Review Article

Review of ice-pavement adhesion study and development of hydrophobic surface in pavement deicing

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HIGHLIGHTS

- A novel pavement deicing approach achieved by hydrophobic surface is proposed.
- Several methods to build hydrophobic pavement surface with nanoscale texture are reviewed.
- Most of hydrophobic pavement is achieved by nano-engineered coating technology.
- Consumable nano/micro structures of lead to poor durability of hydrophobic coatings.
- The long-term effect is the research and development priorities of ice-repelling pavement.

ABSTRACT

Ice adhesion to materials is a significant concern in many fields. Hydrophobic surface has been used for anti-icing in fields of aircraft or transmission line, which prove to be efficacious and economical. However, such technique is seldom employed for road deicing, because of the texture and service environment of pavement. Instead, deicers such as rock salt are frequently used, which leads to serious corrosion problem of roads and bridges. In this paper, a number of studies that characterize mechanism of ice adhesion to common substrates, specifically to pavement, are reviewed. The most important researches undertaken on ice adhesion strength affecting factors are presented. An overview of studies carried out to find hydrophobic surface for asphalt and cement concrete pavement anticing are presented. It was verified that the hydrophobicity had high correlation with icephobicity, and nano-engineered asphalt and cement concrete pavement surface exhibited favorable hydrophobicity, and also had good performance on weakening pavement-ice bonding. However, most ice-repelling pavements obtain hydrophobic surface via low surface energy coating, which could not exist on pavement for a long time under wheel abrasion. And the nano/micro structures on hydrophobic surfaces are also vulnerable and consumable. Thus, the long-term effect of hydrophobic surface still need to be improved, and durability of the hydrophobic surface should be the research and development priorities of ice-repelling pavement.
1. Introduction

Adhesion of ice to structure generates disadvantages in the fields of transportation, power transmission, aviation and coal industry, which has led to great loss in economy and safety. In transportation area, ice adhesion on road mitigates the skid resistance, which could lead to treacherous driving conditions (Gustafson, 1982). In aviation area, ice accumulation on aircraft surface changes the shape of plane, which could lead to the decrease of carrying capacity. In all walks of life, various de-icing methods, such as chemicals, heating, and hydrophobic surface, have been developed. Building hydrophobic surface to mitigate ice bonding is popular in academic circles for its excellent anti-freezing ability and human-power-saving characteristic (Ma et al., 2014b; Wang, 2011).

However, hydrophobic-deicing surface is seldom applied to pavement deicing. Road deicing approaches are usually divided to initiative and passive technologies. Initiative deicing is a kind of preventive strategy achieved by building pavement with self-deicing function, including heating pavement, pavement containing antifreeze fillers (salt-storage pavement), rubber crumb icebreaking pavement, etc. Passive deicing is a kind of retroactively method achieved by physical or chemical means, such as snow plow or deicers and abrasives. The passive deicing methods have a high efficiency of deicing while causing damage and corrosion to structure and environment as well (Shi et al., 2010). For example, abrasives pose significant risk for water quality and may threaten the survivability of aquatic species (Staples et al., 2004). Chloride deicers may cause severe damage to structure and effect on water, soil, plants, animals and human health (Fay and Shi, 2012). On the basis of a field study (Hossain et al., 2014a,b), the minimum application rate of NaCl deicer needed for maintaining pavement bare are shown in Table 1. In addition to chlorides, acetates such as potassium acetate (KAc) and calcium magnesium acetate (CMA) are used for anti-icing. KAc and CMA can be more effective, less corrosive to carbon steel, and not as environmentally harmful as chlorides (Shi et al., 2009). Also available are a variety of agro-based chemicals used either alone or as additives for other winter maintenance chemicals (Hossain et al., 2014a,b, 2016; Nixon and Williams, 2001). Although these naturally sourced chemicals may reduce the deicer corrosivity when applied on roads (Fischel, 2001; Kahl, 2002), but it cost much more than traditional chloride deicers, and still, both acetates and agro-based additives tend to increase the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in water bodies, and might further influence aquatic organisms.

