Review

Design of Icephobic Surfaces by Lowering Ice Adhesion Strength: A Mini Review

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Abstract: Ice accretion can lead to severe consequences in daily life and sometimes catastrophic events. To mitigate the hazard of icing, passive icephobic surfaces have drawn widespread attentions because of their abilities in repelling incoming water droplets, suppressing ice nucleation and/or lowering ice adhesion strength. As time elapses and temperature lowers sufficiently, ice accretion becomes inevitable, and a realistic roadmap to surface icephobicity for various outdoor anti-icing applications is to live with ice but with the lowest ice adhesion strength. In this review, surfaces with icephobicity are critically categorized into smooth surfaces, textured surfaces, slippery surfaces and sub-surface textured surfaces, and discussed in terms of theoretical limit, current status and perspectives. Particular attention is paid to multiple passive anti-icing strategies combined approaches as proposed on the basis of icephobic surfaces. Correlating the current strategies with one another will promote understanding of the key parameters in lowering ice adhesion strength. Finally, we provide remarks on the rational design of state-of-the-art icephobic surfaces with low ice adhesion strength.

Keywords: superhydrophobic surfaces; slippery surfaces; ice adhesion strength; anti-icing; macro-crack initiators (MACI)

1. Introduction

Undesired ice accretion on exposed surfaces becomes a severe issue to the safety operation of instruments and facilities, including aircrafts, wind turbines, solar panels, power lines, vehicles, ships and offshore oil platform [1]. The accretion of ice not only brings inconvenience to our daily life but also causes enormous economic loss each year, through, for example, frozen rain (Southern China, 2008), snow storms (Northeast USA, 2014) and aircraft accidents (Colgan Air Flight 3407, 2009). To mitigate icing problems, active de-icing methods have been widely employed with great efforts, such as mechanical vibration, thermal heating and chemical fluid spray [2]. However, the above de-icing methods suffer from having low efficiency and being energy-intensive and environmentally unfriendly [3]. Given frequent outdoor icing occurrence, these methods are expensive and suboptimal in practical applications.

An alternative approach is to introduce passive icephobic surfaces that require at least one of the following abilities: (1) to repel incoming water droplets, (2) to delay ice nucleation and (3) to lower ice-solid adhesion strength [4,5]. Bio-inspired from lotus leaves, superhydrophobic surfaces (SHSs) (contact angle >150° and contact angle hysteresis <10°) can easily shed off water droplets because of their hierarchical structures and low surface energy, showing excellent water repellency (Figure 1a) [6–10]. When SHSs still keep the ability of repelling water droplets below 0 °C, these SHSs can be called icephobic surfaces. In the meantime, SHSs can delay ice nucleation because of their low surface energy barrier and high thermal barrier (i.e., trapped air among hierarchical structures). For example, Guo et al. decorated ZnO nanohairs on micro-structured stainless-steel plates, and a water...
droplet (7 µL) lasted for a long delay time of 7220 s for ice formation [11]. From the view of ice nucleation, SHSs show much longer ice nucleation time than ordinary surfaces, showing the property of icephobicity below 0 °C. When a water droplet in the Cassie–Baxter state is completely frozen, micro-crack initiators can facilitate the fracture of ice at the interface [12]. Yet, SHSs can lose their water repellency under high vapor pressure, and water droplets on SHSs change from the Cassie–Baxter state (i.e., air is trapped among hierarchical structures and liquid only contacts at top of hierarchical structures) to the Wenzel state (i.e., hierarchical structures are fully wetted by liquid and no air is trapped among hierarchical structures) (or the mixture state) (Figure 1b,c) where “Wenzel ice” (i.e., frozen water in Wenzel state) begins to interlock with hierarchical structures below 0 °C [12]. As time elapses and temperature lowers sufficiently, ice accretion becomes inevitable, and thus a realistic roadmap to surface icephobicity for various outdoor anti-icing applications is to live with ice but with the lowest ice adhesion strength such that ice can spontaneously shed off from exposed surfaces by its own weight, vibration or natural wind [2,13,14]. Recently, many reviews have been reported on icephobic surfaces from the viewpoint of bio-inspired [14,15], durable [16], dynamic [17], elastic [18,19], superhydrophobic [20,21] and slippery surfaces [22,23], providing good insights into surface icephobicity in terms of ice repellency, delay of ice nucleation and/or low ice adhesion, respectively. However, there are only a few review papers focusing on lowering ice adhesion strength, and they lack a summary on the rational design of icephobic surfaces through lowering ice adhesion strength as well as their corresponding mechanisms.

![Figure 1](image.png)

**Figure 1.** Three wetting behaviors: (a) Cassie–Baxter state (i.e., water only contacts with atop of hierarchical structures); (b) mixture state between Cassie–Baxter state and Wenzel state; and (c) Wenzel state (i.e., completely wetted state, cross-sectional view).

