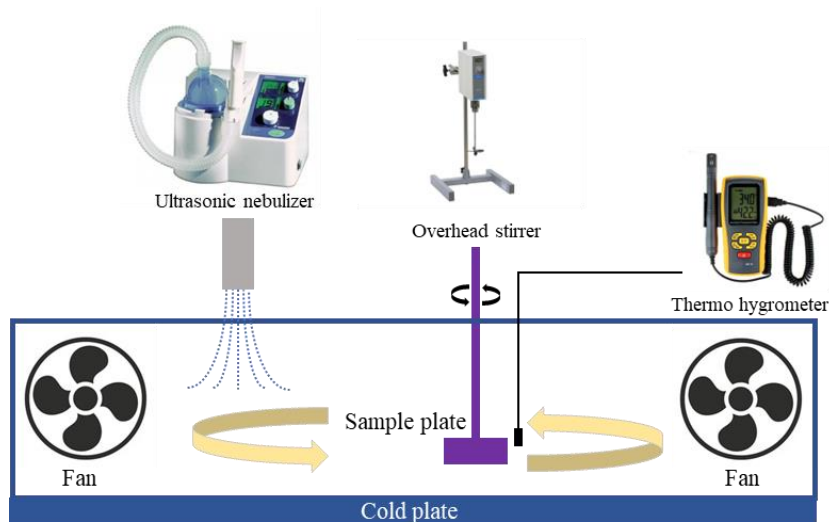


Figure 3.10 Schematic diagram of icing test under frost environment.

3.6.2 Water condensation and icing study using environmental scanning electron microscopy (ESEM)

In-situ water condensation and ice formation process was observed by an ESEM equipped with a Peltier cooling stage (FEI Quanta 650, ThermoFisher). By means of a differential pumping system and a gaseous secondary electron detector (GSED), the hydrated samples could then be imaged. The ESEM column is equipped with a multi-stage differential pressure pumping unit. The pressure in the upper part is about 10^{-6} to 10^{-7} Torr, but pressure ranges from 1-6.5 Torr can be maintained in the observation chamber. When the electron beam (primary electrons) ejects secondary electrons from the surface of the sample, the secondary electrons collide with gas molecules in the ESEM chamber, which in turn function as a cascade amplifier, delivering the secondary electron signal to the positively biased GSED. The positively charged ions are attracted toward the specimen to neutralize the negative charge produced by the electron beam [295].

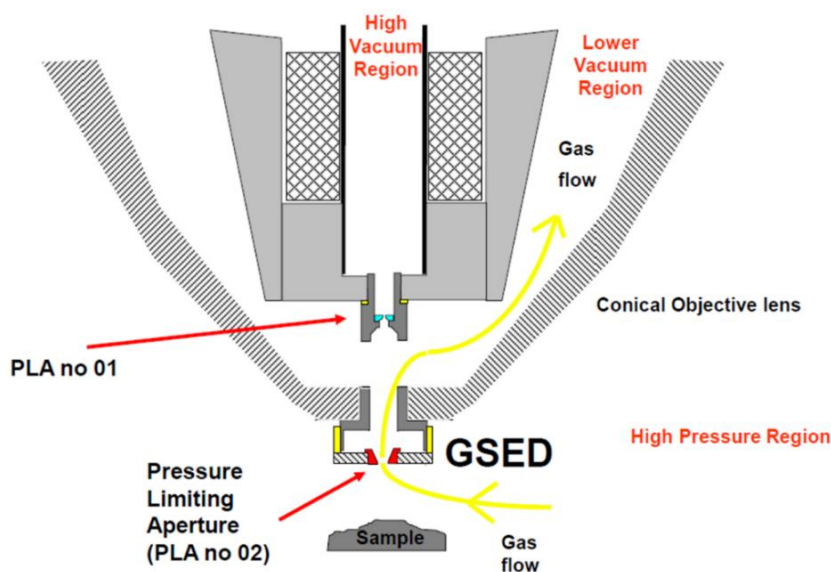


Figure 3.11 Schematic diagram of three zones of ESEM vacuum system (Adapted from Ref [296]).

If the water condensation observation were conducted at room temperature, it could be seen from Figure 3.11 that the required pressure to maintain saturated vapour in the chamber is high. So, it is still not practical to imaging under these conditions. To achieve the saturation state, it is more proper to decrease the temperature of the cooling stage to a bit higher or just above freezing, which could be reflected from the phase diagram shown in Figure 3.11, and then only a modest gas pressure is needed to stabilize water [297]. To ensure a better thermal stability, it would be beneficial to place sample in a well or covering with a washer. The tighter the contact, the better the heat conduction during the observation.

By controlling the pressure and temperature simultaneously, the in-situ wetting and icing could be monitored. Samples that are not thermally conductive would have a larger temperature gradient than thermally conductive samples, mounting can play an important part in minimizing the difference and making an experiment successful. The voltage of the electron beam was 15 kV and the distance of the specimen from the final aperture was about 6-8 mm. During the ESEM observation, the water vapour pressure and humidity of the chamber, the temperature of the cooling stage could be adjusted

according to the phase diagram in Figure 3.12, which would help the water condensation and ice formation and diminishment on sample surfaces. The water condensation and in-situ icing process on different sample surfaces would be analysed in a controlled environment with a certain temperature and humidity. In this study, the water condensation and in-situ icing process of the samples were recorded, at temperature range of $-20.0 \sim 20.0$ °C and relative humidity of 90 ~ 100%.

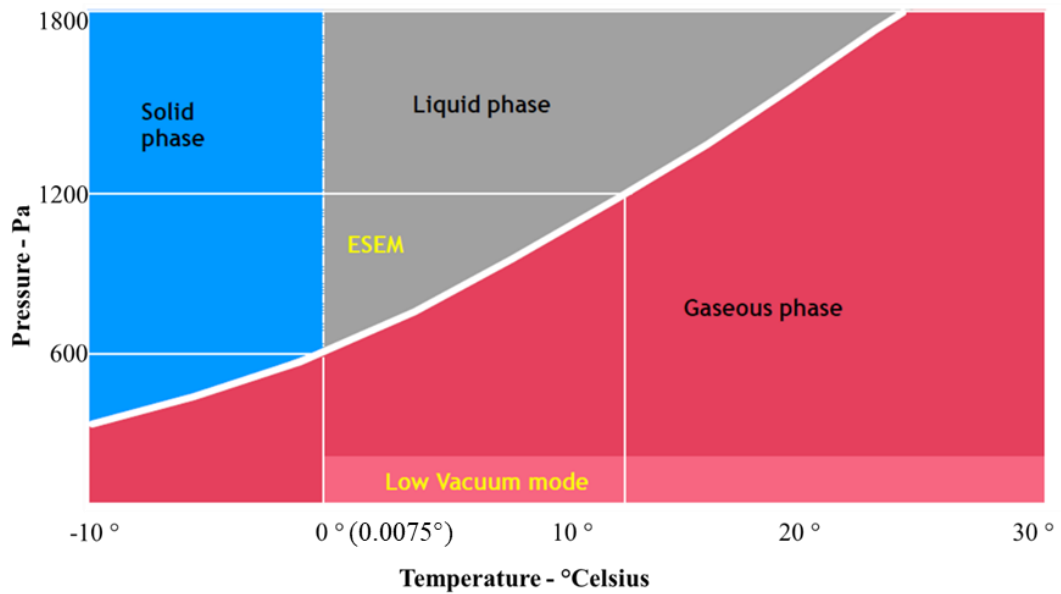


Figure 3.12 Pressure/temperature phase diagram for H₂O (Adapted from Ref [298]).

3.6.3 De-icing evaluation aspects

3.6.3.1 Ice adhesion strength

Ice adhesion strengths were also measured using a horizontal shear test system (as shown in Figure 3.13) with a pre-prepared ice block (volume: 1.31 mL) attached to the sample surface in an environment-controlled cold plate. In essence, the shear test system mainly consists of a force probe, a motion controller as well as the prepared ice block (with diameter of 5 mm) attached to the tested samples. The detailed diagram of the test system is shown in Figure 3.13 (a) for detail. De-ionized water was added into a silicone mould with volume of 1.31 ml using liquid-moving machine. The mould was covered onto the tested samples. They were then kept inside the cold plate with

temperature of -20 °C for 4-6 h, to produce repeatable samples of pure glaze ice on each sample substrate. The iced area between the mould and the sample was 1.38 cm².

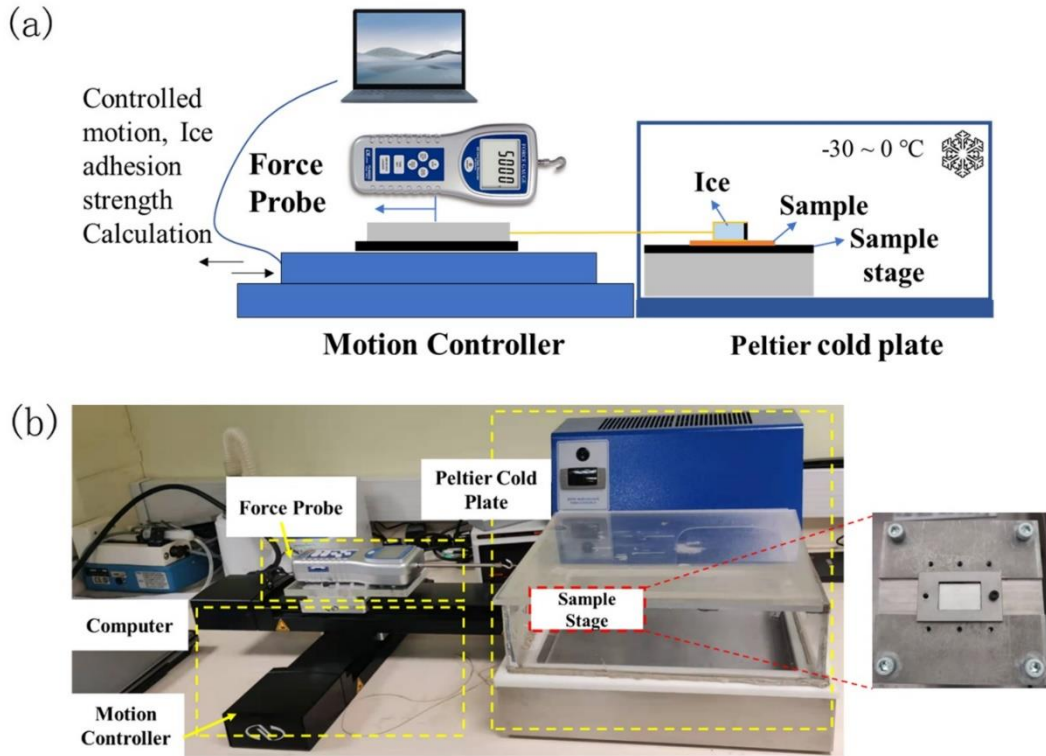


Figure 3.13 (a) Schematic diagram and (b) Pictures of the ice adhesion test setup.

With the induction of the rotor's movement, the prepared ice block/substrate sample would stay with uniform horizontal motion, the force probe was used to propel the ice/sample with a velocity of 0.1 mm/min during the ice adhesion test, and the detailed facility setup was shown in Figure 3.13 (b). The ice would detach from the sample once it is enough to overcome the adhesion strength of the ice to the substrate. With the horizontal shear force keep increasing, the glaze ice block would overcome the shear strength and finally detach from the sample surface. The applied force could be obtained from the probe, ice adhesion strength could then be determined from the equation (3.4) [299]:

$$\tau = F/A \quad (3.4)$$

where τ represents the shear strength (Pa), F refers to applied force (N), and A is the contact area of the ice block on the coating (m^2). Five ice adhesion strength tests were carried out for each tested sample to ensure the data confidence, the standard error was also applied for the tested data.

3.6.3.2 Cyclic icing/de-icing tests

Ice adhesion strength tests measure the force required to detach ice from a surface, usually under controlled laboratory conditions. These tests involve pulling a thin layer of ice from a flat or curved substrate, and the results can be used to evaluate the effectiveness of icephobic coatings or anti-icing materials. They can also be used to study ice adhesion mechanisms and develop new strategies for preventing ice buildup [300]. The ice adhesion strength was reported as the average and standard deviation of several parallel samples during each icing accretion process. Corresponding test reference surfaces (T2024 Al) were used to guide and monitor the ice adhesion at each accretion event, considering possible variations in icing conditions [301]. The ice adhesion strength and mass change versus the cyclic tests were also recorded to evaluate the impact of freezing time on surface icephobicity.

Chapter 4 Microporous Metallic Scaffolds Supported Liquid Infused Icephobic Constructions

In recent years, the slippery liquid-infused porous surfaces (SLIPS) and liquid-infused surfaces (LIS) have drawn a lot of attention [23, 302]. By entrapping liquid inside a porous media through capillary forces, the liquid surfaces would be developed and the smooth nature of the infused lubricants could improve the icephobicity [303]. The liquid surfaces then mitigate the pinning effect of the remaining water droplets and lead to a reduction in ice adhesion strength [304]. But the disadvantages of SLIPS also exist since the liquid layer could be depleted and the ice adhesion then increases inevitably. For example, Rykaczewski et al. reported that the water droplet infused into the bulk of oil where they formed interfaces with solid and the oil film was depleted as they moved onto the nanostructured SHS surfaces [208]. While for LIS, the internal porosities have been substituted with lubricant, the liquidous layer forming on the top surface could prolong the ice formation and reduce the ice adhesion [208, 249]. For the preparation of LIS, it follows three basic principles: 1) sufficient roughness and chemical compositions are needed for the substrates to ensure that the lubricant could adhere to the substrate stably; 2) the infused lubricant requires a better affinity with the substrate than with other liquids and therefore it cannot be replaced with other liquids; 3) the selected lubricant cannot be miscible with the liquid to be repelled [305]. Apart from this, the Cassie-Wenzel wetting state conversion under complex conditions could also be prevented by the formed liquid film [306, 307]. Besides, LIS could enable the rapid recovery ability once the surface suffers damage, which is known as self-healing ability derived from the fluidity of the liquid film [308].

New types of LIS design concepts by infusing other materials into the internal structures have also indicated their good icephobic prospects. The infusion of lubricants could delay the ice formation and decrease the ice adhesion strength. Yamazaki et al. used the ethylene glycols in superhydrophilic matrix to prepare the LIS which exhibited low ice

shear strength of only 17 kPa [309]. Similarly, Sandhu et al. fabricated LIS by infusing perfluoroalkane wax as lubricant into gels, the ice adhesion strength could be as low as 19.6 kPa due to the weaker intermolecular bonding [310]. LIS prepared on polymeric substrates could decrease the ice adhesion strength obviously. Liu et al. used the rubber surfaces to prepare LIS by the electrospray method as well as phase separation [207]. The obtained LIS not only prolong the icing process, but also decrease the ice adhesion by 1 to 2 orders of magnitude compared to conventional materials.

However, the continuous depletion of surface oil layer during the multi icing/de-icing processes could lead to the emergence of degradation in icephobic performance. The serious depletion of lubricants inside the structure is because of the various factors including evaporation, shedding accompanying droplet or bulk ice, mechanic abrasion, etc. For example, the ice adhesion strength of LIS using UV-cured cross-linked silicone resins onto porous anodic aluminum oxide (PAAO) surfaces increased sharply from 10 kPa to 50 kPa after seven icing/de-icing cycles since the resin-oil layer was removed from surfaces under the de-icing process [39]. The interlocks between bulk ice and structure not only increase the ice adhesion strength, but they also result in irreversible damage to the structure under the de-icing process [245, 311]. Therefore, based on the consideration of urgent need of durability improvement, the focus of current research should be paid onto the durability improvement of the icephobic structure which also combines with the excellent icephobicity.

For the aim to combine effective icephobicity and durability in icephobic surface systems, the microporous metallic scaffolds was introduced into the LIS construction to unfold the potentials. Ni scaffolds and PDMS modified silicone oil system were chosen for the LIS construction. The PDMS with silicone oil modification is a typical candidate for LIS construction, but the disadvantage lies in the icephobicity degradation derived from the lack of mechanical durability [32]. With the incorporation of Ni scaffolds, the assumption of mechanical durability enhancement could be achieved. In addition, different distortions could initiated locally from the mismatch in elastic

modulus among Ni scaffolds and LIS polymer matrix, which would further induce the micro-cracks at the ice/solid interface under external loads. Besides, the oil depletion is also expected to be largely alleviated, making contribution to the enhanced durability. Detailed analysis of icephobic performance were also conducted from three different aspects including the formation, growth and removal of ice on sample surfaces, which illustrated the potentials of new LIS construction.

Characterisation details

Several microscopic techniques including OM and SEM were used to investigate the surface morphologies of the as-prepared samples. The microstructural analysis of the different zones was observed by OM (ECLIPSE LV100ND, Nikon, Japan). The image acquisition was conducted at $500\times$ magnification. For SEM observations, they were operated at the voltage of 20 kV, the working distance was maintained at 10 mm. Backscattered electron (BSE) mode was also used to give better revelation for elements difference and cross-sectional areas of as-prepared samples. The 3D surface topography and surface roughness of the samples were measured using a non-contact optical profiler (Zeta-20, KLA-Tencor). For every sample, several separate measurements were carried out to calculate the average penetration (Shore) value and minimise the testing error.

Shore hardness tests were conducted with a SAUTER durometer attached with SAUTER test stands TI-AO and TI-D for Shore hardness A and D scales, respectively. The Shore hardness A scale was used in this part of work. The tensile properties were measured with an Instron 5969 Dual Column Tabletop Universal Testing Systems (Instron, High Wycombe, UK) with utilised clamps (Instron 2710-101). The dimensions of cross-section areas of all tested samples were 20 mm $\times$ 0.3 mm. The length of the gauge was 6 mm. The applied motion rate was stabilized at 1.0 mm/min.

Water contact angle of the surfaces was measured by the contact angle goniometer (FTA200, First Ten Angstroms, Inc) at room temperature. The static water contact angle was measured with a fixed droplet volume of 5 μL and the pumping out rate was stabilized at 1 $\mu\text{L/s}$. The surface free energy of the sample surfaces was acquired using Owens-Wendt method [292]. Three testing liquids including distilled water, formamide and methylene iodide were chosen to determine the surface energy. All of the measurements were conducted under atmospheric conditions at the temperature of 20 $^{\circ}\text{C}$ and the pressure of 1 bar.

Droplet icing tests were performed by observing the icing process of supercooled water droplets on the sample surface in a cold chamber at -20 $^{\circ}\text{C}$. The volume of the droplet was kept at 4 μL and five different spots on each sample were chosen for comparison. The whole icing process was recorded to determine the icing behaviours and durations. Ice growth on the sample surface was investigated by an environmental scanning electron microscopy (Quanta 650 FEG-ESEM, FEI). Water condensation, ice formation and growth were studied under the condition: -10 $\sim$ -2 $^{\circ}\text{C}$, relative humidity: 90-100%, and pressure: 380~700 Pa. The ice growth rate was calculated from equation (4.1) [312]:

$$v = \frac{L}{t} \quad (4.1)$$

where L is the ice growth length (as observed on the ice growth direction) (μm), t is the time (s), and v is the ice growth rate ($\mu\text{m/s}$).

Ice adhesion strengths were measured using a horizontal shear test system with a pre-prepared ice block (volume: 1.31 mL) attached to the sample surface in an environmental chamber with temperature of -20 $^{\circ}\text{C}$. For ice block preparation, a silicone mould was fully filled with 1.31 ml deionised water using pipettor and carefully covered onto the sample surface. Then the samples were kept inside the cold chamber at -20 $^{\circ}\text{C}$ for 3 h, to produce glaze ice block on the samples. The iced area between the

mould and the sample was 1.38 cm². The shear test system mainly consisted of a force probe (with diameter of 5 mm), a motion controller, and an ice block attached on tested samples. The force probe was used to propel the ice/sample with a velocity of 0.1 mm/min during the test.

With the increase of the shear force, the glaze ice block would overcome the bonding strength and finally detach from the sample surface. The applied force was monitored from the probe, and the ice adhesion strength could be determined using equation (4.2) [313]:

$$\tau = \frac{F}{A} \quad (4.2)$$

where τ represents the shear strength (Pa), F refers to the applied force (N), and A is the contact area of the ice block on the sample (m²). Five samples were measured to ensure the data confidence. Most of the samples underwent 50 icing/de-icing cyclic tests with 3-hour re-freezing intervals, while for some reference samples, the anti-icing and de-icing process caused surface damage, and the number of cycles did not reach 50. Therefore, the ice adhesion values from the first 30 cycles were selected for analysis. The ice adhesion strength and mass change versus the cyclic tests were also recorded.

ANSYS software was selected to conduct the comparative 2D plane strain simulation under shear force and gravity on PDMS and Ni-PDMS samples. A combined force including the gravity could be resolved into vertical uniform surface pressure and horizontal shear. An identical force was applied to the two samples.

Calculation methods of internal porosity of Ni scaffolds. The porosity of the Ni scaffolds is measured by the drainage method [314]. The calculated porosity is around 95.6 %.

All sample values were expressed with standard deviation to indicate the range of error. The standard deviation is a commonly used measure of variability in statistical analysis. It is calculated by first finding the mean of a dataset and then computing the square root of the sum of the squared differences between each data point and the mean, divided by the sample size minus one. Mathematically, the formula equation (4.3) for calculating the standard deviation is as follows [315]:

$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n-1}} \quad (4.3)$$

where s is the standard deviation, Σ is the sum, x_i is the value of the i th data point, $\bar{x}$ is the mean of the dataset, and n is the total number of data points.

Initially, the pure PDMS was weighed both before and after the curing process, and subsequently, the mass loss proportion resulting from the curing process was calculated in relation to the total mass of PDMS. This proportion was utilized to determine the actual content of silicon oil in each sample, and the resultant findings are presented in Table 4.1 below:

Table 4.1 Weight percentages of added silicone oil in PDMS after curing.

Sample	In the uncured resin solution (wt%)	In PDMS after curing (wt%)
PDMS-10SO	9.98	10.01
PDMS-20SO	19.85	20.02
PDMS-30SO	29.95	30.03
PDMS-40SO	40.01	40.04
PDMS-50SO	49.98	50.04

4.1 Morphological and Microscopic Characterisations of As-received Ni Scaffolds and NP-SO Samples

4.1.1 Micro-structures of Ni Scaffolds and NP-SO Samples

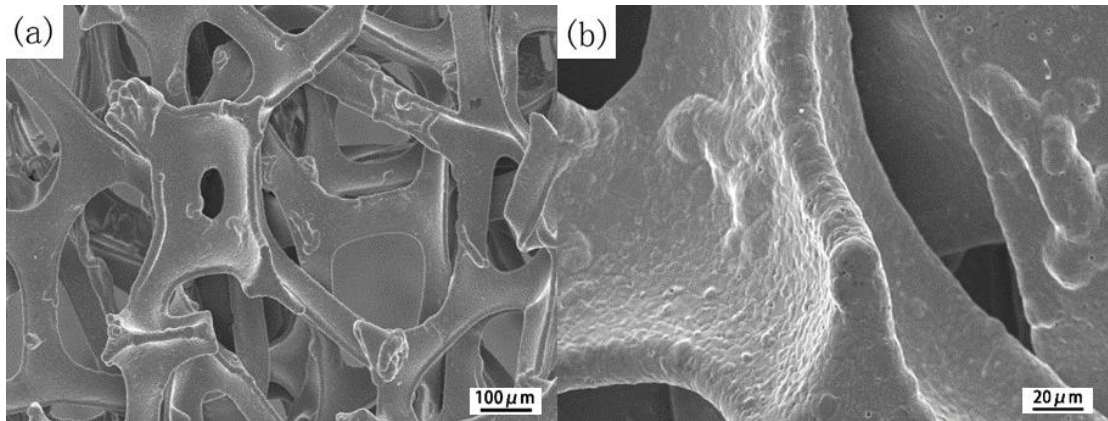


Figure 4.1 SEM images of (a) surface morphology (b) amplified image of Ni scaffold.

Figure 4.1 shows the SEM images of surface morphology and amplified images of Ni scaffold. It clearly shows the highly porous structure of the Ni scaffold with calculated porosity of around 95% (80-110 pores per inch). The pores in the scaffolds range in size from 200-400 μm. The existing numerous pores and foam skeletons could help with the impregnation of hydrophobic/icephobic substances. The material exhibits the uniformity of Ni scaffolds in the entire density range [316].

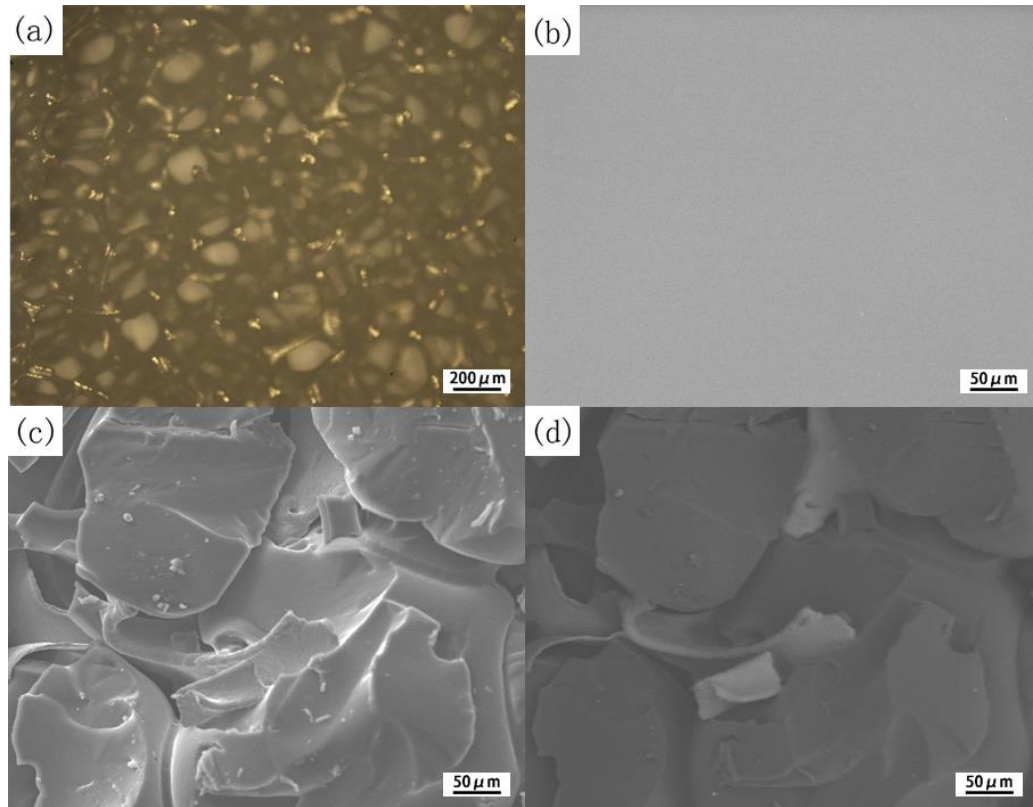


Figure 4.2 (a) Optical microscope images (top view) of Ni-PDMS; (b) SEM surface morphology of Ni-PDMS; (c) SEM cross-sectional images of Ni-PDMS; (d) BSE images of the cross-sectional areas of Ni-PDMS.

The optical and SEM microstructural images of Ni-PDMS surfaces were shown in Figure 4.2. It could be observed in images (a) and (b) that the surface of the Ni scaffolds was completely covered by the infused PDMS, showing as a single layer of PDMS. The internal porosity has also been filled, while no sharp and deep surface pores remain on the surface, which could be beneficial for the later de-icing process [130]. Images (c) and (d) illustrated the SEM and BSE images of the cross-sectional areas of Ni-PDMS. It could be found that the area with obvious edges were Ni scaffolds as well as the areas highlighted with light colour in BSE images. The Ni scaffolds were completely covered by the infused PDMS and the PDMS was also protected by the Ni scaffolds, leading to tighter incorporation between the PDMS and metallic frames.

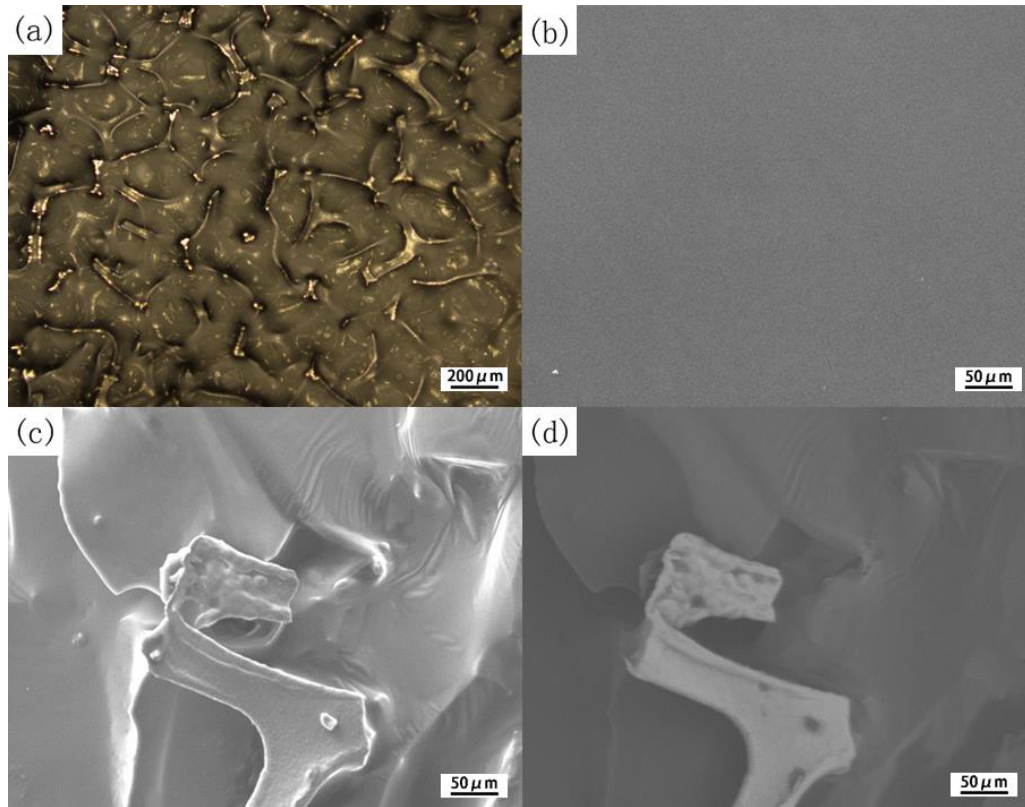


Figure 4.3 (a) Optical microscope images (top view) of NP-40SO; (b) SEM surface morphology of NP-40SO; (c) SEM cross-sectional images of NP-40SO; (d) BSE images of the cross-sectional areas of NP-40SO.

Figure 4.3 showed the optical images and SEM images of NP-40SO (NP-40SO was chosen here as a representative of the studied samples). From Figure 4.3 (a), there was no obvious difference observed, it exhibited smooth and flat throughout the whole modification process. With the PDMS layer on top, the displayed surface morphology still showed as flat and smooth, as depicted in Figure 2 (b), and few surface cavities could be found. No sharp metallic feature could be observed, as well as the profile of the Ni scaffolds cannot be detected from the image. There was also no void and crack on the surface, showing good surface integrity and uniformity. The cross-sectional areas of NP-40SO were also indicated in Figure 4.3. The area with light colours in BSE images were Ni scaffolds, while the areas with dark colours were PDMS, which was the same as that in Ni-PDMS. No voids or cracks could be found on the cross-sectional areas, indicating the good adhesion. With the interconnected network structures

constructed by Ni scaffolds and PDMS filling, the protective effect of the as-prepared icephobic structure could be easily realized. It is thought that the impact energy, wear and shear abrasion from external environment could be decreased effectively. Furthermore, these impacts could be further dispersed and transferred to other larger regions through the interconnecting skeleton [40].

4.1.2 Element composition with EDX spectrum

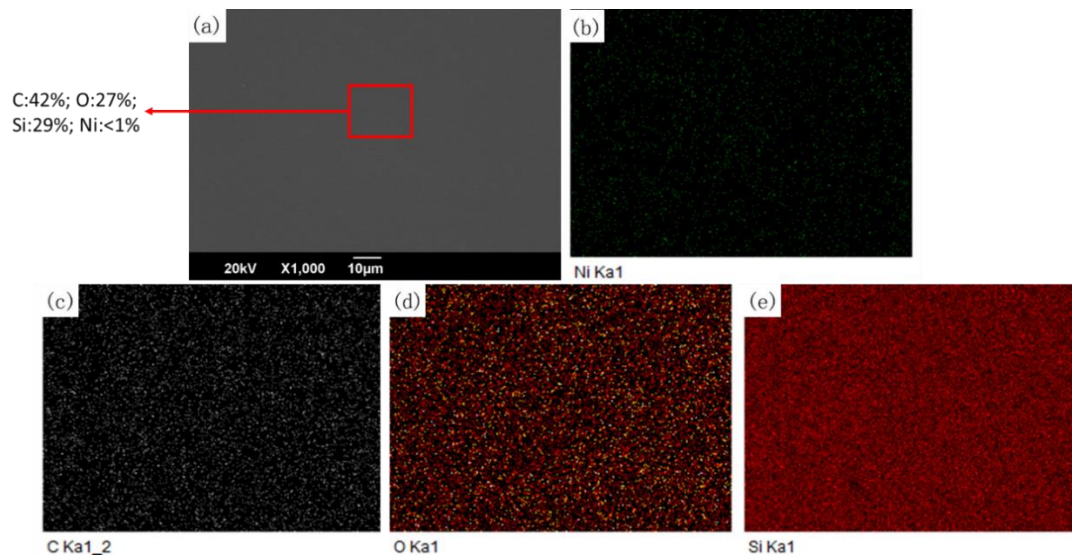


Figure 4.4 SEM images (a) and EDX element mapping results (b) Ni, (c) C, (d) O, (e) Si on NP-40SO.

Figure 4.4 was the EDX spectrum results of the surface of NP-40SO. Figure 4.4 (b) to (e) indicated the element distributions of Ni, C, O, and Si, respectively. On the sample surface, the C, O, Si elements confirmed the PDMS fillings and all these elements were distributed uniformly on the viewfield. Very few Ni could be found on the surface. This confirmed that all Ni scaffolds were fully covered by the top PDMS layer. The Ni scaffold underneath was difficult to observe even though considering the strong penetrability of EDX spectrum. For the other three elements, it was clear to find that all of the mapping results showed uniform distribution. Especially for Si, with the silicone oil addition, there were quite a lot of Si elements on the sample surface, which was also very tightly distributed.

4.1.3 Shore hardness results of PDMS-SO samples

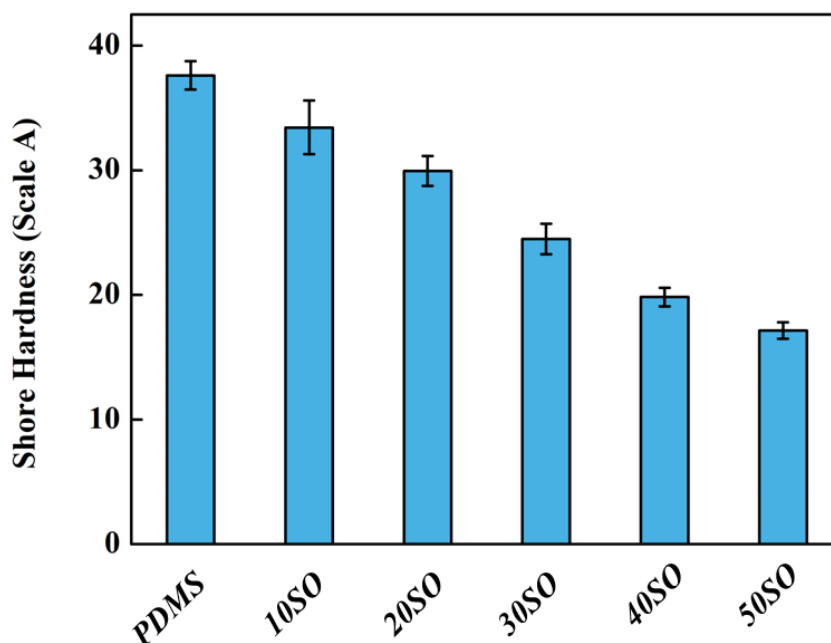


Figure 4.5 Shore hardness results of pure PDMS, PDMS-10SO, PDMS-20SO, PDMS-30SO, PDMS-40SO and PDMS-50SO samples.

The shore hardness results of as-prepared samples with different silicone oil additions were shown in Figure 4.5. The representative values of shore hardness were related to the elastic modulus measured by other typical methods [317]. In comparison, the pure PDMS exhibited a hardness of 37.6 ± 1.1 (Shore A hardness). While for samples with silicone oil incorporation, the hardness (Shore A hardness) of PDMS-10SO, PDMS-20SO, PDMS-30SO and PDMS-40SO were about 33.4 ± 2.1 , 29.9 ± 1.2 , 24.5 ± 1.2 and 19.8 ± 0.7 , respectively. The measured shore hardness showed a steady decreasing trend with increasing silicone oil, which indicated the softening effect of silicone oil infusion. The hardness of PDMS-50SO finally decreased to only 17.1 ± 0.6 (Shore A hardness) when the percentage of oil addition reach 50 wt%. The reason here could be ascribed to the increased gaps among the macromolecular chains [318], leading to the decrease in cross-link density. The description of the microstructure for this phenomenon was also illustrated in Figure 4.6.

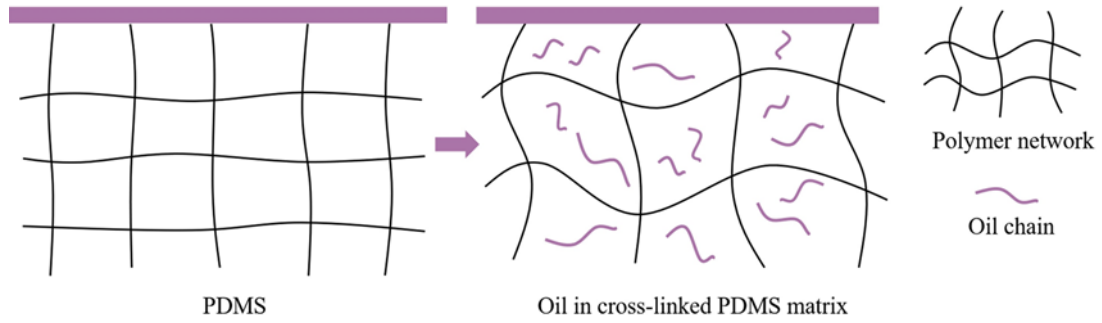


Figure 4.6 Structural changes after the infusion of silicone oil inside the PDMS matrix.

Once the curing process was finished, the PDMS polymer would form a regular matrix, acting as the polymer network. With silicone oil infusion, some of the silicone oil would stay in the cross-linked PDMS matrix. As indicated in the image, with silicone oil infusion, some silicone oil chains remained in the polymer network [318]. This could introduce some soften effect to the sample and lead to a continuously decreasing shore hardness value.

4.2 Detailed Investigation of Involved Surface Properties of NP-SO Samples

4.2.1 Wetting behaviour and roughness of NP-SO samples

Surface roughness of the as-prepared samples has been characterised and compared in Figure 4.7. The surface roughness of as-received Al substrate was $1.40 \pm 0.01 \mu\text{m}$. While for Al-PDMS, with the PDMS layer on top, the measured Ra was $0.75 \pm 0.04 \mu\text{m}$. The as-prepared PDMS layer was smooth and flat, resulting in the decrease of the surface roughness. The average surface roughness of another reference sample-Ni-PDMS was about $0.77 \pm 0.07 \mu\text{m}$, very close to that of Al-PDMS. Regarding the NP samples with different oil additions, only small variations of their surface roughness could be found, ranging from 0.78 to 0.83 μm . The infused silicone oil would keep diffusing into the PDMS cross-linked network, forming a lubricated silicone oil

overlayer [319]. The thin oil layer could alleviate the small surface undulation caused by the combination of soft polymer and Ni scaffolds, which finally led to the similar surface roughness on different samples.

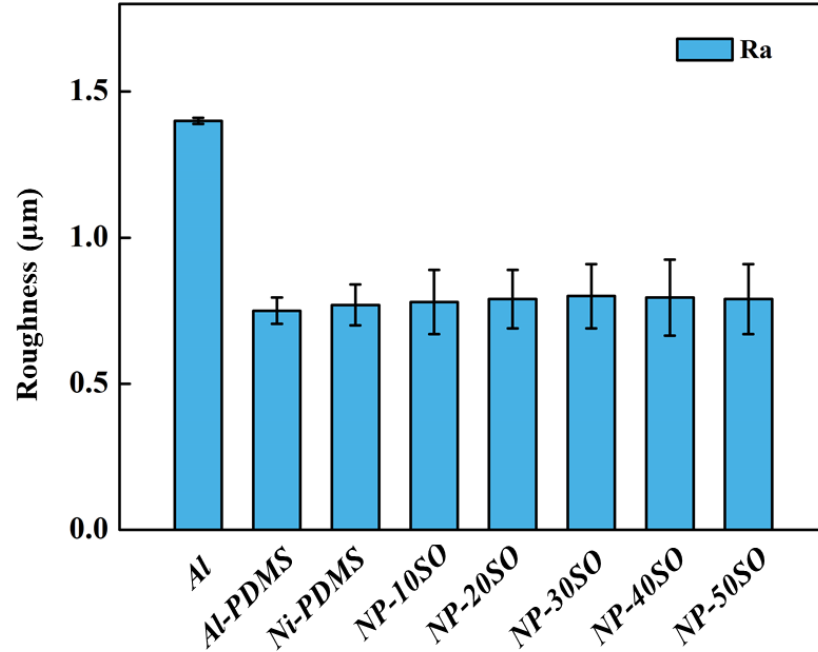


Figure 4.7 Surface roughness and of PDMS, Ni-PDMS and NP-SO series samples.

For the as-prepared NP-SO and the reference samples, water contact angle and contact angle hysteresis (CAH) were measured and shown in Figure 4.8. The static WCA of Al plate and Al-PDMS were $101.2 \pm 2.5^\circ$ and $106.1 \pm 0.9^\circ$, respectively. The minor deviation from the ordinary wettability of pure Al here could be the result of the surface gaseous adsorption derived from the time-dependent wettability [130, 320]. For Ni-PDMS, the WCA value reached $105.6 \pm 0.6^\circ$, which was also consistent with the inherent wettability of pure PDMS (normally around 104° [321]). While for NP-SO series samples, the measured WCAs were normally at the WCA range between 100 to 110° ; for NP-10SO, the WCA was $108.6 \pm 3.0^\circ$, and $110.6 \pm 1.0^\circ$ for NP-20SO, $110.8 \pm 1.7^\circ$ for NP-30SO, $111.8 \pm 2.1^\circ$ for NP-40SO and $116.0 \pm 2.0^\circ$ for NP-50SO, respectively. They showed a steady increasing trend with higher silicone oil addition. The reason for the WCA increase could be the variation in surface energy. The incorporation of silicone oil also played an important role in lowering the surface energy [322], which finally indicated the increased WCAs.

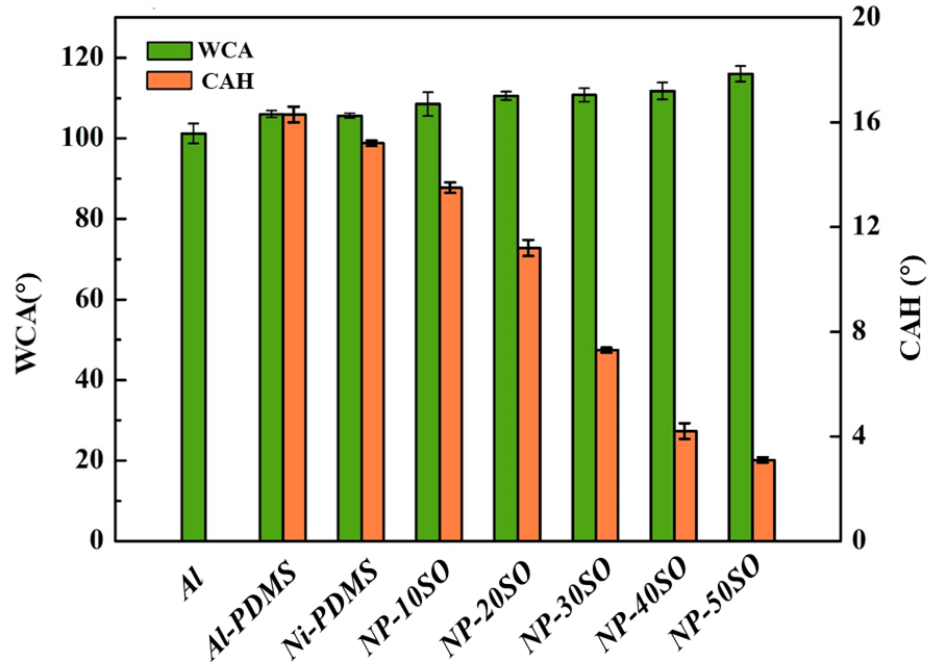


Figure 4.8 Wettability of PDMS, Ni-PDMS and NP-SO series samples.

The CAH of NP-10SO, NP-20SO, NP-30SO, NP-40SO and NP-50SO were $13.5 \pm 0.2^\circ$, $11.2 \pm 0.3^\circ$, $7.3 \pm 0.1^\circ$, $4.2 \pm 0.3^\circ$ and $3.1 \pm 0.1^\circ$, respectively. The detailed advancing and receding WCA results were shown in Table 4.2. With more silicone oil addition, the CAH values also had a clear decreasing trend in Figure 4.7, it could be easier for the sample to present slippery behaviours, the CAH of NP-SO samples kept decreasing to lower than 10° . The excess silicone oil could gradually cover the surface, converting a heterogeneous solid-liquid interface to homogeneous liquid-liquid interface and eliminating the ice pinning points, which further leads to a reduced liquid-solid contact area [37]. The NP-SO samples exhibited nearly defect-free surfaces, as shown in Figure 4.3. The interlocked points at the ice interfaces were reduced, which was favourable to low the adhesion of the ice layer.

Table 4.2 Dynamic contact angles of different samples.

Samples	Adv/ °	Rec/ °	CAH/ °
Al-PDMS	110.1 ±1.6	93.8 ±1.7	16.3 ±0.3
Ni-PDMS	112.5 ±2.0	97.3 ±2.4	15.2 ±0.1
NP-10SO	113.6 ±1.9	100.1 ±2.2	13.5 ±0.2
NP-20SO	114.3 ±2.0	103.1 ±1.7	11.2 ±0.3
NP-30SO	116.4 ±2.5	109.1 ±2.6	7.3 ±0.1
NP-40SO	114.7 ±2.9	110.5 ±2.7	4.2 ±0.3
NP-50SO	119.7 ±3.1	116.6 ±2.9	3.1 ±0.1

4.2.2 Effect of silicone oil addition on surface free energy

The surface free energy of the sample surfaces is a very important parameter for the surface. Surfaces with low surface energy would not only lower the molecular interaction between water and coating surface, but also help with the surface wettability enhancement [323]. As is known, the surface free energy may be defined as the increase in Gibbs free energy of the whole system per unit increase in the interfacial area [324, 325]. It is conceived that the increasing addition and later release of infused silicone oil would affect the surface energy. The detailed values of surface free energy of different samples have been measured and calculated using Owens-Wendt method.

Table 4.3 Surface free energy measurements of Al-PDMS, Ni-PDMS and NP-SO series

Samples	Surface free energy (mJ/m ²)
Al-PDMS	38.2 ±0.4
Ni-PDMS	38.6 ±0.3
NP-10SO	34.0 ±0.5
NP-20SO	33.2 ±0.3
NP-30SO	32.7 ±0.3
NP-40SO	31.8 ±0.4
NP-50SO	29.8 ±0.5

As shown in Table 4.3, the surface energy of reference sample Al-PDMS was 38.2 ± 0.4 mJ/m², while the value of Ni-PDMS was 38.6 ± 0.3 mJ/m². The fairly low surface energy should come from the PDMS layer, while the slight difference came from the surface morphology difference. For NP-SO series samples, the measured surface energy was obviously lower than the two reference samples. They kept decreasing with the increase of silicone oil, from 34.0 ± 0.5 mJ/m² (NP-10SO) to 33.2 ± 0.3 mJ/m² (NP-20SO) to 32.7 ± 0.3 mJ/m² (NP-30SO) to 31.8 ± 0.4 mJ/m² (NP-40SO) to 29.8 ± 0.5 mJ/m² (NP-50SO). The reason here should be that the incorporation of silicone oil also played an important role in lowering the surface energy [322], which resulted in the increased WCAs.

4.2.3 Mechanical performance of as-prepared samples using tensile tests

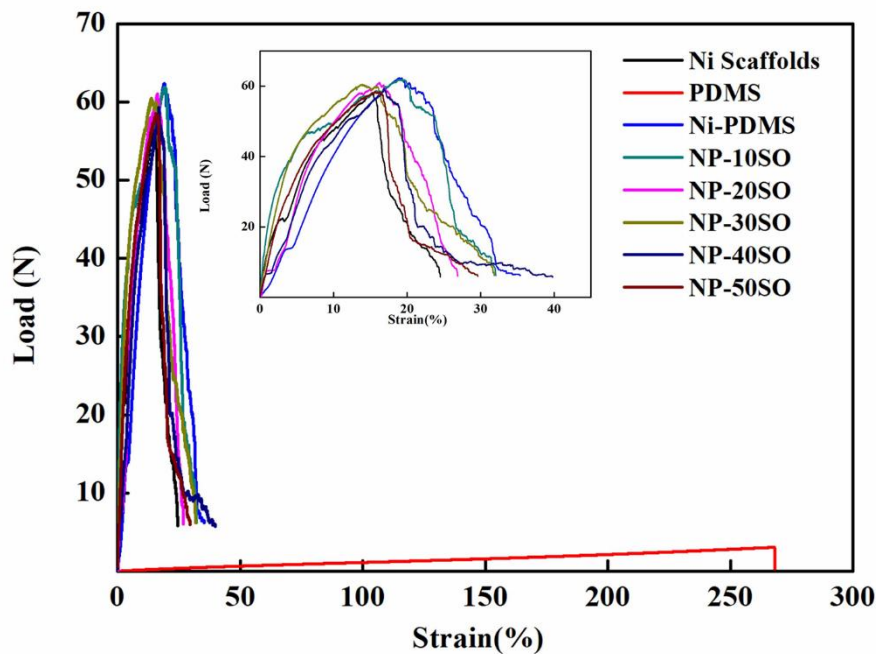


Figure 4.9 Load-extension curves of Ni scaffolds, PDMS, Ni-PDMS and NP-SO series samples

The tensile test results of the samples including Ni scaffolds, PDMS, Ni-PDMS and NP-SO series have been presented in Figure 4.9, showing as the variation curves between load and displacement. The Ni scaffold had the maximum load of 57.7 N, as indicated in the amplified inset. The metallic structures have enough mechanical

properties to withstand the applied load. For the pure PDMS with the same dimensions and thickness, it demonstrated a feature of high elongation, and the fracture strain could reach 268%, while the applied load was only 3.1 N. For Ni-PDMS, with the integration of Ni scaffold and PDMS filling, the sample suffered a much higher load than pure PDMS, which was 62.4 N. The NP-SO series samples had a similar response as Ni-PDMS. The maximum applied loads ranged from 58.5 to 61.9 N, indicating the obvious enhancement in mechanical properties. This also verified the significant importance of the icephobic construction design compared with pure PDMS.

4.3 Determinations of Surface Icephobicity and Durability

4.3.1 Icing delay performance of water droplet

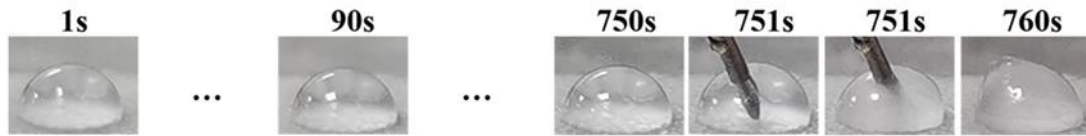


Figure 4.10 Icing process of condensed water droplets on Ni-PDMS surface under $-7\text{ }^{\circ}\text{C}$.

The water droplet icing test was performed by monitoring the icing process of supercooled water droplets on as-prepared samples using a cold plate. As a comparison, most of supercooled droplet icing tests reported previously in related literature were normally conducted at the environment temperature of around $-7\text{ }^{\circ}\text{C}$ [326]. Here, the reason for the selection of temperature $-20\text{ }^{\circ}\text{C}$ was that it really took so long for the supercooled droplet to finish the icing process on NP-SO series samples at the temperature of $-7\text{ }^{\circ}\text{C}$, as indicated in Figure 4.10. The supercooled water droplet remained in liquid state even after 750 s. It did not start the solidification process until the external impact on the droplet. In this way, the ambient temperature inside the cold chamber was maintained at around $-20\text{ }^{\circ}\text{C}$. The reason for the occurrence of the supercooled state was the fact that the sample surfaces were fairly smooth and the

surface energy was quite low, which made it difficult for the sessile droplet to find proper nucleation points on the tested surfaces exposed inside the low-temperature chamber [327]. As reported in the literature, the freezing process for a supercooled droplet could be proceeded in two sequential stages [328]: partial solidification of the droplet and isothermally remaining liquid freezing process. The existing supercooled state before icing could mainly be ascribed to the hydrophobic surfaces. The fairly smooth surface morphology ($R_a < 0.81 \mu\text{m}$) and low surface free energy of PDMS-SO surfaces [329] could firstly delay the absorption process of the released heat by the liquid, and further lowered the rate of heat conduction to the substrate and dissipation to the environment by convection [330]. Also, higher silicone oil addition helped with lower surface roughness and produced reduced CAH and stickiness (it refers to the nonspecific interactions between hydrophobic ligands and binding sites [331]) (as shown in Figure 4.8). Furthermore, the low stickiness of the surface also contributed to fewer ice nuclei formations which could have initiated droplet freezing [94].

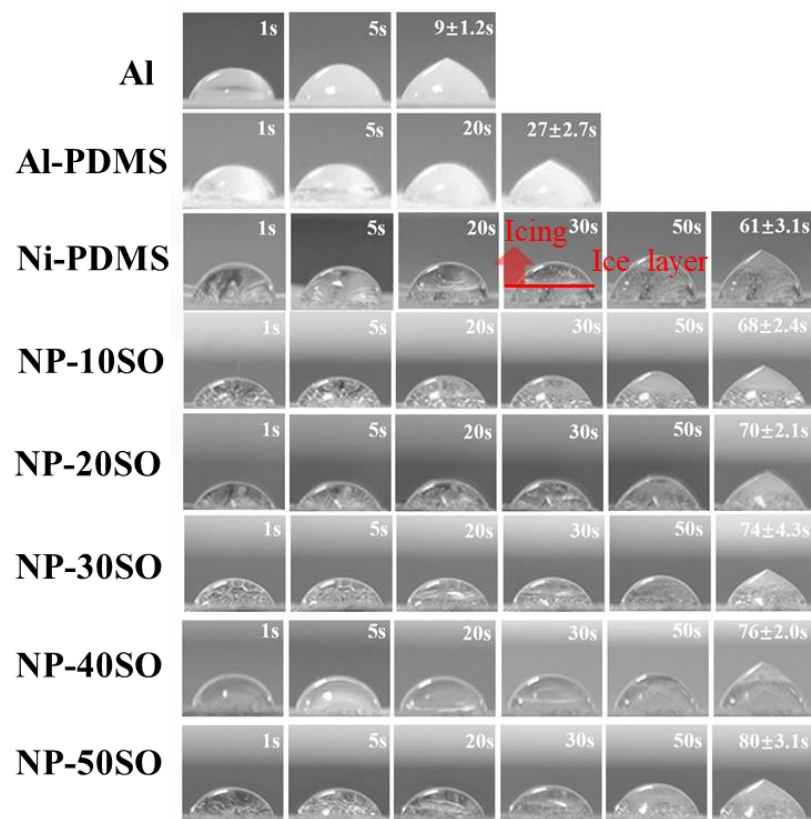


Figure 4.11 Icing process of water droplets on different surfaces: Al plate, Al-PDMS, Ni-PDMS, NP-SO series under -20°C .

The integrated icing process of supercooled water droplets on different samples was illustrated in Figure 4.11. It was obvious that the icing layer always formed from the solid-liquid interface and spread to the top region of the droplet. The ice nucleus was first initiated at the interface, and it then gradually grow into large ice crystals upwards, and finally the whole droplet formed into ice. The water droplet took the shortest time to freeze on pure Al plate, with a duration of only 9 s. While for Ni-PDMS, the total icing duration was prolonged to 61 s. As the two samples possess the same PDMS top layer, the freezing delay was mainly ascribed to the difference in thermal resistance of the different samples. Once the sessile droplets (still at room temperature) were dripped onto the sample surfaces, heat exchange took place. The heat would be released along with the ice-solid interfaces, as shown in Figure 4.12. The prepared top PDMS layer on Al-PDMS and Ni-PDMS have the similar thickness, bringing no difference to the thermal resistance. While for the bottom layers, it was obvious that the thermal conductivity of pure Al substrate (237 W/m K [332]) was much higher than that of Ni/PDMS composite structure (the thermal conductivity of the PDMS filling is only 0.15 W/m K [333]). So the thermal resistance was much higher than that of Al-PDMS, leading to a longer icing duration.