As concerns about deicing chemical pollution greatly increase, self-deicing pavement emerges as the time requires. These self-deicing methods, including salt-storage pavement, heating pavement, rubber crumb pavement, after many laboratory studies and tests on trial road, have proven to be of fine snow-melting ability (Liu et al., 2014, 2015b; Tanga and Mignard, 2012). However, studies have also revealed deficiencies of these self-deicing pavement. As listed in Table 2, the heating pavement requires enormous initial investment and energy dissipation to sustain (Yehia and Tuan, 1998). The salt-storage pavement has functional lifetime shorter than investors expected (Liu et al., 2014). The elastic particles in rubber crumb icebreaking pavement are easily

| Table 1 – Minimum salt application rates (Hossain et al., 2014a,b). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Snow depth (cm) | Average pavement temperature (°C) | Application rate (lb/1000 ft²) by snow-melting time |
|                 |                               | 1 h   | 2 h   | 3 h   | 4 h   | 5 h   | 6 h   | 7 h   | 8 h   |
| 0.5    | −7                            | 85    | 70    | 55    | 45    | 30    | 15    | 0     | 0     |
| 0.5    | −5                            | 70    | 60    | 45    | 30    | 15    | 0     | 0     | 0     |
| 0.5    | −3                            | 60    | 45    | 30    | 15    | 0     | 0     | 0     | 0     |
| 0.5    | −1                            | 45    | 30    | 15    | 0     | 0     | 0     | 0     | 0     |
| 0.5    | 0                             | 40    | 25    | 10    | 0     | 0     | 0     | 0     | 0     |
| 1.0    | −7                            | 90    | 75    | 60    | 45    | 35    | 20    | 5     | 0     |
| 1.0    | −5                            | 75    | 60    | 50    | 35    | 20    | 5     | 0     | 0     |
| 1.0    | −3                            | 65    | 50    | 35    | 20    | 5     | 0     | 0     | 0     |
| 1.0    | −1                            | 50    | 35    | 20    | 5     | 0     | 0     | 0     | 0     |
| 1.0    | 0                             | 40    | 30    | 15    | 0     | 0     | 0     | 0     | 0     |
| 1.5    | −7                            | 95    | 80    | 65    | 50    | 35    | 20    | 10    | 0     |
| 1.5    | −5                            | 80    | 65    | 50    | 35    | 20    | 10    | 0     | 0     |
| 1.5    | −3                            | 65    | 50    | 40    | 25    | 10    | 0     | 0     | 0     |
| 1.5    | −1                            | 50    | 40    | 25    | 10    | 0     | 0     | 0     | 0     |
| 1.5    | 0                             | 45    | 30    | 15    | 5     | 0     | 0     | 0     | 0     |
stripped off from road. In this paper, a kind of rarely-studied self-deicing pavement, based on ice adhesion theory and achieved with hydrophobic surface, will be presented. Due to its chemical stability, hydrophobic-deicing pavement is unlikely to release hazardous substances to the surroundings, therefore, it could be more environmental.

The hydrophobic-deicing pavement focuses on breaking ice-pavement adhesion interface, rather than cleaning up all the ice on pavement. Totally cleaning/melting up ice on road by self-deicing pavement, in practical application, is unrealistic, which needs high cost as well as enormous power consumption (Yehia and Tuan, 1998). It is also proposed in Winter Maintenance Report of Minnesota DOT that the objective of pavement deicing is to break the bonding between ice and pavement so that to create favorable condition for snow plow working rather than melting all the ice and snow accumulating on the road (LRRB, 1995). Unite States Environmental Protection Agency (EPA, 1976) has taken on a fundamental study around adhesion-weakening ability of hydrophobic pavement surface, in which two types of hydrophobic coating were developed. And then the experimental road coated with hydrophobic materials was built, which demonstrated fairly fine anti-freezing effect, and promoted the working efficiency of snow plow. The hydrophobic-deicing pavement, which is based on interface-breaking concept, therefore, has feasibility and own peculiar advantages, and deserves further study.

In this paper, studies of ice adhesion mechanism, ice adhesion characteristic, and development of hydrophobic-deicing pavement are systematically reviewed. In Section 1, concept of hydrophobic-deicing pavement is introduced. In Section 2, as the basic theory of this paper, ice adhesion mechanism studies are presented. In Section 3, ice bonding intensity in diverse surrounding conditions, namely ice adhesion characteristic, is reviewed. And in Section 4, important studies of hydrophobic-deicing pavement are presented. To analyze the particularity of ice bonding on pavement different from other structures, this paper reviews studies in such fields as transportation, power transmission, aviation and coal industry.

2. Mechanism of ice-pavement adhesion

2.1. Ice-general substrates adhesion mechanism

The current researches are inclined to analyze adhesion mechanism of ice with three such aspects as van der Waals bonding, surface free energy, and chemical bonding. Koji’s studies show that the adhesion strength consists of van der Waals bonding, coulomb force, and force generated by surface energy, of which coulomb force and van der Waals bonding are relatively small. Hence, adhesion strength is mainly determined by surface energy (Koji and Daikoku, 2009). Whitworth holds that the influencing factors of ice adhesion include van der Waals bonding, chemical bonding, and electrostatic interaction of ions, among which van der Waals bonding plays a dominant role (Petrenko and Whitworth, 1999). Petrenko (2003) believes that van der Waals bonding, caused by instantaneous polarization, is universal among substrates and is important in ice bonding strength forming, while covalent bonding is a kind of strong molecular bond which only exist in interface between water and certain materials.