Herein, based on the surface morphology and its anti-icing design principles, surfaces with icephobicity are categorized into smooth surfaces, textured surfaces, slippery surfaces and sub-surface textured surfaces (Figure 2). The working mechanism, current status, theoretical limit and perspectives of these surfaces are discussed. The possibility of combining multiple passive anti-icing strategies is investigated to achieve ice adhesion strength as lowest as possible, promoting an understanding of the key parameters in lowering ice adhesion strength. Finally, we provide remarks on state-of-the-art of icephobic surfaces with low ice adhesion in future.
2. Strategies towards Designing of Icephobic Surfaces by Lowering Ice Adhesion Strength

Generally, icephobic surfaces can be defined by ice adhesion strength ($\tau_{\text{ice}}$) below 100 kPa [4,24]. According to the surface properties (i.e., surface chemistry, surface topographies and sub-surface structures), icephobic surfaces can be categorized into smooth surfaces, textured surfaces, slippery surfaces and sub-surface textured surfaces. When comparing the icephobic property of above surfaces via ice adhesion strength, test methods and conditions should be comparable. Factors that influence ice adhesion strength include test method (e.g., horizontal shear, vertical shear, centrifugal shear and tensile strength) [25], test temperature ($-30$ to $0 \degree C$) [25], characterization instrument [5], procedure of ice formation [25–27], type of ice (i.e., precipitation ice, in-cloud ice and bulk water ice) [26], size of ice [28], type of surface (surface chemistry, surface topography, elastic modulus and sub-surface structure) [29], loading rate [30] and failure behavior [25]. For all the data of ice adhesion strength discussed in this paper (Figure 3), the failure behavior refers to the adhesive failure between the substrate and ice but not the cohesive failure within ice or substrate. The instrument is usually test-method-dependent, while the type of ice depends on the icing conditions (i.e., temperature, humidity and vapor pressure). The size of ice (i.e., usually refer to the length of ice) influences ice adhesion on a chosen surface [28,29], whereas the overwhelming majority of the studies on ice adhesion strength do not consider it. Thus, ice adhesion strength of above four types of icephobic surfaces from 162 journal papers has been summarized under the consideration of test method (e.g., horizontal shear, vertical shear, centrifugal shear and tensile strength) and temperature ($-30$ to $0 \degree C$) (Figure 3). Up to now, there are no standards for the preparation of ice cubes and the testing methods of ice adhesion strength, which makes it difficult to directly compare ice adhesion strength by its value. Figure 3 provides an overview that ice adhesion strength can be compared for four types of surfaces under the same test temperature and evaluation method. In general, when test method and temperature are chosen, ice adhesion strength should be comparable. In this section, four types of icephobic surfaces are discussed based on ice adhesion strength in terms of theoretical limitation, current status and perspectives.
Figure 3. Ice adhesion strength plotted against temperature (i.e., range from 0 to −30 °C) by using different ice adhesion test methods (i.e., centrifuge, tensile, horizontal shear and vertical shear): (a) smooth surfaces, (b) textured surfaces, (c) slippery surfaces and (d) sub-surface textured surfaces. Data are collected from the literature [1,2,5,23,24,26,28,31–185].

2.1. Smooth Surfaces

The fabrication process of smooth surfaces is usually facile and cost-effective, which can be easily achieved by machining, depositing, molding, spraying, spin-coating, dip-coating and so on. Smooth surfaces are good candidates for surface icephobicity as long as ice adhesion strength of surfaces is less than 100 kPa [4]. Generally, ice adhesion strength of smooth solid surfaces is below 2 MPa (i.e., horizontal shear test), as shown in Figure 3 [1,4,5,13,24,41]. For example, ice adhesion strength of typical metallic surfaces is larger than 600 kPa (i.e., vertical shear test) [1,5]. For non-textured smooth surfaces with high elastic modulus, a theoretical lower limit for ice adhesion strength is about 150 kPa (i.e., horizontal shear test) [24]. Thus, most of smooth surfaces are not icephobic on the basis of the definition of icephobicity.

From the viewpoint of fracture mechanics, ice adhesion strength can be estimated by the following equation [13,186,187]:

\[ \tau_c = \sqrt{\frac{E^*G}{\pi a\Lambda}} \]  

(1)

where \( E^* \) is the apparent elastic modulus, \( G \) is the surface energy, \( a \) is the length of the interface crack and \( \Lambda \) is a non-dimensional constant determined by the geometric configuration of the crack. According to the equation (1), ice adhesion strength can be reduced by decreasing elastic modulus for a chosen material surface. Thus, ice adhesion strength of smooth surfaces can be further reduced below 100 kPa by tuning elastic modulus and/or surface chemistry as suggested by the equation (1). For example, He et al. decreased elastic modulus and surface energy of polydimethylsiloxane (PDMS) based coatings by
tuning the weight ratio of prepolymer and curing agent ranging from 10:1 to 10:10 and thus lowered ice adhesion strength (Figure 4a) [2]. Beemer et al. developed novel inexpensive, environmentally benign, non-corrosive PDMS gels that offer ultra-low adhesion to ice ($\tau_{\text{ice}} = 5.2 \pm 0.4$ kPa) as well as outstanding mechanical durability by reducing shear modulus of PDMS gels [41]. Moreover, He et al. investigated the correlation between ice adhesion strength and elastic modulus of 24 substrates and found that low elastic modulus of coatings did not guarantee low ice adhesion strength, while surfaces with low ice adhesion strength always show low elastic modulus [5]. In short, ice adhesion strength of coatings with low elastic modulus (i.e., elastomers and organogels) is determined by the failure mechanism of ice as well as the coating thickness.

![Figure 4](image-url). Ice adhesion strength at $-18^\circ$C plotted against (a) PDMS substrates and sandwich-like PDMS sponges with the weight ratio of prepolymer and curing agent ranging from 10:1 to 10:10; (b) correlation between ice adhesion strength and PDMS coating thickness in (a); (c) correlation between ice adhesion strength and shear modulus of PDMS gels; and (d) correlation between ice adhesion strength and coating thickness of PDMS gels in (c). Panel (a,b) reproduced with permission from Ref. [2], Copyright 2018, the Royal Society of Chemistry; panel (c,d) reproduced with permission from Ref. [41], Copyright 2016, the Royal Society of Chemistry.

