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An experimental study on icephobicity and hydrophobicity of concrete surface with Dual crystallization Engineered topical treatment

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ABSTRACT

Ice when formed on structural materials exhibits strong bonds, which poses a major challenge to many industries. To remove the ice, the creation of hydrophobic surfaces is used as a passive ice removal technique by reducing ice adhesion. Concrete surfaces treated by Pavix Dual Crystallization Engineered (DCE) material show strong water-repelling characteristics. However, the effect of such treatment on ice adhesion is yet to be studied. To quantify this effect, a series of direct shear tests were performed on concrete specimens with the top surface treated with a Pavix DCE material. TxDOT standard Class S concrete was used as control concrete and mixed at two water-cement ratios, 0.45 and 0.43. Ice-adhesion shear tests were performed on control and DCE-treated concrete disks using a customized direct shear test device at two controlled sub-freezing temperatures, −1 °C and −10 °C. In addition, water-repellent properties and contact angle were measured using a tensiometer under static and receding conditions. Results show reductions of more than 83% in ice adhesion of ice adhesion and more than 98-degree contact angles for DCE-treated concrete specimens. The measured results quantify the anti-icing benefit of DCE treatment and provide insights into understanding the anti-icing mechanism of the treated concrete.

1. Introduction

In many industries, including transportation, aviation, and power transmission, ice adhesion has been causing hazardous or economic problems [1-3]. Ice removal is a general practice for preventing many unsafe conditions [4,5] and protecting infrastructure from icing [6-8]. For pavements, the fundamental material feature of ice and pavement results in strong bonding between the two and thus makes it difficult to mechanically remove ice off pavements [3,9]. Among pavement types, cement concrete pavements are more hydrophilic in comparison with asphalt mixtures, making their ice adhesion strength higher than asphalt pavements, thus increasing the practical interest in the reduction of their ice bonding [3,10,11]. There are various methods to de-ice pavements, which mainly include three approaches: chemicals, heating, or ice-repelling pavements. Despite the high efficiency of chemicals like chloride-based deicers, they may result in drastic environmental and even some structural damages [12,13]. As an alternative to chemical deicers, making ice-repelling pavements with anti-icing surfaces to reduce ice adhesion strength is one of the most well-received approaches to facilitate the ice-removal process [4,14-16]. The passive method of creating a hydrophobic surface to make it ice-repellent and reduce ice bonding is becoming a popular option to explore in research [17,18].

Different materials and methods have been studied to create hydrophobic surfaces for anti-icing applications in asphalt and concrete pavements. A hydrophobic emulsified asphalt coating was created on asphalt pavement by adding a hydrophobic agent (HPA, Polytetrafluoroethylene powder) to emulsified asphalt [19]. The coated asphalt was reported with the highest contact angle of 94.3° and about a 40% reduction in ice bond strength [19]. In another study, a hydrophobic emulsified asphalt coating was created by using biological antifreeze proteins instead of traditional hydrophobic materials or anti-icing agents [20,21]. A superhydrophobic coating (SHC) was created by painting acrylic acid and spraying carbon nanotube particles onto the asphalt mixture surface. The SHC has a static contact angle of 161.2∘ and a reduction of 85.7% in the ice normal adhesion. Hydrophobic silanol and nano-silica were used as anti-icing coatings for cement

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concrete [22,23]. They tested the effect of abrasion on the hydrophobicity of the treated surfaces and reported an inverse correlation between hydrophobicity and abrasion effect, with an initial contact angle of more than 150° to around 90° after 1000 abrasion cycles. The usage of nanotechnology has been adopted by Sanchez and Sobolev [24] and Sobolev [25] in cement concrete, with goals of hydrophobic surface development as they established a positive correlation between hydrophobicity and icephobocity in cement concrete [14,26]. Nanofibers, nano silica, or nanotubes were proposed as means of hydrophobicity induction based on the composition of cement concrete [27]. The shear test of coated concrete specimens shows ice adhesion about one-sixth of the control samples [28].

The effectiveness of hydrophobic surfaces for anti-icing requires laboratory measurement. A review of test programs to measure ice adhesion on concrete was conducted by Barker et al. [40], and a review of ice- adhesion on asphalt and cement concrete was conducted by Chen et al. [3]. The laboratory testing methods used to measure ice adhesion strength in the past include push or pull-out tests [41,42] and splitting tests [28], but shear tests are among the more popular testing techniques due to their ease of conductance and acceptable results [43]. Ice adhesion on aluminum with various coatings was tested by performing shear tests on ice blocks [44]. Their results suggest a lower ice adhesion strength with a higher contact angle of water, suggesting a positive correlation between hydrophobicity and icephobocity (i.e., non/low-ice adhesion with concrete).

A Dual Crystallization Engineered (DCE) material PAVIX, an aqueous solution used for topical treatment for fresh and fully cured or existing concrete, has been shown to reduce water penetration and enhance the durability of concrete pavements through hydrophobic characteristics combined with hygroscopic and hydrophilic crystallization mechanism [31-35]. The icephobicity and hydrophobicity of DCE-treated concrete surfaces haven't been studied. Evaluation of icephobicity through ice-concrete adhesion calls for a well-established laboratory method. Although there are several existing methods to measure ice adhesion strength in the literature [8,35,36], testing standards are not available and the testing methods vary among research teams [36,37,45]. This lack of standardized testing techniques leads to a challenging cross-examination and comparison between research results [36,39-40].

Therefore, this paper aims to evaluate ice-concrete adhesion strength on cement concrete surfaces treated by PAVIX and measure their contact angles. An ASTM standard direct shear test apparatus was customized for measuring ice-concrete adhesion inside a temperature-controlled freezer box. Concrete samples with a standard mix design were used as control concrete and mixed at two water-cement ratios, 0.45 and 0.43. Cylinder concrete samples of 4 in. diameter were used for PAVIX-surface (topical) treatment to prepare ice-adhesion specimens. Ice-adhesion test was performed with the direct shear test device on control and PAVIX-treated concrete disks cut from the cylinder samples at two controlled sub-freezing temperatures, −1 °C and −10 °C. In addition, water repellent properties and contact angle were measured using a tensiometer under static and receding conditions. The flowchart for this research is shown in Fig. 1.