2.2. Ice-pavement adhesion mechanism

Although the studies about ice adhesion mechanism among general substrates were made great progress, little research has been carried out on ice-pavement bonding mechanism, especially in the bonding of ice-asphalt, ice-aggregate, and ice-cement stone. Strategic Highway Research Program (SHRP) has made a simple classification of possible causes for the adhesion of ice and pavement, which includes van der Waals force (including dispersion, orientation, and induction forces), hydrogen bond, combination of acid and alkali, and macroscopic ice dowels (Penn and Meyerson, 1992). The effect of ice dowels on ice-pavement adhesion strength has been found by Dan et al. (2017). However, it is argued that it is impossible for the chemical bonds to exist in ice-pavement bonding, and consequently ionic bond and covalent bond are not considered. Actually, the bond energy of chemical bond is 400 kJ/mol generally, far more than that of ice-pavement bonding, while the bond energy of hydrogen bond and van der Waals bond is 8–35 kJ/mol and 4–8 kJ/mol (Yang and Jin, 2002). This has also verified the consideration of SHRP from another point of view.

There are also studies trying to illustrate the ice adhesion phenomenon by quasi-liquid layer (QLL) theory. The QLL theory was first proposed by some previous researches carried out to study the properties of the interfacial layer on ice (Gillpin, 1979; Jellinek, 1967). The QLL is a layer of amorphous ice existing between ice crystal and substrate surface, which has significant impact on ice-substrate adhesion. This kind of amorphous ice layer can be regarded as an adhesive between ice and substrate, and the adhesion of ice on a substrate is supposed to be mainly due by the capillary forces created by this QLL (Guerin et al., 2016). According to some previous study conducted on physical properties of QLL (Cai and Bhushan, 2008; Döppenschmidt and Butt, 2000; Jellinek, 2016; Kagi and Karmann, 2015).

<table>
<thead>
<tr>
<th>Heating system</th>
<th>Approximate cost</th>
<th>Annual operating cost</th>
<th>Power consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared heat lamp</td>
<td>$ 96/m² ($ 8.9/ft²)</td>
<td>Not available</td>
<td>75 W/m² (7 W/ft²)</td>
</tr>
<tr>
<td>Electric heating cable</td>
<td>$ 54/m² ($ 5/ft²)</td>
<td>$ 4.8/m² ($ 0.45/ft²)</td>
<td>323–430 W/m² (30–40 W/ft²)</td>
</tr>
<tr>
<td>Hot water</td>
<td>$ 161/m² ($ 15/ft²)</td>
<td>$ 250/storm (76 mm (3 in.) snow)</td>
<td>473 W/m² (44 W/ft²)</td>
</tr>
<tr>
<td>Heated gas</td>
<td>$ 378/m² ($ 35/ft²)</td>
<td>$ 2.1/m² ($ 0.20/ft²)</td>
<td>Not available</td>
</tr>
</tbody>
</table>
ice adhesion strength, $\Delta P$, can be translated as following expression

$$\Delta P = \frac{2\gamma(\cos(\theta_i) + \cos(\theta_s))/b}{a/b - \log(T_f - T_a)}$$

where $\gamma$, $\theta_i$, $\theta_s$, $T_f$ and $T_a$ are the surface tension of the water, the contact angle between ice crystals and the QLL, the contact angle between the QLL and the substrate, the fusion temperature of ice, and the air temperature during precipitation, respectively. And $a$ and $b$ are empirical constants, which are 32 and 20.7, respectively.

From the expression above it could be found that the ice adhesion strength would decrease with the increase of air temperature $T_a$ and decrease of fusion temperature $T_f$ of ice, which is exactly the working mechanism of anti-freezing pavement (Liu et al., 2015a). Besides, it could be also revealed by the expression that the ice-pavement adhesion strength would decrease while pavement has lower surface tension $\gamma$ and higher contact angle $\theta_i$, which might be the theory basis of hydrophobic deicing pavement.

Fig. 1 illustrates the ice-pavement adhesion mechanism in three dimensions, including (a) macroscopic ice dowel structure; (b) microscopic quasi-liquid layer; and (c) van der Waals bond on the atomic scale.

3. Characteristics of ice adhesion

3.1. Characteristics of ice adhesion on general substrates

Based on the study of ice adhesion mechanism, further researches about characteristics of ice adhesion on different substrates have been taken, such as adhesion characteristics between ice and rubber, metals, plastics, high-molecular polymers (Aoyama et al., 2011; Archer and Gupta, 1998; Bascom et al., 1969; Landy and Freiberger, 1967; Nelson and Young, 1994; Raraty, 1958). The ice adhesion strengths of these materials are shown in Table 3. Nowadays, correlation between ice adhesion and hydrophobic properties or surface microstructure is the research hotspot in academic circles (Bharathidasan et al., 2014; Cao et al., 2013; He et al., 2014; Tremblay et al., 2013; Zou et al., 2011). There are specialized researches about ice bonding with pavement in highway industry as well (Bhoopalam and Sandu, 2014; Dan et al., 2014a,b; Klein-Paste and Sinha, 2010a,b).