The failure mechanism at the ice-substrate interface may depend on the size of ice, type of ice and flexibility of the smooth substrate [29]. The removal of ice occurs in a brittle manner for smooth surfaces with high elastic modulus, while ductile behavior occurs for highly elastic smooth surfaces because of surface deformations during the detachment of ice [29]. In the latter case, the ice interface usually behaves like that of a ductile material with little tendency to fracture when smooth surfaces are highly elastic [29]. For example, Beemer et al. reported that air-trapped cavity at the interface between ice and the PDMS gel surface propagated as a separation pulse and resulted in a stick slip motion, as shown in Figure 5a [41,188]. Chaudhury et al. demonstrated that the elastic instability led to the development of interfacial cavities at the interface between glass and PDMS rubber such that it allowed localized deformations [189]. Irajizad et al. introduced stress-localized interfacial cavity between ice and organogel, thereby leading to the propagation of crack at the interface and achieving ice adhesion strength of 1 kPa, as shown in Figure 5b [143]. Moreover, the coating thickness is another factor that correlates with the ductile deformation and the wavelength of elastic instability, which are caused by the interfacial cavitation and
subsequent minimization of the shear and longitudinal deformation energies of the elastic coating and thus influence ice adhesion strength [189,190]. For example, Chaudhury et al. considered the wavy segments as individual cracks during the detachment of ice, leading to the decrease of ice adhesion strength [189]. Wang et al. found that increasing the thickness of PDMS surfaces from 18 to 533 µm can reduce ice adhesion strength when removing a solid from an elastomeric substrate, as suggested by Kendall [53,191]:

\[
P_c \propto \pi a^2 \sqrt{2w_a K / t}
\]  

where there is a correlation of the force \( P_c \) required to remove a rigid cylinder with work of adhesion \( w_a \), bulk modulus \( K \), thickness \( t \) and radius \( a \). Kendall’s theory can be used for the removal of a rigid object from an elastic film in tensile mode, and there is also a relationship between tensile and shear modulus \( K_{\text{tensile}} = 3 K_{\text{shear}} \) [53,192]. This correlation has been also verified by He et al. (that increasing coating thickness can reduce ice adhesion strength), and ice adhesion strength became stable when the thickness of PDMS substrate reached 4.8 mm, as shown in Figure 4b,d [2].

![Figure 5. (a) Schematic illustrating the separation of ice from PDMS gels via separation pulses. During a horizontal shear, air can be trapped into air cavities, and these air cavities can be propagated via separation pulses; (b) stress-localized viscoelastic icephobic material consists of two phases: silicon elastomer (Phase I) and silicon-based organogel (Phase II). The crack forms at the coordinate of phase II with minimal forces. Panel (a) reproduced with permission from Ref. [41], Copyright 2016, the Royal Society of Chemistry; panel (b) reproduced with permission from Ref. [143], Copyright 2019, the Royal Society of Chemistry.](image)

From the above discussion, we find that smooth elastic surfaces can be icephobic and even achieve extremely low ice adhesion strength by tuning surface chemistry, elastic modulus and surface thickness (Figures 3 and 4). Smooth elastic surfaces (i.e., elastomeric surfaces [2], organogels [41], hydrogels [193] and ionogels [194]) have attracted much attention because of low ice adhesion strength. For ice adhesion strength, elastic smooth surfaces may reach their own theoretical limits as affected by the coating thickness and the failure mechanism of ice (i.e., mechanism of separation pulses [41]) during a de-icing process. Thus, it is necessary to seek rational designs of anti-icing surfaces by the combination of multiple passive anti-icing strategies. For example, various kinds of elastic surfaces can be incorporated with polyelectrolytes, ions, salts and lubricants to enhance surface chemistry and interfacial slippage and thus lower ice adhesion strength because of potential synergistic effects of different anti-icing/de-icing strategies. Additionally, these elastic smooth surfaces can be rationally designed to be porous or sub-surface structured such that multi-scale crack initiators can be generated at the interface between ice and substrate due to the stiffness inhomogeneity in both perpendicular and tangential directions.

### 2.2. Textured Surfaces

Textured surfaces with icephobicity usually contain hierarchical structures (i.e., hydrophobic surfaces and SHSs). Taking SHSs, for instance, some surfaces present excellent anti-icing behaviors, while others do not always show icephobicity [156,187,195–197]. This controversial issue arouses researchers’ curiosity in SHS-based icephobicity all over the world. To explain this issue, three factors related to the variable surface icephobicity of SHSs
are discussed as follows. The first factor is condensation. SHSs may lose superhydrophobicity (i.e., water repellency) in a highly humid environment (or supersaturation) [198–200]. Once the vapor pressure reaches critically high, or the droplets are too small, water droplets can slowly permeate hierarchical structures and fully wet the hierarchical structures of SHSs (Figure 6) [199]. For example, the lotus leaf surface became hydrophilic once it experienced water condensation [198]. The second factor is the inter-locking effect between ice and hierarchical structures of SHSs (Figure 6c). The water that has wetted the hierarchical structures of SHSs can freeze to ice, enveloping hierarchical structures at low temperatures (i.e., below 0 °C) [32,167], thereby leading to an increase of ice adhesion strength. The third factor is the sustainability of surface chemistry and hierarchical structures. The surface chemistry and the tips of hierarchical structures may be damaged during icing (i.e., water solidification) and/or de-icing (i.e., ice removal) cycles (Figure 6d) [156,201], resulting in the loss of surface superhydrophobicity. Besides, SHSs can also be applied for frost-resistant surfaces that can withstand several freeze-thaw cycles without damage when these surfaces suffer frost in the saturated state [202], which is different from the definition of icephobic surfaces.