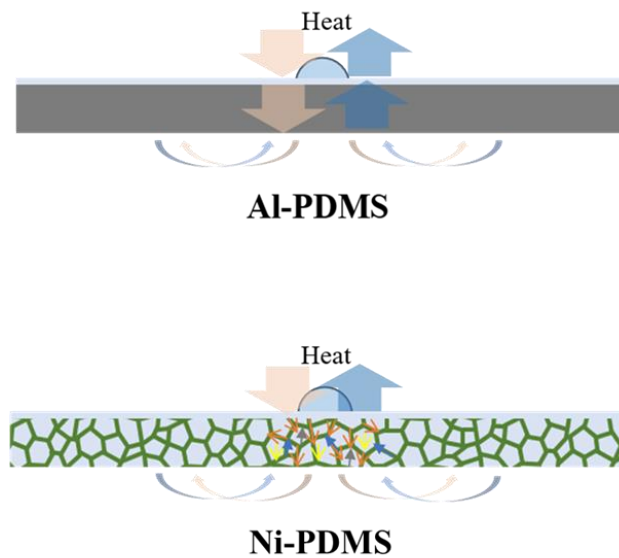


Figure 4.12 Schematic diagram for thermal conduction of Al-PDMS and Ni-PDMS.

As indicated in Figure 4.11, the formed ice on pure Al plate is clear white. As a comparison, the ice on the NP-SO series samples turns out to be transparent with floccule formed inside. The causing factors for the formed white ice in Al sample could be the introduced impurity or the existing internal air bubbles. The icing process from liquid to solid was accompanied by the heat release. Considering the actual icing condition, the freezing would start from the external surface to the middle centre region. Once the external surface becomes solid, it could introduce stress to the internal region of the supercooled droplet, and pose restrictions to the remaining air bubbles when the system tried to drive them away. In this way, the unremoved bubbles would act as the nucleus for later ice formation. Some special structures with non-uniform density distribution would form around the nucleus (existing air bubbles) that is mainly made up of water molecules, leading to the adsorption and scattering of the incident light and the non-transparency of the formed ice [334].

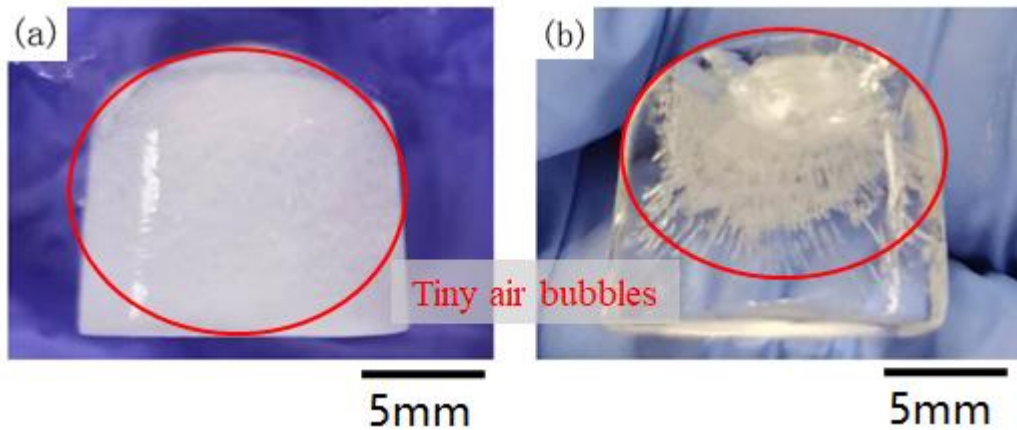


Figure 4.13 Ice blocks formed on the surfaces of (a) Al-PDMS; (b) Ni-SO series.

But for NP-SO series samples, the whole icing duration had been prolonged, the freezing rate is also much slower than that in Al plate sample, the introduced stress was not big enough to imprison the remaining air bubbles at their original location, they were then driven to the center area or top area (as indicated in Figure 4.13), and stayed there without being driven away completely, that is the reason why the white floccules could be observed at the center or top area inside the droplet placed on NP series samples.

When water droplets contacted with NP-SO series samples, the icing time on tested surfaces gradually increased with higher silicone oil infusion. This phenomenon could be explained by the increased energy barrier for ice nucleation. The icing process on ideal lubricated surfaces could be regarded as a homogeneous nucleation process, while for a normal solid surface such as a metallic substrate, the ice formation is mainly classified as a heterogeneous nucleation process [207]. The free energy barriers for homogeneous nucleation (ΔG_{homo}) and heterogeneous nucleation (ΔG_{hete}) could be estimated using the following equations (4.4)-(4.6) [335]:

$$\Delta G_{homo} = -\frac{3}{4}\pi r^3 \Delta G_V + 4\pi r^2 \delta_{IL} \quad (4.4)$$

$$\Delta G_{hete} = \left(-\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \delta_{IL}\right) S(\theta) = \Delta G_{homo} S(\theta) \quad (4.5)$$

$$S(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2 \quad (4.6)$$

where r means the nucleation radius, ΔG_V shows the driving force during the solidification, and δ_{IL} represents the interfacial energy between the ice nucleus and liquid. θ indicates the contact angle of the nucleus on specific solid surface, which is also approximately equal to the measured contact angle of a droplet on a flat surface. The value of $S(\theta)$ is between 0 to 1, as indicated in equation (4.6).

Regarding NP-10SO to NP-50SO, as shown in Figure 4.11 (a), the nucleation could all be classified as heterogeneous. As the formed surface oil layer would be thickened with increasing silicone oil addition, ΔG_{hete} on these samples showed an obvious trend, closing to the value on ideal lubricated surfaces (ΔG_{homo}). More energy was needed for initiating the icing process, resulting in the delayed ice formation. The results of icing delay indicated that with the incorporation of microporous Ni scaffolds, the overall thermal resistance of the multiphase layers was increased, which introduced delay to ice formation. More importantly, the advantage of high energy barrier for ice nucleation on LIS was also kept. The good anti-icing performance of LIS had been well retained with the introduction of the microporous Ni scaffolds.

It is evidenced from relevant literatures that the silicone oil modified surfaces show some icing delay effects. For example, the water droplet froze into ice in only 40 s on silicone oil modified nanofibre membrane based SLIPS at $-10\text{ }^{\circ}\text{C}$ [326]. Another example is that the ice delay performance of fluorinated silica modified PDMS coatings at $-15\text{ }^{\circ}\text{C}$ was around 276.2 s. It is noted that the big differences in testing temperature and other testing standards could pose effect on the results [336]. The delayed-icing time of the water droplets on the same sample decreased when the temperature was decreased from $-5\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$ [337]. Another example is that the ice delay performance of the silicone oil-infused oleamide-PDMS (SiOP) coating was around 405 s at $-10\text{ }^{\circ}\text{C}$ [338], which was longer than that of our results. It should be acknowledged that big variations exist among the results, particularly considering that our results were acquired at $-20\text{ }^{\circ}\text{C}$. It is important to recognize the effectiveness of the anti-icing performance, and careful considerations need to be given to the testing methodology.

4.3.2 Anti-frost performance by frost growth test

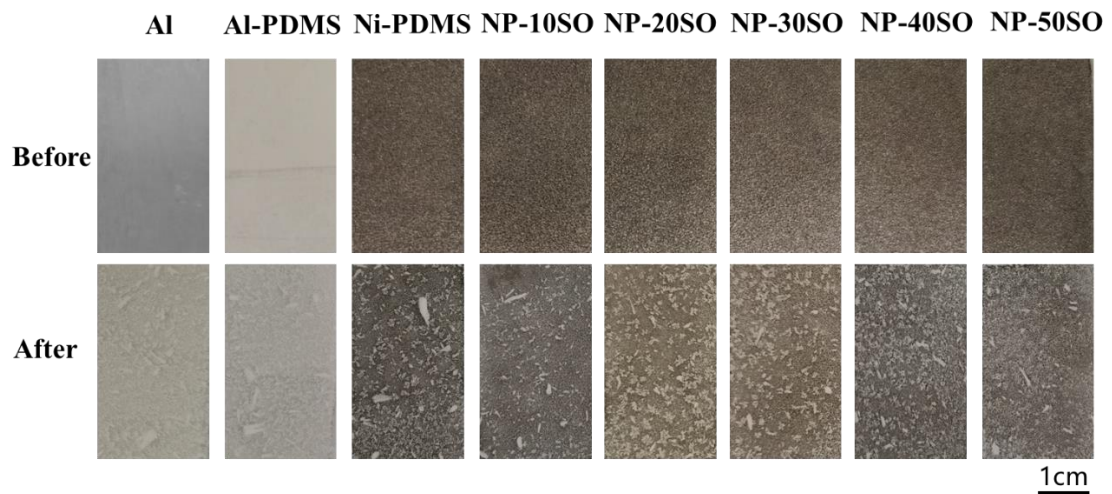


Figure 4.14 Surfaces images of Al, Al-PDMS, Ni-PDMS, NP-SO series samples

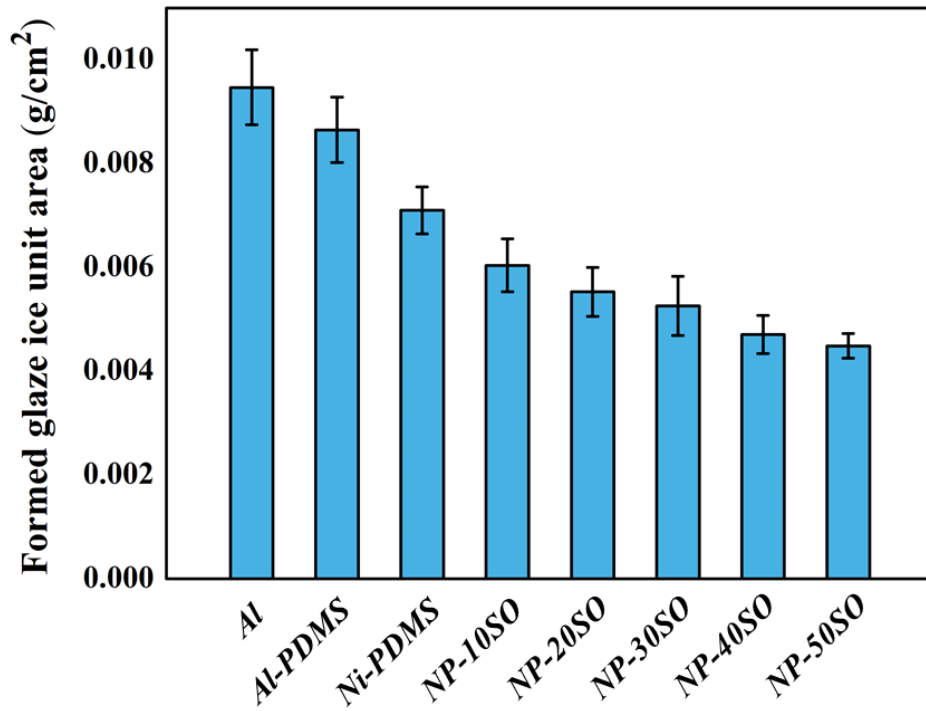


Figure 4.15 Increased mass of formed glaze on Al, Al-PDMS, Ni-PDMS, NP-SO series samples

The static frost formation tests were also carried out among the NP-SO series samples. Figure 4.14 and 4.15 displayed the detailed surface conditions versus the frost formation tests and the detailed value of formed glaze per unit area on different samples, respectively. The detailed results of Al, Al-PDMS and Ni-PDMS reference samples had already been illustrated in the previous section. It was also obvious to find the values of NP-SO series samples were all lower than that of the three samples. With some silicone oil additions, the sample surfaces were modified.

As indicated in Figure 4.15, the measured values of the formed glaze per unit area kept decreasing from NP-10SO to NP-50SO, from $6.1 \pm 0.5 \text{ mg/cm}^2$ (NP-10SO) and $5.5 \pm 0.5 \text{ mg/cm}^2$ (NP-20SO) and $5.3 \pm 0.6 \text{ mg/cm}^2$ (NP-30SO) and $4.7 \pm 0.4 \text{ mg/cm}^2$ (NP-40SO) and $4.5 \pm 0.2 \text{ mg/cm}^2$ (NP-50SO). The surface images in Figure 4.14 also showed that there was less and less frost formed on the surfaces. The incorporation of silicone oil could not join the crosslinking reaction with PDMS, but it could remained on the sample surface and altered the surface hydrophobicity. With the combined effect

of surface chemistry and remained oil layer, the remaining lubricants on the sample surfaces could minimize the ice nucleus points, less glaze could form. The increased oil infusion would lower the possibility of moisture condensation on the layer surfaces.

4.3.3 Evaluation of ice adhesion and structure durability

Figure 4.16 showed the ice adhesion strength results of different samples including Al plate, Al-PDMS, Ni-PDMS, and NP-SO series samples. In Figure 4.16, the ice adhesion strength of Al plate was maintained at 217.9 ± 6.4 kPa during the icing/de-icing cycles at -20 °C. The measured shear strength decreased to 115.9 ± 8.5 kPa when the Al plate was covered with PDMS layer. The sample surface was damaged when the 28th icing/de-icing cycle was conducted. The PDMS top layer was partially peeled off from the Al plate due to the high ice adhesion strength and some breakages and voids could be found on the surface. The surface lost its icephobicity once part of the coating was removed. As a comparison, the ice adhesion strength of Ni-PDMS always remained at low value (around 30 kPa) during the tests. The introduction of Ni scaffolds helped with the good icephobic stability.

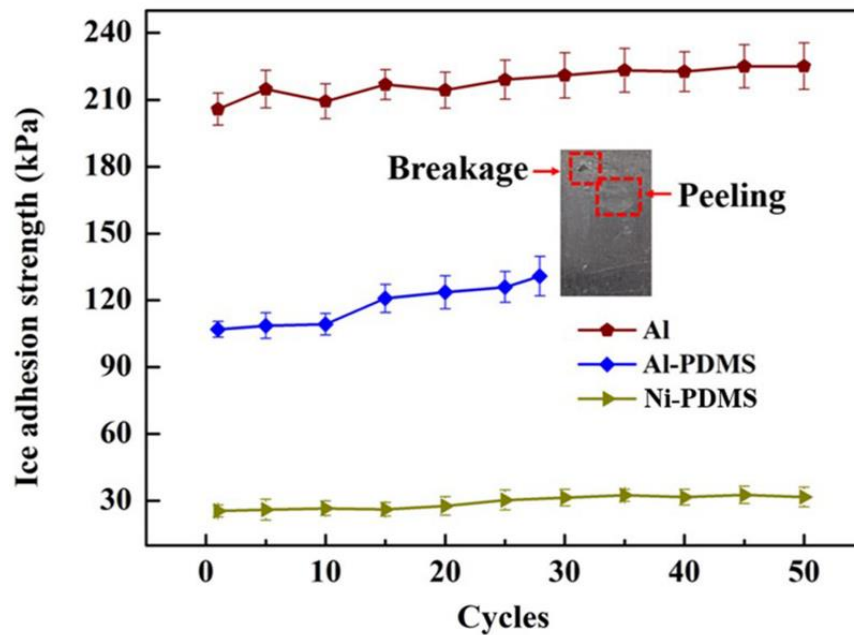


Figure 4.16 Ice adhesion strengths of Al, Al-PDMS, and Ni-PDMS during the cyclic tests.

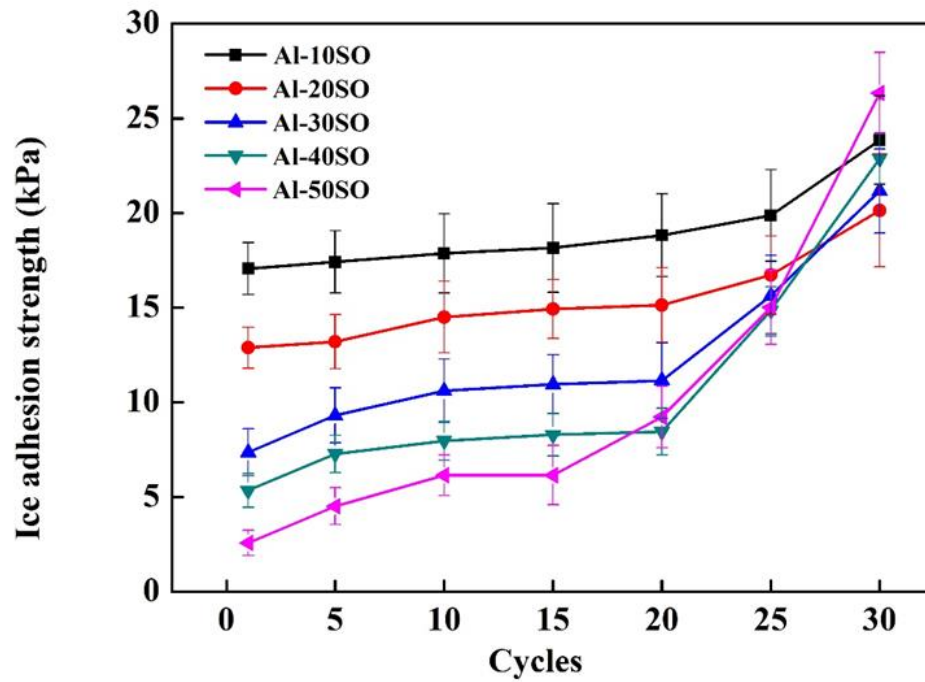


Figure 4.17 Ice adhesion strengths of Al-10SO, Al-20SO, Al-30SO, Al-40SO and Al-50SO during 30 icing/de-icing cycles.

Figure 4.17 showed the ice adhesion strength of Al-SO series samples during 30 icing/de-icing cycles. It is obvious that all of the Al-SO samples showed an obvious increasing trend. The measured ice adhesion strength kept increasing with the tests undergone. Al-10SO was the highest among the samples $\sim 17.1 \pm 1.4$ kPa, while the measured shear strength of the as-prepared samples decreased from 17.1 ± 1.4 kPa to only 2.6 ± 0.7 kPa (Al-50SO) (measured in 1st cycle) with the increase of silicon oil incorporation. Nevertheless, the ice adhesion strength value of all samples kept increasing with the increased icing/de-icing cycles, indicating the deterioration of the de-icing ability. Al-50SO had the highest ice adhesion after the tests $\sim 25.6 \pm 4.4$ kPa, and Al-20SO has the lowest value $\sim 18.9 \pm 3.7$ kPa. Some of the sample surfaces were even damaged after 30th cycle.

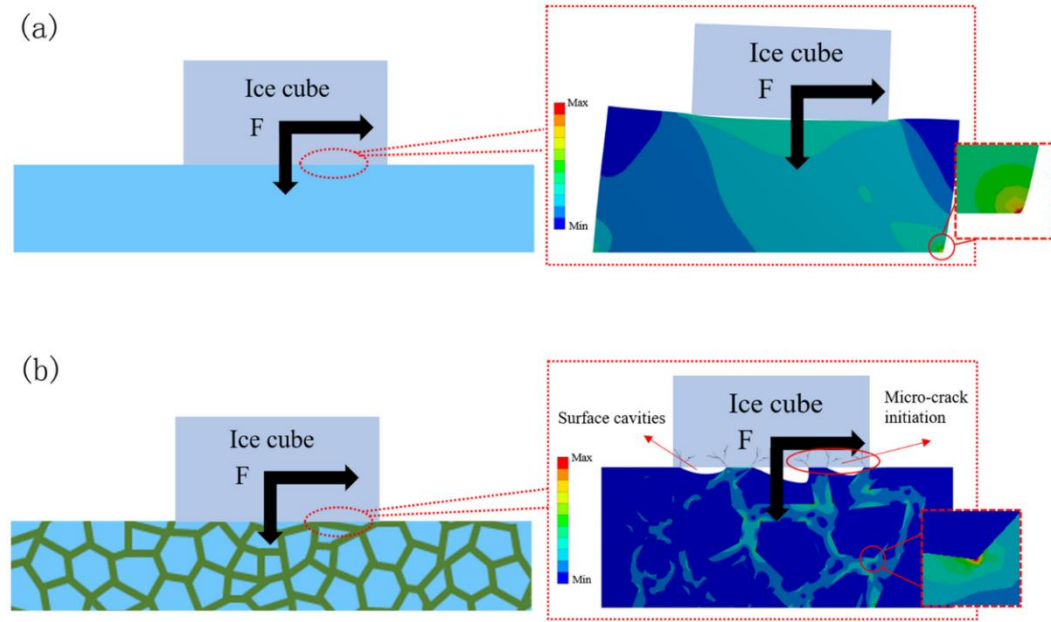


Figure 4.18 2D stress simulation under shear force and gravity on (a) pure PDMS and (b) Ni-PDMS using ANSYS.

As a comparison, for Ni-PDMS samples as shown in Figure 4.16, the addition of microporous Ni scaffold could help to lower the ice adhesion strength to as low as 29.3 ± 2.9 kPa. The detailed mechanism was depicted in Figure 4.18. In the de-icing tests, when a shear force was applied to remove the formed ice block from the surfaces, the combined force including the gravity could be resolved into the vertical uniform surface pressure and the horizontal shear strength. For pure PDMS layer, the maximum stress is mainly located at the bottom right corner area, which also introduces large distortion to the PDMS layer. While for Ni-PDMS, the uniformly distributed Ni scaffolds carries most of the loading compared with PDMS which is reflected from the colour difference. In the Ni-PDMS structure, the stress in the PDMS matrix would be reduced because the major stress would be carried and re-distributed by the microporous Ni network due to the different elastic modulus between Ni scaffolds and PDMS. This also introduces different distortions at the ice/solid interface areas, generating small surface cavities at the interfaces and leading to the initiation of micro-cracks [236, 247]. Compared with pure PDMS layer, the incorporation of Ni scaffolds would significantly improve the mechanical reinforcement effect of LIS constructions and the de-icing performance.

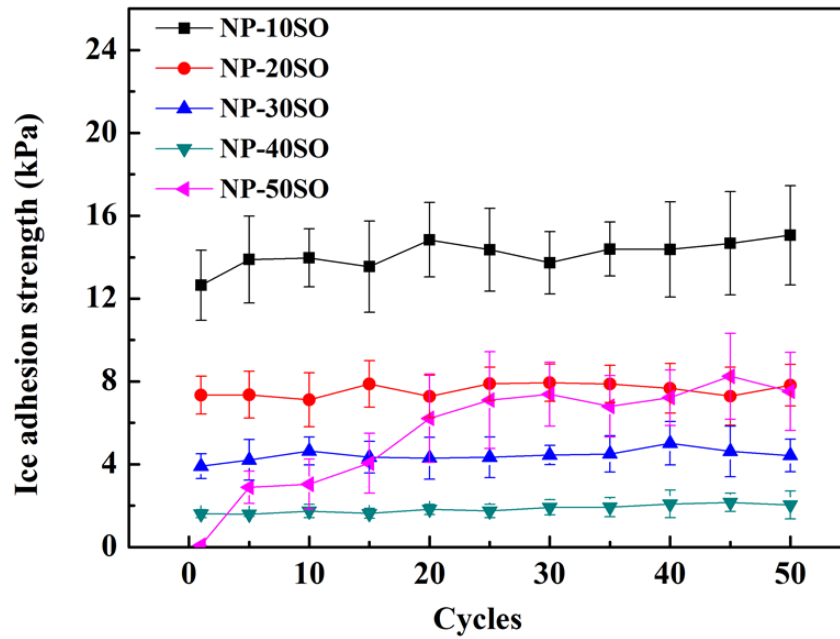


Figure 4.19 Ice adhesion strengths of NP-10SO, NP-20SO, NP-30SO, NP-40SO and NP-50SO during 50 icing/de-icing cycles.

Figure 4.19 indicated the ice adhesion strengths of different NP-SO series samples during 50 icing/de-icing cycles at $-20\text{ }^{\circ}\text{C}$. The measured ice adhesion strength kept decreasing with the increase of silicon oil incorporation. NP-10SO was the highest among the samples $\sim 12.5 \pm 2.8\text{ kPa}$, while the measured shear strength of the as-prepared samples kept decreasing to only $1.6 \pm 0.2\text{ kPa}$ (NP-40SO) (measured in 1st cycle). It is obvious that all of the samples nearly remained unchanged during the icing/de-icing cyclic tests except NP-50SO. NP-50SO showed the highest increasing ratio in ice adhesion after the tests while NP-40SO has the lowest value $\sim 2.0 \pm 0.7\text{ kPa}$. It indicated that the content of silicone oil should be no more than 40 wt%.

With the increasing addition of silicone oil, the ice adhesion strength indicated a decreasing trend. The reason for the continuous decline in ice adhesion could be summarised as below: 1. With the decreasing shore hardness of polymeric layer, the elastic mismatch between the polymer and metallic scaffold would increase. It strengthened the stress concentration effect, and the possibility for the initiation of

micro-cracks at the solid-ice interface also became higher, causing the easier detachment of ice blocks from the surface. 2. Higher oil content would help to maintain a thin oil layer between the ice and solid interface, which was favourable for minimising the ice adhesion strength. While the weight percentage of silicone oil inside the sample surface reached 30 wt%, the existence of surface oil layer could pose an obvious impact on the ice formation process and the ice adhesion strength was lower than 5 kPa (which could also be verified by the homogenous nucleation that was shown in Section 4.4.1).

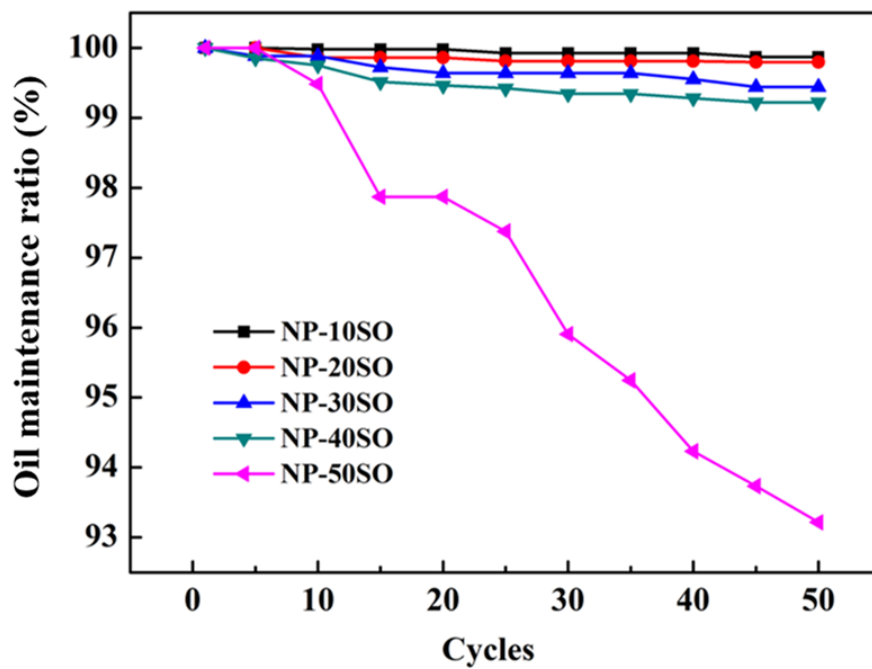


Figure 4.20 The percentages of mass for remaining oil relative to the mass of overall added oil in NP-10SO, NP-20SO, NP-30SO, NP-40SO and NP-50SO

Combined with the results shown in Figure 4.20, it could be observed that the total mass of the sample nearly remained unchanged during the whole icing/de-icing when the weight percentage of silicone oil addition ranged from 0-20 %. While for NP-30SO and NP-40SO, there was a slight decrease in the oil maintenance of the two samples. The reason could be ascribed to the partial depletion of the oil layer during the icing/de-icing cycles. It would not introduce a significant effect on the de-icing performance, because the infused silicone oil inside the PDMS system could keep filtering out,

reforming oil layer, and working as a self-healing system, which also ensured the stability of the de-icing performance [319]. While the weight percentage of silicon oil infusion reached 50 wt%, the ice adhesion strength kept increasing during the whole cycle, from 0.09 ± 0.03 kPa (1st cycle) to 7.5 ± 1.9 kPa (50th cycle), and the surface also suffered obvious damage. The main reason here was that the surface oil layer was so thick that it was easier to be depleted than in other samples, there was not enough time for the supplement of the incorporated silicone oil to recover the surface oil coverage.

From NP-30SO to NP-50SO, the existence of the surface oil layer could pose an obvious impact on the ice formation and the ice adhesion strength was lower than 5 kPa. It was inferred that NP-40SO possessed the most stable ice adhesion strength, which was as low as 1.6 ± 0.2 kPa.

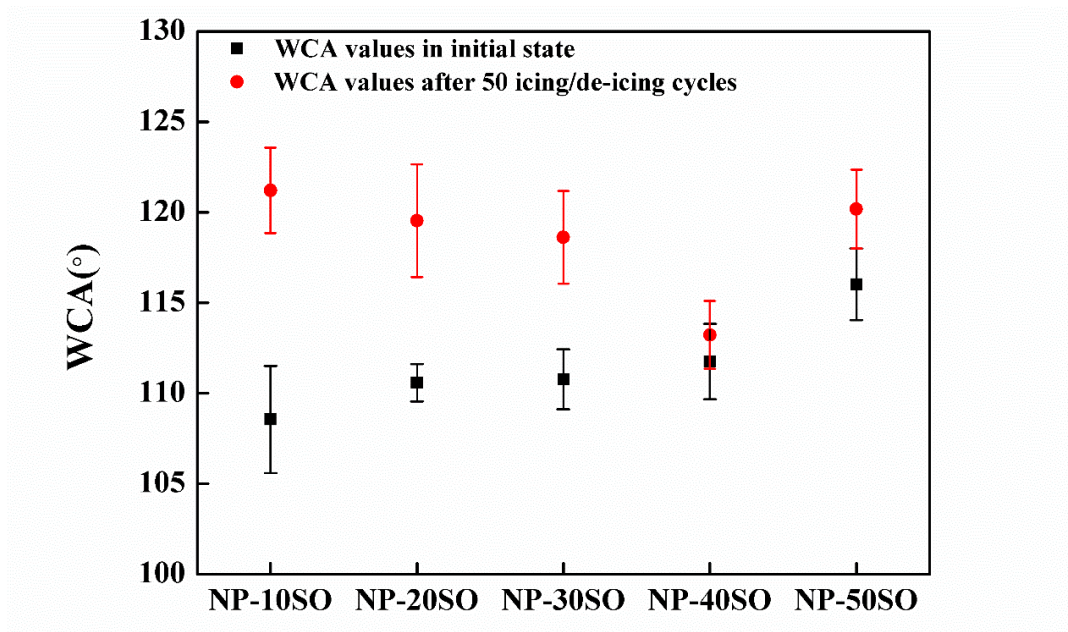


Figure 4.21 WCA variation of NP-SO series samples before and after 50 icing/de-icing cycles.

The WCA variations of NP-SO series samples versus 50 icing/de-icing cycles were also compared in Figure 4.21. The WCA values on NP-40SO had the lowest change, reflecting a minimal surface damage. From NP-10SO to NP-40SO, the increased level of WCA after the 50 cycles were reduced. As the ice adhesion strength from NP-10SO

to NP-40SO decreased, posing less damaging (roughening) effect on the surface. While for NP-50SO, due to the increased ice adhesion strength and thus the increased roughening effect, the change of WCA was higher. Similar phenomenon has been reported that the superhydrophobic SiO_2 nanocomposite films undergo gradual mechanical damage during the repetitive 10 icing/deicing cycles, and the WCA suffered obvious decrease (around 11%) [339]. The possible mechanism for the deteriorated hydrophobicity/ icephobicity could be that some portions of the nano-sized protrusions indent the forming ice and are mechanically damaged (i.e. cracked or spalled) due to the compressive stress generated during ice expansion [339]. Also, infused oil layer could be removed together with the water droplet. The formed ice block could also get into contact with micrometer-scale surface features when the surface is subjected to a number of icing/deicing treatments. There would be a certain amount of force generated in the contacting areas. Thus stress concentrations existed during ice expansion, which posed effect on the remaining silicone oil. As a result, the micro-scale surface structures suffered deformation that could induces stress concentrations, causing the initial crack front formation. Water droplet is then able to nucleate even deeper within the damaged surface which explains the shape change during the formation of the thawed water droplet and the corresponding WCA decrease. With additional icing/deicing cycles occurred, the crack front propagates. It increases the surface area and performs the change in surface height distribution as well as the quantitative behavior of the surface morphological parameters, leading to the continuous increased ice adhesion strength.

As shown in Figure 4.22, the percentage of oil depletion in Al-SO series samples was higher than those in NP-SO series samples. The main reason could be ascribed to that the existence of Ni scaffolds restrained the level of deformation of the polymer matrix (as depicted in Figure 4.18), which helped to retain the infused oil. The enhanced deformation amount could lead to increased extrusion of infused lubricants [340].

With the introduction of the microporous Ni scaffolds to ensure the mechanical enhancement as well as to offer an additional de-icing mechanism, the icephobic

potentials of PDMS-SO surfaces have been further demonstrated. The micro-cracks at the solid-ice interface could be readily induced under the shear force, which further weakens the adhesion strength between the formed ice and the surface, prompting the ice detachment from the sample surface. Furthermore, the interconnected network structure formed by microporous metallic scaffolds and LIS could work effectively in resisting the external impact energy and minimising the oil depletion. The multiphase structure could also help to distribute the external impact to the larger area of the interconnected structure along the metallic scaffolds, thus offering effective protection for the LIS constructions.

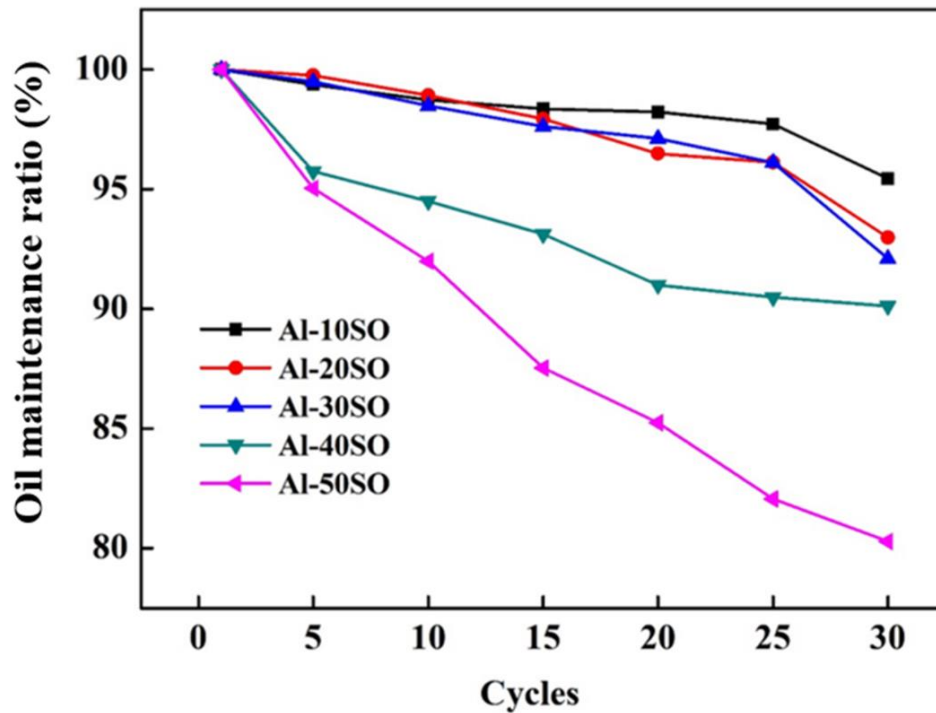


Figure 4.22 The percentages of mass for remaining oil relative to the mass of overall added oil in Al-10SO, Al-20SO, Al-30SO, Al-40SO and Al-50SO.

Compared to the existing reported LIS, the NP-SO samples (Ni scaffolds with PDMS filling infused with silicone oil) exhibit low ice adhesion strength. For example, the ice adhesion strength of PDMS modified superhydrophobic micro-/nano- surface infused with silicone oil was 22 ± 5 kPa, measured at -10 °C, and it finally increased to as high

as 81 kPa after 15 cycles [341]. In addition, another study indicated that PDMS coatings in presence of Pt catalyst with silicone oil infusion exhibited even higher ice adhesion strength ~ 50 kPa (measured at -10 °C, no cyclic test was conducted for this study) [342]. The ice adhesion strength of laser-irradiated Al substrate with replicating micro-textures modified with silicone oil-infused PDMS elastomer was quite competitive ~ 38 kPa, which also remained under the repeated cycles of ice accretion and detachment [343]. Overall, the NP-SO samples show fairly low de-icing and durable performance.

4.4 Water Condensation and Icing Process observed by ESEM

4.4.1 Observation of condensed water and icing formation

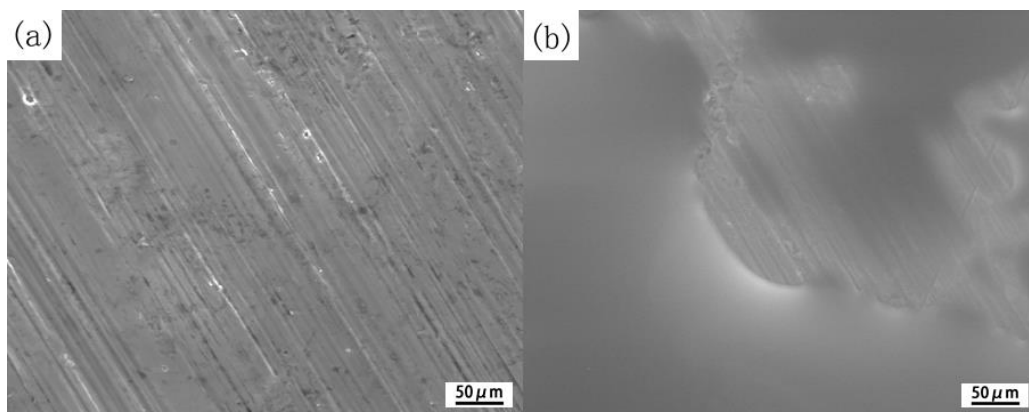


Figure 4.23 Surfaces images of (a) pristine Al plate (b) Al plate being wetted via ESEM.

Figure 4.23 showed the process of water condensation and ice growth on an Al plate under ESEM observation. Figure 4.23 (a) was the pristine Al surface, while Figure 4.23 (b) showed the Al surface which had been wetted by condensed water (with a relative humidity of 99.7%), and Figure 4.24 (a) indicated the shape of the formed ice at the moment when supercooled droplets on Al surface turned into ice instantaneously. For the subsequent ice growth, because of the fairly rough Al surface, the distributed water molecules inside the ESEM chamber could easily attach to the Al surface randomly and constantly, leading to the water condensation, ice nucleation, and ice growth. In Figure

4.24 (b), a piece of ice layer (named as bottom ice layer) was formed beneath the existing ice layer (named as top ice layer) after 10 s, as circled in Figure 4.24 (b).

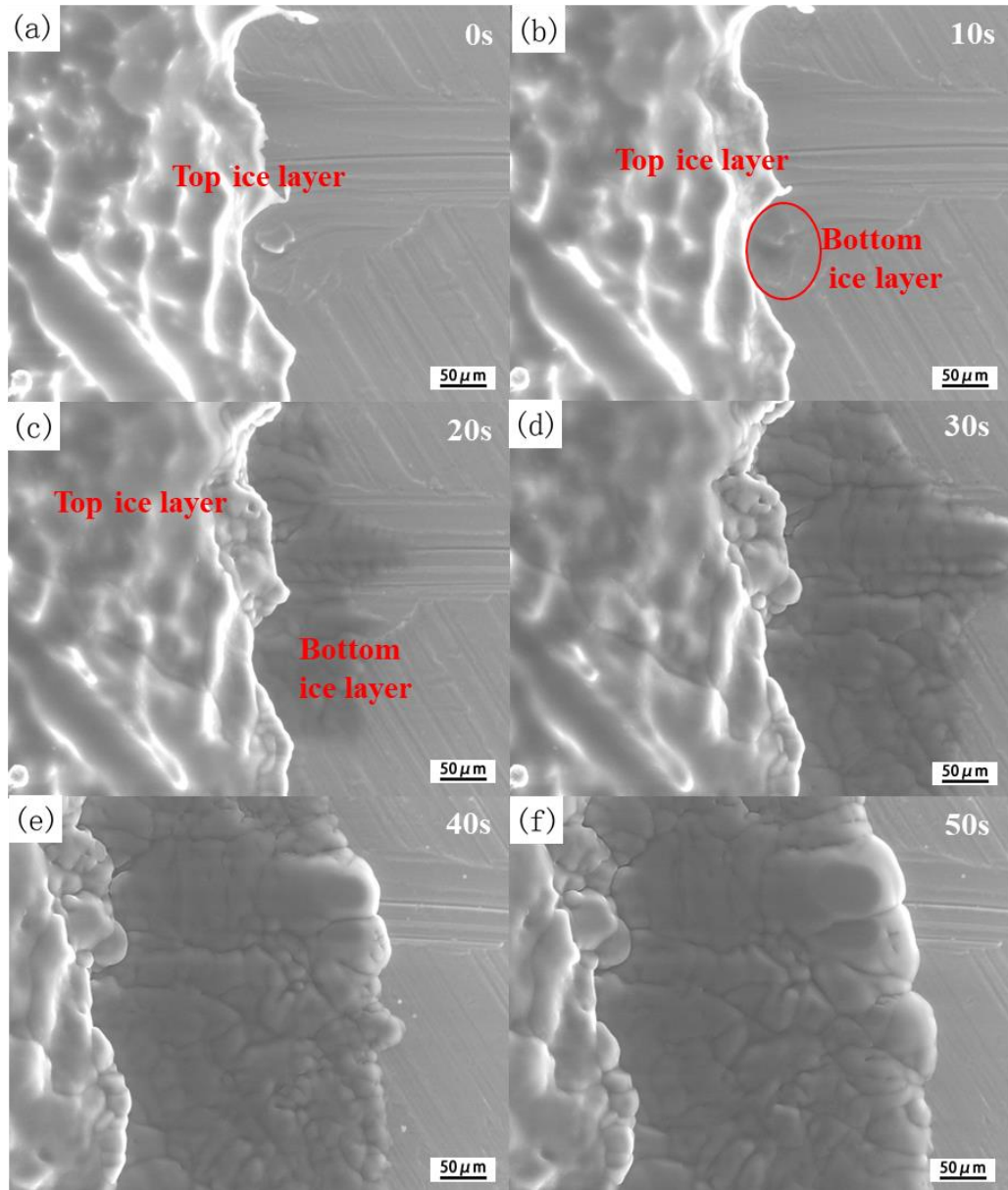


Figure 4.24 (a)-(f) Ice growth and spread of Al plate (a) $t=0$ s (b) $t=10$ s (c) $t=20$ s (d) $t=30$ s (e) $t=40$ s (f) $t=50$ s.

From Figure 4.24 (c) to (f) and Figure 4.25 (a) to (d), the two ice layers exhibited different growth speeds. With the controlled temperature and humidity, the boundary of the bottom ice layer would keep growing forward quickly. After another 60 s, the ice

layer spread to the other side of the field of view. The demarcation line between the top ice layer and bottom ice layer became unclear gradually because the top ice layer eventually integrated with the bottom ice layer, as evidenced in Figure 4.25 (a).

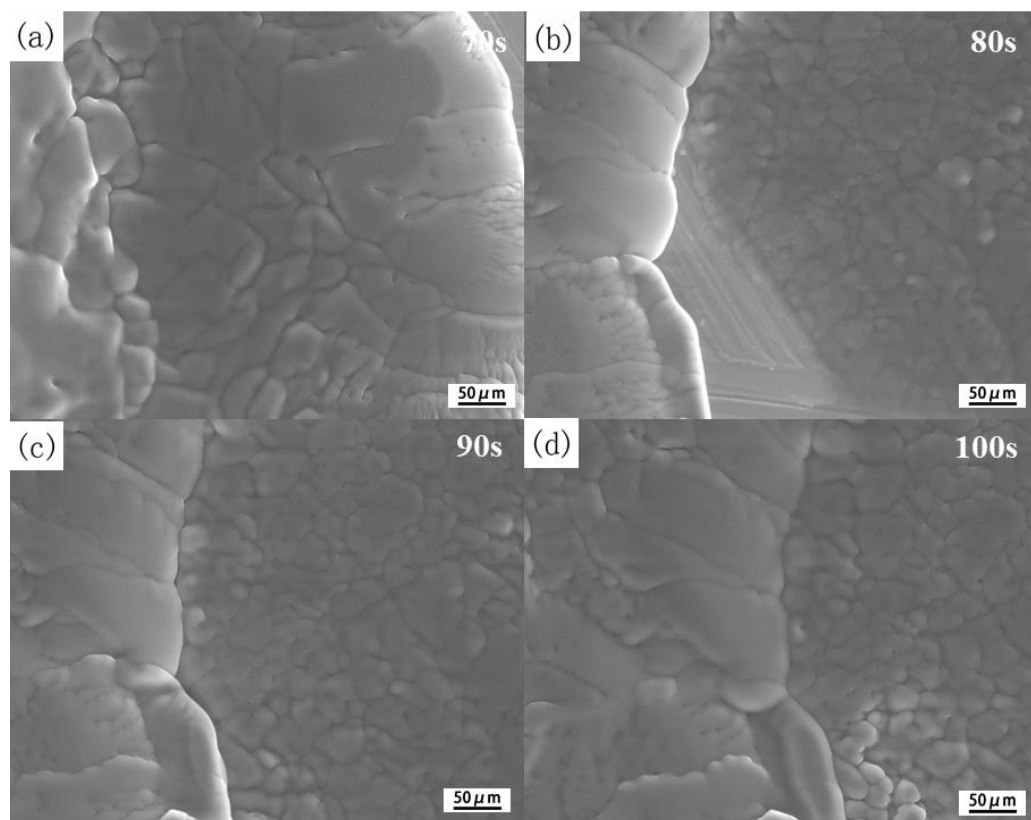


Figure 4.25 (a)-(d) Ice growth and spread on Al plate (a) $t=70$ s (b) $t=80$ s (c) $t=90$ s (d) $t=100$ s
(Image (a) showed the position with a bit slightly rightward shift to image (b)).

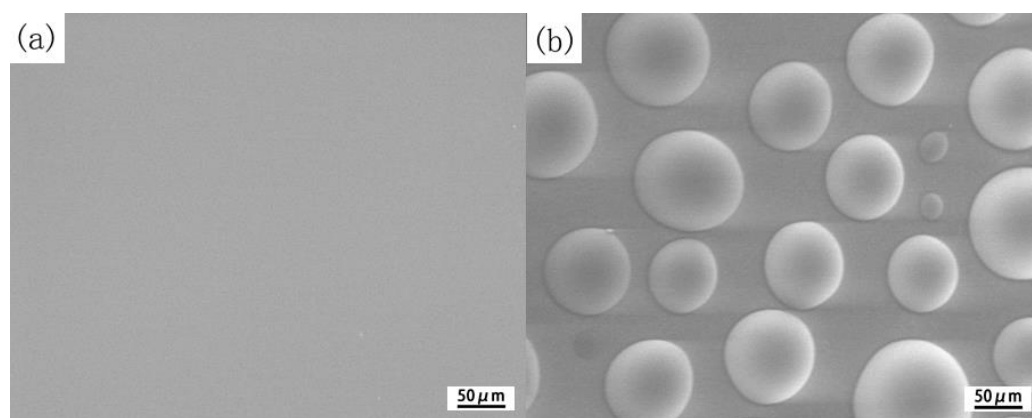


Figure 4.26 Surfaces images of (a) as-prepared Ni-PDMS sample (b) condensation of water droplets on Ni-PDMS sample in ESEM.

Figure 4.26 (a) showed the surface of as-prepared Ni-PDMS sample. The condensed water droplets presented regular spherical shapes on the sample surface. The uniform distribution of the condensed water may be attributed to the hydrophobicity of the Ni-PDMS surface. The simultaneous evaporation of condensed water droplets would take place along with the ice solidification. Ice would first grow on the surface of sample holder and then spread to the Ni-PDMS surface.

To better illustrate the whole procedure, a schematic diagram was drawn in Figure 4.27. The top view and side view of Ni-PDMS inside the ESEM chamber were given in Figure 4.27 (b) and (c)-(f). In Figure 4.27 (d), ice first appeared on the sample holder instead of the Ni-PDMS surface due to its good anti-icing performance. The formed ice would then grow forward to the Ni-PDMS surface, as evidenced in Figure 4.27 (f). The remaining water droplets would also evaporate simultaneously once ice formed.

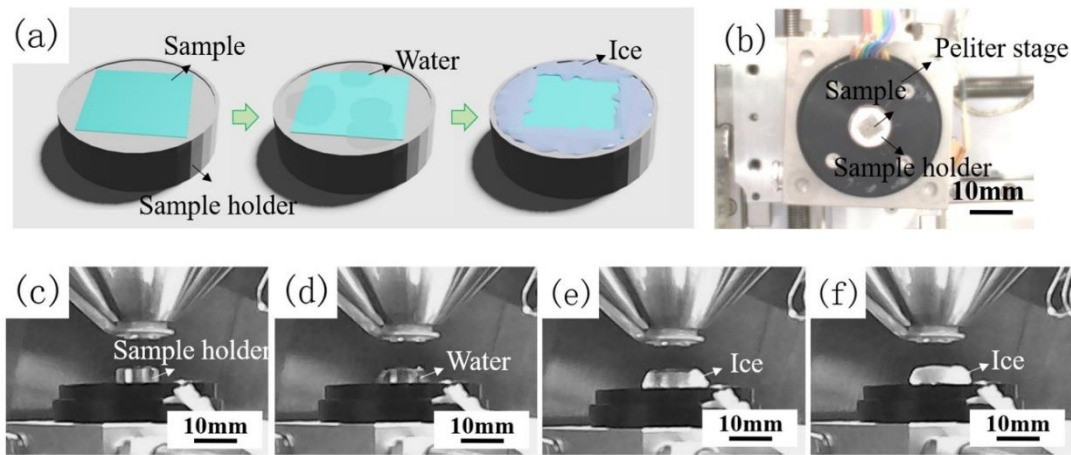


Figure 4.27 (a) Schematic of icing phenomenon on the surface of Ni-PDMS. (b) Top view of the sample stage inside the observation chamber. (c)-(f) Side views of the sample stage during the icing process.

Figure 4.28 (a) indicated that ice started to grow on the sample holder, and then spread to the sample surface gradually. It was essential to form solid ice nucleus for the continuous growth of the ice crystals. Ice tended to nucleate on the sample holder at

first rather than form nucleation points on the Ni-PDMS surface. The reason for the simultaneous evaporation of the remaining water droplet was the decrease of the environmental humidity inside the chamber (from 99.7% to 90.8%) at the moment of the ice formation, and the water molecules in the atmosphere would attach to the formed ice crystal and participate in the ice growth. Meanwhile, due to the exothermic effect of ice formation, the real-time temperature showed a slight increase (from $-6.7\text{ }^{\circ}\text{C}$ to $-4.2\text{ }^{\circ}\text{C}$ at first, then returned to $-6.7\text{ }^{\circ}\text{C}$). The integrated factors including lowered humidity and increased temperature made the condensed water droplets unable to stay on the Ni-PDMS surface.

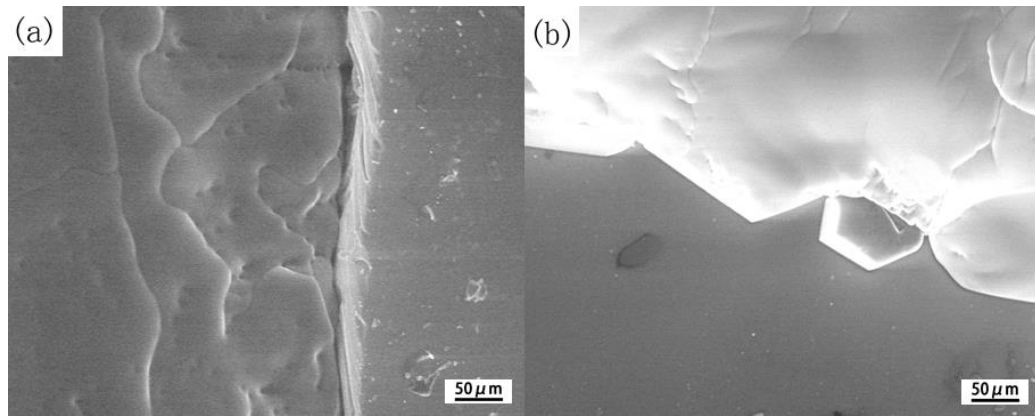


Figure 4.28 (a) Ice growing near the edge of the sample, (b) Ice growing on the surface of Ni-PDMS.

Figure 4.28 (b) showed the ice growth on the Ni-PDMS sample. The formed ice crystal on the sample surface was quite large, and only some small ice crystals grew slowly from the boundary and promoted the ice block expansion. As shown in Figure 4.29 (a), some supercooled water droplets still remained on the sample surface even though most of the droplets disappeared during the ice formation process. Figure 4.29 (b)-(d) clearly indicated the process that the ice layer grew from the supercooled droplets. Once the ice layer contacts the supercooled droplets, the droplet could be quickly absorbed by the ice layer. It changed into ice and integrated with the ice layer. Finally, the continuous spreading of the ice layer was completed.

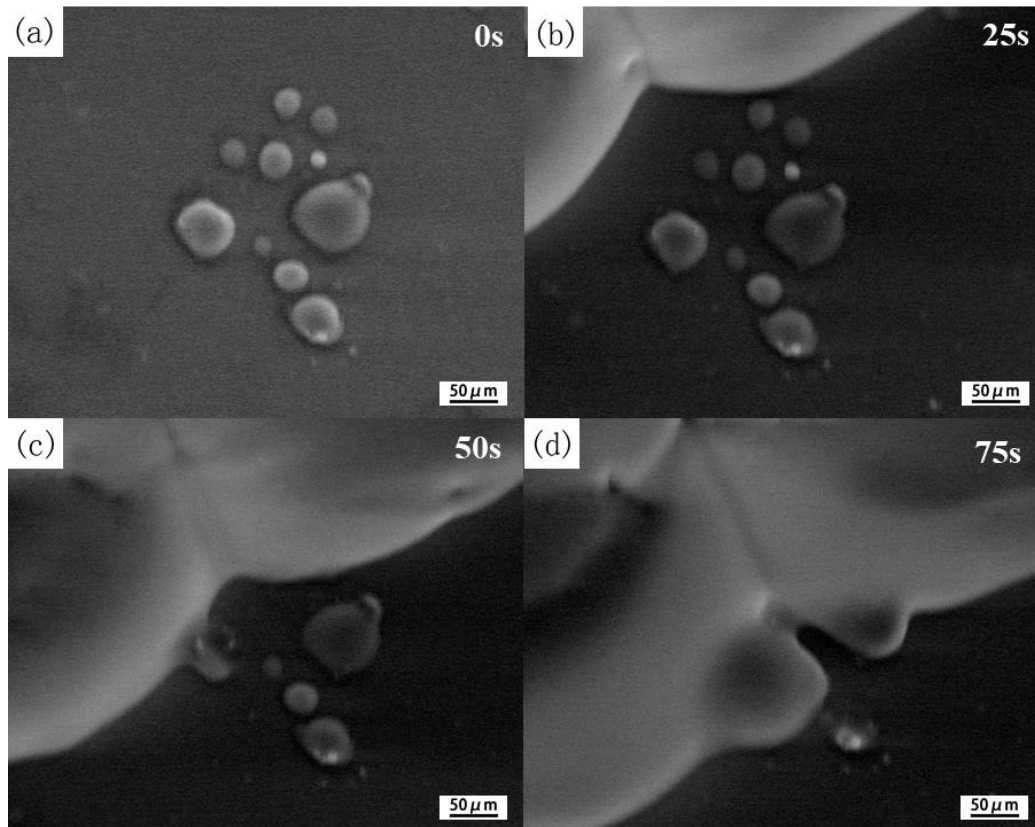


Figure 4.29 (a) Tiny water droplets in supercooled state, (b)-(d) Ice spreading process during the convergency between tiny supercooled water and existing ice crystal.

Figure 4.30 (a) and (b) showed the surface state of NP-40SO without/with wetting, exhibiting similar water condensation and droplet distribution as Ni-PDMS sample. Figure 4.30 (c) showed the ice growth on NP-40SO. Compared with the Ni-PDMS sample, the ice mainly grew in the z direction, leading to the obvious increase in ice thickness on NP-40SO because it was difficult for the ice growth of in the x direction, which could be ascribed to the difficulty of ice nucleation at solid-ice interfaces deriving from the fairly high energy barrier. Therefore, the ice growth on existed ice layer was much faster than that on NP-40SO, forming the accumulated ice layer indicated in Figure 4.30 (c).