2. Materials and methods

2.1. Raw materials

As an alternative to current passive de-icing methods of using coatings for concrete surfaces, a product from the International Chem-Crete Corporation named Chem-Crete® PAVIX® CCC100 is investigated. Chem-Crete PAVIX CCC100 is a patented dual crystallization waterproofing material, penetrating concrete, and masonry sealer [34]. It is a water-based waterproofing aqueous product that combines hygroscopic and hydrophilic crystals for pore-blocking function and hydrophobic material for pore lining. Concrete specimens were prepared with two water-cement (w/c) ratios of 0.45 and 0.43 following the standard TxDOT concrete mix design, commonly used for bridge slabs, top slabs of direct traffic culverts, and approach slabs with a minimum compressive strength of 27.5 MPa. The concrete mix design for 0.45 is shown in Table 1. Concrete specimens needed for different laboratory tests were cast and cured in a standard concrete moisture room for more than 28 days (approximately 60 days) before testing. The curing was chosen to ensure the concrete specimens with fully developed strength and eliminate the curing time effect on the ice-adhesion test results. Cured specimens chosen for PAVIX-DCE treatment were prepared by spraying PAVIX CCC100 on the top surface of the concrete cylinder with a surface coverage of around 3.7 m^2/l. The treated cylinders were allowed to cure for 24 h before being transferred to the moisture room.

2.2. Direct shear test to measure Ice-Concrete adhesion

Snowplows work by shearing the ice off the road surface. Direct shear tests allow the shearing of ice in a similar mechanism and are therefore chosen as a convenient method to measure the ice adhesion strength on concrete. This study adopts a customized direct shear box to measure ice-concrete adhesion. Fig. 2 and Fig. 3 show the schematics and pictures of ice-concrete specimens and the direct shear apparatus, respectively. The ice-concrete disc is placed inside the direct shear box with a concrete disk on the top. The top disc is held fixed with a custom-made aluminum sample holder. The bottom aluminum for making ice is set inside the direct shear box. During shearing, the bottom ice disc moves while the top concrete disc is fixed. As shown in Fig. 2, the sample is sheared with ice on the bottom. The direction of the shearing can also be seen in the schematic. A hollow aluminum block is designed for making an ice disc (6.4 cm dia. and 2.5 cm height) on top of a concrete disk. The ice-concrete specimen is placed inside the customized direct

Table 1
TxDOT class S concrete mix design (w/c = 0.45) used in this study.

Component	ASTM Standard	Specific Gravity	Weight (kg)
Type I/II Cement	C-150	3.15	255.8
2.54 cm Limestone	C-33	2.81	833.7
Concrete Sand	C-33	2.64	645.5
Water	C-1602	1	115.1
Aea 92S	C-260	1.02	0.085
Eucon X-20	C-494	1.01	0.9639

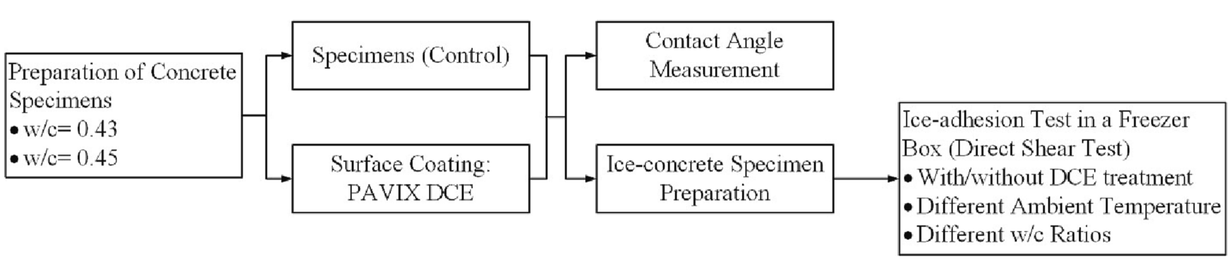


Fig. 1. The research flowchart.

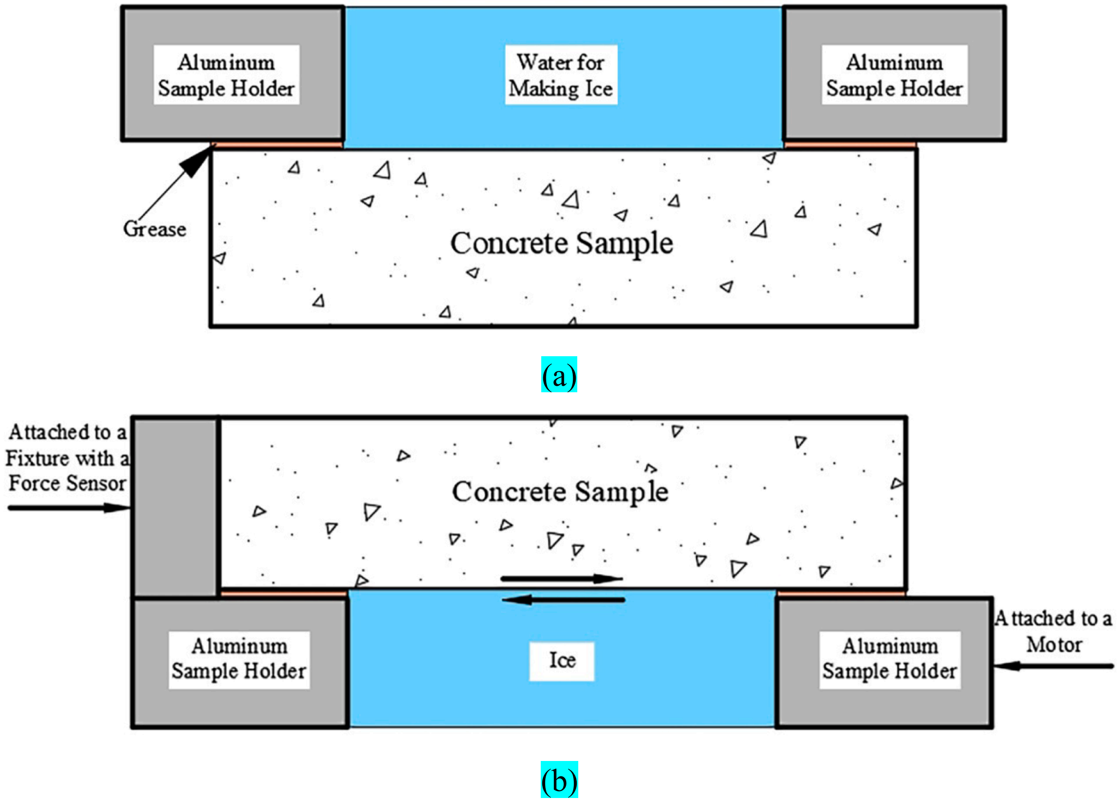


Fig. 2. Schematics of (a): setup for making ice-concrete specimens; (b): the ice adhesion shear test.