SHSs have been demonstrated to be water/ice-repellent in the outdoor applications [203–205]. For example, Cao et al. kept silica-based SHSs coated or uncoated aluminum plates under freezing rain, and they found SHSs showing excellent icephobicity [203]. Boinovich et al. carried out an outdoor test (i.e., a heavy snowfall at −3 °C) and showed the superhydrophobic coating being free of ice in comparison with untreated stainless steel [204]. In real long-term outdoor applications, SHSs will unavoidably lose water/ice-repellent properties as time elapses in cold and harsh environments. An alternative approach to achieving surface icephobicity is to lower ice adhesion strength [2,13]. During a de-icing process, the inter-locking effect between ice and hierarchical structures of SHSs cannot be ignored, which often causes the damage of hierarchical structures and thus induces an increase of ice adhesion strength (Figure 6). Actually, using SHSs as part of an an individual anti-icing strategy is not enough for the design of durable icephobic
surfaces with low ice adhesion strength. Through integration with other passive anti-icing strategies (i.e., elastic substrates and lubricating layers), SHSs can alleviate the inter-locking effect, enhance robustness and lower ice adhesion strength. For example, Wang et al. reported that a flexible superhydrophobic coating showed a water and ice repellency at low temperatures (−20 °C) and high relatively humidity of 90% for up to three months [206]. Vasileiou et al. demonstrated that the collaborative effect of substrate flexibility and surface micro/nanotexture can enhance both icephobicity and the repellency of viscous droplets (i.e., typical of supercooled water) [207]. Wang et al. reported that a robust SHS with flexible micro-ratchet/ZnO nano-rods can recover its icephobicity after a freezing test [208]. Golovin et al. investigated an SHS with flexible PDMS-based micropillars and found its ice adhesion strength of 26 ± 3 kPa for 20 successive icing/de-icing cycles [24]. Barthwal et al. prepared robust and durable lubricating anti-icing coating by infusing silicone oil on super-hydrophobic aluminum surfaces, and ice adhesion strength on this lubricating anti-icing coating was as low as 22 ± 5 kPa [44].

Although hydrophobic or superhydrophobic surfaces cannot be guaranteed as icephobic surfaces for a long time, researchers still try to find correlations between ice adhesion strength and room temperature characteristics, such as wettability, surface roughness, elastic modulus, hardness and water adhesion force [1,5]. Among these characteristics, the value of \( (1 + \cos \theta_{\text{rec}}) \) and water adhesion force have attracted much attention in recent years. For example, Mckinley and Cohen et al. found a linear correlation between ice adhesion strength and the value of \( (1 + \cos \theta_{\text{rec}}) \) in 2010 when ice adhesion strength of surfaces is larger than 150 kPa (Figure 7a) [1], but later in 2017 they found that this correlation become inaccurate for elastomeric surfaces (Figure 7b) [75]. This is because water contact angle only reflects surface chemistry of surfaces, while it cannot indicate elastic modulus of surfaces. Recently, He et al. found that water adhesion force correlates well with ice adhesion strength when ice adhesion strength is larger than 100 kPa (Figure 7c) [2,5]. Below 100 kPa, low ice adhesion strength is associated with low water adhesion force ranging from 160 to 315 µN (Figure 7c,d) [2,5]. The working process of water adhesion force is similar to that of ice detachment, and water adhesion force as well as ice adhesion strength can simultaneously reflect surface chemistry, elastic modulus and sub-surface structures.

In summary, surface icephobicity of SHSs can be easily maintained before ice formation occurs on SHSs. Once accumulated ice covers SHSs, ice adhesion strength can still be low if “Cassie ice” forms on the top of hierarchical structures of SHSs. For real outdoor applications, SHSs as an individual anti-icing approach may be suitable for short-term use, while they are not proper for a long-term use because superhydrophobicity will be gradually destroyed during icing/de-icing cycles. To cope with these drawbacks (i.e., inter-locking effect and degradation of surface chemistry and hierarchical structures) of SHSs, multiple passive anti-icing strategies need to be considered for incorporation with SHSs, including elastic/flexible substrates, sub-surface structures and lubricating layers, to provide robust SHSs with durable icephobicity.

2.3. Slippery Surfaces

Slippery surfaces with icephobicity usually refer to lubricating surfaces, such as organic lubricating layers and aqueous lubricating layers. Organic lubricating layers often contain sacrificial layers (e.g., oils, liquid paraffin, and perfluorinated fluids) that are immiscible with water [24,97,209]. Ice can be easily shed from these surfaces, but at the same time this depletes the organic lubricant. Aqueous lubricating layers consist of hygroscopic polymers that can absorb water and form an interfacial non-frozen layer below 0 °C [38,75,76,185], working as a lubricating layer during a de-icing process. In this section, two kinds of lubricating surfaces with low ice adhesion strength will be discussed, and the possibility of organic lubricating and aqueous lubricating surfaces will be investigated for practical anti-icing applications.
Figure 7. Correlations between ice adhesion strength and the value of \((1 + \cos \theta_{rec})\): (a) ice adhesion strength measured at \(-10^\circ\) C for bare steel and 21 different coatings; (b) ice adhesion strength measured at \(-15^\circ\) C for 17 different polymer coatings and a bare clean silicon wafer. Correlations between ice adhesion strength and water adhesion force (i.e., the water adhesion force was investigated by a Dynamic Contact Angle Tensiometer (DCAT11s, dataphysics) at room temperature): (c) 24 different coatings; and (d) 10 PDMS-based coatings. (a) Reproduced from Ref. [1] with permission, Copyright 2010 American Chemical Society; (b) reproduced from Ref. [75] with permission, Copyright 2017 American Chemical Society; (c) reproduced from Ref. [5] with permission, Copyright 2017 Springer Nature Publishing AG; and (d) reproduced from Ref. [2] with permission, Copyright 2018 the Royal Society of Chemistry.