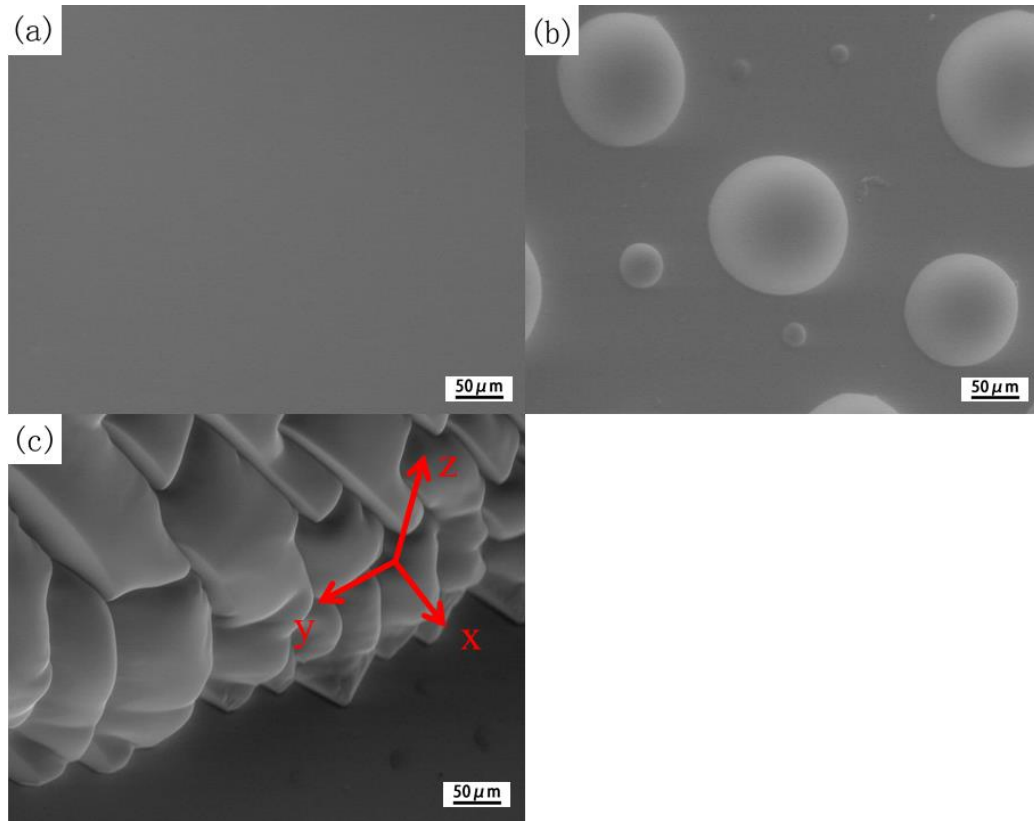


Figure 4.30 ESEM images of Ni-40SO sample: (a) as-prepared state, (b) water condensation, (c) Ice accumulation.

The detailed surface ice growth rates on the different samples were also depicted in Figure 4.31. With respect to the quick ice growth on Al plate (which could reach as high as $7.0 \pm 0.3 \mu\text{m/s}$), the ice growth on Ni-PDMS was also much slower than before, $0.4 \pm 0.1 \mu\text{m/s}$. And the growth rate of ice showed an obvious decrease in NP-SO series sample. The ice growth rate of NP-10SO decreased to only $0.4 \pm 0.09 \mu\text{m/s}$, as well as the NP-20SO ($0.3 \pm 0.01 \mu\text{m/s}$) to NP-50SO ($0.2 \pm 0.01 \mu\text{m/s}$). It indicated that the infusion of silicone oil could slow down the ice growth. Also, no negative impact was observed in the icing process on LIS by the introduction of Ni scaffolds. The results further confirmed that NP-SO series samples exhibited strong inhibiting effects on the spread of ice.

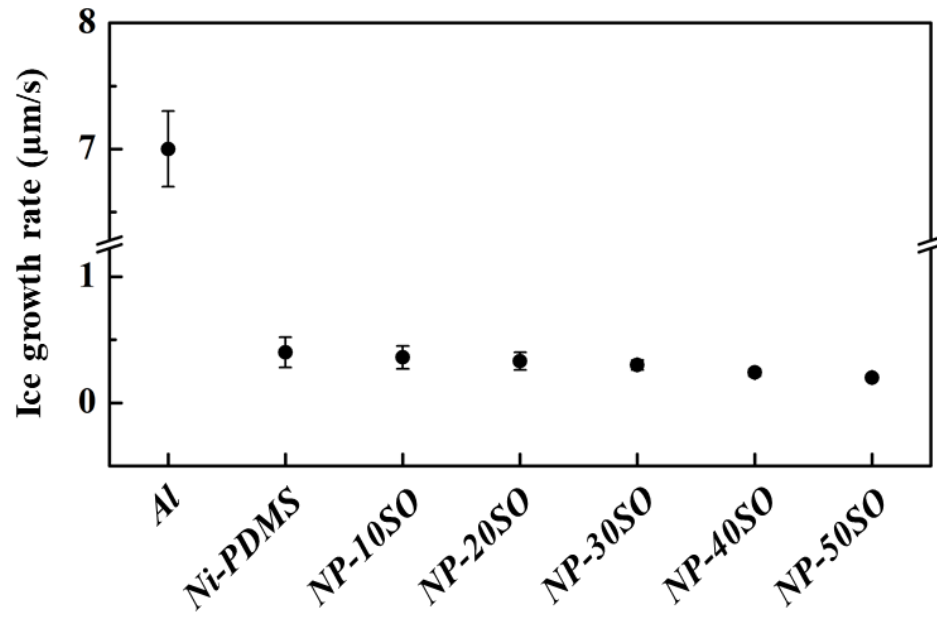
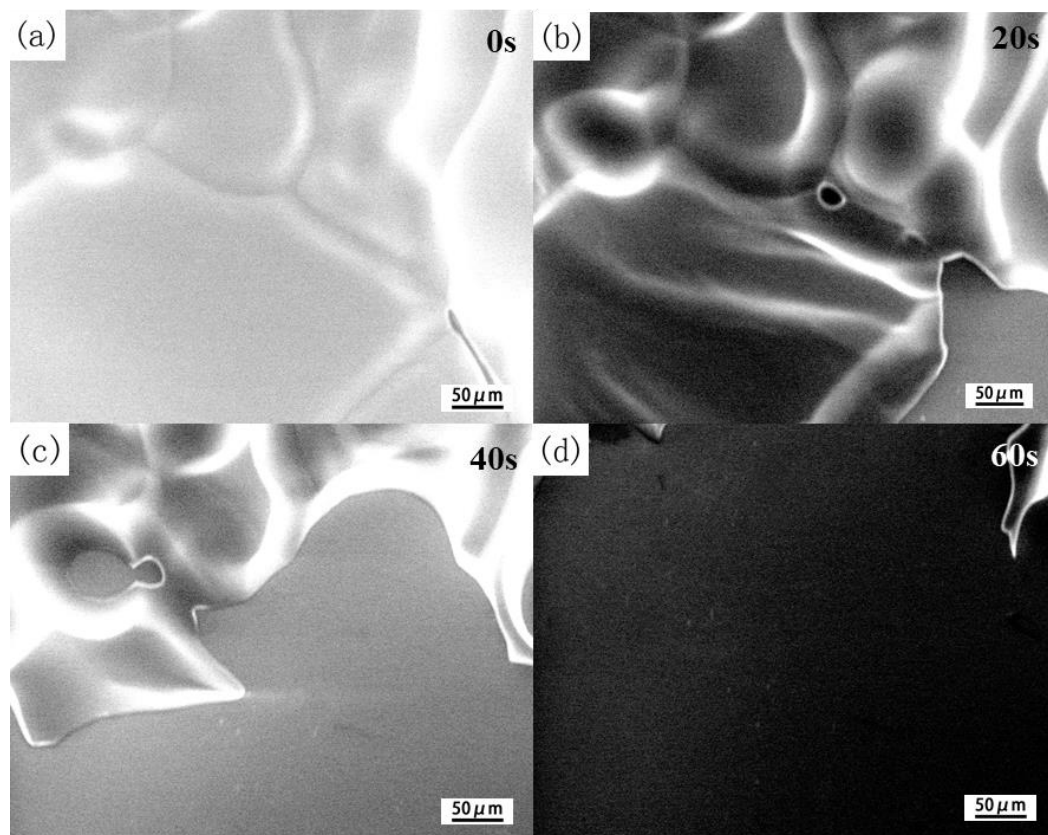


Figure 4.31 Values of ice growth rate on various samples.

4.4.2 Ice diminishing process on different sample surfaces

Figure 4.32 Ice diminishing process on Ni-PDMS (a) $t=0$ s, (b) $t=20$ s, (c) $t=40$ s, (d) $t=60$ s.

The sublimation dynamic of Ni-PDMS observed by the in-situ ESEM observations clearly showed the changes during ice retardation and the effect of PDMS layer. As indicated by Figure 4.32, it is assumed that the ice sublimation had a preference to move with the direction from the bottom up with the reduced chamber humidity. There was also no shift in view field from image (a) to (d), the ice block would keep shrinking and the morphology on the formed ice showed as the angular patterns [344]. Due to the remaining flat and smooth sample surface, there were few interlock ice existing on Ni-PDMS, the formed ice also has less ice-surface contact area between the ice and sample surface. As verified by the low value of ice adhesion strength, the good de-icing performance was confirmed. Besides, no damage was found on the surface, which also showed good durability.

Figure 4.33 demonstrated the detailed in-situ ice diminishing processes on NP-40SO. It took over 450 s for NP-40SO to finish the whole retardation process. Image (a) indicated the initial ice-covered state. The initially covered ice was quite smooth. But with the sublimation kept undergoing, the surface pattern became more angular than before. The displayed colour in different images also varied, the reason here was mainly due to the sudden change in chamber conditions, the focus was not finished before it was captured by the detectors. There were also big holes surrounded by the remaining ice shown in images (c) and (d), the NP-40SO sample surface should pose less effect on the displayed behaviour. The removal of the covered ice layer showed a preference in the order of ice retardation. It was easy to find that it took much longer duration to retract all of the ice. By comparing Figure 4.32 and Figure 4.33, the thickness of the ice layer on NP-40SO was much higher than that on Ni-PDMS. It may be ascribed to that the ice crystal spread at the ice/solid interfaces was more difficult than that on Ni-PDMS, there was more ice grown in the vertical dimension than in the horizontal dimension, leading to the much thicker ice formation.

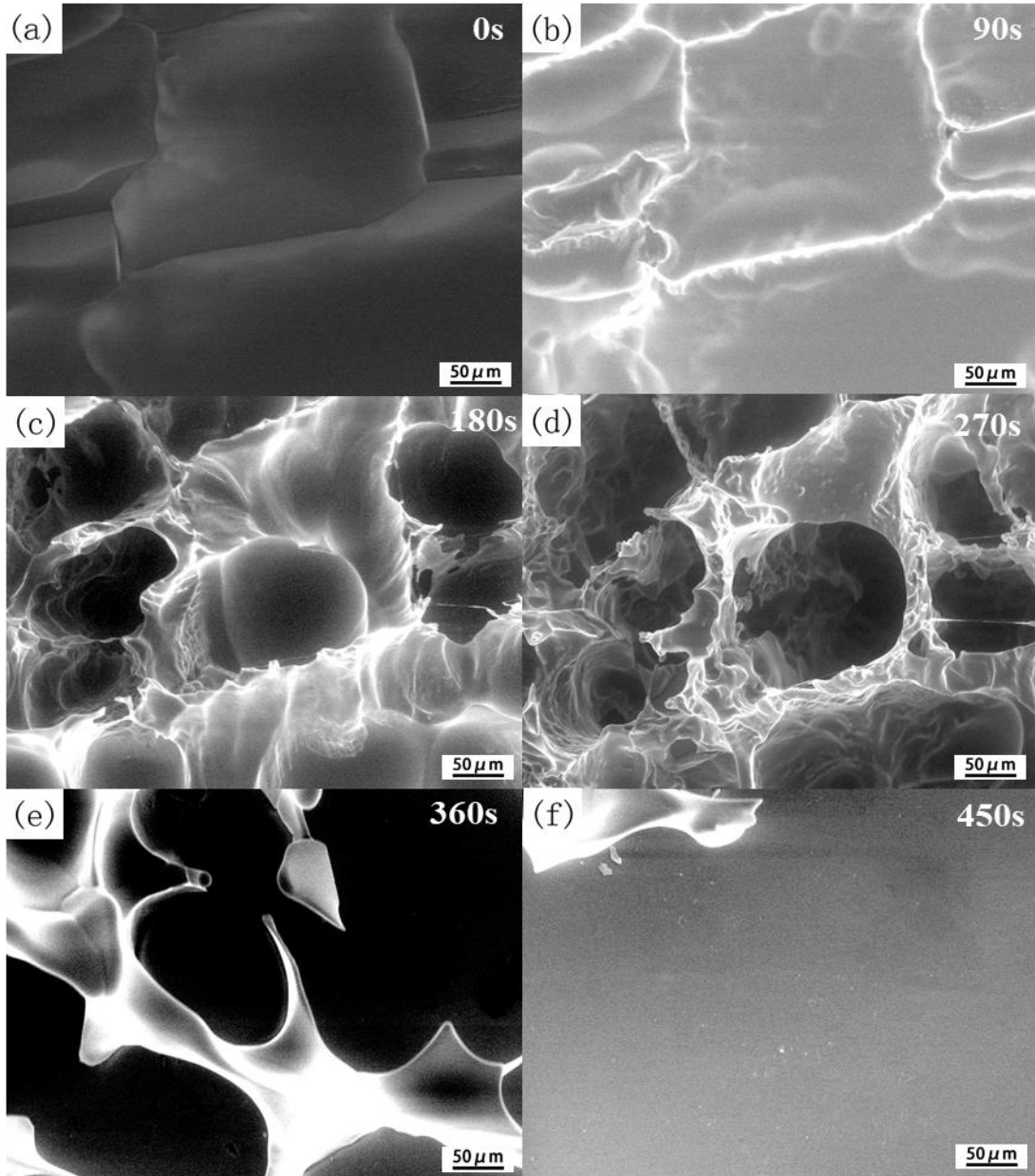


Figure 4.33 Ice diminishing process on NP-40SO (a) $t=0$ s, (b) $t=90$ s, (c) $t=180$ s, (d) $t=270$ s, (e) $t=360$ s, (f) $t=450$ s.

From the displayed results, it could be inferred that NP-40SO possessed the lowest ice adhesion strength, 1.6 ± 0.2 kPa. The value could also maintain stable during the whole 50 icing/de-icing cycles. By combining the durability of two-phase structure and self-repairability derived from PDMS-silicone oil incorporation, the lack of durability and icephobicity could both be taken into consideration and proper solutions could also be supplied using the NP-SO series system.

4.5 Thermal Resistance Analysis of Different Surfaces

All of the tested samples were pre-cooled inside the cold chamber and the temperature of their surfaces should be stabilized at -20 °C. Once the sessile droplet (still at room temperature) was placed onto the sample surfaces, heat exchange took place, the heat would be released along with the ice-sample interface as shown in Figure 4.12. Here, the heat transfer could be simplified into a one-dimensional flux. The total thermal resistance consists of a sum of reciprocal conductivities and could be determined by considering the different parts in series. The total effective thermal conductivity k_{eff} could be calculated using equation (4.7) [345]:

$$k_{eff} = \frac{\sum b}{\sum_{n=1}^{\infty} \frac{b_n}{k}} \quad (4.7)$$

where $\sum b$ is the overall thickness of the multi-lamina panels, and $\sum b/k_{eff}$ refers to the overall heat transfer resistance per unit area. The temperatures at different layers could be calculated using a simple form of Fourier Law and expressed as equation (4.8) and equation (4.9) [346]:

$$q = \frac{\Delta T}{R_{th}} \quad (4.8)$$

$$R_{th} = \frac{L}{A \cdot k} \quad (4.9)$$

where q is the heat flux, ΔT is the temperature difference between two layers, R_{th} is the thermal resistance, L is the layer thickness, A is the conduction area, and k is the thermal conductivity of the material. If one layer possesses poor thermal conductivity, it contributes more to the total thermal resistance and further affected the heat conduction of the whole system. The icing durations of Al, Al-PDMS and Ni-PDMS were different. The reason here could be that the different heat conduction during the whole icing process.

4.6 Influence of Ni Scaffolds Introduction in Lowering Ice Adhesion Strength

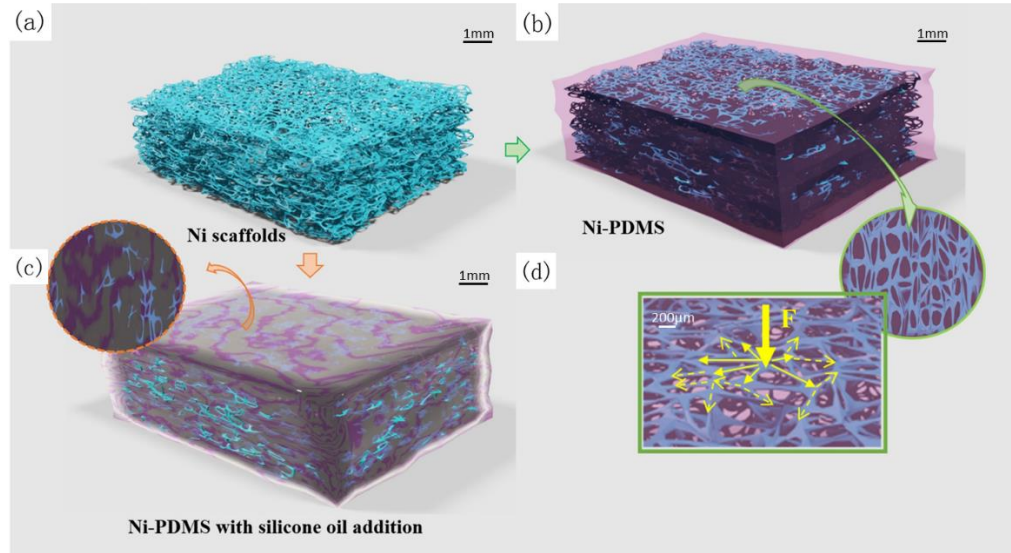


Figure 4.34 Schematic diagram of different sample structures (a) Ni scaffolds; (b) Ni-PDMS; (c) Ni-PDMS with silicone oil addition; (d) Ni metallic framework indicating the mechanism of dispersion and redistribution of impact energy.

The schematic diagrams of involved samples including the as-received Ni scaffolds, Ni-PDMS and Ni-PDMS with silicone oil addition were illustrated in Figure 4.34. Image (a) clearly shows the highly porous structure of the Ni scaffolds with calculated porosity of around 90% (80-110 pores per inch). The existing large number of pores and scaffolds could provide the impregnation of hydrophobic/icephobic substances. As discussed before, the Ni scaffolds could play important roles in increasing the durability to prolong the attended time and accelerate the thermal conduction when doing de-icing applications. The schematic of the cross-sectional area was also displayed, showing a similar morphology as the surface morphology, as evidenced by Figure 4.1. The existing numerous pores showed uniform arrangement on the Ni scaffolds in the entire density range [316]. Figure 4.34 (b) indicated that the Ni scaffolds were completely covered by the PDMS filling. The former existing hierarchical parts and the big pores on the sample surface were filled by controlling the volume of deposited PDMS.

Compared with pure PDMS layer, the incorporation of Ni scaffolds would significantly improve the mechanical reinforcement effect of the layer structure. It is inferred that the stress in the PDMS matrix would be reduced because the major stress would be carried and re-distributed by the Ni network.

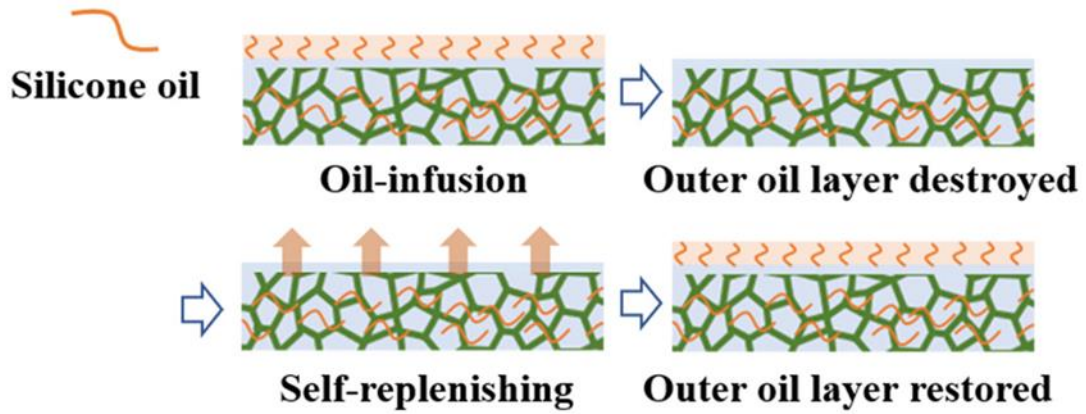


Figure 4.35 Schematic diagram showing the self-replenishment mechanism of the Ni-SO series samples.

While in Figure 4.35, with the infusion of silicone oil, it could introduce some slippery effects into the whole system. There would be some silicone oil diffused out and there was a thin layer of silicone oil covered on top. The thin oil layer could enable the good icephobicity of the layer system. As depicted in Figure 4.33 (d), the protective effect on the as-prepared icephobic layer structure could be easily realized via the interconnected network structures constructed by Ni scaffolds and PDMS filling. It indicated that the impact abrasion could be significantly restrained and the impact energy could be transferred to a much larger area through the Ni scaffold. And the PDMS filling, which is a highly-damped, visco-elastic polymer, also helps such transfer and adsorb most of the energy [40]. Besides, the infused silicone oil could keep diffusing out and existing and coming into effect even taking the oil depletion issue during the de-icing process into consideration. Therefore, the NP-SO layer system could be well maintained under severe impact abrasion and direct shear abrasion. The Ni scaffolds would act as the armour for the filled PDMS and the silicone oil incorporation also contribute a lot to the significant icephobicity.

4.7 Summary

In summary, a universal approach was proposed to introduce microporous metallic scaffolds in the LIS construction to increase the applicability and durability, and the potential of LIS was significantly prompted for ice mitigation. Ni scaffolds and PDMS modified silicone oil system was chosen for the LIS construction, and the multiphase icephobic layer structures have demonstrated good icephobicity and significantly improved durability. In comparison with recent reports [[32](#), [250](#), [319](#), [340](#), [341](#), [347-349](#)] indicated in Table 4.4, the proposed LIS construction in this work demonstrated an obvious advantage in the de-icing aspects. The ice adhesion strength of Ni scaffolds combined with PDMS modified by 40 % silicone oil addition was only 1.6 ± 0.2 kPa and the low ice adhesion strength was maintained even after 50 icing/de-icing cycles. The surface free energy of the samples decreased with the increasing addition of silicone oil. The actual nucleation free energy barrier during the freezing process also increased, which restrained the ice nucleation at the liquid-solid interface and in turn prolonged the icing duration. During the icing/de-icing test, a good level of lubricating effect would be well maintained with minimal oil depletion for the enhanced LIS construction.

Besides, the introduction of microporous Ni scaffolds could help to redistribute the stress during de-icing process, which effectively protected the LIS materials from external load and impact. Meanwhile, the quick depletion of infused oil lubricants derived from the large deformation in polymer could also be restrained, which has solved the oil depletion issues in long-term service environments. The multi-phase LIS construction could further boost the initiation of micro-cracks at the solid-ice interfaces and prompt an easy ice detachment. Additionally, with the microporous scaffolds, the oil depletion from the LIS construction has also been largely reduced, contributing to the durability enhancement.

Table 4.4 Ice adhesion strength of different icephobic surfaces versus icing/de-icing

Reference	Surface type	Ice adhesion		
		1 st cycle (kPa)	Icing/de-icing cycles	Last cycle (kPa)
This work	NP-40SO	1.6	50	2.0
Zhang [32]	1P1S	25.0	24	37.0
	1P2S	15.0	24	28.0
Khammas [347]	FS-PE SLIPS	22.0	4	32.0
Qian [340]	0 SLIPS	27.0	25	24.0
	0.5 SLIPS	22.0	25	23.0
	1 SLIPS	17.0	25	15.0
Barthwal [341]	SIOP	22.0	15	81.0
	SLIPS	45.3	18	89.2
	SLIPNS	48.1	18	61.2
Xing [319]	PDMS-oil-30	4.0	20	38.0
	PDMS-oil-50	2.0	20	28.0
He [250]	PG1-PFO	20.0	50	16.0
Li [349]	Submicrometer porous foam	39.1	50	17.5
Boinovich [348]	SLIPS	253	32	275

The newly developed strategy could effectively alleviate the problem of serious oil depletion and fragility of LIS surfaces by combining the advantage of mechanical durability enhancement and effectiveness in icephobicity. The LIS construction design could also be used in the combinations with diverse polymeric substrates, which further opens the potential in ice protection. For example, the NP-SO system in this work could be developed as gummed tape and attached onto certain engineering surfaces directly like aircraft wings or wind turbines [350].

Chapter 5 Phase Change Oil Modified Icephobic Structures

In chapter 4, the LIS construction was carried out by incorporating metallic scaffolds with the aim to improve applicability and surface durability. With the new LIS design and construction, the level of deformation of the polymer matrix was restrained while the infused oil could be well retained. In this way, little oil depletion would occur, and the good lubricating effect of LIS could be maintained, which significantly prompted the potential for ice mitigation. The Ni scaffolds were introduced into PDMS with silicone oil addition (PDMS-SO) system. Nevertheless, the results indicated that the introduction of metallic scaffolds could help to slow down the oil depletion in LIS system. But if the weight percentage of infused oil in LIS system exceeds the limit of system storage, oil depletion would take place during the repeated icing/de-icing cycles.

To minimise the emergence of this problem fundamentally, the phase change liquids were selected to incorporate with the Ni scaffolds combined with PDMS system. With this combination, it could absorb and release heat over a defined temperature range during the whole phase change process. By infusing the phase change liquid into the polymer matrix, it could supply a new potential design concept by delaying the ice formation and decreasing the ice adhesion on certain exposed surfaces [136]. Under the icing conditions, there would be a lot of heat being released during the phase change process, which further slows down the formation of ice and frost. Meanwhile, the phase change liquids would change into solid state from liquidous state, so oil depletion could be avoided. Moreover, there would also be localized shear stress appearing on the surface, which lowers the existing ice adhesion [236]. In this way, there would be micro-cracks initiated at the interfacial regions and minimise the ice adhesion strength.

To increase the oil storage, aerogel powder is widely thought to possess large specific surface area (the value is normally higher than 300 m²/g [351]) and was used as an absorption material, which could be chosen to absorb and store the oil [352, 353]. For

example, Kim et al. developed icephobic coating with excess oil containing aerogels in polymer. The infusion of silica aerogel not only helped to mitigate the oil drought inside the coating, but also improve the mechanical strength of the matrix. It also achieved very low ice adhesion strength less than 20 kPa even after 20 icing/de-icing cycles [354]. There would be phase change taking place in phase change liquid (from liquidous to solid) when the temperature was lower than the freezing points, thus avoiding the oil depletion during the de-icing process. The heat released during the phase change process also introduced delay effect to the ice formation, which also increased the anti-icing performance [270]. Groundnut oil was selected as the infused phase change liquid because of its phase change temperature ($0 \pm 3\text{ }^{\circ}\text{C}$), which is fairly close to the freezing point of water. It changes from liquid state into solid state when the surrounding temperature decreases to around $0\text{ }^{\circ}\text{C}$. The simultaneous releasing of the heat from phase change also introduce delay to the ice formation on the sample surface. To give better illustration of the effect of phase change material addition to PDMS polymer, several types of oils with different phase change temperatures including coconut oil and silicone oil have been selected as the references, for the aim to investigate the influence of phase change liquid additions to the surface morphology, chemical structure, surface wettability and icephobicity/anti-frost performance. The Ni scaffold is also chosen as the candidate of metallic scaffold in order to improve the mechanical durability of the structure.

Characterisation details:

The surface morphologies of the as-prepared samples were investigated by an Optical Microscope (OM, ECLIPSE LV100ND, Nikon) and a Scanning Electron Microscopy (JSM-6490LV, JEOL). 3D surface topography of the involved samples was measured by a non-contact optical profiler (Zeta-20, KLA-Tencor).

The variations in the chemical composition of the sample surfaces (square pieces of $10\text{mm} \times 10\text{mm}$) were qualitatively analysed using a FTIR spectrometer (Spectrum One,

Perkin Elmer, Akron, OH, USA) operating in attenuated total reflectance (ATR) mode with a diamond ATR crystal. Infrared spectra were recorded with 32 scans over the wavenumber range of 600-4000 cm^{-1} .

Shore hardness tests were conducted with a SAUTER durometer which links to a SAUTER test stands ranging from shore hardness A and D scales (TI-AO and TI-D), respectively. The shore hardness A scale was used in this work. For every sample, five separate measurements were carried out to calculate the average (Shore) value and minimize the existing error.

A contact angle goniometer (FTA200, First Ten Angstroms, Inc) was utilized to evaluate the wettability of the samples via a micro-pipette with pumping out rate of 1 $\mu\text{L/s}$ using a fixed droplet volume of 5 μL at room temperature and humidity.

Icing delay tests were conducted by monitoring the icing process of supercooled water droplets on the sample surface inside a cold chamber at $-20\text{ }^{\circ}\text{C}$. The volume of the droplet was 4 μL for each coated sample, and five spots were tested. The Al substrates were chosen for comparison. The whole icing process was recorded to determine the icing duration.

Ice growth behaviours were investigated with an Environmental Scanning Electron Microscopy (ESEM, Quanta 650 FEG, FEI). Water condensation, ice formation and the subsequent growth processes were all studied under the controlled conditions: $-10 \sim 2\text{ }^{\circ}\text{C}$, humidity: 90-100%, and pressure: 380~700 Pa.

Ice adhesion strengths of the samples were measured using a horizontal shear test system with a pre-prepared ice block (volume: 1.31 mL) attached to the sample surface in a cold chamber with temperature of $-20\text{ }^{\circ}\text{C}$. The shear test system mainly consisted of a force probe (with diameter of 5 mm), a motion controller as well as the pre-prepared ice cube attached onto the tested samples. The force probe was applied to propel the

ice/sample with the velocity of 0.1 mm/min during the ice adhesion tests. Five identical tests were carried out to ensure the data confidence, and the standard deviation was calculated.

Besides, icing/ice detachment cyclic tests were conducted for 50 cycles. The ice adhesion strength and mass change during the cyclic tests were recorded. The freezing time between two cycles was set to 3 h.

The method used to calculate the error bars is consistent with the one presented in Chapter 4.

5.1 Micro-structure of Ni-PDMS Samples Modified by Different Phase Change Oil with Aerogel Addition

With the addition of aerogel powder (size in nanoscale) into the infused oil, the oil storage inside the PDMS polymer matrix could be increased, and it also helps with the continuous existence of the oil layer. The specific surface area of alumina aerogel powder is as high as 85-115 m²/g, it also has good oil adsorption and hydrophobicity. Because of these properties, alumina aerogel was finally chosen as the aerogel powder to improve the adsorption of phase change liquid in this work.

5.1.1 Surface characterisation

Figure 5.1 (a)-(c) showed the optical images of different phase changed oil modified Ni-PDMS samples without aerogel incorporation, and Figure 5.1 (d)-(f) showed the OM images of the samples that were incorporated with aerogel. Among them, images (a) and (d) indicated the Ni-PDMS samples modified by silicone oil with and without aerogel. It could be seen that the metallic Ni scaffold could be easily found in the optical images. The internal porosity was also filled by the PDMS polymer completely. Due to the transparency of the aerogel, there was no obvious difference between the two samples. The infused silicone oil was adsorbed by the aerogel powder and it would not diffuse out onto the sample surface. Figure 5 (b) and (e) corresponded to the Ni-PDMS samples modified by groundnut oil with and without aerogel. They showed obvious differences compared to the previous sample. The added groundnut oil diffused out a lot and remained in spherical shapes on the sample surface. The groundnut oil would stay at the PDMS matrix (as shown in Figure 4.6), with no reaction taking place with the PDMS. The sample changes from pure transparent to white and translucent. In this way, the underneath Ni scaffold was covered and was not easy to be observed. While for Figure 5 (e), with the incorporation of aerogel, the capacity for groundnut oil on the surface was absorbed, there was also oil droplets in large sizes diffused out obviously, showing a smooth and flat surface.

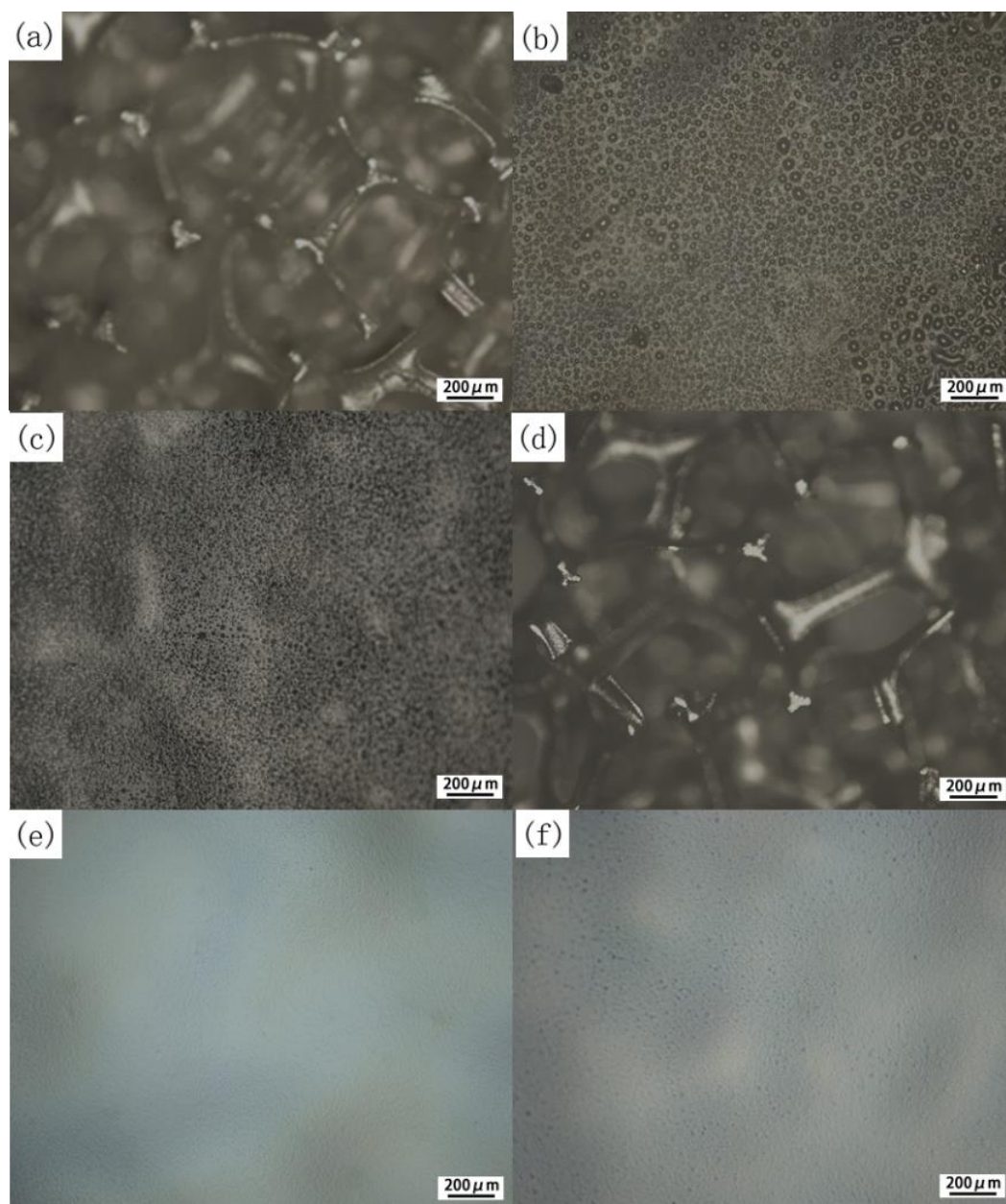


Figure 5.1 Optical images of Ni-PDMS sample modified by (a) silicone oil; (b) groundnut oil; (c) coconut oil; (d) silicone oil with 3wt% aluminiumoxid C; (e) groundnut oil with 3wt% aluminiumoxid C and (f) coconut oil with 3wt% aluminiumoxid C.

Figure 5.1 (c) and (f) were Ni-PDMS samples modified by coconut oil with and without aerogel incorporation. Similar to Figure 5.1 (b), the coconut oil also diffused out to the surface, but the diffused volume was a little lower than that using groundnut oil. While with the aerogel incorporation, the diffusion of coconut oil was decreased. Some small cavities could be observed on the sample surface, which mainly came from the partial volatilization of oil during the curing process. The addition of aerogel powder could

effectively inhibit the exudation of the surface excess oil, which in turn help to store more oil inside the polymer matrix.

5.1.2 Microstructural characterisation

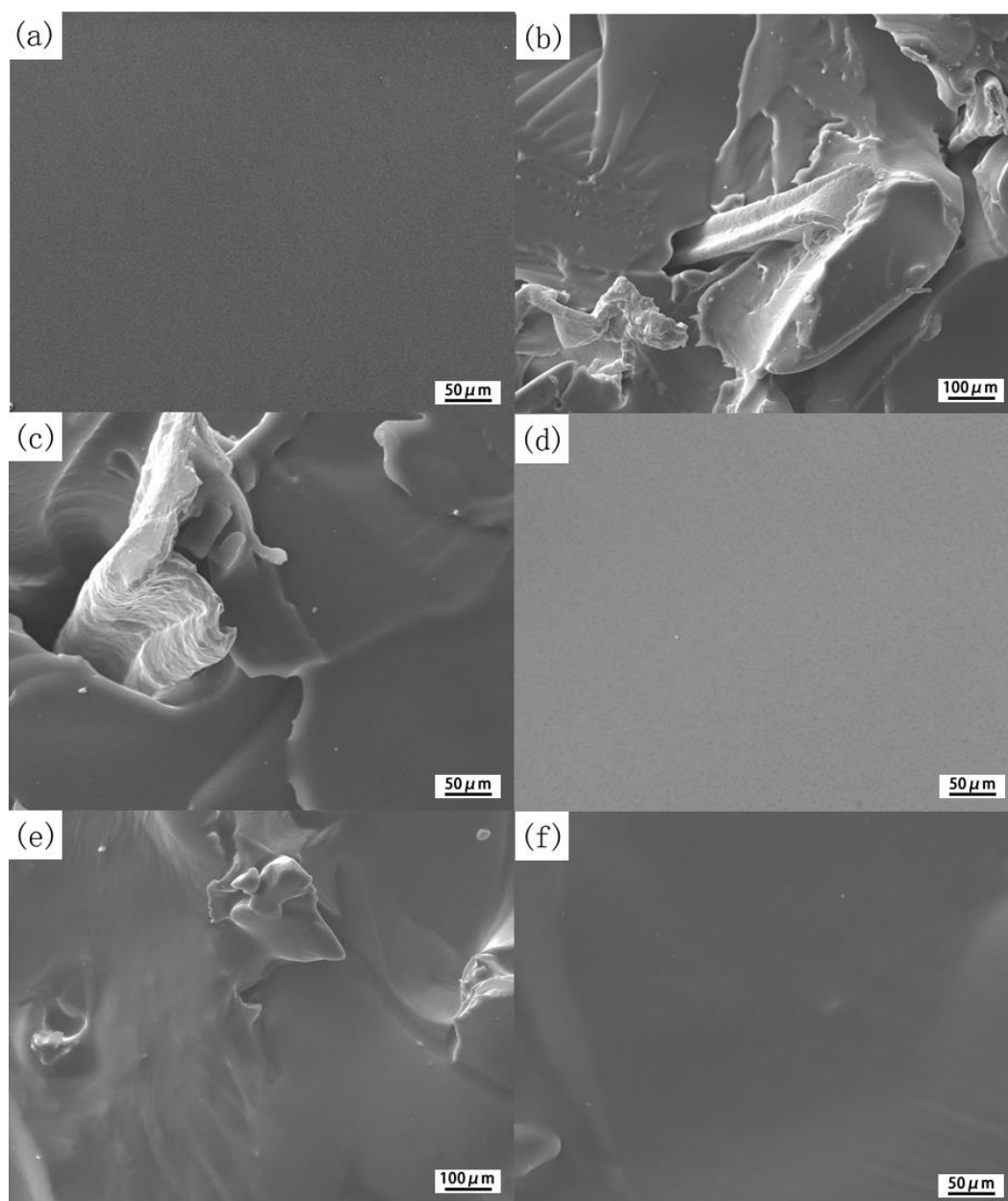


Figure 5.2 SEM images of (a) the surface morphology of Ni-PDMS; (b) and (c) the cross-sectional area of Ni-PDMS; (d) the surface morphology of NP-20SO₃Al; (e) and (f) the cross-sectional area of NP-20SO₃Al.

Figure 5.2 showed the SEM images of surface morphology and cross-sectional areas of Ni-PDMS, and NP-20SO₃Al samples. Figure 5.2 (a)-(c) indicated the details of Ni-PDMS. The surface was fairly flat and smooth with no pores and cracks, displaying an intact surface. It was also obvious to find that the Ni scaffolds have been fully covered by the PDMS. When moving to the cross-sectional areas, the good adherence between the scaffold and the PDMS polymer was also verified. From the amplified image, there was no porosity formed inside the PDMS matrix, which also proved the effect of vacuum impregnation. While for NP-20SO₃Al, it corresponded to Figure 5.2 (d)-(f). The surface morphology of NP-20SO₃Al was also flat and smooth, without any obvious defect on top. Due to the nanometer dimension of the aerogel, it was difficult to be found on the surface. Figures 5.2 (e) and (f) showed the details of the cross-sectional areas, displaying good adherence and no internal porosity.

Figure 5.3 showed the SEM images of surface morphology and cross-sectional areas of NP-20GO₃Al, and NP-20CO₃Al samples. Figure 5.3 (a) to (c) showed the details of 20GO₃Al sample. It is easy to find that there are some shallow cavities distributed randomly on the surface in Figure 5.3 (a), showing a fluctuant surface. The cavities mainly came from the evaporation of the infused groundnut oil during the curing treatment. The incorporation of aerogel was also difficult to be observed in these images. From the cross-sectional images, it showed many differences between the former two samples. The central regions of the samples exhibited numerous porosities, primarily resulting from the evaporation of the infused groundnut oil, whereas the surrounding regions comprised the Ni scaffolds. The observed porosity measured 9.67%. From the amplified image in Figure 5.3 (c), the formed pores were clearer and they varied in the size. For NP-20CO₃Al, the surface cavities were deeper, it also did not show the smooth surface. Due to the smaller size, no obvious aerogel powder could be found from the observation. As for cross-sectional images, the white parts are the broken Ni scaffolds while the black area is PDMS fillings. Quantity of porosities could still be found in the PDMS area. The average size of the formed internal porosities was around 5-10 μm and the porosity was 22.65%, which was higher than that of NP-20GO₃Al sample.

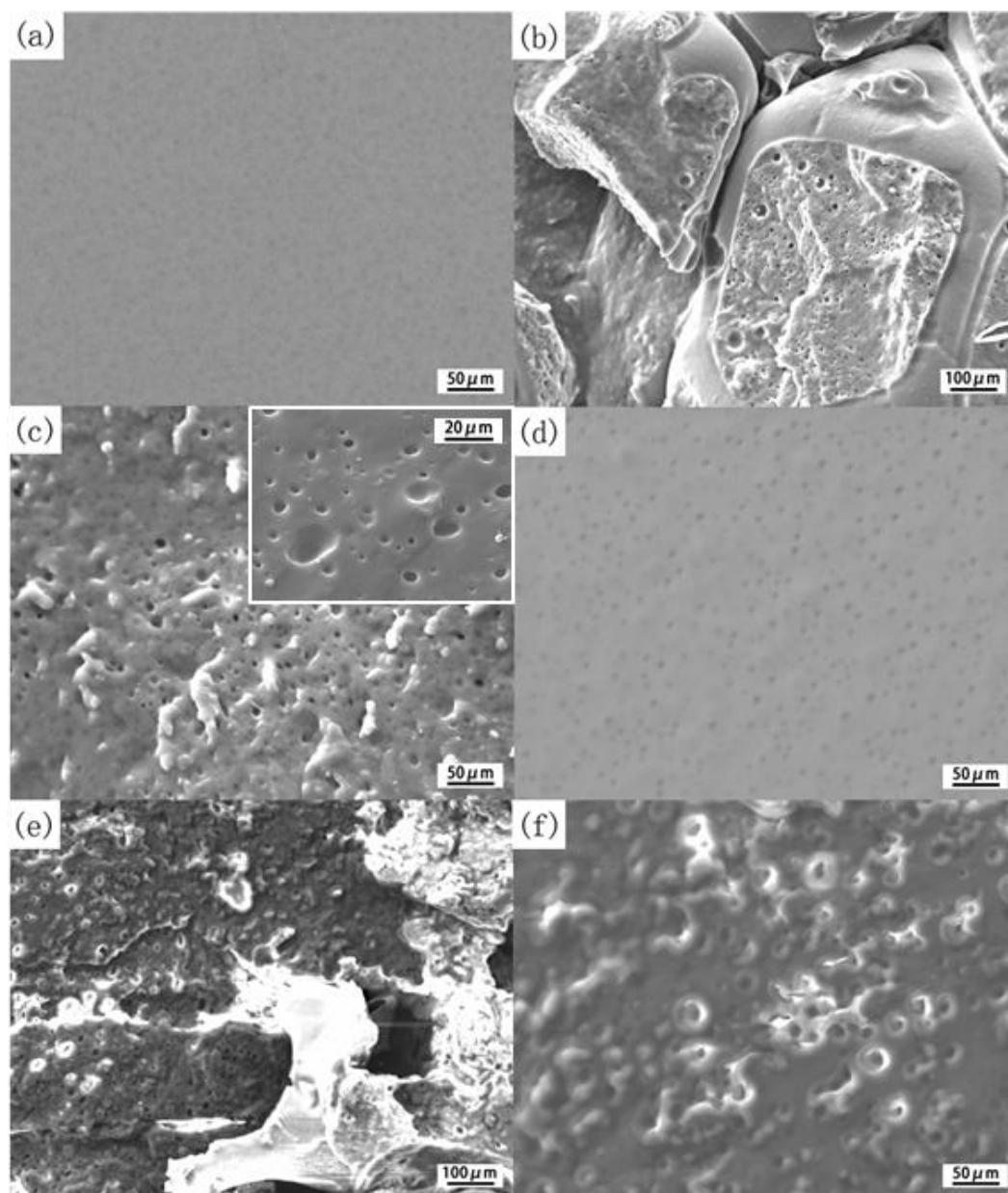


Figure 5.3 SEM images of (a) surface morphology of NP-20GO3Al; (b) and (c) cross-sectional area of NP-20GO3Al; (d) surface morphology of NP-20CO3Al; (e) low magnification and (f) high magnification of cross-sectional area of NP-20CO3Al.

5.1.3 Surface analysis using FTIR spectrum

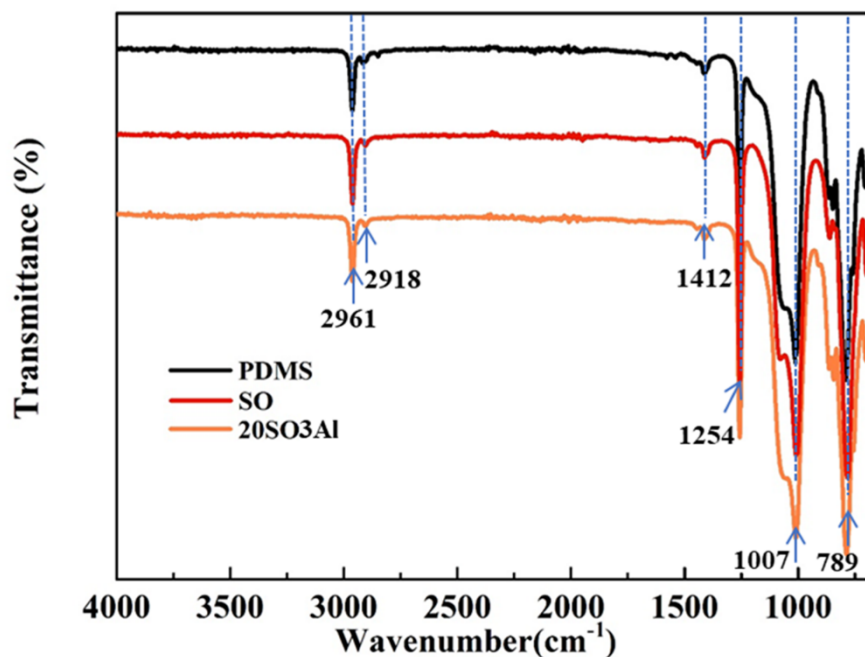


Figure 5.4 ATR-FTIR results of PDMS, pure silicone oil and 20SO3Al.

Figure 5.4 showed the ATR-FTIR results of PDMS, pure silicone oil (liquid) and 20SO3Al. The detailed position of peaks corresponding to the functional groups with different chemical bonds was illustrated in Table 5.1. The peak representing positions at $2850 \sim 2965 \text{ cm}^{-1}$ were characterized by the presence of methyl ($-\text{CH}_3$) functional group at PDMS surface [355]. The symmetric and asymmetric stretching of the methyl group was obtained at 2961 cm^{-1} and 2918 cm^{-1} , respectively, along with the deformation vibration of same group at 1412 cm^{-1} and 1254 cm^{-1} . Peak at 1007 cm^{-1} represented the Si-O-Si asymmetric stretching while the methyl rocking occurred at around 789 cm^{-1} . Because PDMS and silicone oil have the same chemical properties, no functional groups were introduced on the surface of 20SO3Al with the addition of silicone oil and aerogel.

Figure 5.5 showed the ATR-FTIR results of PDMS, pure groundnut oil (liquid) and 20GO3Al. The detailed position of peaks corresponding to the functional groups with different chemical bonds was illustrated in Table 5.1. The peak positions of PDMS were

the same as in Figure 5.4. Notable and characteristic shoulders of the groundnut oil spectrum were attributed to the specific functional groups of fats and oils [356]. The C-CH₂ asymmetric (C-H) stretching (2926 cm⁻¹); CH₂ symmetric stretching (C-H) (2852 cm⁻¹); ester C=O stretching (1742 cm⁻¹); CH₂ wagging (1460 cm⁻¹); -C-O stretching and -CH₂- bending (1155 cm⁻¹) were matched with triglyceride component of the oil. In comparison with the three spectra, there are strong absorption peaks belonging to PDMS at positions of 2961 cm⁻¹, 2912 cm⁻¹, 1406 cm⁻¹, 1254 cm⁻¹, 1012 cm⁻¹ and 789 cm⁻¹ in the spectrums of 20GO3Al, as well as the peaks of groundnut oil at positions of 2926 cm⁻¹, 2852 cm⁻¹, 1742 cm⁻¹, 1460 cm⁻¹, and 1155 cm⁻¹. As indicated from the SEM results, the majority of the groundnut oil has been kept in PDMS even though some of the groundnut oil has volatilized.

Table 5.1 List of ATR-FTIR peaks obtained for the various functional groups present on PDMS, silicone oil, groundnut oil, coconut oil, 20SO3Al, 20GO3Al and 20CO3Al surface in Figure 5.4, Figure 5.5 and Figure 5.6.

Peak position	Wavenumber (cm ⁻¹)	Functional groups
1	2961	Symmetric -CH ₃ stretching in ≡Si-CH ₃
2	2918~2930	Asymmetric -CH ₂ stretching in -C-H(-CH ₂)
3	2912	Asymmetric -CH ₃ stretching in ≡Si-CH ₃
4	2852	Symmetric -CH ₂ stretching in -C-H(-CH ₂)
5	1742	-C=O (Carbonyl ester) stretching
6	1460	-C-H(-CH ₂) bending (scissoring)
7	1406	Deformation vibration of -CH ₃
8	1254	Deformation vibration of -CH ₃
9	1155	-C-O stretching & -CH ₂ - bending
10	1012	Si-O-Si asymmetric deformation
11	789	CH ₃ rocking in -Si-(CH ₃) ₂

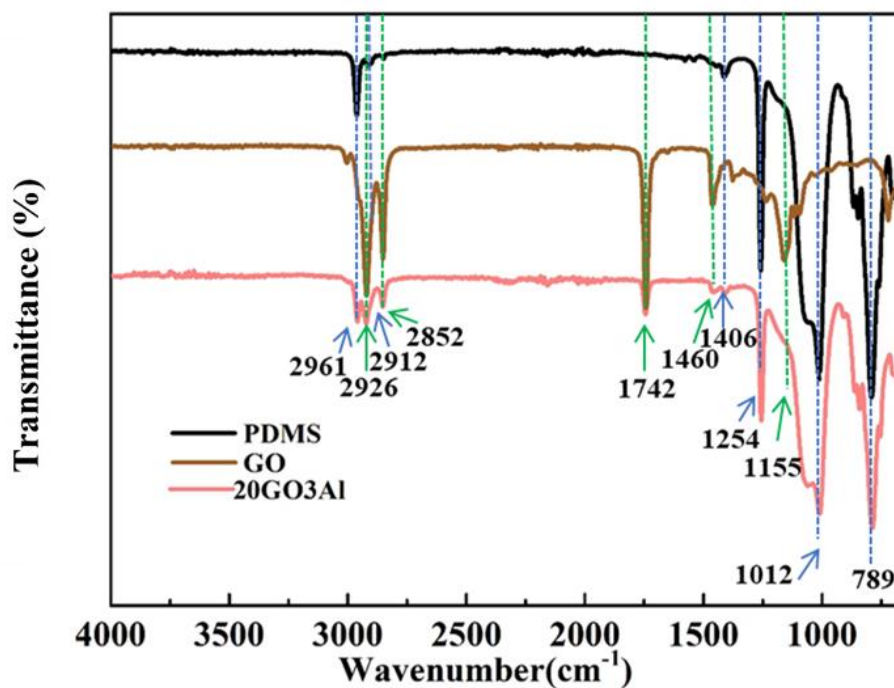


Figure 5.5 ATR-FTIR results of PDMS, pure groundnut oil and 20GO3Al.

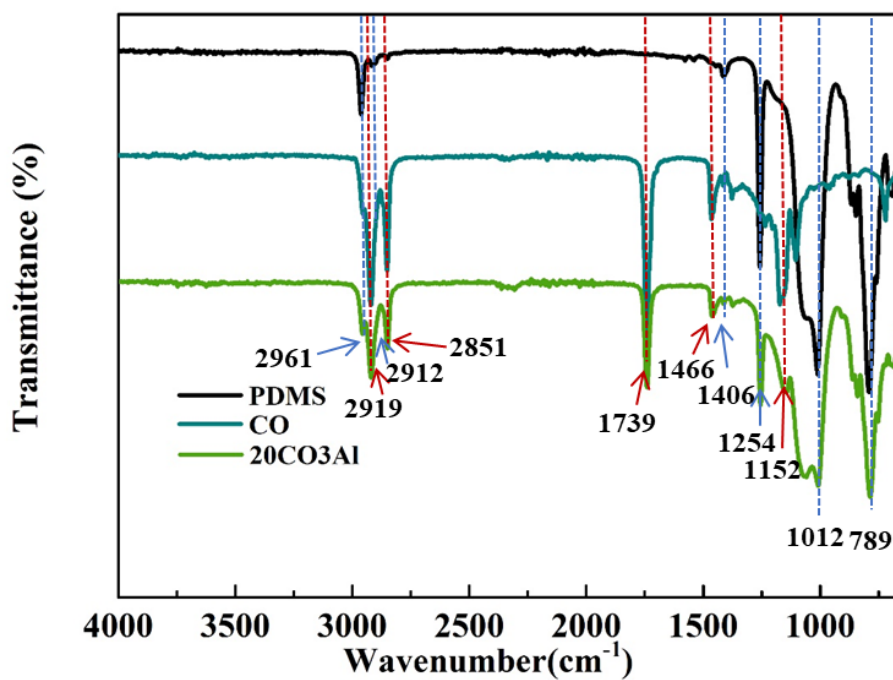


Figure 5.6 ATR-FTIR results of PDMS, pure coconut oil and 20CO3Al.

Figure 5.6 showed the ATR-FTIR results of PDMS, pure coconut oil (liquid) and 20CO3Al. The detailed position of peaks corresponding to the functional groups with

different chemical bonds was illustrated in Table 5.1. It was not difficult to observe that the peak positions of coconut oil were similar to the peak position of groundnut oil. The functional groups on the surface of 20CO3Al were also same as that of 20SO3Al surface. It could be indicated that there was a large quantity of coconut oil remaining in the cross-linked PDMS polymer matrix which has already been dissolved in the matrix. It could also be observed that there was still a large quantity of coconut oil remaining in the PDMS matrix.