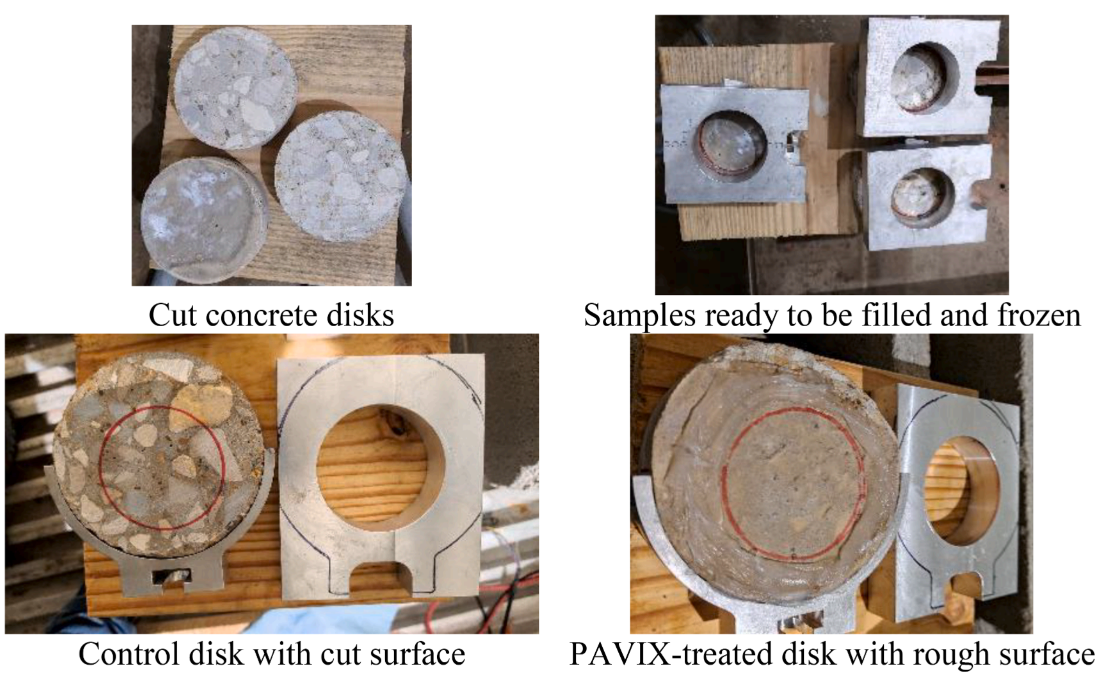


Fig. 3. Steps of specimen preparation for testing ice adhesion.

shear box to allow the shearing of the ice disc laterally at the ice-concrete interface. During shearing, the resistance load and displacement of the ice block are recorded to determine the maximum ice-concrete adhesion. The entire direct shear equipment was placed inside a temperature-controlled freezer container set to a freezing temperature. The freezer temperature is also recorded to ensure the room temperature inside the freezer follows the target set temperature of the freezer. The tested concrete specimens include concrete disk specimens of control type for two water-to-cement ratios and DCE-treated disks of the same concrete. The treated concrete specimens are referred to as DCE-treated in the rest of the paper.

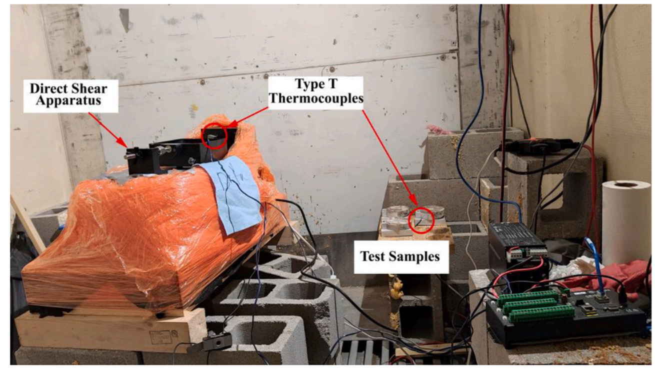
The test program is tabulated in Table 2. Both static and dynamic

Table 2
Summary of test program in this study.

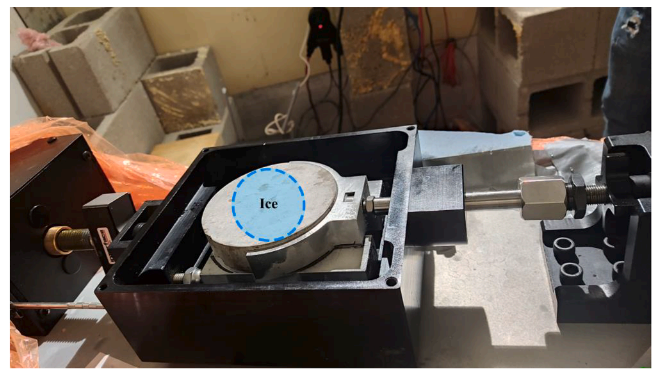
Concrete Sample	Water Cement Ratio	Temperature (°C)	Lab Test
Control PAVIX-treated	0.43, 0.45	−1, −10	Ice-adhesion Direct shear Test
Control PAVIX-treated	0.43, 0.45	Room temperature	Water Contact Angle Static, Dynamic

contact angles for treated specimens were measured. In addition, direct shear tests were performed under various ambient temperatures to investigate ice-adhesion behavior for both treated and untreated specimens. Ice-concrete test specimens were prepared inside the freezer at two controlled temperatures of −1 °C and −10 °C for 24 h to form the ice disc on top of the concrete specimen. This preparation allows evaluation of the temperature effect on the ice concrete adhesion. The 24-hour test duration was verified to form a solid ice disc before shearing. For each test run, three test specimens were prepared to save time and provide identical test conditions for the control and treated concrete specimens. Then the direct shear apparatus was moved inside the freezer, and one ice-concrete specimen was placed inside the shear box. The load cells and LVDTs used in the direct shear apparatus have built-in temperature compensation and were thoroughly checked for temperature calibration. The concrete disc specimen used for these tests are disks of about one inch (2.54 cm) height cut from 10-cm diameter concrete cylinders. To test the effects of DCE surface treatment, the top surfaces of the DCE-treated concrete cylinders were used to measure their ice adhesion. The test specimens were obtained by cutting the cylinder one inch (2.5 cm) from the top surface. In most cases, the rest of the same cylinder was used as the control specimens as the concrete material is almost identical to the DCE-treated one for a better and more accurate comparison of the effects of the treatment. It should be noted that the ice formation and shearing tests on the control specimen were performed on the cut surface of the concrete disk. In contrast, for DCE-treated disks, ice was formed and sheared on the top rough surface of the specimen. Jia et al. (2011) reported a higher ice adhesion value with higher surface roughness in shear tests run on ice and concrete [30]. This phenomenon (surface roughness effect) is considered when analyzing the results from both specimen types.