It is demonstrated in recent studies that surface microstructure in size between nanometer and micrometer can enhance hydrophobicity and achieve remarkable ice repellency of material. He studied hydrophobicity and ice bonding strength of aluminum plate with diverse microstructures.
including micrometer size, nano/micro size, and smooth surface (Fig. 2). It is indicated that substrates with nano/micro composite microstructure size has weakest ice adhesion strength, and smooth surface with weakest hydrophobicity shows strongest bond with ice. He concluded that surface with various kinds of microstructures can reduce contact area of water/ice and substrate, which leads to a decrease of adhesion strength. And the composite structure with nano/micro size, among other microstructures, has the best performance of reducing the contact area and lessening the adhesion strength (He et al., 2014).

Previous researcher (Assel and Herche, 1998; Bharathidasan et al., 2014; Susoff et al., 2013) developed a kind of zero-degree tip cone test to evaluate hydrophobic properties and ice repellencies of hydrophilic, hydrophobic, super-hydrophobic coating. The test equipment is presented in Fig. 3, in which the ice is formed in the annular space between the pile and the mould, and the pile is a cylinder made of aluminum alloy AA6061 with the coating to be tested deposited on its smoothly polished surface. The inner surface is the mould is made rough such that the ice will always fail at the mould–ice interface. A teflon bush is kept in the bottom to align the pile concentric with the mould. The pile is pushed out at a constant velocity by a servo motor while continuously recording the force as the function of the displacement of the pile. Ice-adhesion strength is the shear stress at which the annular ice became detached from the pile surface as indicated by sudden drop of the sensed force to zero and is calculated as the ratio of the maximum load and the contact area. By this test, he got a contrary result that although substrates with super-hydrophobic coating had strong water repellency, their anti-freezing properties tend to

**Fig. 2** – Three kinds of surface microstructure (He et al., 2014). (a) Micro size structure. (b) Nano/micro composite structure. (c) Smooth surface.

**Fig. 3** – Zero-degree tip cone test (Bharathidasan et al., 2014).
be worse than hydrophobic surface (Bharathidasan et al., 2014). Similar results have also shown in other scholars’ studies including Kulinich and Farzaneh (2011), Varanasi et al. (2010), and latest researches taken by Zou et al. (2011) and Yang et al. (2011).

There seems to be a contrast between the results of Bharathidasan and He’s studies. In He’s research, surface with higher hydrophobicity gains stronger ice repellency and super-hydrophobic surface show poor ice repellency in Bharathidasan’s study. As a matter of fact, in the SEM image of their studies, a large number of irregular sharp promontories can be found on the super-hydrophobic surface of Bharathidasan. These promontories are liable to stab into water drop and enlarge adhesion area, which form numerous anchors after freezing and lead to the increase of ice adhesion finally. Hydrophobic coating developed by He has a regular and neat surface microstructure. With this kind of surface, water can’t enter into the void between microstructure, thus the adhesion area is cut down and the adhesion strength is lessened. Accordingly, the adhesion strength is mainly related to the contact area of water drop and substrate on the micro scale, and by changing the contact area, microstructure and hydrophobicity of the surface affect adhesion strength. There is similar phenomenon of ice bonding on pavement in macroscopic scale, which is discussed in the latter section.

3.2. Characteristics of ice adhesion on pavement

As mentioned above, there are many work reported in field of ice adhesion feature on general materials. However, few research has been found directly concerning to ice-pavement adhesion characteristics. Most of studies in this area are mainly focus on the meteorological conditions for pavement freezing, impact of hydrophobic surface and pavement structure on ice adhesion strength.

Studies focusing on ice adhesion feature on pavement are rare currently. Relative works as pavement freezing conditions have been taken. Based on the road temperature data collection of Hubei in China, Li established multiple regression fitting formula of pavement freezing and meteorological conditions Li et al. (2011). According to the data of automatic meteorological station, Lv et al. (2013) discussed the temperature change regulation of air, pavement and bridge deck in winter typical meteorological conditions. Works of Li and Lv contribute to the external factor study of ice-pavement adhesion. However, these studies fail to involve to the essence of ice adhesion on pavement due to different study direction, and as a consequence, they couldn’t explain the relationship between ice adhesion strength and internal factors of road.