5.2 Various Surface Properties of As-prepared Samples

The role of surface micro-structures on icephobicity has already been confirmed previously. In this section, the detailed wetting behavior were displayed to unfold the correlation between wettability and icephobicity. Besides, the shore hardness is also illustrated as a measurement of the surface elastic modulus [357]. The thermal properties evaluated by DSC were also displayed to demonstrate the anti-icing performance.

5.2.1 Detailed wettability of involved samples

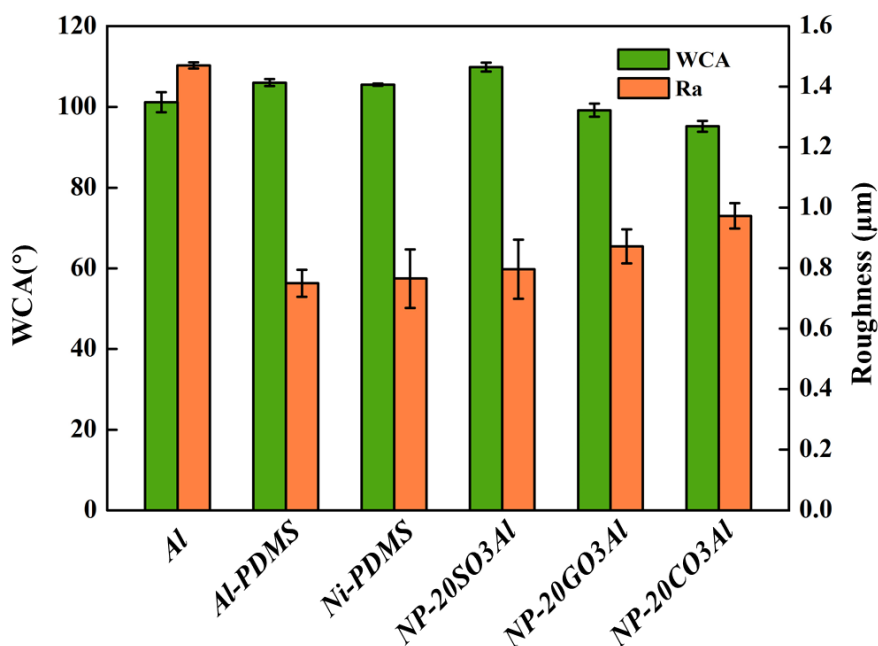


Figure 5.7 WCA and surface roughness results of different samples include Al, Al-PDMS, Ni-PDMS, NP-20SO3Al, NP-20GO3Al and NP-20CO3Al.

Figure 5.7 depicted the detailed wettability and surface roughness of different samples as well as the reference samples. For pure Al, the static WCA was $101.2 \pm 3.5^\circ$, which could be seen as hydrophobic. The surface roughness was $1.45 \pm 0.03 \mu\text{m}$. The as-received Al did not undergo any further treatment, showing the regular surface topography. As for Al-PDMS, with PDMS layer covering on top, the obtained surface became flat and smooth, which was also verified by the low surface roughness $0.75 \pm 0.11 \mu\text{m}$. To some extent, this could lower the static WCA, but the actual measured WCA was $105.3 \pm 1.3^\circ$, which was a bit higher than that of Al. The full PDMS coverage could explain this.

For Ni-PDMS, the WCA was similar to that of Al-PDMS, $104.9 \pm 0.6^\circ$, and the surface roughness is also close to Al-PDMS, around $0.78 \pm 0.14 \mu\text{m}$. With the similar surface topography and the same PDMS layer coverage, no obvious change was introduced. As for NP-20SO3Al, with the addition of silicone oil inside the PDMS matrix, the WCA value was increased to $108.2 \pm 2.2^\circ$. It did not bring much difference to the surface and it still showed as a flat and smooth surface with a surface roughness of $0.81 \pm 0.13 \mu\text{m}$, as indicated from SEM image in Figure 5.2. The usage of aerogel powder posed less effect on the surface roughness change. While for NP-20GO3Al, the phase change liquid has been changed from silicone oil to groundnut oil, the static WCA showed some decrease to around $97.2 \pm 1.9^\circ$. Because of the evaporation behaviour of the infused groundnut oil during the curing process, a lot of pores could form both inside the structure and on the surface. The scattered surface shallow cavities contributed to the surface roughness increase, $0.90 \pm 0.13 \mu\text{m}$. The WCA kept decreasing to $95.5 \pm 1.5^\circ$, the surface roughness increased to $0.95 \pm 0.13 \mu\text{m}$. The static WCA values of NP-20CO3Al should be higher than that of NP-20GO3Al considering the increased surface roughness. But it turned out that the measured WCA value of NP-20CO3Al was actually lower. The reason here could mainly be ascribed to the relatively high surface free energy.

Table 5.2 Surface free energy of Al-PDMS, Ni-PDMS, NP-20SO3Al, NP-20GO3Al and NP-20CO3Al.

Samples	Surface free energy (mJ/m ²)
Al-PDMS	38.2 ± 0.4
Ni-PDMS	38.6 ± 0.3
NP-20SO3Al	34.3 ± 0.4
NP-20GO3Al	39.2 ± 0.3
NP-20CO3Al	39.6 ± 0.3

As shown in Table 5.2, the measured surface free energy of NP-20GO3Al and NP-20CO3Al were 39.2 ± 0.3 mJ/m² and 39.6 ± 0.3 mJ/m², respectively. The hydrophobicity could be affected by two factors: the surface roughness and surface chemistry. Here, with the lowest surface free energy and moderate surface roughness, NP-20SO3Al possessed higher static WCA.

5.2.2 Shore hardness results

Figure 5.8 showed the values of shore hardness of different samples including PDMS, 20SO3Al, 20GO3Al and 20CO3Al. It is reported that the shore hardness could be used to evaluate the elastic modulus that is acquired through other typical methods [317]. The shore hardness value of PDMS was about 37.6 ± 1.1 (Shore A hardness), which was the highest among the samples. For 20SO3Al, the shore hardness suffered an obvious decrease to only 28.6 ± 0.9 (Shore A hardness). The reason could be the soften effect that came from the silicone oil infusion. The 20GO3Al showed the shore hardness value of 13.7 ± 1.0 (Shore A hardness), which was the lowest. The hardness of 20CO3Al was 17.2 ± 1.7 (Shore A hardness). The molecules of the groundnut oil and coconut oil were trapped inside the matrix of PDMS, which could also contribute the softening effect [358].

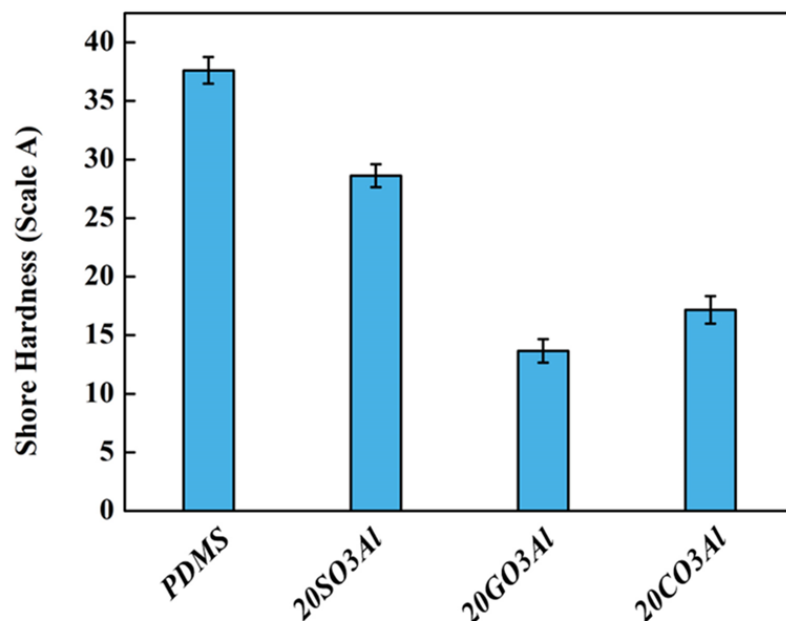


Figure 5.8 Shore hardness results of PDMS, 20SO3Al, 20GO3Al and 20CO3Al.

5.2.3 Thermal properties revealed by DSC measurements

Table 5.3 Thermodynamic parameters of 20GO3Al and 20CO3Al.

Sample	Onset of crystallization (°C)	End of crystallization (°C)	ΔH_m (J/g)
NP-20GO3Al	2.4	-16.0	3.2
NP-20CO3Al	25.5	6.7	3.8

Figure 5.9 showed the detailed DSC results of all of the involved samples including Ni-PDMS, NP-20SO3Al, NP-20GO3Al and NP-20CO3Al. It is acknowledged that all of the phase changing processes were classified as exothermic processes [359]. Table 5.3 indicated the thermodynamic parameters (Onset of crystallization, end of crystallization, and ΔH_m) of NP-20GO3Al and NP-20CO3Al. It could be seen that no peak was observed on the curves of both PDMS and NP-20SO3Al, which indicated that Ni-PDMS and NP-20SO3Al had no phase change taking place within the testing temperature range. While for NP-20GO3Al and NP-20CO3Al, they exhibited the entirely different phase changing temperatures. The phase changing process of NP-20GO3Al occurred at the temperature range between -16.0 °C and 2.4 °C. The phase

changing temperature of NP-20CO3Al is mainly located in the temperature region from 6.7 °C to 25.4 °C. It could be found that the temperature range for phase changing process among NP-20GO3Al and NP-20CO3Al was very close to that of pure groundnut oil and coconut oil [270]. According to Table 5.3, the phase-transition enthalpy of NP-20GO3Al and NP-20CO3Al were 3.2 J/g and 3.8 J/g, respectively. The results indicated that the icing process of water droplets could be significantly affected through the releasing of heat with the temperature decrease during the phase changing process derived from the phase change material in the composite layer. The cooling enthalpies of groundnut oil and coconut oil were found to be 38.1 J/g and 76.4 J/g [360, 361]. The expected theoretical cooling enthalpies for NP-20GO3Al and NP-20CO3Al were calculated to be 7.6 J/g and 15.2 J/g. However, the measured solidification enthalpies of the samples were lower than the theoretical values due to the varying degrees of evaporation of groundnut oil and coconut oil during the curing process. As a result, it can be inferred that the actual residual amounts of groundnut oil and coconut oil in the NP-20GO3Al and NP-20CO3Al samples are approximately 8.4 wt% and 4.7 wt%, respectively.

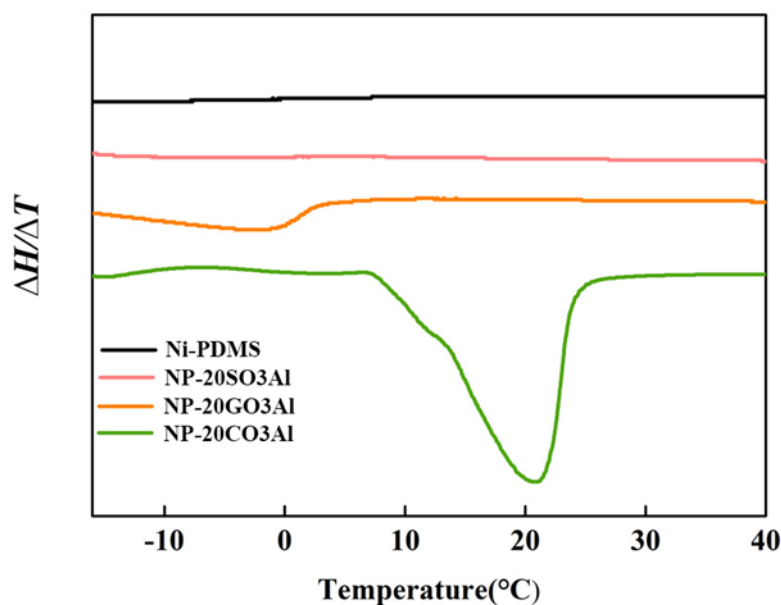


Figure 5.9 DSC curves of PDMS, NP-20SO3Al, NP-20GO3Al and NP-20CO3Al.

5.3 Surface Icephobicity and Durability Evaluations of NP Samples with Phase Change Liquid Modifications

5.3.1 Icing delay of water droplets

Figure 5.10 showed the droplet icing processes on different sample surfaces including Al, Al-PDMS, Ni-PDMS, NP-20SO₃Al, NP-20GO₃Al and NP-20CO₃Al under the temperature of -20 °C.

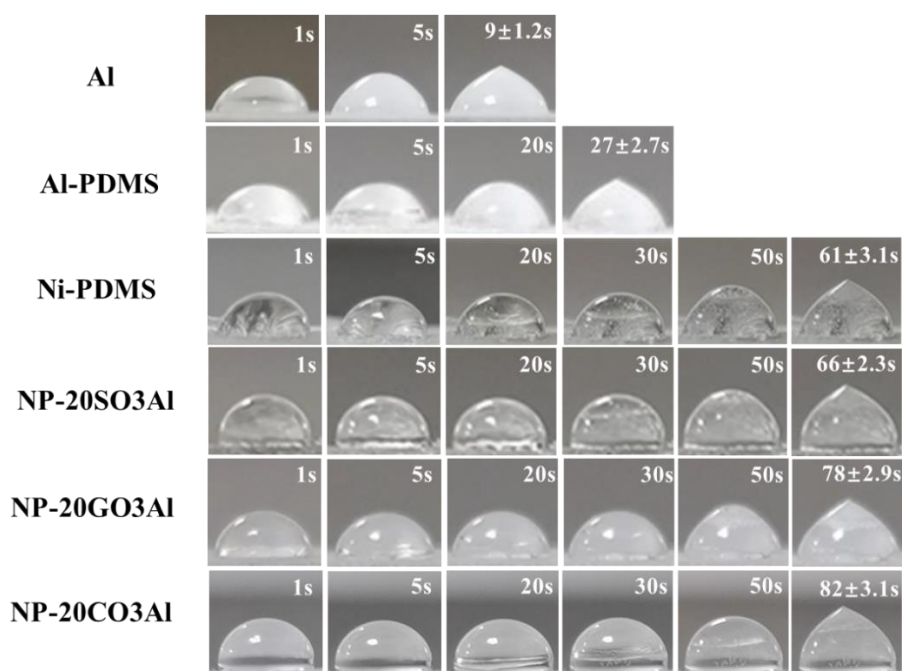


Figure 5.10 Droplet icing observation in anti-icing tests on different surfaces of Al, Al-PDMS, Ni-PDMS, NP-20SO₃Al, NP-20GO₃Al and NP-20CO₃Al.

The icing phenomenon would first appear at the solid-liquid interfaces, and there would be ice nucleus forming at the interfacial areas. It then gradually grew into ice crystals and spread to other regions, finally reaching the top region of the water droplet. Thus, the whole icing of the droplet was completed. The ice nucleation type in this phenomenon was verified as heterogeneous nucleation. As the reference samples, the detailed icing durations of water droplets on Al, Al-PDMS and Ni-PDMS were 9 ± 1.2 s, 27 ± 1.2 s and 61 ± 3.1 s, respectively. The main factors for the freezing delay may include the surface wetting behaviour and the heat transfer efficiency. The big

difference in thermal resistance between different sample surfaces also affected the heat transfer and further the icing delay. The detailed analysis has been discussed in section 4.3 in Chapter 4. While for NP-20SO3Al, the icing time of supercooled water droplets has been prolonged to 66 ± 2.3 s. The main reason could be ascribed to the increased energy barrier for ice nucleation. The incorporation of silicone oil altered the surface chemistry and lowered the surface free energy, which helped with the ice delay effect. The ice nucleation on ideal lubricant-infused surfaces could be regarded as the homogeneous type. And the relationships between the free energy barrier of homogenous nucleation and heterogenous nucleation could be described by equation (5.1) [335]:

$$\Delta G_{hete} = \Delta G_{homo} f(m, x) \quad (5.1)$$

where ΔG_{hete} and ΔG_{homo} represent the free energy barrier of heterogeneous nucleation and homogenous nucleation, respectively, and $f(m, x)$ is the geometric factor, with the range from 0 and 1. The free energy barrier of heterogeneous nucleation on these samples with the silicone oil infusion tended to be closer to that on ideal oil-lubricated surfaces [37]. More energy was needed to overcome the energy barrier and initiate the whole ice nucleation, which led to the delayed ice formation. The icing time on NP-20GO3Al was 78 ± 2.9 s, which was even higher than that of 20SO3Al. As shown in Table 5.4, there was phase change taking place at the temperature range between -16.0 to 2.4 °C, leading to the release of heat, which also prolonged the whole icing duration. But for NP-20CO3Al, there was some coconut oil diffused out to the sample surface from the resin because of the temperature decrease. Because the temperature range for phase change is $6.7 \sim 25.5$ °C, the remaining coconut oil on the surface would solidify when the temperature was lower than 0 °C, forming the structure shown in Figure 5.11. Because of the change, the WCA also increased from 95.5 ± 1.5 ° to 108.9 ± 1.7 °. The contacting area between the sample surface and water droplet was decreased, as well as the areas for ice nucleation, which also introduced some delay to the icing time of water droplet to some extent. The existence of solidified coconut oil

layer could further help with the overall thermal resistance increase. Therefore, the icing time on NP-20CO3Al increased to 82 ± 3.1 s.

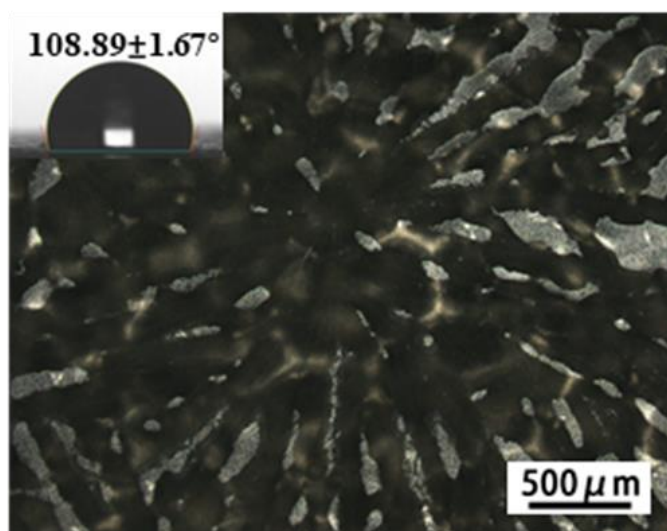


Figure 5.11 Optical microscope and WCA images of formed coconut solid layer on NP-20CO3Al at the temperature below 0 °C.

The proposed groundnut oil and coconut oil modified icephobic surfaces demonstrated advantages in anti-icing aspects. With the addition of phase change materials (PCMs), a certain amount of heat is released during the temperature reduction. More latent heat would be released with more PCMs included. Reports from the current literatures show that the freezing delay performance of supercooled water droplets at -20 °C on fluorosilicone copolymer coating with phase-change microcapsule modification was initiated at 119 s, which is a bit longer than our results [362]. Another study indicated that the freezing time of SiC/SiO₂ coated copper foam has been prolonged to 82 s compared to pristine copper substrate (-30 °C) [363].

5.3.2 Anti-frost performance by frost growth test

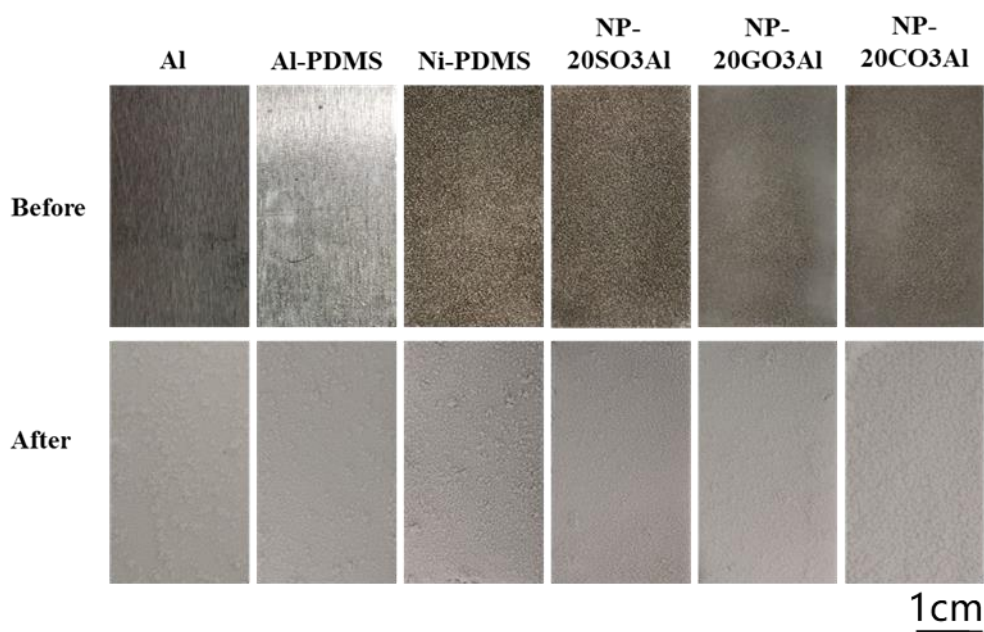


Figure 5.12 Surfaces images of Al, Al-PDMS, Ni-PDMS, NP-20SO₃Al, NP-20GO₃Al and NP-20CO₃Al before and after frost accumulations.

The frost formation tests were carried out to evaluate the anti-icing performance of different samples. Figure 5.12 illustrated the images of surface morphology of Al, Al-PDMS, Ni-PDMS, NP-20SO₃Al, NP-20GO₃Al and NP-20CO₃Al before and after frost accumulation. It was also observed that all of the three sample surfaces had been covered by the formed frost after the frost formation tests. It was also not obvious to find the difference among the samples.

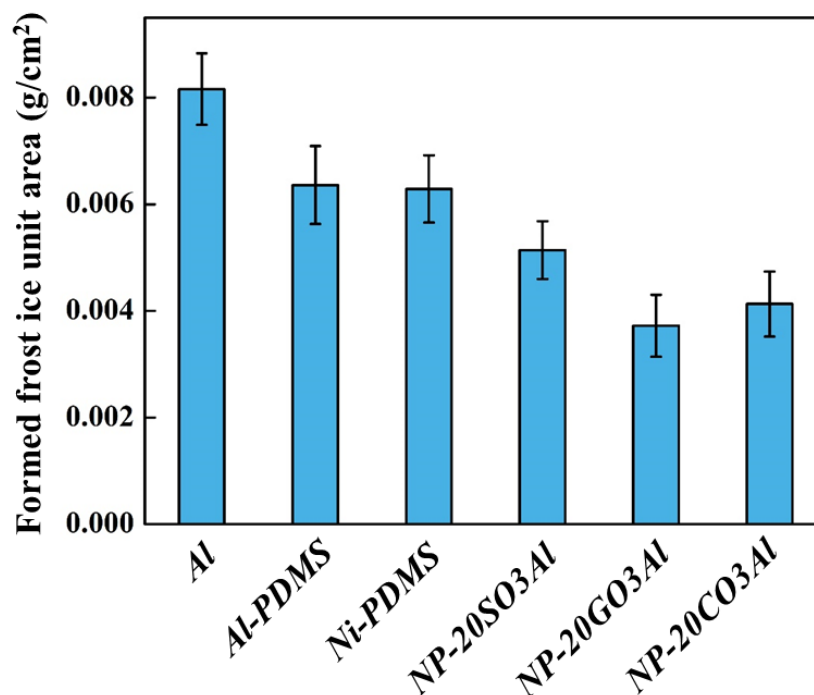


Figure 5.13 Increased mass of formed frost on Al, Al-PDMS, Ni-PDMS, NP-20SO3Al, NP-20GO3Al and NP-20CO3Al.

Figure 5.13 displayed the increased mass of formed frost per unit area on different samples. The frost formed per unit area on Al was $8.2 \pm 0.7 \text{ mg/cm}^2$. It then decreased to $6.3 \pm 0.7 \text{ mg/cm}^2$ after being covered with a PDMS layer on top of Al-PDMS. The reason may be ascribed to the improved hydrophobicity (the static WCA increased to $104.9 \pm 0.6^\circ$). While for Ni-PDMS, the extent of formed frost was similar to that of Al-PDMS, the value of the increased mass of formed frost on Ni-PDMS was $6.2 \pm 0.6 \text{ mg/cm}^2$. The addition of silicone oil into the Ni-PDMS system could easily increase the free energy barrier for ice nucleation, so for NP-20SO3Al, the formed frost per unit area was lowered to $5.1 \pm 0.5 \text{ mg/cm}^2$. As discussed before, there was exothermic reaction taking place during the frost formation tests, so NP-20GO3Al possessed the lowest value, $3.7 \pm 0.6 \text{ mg/cm}^2$. As for NP-20CO3Al, the formed frost per unit area was measured to be $4.1 \pm 0.6 \text{ mg/cm}^2$. There would be a formed layer of solidified coconut oil on NP-20CO3Al surface if the temperature was below 0°C . The static WCA increased because of the existence of coconut oil layer (as shown in Figure 5.11). As is

known, the frost formation process consists of three steps: crystal growth period, frost layer growth period and frost layer full growth period [364]. During the crystal growth period, ice crystals would form on cold surfaces. Enhanced surface hydrophobicity reduces the number of rod-shaped ice crystals and subsequent frost branches, thereby decreasing the formation of glaze ice. Additionally, the exothermic phase change process also contributes to the reduction in glaze ice formation. In this way, the formed frost on NP-20CO3Al was also very low compared to other samples.

5.3.3 Ice adhesion strength and durable performance of different sample surfaces

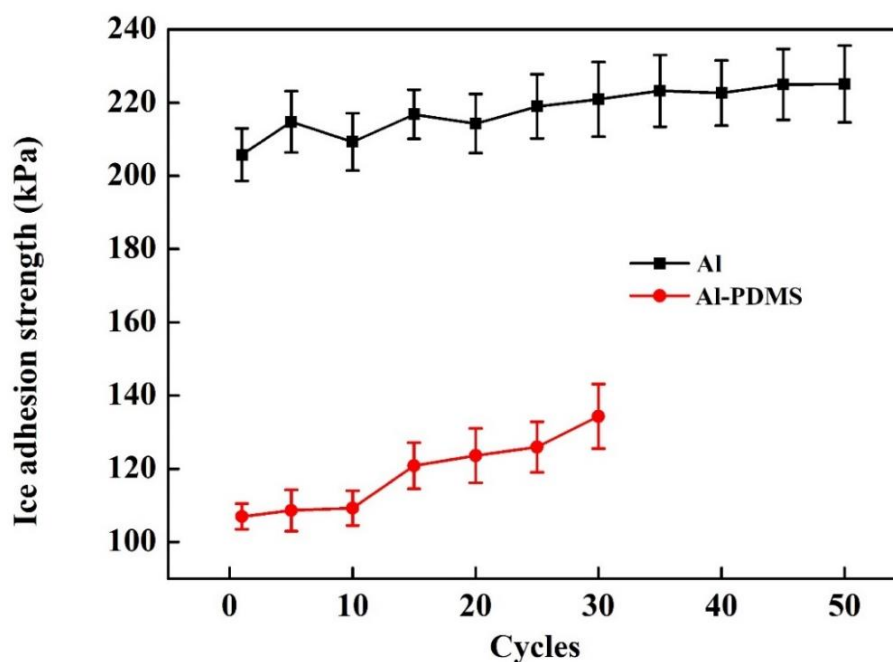


Figure 5.14 Ice adhesion strengths of Al and Al-PDMS during 50 icing/de-icing cycles.

Figure 5.14 showed the detailed changes of ice adhesion strengths of reference samples, including pure-Al and Al-PDMS, during 50 icing/de-icing cycles. For Al plate, the measured shear strength was maintained at around 220 kPa. With a PDMS layer deposited on top, the adhesion strength decreased to 105.9 ± 3.5 kPa. But it was observed that the layer surface had been destroyed during the 30 cycles, there was peeling and breakage emerged, which led to the icephobicity degradation. The

increasing ice adhesion strength could be largely related to the continuous abrasions of PDMS layer.

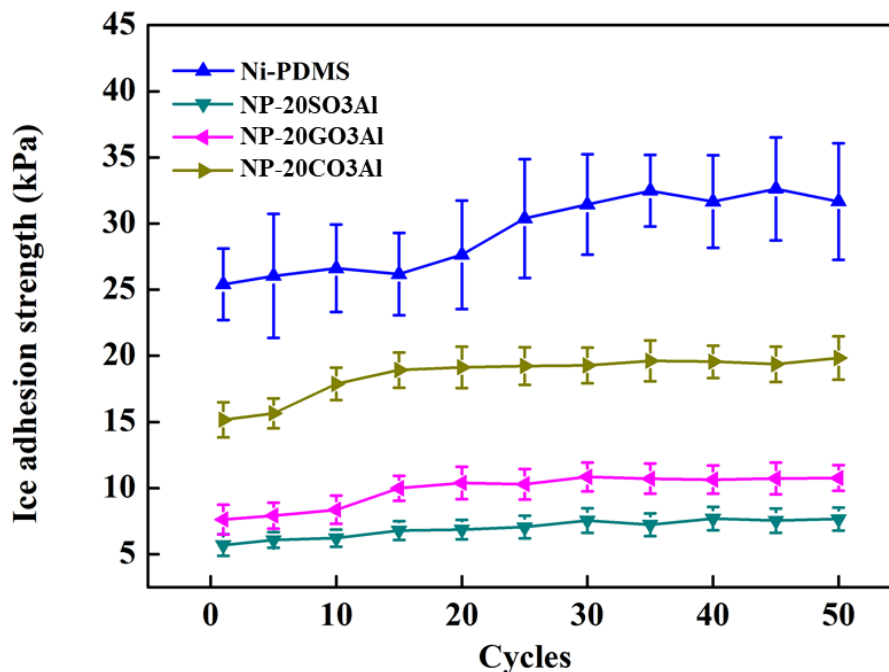


Figure 5.15 Ice adhesion strengths of Ni-PDMS, NP-20SO3Al, NP-20GO3Al and NP-20CO3Al.

Figure 5.15 depicted the ice adhesion strength of different samples including Ni-PDMS, NP-20SO3Al, NP-20GO3Al and NP-20CO3Al during the cyclic icing/de-icing tests. With the replacement of Ni scaffolds instead of Al plate, the average values of ice adhesion decreased to 29.3 ± 2.9 kPa. The causing factor here was that there would be different deformations on the sample surfaces under the same de-icing force due to the big difference in elastic modulus between the Ni scaffolds and PDMS fillings [40]. The elastic modulus of PDMS polymer 2.58 MPa considering the layer thickness and 10:1 curing agent ratio [365]. While for the used Ni scaffolds in this work, it possessed the porosity of around 95%, the elastic modulus could then be inferred with the value of around 60 MPa from the slope of the unloading load-deflection curve taken at approximately the yield strength of the nickel foams [366]). This could introduce the micro-crack initiation mechanism in the ice-solid interfacial areas, and induce the ice

detachment. With the additions of coconut oil and groundnut oil, there would be internal porosities emerging inside the structure and the third gaseous phase was then introduced, which further increased the mismatch gap between the different parts of the material. This could in turn promote the occurrence of micro-cracks at the solid-ice interfaces.

While for NP-20CO3Al, there were some portions of coconut oil diffusing out to the surface because of the low temperature, the released coconut oil remained in solid state at $-20\text{ }^{\circ}\text{C}$, leaving the surface with a layer of solid coconut oil. Because of that, the surface roughness increased which could increase the ice adhesion strength. The ice adhesion strength of NP-20CO3Al was around 18 kPa, which mainly contributed to the interaction effects of solid coconut oil existence and micro-crack initiation mechanism.

As for NP-20GO3Al, the temperature range of phase change was from $-15.9 - 2.4\text{ }^{\circ}\text{C}$, so there was also a thin layer of groundnut oil existing on the surface. It could introduce some delay to the icing process. Besides, the groundnut oil layer was not very thick, so it would not lead to a similar roughness enhancement effect in coconut oil sample (NP-20CO3Al). The measured ice adhesion strength of NP-20GO3Al was around 9 kPa, which was a bit lower than that of NP-20CO3Al. For NP-20SO3Al, the surface shore hardness had been significantly modified by the incorporation of silicone oil, which enlarged the difference in elastic modulus. This also promoted the working effect of micro-crack initiation and helped with the emergence of micro-crack in the interfacial areas. It could also be found that the sample surface was smoother than before with silicone oil addition. Based on the several factors mentioned above, the ice adhesion strength of NP-20SO3Al decreased to about 7 kPa.

The variation in weight percentage of different samples during the 50 icing/de-icing cycles was shown in Figure 5.16. It could be found that the mass of all involved samples showed no obvious change during the whole cycle except Al-PDMS, which suffered surface breakage and mass loss after around 30 cycles. Combined with the results in

Figure 5.15, the ice adhesion strength of oil-infused samples including NP-20SO3Al, NP-20GO3Al, NP-20CO3Al all remained stable during the icing/de-icing cyclic tests. The reasons for the stable ice adhesion strength of the three samples were also different from each other. For NP-20SO3Al, since PDMS and silicone oil possess the same chemical properties, most of silicone oil contents would diffuse into the voids of the cross-linked PDMS network. With the incorporation of Al aerogel, the added silicone oil could be better preserved in the PDMS matrix. Thus, there was no obvious silicone oil depletion taking place during the cyclic tests, the good icephobic performance was always kept. While for NP-20GO3Al and NP-20CO3Al, the diffused oil on the sample surfaces always remained in the solid state, which in turn lowered the loss of oil content and helped with the low ice adhesion strength.

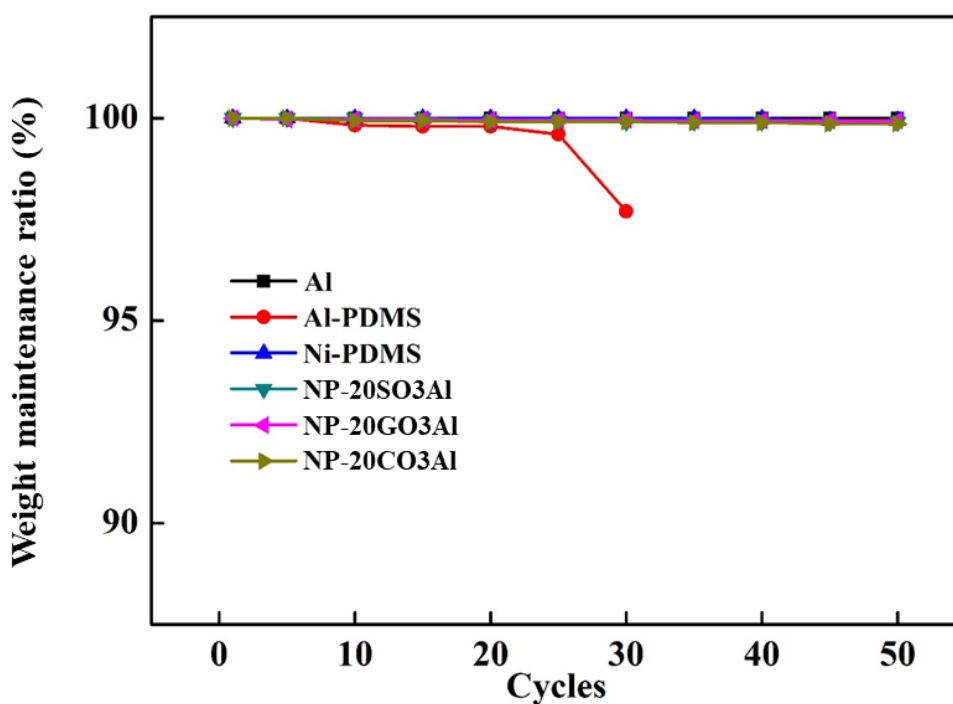


Figure 5.16 Weight maintenance ratio changes of different samples during 50 icing/de-icing cycles.

Compared with Shen's result, the de-icing ability of F-SiO₂@PDMS coatings retained high stability at 26.3 kPa (ice adhesion strength) under the conditions of 30

icing/deicing cycles [367]. Considering Zhang's icephobic construction, which mainly used peanut oil infused porous PDMS, the drain of lubricant was significantly slowed down. Low ice adhesion strength around 16 kPa was maintained even after 30 icing/deicing cycles [270]. Besides, the hybrid polysiloxane coating sample kept exhibiting low ice shear strength value at 35.2 ± 1.6 kPa after 15 icing/deicing cycles [368]. In comparison with the aforementioned results, the sample in this work exhibited a consistent deicing performance, characterized by a sustained low ice bonding strength of 10.8 ± 0.9 kPa over a period of 50 icing/deicing cycles.

5.4 Water Condensation and Icing Study on Phase Change Liquid Modified Icephobic Structures

5.4.1 Icing formation process using ESEM

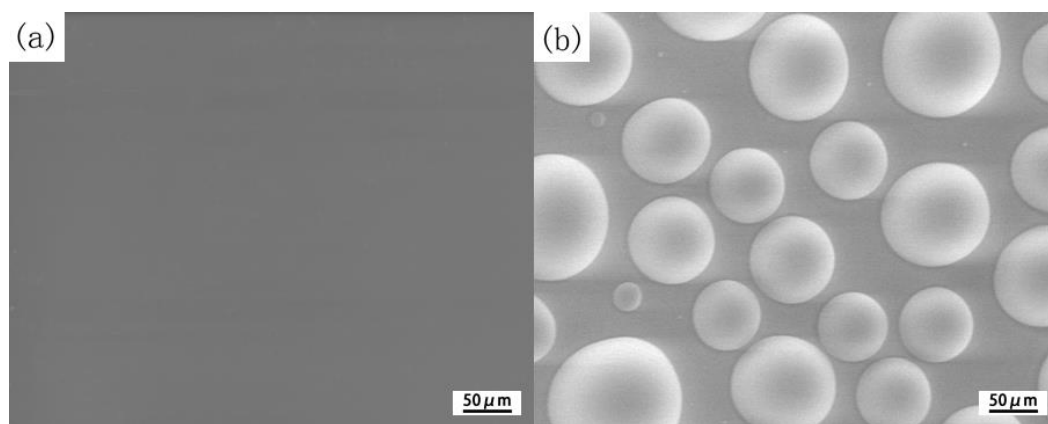


Figure 5.17 Surfaces images of (a) as-prepared NP-20SO₃Al; (b) NP-20SO₃Al being wetted via ESEM.

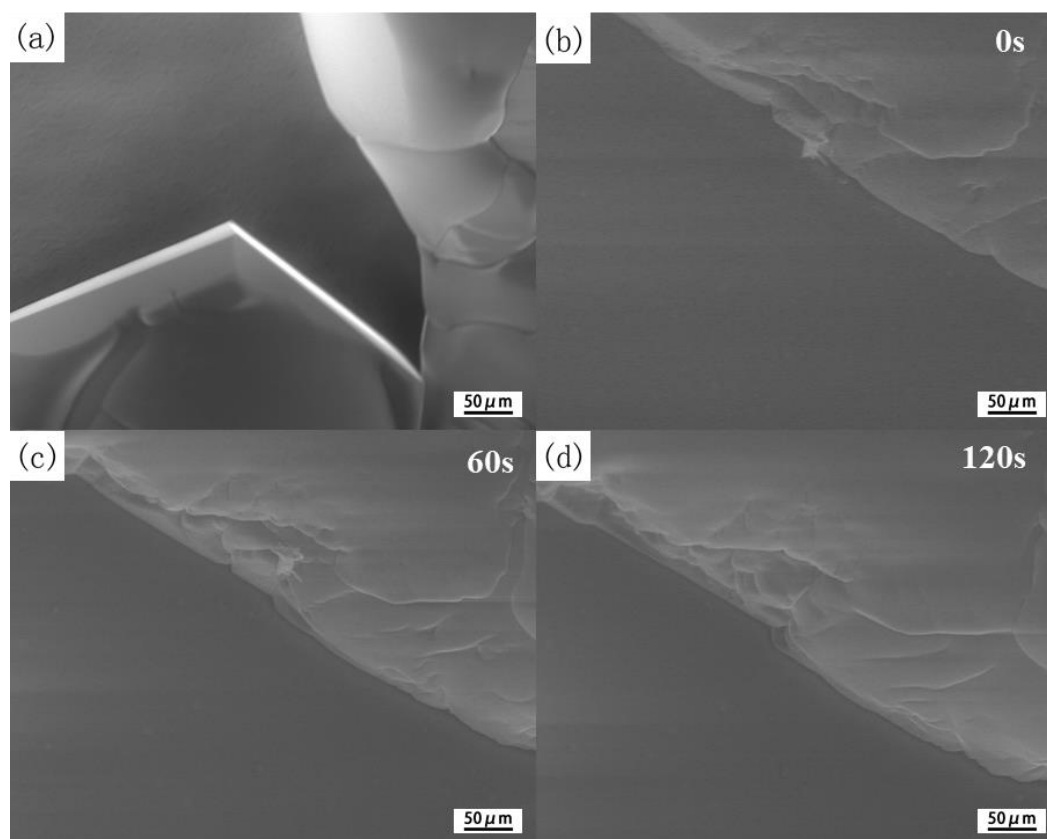


Figure 5.18 ESEM observation of NP-20SO₃Al: (a) Ice growing near the edge of the sample; (b)-(d) Ice growing process.

Figure 5.17 displayed the surface state of NP-20SO₃Al without/with being wet. It could be seen that the sample surface was flat and smooth with no water on top before the water condensation. Then spherical droplets with different sizes emerged and distributed uniformly on the sample surface during the wetting process since supercooled water droplets started to condense. The remaining water droplets could evaporate simultaneously when the icing process took place. The ice nucleus would first form on the sample holder, not on the sample surface due to the anti-icing capability, the formed nucleation points then grew into ice crystals and spread to other areas of the samples. Compared to the icephobic sample surface, the sample holder that is made up of aluminum alloys was more prone to initiation of ice nucleation. Figure 5.18 (a) indicated that ice normally grew at the marginal areas of the sample, while the detailed ice growing process of NP-20SO₃Al was illustrated in Figure 5.18 (b)-(d). Because of the smooth surface and anti-icing performance, the growth direction of the formed ice

on the surface was from the edges to the central areas, and the growth rate of the ice was calculated to be $0.4 \pm 0.04 \mu\text{m/s}$.

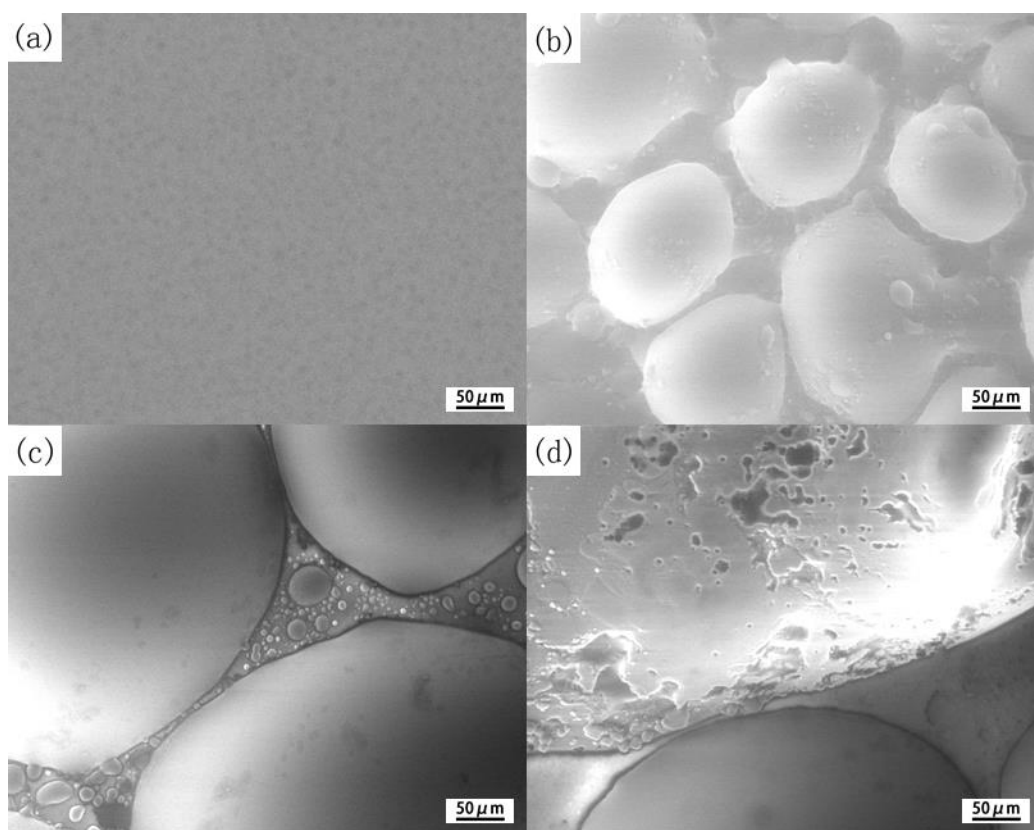


Figure 5.19 Surfaces images of NP-20GO3Al (a) without being wetted; (b) with being wetted at 2 °C; (c) with being wetted at -5 °C; (d) formed ice via ESEM.

Figure 5.19 (a) to (c) showed the detailed surface states of NP-20GO3Al in the initial state, being wetted at -5 °C and 2 °C, respectively. It was clear to find that the surface in the initial state showed no obvious feature, which was almost the same as SEM image of the surface, only some small and shallow cavities could be observed as distributed uniformly on the surface. By controlling and decreasing the temperature inside the observation chamber, some groundnut oil was found to be released from the internal parts of the sample. With the humidity increasing, the sample was then wetted by the condensed water droplet. These droplets could attach and stay onto the released oil layer, forming a composite structure. In this way, the edges of the droplets also became not very clear, as indicated in Figure 5.19 (b). As the temperature kept decreasing, phase change took place among the surface oil layer, they transformed from liquid state to

solid state, making the edges of the water much clearer than before, which was evidenced by Figure 5.19 (c). Due to the sudden environmental condition change, water droplets with small volumes evaporated once the icing phenomenon started, while droplets with large volumes would not disappear, they formed into in-situ state ice at the previous positions. The main factor for this phenomenon was that the surface became less smooth after the oil layer solidified, which made it easier for the attachment of ice nucleus. So, some of the large droplets could form the in-situ state ice, as indicated in Figure 5.19 (d).

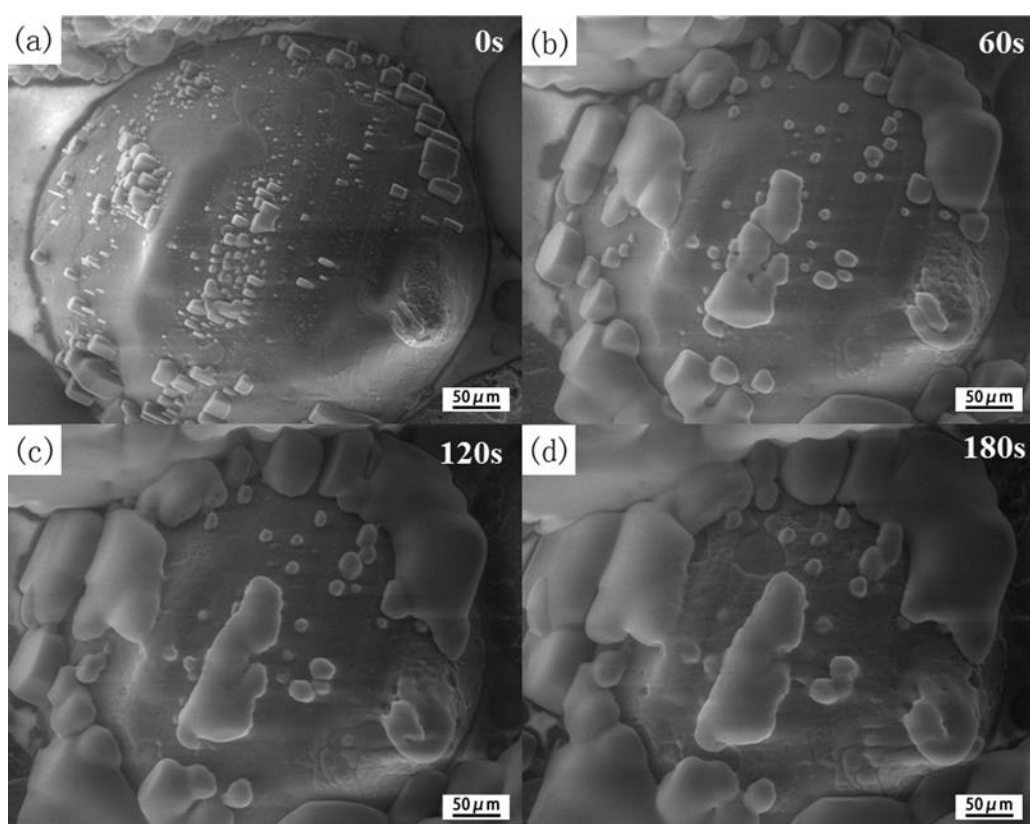


Figure 5.20 ESEM images of ice growing on the initial-formed ice block of NP-20GO3Al surface with different durations (a) 0 s; (b) 60 s; (c) 120 s; (d) 180 s.

Figure 5.20 (a)-(d) exhibited the detailed ice growing processes on initial-formed ice on NP-20GO3Al. It was found that the ice nucleation points were mainly located at the hierarchical surface areas, the formed ice nucleus then integrated with the atmospheric water molecules and gradually grew into ice crystals. With the continuous growth of the ice crystal, they could then cover the initially formed ice. As mentioned before,

some droplets with big volumes could grow in In-situ state, a majority of the ice nucleation occurred on the sample holder and spread gradually to the central areas.

Figure 5.21 (a)-(d) showed the ice growing process on NP-20GO3Al surface. Ice crystals formed at the marginal areas. And the initial-formed ice kept growing on the sample surface. They finally covered the whole sample surface. It was calculated that the growth rate of ice crystal in one direction of the sample surface was $0.3 \pm 0.06 \mu\text{m/s}$. It is also thought that the ice growth rate could not reflect the actual speed of the ice coverage spread because the existence of initial-formed ice could make it even higher than the actual ice growth speed.

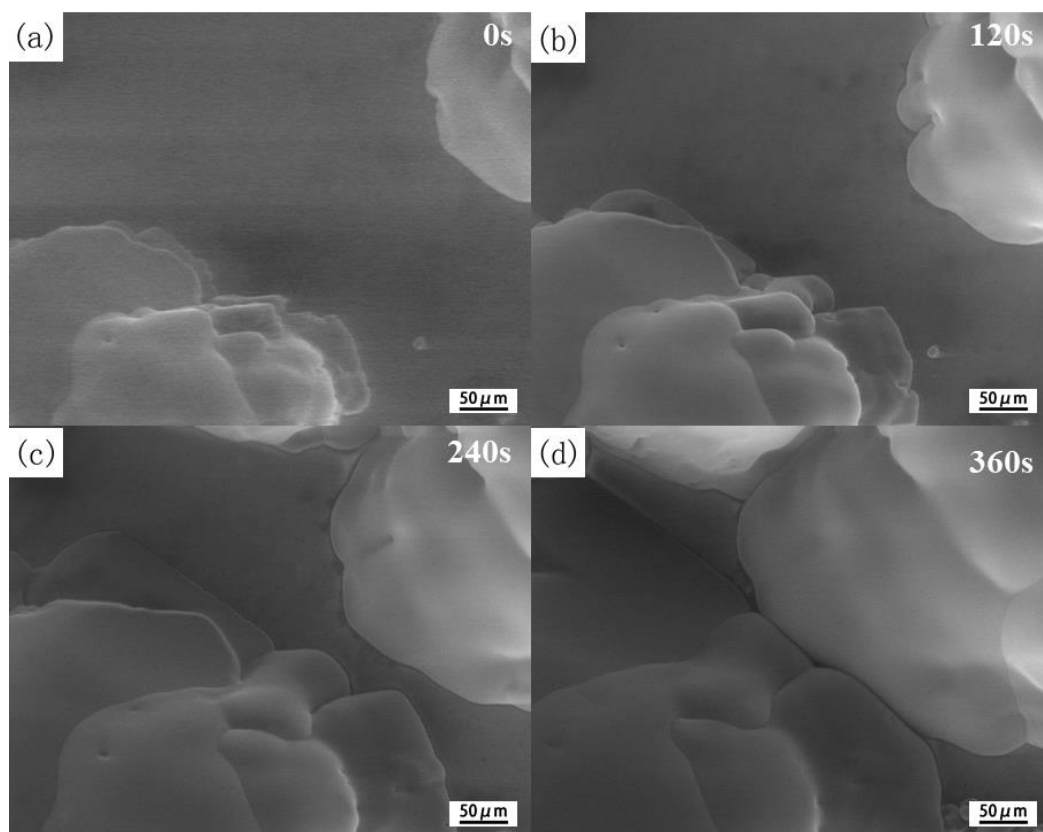


Figure 5.21 ESEM images of ice growing on NP-20GO3Al surface via different durations (a) 0 s; (b) 120 s; (c) 240 s; (d) 360 s.

Figure 5.22 (a) and (b) depicted the surface states on NP-20CO3Al without/with being wet. It is clear to find the surface in the initial state (without being wetted) was similar to that shown in SEM image. The water droplets were all scattered on the sample

surface acting with different sizes and shapes (spherical or axiolitic). There was a small piece of ice crystal formed at the interfacial areas between the solid surface and big volume of water droplets when icing started to occur, which were also circled in red and shown in Figure 5.22 (c). The final results were that the water droplet with a small volume would evaporate during the icing, while the big water droplet formed into In-situ state ice that was shown in Figure 5.22 (d).

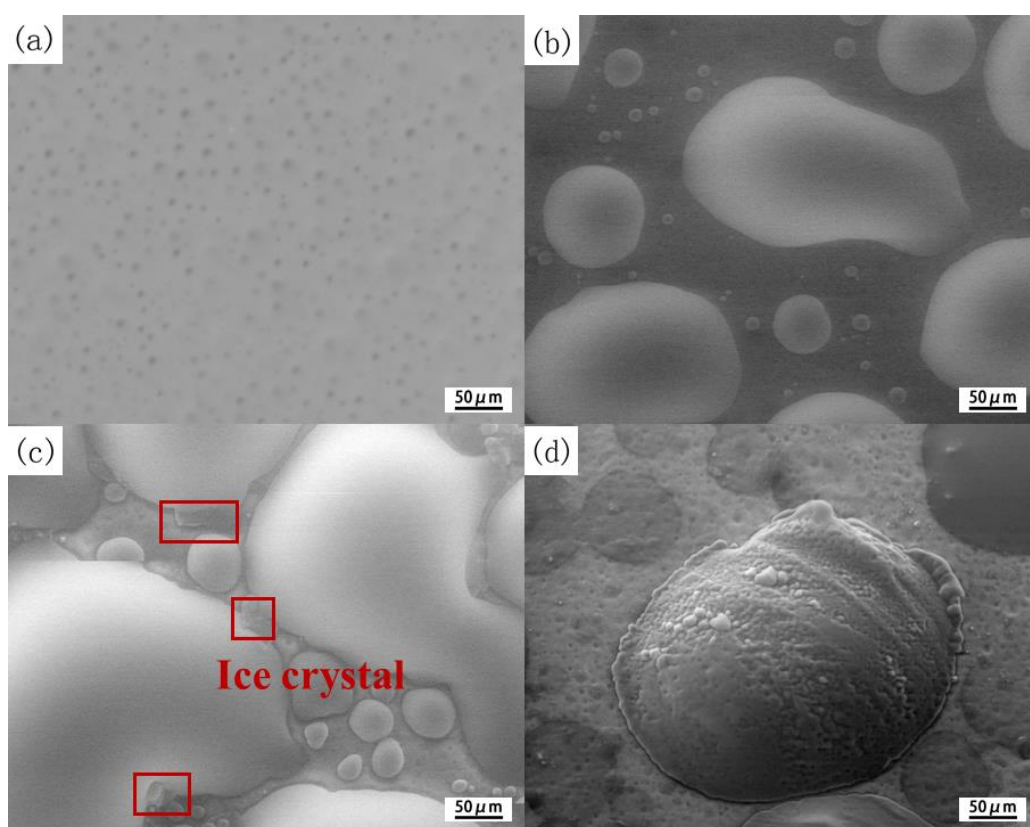


Figure 5.22 Surfaces images of NP-20CO₃Al (a) without being wetted; (b) with being wetted at 2 °C; (c) with being wetted at -3 °C; (d) formed ice via ESEM.

Figure 5.23 (a)-(d) showed the icing processes of the initial-formed ice on NP-20CO₃Al. It could be found that ice nucleation points were formed at the marginal areas of initially-formed ice, and it could work with the water molecules in ambient air to generate ice crystals. The ice kept growing in size and integrated with the surrounding ice crystals, which also kept growing later. It needed to be noted that the water droplets with small volumes in supercooled state would evaporate gradually with the icing

duration. The reason could be that the atmospheric relative humidity kept decreasing with more and more formed ice, some of the small water droplets that attached to the surface would then disappear.