In Fig. 4, the direct shear apparatus ready to be tested can be seen inside the freezer box. One type-T thermocouple records the temperature of the direct shear box where the specimen is put for testing on the apparatus, and another one records the ambient temperature. This allows for verification of the temperature during ice sample preparation and shearing. It must be noted that the tests were all run in a strain control mode. The strain speed is constant during all the tests and is 33 mm/min, which is the maximum strain speed of the apparatus. As previously reported, the strain rate can directly affect the ice adhesion value [29,30]. The reason for chosing the maximum rate is that the ice removal process on roads with a snowplow is a very fast process. To avoid any strain rate effects, this rate is kept constant throughout all tests. A total number of 24 successful tests are reported here. For each water-to-cement ratio of 0.43 and 0.45, at ice formation temperatures of −1 °C and −10 °C, 6 specimens were tested, including 3 treated with DCE and 3 untreated as control specimens.



(a)



(b)

Fig. 4. Setup inside the freezer box during the test, (a) overview and thermocouples, (b) a concrete-ice specimen in the shear box.

2.3. Contact angle test

The objective of the contact angle test is to quantify the effect of DCE on concrete surface wettability using contact angle (static and dynamic) as an indicator. Measuring the contact angle of the treated and non-treated concrete specimen is essential since it is related to the performance of hydrophobicity and icephobocity, as water drops may bounce back when they impact a hydrophobic surface [46]. The tests were performed using a Goniometer/Tensiometer (Ramé-hart Model 250). The sessile drop method (SDM) was adopted to measure the contact angle of a water droplet on a concrete surface. The assumptions of this method for concrete contact angle measurements are that gravitational effects on the drops are negligible, the concrete surface is relatively smooth, and the heterogeneity of the concrete surface is limited.

3. Test results and analysis

3.1. Example direct shear test results

There are various criteria for failure regarding shearing and what displacement would be considered a failure. Throughout all the tests, a displacement limit of 10 mm, which roughly corresponds to 16% of the ice disc diameter, is chosen as an excessive displacement, after which it can be assured that failure has happened already. The displacement limit for conventional direct shear tests is 10% of the soil specimen diameter, corresponding to 6.35 mm. The failure within this range would be characterized by separating ice from the concrete surface. This would be demonstrated as a sharp slope after a peak value in the direct shear test result. The ice adhesion value in this paper is defined as the maximum shear strength recorded during the loading process of the shear test, i.e., the peak of the shear stress-displacement curve. The direct shear result with a steep curve correctly conveys the very brittle nature of the sheared material, as ice is very brittle and, upon shearing, would most likely break off from the concrete. An example direct shear test result is shown in Fig. 5. In this case, the peak value (415 kPa for the control specimen and 8.3 kPa for the treated specimen) is considered the ice adhesion strength for the specimen. Even though the physical description of ice shear adhesion strength would be the bonding in the interface of ice and concrete, in some samples, small residual ice particles were left on the concrete surface of control specimens, indicating a

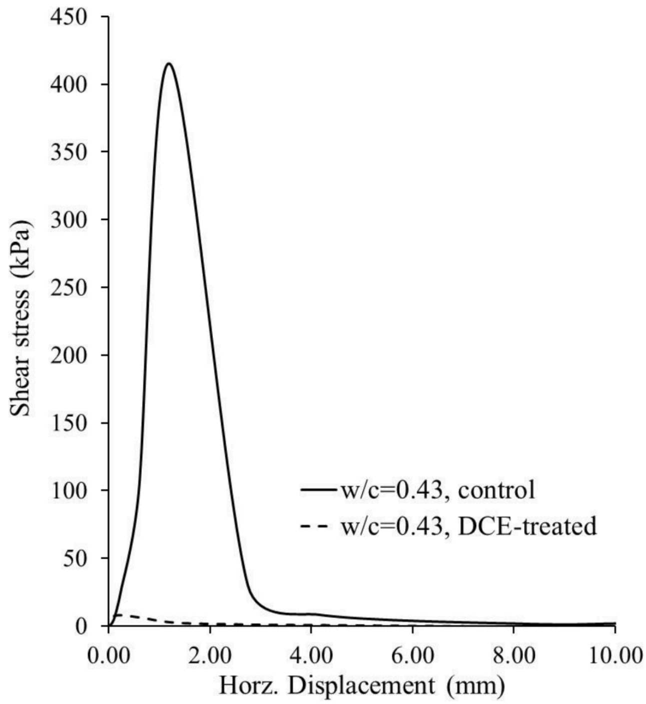


Fig. 5. Sample direct shear test results.

localized shearing failure in ice rather than the interface. These localized failures contribute to the variance seen in the ice-adhesion results, which can be used to better understand the mechanisms involved and better interpret the tests.

The recorded temperatures for the specimens, presented in Fig. 5, are shown in Fig. 6. The temperature recordings are for the set of samples with the freezer set for the temperature of −10 °C. The two temperatures are recorded using the two thermocouples shown in Fig. 4. The ambient temperature recorded the ambient (room) temperature inside the freezer, and the direct shear plate temperature recorded the shear box temperature. These two thermocouples show similar fluctuations, as seen in the initial parts of the graph in Fig. 6, during the 24 h of ice formation. During this period, the shear box thermocouple was not attached to the direct shear box and also recorded the room temperature. When the direct shear equipment was moved inside the freezer and the shear box thermocouple started to record its temperature. Its recorded temperature started to rise as the shear box had a warm initial temperature. Then it started to decrease as being cooled inside the freezer. The average recorded temperature for each test set is reported as follows. The average room temperature (freezer temperature) during the ice formation period of 24 h was −10.44 °C. The freezer temperature during shearing was −10.86 °C, and the direct shear box temperature average was −3.5 °C.

Many environmental and external phenomena can affect the actual temperature for each specific test set. There is an unavoidable increase in the temperature control freezer box, as seen in Fig. 6. from hour 18:00 when the freezer door was open to prepare the test setup. A waiting period was allowed to lower the temperature inside the freezer below freezing and minimize the temperature effect on shearing. As shown, the actual testing time for a set of three specimens is short. The ice-concrete specimens are kept in the freezer for 24 h; this relatively short testing period would ensure minimal effects on the shear properties of the ice.