2.3.1. Organic Lubricating Surfaces

Bio-inspired from Nepenthes pitcher plants, Aizenberg et al. reported a new lubricating surface named slippery liquid-infused porous surface (SLIPS) (Figure 8), which needs to meet three criteria: (1) the organic liquid firmly adhere within the porous substrate, (2) the substrate prefer to be wetted by the organic liquid rather than the external incoming liquid (i.e., water), and (3) the organic liquid and the external incoming liquid are immiscible [209]. This novel strategy opened a new avenue towards designing icephobic surfaces [70,96,150,152,177,210–220], showing low ice adhesion strength as described in Figure 3. From then on, more and more relevant researches have been explored. For example, Kim et al. impregnated a perfluorinated lubricant in polypyrrole-coated aluminum surface to obtain a SLIPS with ice adhesion strength \((\tau_{\text{ice}} = 15.6 \pm 3.6 \text{ kPa})\) [152]. Zhang et al. fabricated a double-layered SLIPS coating on the AZ31 Mg alloy for anti-icing application [70]. Wang et al. obtained a SLIPS by infusing perfluorinated lubricants into a superhydrophobic coating consisting of SiO\(_2\) nanoparticles and poly(methyl methacrylate), which functions remarkable anti-icing ability [211]. Wang et al. infused different lubricants into SHSs to form slippery icephobic surfaces with superior anti-icing properties [213]. Thus, SLIPS with low ice adhesion strength can be utilized in the anti-icing application.
Figure 8. (a) Schematics showing the fabrication of a SLIPS by infiltrating a functionalized porous/textured solid with a low-surface energy, chemically inert liquid. (b) Ice mobility on a SLIPS (highlighted in green) compared to strong adhesion to an epoxy-resin-based nanostructured superhydrophobic surface (highlighted in yellow) when temperature and relative humidity were $-4 \, ^\circ C$ and $\sim 45\%$, respectively. (a,b) Reproduced with permission from [209], Copyright 2011 Macmillan Publishers Limited.

To understand the properties of organic lubricating layers, the stability of organic lubricant layers needs to be clarified. Preston et al. used a model as proposed by van Oss, Chaudhury and Good (vOCG) to predict unknown surface energies for an arbitrary system of solid and lubricant [221], and identified five criteria (Figure 9) for failure of an organic lubricant surface as follows [221]:

1. $S_{ld} \geq 0$, the lubricant spreads over the droplet; the droplet is cloaked,
2. $S_{dl} \geq 0$, the impinging fluid spreads over the lubricant and forms a film instead of discrete droplets,
3. $S_{ls} \leq -\gamma_l R$, the lubricant does not infuse in the hierarchical structures of substrate in the presence of the surrounding vapor,
4. $S_{ls(d)} \leq -\gamma_{dl} R$, the lubricant does not infuse in the hierarchical structures of substrate in the presence of the impinging fluid,
5. $\gamma_{dl} \leq 0$, the lubricant and the impinging fluid are miscible, where subscripts l, d, s refer to lubricant, impinging fluid and substrate, respectively, where $S_{xy}$ represents the spreading parameter for $x$ spreading over $y$, and $R = (r - 1)(r - \phi)$ is a roughness factor calculated using the roughness ($r$) and the solid fraction ($\phi$), and is 0 for a flat substrate and 1 for a very rough substrate [221,222]. Thus, these five criteria need to be considered when a water droplet is on slippery surfaces at low temperature (i.e., before ice nucleation).

For slippery lubricating surfaces, when water droplets are frozen, the amount of lubricants greatly influences ice adhesion strength, accompanied by the depletion of lubricants during icing/de-icing cycles [223,224]. For example, Varanasi et al. demonstrated that ice adhesion strength of a lubricant-impregnated surface with excessive amount of lubricants was lower than that with balanced amount of lubricants by a factor of 15 (Figure 10a–c) [223]. Varanasi et al. also investigated the depletion phenomenon of lubricants before and after freezing and found that the impregnated lubricants can migrate from the wetting ridge and the substrate’s texture to the frozen drop as observed by using the cryo-FIB/SEM images (Figure 10d,e) [224]. Once excessive amount of lubricants is depleted from substrate, inter-locking effect between ice and exposed hierarchical structures occurs, resulting in the increase of ice adhesion strength. Thus, this indicates that long-term
use of SLIPS for surface icephobicity sometimes becomes impractical until the depletion problem of lubricants can be mitigated.

Figure 9. The possible failure modes outlined by Preston et al. for a lubricant/substrate/droplet system. The ideal droplet of impinging fluid on a slippery surface rests atop a combined lubricant-solid layer. Reproduced with permission from Ref. [221]. Copyright 2017 American Chemical Society.