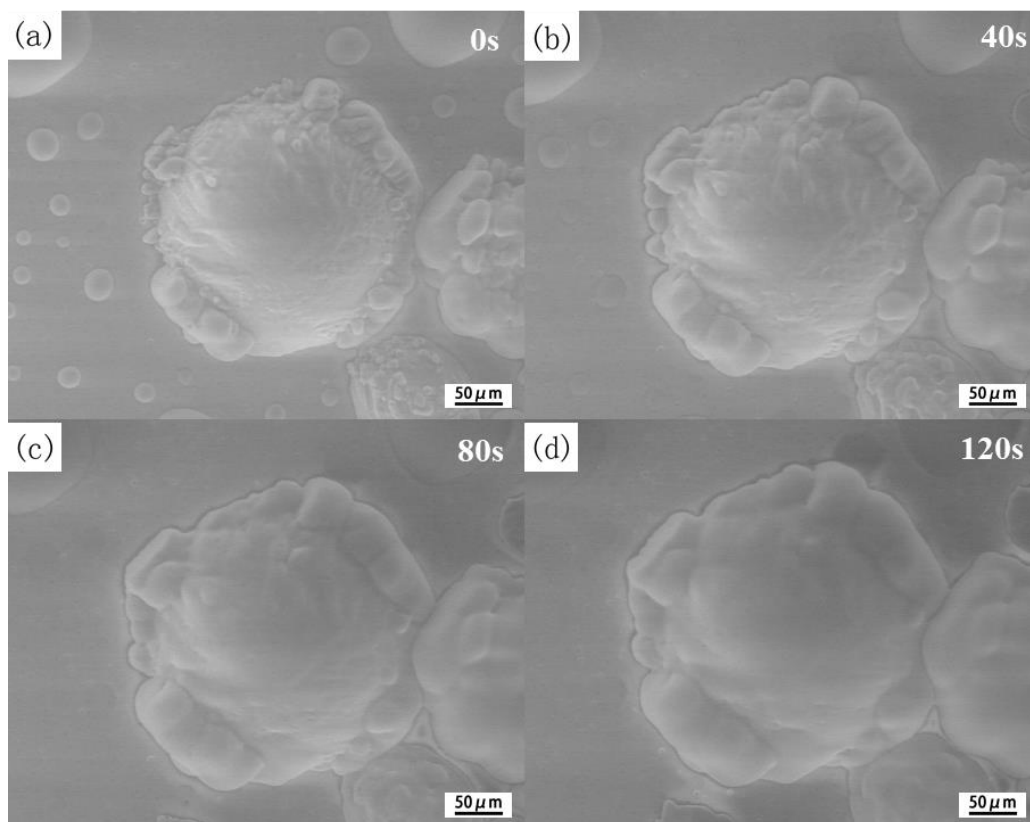


Figure 5.23 ESEM images of ice growing on the initial-formed ice block of NP-20CO₃Al surface during different durations (a) 0 s; (b) 40 s; (c) 80 s; (d) 120 s.

Figure 5.24 (a)-(d) displayed the detailed process of ice growth on NP-20CO₃Al. It could be seen that the big block of ice crystal kept spreading on the surface and they finally merged with each other, which was quite similar to the process taking place on NP-20GO₃Al. But the speed of ice spread was higher than that on NP-20GO₃Al, which could reach $0.6 \pm 0.04 \mu\text{m/s}$. Here, the calculated speed for the ice coverage should be lower than the actual speed due to the existence of in-situ ice, indicating the similar reason as NP-20GO₃Al.

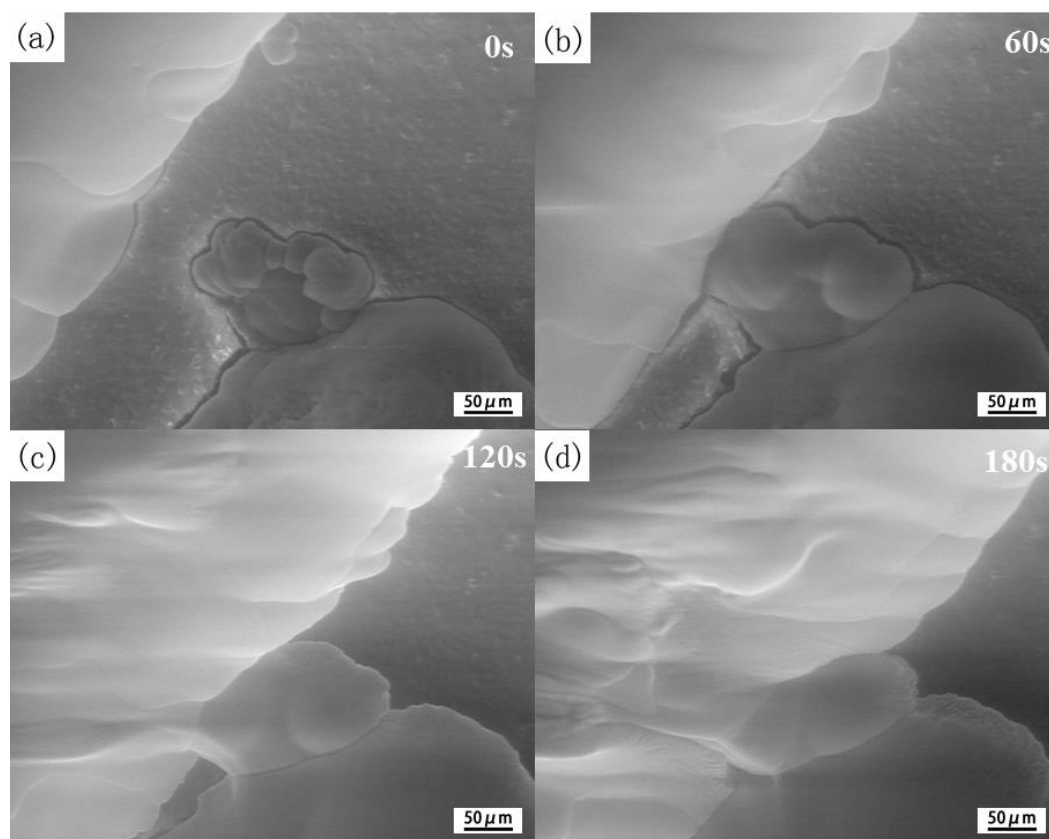


Figure 5.24 ESEM images of ice growing on NP-20CO₃Al surface during different durations

(a) 0 s; (b) 60 s; (c) 120 s; (d) 180 s.

5.4.2 Ice diminishing process via ESEM observation

The detailed ice diminishing processes on the surfaces of NP-20SO₃Al, NP-20GO₃Al and NP-20CO₃Al were displayed in Figure 5.25, Figure 5.26 and Figure 5.27, respectively. With proper humidity and temperature control, the existing ice would sublime [[369](#), [370](#)].

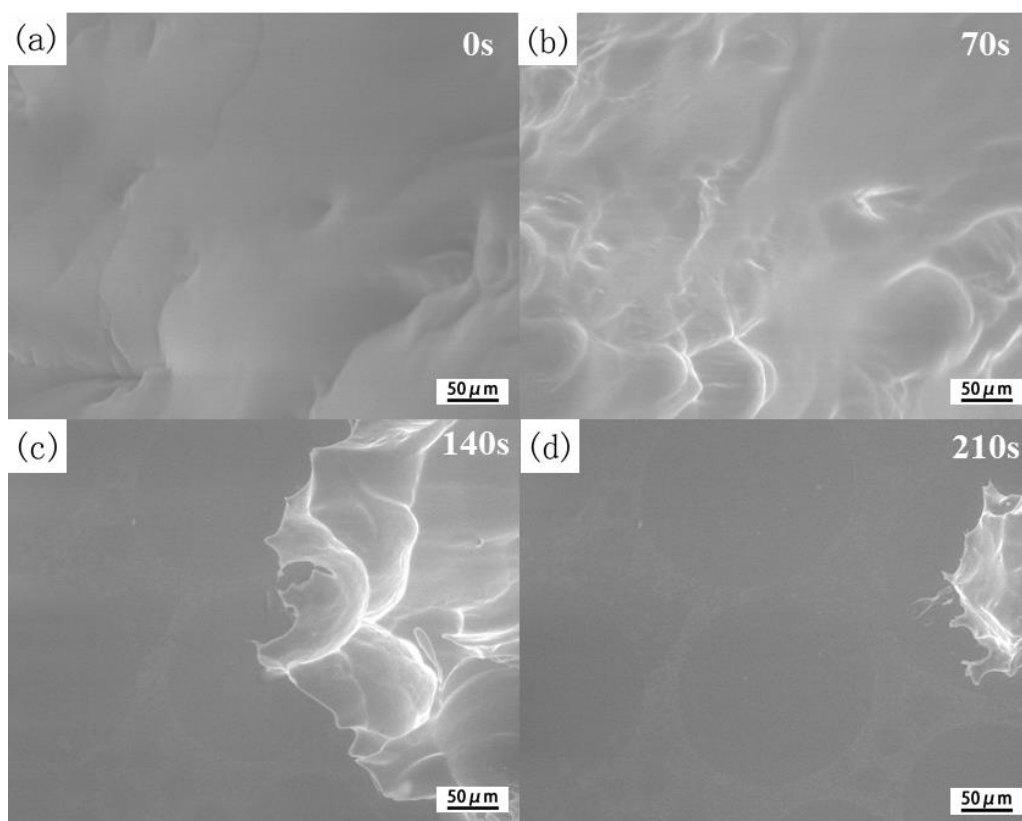


Figure 5.25 Ice diminishing process on NP-20SO₃Al surface (a) $t=0$ s; (b) $t=70$ s; (c) $t=140$ s; (d) $t=210$ s.

First, for NP-20SO₃Al, the surface was covered by a big block of ice. With reduced system humidity, the snapshot images of the whole ice diminishment were illustrated. It could also be observed that the surface morphology of NP-20SO₃Al remained intact during the receding process of the ice crystal. It took over 210 s to sublimate all of the ice in the view field. The ice layer first became thinner from Figure 5.25 (a) to (b), which could be observed from the changing morphology of the covered ice. As shown in Figure 5.25 (c), due to the smooth and flat surface structure, few anchoring points could be found on the sample surface. The formed ice block has much less ice-surface contact area with the sample surface. It could also verify the low value of ice adhesion strength, showing good de-icing performance. It was also thought that there was no specific ice receding direction since the surface could be seen as a homogenous surface.

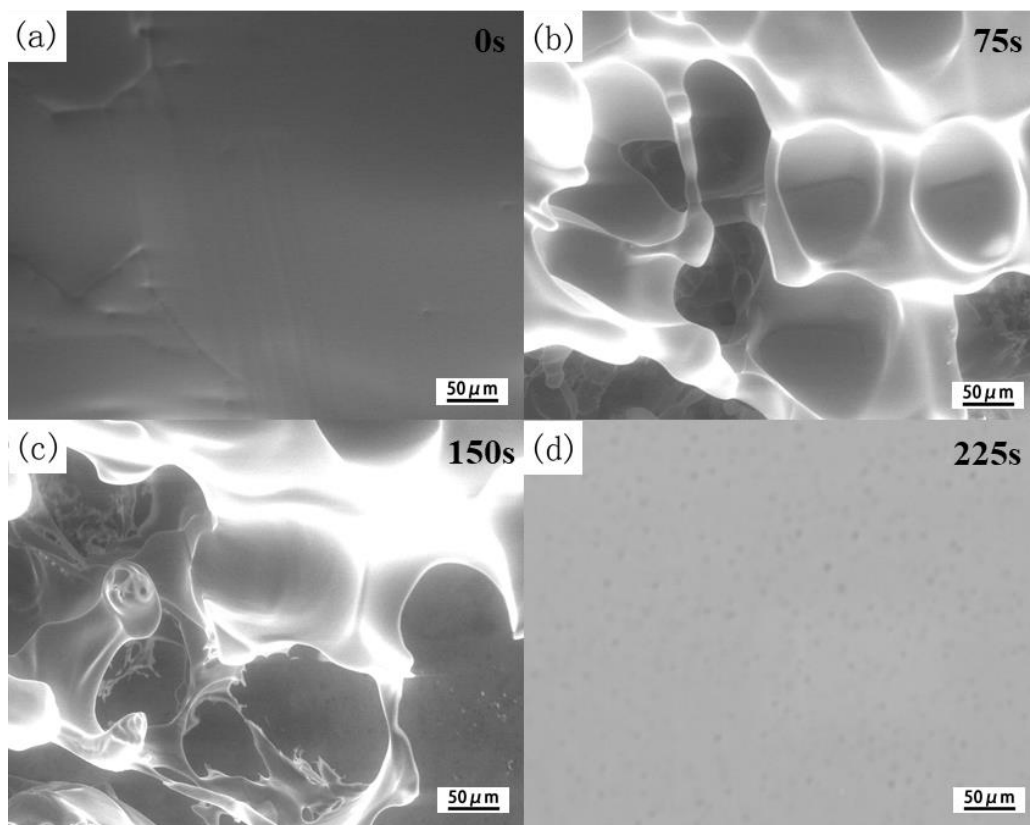


Figure 5.26 Ice diminishing process on NP-20GO3Al surface (a) $t=0$ s; (b) $t=75$ s; (c) $t=150$ s; (d) $t=225$ s.

While for NP-20GO3Al, the initial ice-covered state was similar to that on NP-20SO3Al. The ice sublimation process also occurred by monitoring the chamber conditions. It could be observed that the ice retracting process was quite similar to that took place on NP-20SO3Al. The ice would diminish along some directions, which mainly showed an upward retraction. Some morphology changes could also be clearly observed on the formed ice, as shown in Figure 5.26 (b) and (c). It also took around 220 s for the ice sublimation process to finish. This indicated the similar role between silicone oil and groundnut oil in the ice retraction process. The sample surface morphology remained unchanged during the whole process. For NP-20SO3Al and NP-20GO3Al, they both showed smooth surfaces, so the overall speeds of sublimation of the two samples were also close to each other.

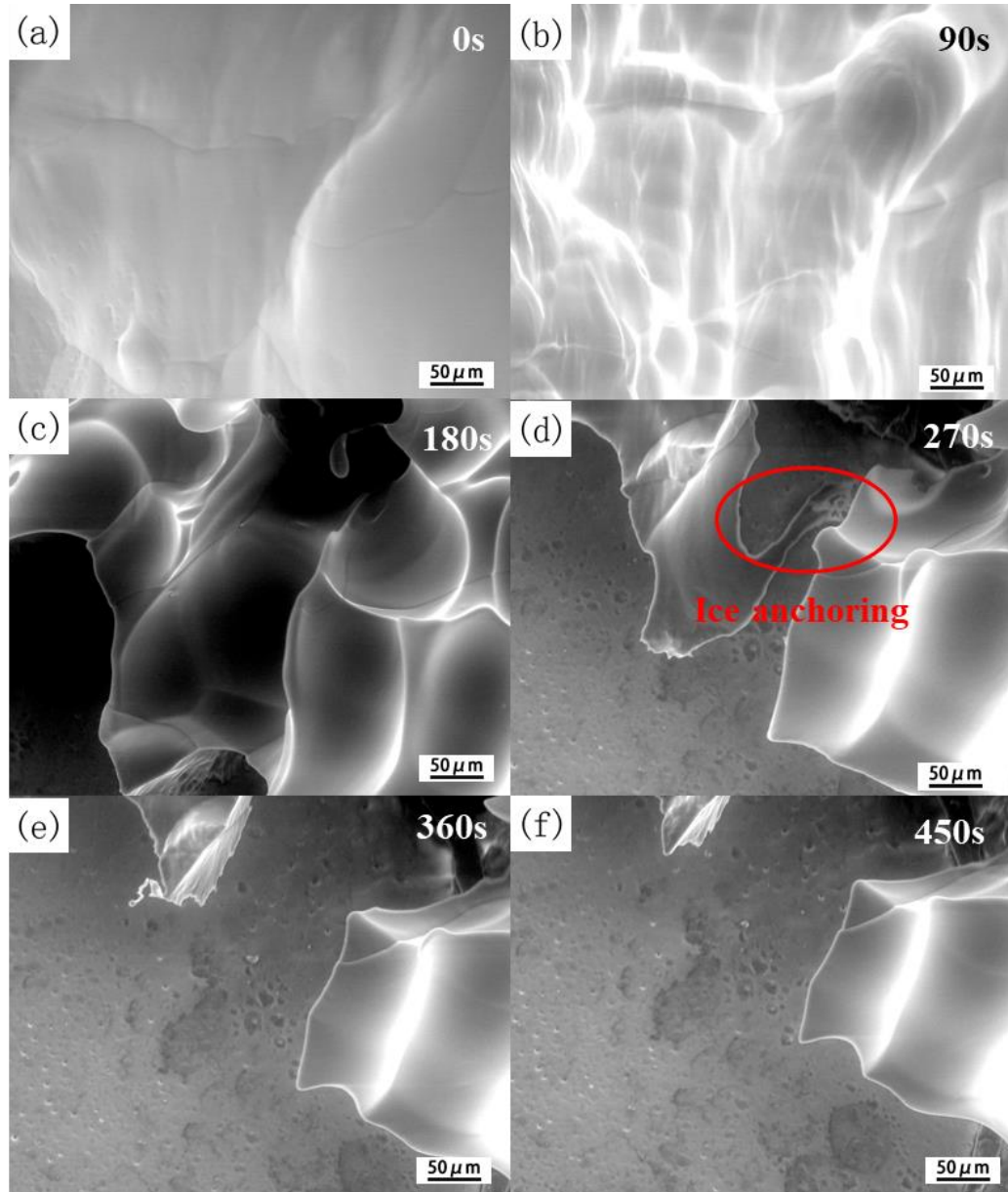


Figure 5.27 Ice diminishing process on 20CO3Al (a) $t=0$ s; (b) $t=90$ s; (c) $t=180$ s; (d) $t=270$ s; (e) $t=360$ s; (f) $t=450$ s.

Figure 5.27 displayed a more detailed process for the whole ice sublimation on NP-20CO3Al. The whole duration was prolonged to 450s. From Figure 5.27 (a) to (b), the ice layer becomes thinner and the edge changes from rounded to angular. By comparing it with previous images in Figure 5.19, the direction of the disappearance of the formed ice crystal was just opposite to the propagation direction. Due to the existence of surface solid coconut oil layer and increased surface roughness, the surface roughness could increase with the surface undulations (which could be easily verified from Figure 5.27

(d)). Nevertheless, it could lead to some mechanical interlocks between the ice and surfaces, as shown in Figure 5.27 (e), which may provide some difficulties in the ice removal. The increased mechanical interlocks also led to higher ice adhesion and further the longer duration of ice sublimation. From this point, it can be concluded that the different oil infusions would affect the ice formation and ice disappearance.

5.5 Mechanisms on Icephobicity and Durability Improvements Derived from Oil Infusion

5.5.1 Effect of different oil infusions in delaying ice/frost formation

The delay effect on the condensation mechanism of ice/frost introduced by the addition of groundnut oil was illustrated in Figure 5.28.

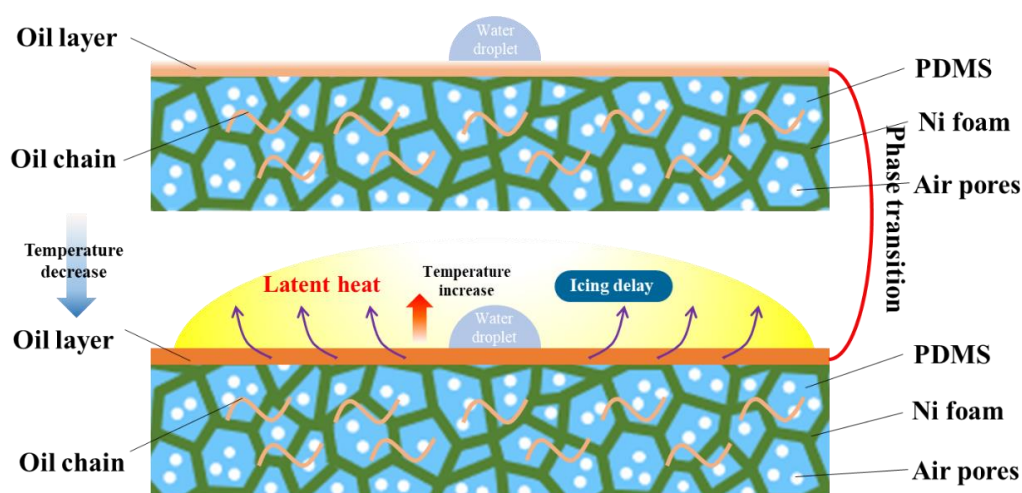


Figure 5.28 Schematic diagram of icing delay process.

With the temperature kept decreasing, there would be more oil diffused out to the surface, leading to the formation of thin oil layer on the sample surface. It was also obtained from the DSC results that the estimated phase changing temperature range of groundnut oil in NP-20GO3Al was from $-16.0\text{ }^{\circ}\text{C}$ to $2.7\text{ }^{\circ}\text{C}$. The phase change process would keep occurring within the temperature range and it was also an exothermic process [137]. The temperature at the sample and water droplet interfaces would not suffer a serious increase due to the continuous releasing of heat which came from the

phase change [371]. The decreasing trend of the temperature would be lowered and it then helped to delay the surface icing process.

The results from ice formation tests and static frost formation tests were also verified. It needed to be noted that the actual icing temperature for the supercooled droplet on NP-20GO3Al was the lowest among the samples even under high humidity (relative humidity: 98-100%), as shown in Table 5.4. This also indicated that the phase change mechanism of groundnut oil played a significant role in delaying the icing/frost formation process. In addition, the cavities formed by the volatilization behaviour of oil droplets during the curing process could also increase the overall thermal resistance and slowed down the cooling speed of the layer system [372], which contributed to the anti-icing performance to some extent.

Table 5.4 Ice formation temperature of different samples (humidity: 98% - 100%) via ESEM.

Samples	NP-20SO3Al	NP-20GO3Al	NP-20CO3Al
Ice formation Temperatures (°C)	-6	-10	-3

For NP-20SO3Al, because of the similar chemical properties between silicone oil and PDMS, most of the silicone oil would disperse uniformly in the PDMS filling and no internal cavity was formed. The diffused silicone oil layer was also thinner compared to the thickness of NP-20GO3Al and NP-20CO3Al, which has less impact on the anti-icing performance. For NP-20CO3Al, the surface remaining coconut oil layer solidified completely before the water froze into ice since the solidification temperature range of coconut oil is 6.7-25.4 °C. The formed coconut solid layer was also observed in Figure 5.11, which could help to increase the water contact angle and decrease the contact areas between water droplets and surfaces. Nevertheless, the existence of solidified coconut oil layer and internal gaseous cavities also contributed to the increase of thermal resistance of the system, which led to good anti-icing performance.

5.5.2 Influence of groundnut oil infusion in lowering ice adhesion strength

As indicated in Figure 5.29, there were three types of materials with different elastic modulus inside the NP-20GO3Al. The first one was the Ni scaffold, and the second material was the modified polymer after groundnut oil infusion, while the third phase was the internal cavities generated during the curing process which was filled with ambient air. Meanwhile, there would be some groundnut oil diffusing out from the polymer resin and forming a thin oil layer on the sample surface. The ice adhesion strength could be affected by the multi-phase composite structure from several factors: first, the shore hardness value of the resin was decreased and the difference in elastic modulus between polymer and Ni scaffolds was further enlarged due to the combined factors from groundnut oil infusion and introduced cavities, which was verified previously in Figure 5.8. The big difference in elastic modulus led to different micro-distortions on Ni scaffolds and PDMS fillings during the ice detachment. Then micro-crack could be initiated at the interfacial areas and weaken the adhesion between the formed ice and solid surface, which resulted in the decrease in ice adhesion strength. The micro-crack initiation mechanism during the ice detachment may be derived from the integrated factors of remaining smooth surface cavities and the difference in elastic modulus between Ni scaffolds and polymer fillings.

The incompatibility in interfacial deformation and inhomogeneity in stiffness between different phases were beneficial to the formation of the crack initiation mechanism [373]. The larger the difference in elastic modulus, the higher the difference in deformation between different phases, making it easier to initiate the micro-crack [139, 374]. On one hand, the diffused groundnut oil could fill in the internal cavities which came from the oil evaporation, making the sample surface smoother and avoiding the emergence of mechanical interlock during the de-icing processes. On the other hand, the diffused oil would transfer from liquid state to solid state, which lowered the oil depletion during the de-icing process. This enabled the good de-icing performance of the sample even after 50 icing/de-icing cyclic tests.

Though the decreasing effect of silicone oil addition on shore hardness was not as strong as that of groundnut oil, the silicone oil could remain in the liquid state at a temperature near the freezing point and enabled the surface with certain slippage by forming oil layer on top. So the ice adhesion strength of NP-20SO3Al was the lowest among the three. When moving to NP-20CO3Al, the rough structures on the solidified coconut oil layer could increase the degree of mechanical interlock between the surface and ice, which made the ice adhesion strength a bit higher than that of NP-2GO3Al.

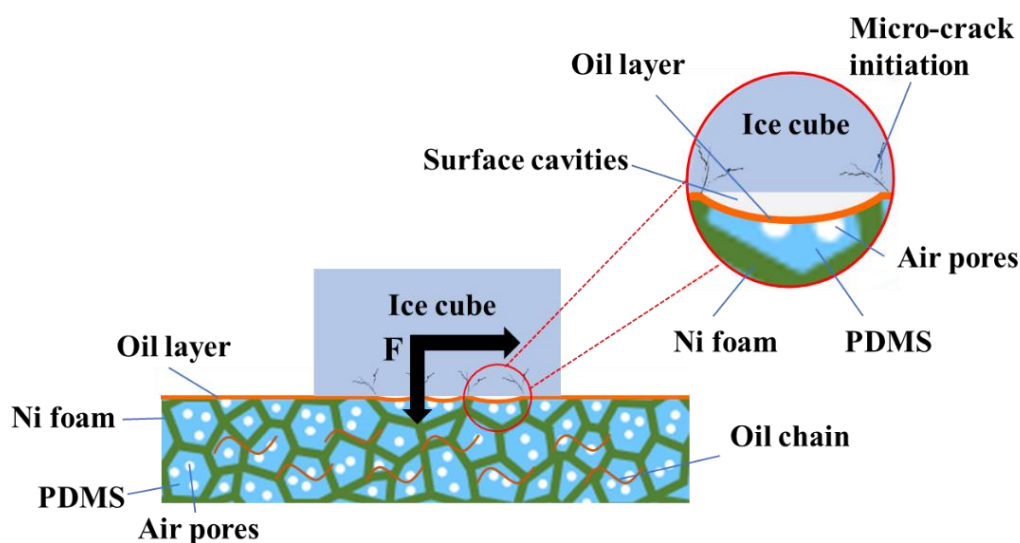


Figure 5.29 Schematic diagram of ice adhesion mechanism.

5.6 Summary

In summary, a new type of highly durable icephobic layer structures using porous Ni scaffolds, PDMS filling and phase change oil infusion by two-step methods (vacuum impregnation and spinning coating) was developed. With the adsorption effect from aerogel, the infused oil could be maximumly retained inside the polymer matrix. Compared with previous studies, the liquidous lubricating oil was replaced with phase change oil. The released heat derived from phase change oil could be applied to prolong the ice formation. Meanwhile, the phase change oil could prevent the oil depletion effectively during the de-icing process when compared to the liquidous lubricating oil that is easily worn, making the icephobicity more stable. In this study, some portions of the groundnut oil and coconut oil evaporated during the curing process of PDMS,

resulting in the uniform formation of internal and surface cavities. The infusion of layers at low temperature range could help to form an oil layer coverage on the sample surface. In the anti-icing performance tests, the emergence of internal cavities helped with the increase of thermal resistance in NP-20GO3Al and NP-20CO3Al. For NP-20GO3Al, there would be phase change taking place in the groundnut oil layer during the icing process, which also helped to delay the ice formation. But for NP-20CO3Al, the coconut oil layer in solid state increased the water contact angle as well as the thermal resistance, which helped to prolong the ice formation time. On the other aspect, the remaining surface mechanical interlock also increased due to the existence of solidified coconut oil layer, leading to the poorer de-icing capability among the three researched samples. Here, NP-20SO3Al showed a very low ice adhesion strength of only 7.6 ± 0.9 kPa after 50 icing/de-icing cyclic tests. Table 5.5 showed the comparison of the de-icing performance of NP-20SO3Al, NP-20GO3Al, and NP-20CO3Al with existing findings [270, 375-378]. The study suggested that while NP-20GO3Al ($\sim 10.8 \pm 0.9$ kPa at 50th cycle) and NP-20CO3Al ($\sim 19.8 \pm 1.7$ kPa at 50th cycle) exhibit higher ice adhesion strength than NP-20SO3Al, their overall performance remained low as a result of the introduced micro-crack initiation mechanism. For anti-icing performance, NP-20SO3Al did not appear as good as NP-20GO3Al and NP-20CO3Al. The ESEM observation results showed that NP-20GO3Al has good anti-icing performance with the icing temperature of as low as -10 °C under high humidity environment.

Considering both anti-icing and de-icing performance and the effect of infused phase change liquids, NP-20GO3Al exhibited a better icephobicity when compared to the three involved samples: the ice delay duration was 78.0 ± 2.1 s; the formed frost per unit area was 3.7 ± 0.6 mg/cm²; the ice adhesion strength was maintained at around 9.8 ± 1.2 kPa during the 50 icing/de-icing cyclic tests. The results indicated that the infusion of oil with phase change temperature around 0 °C could pose a positive effect on the icephobicity of the Ni/PDMS system. The design concept using the incorporation of phase change oil could provide new insight into the design of novel icephobic surfaces.

And it also provides new feasibility and insights into the R&D of durable icephobic surfaces.

Table 5.5 Ice adhesion strength results of reported icephobic surfaces versus icing/de-icing cycles

Reference	Surface type	Ice adhesion		
		1 st cycle (kPa)	Icing/de-icing cycles	Final cycle (kPa)
This work	NP-20SO3Al	5.7	50	7.6
	NP-20GO3Al	7.8	50	10.8
	NP-20CO3Al	15.0	50	19.8
Zhang [270]	PTSLIPS	4.5	30	16.0
Ragogna [375]	Silyated PAAO	22.0	4	359.0
	Oil-only SLIPS	36.0	10	115.0
	Ebecryl 350	12.0	3	96.0
	Ebecryl 1360	23.0	3	255.0
	Oil+350 SLIPS	8.0	5	17.0
	Oil+1360 SLIPS	7.0	5	22.0
Gao [376]	SLNTMC	11.8	21	20.0
			30	60.0
Wang [377]	SLIPNS05	19.1	20	64.6
	SLIPNS30	24.6	20	40.6
	SLIPNS60	48.0	20	162.2
Pakkanen [378]	LC-10-0	28.0	3	52.0
	LC-15-0	25.0	3	58.0
	LC-20-0	19.0	3	20.0

Chapter 6 Icephobic Layer System Modified by Ice Depressing Liquids

The comprehensive understanding of surface icephobicity could mainly be controlled from four different aspects [379]: thermodynamics of phase transition on supercooled water droplet surfaces, heat transfer during ice formation process, mechanics of iced surface systems, and long-term mechanical, chemical, and environmental durability controlled by material property. According to the above definition, ideal icephobic surfaces mainly are reflected by average delay time of ice formation, ratio of ice accretion on certain surfaces, ice adhesion at the ice-solid interface, and long-term effective surface ice repellency [380].

The current improvement in icephobicity is mainly reported in one or two aspects. Shen et al. prepared superhydrophobic nano structures with closed layered holes and open cones by wet chemical method. The icing delay time could be prolonged to 170 s [381]. But it is difficult for superhydrophobic structures to meet the demands of ice mitigation in different working environments [110, 382]. The superhydrophobicity could have deteriorated under low temperature and high humidity environments with high-speed impacting water droplets, and supercooled droplets could easily be fixed onto the hierarchical micro-nano coating structures, leading to ice accumulation and increasing the difficulty of de-icing process [18, 31, 239]. The problems of poor mechanical performance, fragility and lack of wear resistance among low-elastic icephobic coatings always limit the wide applications [383, 384]. It is a critical challenge to design icephobic structures to meet all the criteria simultaneously (good anti-icing performance, low ice adhesion, low ice accretion rate and durability).

The introduction of ice depressing liquids could help to improve the anti-icing performance. Halar et al. [43] reported the design concept of imitating liquid droplets in cetaceans' skin to improve icephobic performance. The ice depressing liquid (ice

inhibitor) was added into reinforced composite coatings to inhibit the formation of ice nucleus. However, the de-icing aspect especially for the ice adhesion strength could be deteriorated because of the effusion of large volume of hydroxyl groups [44], which is contrary to the initial ice protection purpose. To solve the problem, the construction of multi-phase structure system has been raised. Irajizad et al. [236] proposed that icephobic surfaces could be achieved using surface elastoplastic differentiation by incorporating different elastomers having big mismatches in elastic modulus. Silicon-based elastomers with high elastic modulus were used to form the matrix, while organosilicon-based gel with fairly low elastic modulus was added to construct the icephobic structure.

From our former studies in Chapter 5, the addition of Ni scaffolds could improve the mechanical durability as well as alleviate the oil depletion problem. To solve the problem essentially, the phase changed liquids were considered to introduce into the metallic substrate - polymeric network. In Chapter 6, although the released heat energy during the phase transition process could postpone the ice formation on the surface, the formed solidified oil layer also increase the surface roughness, thus affecting the ice adhesion strength.

The majority of the reported work could only meet some aspects of the surface icephobicity, including anti-icing performance, de-icing ability and mechanical stability, and it is difficult to achieve all of these requirements simultaneously. In the present work, a new icephobic structure was proposed and constructed to provide a solution for such a challenge. Ni scaffolds were introduced to incorporate with ice depressing liquid and PDMS matrix, and impressive icephobicity and durability enhancement have been achieved simultaneously, demonstrating the effectiveness of new icephobic construction.

Characterisation details:

The cross-section and top view morphology were investigated by a JEOL 6490LV scanning electron microscope (SEM) under an acceleration voltage of 10 kV after Pt was deposited on the samples to prevent charging by the electron beam. Fourier transform infrared (FTIR) spectra were recorded by a spectrometer (Spectrum One, Perkin Elmer, Akron, OH, USA) using attenuated total reflection mode.

The surface roughness was evaluated out using a Zeta-20 non-contact optical profiler. 100× magnification was used for surface roughness measurements and 5× magnification was used for 3D surface profiling images. Surface roughness values in this study were based on the average of several measurements.

Water contact angles (WCAs) were measured using the sessile drop technique on FTÅ200 goniometer and the volume of one water drop was kept constant at 5 μ l. For dynamic water contact angle measurement, water pumping out rate of 0.05 mL/s was used, similar to the testing condition reported by Esmaeili et al. [385]. The tests were conducted at room temperature and humidity conditions. Several repeating measurements were conducted to ensure data accuracy.

Droplet icing test was carried out by determining the duration of ice formation from water droplets with a volume of 4 μ L on five different points on the coated samples and the substrates for comparison on a cold plate at $-10\text{ }^{\circ}\text{C}$. By video recording the icing of water droplets, the icing times of the coatings were obtained.

The detailed ice adhesion strength were measured via a horizontal shear test system. A controlled volume of de-ionized water was filled in silicone molds, the molds were then flipped upside down and kept against gravity for overnight freezing at $-20\text{ }^{\circ}\text{C}$. The pre-prepared ice block (mass of 1.3 g) was then attached to the sample surface in a cold chamber. The ice/sample was propelled by the force probe at the velocity of 0.1 mm/min

during the tests. Five identical tests were carried out to ensure the data confidence, and the standard deviation was calculated.

In-situ water condensation and ice formation process was studied using a FEI Quanta650 eSEM system. The system is capable of generating micro-level HD surface images, under controlled humidity and temperature by a Peltier cooling stage. The observation of water condensation process was operated in a controlled environment at temperature of 2.0 ± 1.0 °C and relative humidity of $95 \pm 5\%$, while in the observation of ice formation process, the temperature was set to -5.0 ± 2.0 °C with relative humidity of $95 \pm 5\%$.

The method used to calculate the error bars is consistent with the one presented in Chapter 4.

6.1 Microstructural Characterisation of Ni-PDMS Sample Modified by Ice Depressing Liquid

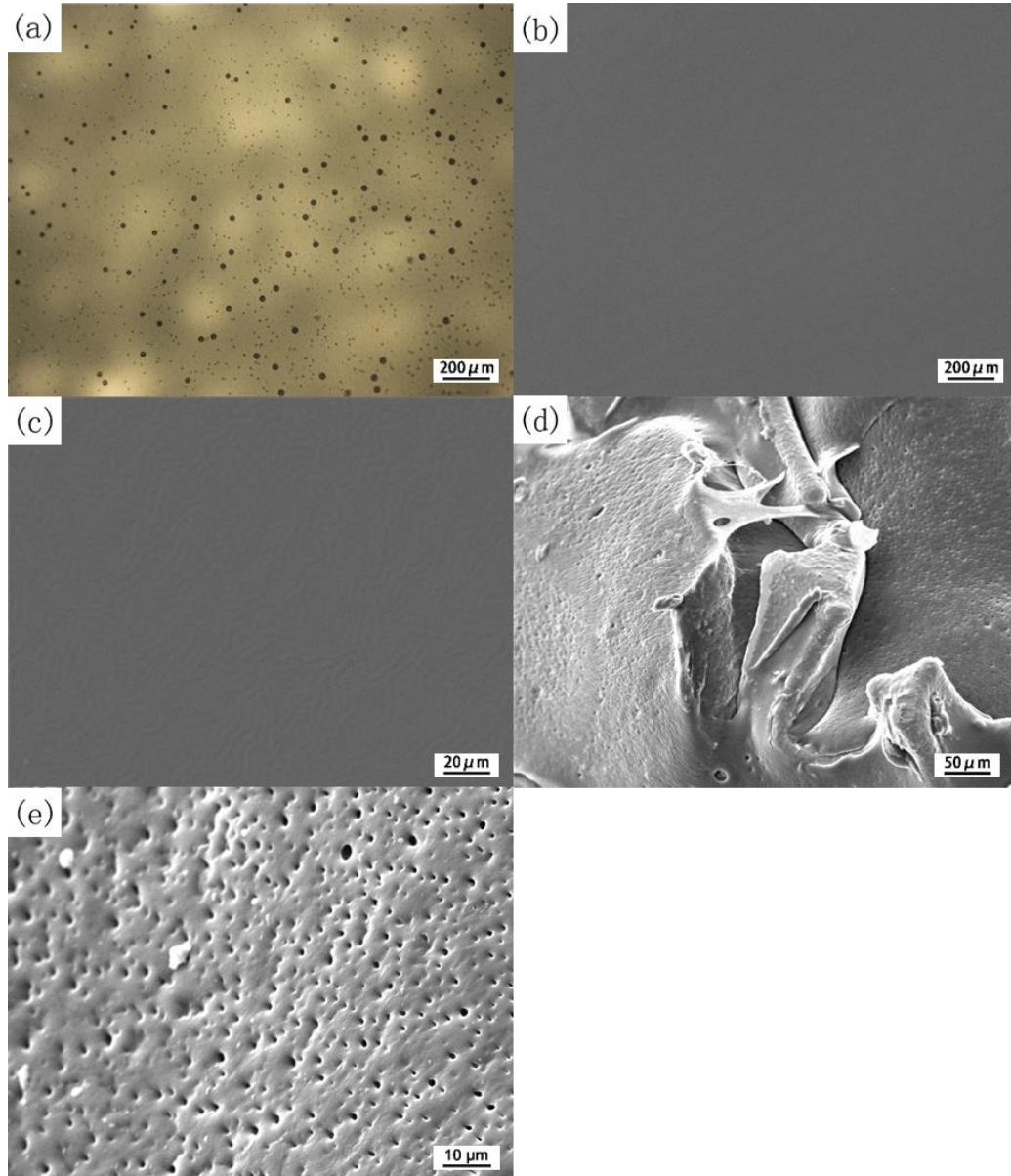


Figure 6.1 (a) Optical microscope images (top view) of NP-glycol; (b) and (c) SEM images of the surface morphology of NP-glycol; (d) and (e) SEM images of the cross-sectional area of NP-glycol.

Figure 6.1 showed the surface morphology of NP-glycol observed by optical microscopy and SEM. Figure 6.1 (a) was the image obtained from optical microscopy. It can be clearly seen from image (a) that there were a lot of black dots distributed on

the surface of NP-glycol. These black dots were actually the generated internal pores inside the PDMS fillings. Some of the ice depressing liquid suffered volatilization and diffused out, leaving the remaining porosities. Because of the advantages of OM, these pores could be found under observation, which also confirmed the existence of the internal porosities. While moving to images (b) and (c), it was difficult for the secondary electrons to detect and display the internal porosities by SEM observation. The observed surface morphology was still smooth and flat, no obvious features including cracks and voids could be found in the images. The former porosities displayed in image (a) were also not found and the profile of the Ni scaffolds could not be detected from the high magnification images. To better characterise the samples, the SEM images of the cross-sectional areas of the NP-glycol sample were detected and shown in Figure 6.1 (d) and (e). It displayed a similar morphology as the NP-SO samples, the Ni scaffolds were well wrapped in the PDMS filling. The good combination between Ni scaffolds and PDMS filling could be verified in Figure 6.1 (d). The existed internal porosities were also cross-authenticated from the enlarged area shown in the amplified image with high magnification in image (e). The pores were quite uniformly distributed, and the sizes of the pores also varied, which may come from the different volatilization behaviours. These internal porosities could act as the storage location for the infused anti-freezing liquids including glycol and glycerol.

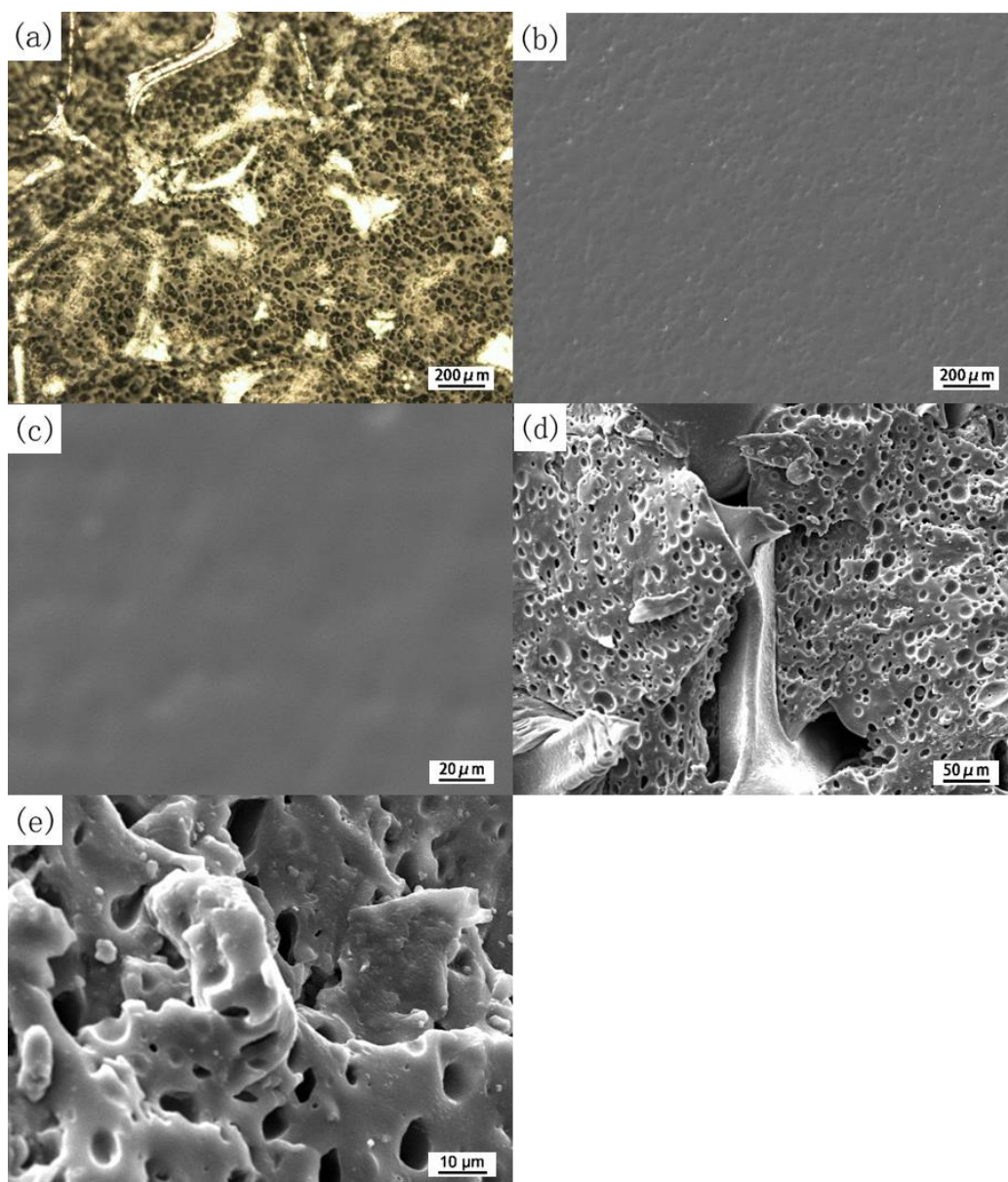


Figure 6.2 (a) Optical microscope images (top view) of NP-glycerol; (b) and (c) SEM images of the surface morphology of NP-glycerol; (d) and (e) SEM images of the cross-sectional area of NP-glycerol.

Then for NP-glycerol, the optical microscope images and SEM images of NP-glycerol were also shown in Figure 6.2. As indicated in Figure 6.2 (a), it was obvious that the size of the generated internal pores around the PDMS filling was much larger than that in NP-glycol. With the same weight percentage addition as glycol, the incorporated glycerol liquids were more likely to volatilize and diffuse away, resulting in the much-increased number of pores. The Ni scaffolds underneath could also be observed from

the optical image. Image (a) showed a quite rough and hierarchical morphology. Due to the existing internal porosities, the surface morphology observed by SEM was also affected, as shown in Figure 6.2 (b) and (c), the as-prepared sample surface was no longer smooth and flat with a lot of fluctuations emerging which should mainly be ascribed to the porosities. Even though a lot of pores exist in the optical images, there were actually no pores on the sample surface. It needed to be noted that the surface of NP-glycerol was still intact without any surface pores. The volatilization behaviours changed the surface and made it a bit more hierarchical than that of NP-glycol, the measured surface roughness (as shown in Section 6.3) also indicated the change. To better illustrate the formed internal pores, the cross-sectional images were displayed in Figure 6.2 (d) and (e), which also showed the uniformly distributed pores inside the PDMS fillings, while the spherical shapes of the remaining pores also reflected the former locations of the infused glycerol before the curing treatment, as observed in Figure 6.2 (e). There were some interspaces between the PDMS filling and the Ni scaffolds, which may lead to weak adherence. The amplified image showed that the sizes of the pores ranged from 3 μm to 7 μm . Some of the remaining spaces could then be used to store the ambient air which acted as the gaseous phase.

Figure 6.3 (a) to (e) showed the details of Ni-PDMS. As a comparison, no glycol or glycerol was added, it can be seen in Figure 6.3 (a) that no obvious pores could be found inside the sample surface, the Ni scaffolds underneath the PDMS layer with lighter colour was easy to be observed. While moving to the SEM observation, the sample surface exhibited regular smooth and flat topography and no obvious feature could be found in the images. Images with high magnification also indicated no surface features including cracks and pores, as indicated in images (b) and (c). When moving to the cross-sectional area shown in Figure 6.3 (d) and (e), no pore could be detected, displaying the intact cross-section morphology as well as the good adhesion between the PDMS and Ni scaffolds. The infusion of glycol and glycerol inside the PDMS filling could help with the formation of uniform distribution of internal pores, which further enabled the multi-phase structure system [386].

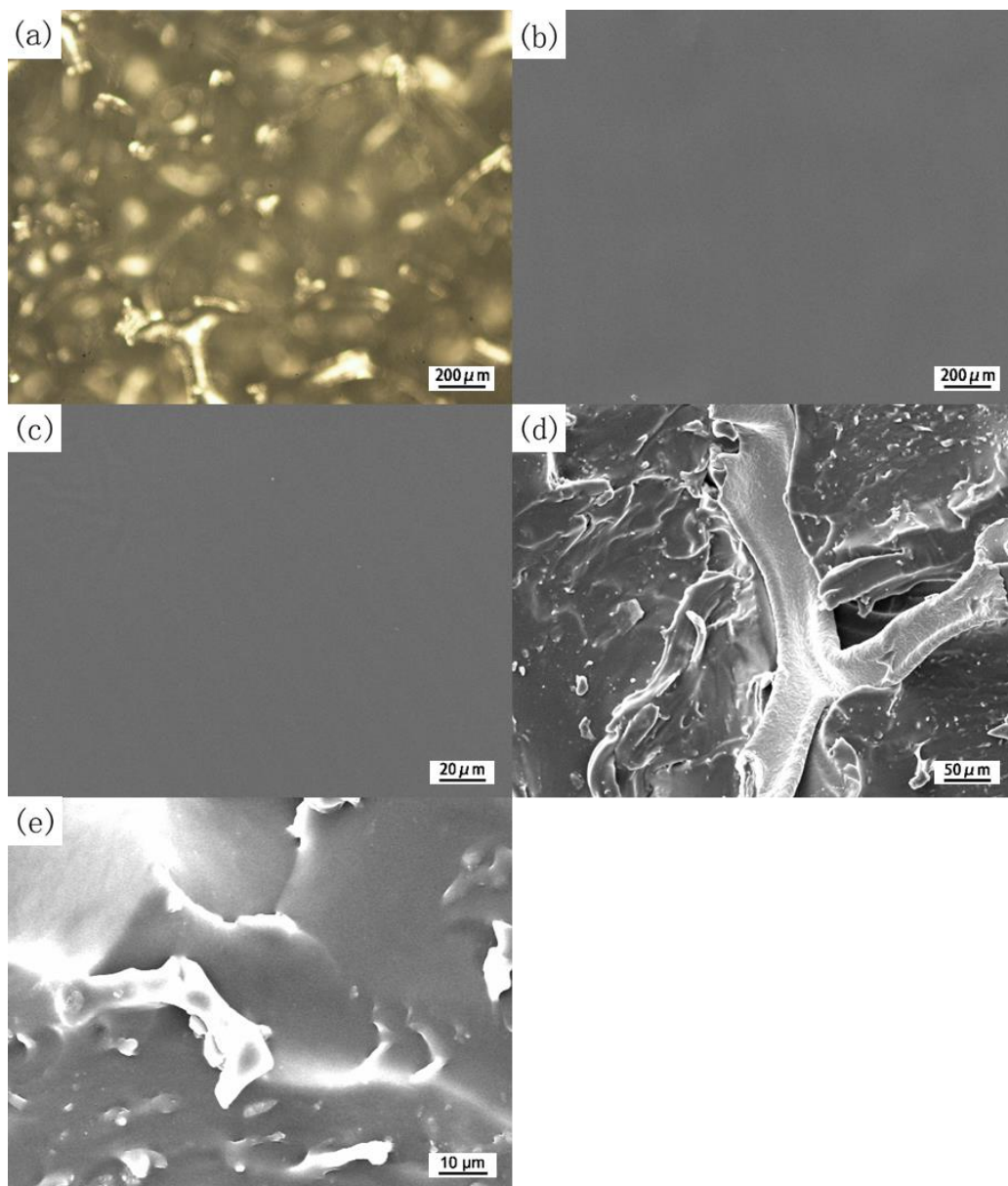


Figure 6.3 (a) Optical microscope images (top view) of Ni-PDMS; (b) and (c) SEM images of the surface morphology of Ni-PDMS; (d) and (e) SEM images of the cross-sectional area of Ni-PDMS.

6.2 Surface Analysis of the As-prepared Samples

6.2.1 Wetting performance and surface topography of Ni-PDMS sample modified by ice depressing liquid

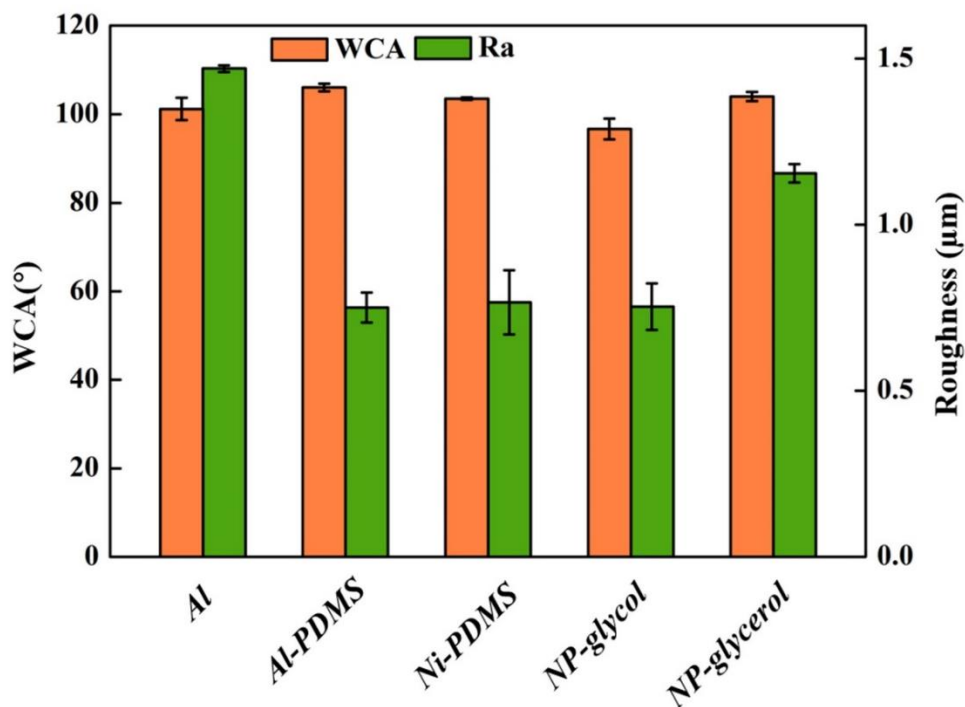


Figure 6.4 Surface roughness and wettability of Al, Al-PDMS, Ni-PDMS, NP-glycol and NP-glycerol.

The detailed wettability results as well as the surface roughness of NP-glycol, NP-glycerol and reference samples were shown in Figure 6.4, respectively. The WCA of pure Al was around 100°, which could mainly be the promoting effect of the time-dependent wettability, exhibiting the metastable hydrophobicity. The rough surface (with the measured surface roughness of $1.41 \pm 0.03 \mu\text{m}$) could introduce the huge specific surface area and lead to time-dependent wettability to the Ni scaffold substrate, the WCA would easily decrease after the adsorbed species and air pockets have been removed [130, 320]. For Al-PDMS, with a PDMS layer on top, the static WCA was a bit higher than that of Al. The measured roughness was also lower, only $0.75 \pm 0.05 \mu\text{m}$. The displayed WCA was also close to the inherent value of pure PDMS polymer

[321, 387]. Then the WCA of Ni-PDMS was similar to that of Al-PDMS. They both reflected the exact wettability of pure PDMS without any modification. The surface roughness was also close to the value of Al-PDMS, only $0.76 \pm 0.10 \mu\text{m}$, indicating that the PDMS filling had nearly covered all of the surface porosities on Ni scaffolds. Table 6.1 illustrated that the measured surface free energy of Al-PDMS was 38.2 mJ/m^2 . And the result of Ni-PDMS was 38.6 mJ/m^2 , which was close to each other. Then moving to NP-glycol, it was obvious to find that the WCA of NP-glycol was lower than the three reference samples, with the value of around $96.7 \pm 2.4^\circ$. It was observed that no big difference occurred in the surface roughness, the Ra of NP-glycol was still as low as $0.75 \pm 0.07 \mu\text{m}$. There would be some hydroxyl groups (-OH) existing on the sample surface. It also results in the increase of the surface apparent free energy, the surface free energy of NP-glycol was $39.8 \pm 0.5 \text{ mJ/m}^2$, which could be evidenced in Table 6.1.

Table 6.1 Surface free energy results of Al-PDMS, Ni-PDMS, NP-20SO₃Al, NP-glycol and NP-glycerol.

Samples	Surface free energy (mJ/m^2)
Al-PDMS	38.2 ± 0.4
Ni-PDMS	38.6 ± 0.3
NP-glycol	39.8 ± 0.5
NP-glycerol	38.4 ± 0.4

The increased surface free energy could help to enlarge the liquid-solid contact area and affect the hydrophobicity. Upon transition to NP-glycerol, the measured water contact angle (WCA) was found to be higher compared to that of NP-glycol, with a value of $104.0 \pm 1.1^\circ$. Additionally, the corresponding surface roughness, as measured by Ra, was determined to be $1.15 \pm 0.02 \mu\text{m}$. The glycerol was diffused into the PDMS on sample surface, which also increased the surface energy, with the value of $38.4 \pm 0.4 \text{ mJ/m}^2$. However, the rough surface morphology of NP-glycerol posed more

contribution to the hydrophobicity, resulting in a higher WCA value. The difference in surface free energy between the samples could also explain the variation in ice adhesion strength, which would be further discussed in Section 6.3.3.