3.2. *Effect of DCE treatment on ice adhesion*

A total of 24 tests, as shown in Table 3, were successfully conducted on concrete samples of two water-to-cement ratios, including both control and DCE-treated specimens with initial ice formation temperatures of −10 °C and −1 °C, respectively. Table 3 presents the statistical results of all 24 direct shear test results. These include three tests on identical disks of the same type with the same treatment and with ice formed at the same temperature. The three repetitive tests provide the sample average and variance of each sample type for each treatment. All the results of the ice adhesion shear tests can be seen in Figs. 7 and 8. The obtained ice-adhesion for the concrete mixed with a w/c ratio of 0.45 is 537.31 kPa and 581.92 kPa at −1 °C and −10 °C, respectively. The average result for the two concrete mixes at two temperatures is around 550 kPa. This is very close to the reported value in the literature. For

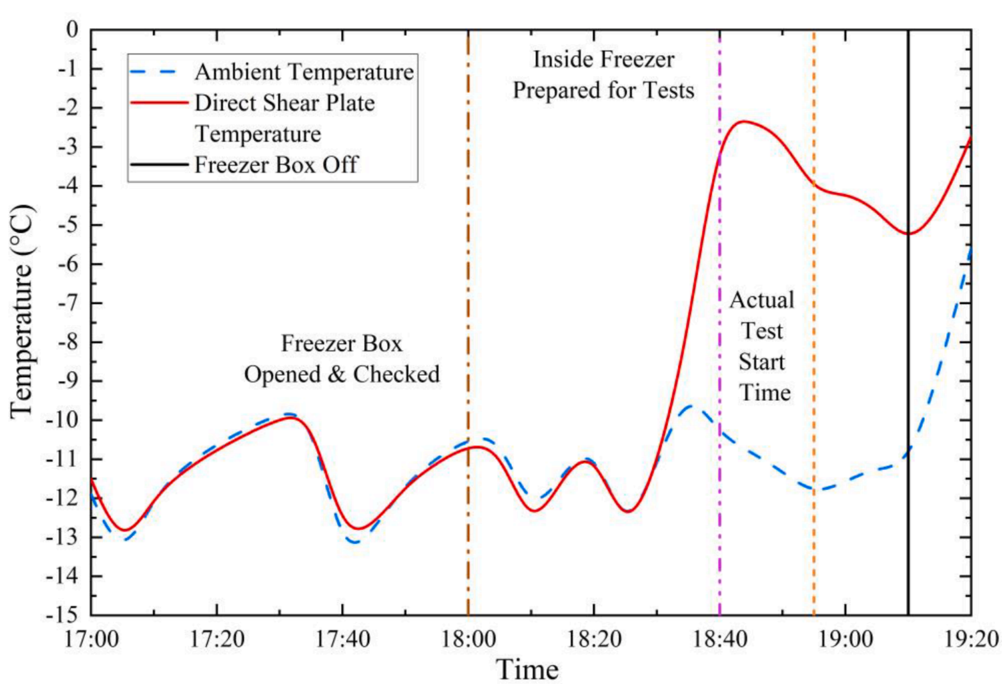


Fig. 6. Sample temperature records in the freezer box.

Table 3
Ice adhesion test results for two water contents (w/c = 0.43 and 0.45).

Test Temp.	Sample Type	Adhesion of Ice to Concrete Surface (kPa)						Standard Deviation (SD.)		Change	
		Average		Minimum		Maximum					
		w/c = 0.45	w/c = 0.43	w/c = 0.45	w/c = 0.43	w/c = 0.45	w/c = 0.43	w/c = 0.45	w/c = 0.43	w/c = 0.45	w/c = 0.43
	Control	581.92	486.77	468.84	398.52	674.31	592.95	102.73	100.18	–	–
−10 °C	PAVIX	99.70	69.64	0*	8.27	275.79	128.93	139.62	59.98	**−82.8%**	**−85.6%**
−1 °C	Control	537.31	599.15	372.32	453.68	703.27	679.82	165.47	114.45	–	–
	PAVIX	13.79	13.10	9.65	3.45	18.62	31.03	4.48	13.79	**−97.4%**	**−97.8%**

* The ice-disc was separated from the concrete disc before shearing.

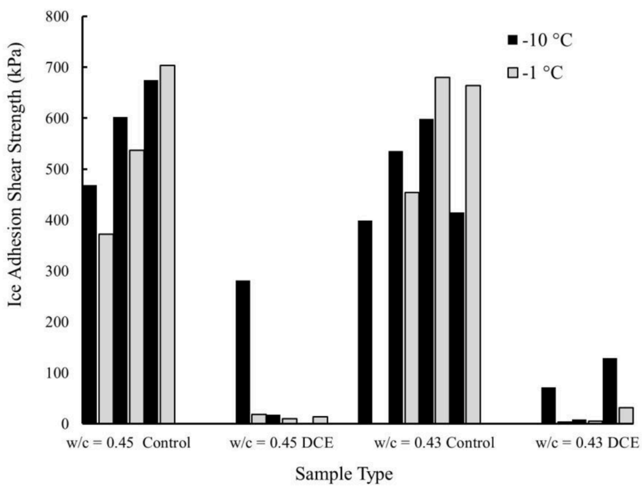


Fig. 7. Results of all ice adhesion tests.

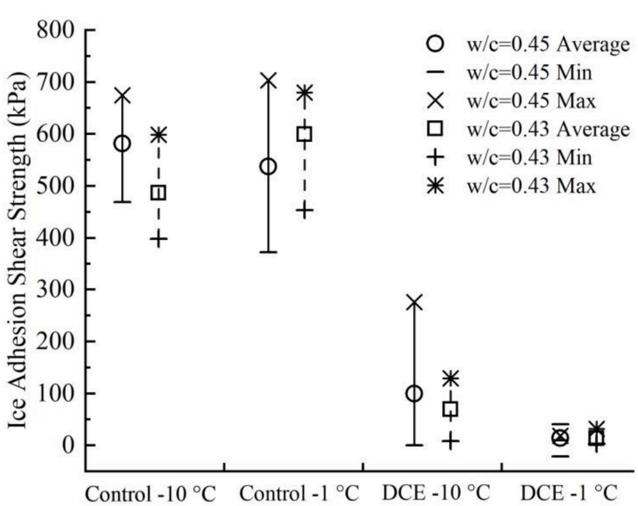


Fig. 8. Ice adhesion of test specimens – sample variance.

example, 600 kPa was reported as the ice-adhesion value for bare concrete measured on shearing an ice block off a bare concrete wall (Makkonen et al. 1986). This agreement emphasizes the validity of the experimental setup.

The results show a clear performance of the DCE surface treatment on the reduction of ice adhesion values. For the ice sample prepared at −10 °C, DCE-treated specimens exhibit around 97% reduction in ice adhesion compared to the control samples for both concrete mixes. For the ice-sample prepared at −1 °C, reductions of 82.8% and 85.6% are observed for the two concrete mixes. It should be noted that the reduction neglects the rough surface effects of the DCE-treated samples versus the smooth cut surfaces of the control samples. As the higher roughness increases the shear stress, it can be concluded that the actual reduction is expected to be higher [29]. This roughness could also explain the anomalous single test result of the 0.45 w/c DCE-treated disk with a higher adhesion value.