To mitigate the depletion of lubricants, many efforts have been made to prepare durable SLIPS [24,35,68,73,74,90,132,225–227]. One strategy is to mix organic lubricants (e.g., oils) with polymer networks during synthesis; then, the added oils are released gradually under shear stress. For example, Golovin et al. fabricated a class of organic lubricants impregnated with durable elastomers with low ice adhesion strength [24]. Zhu et al. introduced a liquid-infused porous PDMS surface for icephobic coatings and achieved ice adhesion strength below 50 kPa (tensile test) and 40 kPa (shear test) [73]. Coady et al. developed an approach that utilized UV cross-linked, interpenetrated siloxane polymer networks to enhance SLIPS durability, obtaining ice adhesion strength below 10 kPa [68]. Yeong et al. reported a flexible oil-infused superhydrophobic elastomer with ice adhesion strength of ~38 kPa [90]. Pang et al. obtained waterborne anti-icing coatings with silicone oil microcapsules in latex paints for a long-term use [225]. Tao et al. prepared a durable slippery surface from polysiloxane and fluorinated POSS, which possessed an extremely low ice adhesion strength of 3.8 ± 1.8 kPa [226]. Gao et al. fabricated a durable, self-lubricating icephobic elastomer coating with ultra-low ice adhesion strength by optimizing silicone oil infusion levels [227]. Although the lubricants can be generated continuously during icing/de-icing cycles, the lubricant at the interface between ice and substrate is still easy to be depleted. To further improve the durability of SLIPS, new rational designs of organic lubricating layers have been proposed. Wang et al. used peanut oil as the lubricant that can have a phase transformation from liquid to solid state before water freezing and thus enhance the durability of obtained SLIPS [56].
In short, we discuss the design criteria and drawbacks of organic lubricating surfaces with icephobicity and summarize approaches towards improving the durability of organic lubricating surfaces during icing/de-icing cycles. Regarding lubricants, they need to be firmly locked by hierarchical (or porous) substrates and possess durable, regenerable, continuously released and/or phase transition properties during icing/de-icing cycles. For substrates, the anti-icing strategy of organic lubricating layers can be combined with other passive anti-icing strategies (e.g., low elastic and flexible substrates, sub-surface textured substrates, etc.) to achieve synergistic effects and thus promote low ice adhesion strength. For organic lubricating layers, durability and longevity are still critical parameters that restrict practical applications. Considering the complexity of outdoor conditions and atmospheres, organic lubricating layers need to be properly chosen and utilized when used in the anti-icing field.

2.3.2. Aqueous Lubricating Surfaces

Compared with organic lubricating layers, aqueous lubricating layers for anti-icing application are due to a non-frozen liquid-like water layer that grafts hygroscopic molecules or polymers and then forms hydrophilic surfaces. This non-frozen liquid-like layer can exist at the ice-substrate interface below 0 °C and thus serves as a lubricating layer during a de-icing test [38,75,95,228–231]. Actually, the crucial question “Does the liquid-like layer exist at temperatures below 0 °C?” aroused researchers’ curiosity for more than one century. As early as 1859, Michael Faraday hypothesized that a non-frozen liquid-like water layer covered ice even at temperatures well below freezing [229]. There are three interesting issues attracting researchers’ attention: (1) temperatures that the non-frozen liquid layer begins to form; (2) the thickness of this non-frozen liquid layer; and (3) the reduction of ice adhesion strength caused by this non-frozen liquid layer.

With great effort, scientists have tried to found theories for the liquid-like non-frozen layer on ice. For example, in 1968 Fletcher developed a quantitative theory associated with the liquid-like water layer, and Fletcher’s model predicts that the transition between the
crystalline ice surface and the liquid-like water layer occurs at a well-defined temperature in the range from $-6$ to $-3 \, ^\circ C$ [232]. Much experimental evidence, such as nuclear magnetic resonance (NMR), proton backscattering, X-ray diffraction and atomic force microscopy, shows that the liquid-like layer starts to form at a temperature range from $-35$ to $0 \, ^\circ C$ [229]. Dou et al. have experimentally verified the existence of the aqueous lubricating layer as low as $-53 \, ^\circ C$ [36]. Besides, Xiao et al. demonstrated the presence of this liquid-like non-frozen layer by molecular dynamics simulation and showed a reduction of ice adhesion strength up to 60% [228]. Thus, the non-frozen liquid-like water layer may exist for the majority of de-icing tests on aqueous lubricating layers.

The thickness of the liquid-like layer can vary at different temperatures. For example, Döppenschmidt et al. used atomic force microscope (AFM) to investigate surface properties of ice in a temperature range from $-24$ to $-0.7 \, ^\circ C$ and found the thickness of the liquid-like water layer varying between ~12 nm at $-24 \, ^\circ C$ and ~70 nm at $-0.7 \, ^\circ C$ [233]. Hetland et al. reported that as temperature decreased, the slope of the film-thickness versus temperature curve changed depending on the relative strengths of van der Waals and Coulombic interactions because of the amount of impurity [234]. Ikeda-Fukazawa et al. performed molecular-dynamics studies of surface of ice Ih and found the thickness of liquid-like film as a function of temperature due to the surface melting of ice crystal and low friction [235]. Chen et al. found that for the hydrophobic surfaces, the interaction between water/ice and the substrate was dominated by van der Waal’s forces [236], and the increased thickness of the water depletion layer at the interface weakened the van der Waal’s interaction [75].