6.2.2 Surface analysis using FTIR spectrum

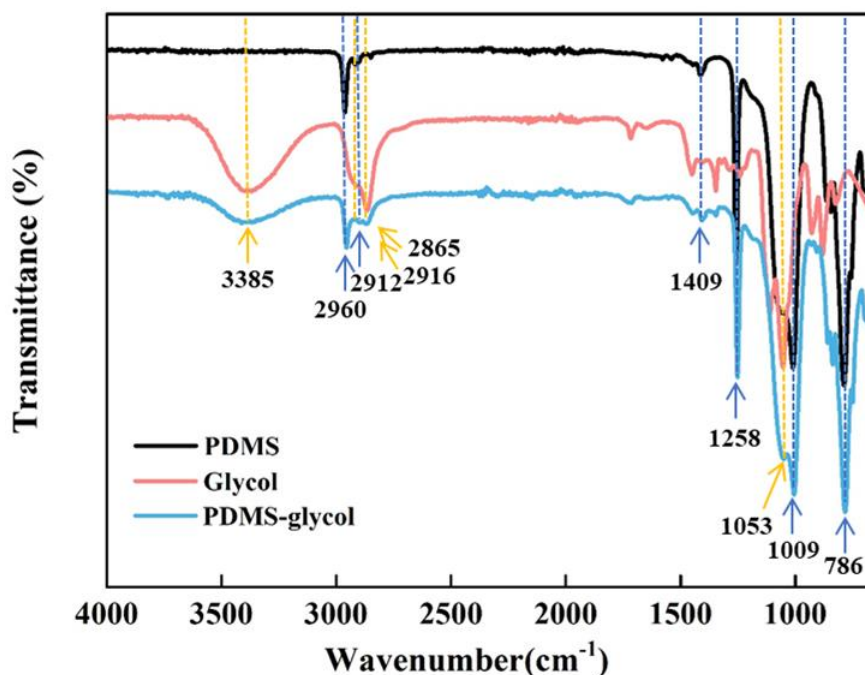


Figure 6.5 ATR-FTIR results of PDMS, glycol and PDMS-glycol.

Figure 6.5 showed the ATR-FTIR results of PDMS-glycol, PDMS, and pure glycol (liquid). The detailed position of peaks corresponding to the functional groups with different chemical bonds was also demonstrated in Table 6.2. Peaks at 2960 cm^{-1} , 2912 cm^{-1} , 1409 cm^{-1} , 1258 cm^{-1} and 786 cm^{-1} were characterised by the presence of methyl ($-\text{CH}_3$) functional groups on PDMS surface, which were also commonly used in Ref [355]. Among the referred positions, the peaks of symmetric $-\text{CH}_3$ stretching and asymmetric $-\text{CH}_3$ stretching were observed at 2960 cm^{-1} and 2912 cm^{-1} , respectively. But for PDMS, the peaks of $-\text{CH}_3$ appeared at the positions including 1409 cm^{-1} , 1258 cm^{-1} and 786 cm^{-1} . The peak at 1009 cm^{-1} indicated the asymmetric deformation of Si-O-Si. By comparing the data of glycol with PDMS, the most obvious difference in FTIR spectrum of glycol was the O-H stretching vibration located at 3385 cm^{-1} [388]. The

peak at 2916 cm^{-1} belonged to the asymmetric -CH_2 stretching, while the one at 2865 cm^{-1} was attributed to the symmetric -CH_2 stretching of glycol. The C-C stretching vibration also appeared at the position of 1053 cm^{-1} as a peak with high intensity. It was not difficult to observe that there were also peaks that belonged to glycol that appear apart from the peaks of PDMS. This could also verify the mentioned surface morphology results shown in Figure 6.2 (b) that even some of the glycol volatilize, parts of the glycol could remain in the PDMS filling and participate in the cross-linking.

For Figure 6.6, it indicated the ATR-FTIR results of pure glycerol (liquid) and PDMS-glycerol. The results of PDMS were also used to guide the position references. Table 6.2 showed the results of specific corresponding peak positions of functional groups containing different chemical bonds [389]. Among the spectrum of glycerol, there was an intensified absorption peak at 3301 cm^{-1} that was characterized by -OH stretching. Similar to the spectrum of glycol, there were also two peaks of -CH_2 stretching located at the positions of 2930 cm^{-1} (asymmetric -CH_2 stretching) and 2880 cm^{-1} (symmetric -CH_2 stretching), respectively. The -OH stretching could still be observed among the PDMS-glycerol spectrum, displaying decreased peak intensity. The reason could be ascribed to the low content of glycerol inside the sample (only 20 wt%). Several -CH_3 stretching peaks belonging to PDMS could also appear in the spectrum of PDMS-glycerol, as well as the C-OH stretching peak (containing -OH functional group) which came from the glycerol. It turned out that there was some glycerol contributing to the diffusion into PDMS even though some glycerol volatilized during the curing process, which was quite similar to the FTIR results of PDMS-glycol.

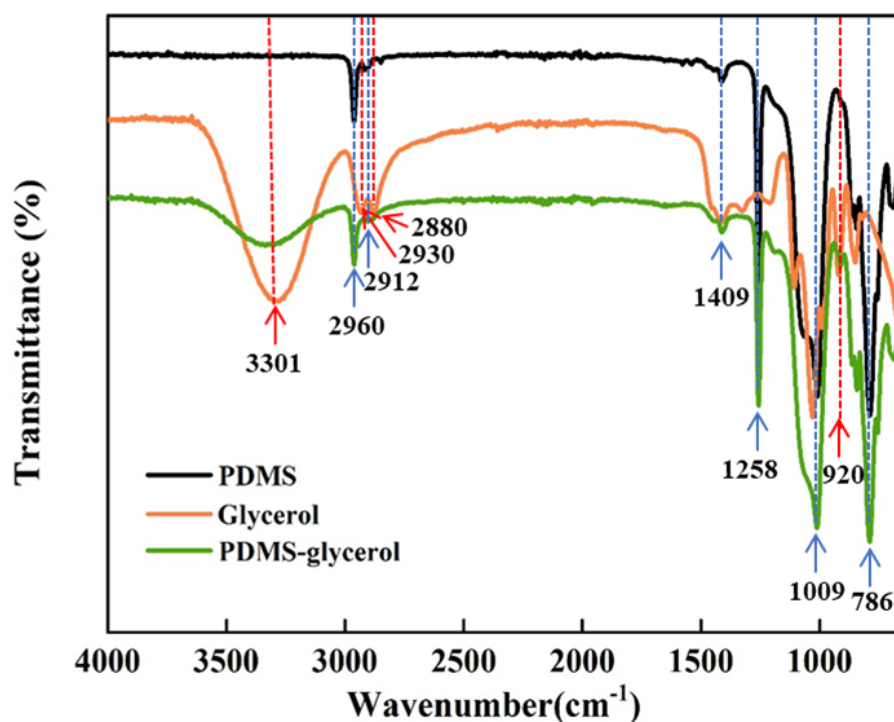


Figure 6.6 ATR-FTIR results of PDMS, glycerol and PDMS-glycerol.

Table 6.2 Obtained ATR-FTIR peaks of the various functional groups presented on PDMS, glycol, PDMS-glycol, glycerol, PDMS-glycerol surfaces [389].

Peak position	Wavenumber (cm-1)	Functional group
1	3300~3390	Stretching vibration of O-H
2	2960	Symmetric -CH ₃ stretching in ≡Si-CH ₃
3	2912	Asymmetric -CH ₃ stretching in ≡Si-CH ₃
4	2915~2930	Asymmetric -CH ₂ stretching
5	2860~2880	Symmetric -CH ₂ stretching
6	1409	Deformation vibration of -CH ₃
7	1258	Deformation vibration of -CH ₃
8	1053	Stretching vibration of C-C
9	1009	Si-O-Si asymmetric deformation
10	920	Stretching vibration of C-OH
11	786	CH ₃ rocking in -Si-(CH ₃) ₂

6.2.3 Shore hardness analysis

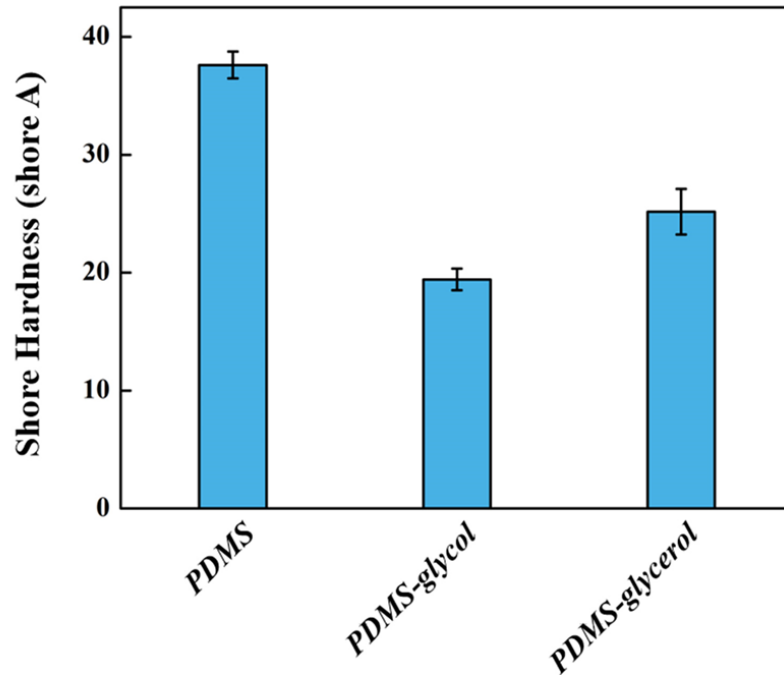


Figure 6.7 Shore hardness results of pure PDMS, PDMS-glycol and PDMS-glycerol.

Figure 6.7 depicted the values of shore hardness of involved samples including PDMS, PDMS-glycol and PDMS-glycerol. For certain samples, as was reported, the shore hardness could be utilized to evaluate the elastic modulus confirmed using other typical methods [317]. The PDMS showed a hardness of about 37.6 ± 1.1 (Shore A hardness), which was the highest among the three samples. For PDMS-glycol, the hardness suffered an obvious decrease to only 19.4 ± 0.9 (Shore A hardness). The reason could be the soften effect derived from the glycol infusion. The PDMS-glycerol showed the value of 25.2 ± 1.9 (Shore A hardness), which was in between the values of PDMS and PDMS-glycol.

6.3 Surface Icephobicity and Durability Evaluations of Ni-PDMS

Sample Modified by Ice Depressing Liquid

6.3.1 Icing delay performance of water droplets

Figure 6.8 showed the detailed processes of ice formation results in anti-icing tests on different surfaces including Al, Al-PDMS, and Ni-PDMS. A thin icing layer would first emerge at the interfacial area between the liquid-solid areas. It then grew slowly from the interface to the top region of the droplet. The phenomenon showed that the ice nuclei would first form at the liquid-solid interface and then gradually grew into ice crystals, which continued to spread from the interfacial area to the topped area until the icing process was completed. The nucleation type that nucleates at the liquid-solid interface firstly was recognized as heterogeneous nucleation process [390].

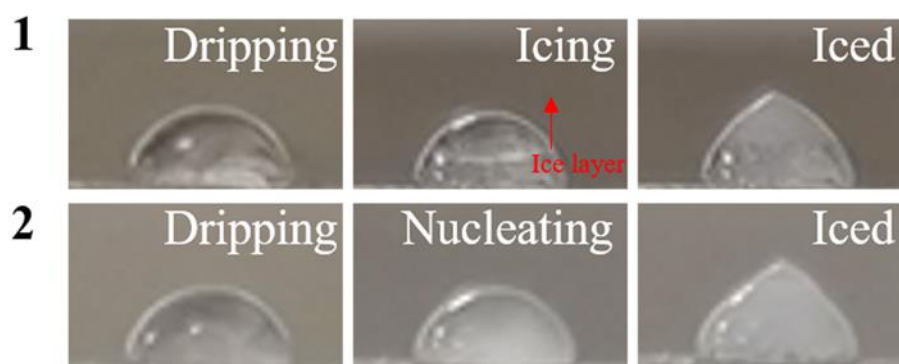


Figure 6.8 Typical ice formation processes on different surfaces: 1. Al, Al-PDMS, and Ni-PDMS; 2. NP-glycol and NP-glycerol.

While for NP-glycol and NP-glycerol, the specific ice formation processes were displayed in image set 2 of Figure 6.8. No thin icing layer would appear but the color of the supercooled droplets changed from transparent to white rapidly at specific timepoints, and phase change of the whole droplet was then completed quickly. Two different ice nucleation mechanisms appeared during the icing phenomena, which are termed as heterogeneous and homogeneous nucleation. Here, homogeneous nucleation

indicates equal probability of nucleation all over the places in the system, regardless of the effect of external particles or surface presence. For heterogeneous nucleation, it could be more easily induced with a lower nucleation free energy, since an existing solid surface is able to reduce the energy barrier for the ice nucleation [206].

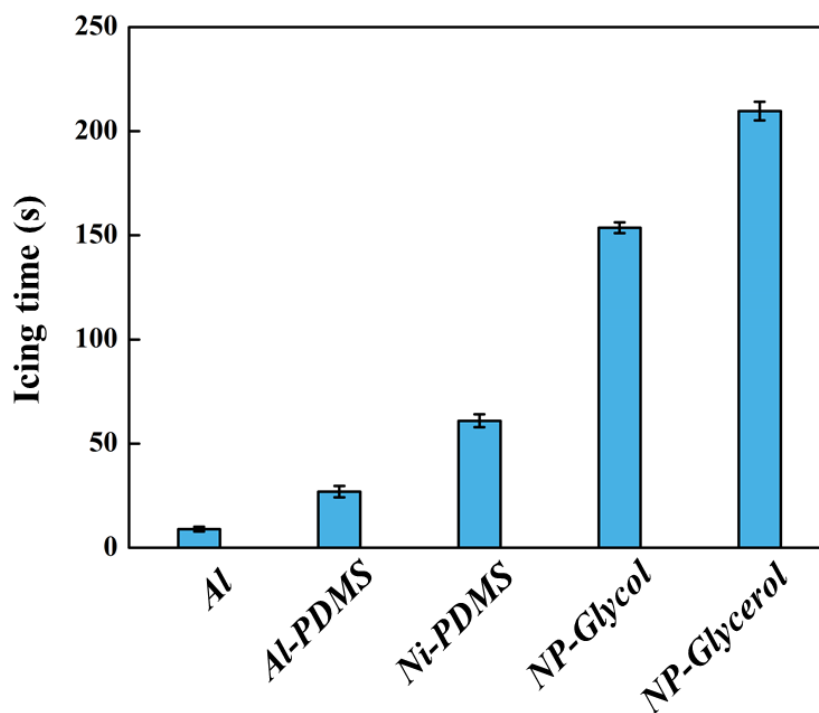


Figure 6.9 Icing durations of supercooled droplets on different sample surfaces.

The icing durations of NP-glycol, NP-glycerol and reference samples were shown in Figure 6.9, respectively. The columns indicated the ice delay time. It is an important parameter for icephobicity evaluation and reflects the duration required for a water droplet to become ice on certain surfaces with constant temperature [15]. It is also closely related to the ability of thermal transmission at the apparent solid-liquid contact interface [391]. The droplets remaining on a cold surface would lose heat to the cold substrate through thermal conduction. The icing time of pure Al plate was only 9.1 ± 1.2 s, which was the shortest among the samples. This could be ascribed to the good thermal conductivity of Al plate (the thermal conductivity of Al could reach 237 W m/K, which is fairly high), and the thickness of Al plate is also very thin (only around 50 μm), which makes the thermal transfer more effectively. With the coverage of PDMS

layer in Al-PDMS, the surface energy was decreased and the overall thermal resistance also increased, the value of icing delay duration was prolonged to 27.2 ± 2.7 s. Some hydrophobic characteristic was also introduced to the sample. While for Ni-PDMS, considering the replaced Ni scaffolds and filled PDMS, the whole thermal resistance could further increase, leading to the icing time of 61.8 ± 3.1 s. Then for NP-glycol and NP-glycerol, the icing process on NP-glycol and NP-glycerol had been significantly delayed with respect to the substrates and the two samples took prolonged periods of 153.7 ± 2.5 s and 209.7 ± 4.5 s, respectively.

For example, the static water droplet icing delay duration on sample with 20 % glycerol infused inside polyurethane matrix was 364 s measured at -10 °C while the distilled water droplets froze in only 7 seconds on the aluminium substrates [43]. The icing delay performance derived from the static anti-icing experiments of lubricant-infused (with glycol incorporation) on ultra-slippery aluminum alloy surfaces at -10 °C was 120 s [392]. Upon comparison with the obtained data from previous literature, it is evident that NP-glycol and NP-glycerol exhibited better anti-icing properties.

6.3.2 Anti-frost performance by frost growth tests

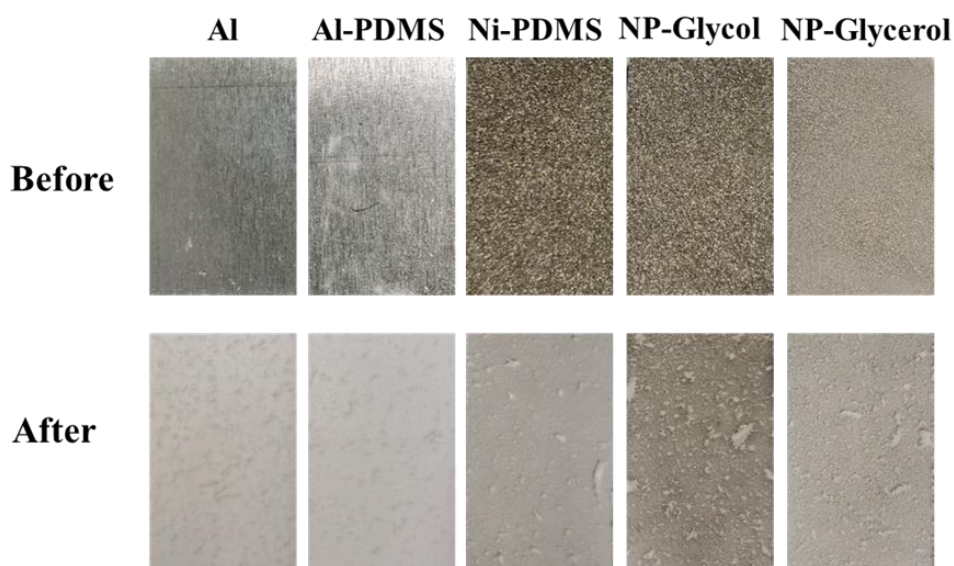


Figure 6.10 Surfaces images of Al, Al-PDMS, Ni-PDMS, NP-glycol and NP-glycerol.

The static frost formation tests were carried out to evaluate the anti-icing performance of the involved samples. The surface images reflecting the detailed conditions of the samples before and after the frost formation tests including Al, Al-PDMS, Ni-PDMS, NP-glycol and NP-glycerol were displayed in Figure 6.10, respectively. Figure 6.11 displayed the mass of formed glaze per unit area on different samples. Here, the mass of the formed glaze on certain surfaces indicated the anti-icing performance. The frost formation process consists of three steps: crystal growth period, frost layer growth period, and frost layer full growth period. During the crystal growth period, ice crystals formed on the cold surface. With deteriorated wettability, there would be more rod-type crystals on the surface and more frost branches would form later and lead to the increased formed glaze [393].

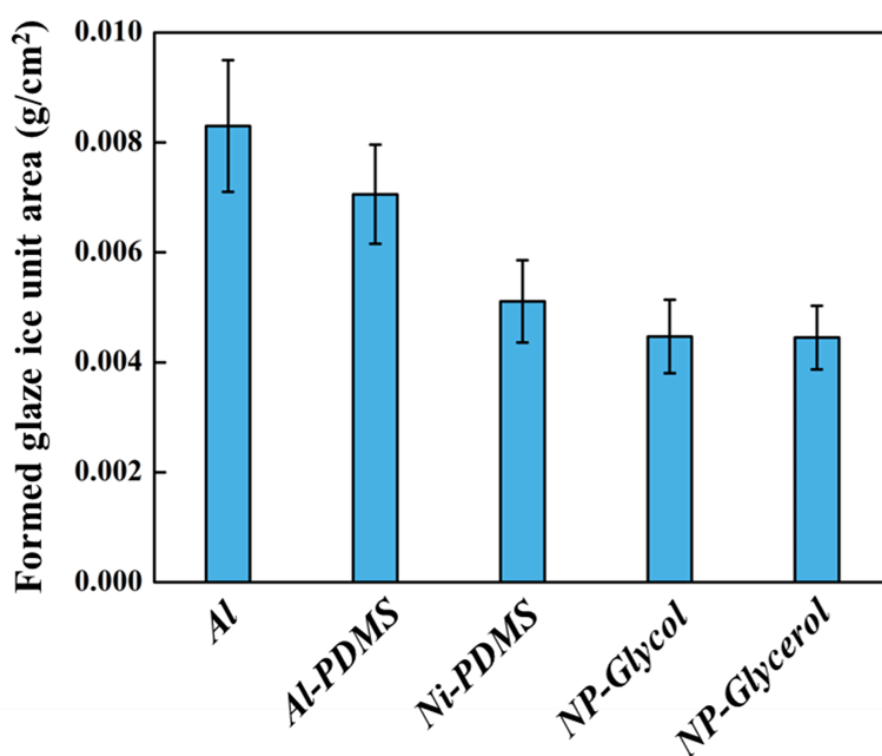


Figure 6.11 Increased mass of formed glaze on Al, Al-PDMS, Ni-PDMS, NP-glycol and NP-glycerol.

There was glaze formed indiscriminately on the Al surfaces. It could be seen that the Al surface was fully covered by the formed frost after the tests and there was a lot of

glaze ice scattered on the sample surface. The glaze formed per unit area on Al reference sample was $8.3 \pm 1.2 \text{ mg/cm}^2$. The large volume of formed glaze could come from the lowered hydrophobicity. The hydrophilic surfaces could supply a lot of hydrophobic defects and act as the ice nucleation points and help with frost formation. While for Al-PDMS, with a prepared PDMS layer on top and the relatively low surface roughness, the value was lower than before, around $7.1 \pm 0.9 \text{ mg/cm}^2$. It can be seen in Figure 6.10 that the formed glaze was less than before. With PDMS layer coverage, the surface hydrophobicity was improved and the surface morphology was also smoother and flatter than before. When moving to Ni-PDMS, the Ni scaffolds were used to replace the Al plate substrate. The formed glaze per unit area kept decreasing to $5.1 \pm 0.8 \text{ mg/cm}^2$. After the frost formation, the surface was a bit different from before, the whole surface was fully covered by the formed frost. The improved hydrophobicity helped with the low glaze formation under a high humidity environment. The results were also consistent with the conclusion obtained before, the anti-icing performance also improved. As for NP-glycol and NP-glycerol, the measured values of the formed glaze per unit area were similar to each other, which were also the lowest among the samples, $4.7 \pm 0.7 \text{ mg/cm}^2$ and $4.5 \pm 0.6 \text{ mg/cm}^2$, respectively. The remaining hydroxyl groups released from ice depressing liquids on the sample surfaces could decrease the freezing point, less glaze could form. The images in Figure 6.10 also indicated the obviously decreased the glaze formation. The increased hydrophobicity would lower the possibilities of moisture condensation on the coating surfaces [394].

6.3.3 Evaluation of ice adhesion strength and durability of Ni-PDMS sample modified by ice depressing liquid

Figure 6.12 showed the detailed variations of ice adhesion strength values of the reference samples including Al and Al-PDMS during the 50 icing/de-icing cyclic tests. The values represented the measured shear strengths. It indicated how easily the formed ice could be removed from the substrate. As well known, icing is an inevitable process

under the condition of sufficient supercooling [395]. The measured ice adhesion strength of Al was maintained at around 217.9 ± 6.4 kPa during the cycles, exhibiting little changes, which showed the good durability of pure Al metallic surface. This also indicated that the ice formed on the Al plate conformed to the Wenzel state. Ice adhesion strength is largely related to hydrogen bonding, van der Waals forces, and electrostatic interaction. Among them, the electrostatic interaction could be the dominant factor [24]. Icephobic coating with low surface energy would lower the electrostatic interaction between ice and the layer surface. So for Al-PDMS, the initial ice shear strength decreased sharply to around 106.0 ± 3.5 kPa when the Al surface was covered with a layer of PDMS possessing hydrophobicity and low surface free energy. With the cycles undergoing, there was also some increase in the ice adhesion strength. Some breakages could be observed on the surface of Al-PDMS after 30 cycles. The partial PDMS layer was removed and the Al substrate was exposed, which led to the deterioration of icephobicity. The reason could be the repetitious deformation of the PDMS layer surface under the loads during the cyclic tests which mainly come from the relatively low elastic modulus. The repetitious deformation could lead to damage to the PDMS layer.

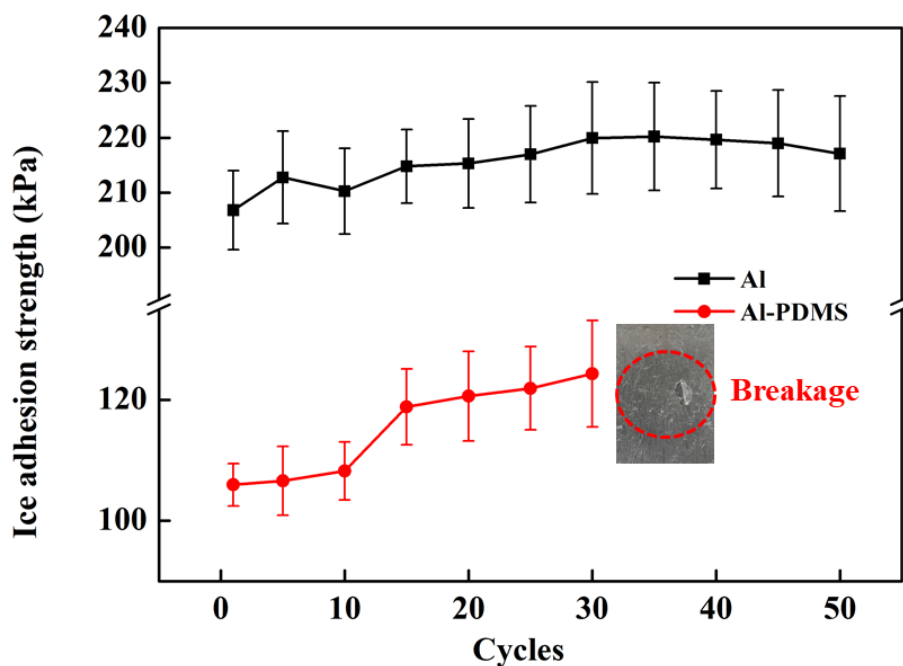


Figure 6.12 Variations of ice adhesion strength values of Al, Al-PDMS during 50 icing/de-icing cycles.

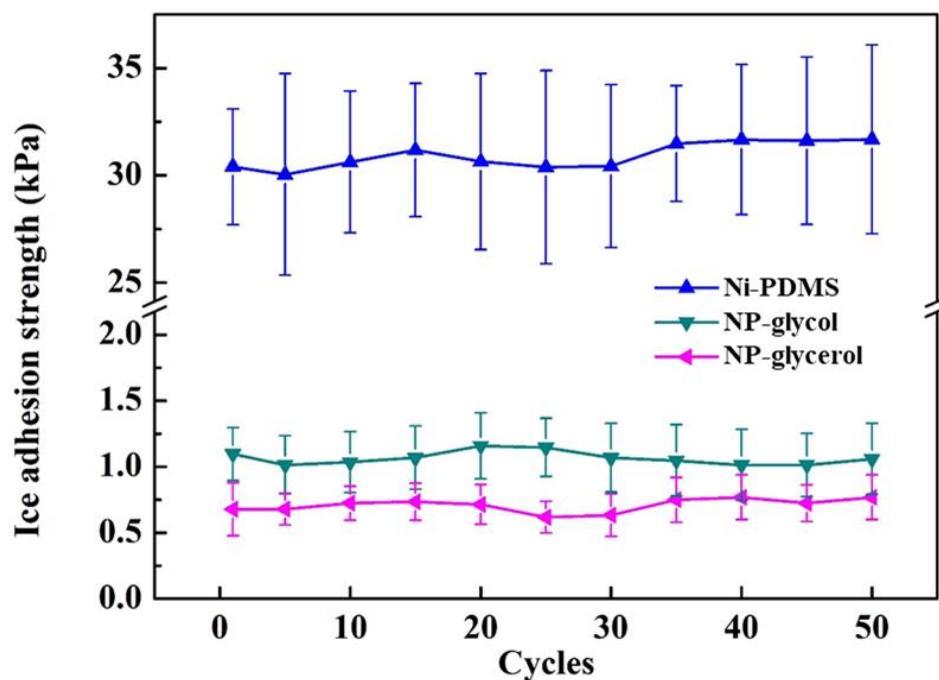


Figure 6.13 Variations of ice adhesion strength results of Ni-PDMS, NP-glycol and NP-glycerol during 50 icing/de-icing cycles.

Figure 6.13 shows the detailed changes in ice adhesion results of NP-glycol and NP-glycerol as well as Ni-PDMS. While for Ni-PDMS, with the addition of Ni scaffold, the ice adhesion strength has further been decreased to 29.8 ± 2.9 kPa. Here, the full coverage of PDMS layer reduced the surface free energy significantly. Then the ice adhesion strength of NP-glycol and NP-glycerol were around 1.1 ± 0.2 kPa and 0.7 ± 0.1 kPa, respectively. The low ice adhesion may come from a combined factor of, ice depressing liquid infusion and multi-phase construction. There was large mismatch in elastic modulus between the metallic scaffolds and the polymer filling, which could initiate different micro-distortions between the Ni scaffolds and PDMS matrix. It could help with the micro-crack initiation at the solid-ice interfaces and the decrease of ice adhesion strength. The combination of Ni scaffolds and modified PDMS built a unique interconnected structure which could disperse the load to other larger regions of the Ni scaffolds/PDMS network structure. Therefore, the shear strength remained stable during the whole icing/de-icing cycles. The micro-crack initiation mechanism could further be enhanced with the introduction of porosity in the matrix. As shown in Figure

6.13, the ice adhesion strength was decreased to lower than 2 kPa. Because of the differences among the internal porosity size and hardness among NP-glycerol and NP-glycol, the differences could lead to larger difference in elastic modulus. While the surface roughness posed little influence on the ice adhesion strength, the ice adhesion strength of NP-glycerol was lower even though the surface roughness of NP-glycerol is larger than that of NP-glycol.

To demonstrate the de-icing performance of the as-prepared samples, a selection of representative cases are referenced for comparative analysis. For example, the ice adhesion strength of glycerol triglycidyl ether modified PDMS sample remained similar to the value in the first test ~ 30 kPa after 20 icing/deicing cycles [239]. In addition, the slippery liquid-injected porous surfaces could maintain their low ice shear strength after 20 icing/de-icing cycles around 40.56 kPa to 64.58 kPa [377]. Compared with the referred literature results, NP-glycol and NP-glycerol show fairly competitiveness, which can fully meet the identified low ice adhesion standard ($\tau < 30$ kPa) [396].

6.4 Icing and De-icing Studies via ESEM Observation

6.4.1 Icing formation process

Figure 6.14 (a) and (b) showed the big differences on surfaces of NP-glycol samples being/ without being wet. It could be obviously found that water droplets with different spherical sizes scattered on the surfaces when compared with the ones without being wet. The WCA could be reflected from the displayed formed water droplet. There was no obvious preference for the condensed droplets to gather on NP-glycol. With the condensed water, the hydrophobic characteristic could be confirmed. Figure 6.14 (c) indicated the supercooled water left after the droplet evaporation when icing progress occurred simultaneously. Once the transition from water to ice took place, the water molecules in the ambient atmosphere could integrate with the ice nucleus and form ice

crystals, which also lowered the humidity inside the chamber. It was noted that the icing of water was an exothermic reaction, the released heat could also increase the temperature inside the ESEM chamber. The sudden changes in both humidity and temperature could result in the evaporation of water droplets on the surface, leaving some remaining supercooled water.

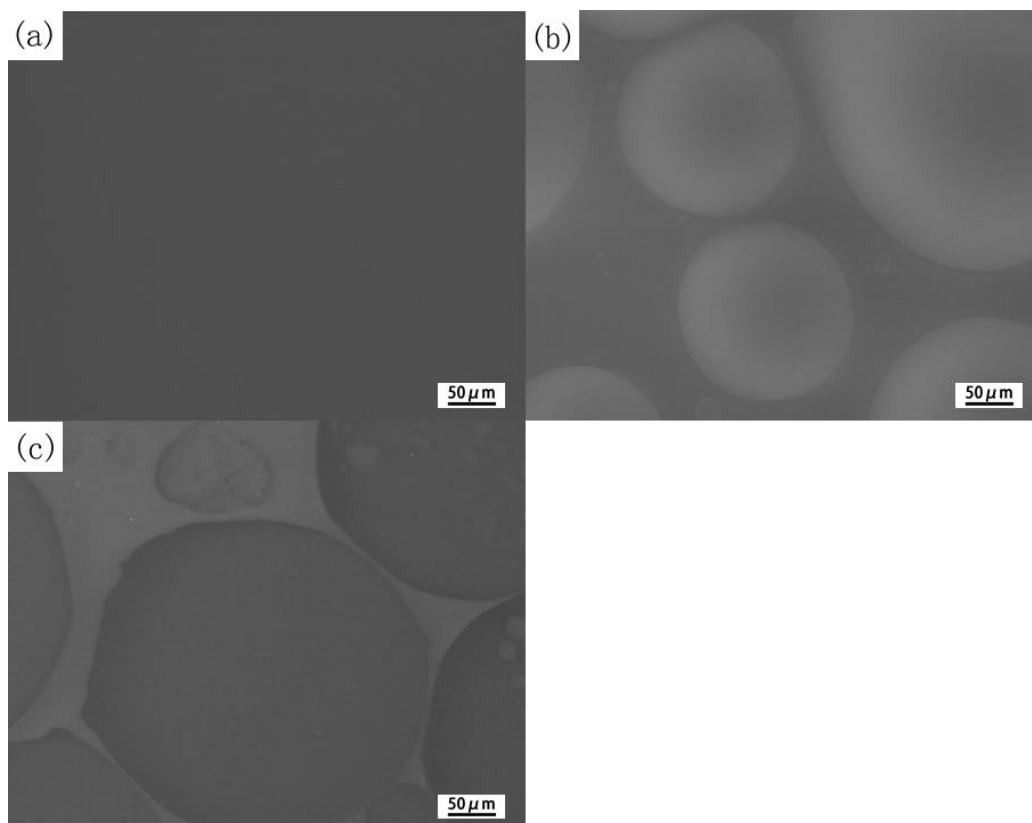


Figure 6.14 Water condensation and icing behaviour on NP-glycol via ESEM observation: (a) As-prepared surface (b) Condensed water distribution (c) Remained supercooled water after evaporation.

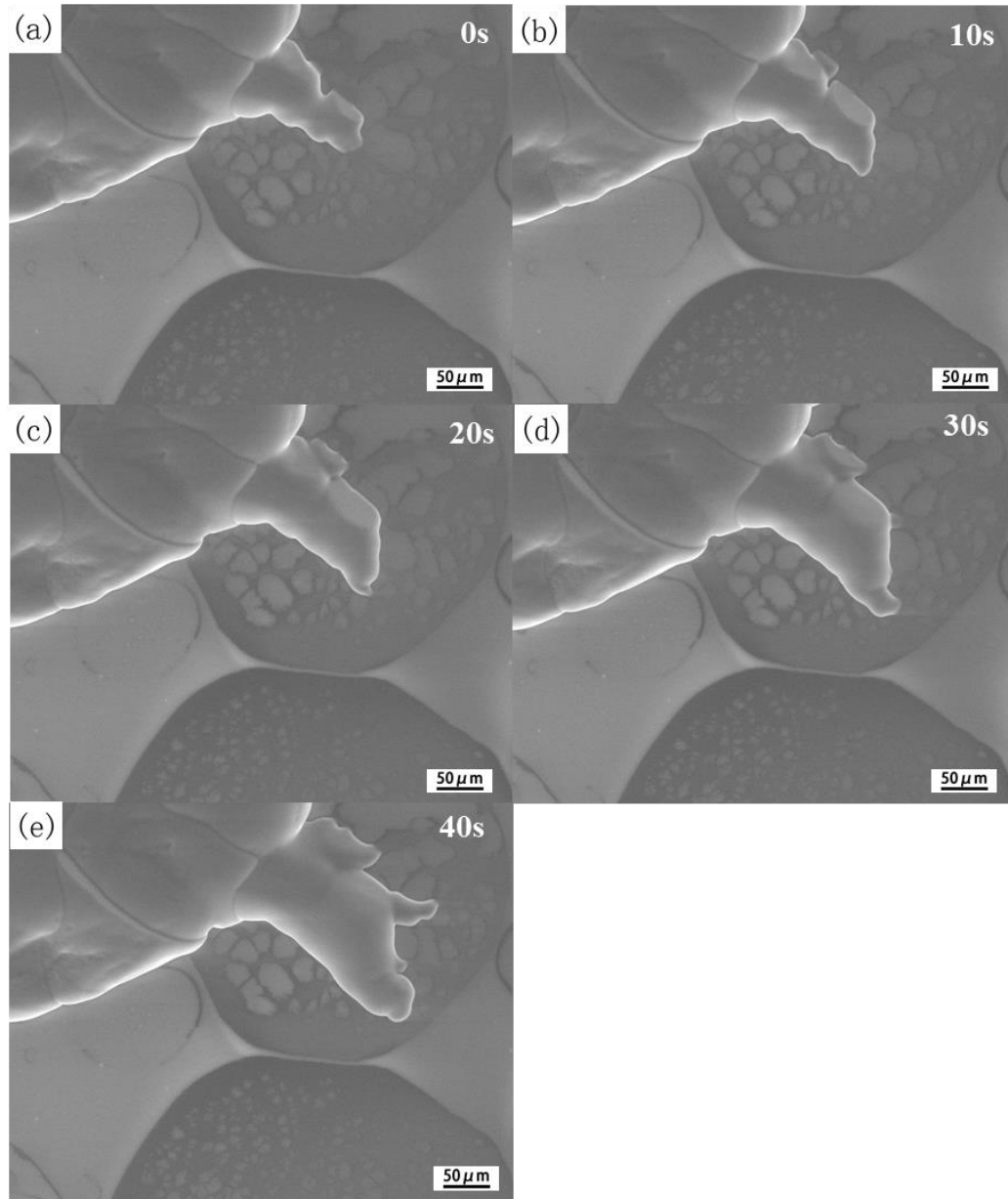


Figure 6.15 Ice formation and spread processes on NP-glycol via ESEM observation (a) to (e) ice growth from left to right.

Because of the good surface icephobicity, an ice nucleus would first form on the sample holder that was made up of aluminium alloy, and the growing ice then spread to the sample surface. As shown in Figure 6.15 (a) to (e), the ice could grow along with the direction that the existing supercooled water spread when the expansion of the ice boundary merged with the remaining supercooled water. These remaining supercooled water could help to speed up the ice crystals spread on iced surface. The areas with remaining supercooled water seemed to have preferences for icing.

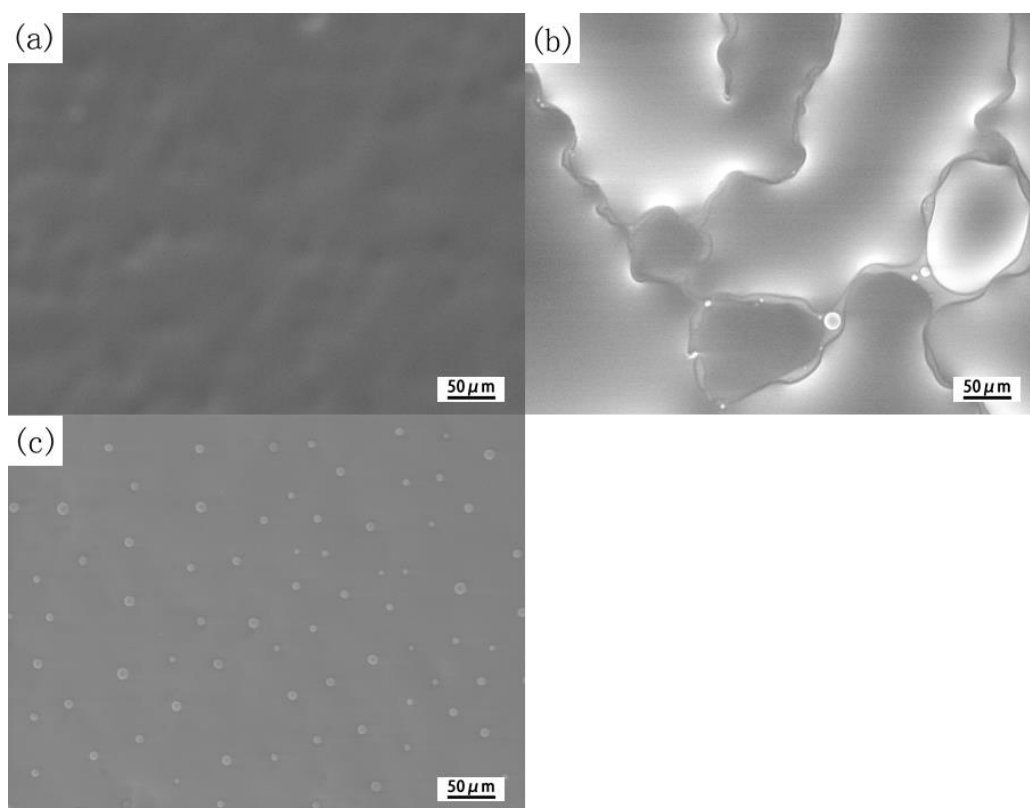


Figure 6.16 Water condensation and icing behaviour on NP-glycerol via ESEM observation: (a) As-prepared surface; (b) Condensed water distribution; (c) Remained supercooled water droplets after evaporation.

Figure 6.16 (a) and (b) also showed the variations in the sample surface on NP-glycerol being/without being wet. Due to the slight hierarchical surface morphology, the dispersed water droplets could not appear as the regular spherical shape, but showed as the ordinary big pieces of water, they merged with each other without showing any regular rules. Once ice formed on the sample surface, the remaining water droplet also evaporated instantly, only leaving some tiny supercooled water droplets scattered at the shallow cavities of the surface. The ice crystals at the boundary areas could combine with the water molecules and further promote the movement of the ice while the formed ice kept spreading to these droplets.

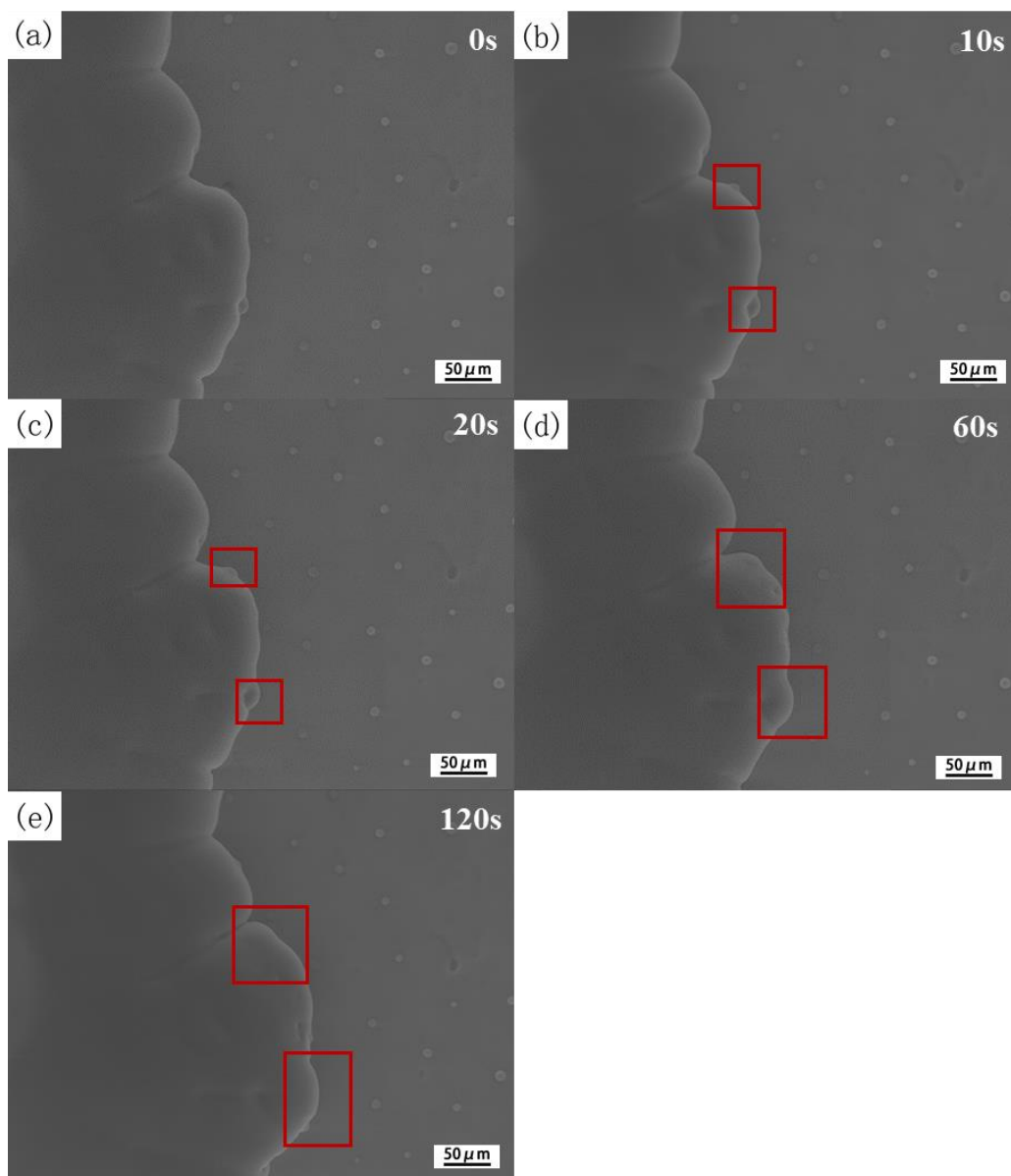


Figure 6.17 (a) to (e) Ice formation and spread processes on NP-glycol via ESEM observation.

Snapshot images of the nucleation and growth of ice on NP-glycerol were shown in Figure 6.17. In Figure 6.17 (a), there was already a large piece of formed ice covering the surface. The images demonstrated that ice formed discriminately over the surface on condensed supercooled droplets. There were several condensed supercooled droplets distributed on the surface, as red circled in the images. The initiated ice crystal would grow from the left side to the central area as indicated in Figure 6.15 (b) to (e). The area with condensed supercooled droplets was more likely to form ice. These condensed supercooled droplets would act as the preferential ice nucleation sites to

form ice and finally lead to the full coverage of ice on the surface. It is reported that the saturated water vapour pressure around the condensated supercooled droplets would always be higher than the ice-covered area at a constant temperature. Because of this, some of these condensated supercooled droplets would evaporate and migrate into the ice crystal, which could form ice bridges toward the condensates [397]. If an ice bridge touched the nearby condensated droplet, the supercooled droplet would freeze much more quickly. The phenomenon could be explained by Wegener-Bergeron-Findeisen process in meteorology: the propagation characteristic of ice crystal which comes from the saturated water vapour pressure difference between formed ice and supercooled droplets [398]. Because of the smooth surface topography, the formed ice block would have much less contact area with the sample surface, this could also be favourable for reducing the ice adhesion strength, which has been further verified in Section 6.5.

By comparing Figure 6.15 and Figure 6.17, it could be easy to find the degree of promoting effect of supercooled water droplets for ice growth on sample surfaces of NP-glycol and NP-glycerol vary because the existing form of supercooled water droplets on them had exhibited relatively large differences. The growth rate of ice on NP-glycerol was much lower than that on NP-glycol, which was also consistent with the results from ice delay tests shown in Section 6.4.

6.4.2 Ice diminishing process

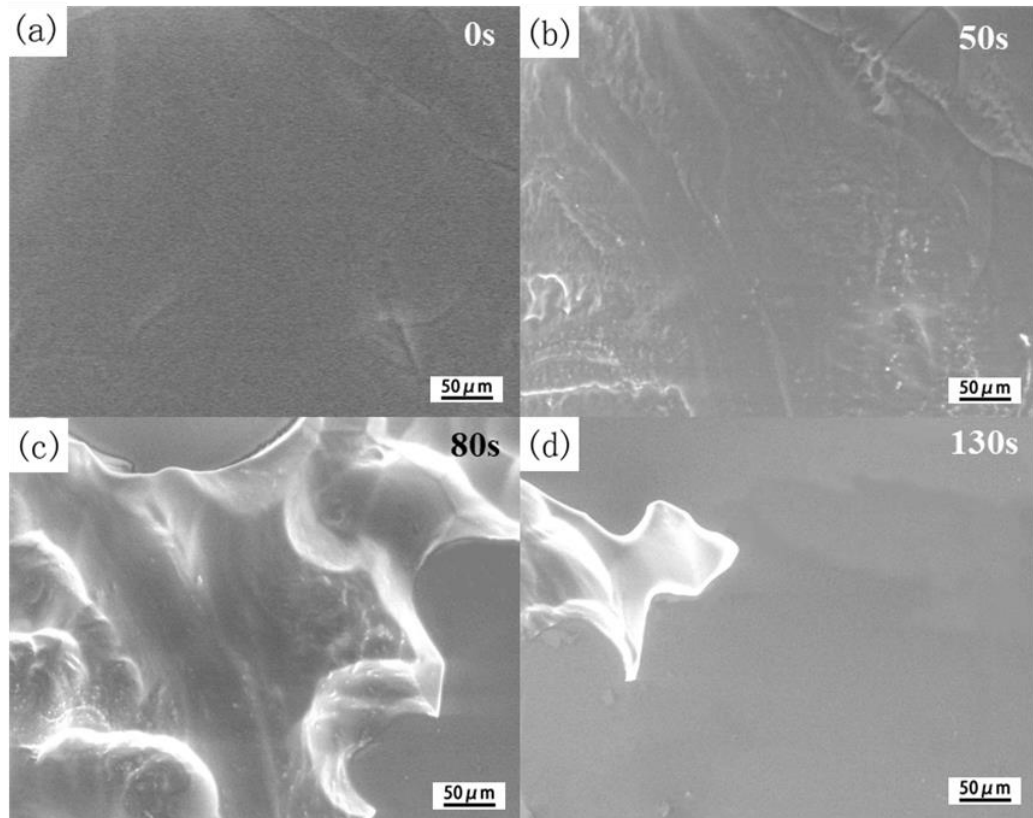


Figure 6.18 Ice diminishing process on NP-glycol (a) $t=0$ s (b) $t=50$ s (c) $t=80$ s (d) $t=130$ s.

Figure 6.18 showed the ice retardation process on NP-glycol. With reduced system humidity, sublimation would occur and ice diminishment would take place. The surface morphology of NP-glycol remained unchanged during the whole process. The edges of the formed ice also changed into angular shape from the initial rounded shape, as indicated in Figure 6.18 (a) to (b). With time going on, the ice layer kept becoming thinner. The direction of ice retraction was also opposite to the ice growth and spread direction. Considering the smooth and flat surface, no ice anchoring or retardation of ice movement was found. The only difference was that it took around 130 s for the whole ice layer to sublime, which was much quicker. And it indicated a thinner ice layer thickness, which showed that the ice layer spread could be easier than that of NP-glycol.

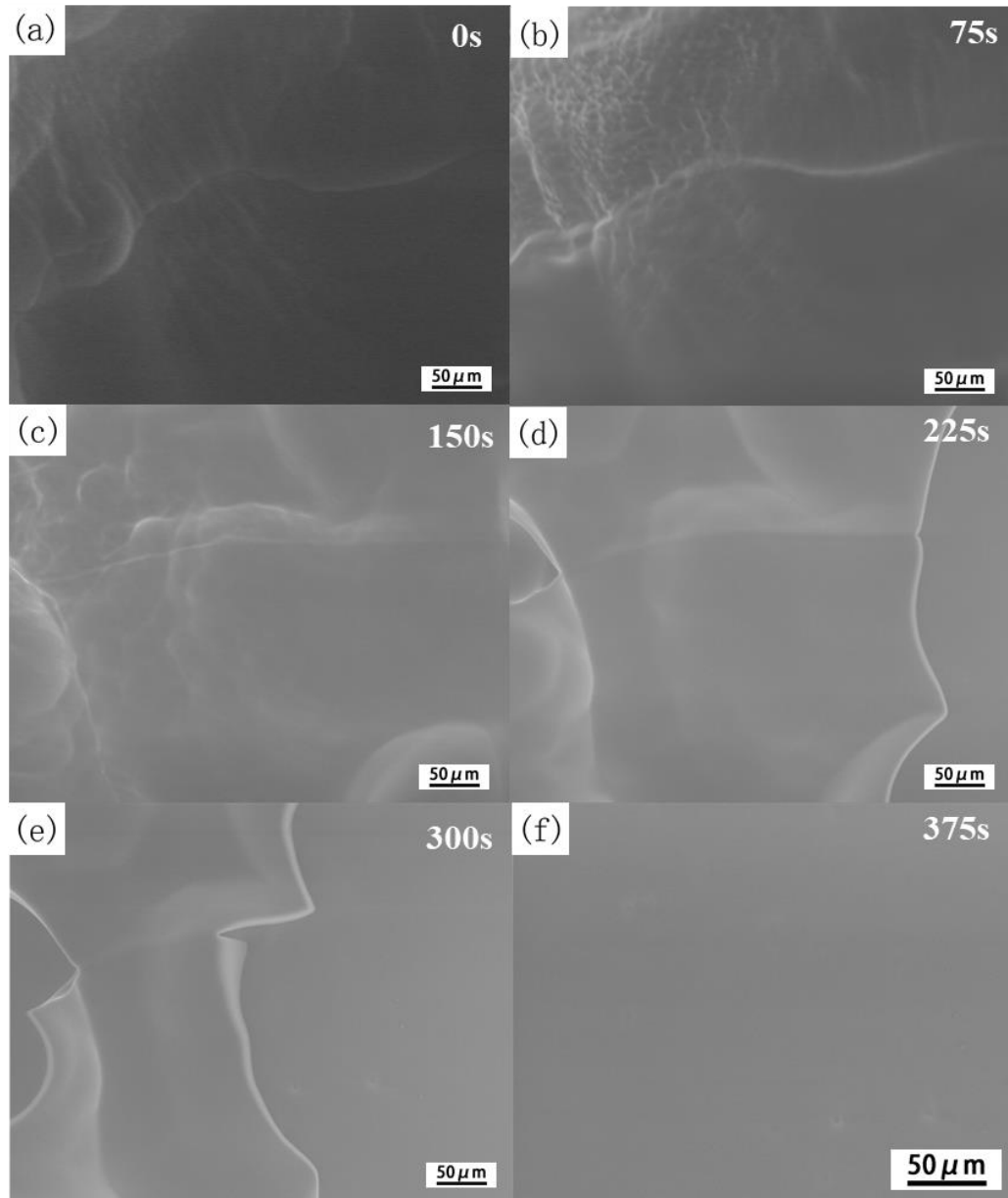


Figure 6.19 Ice diminishing process on NP-glycerol (a) $t=0$ s (b) $t=75$ s (c) $t=150$ s (d) $t=225$ s (e) $t=300$ s (f) $t=375$ s.

Figure 6.19 showed the diminishment process of ice on NP-glycerol. The whole process seemed to be quite similar to that of NP-glycol. It could be found that the surface morphology of NP-glycerol maintained intact when the ice crystal receded during the sublimation. From Figure 6.19 (a) to (b), the ice layer seemed to become thinner. The thickness of the ice layer kept reducing with reduced system humidity. The edges also changed from rounded to angular, as shown in image (d). The main changes took place

on the formed surface ice block, less phenomenon between the sample/ice interfaces could be found until image (d). The disappearance direction of the formed ice crystal was just the opposite of the propagation direction. It took more than 300 s to finish the whole process, and no surface damage could be found on the surface. With smooth and flat surface, there was also no ice anchoring or retardation of ice movement observed during the whole process. This could also verify the low value of ice adhesion strength, indicating good potential in de-icing applications.