3.3. Effect of temperature and w/c ratio on ice adhesion

As it can be seen in Fig. 8, even with specimens of the same type, there is a considerable variance in the ice adhesion results. In addition to sample variance, temperature is one possible external factor for the variance of the results. The actual temperature for ice formation can directly influence the strength characteristics of the solid ice specimen. The variation of ice adhesion strength against ice formation temperature is presented in Fig. 9. The ice formation temperature represented are the 24-hour average recorded temperatures inside the freezer box. For both figures, no clear trend is observed on the effect of temperature on ice-adhesion. From Table 3, the test temperature effect on ice-adhesion of control samples is not conclusive. However, the DCE-treatment effect on shear strength reduction is correlated with the test temperature. Higher shear strength and lower reduction are observed for the results tested at −10 °C when compared to the results at −1 °C.

The expected higher ice adhesion at lower temperatures for control samples is not clearly seen. Nevertheless, there are major reductions in the ice adhesion strength when the concrete surface is treated with DCE. An in-depth investigation of the mechanisms that contribute to this ice adhesion reduction is needed to better understand this phenomenon. Icephobicity can be correlated with hydrophobicity [46]: Increasing the hydrophobicity of a surface increases the icephobocity since the water drops may bounce back when they impact the surface and the surface is not wetted well with water if the drops remain on it. Then, if they settle on the surface, the contact area is going to be very small due to the high contact angle. The DCE treatment of a concrete surface increases the hydrophobicity of the surface [31] and hence creates the icephobocity characteristics. Hydrophobicity has also been reported previously on ice adhesion reduction on metallic surfaces at various times [47,48].

3.4. Contact angle and hydrophobicity

Contact angle as the angle a drop of water forms on the surface of the concrete can be used as a property to measure hydrophobicity of a surface. Samples of treated and untreated concrete were tested for this. Figure 10 shows images of the water droplets on the surfaces of control, and Pavix-treated samples for the cases of w/c ratios. The summary of contact angles of concrete surfaces is tabulated in Table 4 for the two investigated water-cement ratios and treatments. The contact angle of the control sample with w/c = 0.43 is around 56.6°, meaning that the surface is hydrophilic, as shown in Fig. 10(a). The static contact angle for the control sample with w/c = 0.45 was difficult to measure since the specimen surface was highly hydrophilic with a bunch of small cracks. When a water droplet was put on the surface, water was quickly dissipated by those cracks. The static contact angles of top-treated specimens with w/c = 0.45 and w/c = 0.43 are 104.7° and 98.1°, respectively, as shown in Fig. 10(b). The results illustrate that after applying DCE on a concrete block surface, the surface becomes hydrophobic, as confirmed

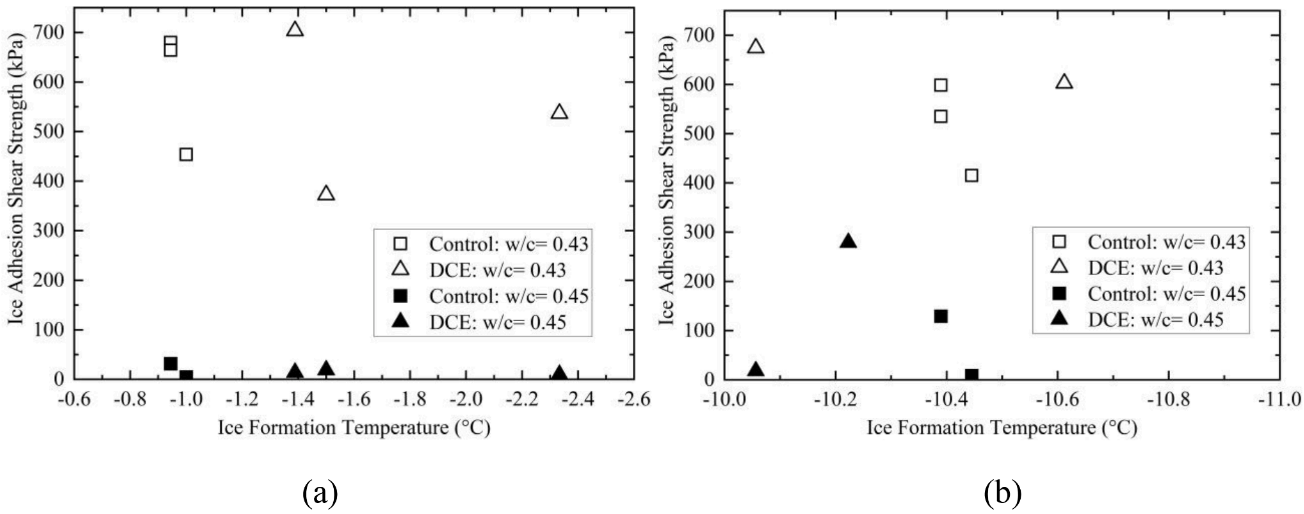


Fig. 9. Variation of ice adhesion shear strength versus ice formation temperature, (a) freezer set for at −1 °C, (b) freezer set for at −10 °C.