Wu studied the correlation between adhesion strength and freezing period, radial thickness of ice, and pavement types (Wu et al., 2014). The result shows that the freezing period and radial thickness have little correlation with adhesion strength, and the asphalt pavement has only 40% adhesion strength of concrete pavement. Wu hold that a discontinuous interface exists between water and hydrophobic asphalt surface in freezing progress, and the ice adhesion is weakened as a consequence.

Hossain studied the friction characteristics and slipping risks of pavement with winter contaminants (Hossain et al., 2015). It is found that the pavement with contaminants of ice, slush, and plowed-bonded snow is of the highest risk of slipping, followed by pavement with unplowed-bonded snow and unplowed-unbonded snow, and the pavement with plowed-unbonded snow has lowest risk of slipping. It is also revealed that asphalt pavement has higher coefficient of friction than Portland cement concrete, no matter for pavement under wet bare condition, or pavement with covering snow. Hossain’s study shows that the friction characteristics between asphalt concrete and cement concrete pavement are quite different under snow condition, which might be caused by pavement texture, but also could be illustrated by different hydrophobicity between asphalt concrete pavement and cement concrete pavement.

Dan has studied the condensation mechanism on humid pavement and skid resistance capacity of freezing pavement (Dan et al., 2014b), and the ice bond properties of asphalt pavement (Dan et al., 2014a). Large-scale freezing laboratory has been established to create steady low temperature moist environment. Full-scale pavement model was built to explore correlation between mean texture depth (MTD), pavement temperature and normal, tangential adhesion strength. The results show that the relationship of adhesive strength and temperature is close to log curve, and the pavement with deeper MTD has stronger ice bonding. The experimental details are shown in Fig. 4(a) and (b), and the specific results are presented in Fig. 4(c) and (d).

Similar results are reported on Tan’s research (Tan et al., 2013), by which adhesive strengths of pavements made with various materials (OGFC-16, AC-16, AC-13) in different temperatures are studied. The study adopted pull-off experiment, which was similar to Dan’s study, and normal ice adhesion force and ice shedding rate were used as evaluation indexes. It is found that pavement with open grade has stronger ice bond than pavement with close grade. Moreover, there is a positive correlation between the maximum nominal size and adhesive strength.

In Dan’s work, MTD is a rough index that indicates the contact area of ice and pavement, which has similar role to maximum nominal size and material types. It can be concluded that the contact area also contributes to ice adhesive strength, which is similar to the results of adhesion properties studies of general substrates in microscopic scale, and may shed light on the directions of further study about the relationship between the pavement material and the ice adhesion strength.

Due to the complexity of surface structures and service conditions of pavement, studies conducted on ice-pavement adhesion are mostly from macroscopic scale at present, and the results of these studies are hard to meet the same accuracy as adhesion-feature studies of common substrates such as plastic or metal. Furthermore, the ice-pavement adhesion strength obtained by common approaches such as pulling test or shearing test, would be fluctuant because the porous structures and the texture depths (TDs) of pavement. Besides, service time has the increasing impact on ice adhesion condition, making adhesion-feature of pavement and ice a dependent variable of time.

To advance veracity of ice adhesion study, and ice-pavement adhesion study from macroscopic statistics research to
microscopic precise computation, we hold the opinion that the ice adhesion of pavement is, actually, ice adhesion of certain substrates (asphalt, cement stone, aggregates) in specific space structure (texture of pavement). Therefore, studies of adhesion on pavement should be divided into two parts, including adhesion of structure and adhesion of materials.

(1) Study of adhesion strength between ice and raw materials (asphalt, cement stone, aggregates). Essence of ice bonding on pavement is the adhesion between ice and road materials. Thus materials adhesion is the basic of adhesion and anti-adhesion technologies of pavement.

(2) Study of adhesion amplifying factor derived from pavement structure, means research of relevance between amplifying factor and different pavement structure such as mix proportion, texture depth, porosity and aggregate types. The formulas for amplifying factor is as follows.

\[
AF = \frac{S'}{S}
\]

where \(AF\) is amplifying factor for a certain type of pavement structure, \(S\) is adhesion strength of materials, \(S'\) is adhesion strength of pavement.

4. Repelling ice by hydrophobic pavement technologies

According to the fundamental studies mentioned above, many researches have explored the feasibility of hydrophobic surface which has low ice adhesion strength applied in ice repelling. These have been applied successfully in anti-freezing of aircraft, power transmit, and transportation area.

4.1. Hydrophobic coating on general substrates

Nowadays hydrophobic surfaces are mainly based on bionics of lotus leaf, on which micrometer/nanometer texture are built to form the repellent of water and reduce the adhesion of ice. Thus, the hydrophobicity can reach a fairly high level, and ice forming will be postponed. However, due to the
demolishing of the surface texture in deicing recycle, the endurance of hydrophobic surface needs improving.