The investigation of non-frozen liquid-like lubricating layer for reducing ice adhesion strength becomes active in the recent decade. Usually, hydrophilic polymers can collect water in their vicinity as temperature decreases. For example, Chen et al. utilized several hydrophilic polymers to prepare aqueous lubricating layers with iced-hobicity, including hyaluronic acid-dopamine [38], poly(acrylic acid) (PAA) (Figure 11a) [76] and poly(acrylic acid)–dopamine [125], respectively. Dou et al. achieved ice adhesion strength of $27 \pm 3 \, kPa$ at $-15 \, ^\circ C$ on dimethylolpropionic acid/polystyrene surfaces [36]. Ozbay et al. used water, ethylene glycol, formamide and water-glycerine mixture as hydrophilic lubricants to prepare hydrophobic surfaces with a lowest ice adhesion strength of $16 \pm 3 \, kPa$ [230]. Some researchers chose amphiphilic lubricants to replace traditional hydrophilic or hydrophobic lubricants to prepare lubricating surfaces, and potential synergistic effects of hydrophilic and hydrophobic segments of amphiphilic lubricants showed high stability and excellent surface iced-hobicity [87,105,237,238]. Similarly, anti-freeze proteins [155,239], polyelectrolyte brush layers [77,240–244], hydrogels [139,245,246] and iongels [194] also contain hydrophilic and hydrophobic parts and can exhibit surface iced-hobicity. For example, Zhang et al., Yamazaki et al. and Wang et al. used anti-freeze hydrophilic liquids to obtain lubricating surfaces with excellent iced-hobicity at extremely low temperatures, including polyols [69], ethylene glycol [65] and ethanol (Figure 11b–d) [100]. Particularly, Wang et al. used the continuous release of ethanol molecules to generate the non-frozen liquid-like layer and realize low ice adhesion strength at low temperatures (Figure 11b–d) [100].
In brief, aqueous lubricating layers show low ice adhesion strength because of the non-frozen liquid-like water layer below 0 °C. The non-frozen liquid-like layer forms from −53 to 0 °C, and the thickness of non-frozen liquid-like layer usually ranges from 0 to 100 nm, depending on temperatures and the impurity amount of water. Similar to other passive anti-icing strategies (e.g., organic lubricating layers, organogels), aqueous lubricating layers can realize super-low ice adhesion strength. The critical issue for aqueous lubricating layers is the sustainability of hygroscopic (or hydrophilic) polymers and thus the functional durability. Although much attention has been paid to the icing/de-icing cycles of aqueous lubricating layers, variations of chemical structures and morphologies of hygroscopic or hydrophilic polymers still need to be analyzed and explored after de-icing tests. Additionally, aqueous lubricating layers can be combined with other passive anti-icing strategies (i.e., elastic substrate and sub-surface structures) to achieve potential synergistic effects and thus facilitate lower ice adhesion strength. For the outdoor anti-icing application, however, the rational design of aqueous lubricating surfaces with durability and longevity at low temperature is still a challenge.

2.4. Sub-Surface Textured Surfaces

For textured surfaces, “Cassie ice” can be formed on hierarchical structures of SHSs, and micro-voids where trapped air exists become micro-cracks during a shear test. For example, Nosonovsky et al. explained why superhydrophobic surfaces were not always icephobic and concluded the correlation of ice adhesion strength with the receding contact angle and the initial size of interfacial cracks [187]. Ling et al. reported that the formation of micro-cracks that act as interfacial stress concentrators can reduce ice adhesion strength on textured metallic surfaces [170]. Therefore, the key factor for textured surfaces with low ice adhesion strength is to form micro-cracks between ice and substrate and hence maximize interfacial cracking during a de-icing test.

According to the correlation between ice adhesion strength (τ<sub>ice</sub> >100 kPa) and (1 + cosθ<sub>rec</sub>) proved by Meuler et al. [1] and He et al. [9], ice adhesion strength theoretically approaches zero when θ<sub>rec</sub> becomes 180°. However, it is difficult to experimentally realize such a high receding contact angle. Thus, an alternative approach to obtaining low ice adhesion strength is proposed: hydrophobic surfaces (low surface energy) combining
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with sub-surface textured structures (potential crack initiators during the detachment of ice) (Figure 12a).

![Figure 12. (a) Multiscale crack-initiator mechanisms at an ice–substrate interface. The red line represents nanoscale-initiator (NACI) mechanism. The yellow line denotes microscale-initiator (MICI) mechanism. The green lines show the proposed macroscale-initiator (MACI) mechanism that can function on any surfaces with deformation incompatibility, and bring ice adhesion strength down to the super-low regime. 2D plane strain finite element analyses using ABAQUS to illustrate the MACI mechanism, (b) ice adhesion test on a homogenous film and (c) ice adhesion test on the proposed film with substructures. The black arrows resemble the applied forces. (a–d) reproduced with permission from [13], Copyright 2017 the Royal Society of Chemistry.](image)

From the viewpoint of fracture mechanics, it is hypothesized that multi-scale crack initiator-promoted surfaces with super-low ice adhesion strength can be obtained, and multi-scale crack initiators at the interface between ice and substrate can be divided into three types (Figure 12a): (1) nano-crack initiator (NACI) induced by the surface chemistry; (2) micro-crack initiator (MICI) formed by the micro-voids between the solid surface and the so-called “Cassie ice”; and (c) macro-crack initiator (MACI) induced by the stiffness inhomogeneity in both perpendicular and tangential directions (Figure 12b) to maximizing the length of crack (a) as suggested by the equation (1) during a shear test [13,140]. The experimental results confirmed that MACI originates from the deformation incompatibility, which was fundamentally different from NACI and MICI as illustrated by finite element analyses (Figure 12b,c) [13].