6.5 Relationship between Structure Icephobicity/Durability

Improvements with Ice Depressing Liquid Incorporation

6.5.1 Influence of ice depressing liquid incorporation on sample structures

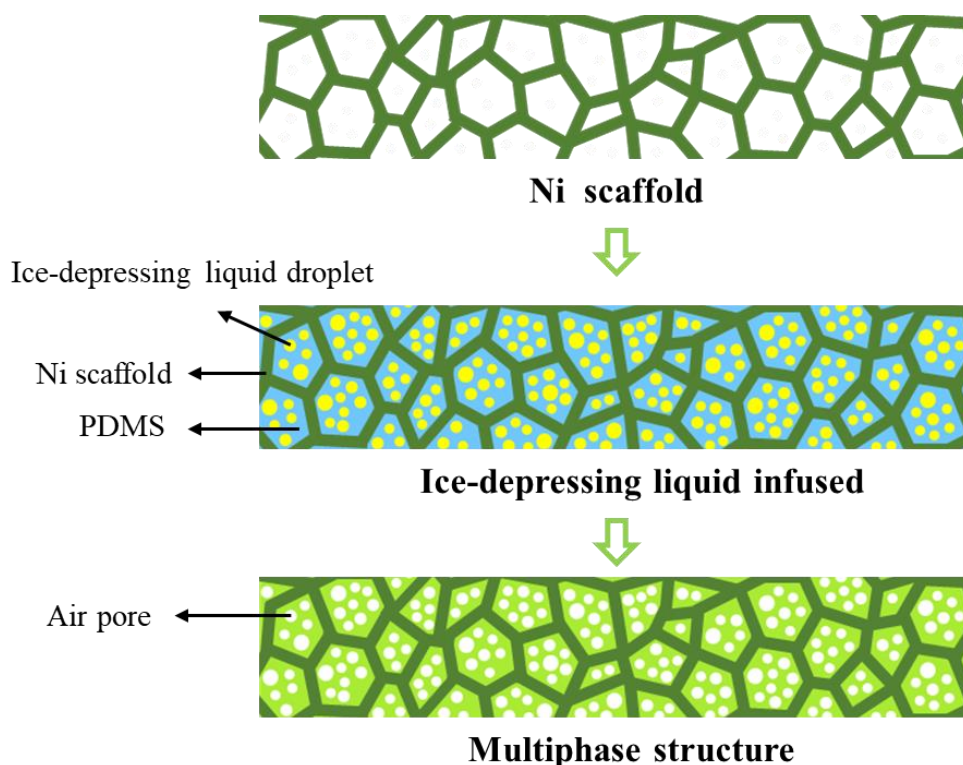


Figure 6.20 Schematic diagram indicating the effect of ice depressing molecules on the sample structures during the curing process.

The additions of ice depressing liquid and Ni scaffold made huge differences in the structure and the icephobic performance. Figure 6.20 illustrated the influence of ice depressing liquid on the sample structures during the curing process. As indicated in the Section 6.1.2, the ice depressing liquid suffered the volatilization and diffused out during the curing treatment. Ice depressing liquid could distribute inside the PDMS matrix in the form of droplets. Some portions of the ice depressing liquid were released slowly. Some of the ice depressing molecules still remained inside the matrix [399]. Due to the differences in interfacial tension between the PDMS resin and the infused liquid (including glycol and glycerol), there would be big variations among the dimension and density of the formed internal porosities which came from the curing of the mixtures derived from the difference in dispersed states [400]. By comparing the FTIR spectrum results of pure PDMS, the -OH stretching was found to be the supporting evidence of the existence of ice depressing liquid. Some portions of the ice depressing liquid were dispersed inside PDMS cross-linked network. The results proved that there would be ice depressing liquid molecules remaining inside the samples even if some volatilization has taken place during the post-baking treatments.

6.5.2 Effect of different oil infusions in delaying ice formation

Figure 6.8 indicated the two different ice nucleation behaviours including heterogeneous and homogenous nucleations. The nucleation process at the liquid-solid interfaces (shown in Set 1) was recognized that the heterogeneous nucleation played a dominant role throughout the whole process [390]. As for Set 2, when nucleation took place indiscriminately both inside the droplet and at the gas-liquid interfaces [401], the homogenous nucleation contributes the majority of the whole phase change process. Due to the different nucleation processes, the icing durations of water droplet on samples with ice depressing liquids was much longer than that on samples without any addition. The relationships between the free energy barrier of homogenous nucleation and heterogenous nucleation could be described by equation (6.1) [335]:

$$\Delta G_{hete} = \Delta G_{homo} f(m, x) \quad (6.1)$$

where ΔG_{hete} and ΔG_{homo} represent the free energy barrier of heterogeneous nucleation and homogenous nucleation, respectively. $f(m, x)$ is the geometric factor, with the range from 0 and 1. Therefore, the energy barrier overcome by homogeneous nucleation during the ice nucleation is always larger than that of heterogeneous nucleation. The ice delay duration of samples with ice depressing liquids (mainly homogeneous nucleation) would be longer when compared with the value of samples without ice depressing liquids infusion.

Combined with the surface chemistry analysis, it indicated that the hydroxyl groups play vital roles in delaying the ice formation which mainly comes from the ice depressing molecules. The hydroxyl groups could form hydrogen bond networks with free water molecules, which also decreased the effective concentration variation between ice and the free water molecules [402]. Therefore, the freezing point of the water droplet at the solid-liquid interfaces decreased.

The relationship between Gibbs free energy (ΔG) and ice embryo radius (r) shows that if the radius of the ice embryo is higher than the critical value r_c , the growth of the ice embryo in energy aspects could help more with the homogenous nucleation [112]. It is thought that the water molecules at the gas-liquid interface contributed more to the growth of ice embryos than that at the solid-liquid interface, thus promoting the homogenous nucleation progress.

Ice nucleation delay time τ was related to the nucleation free energy ΔG_n , as shown in equation (6.2) [379]:

$$J(T) = \tau^{-1} = K \exp\left(-\frac{\Delta G_n}{k_B T}\right) \quad (6.2)$$

ΔG_n can be further calculated by equation (6.3) [403, 404]:

$$\Delta G_n = \frac{16\pi\gamma_{lw}^3}{3\Delta G_v^2} f(m, x) \quad (6.3)$$

Here, ΔG_v represents the volumetric free energy during the phase-change, which can be calculated by equation (6.4):

$$\Delta G_v = \Delta H_v \frac{(T_m - T)}{T_m} \quad (6.4)$$

where $J(T)$ shows the nucleation rate, k_B is the Boltzmann constant (non-dimensional), K is kinetic constant. ΔH_v represents the enthalpy of phase-change, T_m means phase-transition temperature and γ_{lw} is ice-water interfacial energy. $f(m, x)$ is a surface factor that is governed by the energy and geometry of the involved interfaces. The value of $f(m, x)$ is in the range from 0 to 1.

Ice depressing molecules addition was used to decrease freezing point of water (T_m), so ΔG_v would decrease and ΔG_n then increase. Besides, the value of $f(m, x)$ equals to 1 when the homogenous nucleation takes place, and ΔG_n increases. To summarize, the addition of ice depressing liquid contributes to the increase of the icing duration τ .

6.5.3 Evaluation of mechanical durability

Although the introduction of ice depressing molecules shows good advantages in ice formation delay, surfaces that incorporate hydroxyl groups can in turn increase ice adhesion through the hydrogen bonding. Multiphase icephobic layer construction was designed to minimize the effect of hydroxyls to surfaces and lower the ice adhesion strength. The introduction of ice depressing molecules also helped with the formation of the porous polymer matrix, forming the three phase structures (porosity/metallic scaffold/polymer). The mismatch in elastic modulus between the metallic scaffolds and the matrix further promoted the initiation of the micro-crack on the surface.

The values of ice adhesion strength of different samples during 50 icing/de-icing cycles were shown in Figure 6.12 and Figure 6.13. It indicated that the ice adhesion strength of both NP-glycol and NP-glycerol were always maintained at 1.1 kPa and 0.7 kPa during the whole 50 cycles. The extremely low value of ice adhesion strength mainly comes from the multi-phase structure of NP-glycol and NP-glycerol. The introduction of ice depressing liquid could help to form the porous polymer, which further contributes to the three-phase system (porosity/metallic scaffold/polymer). The difference in the elastic modulus further promoted the initiation of micro-cracks on the surface. Because the size and distribution density of internal porosity in NP-glycerol was obviously larger than that in NP-glycol, it also led to a larger difference in elastic modulus. While for surface roughness, it could pose less effect on the ice adhesion strength than elastoplastic difference, the ice adhesion strength of NP-glycerol was just below that of NP-glycol even though the surface roughness of NP-glycerol was larger than the Ra of NP-glycol.

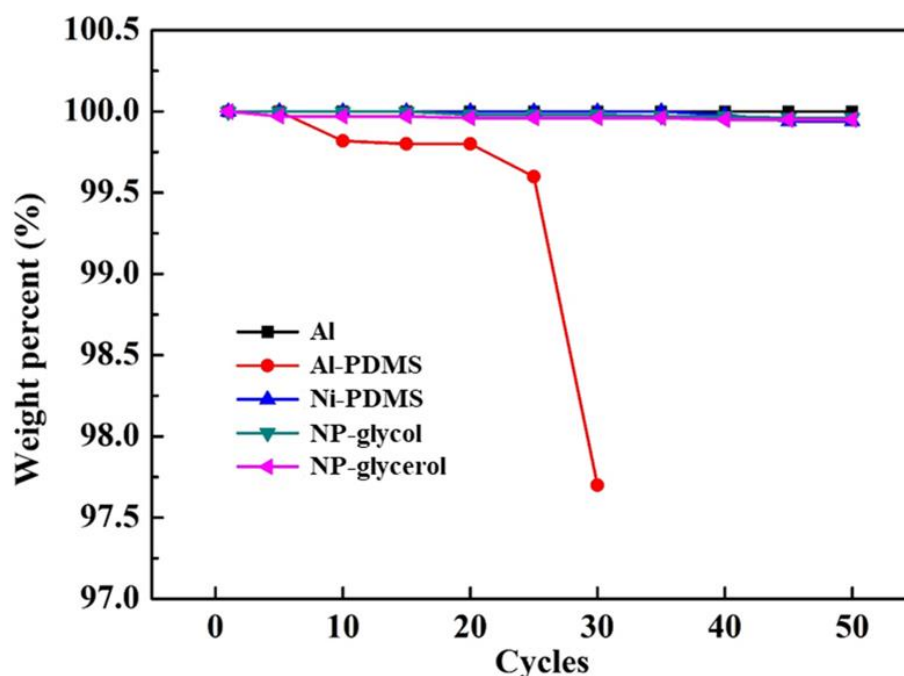


Figure 6.21 Weight maintenance ratio variations of different samples during 50 icing/de-icing cycles.

Figure 6.21 depicted the variation in the mass of the involved samples during the 50 icing/de-icing cycles. There was no big change taking place in the mass of the tested samples except for the breakage of PDMS layer in Al-PDMS, leading to some mass decrease, which was also mentioned in Figure 6.12. For other samples, especially the NP-glycol and NP-glycerol, the introduction of Ni scaffold could improve their mechanical durability. This also proved the good durability enhancement of the Ni scaffold addition to the PDMS polymer. The combination between Ni scaffolds and polymer helped to enable the good icephobic stability of NP-glycerol and NP-glycol.

6.6 Summary

In this work, the multi-phase icephobic system that was made up of gas (internal pores)/polymer/metallic scaffold was designed and prepared. With the introduction of ice depressing liquids, there would be hydroxyl groups attached to the surface on the one hand, which could integrate with the water molecules and form the hydrogen-bond network. This would decrease the effective concentration between the formed ice and the unbound water molecules, leading to a lower freezing point at the interfaces. This also in turn improved the anti-icing performance of the as-prepared sample. On the other hand, because of the formed internal pores caused by the partial evaporation of ice depressing liquid and also the combination with the metal scaffold/polymer interconnected structure, it could help to form the multi-phase composite structure. In this case, the elastic-plastic difference between the various phases of the system increased, which promoted the initiation of surface micro-cracks and introduce a reduction to the ice adhesion strength. The de-icing ability has also been improved. The freezing duration of supercooled water droplets at $-20\text{ }^{\circ}\text{C}$ was delayed to as large as $153.7 \pm 2.5\text{ s}$ and $209.7 \pm 4.5\text{ s}$ on the surfaces of NP-glycol and NP-glycerol, respectively. The ice adhesion strength of the two samples also remained at around $1.1 \pm 0.2\text{ kPa}$ and $0.7 \pm 0.1\text{ kPa}$ after 50 icing/de-icing cyclic tests. NP-glycol and NP-glycerol showed more stability and lower ice adhesion strength in a higher quantity of

icing/de-icing cyclic tests compared to the reported findings [260, 318, 405-409]. The incorporation of ice depressing liquid, as well as the combination with metallic scaffold and polymer, could unfold the full potential of icephobic structures in ice protection areas.

Table 6.3 Ice adhesion strength results of reported icephobic surfaces versus icing/de-icing cycles

Reference	Surface type	Ice adhesion		
		1 st cycle (kPa)	Icing/de-icing cycles	Last cycle (kPa)
This work	NP-glycol	1.1	50	1.2
	NP-glycerol	0.7	50	0.8
Wang [405]	LP-OG	2.0	35	8.1
Donadei [406]	LIC3	23.0	4	63.0
Zhan [260]	SLI-EG	1.0	3	21.0
Henna [407]	Perfluorinated oil	8.0	4	10.0
Kim [318]	50%SO (100cst)	10.2	20	15.0
	50%SO (350cst)	16.3	20	20.8
	70%SO (100cst)	5.3	20	24.1
	70%SO (350cst)	8.3	20	18.9
Sun [408]	SHN1-1	6	10	29
	TSN1-1	14	10	37
Deng [409]	LIMNSMC	19.0	10	86.0

Chapter 7 Conclusions and Future Work

7.1 Conclusions

The aim of this work was to investigate and design novel icephobic structures with prospective utilization in the aerospace sectors. The literature review in Chapter 2 encompassed an examination of the importance of ice protection, principles and theories underlying icephobicity, surface wettability, challenges, and perspectives in associated domains. Standard and custom-built equipment were used to conduct in-situ characterisation, icephobic evaluations and durability analysis on the developed substrates as detailed in Chapter 3. This study examined three icephobic structures with unique concepts, namely the incorporation of Ni scaffolds to alleviate oil depletion in the PDMS-silicone system (Chapter 4), the application of phase change liquid to extend the icing delay time at the solid-liquid interface (Chapter 5), and the addition of ice depressing liquid to improve the anti-icing properties of the surface (Chapter 6). The three icephobic structures demonstrated low ice adhesion strength attributable to the micro-cracks initiation caused by the discrepancy in the elastic modulus of the multi-phase constructions. The experimental study was meticulously designed to achieve an equitable research outcome on the fundamental aspects of icephobicity investigation and to impart the understanding for the innovative and durable icephobic structures.

Initially, Ni scaffolds with microporous structures was incorporated into the LIS construction, followed by the application of PDMS with varying silicone oil content through vacuum impregnation and spinning coating techniques. The processing parameters for the layer structure preparation were investigated. The inclusion of Ni scaffolds facilitated stress redistribution during de-icing, thereby safeguarding the LIS material from external loads and impacts. The experimental outcomes suggest that the incorporation of Ni scaffolds and PDMS modified with 40 wt% silicone oil addition (NP-40SO) yielded surfaces that were smooth and flat with a surface roughness value of $0.81 \pm 0.13 \text{ } \mu\text{m}$. The NP-40SO surfaces exhibited exceptional icephobic

characteristics, as evidenced by the ice adhesion strength value of 1.6 ± 0.2 kPa, which was significantly lower than that of conventional surfaces. Furthermore, the NP-40SO surfaces displayed remarkable de-icing performance stability even after undergoing 50 icing/de-icing cycles. In addition, the anti-icing mechanisms of NP-40SO were investigated through ice/frost formation tests and Environmental Scanning Electron Microscopy (ESEM) observation. The wetting behavior of water contact angle (WCA) of 111.75° and contact angle hysteresis (CAH) of 4.2° were also recorded. With the increasing addition of silicone oil, the measured hardness and surface free energy of the NP-SO samples decreased. The increase in the actual nucleation free energy barrier during the freezing process resulted in a delay in ice nucleation at the liquid-solid interface and an extension of the icing duration. Specifically, the icing duration was prolonged by approximately 20 seconds, as the NP-50SO samples had an average icing duration of 80 ± 3.1 s compared to the Ni-PDMS surface. The inclusion of Ni scaffolds during the de-icing process aided in stress redistribution, which effectively protected the LIS structures from external loads and impacts. Additionally, it prevented quick depletion of infused oil lubricants caused by large polymer deformation. The multiphase construction significantly reduced oil depletion by over three times after 50 cycles of anti-icing/de-icing tests, thus addressing concerns regarding oil depletion in extended service environments. Moreover, the multiphase LIS construction promoted the initiation of micro-cracks at the solid-ice interfaces, which facilitated easy ice detachment. The NP-SO samples with Ni scaffolds showed an ice adhesion strength of down to 2.0 ± 0.7 kPa after 50 cycles of anti-icing/de-icing tests, while samples without Ni scaffolds exhibited surface damage after only 30 cycles.

Phase change liquids were introduced into a multi-phase icephobic structure composed of Ni scaffolds and PDMS to enhance its anti-icing performance. Two phase change materials, groundnut oil and coconut oil, with varying phase change temperatures were chosen along with silicone oil as a reference material and were incorporated into the Ni scaffolds/PDMS system. The phase change liquids were able to absorb and release heat over a specific temperature range during the phase change process. The release of heat

from the phase change material could raise the temperature on the sample surface, which could delay the icing process of the supercooled water droplet. Ni scaffolds/PDMS modified with 20 wt% groundnut oil and 3 wt% Alumina aerogel (NP-20GO3Al) were prepared to enhance the anti-icing performance of the multi-phase icephobic structure. The surface chemical properties of NP-20GO3Al were analyzed using FTIR spectrometry and differential scanning calorimetry, which showed that groundnut oil was diffused into PDMS matrix and the phase change properties (phase transition temperature interval: $-16.0\text{ }^{\circ}\text{C}$ to $2.4\text{ }^{\circ}\text{C}$) of PDMS were well retained. The heat transfer efficiency during the phase change was 3.2 J/g . Environmental Scanning Electron Microscopy (ESEM) observations revealed the importance of the phase change liquid and the presence of the oil layer in delaying the icing time to $78 \pm 2.9\text{ s}$ and reducing the formed frost per unit area to $3.7 \pm 0.6\text{ mg/cm}^2$. Moreover, the freezing time of droplets on the sample surface was found to be 7-8 times longer compared to that observed on aluminum alloy. The actual freezing temperature of the water on the samples surface was reduced to $-10\text{ }^{\circ}\text{C}$. The ice adhesion strength was maintained at around $9.8 \pm 1.2\text{ kPa}$ during the 50 icing/de-icing cyclic tests due to the addition of Ni scaffolds. The mechanism identified in this study could be transferable to other icephobic coatings and surfaces.

In order to reduce the freezing points of water on the sample surface, ice depressing liquid was introduced into the Ni scaffolds/PDMS. Glycol and glycerol were selected as the ice depressing liquids infused in the Ni scaffolds/PDMS system. SEM results indicated the formation of internal pores in the multi-phase structures, while the ice depressing liquid experienced volatilization and diffusion during the curing process. However, the surface of the structure remained smooth, without visible pores, and the roughness remained at $Ra \approx 1\text{ }\mu\text{m}$. The incorporation of ice depressing liquids in the form of glycol and glycerol facilitated the formation of a porous polymer, thereby contributing to the development of a three-phase system that included porosity, metallic scaffold, and polymer. This system was observed to initiate micro-cracks on the surface due to the difference in the elastic modulus. The study found that the retention of

significantly low ice adhesion strength (1.1 ± 0.2 kPa and 0.7 ± 0.1 kPa, respectively) was achieved for 50 icing/de-icing cycles by incorporating glycol and glycerol in the multi-phase structures. In contrast, the reference value for Ni-PDMS samples was 29.8 ± 2.9 kPa. The freezing duration of supercooled water droplets at -20 °C was delayed to 153.7 ± 2.5 s and 209.7 ± 4.5 s on the surfaces of NP-glycol and NP-glycerol, respectively. This can be attributed to the formation of hydrogen bond networks between the hydroxyl groups and the free water molecules, which decreased the effective concentration between ice and the free water molecules. Moreover, the in-situ ESEM observation demonstrated the process of ice accretion and diminishment on the NP-glycol and NP-glycerol surfaces. The combination of the mechanical advantages offered by Ni scaffolds and the favorable icephobicity provided by ice depressing liquid modified PDMS presents a promising approach for the development of durable icephobic surfaces. This strategy offers a new feasibility and provides valuable insights for designing robust icephobic surfaces.

7.2 Future Work

The present doctoral project has a specific scope aimed at investigating the fundamental science underlying durability and anti-icing mechanisms, developing anti-icing layer structures with exceptional mechanical durability, and practically applying the resulting anti-icing coatings. Accordingly, a number of specific domains have been identified for future research that aims to advance the field of icephobicity science.

In the present study, it was found that there is room for improvement in the selection of metal phases and polymers in multiphase systems, in addition to the Ni scaffolds and PDMS used. The research presented in this thesis provides insightful guidance on the phase composition of multiphase durable anti-icing structures. Due to the random pore distribution of the Ni scaffolds utilized in this study, a more detailed control of the distribution of the metal mesh is necessary to elucidate the relationship between the

distribution status of the metal mesh and the mechanism of micro-crack generation. The distribution of the metal mesh can be more precisely controlled by lithography and dry etching on a silicon substrate, which can be patterned with the required shape, followed by sputtering a nickel seed layer on the substrate and electroplating to fabricate the Ni scaffold. The results of this study may also aid in developing a theoretical relationship between the difference in elastic modulus and ice adhesion strength. Further investigations can be conducted to explore the synergy between the distribution of the multiphase structure and its related correlation, and to determine the appropriate phase composition that maximizes the icephobic performance. Furthermore, the scope of this study can be expanded to include the use of various polymers, such as polytetrafluoroethylene (PTFE), polyurethane (PU), polyoxymethylene copolymer thermoplastic (POTs), and others, to validate the findings.

To gain a deeper comprehension and accurate measurement of the icephobicity of diverse surfaces, a variety of prototype tests must be performed to evaluate different icephobic performances. These evaluations may entail assessments conducted under simulated working conditions, such as wind tunnel tests designed for airfoil applications, as well as tests conducted in real-world conditions. Moreover, it is crucial to take into account the specific application for which the anti-icing or de-icing surface will be used, as the desired icephobic performance can be significantly impacted. For instance, a surface that is highly effective in mitigating ice adhesion on an airplane wing may not exhibit comparable results when applied to a power line or a car windshield. Therefore, it is imperative to obtain a comprehensive understanding of the various properties and behaviors that contribute to icephobicity, and to customize the design and testing of anti-icing and de-icing surfaces accordingly.

To further advance the research and development of icephobic coatings, additional simulation analysis work could be conducted to provide more precise guidance. This may include stress analysis, thermal transfer analysis, and material response under erosion impact using finite element analysis. To better capture the intricacies of ice

adhesion and icephobicity, modelling at different scales, such as macroscale, microscale, and nanoscale, may be necessary. Various simulation methods, such as finite element analysis, molecular dynamics, or other appropriate techniques, could be applied to uncover the underlying mechanisms of ice adhesion and detachment. By utilizing a multi-scale simulation approach, the complex interplay between surface morphology, surface energy, and ice accretion can be more comprehensively investigated, leading to the development of more effective icephobic coatings with tailored properties for different applications. The results of these simulations can provide valuable insights into the design and optimization of icephobic coatings, by predicting performance under varying conditions and informing the selection of materials and surface structures. Moreover, simulation work can provide a cost-effective and efficient means of testing and evaluating different coating designs before physical testing is conducted, reducing the time and expense involved in the development process. Therefore, further exploration and application of simulation analysis in the research and development of icephobic coatings are crucial for advancing this field and improving the performance and durability of icephobic coatings in various applications.

References

- [1] J. Jeevahan, M. Chandrasekaran, G.B. Joseph, R. Durairaj, G. Mageshwaran, Superhydrophobic surfaces: A review on fundamentals, applications, and challenges, *Journal of Coatings Technology and Research* 15(2) (2018) 1-20.
- [2] R. Gent, N. Dart, J. Cansdale, Aircraft icing, *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 358(1776) (2000) 2873-2911.
- [3] J. Laforte, M. Allaire, J. Laflamme, State-of-the-art on power line de-icing, *Atmospheric Research* 46(1-2) (1998) 143-158.
- [4] X. Shi, S.M. Quilty, T. Long, A. Jayakaran, L. Fay, G. Xu, Managing airport stormwater containing deicers: challenges and opportunities, *Frontiers of Structural and Civil Engineering* 11(1) (2017) 35-46.
- [5] P.F. Ibáñez-Ibáñez, F.J. Montes Ruiz-Cabello, M.A. Cabrerizo-Vélez, M.A. Rodríguez-Valverde, Ice adhesion of PDMS surfaces with balanced elastic and water-repellent properties, *Journal of Colloid and Interface Science* 608 (2022) 792-799.
- [6] D. Yang, R. Bao, A.T. Clare, K.-S. Choi, X. Hou, Hydrophobically/oleophilically guarded powder metallurgical structures and liquid impregnation for ice mitigation, *Chemical Engineering Journal* 446 (2022) 137115.
- [7] P. Wang, Z. Li, Q. Xie, W. Duan, X. Zhang, H. Han, A passive anti-icing strategy based on a superhydrophobic mesh with extremely low ice adhesion strength, *Journal of Bionic Engineering* 18(1) (2021) 55-64.
- [8] T. Wu, W.-h. Xu, K. Guo, H. Xie, J.-p. Qu, Efficient fabrication of lightweight polyethylene foam with robust and durable superhydrophobicity for self-cleaning and anti-icing applications, *Chemical Engineering Journal* 407 (2021) 127100.
- [9] A. Volpe, C. Gaudiuso, A. Ancona, Laser Fabrication of Anti-Icing Surfaces: A Review, *Materials* 13(24) (2020) 5692.
- [10] Y. Zhuo, S. Xiao, V. Håkonsen, J. He, Z. Zhang, Anti-icing ionogel surfaces: inhibiting ice nucleation, growth, and adhesion, *ACS Materials Letters* 2(6) (2020) 616-

623.

- [11] M.S. Park, Aircraft De-Icing System Using Thermal Conductive Fibers, (2015).
- [12] H. Hou, X. Yin, Q. Chen, G. Tong, D. You, B. Wang, X. He, H. Liu, Analysis of vulnerabilities in China's Southern Power System using data from the 2008 snow disaster, 2009 IEEE Power & Energy Society General Meeting, IEEE, (2009) 1-7.
- [13] Y. Zhuo, F. Wang, S. Xiao, J. He, Z. Zhang, One-step fabrication of bioinspired lubricant-regenerable icephobic slippery liquid-infused porous surfaces, ACS omega 3(8) (2018) 10139-10144.
- [14] S. Gao, B. Liu, J. Peng, K. Zhu, Y. Zhao, X. Li, X. Yuan, Icephobic durability of branched PDMS slippage coatings co-cross-linked by functionalized POSS, ACS applied materials & interfaces 11(4) (2019) 4654-4666.
- [15] Y. Shen, J. Tao, H. Tao, S. Chen, L. Pan, T. Wang, Anti-icing potential of superhydrophobic Ti6Al4V surfaces: ice nucleation and growth, Langmuir 31(39) (2015) 10799-10806.
- [16] H. Guo, Y. Xing, H. Yuan, R. Zhang, Y. Zhang, P. Deng, Improving the anti-icing performance of superhydrophobic surfaces by nucleation inhibitor, Surface Engineering 36(6) (2020) 621-627.
- [17] G. Wang, Y. Shen, J. Tao, X. Luo, M. Jin, Y. Xie, Z. Li, S. Guo, Facilely constructing micro-nanostructure superhydrophobic aluminum surface with robust ice-phobicity and corrosion resistance, Surface and Coatings Technology 329 (2017) 224-231.
- [18] X. Wu, F. Yang, G. Lu, X. Zhao, Z. Chen, S. Qian, A breathable and environmentally friendly superhydrophobic coating for anti-condensation applications, Chemical Engineering Journal 412 (2021) 128725.
- [19] S. Barthwal, B. Lee, S.-H. Lim, Fabrication of robust and durable slippery anti-icing coating on textured superhydrophobic aluminum surfaces with infused silicone oil, Applied Surface Science 496 (2019) 143677.
- [20] Y. Shen, K. Li, H. Chen, Z. Wu, Z. Wang, Superhydrophobic F-SiO₂@ PDMS composite coatings prepared by a two-step spraying method for the interface erosion mechanism and anti-corrosive applications, Chemical Engineering Journal 413 (2021)

127455.

[21] X. Shi, X. Lv, J. Lu, Y. Xu, W. Yuan, Y. He, Anti-icing polyimide thin film with microcolumns fabricated by RIE with cooling and PCVD, *Micro & Nano Letters* 17(1) (2022) 1-8.

[22] L. Xiao, J. Li, S. Mieszkin, A. Di Fino, A.S. Clare, M.E. Callow, J.A. Callow, M. Grunze, A. Rosenhahn, P.A. Levkin, Slippery liquid-infused porous surfaces showing marine antibiofouling properties, *ACS applied materials & interfaces* 5(20) (2013) 10074-10080.

[23] T.-S. Wong, S.H. Kang, S.K. Tang, E.J. Smythe, B.D. Hatton, A. Grinthal, J. Aizenberg, Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity, *Nature* 477(7365) (2011) 443-447.

[24] T. Li, P.F. Ibáñez-Ibáñez, V. Håkonsen, J. Wu, K. Xu, Y. Zhuo, S. Luo, J. He, Z. Zhang, Self-deicing electrolyte hydrogel surfaces with Pa-level ice adhesion and durable antifreezing/antifrost performance, *ACS applied materials & interfaces* 12(31) (2020) 35572-35578.

[25] H.N. Kim, S.J. Kim, W. Choi, H.J. Sung, S.J. Lee, Depletion of lubricant impregnated in a cavity of lubricant-infused surface, *Physics of Fluids* 33(2) (2021) 022005.

[26] G. Chen, Z. Sun, Y. Wang, J. Zheng, S. Wen, J. Zhang, L. Wang, J. Hou, C. Lin, Z. Yue, Designed preparation of silicone protective materials with controlled self-healing and toughness properties, *Progress in Organic Coatings* 140 (2020) 105483.

[27] G. Chen, S. Liu, Z. Sun, S. Wen, T. Feng, Z. Yue, Intrinsic self-healing organogels based on dynamic polymer network with self-regulated secretion of liquid for anti-icing, *Progress in Organic Coatings* 144 (2020) 105641.

[28] M. Carlotti, I. Cesini, V. Mattoli, A Simple Approach for Flexible and Stretchable Anti-icing Lubricant-Infused Tape, *ACS applied materials & interfaces* 13(37) (2021) 45105-45115.

[29] R. Dou, J. Chen, Y. Zhang, X. Wang, D. Cui, Y. Song, L. Jiang, J. Wang, Anti-icing Coating with an Aqueous Lubricating Layer, *ACS Applied Materials & Interfaces* 6(10) (2014) 6998-7003.

- [30] X. Tan, Y. Wang, Z. Huang, S. Sabin, T. Xiao, L. Jiang, X. Chen, Facile Fabrication of a Mechanical, Chemical, Thermal, and Long-Term Outdoor Durable Fluorine-Free Superhydrophobic Coating, *Advanced Materials Interfaces* 8(11) (2021) 2002209.
- [31] M.J. Kreder, J. Alvarenga, P. Kim, J. Aizenberg, Design of anti-icing surfaces: smooth, textured or slippery?, *Nature Reviews Materials* 1(1) (2016) 1-15.
- [32] J. Zhang, B. Liu, Y. Tian, F. Wang, L. Ma, Facile One-Step Method to Fabricate a Slippery Lubricant-Infused Surface (LIS) with Self-Replenishment Properties for Anti-Icing Applications, *Coatings* 10(2) (2020) 119.
- [33] M. Khalifa, A. Berndt, S. C., S. Pichler, H. Lammer, G. Wuzella, Hybridization effect of cellulose paper and postcuring conditions on the mechanical properties of flax fiber reinforced epoxy biocomposite, *Journal of Applied Polymer Science* 140(2) (2023) e53297.
- [34] Q. Rao, Y. Lu, L. Song, Y. Hou, X. Zhan, Q. Zhang, Highly efficient self-repairing slippery liquid-infused surface with promising anti-icing and anti-fouling performance, *ACS Applied Materials & Interfaces* 13(33) (2021) 40032-40041.
- [35] J.S. Wexler, A. Grosskopf, M. Chow, Y. Fan, I. Jacobi, H.A. Stone, Robust liquid-infused surfaces through patterned wettability, *Soft Matter* 11(25) (2015) 5023-5029.
- [36] M. Villegas, Y. Zhang, N. Abu Jarad, L. Soleymani, T.F. Didar, Liquid-Infused Surfaces: A Review of Theory, Design, and Applications, *ACS Nano* 13(8) (2019) 8517-8536.
- [37] S. Heydarian, R. Jafari, G. Momen, Recent progress in the anti-icing performance of slippery liquid-infused surfaces, *Progress in Organic Coatings* 151 (2021) 106096.
- [38] J. Cui, D. Daniel, A. Grinthal, K. Lin, J. Aizenberg, Dynamic polymer systems with self-regulated secretion for the control of surface properties and material healing, *Nature Materials* 14(8) (2015) 790-795.
- [39] M.J. Coady, M. Wood, G.Q. Wallace, K.E. Nielsen, A.-M. Kietzig, F. Laguë Labarthe, P.J. Ragogna, Icephobic Behavior of UV-Cured Polymer Networks Incorporated into Slippery Lubricant-Infused Porous Surfaces: Improving SLIPS Durability, *ACS Applied Materials & Interfaces* 10(3) (2018) 2890-2896.
- [40] J. Wang, M. Wu, J. Liu, F. Xu, T. Hussain, C. Scotchford, X. Hou, Metallic skeleton

promoted two-phase durable icephobic layers, *Journal of Colloid and Interface Science* 587 (2021) 47-55.

[41] X. Xiao, P. Zhang, M. Li, Effective thermal conductivity of open-cell metal foams impregnated with pure paraffin for latent heat storage, *International Journal of Thermal Sciences* 81 (2014) 94-105.

[42] Y. Zhuo, S. Xiao, A. Amirfazli, J. He, Z. Zhang, Polysiloxane as icephobic materials–The past, present and the future, *Chemical Engineering Journal* 405 (2021) 127088.

[43] H. Memon, D.S. De Focatiis, K.-S. Choi, X. Hou, Toward Exceptional Icephobicity with Chionophile-Inspired Durable Biomimetic Coatings, *ACS Applied Polymer Materials* 3(8) (2021) 4184-4194.

[44] Petrenko, F. V., Peng, S., Reduction of ice adhesion to metal by using self-assembling monolayers (SAMs), *Canadian Journal of Physics* 81(1-2) (2003) 387-393.

[45] B. Traveller, Snow disruption to cost BA £50m., (2011).

[46] M. Politovich, Aircraft icing. *Encyclopedia of Atmospheric Science*, JR Holton, JA Curry, and JA Pyle, Eds, Academic Press (2003).

[47] H. Hou, Y. Li, J. Dong, N. Lu, A. Tang, Ice disaster prevention measure optimization model, *International Journal of Security and Its Applications* 9(9) (2015) 179-188.

[48] H. Hou, X. He, Z.-t. Li, A. Tang, H.-l. Fang, Risk assessment of power system under typhoon disaster, *International Journal of Security and its Applications* 8(3) (2014) 289-296.

[49] S.V. Venna, Y.-J. Lin, G. Botura, Piezoelectric Transducer Actuated Leading Edge De-Icing with Simultaneous Shear and Impulse Forces, *Journal of Aircraft* 44(2) (2007) 509-515.

[50] Q. Sun, Y. Zhao, K.-S. Choi, X. Mao, Molecular dynamics simulation of thermal de-icing on a flat surface, *Applied Thermal Engineering* 189 (2021) 116701.

[51] W.J. Baars, R.O. Stearman, C.E. Tinney, Wind Tunnel Studies Employing Higher Order Statistics to Detect Icing Induced Upsets, *International Forum on Aeroelasticity and Structural Dynamics*. Seattle, Washington: IFASD (IFASD Paper 2009-012),

(2009).

[52] F.T. Lynch, A. Khodadoust, Effects of ice accretions on aircraft aerodynamics, *Progress in Aerospace Sciences* 37(8) (2001) 669-767.

[53] T. Irvine, S. Kevdzija, D. Sheldon, D. Spera, Overview of the icing and flow quality improvements program for the NASA-Glenn Icing Research Tunnel, 39th Aerospace Sciences Meeting and Exhibit (2001) 229.

[54] H.E. Addy, Ice accretions and icing effects for modern airfoils, National Aeronautics Administration, Glenn Research Center, (2000).

[55] X. Wang, W. Song, Z. Li, Q. Cong, Fabrication of superhydrophobic AAO-Ag multilayer mimicking dragonfly wings, *Chinese Science Bulletin* 57(35) (2012) 4635-4640.

[56] P. Hao, C. Lv, F. He, Evaporating behaviors of water droplet on superhydrophobic surface, *Science China Physics, Mechanics and Astronomy* 55(12) (2012) 2463-2468.

[57] J. Shim, J. Chung, K. Le, A computational investigation of ice geometry effects on airfoil performances, 39th Aerospace Sciences Meeting and Exhibit, (2001), p. 540.

[58] X. Huang, N. Tepylo, V. Pommier-Budinger, M. Budinger, E. Bonaccorso, P. Villedieu, L. Bennani, A survey of icephobic coatings and their potential use in a hybrid coating/active ice protection system for aerospace applications, *Progress in Aerospace Sciences* 105 (2019) 74-97.

[59] O. Parent, A. Ilinca, Anti-icing and de-icing techniques for wind turbines: Critical review, *Cold Regions Science and Technology* 65(1) (2011) 88-96.

[60] L. Vertuccio, F. Foglia, R. Pantani, L. Guadagno, New Aircraft Anti/de-Icing Technologies, *IOP Conference Series: Materials Science and Engineering*, IOP Publishing, (2021), p. 012012.

[61] Q. Su, S. Chang, Y. Zhao, H. Zheng, C. Dang, A review of loop heat pipes for aircraft anti-icing applications, *Applied Thermal Engineering* 130 (2018) 528-540.

[62] A. Shinkafi, C. Lawson, Enhanced method of conceptual sizing of aircraft electro-thermal de-icing system, *International Journal of Aerospace and Mechanical Engineering* 8(6) (2014) 1073-1080.

[63] Y. Zhu, J. Palacios, J. Rose, E. Smith, De-icing of Multi-Layer Composite Plates

Using Ultrasonic Guided Waves, 49th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, 16th AIAA/ASME/AHS Adaptive Structures Conference, 10th AIAA Non-Deterministic Approaches Conference, 9th AIAA Gossamer Spacecraft Forum, 4th AIAA Multidisciplinary Design Optimization Specialists Conference.

[64] L. Battisti, A. Brighenti, S. Dal Savio, S. Dell'Anna, Evaluation of anti-icing energy and power requirement for wind turbine rotors in cold climates, BOREAS VII. FMI, Saariselkä Finland 13 (2005).

[65] F. Zhang, C.-L. Zhang, L. Song, R.-C. Zeng, L.-Y. Cui, H.-Z. Cui, Corrosion resistance of superhydrophobic Mg–Al layered double hydroxide coatings on aluminum alloys, *Acta Metallurgica Sinica (English Letters)* 28(11) (2015) 1373-1381.

[66] E. Huttunen-Saarivirta, H. Korpiniemi, V.T. Kuokkala, H. Paajanen, Corrosion of cadmium plating by runway de-icing chemicals: Study of surface phenomena and comparison of corrosion tests, *Surface and Coatings Technology* 232 (2013) 101-115.

[67] G. Jiang, Z. Liu, J. Hu, Superhydrophobic and Photothermal PVDF/CNTs Durable Composite Coatings for Passive Anti-Icing/Active De-Icing, *Advanced Materials Interfaces* 9(2) (2022) 2101704.

[68] N. Gao, Y. Yan, Modeling superhydrophobic contact angles and wetting transition, *Journal of Bionic Engineering* 6(4) (2009) 335-340.

[69] C. Neinhuis, W. Barthlott, Characterization and distribution of water-repellent, self-cleaning plant surfaces, *Annals of botany* 79(6) (1997) 667-677.

[70] Q. Xie, J. Xu, L. Feng, L. Jiang, W. Tang, X. Luo, C.C. Han, Facile creation of a super-amphiphobic coating surface with bionic microstructure, *Advanced materials* 16(4) (2004) 302-305.

[71] Q. Xie, G. Fan, N. Zhao, X. Guo, J. Xu, J. Dong, L. Zhang, Y. Zhang, Facile creation of a bionic super-hydrophobic block copolymer surface, *Advanced materials* 16(20) (2004) 1830-1833.

[72] J.F. Maissan, Wind power development in sub-arctic conditions with severe rime icing, *Northern Review* (24) (2001).

[73] R. Chatterjee, H. Bararnia, S. Anand, A Family of Frost-Resistant and Icephobic

Coatings, *Advanced Materials* 34(20) (2022) 2109930.

[74] Y. Zheng, J. Wang, J. Liu, K.-S. Choi, X. Hou, Energy saving strategy for the development of icephobic coatings and surfaces, *Thin Solid Films* 687 (2019) 137458.

[75] P. Guo, Y. Zheng, M. Wen, C. Song, Y. Lin, L. Jiang, Icephobic/anti-icing properties of micro/nanostructured surfaces, *Advanced Materials* 24(19) (2012) 2642-2648.

[76] A.M. Coclite, R.M. Howden, D.C. Borrelli, C.D. Petruczok, R. Yang, J.L. Yagüe, A. Ugur, N. Chen, S. Lee, W.J. Jo, 25th anniversary article: CVD polymers: a new paradigm for surface modification and device fabrication, *Advanced Materials* 25(38) (2013) 5392-5423.

[77] A.J. Meuler, G.H. McKinley, R.E. Cohen, Exploiting topographical texture to impart icephobicity, *ACS nano* 4(12) (2010) 7048-7052.

[78] D.Y. Kwok, A.W. Neumann, Contact angle measurement and contact angle interpretation, *Advances in colloid and interface science* 81(3) (1999) 167-249.

[79] G. Whyman, E. Bormashenko, T. Stein, The rigorous derivation of Young, Cassie–Baxter and Wenzel equations and the analysis of the contact angle hysteresis phenomenon, *Chemical Physics Letters* 450(4-6) (2008) 355-359.

[80] P.W. Atkins, J. De Paula, J. Keeler, *Atkins' physical chemistry*, Oxford university press (2018).

[81] T. Young, III. An essay on the cohesion of fluids, *Philosophical transactions of the royal society of London* (95) (1805) 65-87.

[82] R.N. Wenzel, Resistance of solid surfaces to wetting by water, *Industrial & Engineering Chemistry* 28(8) (1936) 988-994.

[83] A. Cassie, S. Baxter, Wettability of porous surfaces, *Transactions of the Faraday society* 40 (1944) 546-551.

[84] G. Morán, R. Mállet-Renault, Superhydrophobic Surfaces Toward Prevention of Biofilm-Associated Infections, *Bacterial Pathogenesis and Antibacterial Control*, IntechOpen (2017).

[85] F. Leroy, F. Müller-Plathe, Rationalization of the behavior of solid– liquid surface free energy of water in Cassie and Wenzel wetting states on rugged solid surfaces at the

- nanometer scale, *Langmuir* 27(2) (2011) 637-645.
- [86] H. Tavana, A. Neumann, Recent progress in the determination of solid surface tensions from contact angles, *Advances in colloid and interface science* 132(1) (2007) 1-32.
- [87] R.E. Johnson Jr, R.H. Dettre, Contact angle hysteresis. III. Study of an idealized heterogeneous surface, *The journal of physical chemistry* 68(7) (1964) 1744-1750.
- [88] A. Gatenby, Initiation to Contact Angle, *CSC Scientific Blog* 11 (2016).
- [89] C. Furmidge, Studies at phase interfaces. I. The sliding of liquid drops on solid surfaces and a theory for spray retention, *Journal of colloid science* 17(4) (1962) 309-324.
- [90] S. Michielsen, J. Zhang, J. Du, H.J. Lee, Gibbs Free Energy of Liquid Drops on Conical Fibers, *Langmuir* 27(19) (2011) 11867-11872.
- [91] D. Qu é é Wetting and roughness, *Annu. Rev. Mater. Res.* 38 (2008) 71-99.
- [92] C. Ran, G. Ding, W. Liu, Y. Deng, W. Hou, Wetting on nanoporous alumina surface: transition between Wenzel and Cassie states controlled by surface structure, *Langmuir* 24(18) (2008) 9952-9955.
- [93] C. Yuan, M. Huang, X. Yu, Y. Ma, X. Luo, A simple approach to fabricate the rose petal-like hierarchical surfaces for droplet transportation, *Applied Surface Science* 385 (2016) 562-568.
- [94] A. Lafuma, D. Qu é é Superhydrophobic states, *Nature materials* 2(7) (2003) 457-460.
- [95] S. Academy, Unit 5: States of Matter, *CHEM101: General Chemistry I* (2009).
- [96] A. Dotan, H. Dodiuk, C. Laforte, S. Kenig, The relationship between water wetting and ice adhesion, *Journal of Adhesion Science and Technology* 23(15) (2009) 1907-1915.
- [97] J.A. Dolan, ERDC/CRREL TR-09-14 Report, Publications of the U.S. Army Engineer Research and Development Center (2017).
- [98] O. Mishima, H.E. Stanley, The relationship between liquid, supercooled and glassy water, *Nature* 396(6709) (1998) 329-335.
- [99] S. Sastry, Sculpting ice out of water, *Nature* 416(6879) (2002) 376-377.

- [100] G.M. Pound, Selected values of critical supersaturation for nucleation of liquids from the vapor, *Journal of Physical and Chemical Reference Data* 1(1) (1972) 119-133.
- [101] G.J. Morris, E. Acton, Controlled ice nucleation in cryopreservation—a review, *Cryobiology* 66(2) (2013) 85-92.
- [102] H. Yu, W.F. van Gunsteren, Charge-on-spring polarizable water models revisited: From water clusters to liquid water to ice, *The Journal of chemical physics* 121(19) (2004) 9549-9564.
- [103] P.V. Hobbs, *Ice physics*, Oxford university press (2010).
- [104] T.F. Whale, M. Rosillo-Lopez, B.J. Murray, C.G. Salzmann, Ice nucleation properties of oxidized carbon nanomaterials, *The journal of physical chemistry letters* 6(15) (2015) 3012-3016.
- [105] E.B. Moore, V. Molinero, Structural transformation in supercooled water controls the crystallization rate of ice, *Nature* 479(7374) (2011) 506-508.
- [106] X. Wang, S. Wang, Q. Xu, J. Mi, Thermodynamics of ice nucleation in liquid water, *The Journal of Physical Chemistry B* 119(4) (2015) 1660-1668.
- [107] M. Fitzner, G.C. Sosso, S.J. Cox, A. Michaelides, The many faces of heterogeneous ice nucleation: Interplay between surface morphology and hydrophobicity, *Journal of the American Chemical Society* 137(42) (2015) 13658-13669.
- [108] H.R. Pruppacher, J.D. Klett, Microphysics of clouds and precipitation, *Nature* 284(5751) (1980) 88-88.
- [109] S. Suzuki, A. Nakajima, N. Yoshida, M. Sakai, A. Hashimoto, Y. Kameshima, K. Okada, Freezing of water droplets on silicon surfaces coated with various silanes, *Chemical Physics Letters* 445(1-3) (2007) 37-41.
- [110] Y. Shen, X. Wu, J. Tao, C. Zhu, Y. Lai, Z. Chen, Icephobic materials: Fundamentals, performance evaluation, and applications, *Progress in Materials Science* 103 (2019) 509-557.
- [111] A. Alizadeh, V. Bahadur, A. Kulkarni, M. Yamada, J.A. Ruud, Hydrophobic surfaces for control and enhancement of water phase transitions, *MRS bulletin* 38(5) (2013) 407-411.

- [112] T.M. Schutzius, S. Jung, T. Maitra, P. Eberle, C. Antonini, C. Stamatopoulos, D. Poulidakos, Physics of icing and rational design of surfaces with extraordinary icephobicity, *Langmuir* 31(17) (2015) 4807-4821.
- [113] H. Inaba, K. Takeya, S. Nozu, Fundamental study on continuous ice making using flowing supercooled water, *JSME International Journal Series B Fluids and Thermal Engineering* 37(2) (1994) 385-393.
- [114] S. Wakamoto, K. Nakao, N. Tanaka, H. Kimura, Study of the stability of supercooled water in an ice generator, *American Society of Heating, Refrigerating and Air-Conditioning Engineers* (1996).
- [115] S. Okawa, A. Saito, H. Suto, The experimental study on freezing of supercooled water using metallic surface, *International journal of refrigeration* 25(5) (2002) 514-520.
- [116] M. Fauchaux, G. Muller, M. Havet, A. LeBail, Influence of surface roughness on the supercooling degree: Case of selected water/ethanol solutions frozen on aluminium surfaces, *International journal of refrigeration* 29(7) (2006) 1218-1224.
- [117] P. Papon, *Physique des transitions de phases*, (1999).
- [118] Y. Zhang, E. Anim-Danso, S. Bekele, A. Dhinojwala, Effect of surface energy on freezing temperature of water, *ACS applied materials & interfaces* 8(27) (2016) 17583-17590.
- [119] L. Lupi, A. Hudait, V. Molinero, Heterogeneous nucleation of ice on carbon surfaces, *Journal of the American Chemical Society* 136(8) (2014) 3156-3164.
- [120] L. Vrbka, P. Jungwirth, Homogeneous freezing of water starts in the subsurface, *The Journal of Physical Chemistry B* 110(37) (2006) 18126-18129.
- [121] V.F. Petrenko, I.A. Ryzhkin, Surface states of charge carriers and electrical properties of the surface layer of ice, *The Journal of Physical Chemistry B* 101(32) (1997) 6285-6289.
- [122] I.A. Ryzhkin, V.F. Petrenko, Physical mechanisms responsible for ice adhesion, *The Journal of Physical Chemistry B* 101(32) (1997) 6267-6270.
- [123] R. Godawat, S.N. Jamadagni, S. Garde, Characterizing hydrophobicity of interfaces by using cavity formation, solute binding, and water correlations,

- Proceedings of the National Academy of Sciences 106(36) (2009) 15119-15124.
- [124] V.F. Petrenko, Study of the surface of ice, ice/solid and ice/liquid interfaces with scanning force microscopy, *The Journal of Physical Chemistry B* 101(32) (1997) 6276-6281.
- [125] L. Wilen, J. Wettlaufer, M. Elbaum, M. Schick, Dispersion-force effects in interfacial premelting of ice, *Physical Review B* 52(16) (1995) 12426.
- [126] D.T. Möhlmann, The influence of van der Waals forces on the state of water in the shallow subsurface of Mars, *Icarus* 195(1) (2008) 131-139.
- [127] K. Eisenberg, Eisenberg, D., Kauzmann, W. *The Structure and Properties of Water* (1969).
- [128] J. Liu, X. He, J.Z. Zhang, L.-W. Qi, Hydrogen-bond structure dynamics in bulk water: insights from ab initio simulations with coupled cluster theory, *Chemical science* 9(8) (2018) 2065-2073.
- [129] J.D. Bernal, R.H. Fowler, A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions, *The Journal of Chemical Physics* 1(8) (1933) 515-548.
- [130] J. Wang, H. Memon, J. Liu, G. Yang, F. Xu, T. Hussain, C. Scotchford, X. Hou, Effect of surface adsorption on icing behaviour of metallic coating, *Surface and Coatings Technology* 380 (2019) 125068.
- [131] J. Lv, Y. Song, L. Jiang, J. Wang, Bio-inspired strategies for anti-icing, *ACS nano* 8(4) (2014) 3152-3169.
- [132] F. Guerin, C. Laforce, M.-I. Farinas, J. Perron, Analytical model based on experimental data of centrifuge ice adhesion tests with different substrates, *Cold Regions Science and Technology* 121 (2016) 93-99.
- [133] M. Goertz, X.-Y. Zhu, J. Houston, Exploring the liquid-like layer on the ice surface, *Langmuir* 25(12) (2009) 6905-6908.
- [134] W.J. Smit, H.J. Bakker, The surface of ice is like supercooled liquid water, *Angewandte Chemie* 129(49) (2017) 15746-15750.
- [135] H. Jellinek, Ice adhesion, *Canadian journal of physics* 40(10) (1962) 1294-1309.
- [136] M. Matsumoto, S. Saito, I. Ohmine, Molecular dynamics simulation of the ice

- nucleation and growth process leading to water freezing, *Nature* 416(6879) (2002) 409-413.
- [137] E. Assem, A. Meguid, Development of novel icephobic surfaces using siloxane-modified epoxy nanocomposites, *Chemical Engineering Journal* 433 (2022): 133637.
- [138] A. Vakis, V. Yastrebov, J. Scheibert, L. Nicola, D. Dini, C. Minfray, A. Almqvist, M. Paggi, S. Lee, G. Limbert, Modeling and simulation in tribology across scales: An overview, *Tribology International* 125 (2018) 169-199.
- [139] Z. He, S. Xiao, H. Gao, J. He, Z. Zhang, Multiscale crack initiator promoted super-low ice adhesion surfaces, *Soft matter* 13(37) (2017) 6562-6568.
- [140] H.-H. Lee, Finite element simulations with ANSYS Workbench 18, SDC publications (2018).
- [141] F. Brezzi, R.S. Falk, L.D. Marini, Basic principles of mixed virtual element methods, *ESAIM: Mathematical Modelling and Numerical Analysis* 48(4) (2014) 1227-1240.
- [142] J. Geng, W. Yan, W. Xu, Application of the finite element method in implant dentistry, Springer Science & Business Media (2008).
- [143] J.-Y. Huang, C.-Y. Gau, Modelling and designing a low-cost high-fidelity mobile crane simulator, *International journal of human-computer studies* 58(2) (2003) 151-176.
- [144] H.-H. Lee, Finite Element Simulations with ANSYS Workbench 2020, SDC publications (2020).
- [145] C.B. Pinca, G.O. Tirian, A. Josan, Application of finite element method to an overhead crane bridge, *Wseas transactions on applied and theoretical mechanics* 4(2) (2009) 64-73.
- [146] W. Yu, P. Sinigh, Application of cad in product packaging design based on green concept, *Computer-Aided Design and Applications* 19(S2) (2021) 124-133.
- [147] T. Stolarski, Y. Nakasone, S. Yoshimoto, Engineering analysis with ANSYS software, Butterworth-Heinemann (2018).
- [148] X. Chen, Y. Liu, Finite element modeling and simulation with ANSYS Workbench, CRC press (2018).
- [149] S.S. Rao, The finite element method in engineering, Butterworth-heinemann

(2017).

[150] N.S. Gokhale, Practical finite element analysis, Finite to infinite (2008).

[151] T. Chandrupatla, A. Belegundu, Introduction to finite elements in engineering, Cambridge University Press (2021).

[152] T. Langbecker, Kinematic analysis of deployable scissor structures, International Journal of Space Structures 14(1) (1999) 1-15.

[153] S. Moaveni, Finite element analysis theory and application with ANSYS, 3/e, Pearson Education India (2011).

[154] H. Tian, F. Wang, S. Ge, J. Ou, W. Li, S. Yu, A simple and effective way to fabricate mechanical robust superhydrophobic surfaces, RSC Advances 6(34) (2016) 28563-28569.

[155] Y. Wu, L. Dong, X. Shu, Y. Yang, W. She, Q. Ran, A review on recent advances in the fabrication and evaluation of superhydrophobic concrete, Composites Part B: Engineering 237 (2022) 109867.

[156] Z. He, H. Xie, M.I. Jamil, T. Li, Q. Zhang, Electro-/Photo-Thermal Promoted Anti-Icing Materials: A New Strategy Combined with Passive Anti-Icing and Active De-Icing, Advanced Materials Interfaces 9 (16) (2022) 2200275.

[157] X. Zhou, Y. Sun, J. Liu, Designing Anti-Icing Surfaces by Controlling Ice Formation, Advanced Materials Interfaces 8(17) (2021) 2100327.

[158] W. Li, Y. Zhan, S. Yu, Applications of superhydrophobic coatings in anti-icing: Theory, mechanisms, impact factors, challenges and perspectives, Progress in Organic Coatings 152 (2021) 106117.

[159] V. Donadei, H. Koivuluoto, E. Sarlin, P. Vuoristo, Durability of Lubricated Icephobic Coatings under Various Environmental Stresses, Polymers 14(2) (2022) 303.

[160] J. Zheng, R. Liu, D. Liu, Z. Weng, G. Song, W. Li, Z. Wang, Slippery liquid infused porous surfaces with anti-icing performance fabricated by direct laser interference lithography, Progress in Organic Coatings 175 (2023) 107308.

[161] Y. Yuan, H. Xiang, G. Liu, L. Wang, H. Liu, R. Liao, Self-Repairing Performance of Slippery Liquid Infused Porous Surfaces for Durable Anti-Icing, Advanced Materials Interfaces 9(10) (2022) 2101968.