Wang investigated the ice repellency and ice forming progress on superhydrophobic surface with nano-fluorocarbon coating (Wang et al., 2012). The hydrogen fluoride was first dissolved in ethyl alcohol and afterward modified by nitric derivate of perfluoropolyoxyalkyl carbonate, and lastly sprayed on copper plate with average thickness around 10 nm. The contact angle was up to 164.62° in –8 °C, and the angle reached 6.17°. Compared with the original substrate, the freezing time was delayed about 30 s and water droplet moved more easily on the nano-fluorocarbon surface.

Foroughi-Mobarakeh et al. (2013) built superhydrophobic coating of hexamethyl disiloxane on aluminum plate. The low pressure plasma polymerization was adopted and the contact angle met 158°. With freezing test under simulated atmospheric condition in wind tunnel and adhesion strength test with centrifugal machine, it is found that the ice adhesion strength of hexamethyl disiloxane decreases to 28% of the aluminum plate, and to rise to 71% again after 15 times of freezing-deicing recycles.

Kulinich and Farzaneh (2011) built two types of superhydrophobic coating with microscopic texture by fluorine-containing polymer mixed with nano-particles and organosilane smearing on surface-etched aluminum plate (Fig. 5). Undercooling water droplet was dripped on substrate to form glaze ice. Centrifuge adhesion strength test was adopted, and it is found that, after several freezing-deicing recycles, microscopic texture made by surface-etched kept better ice repellent performance than nano-particles. Kulinich hold that deicing progress can damage nano-structure on the surface, which results in a decrease of ice repellency.

The hydrophobic coating mentioned above, which simulates lotus leaf, gains great hydrophobicity and ice repellency by nanoscale texture surface. However, the vulnerable surface structure easily damaged by friction of deicing, has a great impact on its application in engineering, especially for pavement deicing. Simulating common nepenthens, Tak-Sing Wong from Harvard developed a kind of slippery liquid-infused porous surfaces (SLIPS) (Wong et al., 2011). According to different requirements, porous structure can lock various lubricants on the surface of SLIPS. Thus, multiple liquid and solid can be repelled and the liquid-repellency will recover rapidly after physical injury (0.1–1 s). SLIPS has better abrasion resistance than nanoscale texture surface, while lubricants may reduce anti-slip performance, and its application feasibility of practical engineering, therefore, it is still remain to be evaluated.

4.2. Hydrophobic asphalt pavement development status

Since the deicing chemicals could bring some disadvantageous influences to environment, the hydrophobic anti-icing technologies have been promoted by some environmental agencies, and studies have been taken to explore probability of hydrophobic surface to mitigate ice adhesion on pavement. Technically speaking, hydrophobic could be achieved by two approaches: building a structural pavement layer which is hydrophobic, or painting a hydrophobic coating on pavement. Considering the wheel load and abrasion on pavement, it seems to be difficult for hydrophobic coating to stay on pavement for enough long time, and hydrophobic structural layer seems to be more promise, for it is supposed to have much longer life of validity. However, in nearly all researches conducted on hydrophobic de-icing pavement, the hydrophobic coating, rather than hydrophobic pavement layer was adopted. And nearly all kinds of existing hydrophobic pavement gain their water/ice repellence through hydrophobic coating. It is believed that although hydrophobic structural pavement layer might have longer effective life, the price of this kind of hydrophobic pavement would be much higher. And coating technology could quickly endow pavement with surface of low surface energy, making pavement hardly wetted by water, and finally hardly adhered with ice. However, due to abrasion existing between pavement and tire, the service life of the hydrophobic coating could be influenced.

For reducing the dosage of deicing agent, United States Environmental Protection Agency (US EPA) has taken a series of works in 1970s developing hydrophobic substances to mitigate pavement ice adhesion (EPA, 1976; Krukar and Cook, 1978; Murray and Eigerman, 1972). In EPA’s research, 54 types of materials including organic silicone and fluorine-containing materials were screened by index of surface energy, solubility and infrared spectroscopic analysis, and two kinds of coating materials having room temperature curing silicone rubber were selected to apply on test-road study. The result

![Fig. 5 – Surface images of fluorine-containing polymer coating taken by optical profiler (Kulinich and Farzaneh, 2011). (a) Spin-coating forming. (b) Spraying forming.](Image)
demonstrated that room temperature curing silicone rubber coating gained relatively high hydrophobicity and ice-repellency. The coating had enough slip resistance and chemical stability that could satisfy pavement function and environmental requirement, while the endurance performance was poor and could just meet half level of research target (150,000–30,000 times of wheel wearing). Study of US EPA systematically explored the application of hydrophobic surface on road ice-proofing. However, 54 kinds of coating materials were just selected from commercially available painting product, which were produced by several big companies, to ensure mass production after its feasibility is verified.