Recently, multi-scale crack initiator-promoted surfaces with low ice adhesion strength have been developed by many researchers. For example, He et al. prepared sandwich-like PDMS sponges and realized durable super-low ice adhesion strength of 0.9 kPa by introducing MACI at the ice-substrate interface [2]. To understand the mechanism of MACI, He et al. investigated the effects of parameters on ice adhesion strength, including hollow sub-surface structure geometry (e.g., the heights, shapes, and distributions) and the directions of the applied shear force [140]. It is found that the number of potential crack initiation sites dictates the ice adhesion strength, and directions of the applied shear force can also influence the ice adhesion strength if the maximum length of an initiated crack is different [140]. Irajizad et al. developed interfacial crack-promoted icerphobic surfaces...
with ice adhesion strength in order of 1 kPa and exceptional mechanical, chemical and environmental durability [143]. Chen et al. utilized a swelling force to induce the interfacial cracks and thus reduced ice adhesion strength of icephobic surfaces [247]. Chen et al. proposed a de-icing model that established a phase-change temperature gradient (ethanol solutions with different concentrations) at the interface to alter the contact stability between ice and substrate [248]. Jamil et al. obtained durable icephobic coatings by introducing Cassie–Baxter superhydrophobicity and cracks as caused by the incorporation of candle soot embedding and RTV-1 [146]. From the above discussion, the hypothesis on MACI promoted surfaces with super-low ice adhesion strength, providing new insight into the rational design of icephobic surfaces.

All in all, multi-scale crack initiator-promoted low ice adhesion surfaces (i.e., MACI) still need to be investigated both theoretically and experimentally, including the stability and durability of surfaces with sub-surface textured structures. Similarly, multi-scale crack initiator-promoted icephobic surfaces can be combined with other passive anti-icing strategies (i.e., aqueous/organic lubricating surfaces, SHSs and low elastic modulus surfaces) such that potential synergistic effects can help to overcome limitations of each individual anti-icing strategy and facilitate lowering ice adhesion strength.

3. Synergy of Multiple Anti-Icing Strategies

Individual passive anti-icing strategies have own drawbacks and ice adhesion strength on these strategies based icephobic surfaces may reach the theoretical limit. Thus, it is worth combining multiple passive anti-icing strategies to break the limitation of each individual strategy and further lower ice adhesion strength. For example, He et al. combined low elastic modulus substrate with aqueous lubricating layers [185] and multi-scale interfacial cracks [2,13,140] to achieve icephobic surfaces with low ice adhesion strength. Golovin et al. introduced organic lubricants into elastomers and obtained icephobic surfaces with extremely low ice adhesion strength [24,35]. Liu et al. integrated a superhydrophobic copper mesh with an intelligent organogel that can secrete anti-freezing agent (the mixture of ethylene glycol and water) autonomously in response to temperature, showing excellent icephobic properties [172]. Wang et al. prepared a robust anti-icing surface by combining low elastic modulus substrates with SHSs [206]. The synergistic effects of combining multiple passive anti-icing strategies can significantly reduce ice adhesion strength and offer a new solution to avoiding drawbacks and theoretical limits of passive anti-icing surfaces. Currently, some researchers have introduced active anti-icing strategies (i.e., electro-thermal, photo-thermal and magnetic responsive stimulus) into passive icephobic surfaces to achieve the reliability and efficiency of de-icing, including magnetic-responsive icephobic surfaces [69,249,250], photo-thermal promoted icephobic surfaces [3,67,148,151,251–255] and electro-thermal icephobic surfaces (Figure 13) [104,151,256–258]. In this review, we focus on the rational design of passive anti-icing strategies by lowering ice adhesion strength, and the goal of the state-of-the-art icephobic surfaces is to realize ice adhesion strength as lowest as possible. In future, the combination of active and passive anti-icing strategies is potentially a good choice for real outdoor anti-icing applications because such combined anti-icing strategy does not require achieving lowest ice adhesion strength but only needs to reach a certain value of ice adhesion strength and realize a rapid de-icing process with the assistance of active anti-icing strategies (i.e., magnetic-responsive, photo-thermal and electro-thermal stimulus). Thus, more relevant research needs to be investigated to study de-icing mechanisms and synergistic effects of active anti-icing strategies that promoted icephobic surfaces with low ice adhesion strength.
4. Summary and Outlooks

Design and preparation of low ice adhesion surfaces for a long-term use is still a big challenge. Passive anti-icing strategies towards designing icephobic surfaces (i.e., smooth surfaces, textured surfaces, slippery surfaces and sub-surface textured surfaces) have their own advantages and disadvantages. For smooth surfaces, they usually need to be tuned by surface chemistry and elastic modulus to lower ice adhesion strength, which can incorporate with other anti-icing strategies (i.e., aqueous/organic lubricating layers and sub-surface structures) to reduce ice adhesion strength. For textured surfaces, the sustainability of surface chemistry and hierarchical structures becomes a critical issue to maintain surface icephobicity during icing/de-icing cycles. To enhance surface icephobicity, textured surfaces can introduce elastic/flexible substrates and/or hollow sub-surface structures (i.e., MACI) to lower ice adhesion strength. For slippery surfaces, low ice adhesion can be realized by rationally designing lubricating mechanisms and combining other passive anti-icing strategies (i.e., SHSs and sub-surface structures). For sub-surface textured surfaces (i.e., MACI), the combination of sub-surface textured surfaces with other passive anti-icing strategies becomes realistic, while the stability and longevity of the MACI strategy need to be investigated both theoretically and experimentally. Moreover, active anti-icing strategies (i.e., magnetic-responsive, photo-thermal and electro-thermal stimulus) can also be considered to combine with passive anti-icing strategies. In summary, each passive anti-icing strategy may have theoretical limits, and multiple passive (and/or active) anti-icing combined strategies promoted by low ice adhesion surfaces provide new insights and open an avenue towards designing novel icephobic surfaces in future.

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