- [162] H.-C. Lu, J.-L. You, Y.-C. Liao, Total Liquid Transfer with Enhanced Contact Line Slippage, *Langmuir* 38(46) (2022) 14238-14248.
- [163] R. Menini, Z. Ghalmi, M. Farzaneh, Highly resistant icephobic coatings on aluminum alloys, *Cold Regions Science and Technology* 65(1) (2011) 65-69.
- [164] S. Farhadi, M. Farzaneh, S. Kulinich, Anti-icing performance of superhydrophobic surfaces, *Applied Surface Science* 257(14) (2011) 6264-6269.
- [165] L.B. Boinovich, A.M. Emelyanenko, Anti-icing potential of superhydrophobic coatings, *Mendeleev Communications* 1(23) (2013) 3-10.
- [166] T. Darmanin, F. Guittard, Recent advances in the potential applications of bioinspired superhydrophobic materials, *Journal of Materials Chemistry A* 2(39) (2014) 16319-16359.
- [167] W. Barthlott, C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta* 202(1) (1997) 1-8.
- [168] J.B. Boreyko, C.-H. Chen, Self-propelled dropwise condensate on superhydrophobic surfaces, *Physical review letters* 103(18) (2009) 184501.
- [169] P. Tourkine, M. Le Merrer, D. Quéré Delayed freezing on water repellent materials, *Langmuir* 25(13) (2009) 7214-7216.
- [170] A. Alizadeh, M. Yamada, R. Li, W. Shang, S. Otta, S. Zhong, L. Ge, A. Dhinojwala, K.R. Conway, V. Bahadur, Dynamics of ice nucleation on water repellent surfaces, *Langmuir* 28(6) (2012) 3180-3186.
- [171] H. Saito, K. Takai, G. Yamauchi, Water-and ice-repellent coatings, *Surface Coatings International* 80(4) (1997) 168-171.
- [172] C. Ukiwe, D.Y. Kwok, On the maximum spreading diameter of impacting droplets on well-prepared solid surfaces, *Langmuir* 21(2) (2005) 666-673.
- [173] Y. Son, C. Kim, D.H. Yang, D.J. Ahn, Spreading of an inkjet droplet on a solid surface with a controlled contact angle at low Weber and Reynolds numbers, *Langmuir* 24(6) (2008) 2900-2907.
- [174] G. Chaudhary, R. Li, Freezing of water droplets on solid surfaces: An experimental and numerical study, *Experimental Thermal and Fluid Science* 57 (2014) 86-93.

- [175] C. Wang, S. Chang, H. Wu, J. Xu, Modeling of drop breakup in the bag breakup regime, *Applied Physics Letters* 104(15) (2014) 154107.
- [176] S. Kulinich, S. Farhadi, K. Nose, X. Du, Superhydrophobic surfaces: are they really ice-repellent?, *Langmuir* 27(1) (2011) 25-29.
- [177] Y. Wang, M. Li, T. Lv, Q. Wang, Q. Chen, J. Ding, Influence of different chemical modifications on the icephobic properties of superhydrophobic surfaces in a condensate environment, *Journal of Materials Chemistry A* 3(9) (2015) 4967-4975.
- [178] U. Tuvshindorj, A. Yildirim, F.E. Ozturk, M. Bayindir, Robust cassie state of wetting in transparent superhydrophobic coatings, *ACS applied materials & interfaces* 6(12) (2014) 9680-9688.
- [179] Y. Cao, L. Yuan, B. Hu, J. Zhou, Three-tier rough superhydrophobic surfaces, *Nanotechnology* 26(31) (2015) 315705.
- [180] A. Tuteja, W. Choi, M. Ma, G.C. Rutledge, G.H. McKinley, R.E. Cohen, S.A. Mazzella, J.M. Mabry, Designing Superoleophobic Surfaces (Postprint), Air Force Research Lab Edwards AFB CA Propulsion Directorate, (2007).
- [181] T. Liu, C.-J. Kim, Turning a surface superrepellent even to completely wetting liquids, *Science* 346(6213) (2014) 1096-1100.
- [182] D. Wang, Q. Wang, Z. Zhang, G. Chen, ZnO nanorod array polydimethylsiloxane composite solid phase micro-extraction fiber coating: fabrication and extraction capability, *Analyst* 137(2) (2012) 476-480.
- [183] R. Enright, N. Miljkovic, J. Sprittles, K. Nolan, R. Mitchell, E.N. Wang, How coalescing droplets jump, *ACS nano* 8(10) (2014) 10352-10362.
- [184] Z. Guo, W. Liu, B.-L. Su, Superhydrophobic surfaces: from natural to biomimetic to functional, *Journal of colloid and interface science* 353(2) (2011) 335-355.
- [185] D. Wang, Q. Sun, M.J. Hokkanen, C. Zhang, F.-Y. Lin, Q. Liu, S.-P. Zhu, T. Zhou, Q. Chang, B. He, Design of robust superhydrophobic surfaces, *Nature* 582(7810) (2020) 55-59.
- [186] A. Milionis, E. Loth, I.S. Bayer, Recent advances in the mechanical durability of superhydrophobic materials, *Advances in colloid and interface science* 229 (2016) 57-79.

- [187] K. Golovin, S.P. Kobaku, D.H. Lee, E.T. DiLoreto, J.M. Mabry, A. Tuteja, Designing durable icephobic surfaces, *Science advances* 2(3) (2016) e1501496.
- [188] M.I. Jamil, X. Zhan, F. Chen, D. Cheng, Q. Zhang, Durable and scalable candle soot icephobic coating with nucleation and fracture mechanism, *ACS applied materials & interfaces* 11(34) (2019) 31532-31542.
- [189] W.A. Zisman, Relation of the equilibrium contact angle to liquid and solid constitution, ACS Publications (1964).
- [190] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, The lowest surface free energy based on— CF₃ alignment, *Langmuir* 15(13) (1999) 4321-4323.
- [191] D. Fuard, T. Tzvetkova-Chevolleau, S. Decossas, P. Tracqui, P. Schiavone, Optimization of poly-di-methyl-siloxane (PDMS) substrates for studying cellular adhesion and motility, *Microelectronic Engineering* 85(5-6) (2008) 1289-1293.
- [192] E. Yilg r, I. Yilg r, Silicone containing copolymers: Synthesis, properties and applications, *Progress in Polymer Science* 39(6) (2014) 1165-1195.
- [193] H. Murase, K. Nanishi, H. Kogure, T. Fujibayashi, K. Tamura, N. Haruta, Interactions between heterogeneous surfaces of polymers and water, *Journal of Applied Polymer Science* 54(13) (1994) 2051-2062.
- [194] A.J. Meuler, J.D. Smith, K.K. Varanasi, J.M. Mabry, G.H. McKinley, R.E. Cohen, Relationships between water wettability and ice adhesion, *ACS applied materials & interfaces* 2(11) (2010) 3100-3110.
- [195] K. Golovin, A. Dhyani, M. Thouless, A. Tuteja, Low–interfacial toughness materials for effective large-scale deicing, *Science* 364(6438) (2019) 371-375.
- [196] A. Dhyani, C. Pike, J.L. Braid, E. Whitney, L. Burnham, A. Tuteja, Facilitating Large-Scale Snow Shedding from In-Field Solar Arrays using Icephobic Surfaces with Low-Interfacial Toughness, *Advanced Materials Technologies* 7(5) (2022) 2101032.
- [197] M. Liu, Y. Hou, J. Li, L. Tie, Z. Guo, Transparent slippery liquid-infused nanoparticulate coatings, *Chemical Engineering Journal* 337 (2018) 462-470.
- [198] C. Delacour, B. Pannetier, J.-C. Villegier, V. Bouchiat, Quantum and Thermal Phase Slips in Superconducting Niobium Nitride (NbN) Ultrathin Crystalline Nanowire: Application to Single Photon Detection, *Nano Letters* 12(7) (2012) 3501-3506.

- [199] A. Leh, H.E. N'guessan, J. Fan, P. Bahadur, R. Tadmor, Y. Zhao, On the role of the three-phase contact line in surface deformation, *Langmuir* 28(13) (2012) 5795-5801.
- [200] J. Chen, R. Dou, D. Cui, Q. Zhang, Y. Zhang, F. Xu, X. Zhou, J. Wang, Y. Song, L. Jiang, Robust prototypical anti-icing coatings with a self-lubricating liquid water layer between ice and substrate, *ACS applied materials & interfaces* 5(10) (2013) 4026-4030.
- [201] F. Schellenberger, J. Xie, N. Encinas, A. Hardy, M. Klapper, P. Papadopoulos, H.-J. Butt, D. Vollmer, Direct observation of drops on slippery lubricant-infused surfaces, *Soft Matter* 11(38) (2015) 7617-7626.
- [202] P. Kim, T.-S. Wong, J. Alvarenga, M.J. Kreder, W.E. Adorno-Martinez, J. Aizenberg, Liquid-infused nanostructured surfaces with extreme anti-ice and anti-frost performance, *ACS nano* 6(8) (2012) 6569-6577.
- [203] A.J. Meuler, J.D. Smith, K.K. Varanasi, J.M. Mabry, G.H. McKinley, R.E. Cohen, Relationships between Water Wettability and Ice Adhesion, *ACS Applied Materials & Interfaces* 2(11) (2010) 3100–3110.
- [204] Y. Long, X. Yin, P. Mu, Q. Wang, J. Hu, J. Li, Slippery liquid-infused porous surface (SLIPS) with superior liquid repellency, anti-corrosion, anti-icing and intensified durability for protecting substrates, *Chemical Engineering Journal* 401 (2020) 126137.
- [205] S.B. Subramanyam, K. Rykaczewski, K.K. Varanasi, Ice adhesion on lubricant-impregnated textured surfaces, *Langmuir* 29(44) (2013) 13414-13418.
- [206] S. Ozbay, C. Yuceel, H.Y. Erbil, Improved icephobic properties on surfaces with a hydrophilic lubricating liquid, *ACS applied materials & interfaces* 7(39) (2015) 22067-22077.
- [207] Q. Liu, Y. Yang, M. Huang, Y. Zhou, Y. Liu, X. Liang, Durability of a lubricant-infused Electrospray Silicon Rubber surface as an anti-icing coating, *Applied Surface Science* 346 (2015) 68-76.
- [208] K. Rykaczewski, S. Anand, S.B. Subramanyam, K.K. Varanasi, Mechanism of frost formation on lubricant-impregnated surfaces, *Langmuir* 29(17) (2013) 5230-5238.
- [209] R. Rosenberg, Why is ice slippery?, *Physics Today* 58(12) (2005) 50.

- [210] K. Alasvand Zarasvand, C. Pope, M. Mohseni, D. Orchard, C. Clark, K. Golovin, Metallic plate buckling as a low adhesion mechanism for durable and scalable icephobic surface design, *Advanced Materials Interfaces* 9(1) (2022) 2101402.
- [211] J. Ayres, W. Simendinger, C. Balik, Characterization of titanium alkoxide sol–gel systems designed for anti-icing coatings: I. Chemistry, *Journal of Coatings Technology and Research* 4(4) (2007) 463-471.
- [212] T. Chang, G. Zhao, Ice inhibition for cryopreservation: materials, strategies, and challenges, *Advanced Science* 8(6) (2021) 2002425.
- [213] X. Deng, L. Mammen, H.-J. Butt, D. Vollmer, Candle soot as a template for a transparent robust superamphiphobic coating, *Science* 335(6064) (2012) 67-70.
- [214] K. Chen, S. Zhou, S. Yang, L. Wu, Fabrication of all-water-based self-repairing superhydrophobic coatings based on UV-responsive microcapsules, *Advanced Functional Materials* 25(7) (2015) 1035-1041.
- [215] Y. Bourgault, H. Beaugendre, W.G. Habashi, Development of a shallow-water icing model in FENSAP-ICE, *Journal of Aircraft* 37(4) (2000) 640-646.
- [216] M. Grizen, M.K. Tiwari, Icephobic surfaces: features and challenges, *Ice Adhesion: Mechanism, Measurement and Mitigation* Chapter 14 (2020) 417-466.
- [217] L. Bocquet, E. Lauga, A smooth future?, *Nature materials* 10(5) (2011) 334.
- [218] Stiffness — an unknown world of mechanical science?, *Injury* 31 (2000) 14-84.
- [219] J.S. Wexler, I. Jacobi, H.A. Stone, Shear-driven failure of liquid-infused surfaces, *Physical review letters* 114(16) (2015) 168301.
- [220] M. Wu, J. Wang, S. Ling, R. Wheatley, X. Hou, Microporous metallic scaffolds supported liquid infused icephobic construction, *Journal of Colloid and Interface Science* 634 (2023) 369-378.
- [221] J. Groten, J.r. Rühe, Surfaces with combined microscale and nanoscale structures: a route to mechanically stable superhydrophobic surfaces?, *Langmuir* 29(11) (2013) 3765-3772.
- [222] J. Gong, y. Katsuyama, T. Kurokawa, Double - network hydrogels with extremely high mechanical strength, *Adv. Mater* 15(14) (2003) 1155-1158.
- [223] E. Ducrot, Y. Chen, M. Bulters, R.P. Sijbesma, C. Creton, Toughening elastomers

- with sacrificial bonds and watching them break, *Science* 344(6180) (2014) 186-189.
- [224] X. Zhang, J. Liu, Z. Zhang, S. Wu, Z. Tang, B. Guo, L. Zhang, Toughening elastomers using a mussel-inspired multiphase design, *ACS applied materials & interfaces* 10(28) (2018) 23485-23489.
- [225] N. Wang, D. Xiong, Y. Deng, Y. Shi, K. Wang, Mechanically robust superhydrophobic steel surface with anti-icing, UV-durability, and corrosion resistance properties, *ACS applied materials & interfaces* 7(11) (2015) 6260-6272.
- [226] E. Huovinen, L. Takkunen, T. Korpela, M. Suvanto, T.T. Pakkanen, T.A. Pakkanen, Mechanically robust superhydrophobic polymer surfaces based on protective micropillars, *Langmuir* 30(5) (2014) 1435-1443.
- [227] X. Deng, L. Mammen, Y. Zhao, P. Lellig, K. Müllen, C. Li, H.J. Butt, D. Vollmer, Transparent, thermally stable and mechanically robust superhydrophobic surfaces made from porous silica capsules, *Advanced materials* 23(26) (2011) 2962-2965.
- [228] X. Wang, X. Liu, F. Zhou, W. Liu, Self-healing superamphiphobicity, *Chemical communications* 47(8) (2011) 2324-2326.
- [229] H. Sojoudi, M. Wang, N. Boscher, G. McKinley, K. Gleason, Durable and scalable icephobic surfaces: similarities and distinctions from superhydrophobic surfaces, *Soft matter* 12(7) (2016) 1938-1963.
- [230] S. Qiang, K. Chen, Y. Yin, C. Wang, Robust UV-cured superhydrophobic cotton fabric surfaces with self-healing ability, *Materials & Design* 116 (2017) 395-402.
- [231] S.-H. Park, E.-H. Cho, J. Sohn, P. Theilmann, K. Chu, S. Lee, Y. Sohn, D. Kim, B. Kim, Design of multi-functional dual hole patterned carbon nanotube composites with superhydrophobicity and durability, *Nano Research* 6(6) (2013) 389-398.
- [232] C. Tan, Q. Li, P. Cai, N. Yang, Z. Xi, Fabrication of color-controllable superhydrophobic copper compound coating with decoration performance, *Applied Surface Science* 328 (2015) 623-631.
- [233] S. Khorsand, K. Raeissi, F. Ashrafizadeh, M.A. Arenas, Super-hydrophobic nickel-cobalt alloy coating with micro-nano flower-like structure, *Chemical Engineering Journal* 273 (2015) 638-646.
- [234] S. Zheng, C. Li, Q. Fu, T. Xiang, W. Hu, J. Wang, S. Ding, P. Liu, Z. Chen,

Fabrication of a micro-nanostructured superhydrophobic aluminum surface with excellent corrosion resistance and anti-icing performance, *RSC Advances* 6(83) (2016) 79389-79400.

[235] L.B. Boinovich, A.M. Emelyanenko, V.K. Ivanov, A.S. Pashinin, Durable icephobic coating for stainless steel, *ACS applied materials & interfaces* 5(7) (2013) 2549-2554.

[236] P. Irajizad, A. Al-Bayati, B. Eslami, T. Shafquat, M. Nazari, P. Jafari, V. Kashyap, A. Masoudi, D. Araya, H. Ghasemi, Stress-localized durable icephobic surfaces, *Materials Horizons* 6(4) (2019) 758-766.

[237] R. Menini, M. Farzaneh, Advanced icephobic coatings, *Journal of adhesion science and technology* 25(9) (2011) 971-992.

[238] M. Li, Y. Chen, W. Luo, X. Cheng, Durable and Flexible Hydrophobic Surface with a Micropatterned Composite Metal–Polymer Structure, *Langmuir* 37(19) (2021) 5838-5845.

[239] M. Liu, S. Wang, L. Jiang, Nature-inspired superwettability systems, *Nature Reviews Materials* 2(7) (2017) 1-17.

[240] J. Sun, H. Li, Y. Huang, X. Zheng, Y. Liu, J. Zhuang, D. Wu, Simple and affordable way to achieve polymeric superhydrophobic surfaces with biomimetic hierarchical roughness, *Acs Omega* 4(2) (2019) 2750-2757.

[241] W. Cui, Y. Jiang, K. Mielonen, T.A. Pakkanen, The verification of icephobic performance on biomimetic superhydrophobic surfaces and the effect of wettability and surface energy, *Applied Surface Science* 466 (2019) 503-514.

[242] Z. Zhang, L. Ma, Y. Liu, J. Ren, H. Hu, An experimental study of rain erosion effects on a hydro-/ice-phobic coating pertinent to Unmanned-Aerial-System (UAS) inflight icing mitigation, *Cold Regions Science and Technology* 181 (2021) 103196.

[243] X. Wu, Y. Shen, S. Zheng, Z.-T. Hu, Z. Chen, Clarifying the Correlation of Ice Adhesion Strength with Water Wettability and Surface Characteristics, *Langmuir* 36(41) (2020) 12190-12201.

[244] R. Karmouch, G.G. Ross, Experimental study on the evolution of contact angles with temperature near the freezing point, *The Journal of Physical Chemistry C* 114(9)

(2010) 4063-4066.

[245] H. Memon, J. Liu, D.S. De Focatiis, K.-s. Choi, X. Hou, Intrinsic dependence of ice adhesion strength on surface roughness, *Surface and Coatings Technology* 385 (2020) 125382.

[246] S. Jung, M. Dorrestijn, D. Raps, A. Das, C.M. Megaridis, D. Poulikakos, Are superhydrophobic surfaces best for icephobicity?, *Langmuir* 27(6) (2011) 3059-3066.

[247] Z. He, Y. Zhuo, F. Wang, J. He, Z. Zhang, Design and preparation of icephobic PDMS-based coatings by introducing an aqueous lubricating layer and macro-crack initiators at the ice-substrate interface, *Progress in Organic Coatings* 147 (2020) 105737.

[248] Z. He, M.I. Jamil, T. Li, Q. Zhang, Enhanced surface icephobicity on an elastic substrate, *Langmuir* 38(1) (2021) 18-35.

[249] P.W. Wilson, W. Lu, H. Xu, P. Kim, M.J. Kreder, J. Alvarenga, J. Aizenberg, Inhibition of ice nucleation by slippery liquid-infused porous surfaces (SLIPS), *Physical Chemistry Chemical Physics* 15(2) (2013) 581-585.

[250] T. Li, Y. Zhuo, V. Håkonsen, J. He, Z. Zhang, Durable Low Ice Adhesion Foams Modulated by Submicrometer Pores, *Industrial & Engineering Chemistry Research* 58(38) (2019) 17776-17783.

[251] R. Masoudi Nejad, F. Berto, G. Wheatley, M. Tohidi, W. Ma, On fatigue life prediction of Al-alloy 2024 plates in riveted joints, *Structures* 33 (2021) 1715-1720.

[252] R. Matsumoto, H. Sakaguchi, M. Otsu, H. Utsunomiya, Plastic joining of open-cell nickel foam and polymethyl methacrylate (PMMA) sheet by friction stir incremental forming, *Journal of Materials Processing Technology* 282 (2020) 116691.

[253] M.S. Aly, Tensile properties of open-cell nickel foams, *Materials & Design* 31(4) (2010) 2237-2240.

[254] A. Hussain, C.Y. Tso, C.Y. Chao, Experimental investigation of a passive thermal management system for high-powered lithium ion batteries using nickel foam-paraffin composite, *Energy* 115 (2016) 209-218.

[255] C.C. Ryerson, Assessment of superstructure ice protection as applied to offshore oil operations safety: problems, hazards, needs, and potential transfer technologies, (2008).

- [256] S. Xia, Y. Chen, J. Tian, J. Shi, C. Geng, H. Zou, M. Liang, Z. Li, Superior Low-Temperature Reversible Adhesion Based on Bio-Inspired Microfibrillar Adhesives Fabricated by Phenyl Containing Polydimethylsiloxane Elastomers, *Advanced Functional Materials* 31(26) (2021) 2101143.
- [257] S.L. Sivas, B. Riegler, R. Thomaier, K. Hoover, A silicone-based ice-phobic coating for aircraft, NuSil Technology LLC, 37th ISTC (2007).
- [258] H. Wang, M. Yang, Q. Tang, X. Zhao, Y. Tong, Y. Liu, Flexible, conformal organic synaptic transistors on elastomer for biomedical applications, *Advanced Functional Materials* 29(19) (2019) 1901107.
- [259] S. Bomdurant, V. Ernster, R. Herdman, Safety of silicon breast implants: report of the committee on the safety of silicon breast implants (IOM), National Academy Press Washington, 1999.
- [260] G. Zhang, Q. Zhang, T. Cheng, X. Zhan, F. Chen, Polyols-infused slippery surfaces based on magnetic Fe₃O₄-functionalized polymer hybrids for enhanced multifunctional anti-icing and deicing properties, *Langmuir* 34(13) (2018) 4052-4058.
- [261] N. Vogel, R.A. Belisle, B. Hatton, T.-S. Wong, J. Aizenberg, Transparency and damage tolerance of patternable omniphobic lubricated surfaces based on inverse colloidal monolayers, *Nature communications* 4(1) (2013) 1-10.
- [262] Q. Zheng, J. Lv, J. Zhang, J. Feng, Fabrication and application of icephobic silicone coatings on epoxy substrate, *Progress in Organic Coatings* 161 (2021) 106483.
- [263] Y. Li, R. Grigoriev, M. Yoda, Experimental study of the effect of noncondensables on buoyancy-thermocapillary convection in a volatile low-viscosity silicone oil, *Physics of Fluids* 26(12) (2014) 122112.
- [264] C. Liu, Y. Li, C. Lu, Y. Liu, S. Feng, Y. Liu, Robust slippery liquid-infused porous network surfaces for enhanced anti-icing/deicing performance, *ACS applied materials & interfaces* 12(22) (2020) 25471-25477.
- [265] A. Hai, G. Bharath, M. Daud, K. Rambabu, I. Ali, S.W. Hasan, P. Show, F. Banat, Valorization of groundnut shell via pyrolysis: Product distribution, thermodynamic analysis, kinetic estimation, and artificial neural network modeling, *Chemosphere* 283 (2021) 131162.

- [266] A. Sodamade, T. Oyedepo, O. Bolaji, Fatty acids composition of three different vegetable oils (soybean oil, groundnut oil and coconut oil) by high-performance liquid chromatography, *Extraction* 3(7) (2013) 126-178.
- [267] B. Oktay, E. Baştürk, M.V. Kahraman, N.K. Apohan, Designing Coconut Oil Encapsulated Poly (stearyl methacrylate-co-hydroxylethyl metacrylate) Based Microcapsule for Phase Change Materials, *ChemistrySelect* 4(17) (2019) 5110-5115.
- [268] C.A. Saleel, A review on the use of coconut oil as an organic phase change material with its melting process, heat transfer, and energy storage characteristics, *Journal of Thermal Analysis and Calorimetry* (2021) 1-22.
- [269] F. Wang, S. Luo, S. Xiao, W. Zhang, Y. Zhuo, J. He, Z. Zhang, Enabling phase transition of infused lubricant in porous structure for exceptional oil/water separation, *Journal of hazardous materials* 390 (2020) 122176.
- [270] F. Wang, W. Ding, J. He, Z. Zhang, Phase transition enabled durable anti-icing surfaces and its DIY design, *Chemical Engineering Journal* 360 (2019) 243-249.
- [271] Z. Wang, Y. Zhu, X. Liu, Z. Zhao, J. Chen, X. Jing, H. Chen, Temperature self-regulating electrothermal pseudo-slippery surface for anti-icing, *Chemical Engineering Journal* 422 (2021) 130110.
- [272] J.K. Mannekote, S.V. Kailas, K. Venkatesh, N. Kathyayini, Environmentally friendly functional fluids from renewable and sustainable sources-A review, *Renewable and sustainable energy reviews* 81 (2018) 1787-1801.
- [273] B. Libisch, H.K. French, T. Hartnik, A. Anton, B. Biró, Laboratory-scale evaluation of a combined soil amendment for the enhanced biodegradation of propylene glycol-based aircraft de-icing fluids, *Environmental technology* 33(6) (2012) 717-724.
- [274] S. Rebsdatt, D. Mayer, Ethylene glycol, *Ullmann's Encyclopedia of Industrial Chemistry* 33 (2000) 531-546.
- [275] Y. Li, H. Meng, Y. Liu, A. Narkar, B.P. Lee, Gelatin microgel incorporated poly (ethylene glycol)-based bioadhesive with enhanced adhesive property and bioactivity, *ACS applied materials & interfaces* 8(19) (2016) 11980-11989.
- [276] Y. Feng, G. Han, T.-S. Chung, M. Weber, N. Widjojo, C. Maletzko, Effects of polyethylene glycol on membrane formation and properties of hydrophilic sulfonated

- polyphenylenesulfone (sPPSU) membranes, *Journal of Membrane Science* 531 (2017) 27-35.
- [277] F. Liu, Z. Wang, Q. Pan, Intelligent icephobic surface toward self-deicing capability, *ACS Sustainable Chemistry & Engineering* 8(2) (2019) 792-799.
- [278] D.P. Makris, S. Lalas, Glycerol and glycerol-based deep eutectic mixtures as emerging green solvents for polyphenol extraction: The evidence so far, *Molecules* 25(24) (2020) 5842.
- [279] D. Cobb, M. Vargas, T. Fridrich, M. Bouschlicher, Metal surface treatment: characterization and effect on composite-to-metal bond strength, *Operative dentistry* 25(5) (2000) 427-433.
- [280] S.L. Sivas, B. Riegler, R. Thomaier, K. Hoover, A silicone-based ice-phobic coating for aircraft, 39th International Society for the Advancement of Materials and Process Engineering Technical Conference, (2007) 53-58.
- [281] K. Efimenko, W.E. Wallace, J. Genzer, Surface Modification of Sylgard-184 Poly(dimethyl siloxane) Networks by Ultraviolet and Ultraviolet/Ozone Treatment, *Journal of Colloid and Interface Science* 254(2) (2002) 306-315.
- [282] A. Mishra, N. Bhatt, A. Bajpai, Nanostructured superhydrophobic coatings for solar panel applications, *Nanomaterials-Based Coatings*, Elsevier (2019) 397-424.
- [283] S. Kawata, O. Nakamura, S. Minami, Optical microscope tomography. I. Support constraint, *JOSA A* 4(1) (1987) 292-297.
- [284] D. Hanaor, Y. Gan, I. Einav, Static friction at fractal interfaces, *Tribology International* 93 (2016) 229-238.
- [285] E. Gadelmawla, M. Koura, T. Maksoud, I. Elewa, H. Soliman, Roughness parameters, *Journal of materials processing Technology* 123(1) (2002) 133-145.
- [286] F. Marinello, P. Bariani, A. Pasquini, L. De Chiffre, M. Bossard, G.B. Picotto, Increase of maximum detectable slope with optical profilers, through controlled tilting and image processing, *Measurement Science and Technology* 18(2) (2007) 384.
- [287] X. Song, W. Dong, Z. Yuan, X. Lu, Z. Li, Q. Duanmu, Investigation of the linearity of the NIM FTIR infrared spectral emissivity measurement facility by means of flux superposition method, *Infrared Physics & Technology* 109 (2020) 103416.

- [288] C. Schick, Differential scanning calorimetry (DSC) of semicrystalline polymers, *Analytical and bioanalytical chemistry* 395(6) (2009) 1589-1611.
- [289] I. Zapf, T. Fekecs, A. Ferencz, G. Tizedes, G. Pavlovics, E. Kálmán, D. Lőrinczy, DSC analysis of human plasma in breast cancer patients, *Thermochimica acta* 524(1-2) (2011) 88-91.
- [290] Z. Shi, Y. Zhang, M. Liu, D.A. Hanaor, Y. Gan, Dynamic contact angle hysteresis in liquid bridges, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 555 (2018) 365-371.
- [291] A. Rudawska, E. Jacniacka, Analysis for determining surface free energy uncertainty by the Owen–Wendt method, *International Journal of Adhesion and Adhesives* 29(4) (2009) 451-457.
- [292] L. Mazzola, Aeronautical livery coating with icephobic property, *Surface Engineering* 32(10) (2016) 733-744.
- [293] A. Siddiqui, M. Braden, M.P. Patel, S. Parker, An experimental and theoretical study of the effect of sample thickness on the Shore hardness of elastomers, *Dental materials* 26(6) (2010) 560-564.
- [294] N.N. Lebedev, I.S. Ufliand, Axisymmetric contact problem for an elastic layer, *Journal of Applied Mathematics and Mechanics* 22(3) (1958) 442-450.
- [295] Y. Jung, B. Bhushan, Wetting behaviour during evaporation and condensation of water microdroplets on superhydrophobic patterned surfaces, *Journal of microscopy* 229(1) (2008) 127-140.
- [296] M. Mazumder, R. Ahmed, A.W. Ali, S.-J. Lee, SEM and ESEM techniques used for analysis of asphalt binder and mixture: A state of the art review, *Construction and Building Materials* 186 (2018) 313-329.
- [297] S. Kirk, J. Skepper, A. Donald, Application of environmental scanning electron microscopy to determine biological surface structure, *Journal of microscopy* 233(2) (2009) 205-224.
- [298] E. Gromnitskaya, O. Stal'gorova, V. Brazhkin, A. Lyapin, Ultrasonic study of the nonequilibrium pressure-temperature diagram of H₂O ice, *Physical Review B* 64(9) (2001) 094205.

- [299] S. Rønneberg, J. He, Z. Zhang, The need for standards in low ice adhesion surface research: a critical review, *Journal of Adhesion Science and Technology* 34(3) (2020) 319-347.
- [300] H. Memon, K. Mirshahidi, K.A. Zarasvand, K. Golovin, D.S. De Focatiis, K.-S. Choi, X. Hou, Comparative study on the influence of surface characteristics on de-icing evaluation, *Journal of Materials Science* 56(30) (2021) 17337-17352.
- [301] H. Niemelä-Anttonen, J. Kiilakoski, P. Vuoristo, H. Koivuluoto, Icephobic performance of different surface designs and materials, *Proceedings of the International Workshop on Atmospheric Icing of Structures (IWAIS)*, (2019) 1-5.
- [302] A. Lafuma, D. Quéré Slippery pre-suffused surfaces, *EPL (Europhysics Letters)* 96(5) (2011) 56001.
- [303] H.F. Bohn, W. Federle, Insect aquaplaning: *Nepenthes* pitcher plants capture prey with the peristome, a fully wettable water-lubricated anisotropic surface, *Proceedings of the National Academy of Sciences* 101(39) (2004) 14138-14143.
- [304] J.D. Smith, R. Dhiman, S. Anand, E. Reza-Garduno, R.E. Cohen, G.H. McKinley, K.K. Varanasi, Droplet mobility on lubricant-impregnated surfaces, *Soft Matter* 9(6) (2013) 1772-1780.
- [305] G. Wang, Z. Guo, Liquid infused surfaces with anti-icing properties, *Nanoscale* 11(47) (2019) 22615-22635.
- [306] N. Wang, D. Xiong, S. Pan, K. Wang, Y. Shi, Y. Deng, Robust superhydrophobic coating and the anti-icing properties of its lubricants-infused-composite surface under condensing condition, *New Journal of Chemistry* 41(4) (2017) 1846-1853.
- [307] M. Muschi, B. Brudieu, J. Teisseire, A. Sauret, Drop impact dynamics on slippery liquid-infused porous surfaces: influence of oil thickness, *Soft Matter* 14(7) (2018) 1100-1107.
- [308] C. Howell, T.L. Vu, J.J. Lin, S. Kolle, N. Juthani, E. Watson, J.C. Weaver, J. Alvarenga, J. Aizenberg, Self-replenishing vascularized fouling-release surfaces, *ACS applied materials & interfaces* 6(15) (2014) 13299-13307.
- [309] T. Yamazaki, M. Tenjimbayashi, K. Manabe, T. Moriya, H. Nakamura, T. Nakamura, T. Matsubayashi, Y. Tsuge, S. Shiratori, Antifreeze liquid-infused surface

- with high transparency, low ice adhesion strength, and antifrosting properties fabricated through a spray layer-by-layer method, *Industrial & Engineering Chemistry Research* 58(6) (2019) 2225-2234.
- [310] A. Sandhu, O.J. Walker, A. Nistal, K.L. Choy, A.J. Clancy, Perfluoroalkane wax infused gels for effective, regenerating, anti-icing surfaces, *Chemical communications* 55(22) (2019) 3215-3218.
- [311] Z.A. Janjua, The influence of freezing and ambient temperature on the adhesion strength of ice, *Cold Regions Science and Technology* 140 (2017) 14-19.
- [312] M.F. Butler, Instability formation and directional dendritic growth of ice studied by optical interferometry, *Crystal Growth & Design* 1(3) (2001) 213-223.
- [313] C. Laforte, C. Blackburn, J. Perron, R. Aubert, Icephobic coating evaluation for aerospace application, 55th AIAA/ASMe/ASCE/AHS/SC Structures, Structural Dynamics, and Materials Conference, (2014) 1327.
- [314] Z. Mu, X. Liu, H. Shi, C. Song, C. Dang, K. Gao, N. Sun, C. Tian, H. Zheng, X. Wang, Y. Xuan, A highly efficient solar-driven CO₂ reforming of methane on Ni/MgAlO_x-LDH loaded Ni foam reactors with heat recovery: Experimental measurements and numerical simulations, *Chemical Engineering Journal* 446 (2022) 137437.
- [315] D.K. Lee, J. In, S. Lee, Standard deviation and standard error of the mean, *Korean journal of anesthesiology* 68(3) (2015) 220-223.
- [316] V. Paserin, S. Marcuson, J. Shu, D.S. Wilkinson, CVD technique for Inco nickel foam production, *Advanced engineering materials* 6(6) (2004) 454-459.
- [317] I.M. Meththananda, S. Parker, M.P. Patel, M. Braden, The relationship between Shore hardness of elastomeric dental materials and Young's modulus, *Dental materials* 25(8) (2009) 956-959.
- [318] J.H. Kim, M.J. Kim, B. Lee, J.M. Chun, V. Patil, Y.-S. Kim, Durable ice-lubricating surfaces based on polydimethylsiloxane embedded silicone oil infused silica aerogel, *Applied Surface Science* 512 (2020) 145728.
- [319] K. Xing, Z. Li, Z. Wang, S. Qian, J. Feng, C. Gu, J. Tu, Slippery coatings with mechanical robustness and self-replenishing properties as potential application on

- magnesium alloys, *Chemical Engineering Journal* 418 (2021) 129079.
- [320] J. Wang, J. Liu, N. Neate, M. Bai, F. Xu, T. Hussain, C. Scotchford, X. Hou, Investigation on time-dependent wetting behavior of Ni-Cu-P ternary coating, *Journal of Alloys and Compounds* 765 (2018) 221-228.
- [321] E. Gee, G. Liu, H. Hu, J. Wang, Effect of varying chain length and content of poly (dimethylsiloxane) on dynamic dewetting performance of NP-GLIDE polyurethane coatings, *Langmuir* 34(34) (2018) 10102-10113.
- [322] T. Svitova, O. Theodoly, S. Christiano, R. Hill, C. Radke, Wetting behavior of silicone oils on solid substrates immersed in aqueous electrolyte solutions, *Langmuir* 18(18) (2002) 6821-6829.
- [323] B. Liu, K. Zhang, C. Tao, Y. Zhao, X. Li, K. Zhu, X. Yuan, Strategies for anti-icing: low surface energy or liquid-infused?, *RSC Advances* 6(74) (2016) 70251-70260.
- [324] R.A.L. Jones, *Polymers at surfaces and interfaces*, Cambridge University Press 1999.
- [325] L. Holysz, E. Chibowski, K. Terpilowski, Influence of ambient humidity on the apparent surface free energy of poly (methyl methacrylate)(PMMA), V: Contact angle, wettability and adhesion 5 (2008) 95-111.
- [326] T. Mahmut, H. Memon, F. Xu, I. Ahmed, X. Hou, Electrospun nanofibre membrane based transparent slippery liquid-infused porous surfaces with icephobic properties, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 585 (2020) 124177.
- [327] S. Jung, M.K. Tiwari, N.V. Doan, D. Poulikakos, Mechanism of supercooled droplet freezing on surfaces, *Nature communications* 3(1) (2012) 1-8.
- [328] S.H. Davis, *Theory of solidification*, Cambridge University Press (2001).
- [329] M.K. Chaudhury, G.M. Whitesides, Correlation between surface free energy and surface constitution, *Science* 255(5049) (1992) 1230-1232.
- [330] S. Jung, M.K. Tiwari, N.V. Doan, D. Poulikakos, Mechanism of supercooled droplet freezing on surfaces, *Nature communications* 3 (2012) 615.
- [331] L.C. James, D.S. Tawfik, The specificity of cross-reactivity: Promiscuous antibody binding involves specific hydrogen bonds rather than nonspecific hydrophobic

stickiness, *Protein Science* 12(10) (2003) 2183-2193.

[332] R. Brandt, G. Neuer, Electrical resistivity and thermal conductivity of pure aluminum and aluminum alloys up to and above the melting temperature, *International Journal of Thermophysics* 28(5) (2007) 1429-1446.

[333] J. Mark, *Polymer Data Handbook* Oxford Univ, Press New York, NY 363 (1999).

[334] E. Langham, B.J.-N. Mason, The heterogeneous and homogeneous nucleation of supercooled water, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 247(1251) (1958) 493-504.

[335] C. Wei, B. Jin, Q. Zhang, X. Zhan, F. Chen, Anti-icing performance of super-wetting surfaces from icing-resistance to ice-phobic aspects: Robust hydrophobic or slippery surfaces, *Journal of Alloys and Compounds* 765 (2018) 721-730.

[336] Y. Shen, Y. Wu, J. Tao, C. Zhu, H. Chen, Z. Wu, Y. Xie, Spraying Fabrication of Durable and Transparent Coatings for Anti-Icing Application: Dynamic Water Repellency, Icing Delay, and Ice Adhesion, *ACS Applied Materials & Interfaces* 11(3) (2019) 3590-3598.

[337] H. Peng, T. Shi, H. Yang, Y. Liu, Q. Wang, Z. Su, Z. Xia, Experimental investigation on the impacting and freezing characteristics of water droplets on a PDMS-decorated superhydrophobic aluminum alloy surface, *Physica Scripta* 98(1) (2022) 015711.

[338] S.J. Lee, G.D. Park, Effective Icephobicity of Silicone Oil-Infused Oleamide–Polydimethylsiloxane with Enhanced Lubrication Lifetime, *ACS Omega* 7(24) (2022) 21156-21162.

[339] A. Lazauskas, A. Guobienė, I. Prosyčėvas, V. Baltrušaitis, V. Grigaliūnas, P. Narmontas, J. Baltrusaitis, Water droplet behavior on superhydrophobic SiO₂ nanocomposite films during icing/deicing cycles, *Materials Characterization* 82 (2013) 9-16.

[340] H. Qian, B. Liu, D. Wu, W. Liu, T. Chowwanonthapunya, D. Zhang, Facile fabrication of slippery lubricant-infused porous surface with pressure responsive property for anti-icing application, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 618 (2021) 126457.

- [341] S. Barthwal, B. Lee, S.H. Lim, Fabrication of robust and durable slippery anti-icing coating on textured superhydrophobic aluminum surfaces with infused silicone oil, *Applied Surface Science* 496 (2019) 143677.
- [342] L. Zhu, J. Xue, Y. Wang, Q. Chen, J. Ding, Q. Wang, Ice-phobic Coatings Based on Silicon-Oil-Infused Polydimethylsiloxane, *ACS Applied Materials & Interfaces* 5(10) (2013) 4053-4062.
- [343] Y.H. Yeong, C. Wang, K.J. Wynne, M.C. Gupta, Oil-Infused Superhydrophobic Silicone Material for Low Ice Adhesion with Long-Term Infusion Stability, *ACS Applied Materials & Interfaces* 8(46) (2016) 32050-32059.
- [344] E. Ghabache, C. Josserand, T. S éon, Frozen impacted drop: from fragmentation to hierarchical crack patterns, *Physical review letters* 117(7) (2016) 074501.
- [345] J.P. Holman, *Heat transfer*, McGraw-hill (2010).
- [346] K.V. Zhukovsky, H.M. Srivastava, Analytical solutions for heat diffusion beyond Fourier law, *Applied Mathematics and Computation* 293 (2017) 423-437.
- [347] R. Khammas, H. Koivuluoto, Durable Icephobic Slippery Liquid-Infused Porous Surfaces (SLIPS) Using Flame- and Cold-Spraying, *Sustainability* 14(14) (2022) 8422.
- [348] L.B. Boinovich, K.A. Emelyanenko, A.M. Emelyanenko, Superhydrophobic versus SLIPS: Temperature dependence and the stability of ice adhesion strength, *Journal of Colloid and Interface Science* 606 (2022) 556-566.
- [349] Z. He, C. Wu, M. Hua, S. Wu, D. Wu, X. Zhu, J. Wang, X. He, Bioinspired Multifunctional Anti-icing Hydrogel, *Matter* 2(3) (2020) 723-734.
- [350] L. Wang, M. Wen, M. Zhang, L. Jiang, Y. Zheng, Ice-phobic gummed tape with nano-cones on microspheres, *Journal of Materials Chemistry A* 2(10) (2014) 3312-3316.
- [351] X. Yue, J. Xiang, J. Chen, H. Li, Y. Qiu, X. Yu, High surface area, high catalytic activity titanium dioxide aerogels prepared by solvothermal crystallization, *Journal of Materials Science & Technology* 47 (2020) 223-230.
- [352] S. Heydarian, R. Jafari, G. Momen, Fabrication of lubricant-impregnated Icephobic surfaces with Improved Stability. *IWAIS* (2022).
- [353] C.J. Prakash, R. Prasanth, Recent trends in fabrication of nepenthes inspired SLIPs: Design strategies for self-healing efficient anti-icing surfaces, *Surfaces and*

Interfaces 21 (2020) 100678.

[354] H. Jin, J. Mi, B. Bl, M. Ji, A. Vp, A. Ysk, Durable ice-lubricating surfaces based on polydimethylsiloxane embedded silicone oil infused silica aerogel, *Applied Surface Science* 512 (2020): 145728.

[355] D. Maji, S. Lahiri, S. Das, Study of hydrophilicity and stability of chemically modified PDMS surface using piranha and KOH solution, *Surface and Interface analysis* 44(1) (2012) 62-69.

[356] V. Balamurugan, J. Haritha, R. ArunChendhuran, S. Srivel, J.N. AmalaJerrin, S. Kishore, M. Pachamuthu, Classification of Groundnut Oil Using Advanced ATR-MIR Spectroscopy and Chemometrics, *Food Analytical Methods* 15(7) (2022) 1778-1786.

[357] M. Li, J. Xie, Q. Dai, W. Huang, X. Wang, Effect of wetting case and softness on adhesion of bioinspired micropatterned surfaces, *Journal of the Mechanical Behavior of Biomedical Materials* 78 (2018) 266-272.

[358] A. Cefalas, E. Sarantopoulou, Z. Kollia, M. Kitsara, I. Raptis, E. Bakalis, Entropic nanothermodynamic potential from molecular trapping within photon induced nano-voids in photon processed PDMS layers, *Soft Matter* 8(20) (2012) 5561-5574.

[359] W. Si, X.-y. Zhou, B. Ma, N. Li, J.-p. Ren, Y.-j. Chang, The mechanism of different thermoregulation types of composite shape-stabilized phase change materials used in asphalt pavement, *Construction and Building Materials* 98 (2015) 547-558.

[360] Y. Srivastava, A.D. Semwal, V.A. Sajeevkumar, G.K. Sharma, Melting, crystallization and storage stability of virgin coconut oil and its blends by differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR), *Journal of Food Science and Technology* 54(1) (2017) 45-54.

[361] A. Devi, B. Khatkar, Thermo-physical properties of fats and oils, *Int. J. Eng. Technocal Res* 7 (2017) 45.

[362] K. Zhu, X. Li, J. Su, H. Li, Y. Zhao, X. Yuan, Improvement of anti-icing properties of low surface energy coatings by introducing phase-change microcapsules, *Polymer Engineering & Science* 58(6) (2018) 973-979.

[363] H. Xie, W.-h. Xu, C. Fang, T. Wu, Efficient and economical approach for flexible photothermal icephobic copper mesh with robust superhydrophobicity and active

deicing property, *Soft Matter* 17(7) (2021) 1901-1911.

[364] J. Song, Q. Li, X. Wang, J. Li, S. Zhang, J. Kjems, F. Besenbacher, M. Dong, Evidence of Stranski–Krastanov growth at the initial stage of atmospheric water condensation, *Nature communications* 5(1) (2014) 1-8.

[365] Z. Wang, A.A. Volinsky, N.D. Gallant, Crosslinking effect on polydimethylsiloxane elastic modulus measured by custom-built compression instrument, *Journal of Applied Polymer Science* 131(22) (2014).

[366] S.-f. Fan, T. Zhang, K. Yu, H.-j. Fang, H.-q. Xiong, Y.-l. Dai, J.-j. Ma, D.-y. Jiang, H.-l. Zhu, Compressive properties and energy absorption characteristics of open-cell nickel foams, *Transactions of Nonferrous Metals Society of China* 27(1) (2017) 117-124.

[367] Y. Shen, Y. Wu, J. Tao, C. Zhu, H. Chen, Z. Wu, Y. Xie, Spraying fabrication of durable and transparent coatings for anti-icing application: dynamic water repellency, icing delay, and ice adhesion, *ACS applied materials & interfaces* 11(3) (2018) 3590-3598.

[368] C. Tao, X. Li, B. Liu, K. Zhang, Y. Zhao, K. Zhu, X. Yuan, Highly icephobic properties on slippery surfaces formed from polysiloxane and fluorinated POSS, *Progress in Organic Coatings* 103 (2017) 48-59.

[369] M. Nair, A. Husmann, R.E. Cameron, S.M. Best, In situ ESEM imaging of the vapor-pressure-dependent sublimation-induced morphology of ice, *Physical Review Materials* 2(4) (2018) 040401.

[370] M. Cascajo-Castresana, S. Morin, A.M. Bittner, The ice–vapour interface during growth and sublimation, *Atmospheric Chemistry and Physics* 21(24) (2021) 18629-18640.

[371] E. Shchukina, M. Graham, Z. Zheng, D. Shchukin, Nanoencapsulation of phase change materials for advanced thermal energy storage systems, *Chemical Society Reviews* 47(11) (2018) 4156-4175.

[372] L. Liang, X. Li, H. Hu, J. Zhang, Y. Peng, C. Liu, M. Yang, Preparation of a novel Janus-cotton via the in-situ dual-phase formation and volatilization-induced fabrication method for oil/water separation with single and double layers, *Journal of Environmental*

Chemical Engineering 9(6) (2021) 106444.

[373] Q. Li, F.K. Yan, N.R. Tao, D. Ponge, D. Raabe, K. Lu, Deformation compatibility between nanotwinned and recrystallized grains enhances resistance to interface cracking in cyclic loaded stainless steel, *Acta Materialia* 165 (2019) 87-98.

[374] Z. Kamio, H. Matsushita, B. Strnadel, Statistical analysis of ice fracture characteristics, *Engineering Fracture Mechanics* 70(15) (2003) 2075-2088.

[375] M.J. Coady, M. Wood, G.Q. Wallace, K.E. Nielsen, A.-M. Kietzig, F.o. Lagugné-Labarthe, P.J. Ragona, Icephobic behavior of UV-cured polymer networks incorporated into slippery lubricant-infused porous surfaces: Improving SLIPS durability, *ACS applied materials & interfaces* 10(3) (2018) 2890-2896.

[376] Y. Zhang, H. Guo, J. Gao, W. Wei, M. Liu, C. Zheng, P. Deng, Self-lubricated anti-icing MOF coating with long-term durability, *Progress in Organic Coatings* 151 (2021) 106089.

[377] X. Wei, Y. Zhong, Y. Feng, J. Wei, J. Wang, A Slippery Liquid-Infused Network-like Surface with Anti/De-icing Properties Constructed Based on the Phosphating Reaction, *Langmuir* 38(46) (2022) 14118-14128.

[378] W. Cui, T.A. Pakkanen, Icephobic performance of one-step silicone-oil-infused slippery coatings: Effects of surface energy, oil and nanoparticle contents, *Journal of colloid and interface science* 558 (2020) 251-258.

[379] P. Irajizad, S. Nazifi, H. Ghasemi, Icephobic surfaces: Definition and figures of merit, *Advances in colloid and interface science* 269 (2019) 203-218.

[380] P. Eberle, M.K. Tiwari, T. Maitra, D. Poulikakos, Rational nanostructuring of surfaces for extraordinary icephobicity, *Nanoscale* 6(9) (2014) 4874-4881.

[381] Y. Shen, X. Xie, Y. Xie, J. Tao, J. Jiang, H. Chen, Y. Lu, Y. Xu, Statistically understanding the roles of nanostructure features in interfacial ice nucleation for enhancing icing delay performance, *Physical Chemistry Chemical Physics* 21(36) (2019) 19785-19794.

[382] C. Zhou, X. Zhao, X. Zhao, H. Li, S. Zhang, W. Feng, Y. Zhang, Low Ice Adhesion Surfaces Based on Flexible Fluorinated Polymers with a Polynorbornene Backbone, *ACS Applied Materials & Interfaces* 12(47) (2020) 53494-53502.

- [383] D. Wu, L. Ma, F. Zhang, H. Qian, B. Minhas, Y. Yang, X. Han, D. Zhang, Durable deicing lubricant-infused surface with photothermally switchable hydrophobic/slippy property, *Materials & Design* 185 (2020) 108236.
- [384] R. Pan, H. Zhang, M. Zhong, Triple-scale superhydrophobic surface with excellent anti-icing and icephobic performance via ultrafast laser hybrid fabrication, *ACS Applied Materials & Interfaces* 13(1) (2020) 1743-1753.
- [385] A.R. Esmaeili, N. Mir, R. Mohammadi, A facile, fast, and low-cost method for fabrication of micro/nano-textured superhydrophobic surfaces, *Journal of Colloid and Interface Science* 573 (2020): 317-327.
- [386] Z. He, Y. Zhuo, J. He, Z. Zhang, Design and preparation of sandwich-like polydimethylsiloxane (PDMS) sponges with super-low ice adhesion, *Soft Matter* 14(23) (2018) 4846-4851.
- [387] M.S. Selim, H. Yang, F.Q. Wang, N.A. Fatthallah, X. Li, Y. Li, Y. Huang, Superhydrophobic silicone/SiC nanowire composite as a fouling release coating material, *Journal of Coatings Technology and Research* 16(4) (2019) 1165-1180.
- [388] Y.-C. Guo, C. Cai, Y.-H. Zhang, Observation of conformational changes in ethylene glycol–water complexes by FTIR–ATR spectroscopy and computational studies, *Aip Advances* 8(5) (2018) 055308.
- [389] S. Salehpour, M.A. Dubé, Reaction Monitoring of Glycerol Step-Growth Polymerization Using ATR-FTIR Spectroscopy, *Macromolecular Reaction Engineering* 6(2-3) (2012) 85-92.
- [390] S.J. Cox, S.M. Kathmann, B. Slater, A. Michaelides, Molecular simulations of heterogeneous ice nucleation. I. Controlling ice nucleation through surface hydrophilicity, *The Journal of chemical physics* 142(18) (2015) 184704.
- [391] A. Ganne, V.O. Lebed, A.I. Gavrilov, Combined wet chemical etching and anodic oxidation for obtaining the superhydrophobic meshes with anti-icing performance, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 499 (2016) 150-155.
- [392] B. Zhang, W. Xu, D.-H. Xia, X. Fan, J. Duan, Y. Lu, Comparison study of self-cleaning, anti-icing, and durable corrosion resistance of superhydrophobic and

- lubricant-infused ultraslippery surfaces, *Langmuir* 37(37) (2021) 11061-11071.
- [393] Y. Hayashi, A. Aoki, S. Adachi, K. Hori, Study of frost properties correlating with frost formation types, 99(2) (1977): 239-245.
- [394] S. Bhat, P.K. Agarwal, The effect of moisture condensation on the spontaneous combustibility of coal, *Fuel* 75(13) (1996) 1523-1532.
- [395] M. Zou, S. Beckford, R. Wei, C. Ellis, G. Hatton, M. Miller, Effects of surface roughness and energy on ice adhesion strength, *Applied Surface Science* 257(8) (2011) 3786-3792.
- [396] J. Sun, C. Wang, J. Song, L. Huang, Y. Sun, Z. Liu, C. Zhao, Y. Li, Multi-functional application of oil-infused slippery Al surface: from anti-icing to corrosion resistance, *Journal of Materials Science* 53 (2018) 16099-16109.
- [397] J.B. Boreyko, C.P. Collier, Delayed frost growth on jumping-drop superhydrophobic surfaces, *ACS nano* 7(2) (2013) 1618-1627.
- [398] M.-H. Kim, H. Kim, K.-S. Lee, D.R. Kim, Frosting characteristics on hydrophobic and superhydrophobic surfaces: A review, *Energy Conversion and Management* 138 (2017) 1-11.
- [399] K. Zhu, X. Li, J. Su, H. Li, Y. Zhao, X. Yuan, Improvement of anti-icing properties of low surface energy coatings by introducing phase-change microcapsules, *Polymer Engineering & Science* 58(6) (2018) 973-979.
- [400] M. Kunieda, K. Nakaoka, Y. Liang, C.R. Miranda, A. Ueda, S. Takahashi, H. Okabe, T. Matsuoka, Self-Accumulation of Aromatics at the Oil–Water Interface through Weak Hydrogen Bonding, *Journal of the American Chemical Society* 132(51) (2010) 18281-18286.
- [401] T.M. Schutzius, S. Jung, T. Maitra, P. Eberle, C. Antonini, C. Stamatopoulos, D. Poulikakos, Physics of icing and rational design of surfaces with extraordinary icephobicity, *Langmuir* 31(17) (2014) 4807-4821.
- [402] X. Liu, Y. Pan, F. Liu, Y. He, Q. Zhu, Z. Liu, X. Zhan, S. Tan, A Review of the Material Characteristics, Antifreeze Mechanisms, and Applications of Cryoprotectants (CPAs), *Journal of Nanomaterials* 2021 (2021): 1-14.
- [403] N.H. Fletcher, Size effect in heterogeneous nucleation, *The Journal of chemical*

physics 29(3) (1958) 572-576.

[404] A.A. Yancheshme, G. Momen, R.J. Aminabadi, Mechanisms of ice formation and propagation on superhydrophobic surfaces: A review, *Advances in Colloid and Interface Science* 279 (2020) 102155.

[405] Y. Wang, X. Yao, J. Chen, Z. He, J. Liu, Q. Li, J. Wang, L. Jiang, Organogel as durable anti-icing coatings, *Science China Materials* 58 (2015) 559-565.

[406] V. Donadei, H. Koivuluoto, E. Sarlin, H. Niemelä-Anttonen, T. Varis, P. Vuoristo, The effect of mechanical and thermal stresses on the performance of lubricated icephobic coatings during cyclic icing/deicing tests, *Progress in Organic Coatings* 163 (2022) 106614.

[407] H. Niemelä-Anttonen, H. Koivuluoto, M. Tuominen, H. Teisala, P. Juuti, J. Haapanen, J. Harra, C. Stenroos, J. Lahti, J. Kuusipalo, Icephobicity of slippery liquid infused porous surfaces under multiple freeze–thaw and ice accretion–detachment cycles, *Advanced materials interfaces* 5(20) (2018) 1800828.

[408] Z. Zhu, H. Liang, D.-W. Sun, Infusing Silicone and Camellia Seed Oils into Micro-/Nanostructures for Developing Novel Anti-Icing/Frosting Surfaces for Food Freezing Applications, *ACS applied materials & interfaces* 15(11) (2023) 14874-14883.

[409] J. Gao, Y. Zhang, W. Wei, Y. Yin, M. Liu, H. Guo, C. Zheng, P. Deng, Liquid-infused micro-nanostructured MOF coatings (LIMNSMCs) with high anti-icing performance, *ACS applied materials & interfaces* 11(50) (2019) 47545-47552.