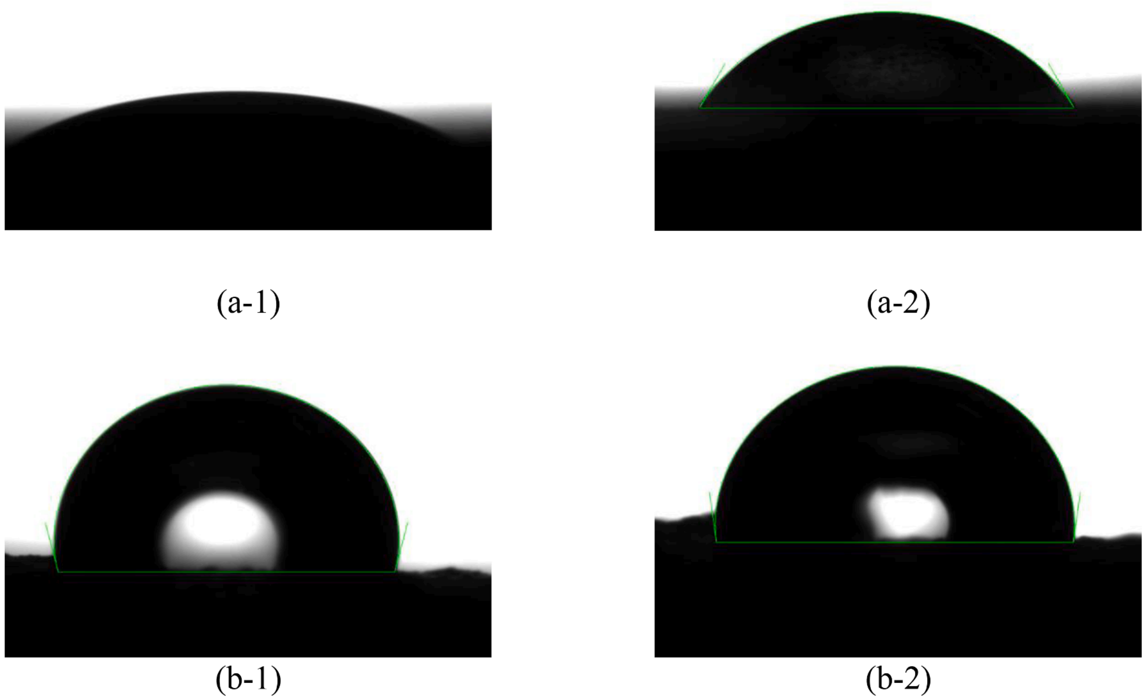


Fig. 10. Contact angle measurement for (a) control samples and (b) top treated samples (1) w/c = 0.45, (2) w/c = 0.43.

Table 4
Summary of contact angles for all specimens.

Test ID	Specimen	Water cement ratio (w/c)	Contact angle (°)	
			Static	Advancing/receding
1	Control	0.45	–	–
2	Top treated		104.7	92.2/47.7
3	Control	0.43	56.6	–
4	Top treated		98.1	100.3/40.8

by having the contact angle of the treated surface above 90°. In addition, the water-cement ratio has less effect on specimen surface wettability. The level of hydrophobicity obtained by Pavix treatment is believed to be dependent on the mix design of the concrete. A recent report has indicated that a nearly over-hydrophobic surface (with a contact angle of 120°) could be obtained with Pavix treatment on a concrete involving fly ash as a partial replacement of the cement (Kevern et al. 2022).

In addition to static contact angle measurement, dynamic contact angle measurements for top-treated samples were also conducted. Figure 11 presents the advancing and receding contact angles for treated samples. Ideally, a perfectly homogeneous surface has a theoretical contact angle hysteresis of 0°. The hysteresis here means the difference between advancing and receding contact angles. However, in this study average contact angle hysteresis is 52°. This large hysteresis indicates a chemical heterogeneity on the concrete surface after applying DCE.

4. Discussion

In general, there are three defensive lines against ice adhesion on

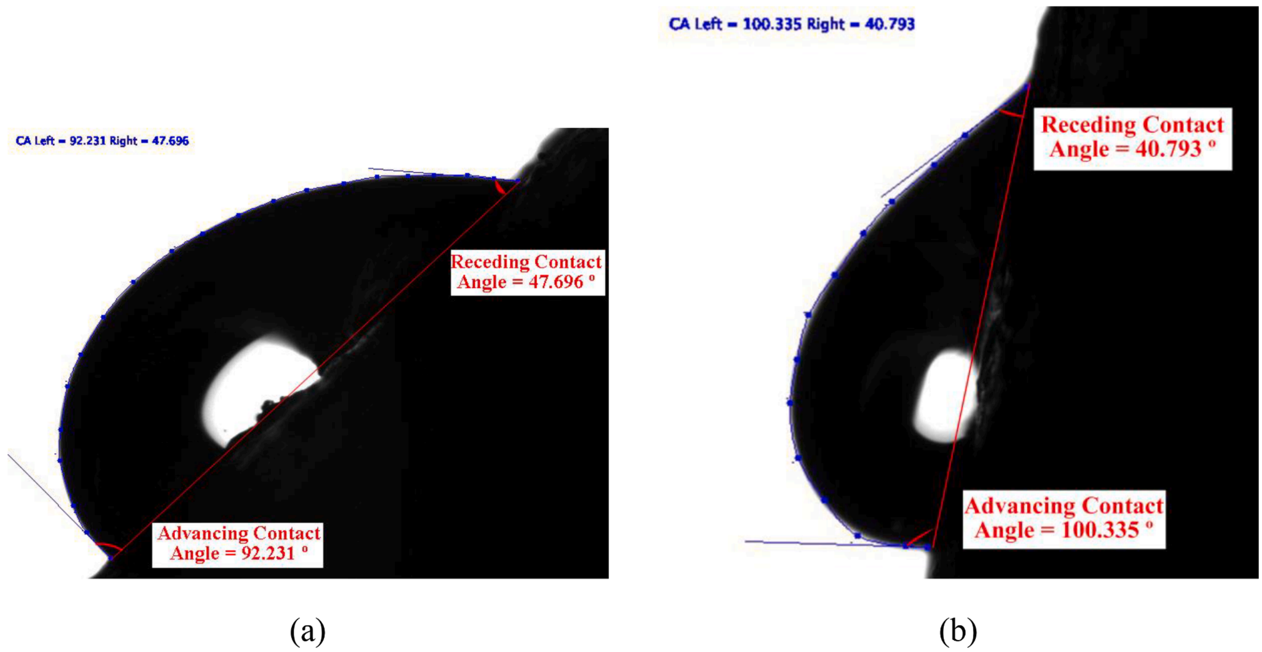


Fig. 11. Dynamic contact angle measurement for treated samples: (a) w/c = 0.45, (b) w/c = 0.43.

concrete surfaces: (1) the hydrophobicity can prevent the wetting of the surface and hence can detach water drops from the surface before they undergo thermal changes, (2) the rapid detachment of water from the surface can reduce the contact time (and contact surface) of the water drop on the concrete and hence can minimize the net rate of ice formation and (3) if the ice is formed under these water repelling conditions, it is associated with a reduction in the strength of ice adhesion, and hence it is easy to be removed. The impact of capillary condensation within concrete is also an important parameter [46], and thus reducing porosity is a governing parameter. Overall, icephobic concrete surfaces must combine the characteristics of (1) water repelling (high water contact angle), (2) resisting water freezing (from condensing or flowing water), and (3) having low adhesion strength of ice and thus ice can be easily detached from the surface.

The mechanisms of ice adhesion include physical and chemical interactions between ice and solid surface, and they are dependent on the forces of adhesion between them. The physicochemical bonds occur at the nano level, while the mechanical bonds occur at a larger level in the micrometer level. The mechanism of DCE in reducing ice adhesion works at the two levels: nano and micro-levels, and it reduces both the physicochemical and the mechanical bonding, as described below.