Machado et al. (2011) modified fluorine-containing polymer with nano-CaO particle in dispersion system and developed a hydrophobic coating for asphalt pavement. The contact angle of asphalt concrete rose to 163° from 98° (Fig. 6). Results of Scanning Transmission Electron Microscopy (STEM) and Dynamic Light Scattering (DLS) indicated that the size distribution of fluorine-containing polymer and CaO particle on asphalt pavement ranged in 100–500 nm. The contact angle of Machado’s coating reached a rare high degree, but whether such a high hydrophobicity is necessary for pavement ice shedding still needs experimental proof.

Gao et al. have carried out a series researches on superhydrophobic asphalt and concrete pavement (Gao et al., 2017a,b,c, 2016a,b). Coating technology was also the core implementation of superhydrophobic asphalt pavement in Gao’s study. The coating emulsion was prepared by silanol and nano-sized SiO₂. The surface contact angle with water reached 150.7°, and a series tests were adopted to assess the ice-proof properties of superhydrophobic asphalt pavement, including rolling test, hammering test, and frosting test. It was found that in these mechanical ice-removing tests, the amount of residue ice on hydrophobic asphalt pavement was much smaller than control group. However, the abrasion resistance of the asphalt pavement coating was not discussed in Gao’s studies, which makes the studies incomplete.

Arabzadeh investigated Poly Tetra Fluoroethylene (PTFE) superhydrophobic asphalt pavement (Arabzadeh et al., 2016; Ceylan et al., 2016). Epoxy resin was firstly dissolved in xylene and then sprayed on asphalt pavement, and then the PTFE dispersed in acetone was sprayed over the epoxy resin by different weight percentages of epoxy resin. The contact angle was up to 166° and the average value was 156° when spraying time was 6 s and PTFE dosage was 30%. The friction coefficient was highly associated with PTFE dosage and spraying time, and 30% and 40% PTFE dosage groups averagely exhibited higher skid resistance than control group. However, no ice-adhesion strength test or abrasion resistance data was available, and the application value was still unknown.

A more practice-stress-relative assessing method for icephobic performance of pavement was adopted in Ma’s study, which was combined with rutting and shearing test (Ma et al., 2014a). SILQUEST® YC-1005G-NT and SILRES® BS290 were adopted as hydrophobic coating materials, which contained organo-silicon and were used as road preventive maintenance in practice. The contact angle of coated pavement was 100.2° and the shear stress was weakened from 3.5 MPa to 0.06 MPa. The water was directly frozen on rut boards or marshall specimen to obtain complex specimens composed with ice and asphalt concrete, of which the status after rutting or shearing tests was used for evaluate ice shedding properties. Fig. 7 presents the ice shedding condition on coated/uncoated specimens. It was found that the ice on the uncoated pavement tended to break into pieces or powder in shearing test, while ice on the coated pavement tended to peel off in whole one-piece, which gave an obvious proof of the advantages of hydrophobic pavement in road winter maintenance. Coated pavement also showed better ice shedding ability than uncoated pavement in ice-rutting test.

Apart from hydrophobic and ice shedding property researches mentioned above, a growing concern about the slip resistance of hydrophobic pavement has come up. Xu adopts TDs to evaluate the anti-skip property of pavement coated with a icephobic material (Xu and Hua, 2012). Result suggests that there was a TD decrease of 0.1–0.2 mm after coating, which could still satisfy specification requirements, 0.55 mm. Similar concern has been taken into consideration in Ma’s study as well (Ma et al., 2014a). British Pendulum Number (BPN) and TDs were used to estimate skid resistance of hydrophobic surface of pavement, which demonstrated that the decrease around 6 and 0.26 mm of BPN and TDs were brought by hydrophobic materials coating. However, estimating anti-skip ability by TDs is obviously not all-inclusive, while BPN has excess random error for a safety assessment. As a result, there are still not conclusive studies reported to allege antiquate anti-skip properties of this kind of pavement, even if the BPN and TDs could satisfy specification.
In conclusion, much research has verified favorable ice-shedding capacity of hydrophobic pavement and its great potency of practical application in road ice-proofing in winter maintenance. Nevertheless, the lack of endurance and the unverified skid resistance are the two blocks which limit the application of this technology, which may well be the future study orientation of hydrophobic pavement.

4.3. Hydrophobic concrete pavement development status

Compared with asphalt mixture, cement concrete is much more hydrophilic. Water can easily spread out on the surface of cement concrete, which causes much stronger ice bonding strength. Thus, development of hydrophobic cement concrete pavement to mitigate ice adhesion strength, can be even more difficult, and has significant practical interest.

Nowadays, a considerable amount of studies has been conducted on nano-engineered cement concrete and its ice proofing properties. Similarly, most of these studies used coating methods to endow the cement concrete with hydrophobic surface, and consequently, the durability became kind of the weakness of hydrophobic cement concrete.

Gao prepared cement concrete hydrophobic coating using silanol and nano-silica (Gao et al., 2016a, 2017c, 2018). The hydroxide radical in cement concrete would have condensation reaction with nano-silica and hydroxide radical in silanol, which made hydroxide radical on cement surface much more hydrophobic. The contact angle of hydrophobic cement concrete reached nearly 160°, while the rolling angle was lowering as 2.3°. Notably, Gao gave the relationship between abrasion and hydrophobicity (Fig. 8). It was found on first 100 cycles, the contact angle of cement concrete lost 60°, and then the contact angle stayed at about 90° with abrasion increased.

Young compared the performances of multiple hydrophobic coatings on cement concrete, including PTFE, ZnO/PTFE, PTFE/PEEK, DE, and epoxy resin. It was found that the higher wettability of the ZnO/PTFE coating was attributed to the natural hydrophilic properties of an unstructured and continuous ZnO layer. The results of Young’s study indicated that the hierarchically structured particles of the PTFE/PEEK and DE coatings resulted in measured Ra and friction values that were significantly higher than those of PTFE and ZnO/PTFE coatings that were composed of a single average particle size distribution and smaller particles, respectively.

Sobolev et al. have conducted much researches on nano engineered cement concrete (Flores-Vivian et al., 2013; Muzenski et al., 2015; Ramachandran et al., 2016; Sanchez and Fig. 8 – Relationship between contact angle and abrasion cycles.

Sobolev, 2010; Sobolev, 2016; Susoff et al., 2013). Firstly, Sobolev and Hejazi investigated the parallelism between the hydrophobicity and icephobicity, and suggested a definition of icephobicity which combines various requirements for anti-icing surfaces, namely, weak adhesion with the solid substrate and the ability to repel incoming droplets (Hejazi et al., 2013). The theoretical force analysis showed that the main parameter affecting droplet adhesion to a solid surface was CA hysteresis, while for ice particles both receding CA and the size of voids/defects were important. Based on the relationship between hydrophobicity and icephobicity and scale composition of original cement concrete (Fig. 9), Sobolev proposed to build cement concrete hydrophobic by nano-fibers, nanosilica, or nano-tubes.

Sobolev developed a kind of self-assembling particlesiloxane coating (Flores-Vivian et al., 2013; Sobolev et al., 2013). According to him, siloxane emulsion was dispersed with nano silicon dioxide powder, and then a low surface energy coating with nanoscale texture could be autonomously built up after the emulsion smearing on concrete surface. Contact angle and physical properties including impact, tensile, shear test were adopted to characterize ice-proofing performance (Fig. 10), which indicated that the contact angle of concrete rose averagely to $127^{\circ}$, and the ice-concrete adhesion strength decreased to 10% of raw specimen. Sobolev group adopted a series of physical tests which could give a comparatively reliable assessment of hydrophobic surface’s icephobicity, while the hydrophobic of this coating needs to be upgraded according to the average contact angle of $127^{\circ}$. Meanwhile, an abrasion resistance is still needed to investigate the life cycle in further studies.

5. Conclusions

This article reviews the studies concerning with ice adhesion mechanism, characteristic and hydrophobic surface anti-icing technologies. And it is found that.

1. Compared with ice adhesion mechanism and characteristic studies in aircraft and power transmit fields, there lies a distinct gap of studies in road anti-icing field. More emphasis has been placed on practical deicing method researching, while fewer studies were found in ice adhesion mechanism and characteristic.

2. Different from relevant areas, complex structure of pavement surface, including texture and porosity, make it an intricate problem to understand and explore the ice-pavement bonding mechanism and characteristic in micro scale. It is suggested that ice adhesion on pavement could be better understood from two perspectives, the materials adhesion and the structure adhesion.

3. Hydrophobic surface, an autonomously ice-proofing technology, based on the ice adhesion mechanism and characteristic studies, has proven to be of great energy conservation and environmental protection. A lot of studies verified the great potential of hydrophobic pavement applied in winter anti-icing maintenance. And in the authors’ opinion, the two following works of hydrophobic pavement, i.e., the improvement of its endurance and skid resistance, need further study.

Fig. 9 – The scale ranges related to concrete (Flores-Vivian et al., 2017).
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Fig. 10 – Splitting test and result (Sobolev et al., 2013). (a) Schematic plot of splitting test. (b) Status of uncoated specimen after test. (c) Status of coated specimen after test. (d) Load-extension curve of uncoated specimen. (e) Load-extension curve of coated specimen.

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