The adhesion or cohesive forces arise from the physicochemical bonds between the ice and the surface. These include hydrogen bonding (which involves water molecules interactions) and van der Waals forces [49]. They are also related to the water adsorption onto the surface and water contact angle with surfaces [50]. The use of DCE would initiate a mechanism that utilizes part of penetrated water in crystal growth and then utilize it in the hygroscopic crystals and hence minimize its availability for freezing and hence reduce the physicochemical bonds between the ice and the surface. The mechanical forces (e.g., entanglement and interlocking of ice structure [50]) arise from the roughness of the surface solid surface and the porosity that creates “legs” for the ice within the concrete pores and capillaries. These legs are created due to the penetration of water and the porosity of concrete. The use of DCE reduces the penetration of water and consumes a major part of the penetrated water in crystal growth (the hygroscopic and hydrophilic crystals) and consequently “cuts the legs” of surface ice.

For a porous surface, the interface surface area between the ice and concrete is high, and thus mechanical forces (interlocking) are also high so that the ice detachment may not be a pure adhesion failure [8]. In such a case, the fracture may occur within ice structure itself. This may explain why in some samples, small residual ice particles were left on the concrete surface since the strength of the ice adhesion strength exceeds the shear strength of the concrete structure itself, as highlighted in section 3.1. The use of DCE reduces the porosity of concrete and hence reduces the interlocking. From thermodynamic perspectives, ice formation is dependent on the temperatures of the surface and surrounding air (and which is colder) and on the level of the capillary action and condensation due to air cooling. Additionally, increasing the hydrophobicity (by increasing the water contact angle) of a surface decreases the freezing temperature of water at that surface, and hence it is expected to decrease the freezing rate at a given temperature (it has been reported that the water freezing requires lower temperatures when the degree of hydrophobicity (contact angle) increases [51]). Such phenomena reinforce the icephobocity effects of a hydrophobic treatment like DCE on the surface of the concrete.

5. Conclusions

An aqueous waterproofing material Chem-Crete PAVIX-DCE was used to treat the top surface of concrete specimens of a standard mix. The ice-concrete adhesion strength of the treated concrete was successfully measured for the first time with a customized ASTM standard direct shear apparatus. Contact angle tests of the concrete specimens were performed using a tensiometer under static and receding conditions at room temperature. The ice-adhesion tests were performed at two ice-formation temperatures on concrete specimens of two water-cement ratios. For both tests, treated samples and their control samples were tested at the same test conditions for comparisons. Despite the variations among the repetitive samples due to the complex nature of ice adhesion at the concrete and ice interface, a clear trend regarding the performance of the DCE-treatment can be observed. The correlation between icephobocity and hydrophobicity of the treated concrete is validated, and the advantage of hygroscopic crystallization waterproofing in enhancing the icephobocity is demonstrated. The conclusions are drawn from the test results as follows:

- The average ice-concrete adhesion for the two control concrete mixes at −1 °C and −10 °C is around 550 kPa.
- DCE surface treatment of concrete has shown a more than 83% reduction in ice adhesion compared to the control specimens. The reduction is consistent for the two concrete mixes.
- The ice-adhesion reduction increases with the increase in temperature. The ice-adhesion reduction is more than 97% at −1 °C.
- Control specimens have hydrophilic surfaces with a contact angle of less than 90°.
- Concrete specimens with surface treatment using DCE show a strong hydrophobic surface with contact angles significantly greater than 90°.
- Water to cement ratio has a minor effect on concrete surface wettability.
- Larger hysteresis is obtained for dynamic contact angle for DCE-treated concrete surface, meaning that a heterogeneous chemical layer was formed after the treatment.

The test results on DCE-treated concrete demonstrate the potential of such treatment to road surfaces to provide better anti-icing and pavement safety performance during winter weather events. This research focuses on the ice adhesion on concrete. Future research should be conducted to investigate surface friction, skid resistance, durability, life cycle cost, and environmental impact. Similar tests shall be performed on asphalt concrete to evaluate the DCE-treatment on its icephobicity and hydrophobicity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] Gustafson. Icing conditions on different pavement structures. Transportation Research Record 1982;860:21.
[2] A.M. Palacios, J.L. Palacios, L. Sánchez, Eliciting a human understandable model of ice adhesion strength for rotor blade leading edge materials from uncertain experimental data, Expert Syst. Appl. 39 (11) (2012) 10212–10225, https://doi.org/10.1016/j.eswa.2012.02.155.
[3] H. Chen, Y. Wu, H. Xia, B. Jing, Q. Zhang, Review of ice-pavement adhesion study and development of hydrophobic surface in pavement deicing, Journal of Traffic and Transportation Engineering (English Edition) 5 (3) (2018) 224–238, https://doi.org/10.1016/j.jtte.2018.03.002.
[4] J. Lv, Y. Song, L. Jiang, J. Wang, Bio-inspired strategies for anti-icing, ACS Nano 8 (4) (2014) 3152–3169, https://doi.org/10.1021/nn406522n.
[5] K. Mittal, Editorial Note, J. Adhes. Sci. Technol. 26 (4–5) (2012) 405–406, https://doi.org/10.1163/156856111X619325.
[6] L. Makkonen, Modeling power line icing in freezing precipitation, Atmospheric Research 46 (1–2) (1998) 131–142, https://doi.org/10.1016/s0169-8095(97)00056-2.
[7] L. Makkonen, T. Laakso, M. Marjaniemi, K.J. Finstad, Modelling and Prevention of Ice Accretion on Wind Turbines, Wind Eng. 25 (1) (2001) 3–21, https://doi.org/10.1260/0309524011495791.
[8] L. Makkonen, Ice Adhesion —Theory, Measurements and Countermeasures, J. Adhes. Sci. Technol. 26 (4–5) (2012) 413–445, https://doi.org/10.1163/016942411X574583.
[9] Penn LS, Meyerson A. Ice-pavement bond prevention: fundamental study; 1992.
[10] E. Turbay, G. Martinez-Arguelles, T. Navarro-Donado, E. Sánchez-Cotte, R. Polo-Mendoza, E. Covilla-Valera, Rheological Behaviour of WMA-Modified Asphalt Binders with Crumb Rubber, Polymers (Basel) 14 (19) (2022), https://doi.org/10.3390/polym14194148.
[11] R. Polo-Mendoza, G. Martinez-Arguelles, L.F. Walubita, F. Moreno-Navarro, F. Giustozzi, L. Fuentes, T. Navarro-Donado, Ultraviolet ageing of bituminous materials: A comprehensive literature review from 2011 to 2022, Constr. Build. Mater. 350 (2022) 128889.
[12] L. Fay, X. Shi, Environmental Impacts of Chemicals for Snow and Ice Control: State of the Knowledge, Water Air Soil Pollut 223 (5) (2012) 2751–2770, https://doi.org/10.1007/s11270-011-1064-6.
[13] Shi X, Liu Y, Mooney M, Berry M, Hubbard B, Fay L et al. Effect of chloride-based deicers on reinforced concrete structures; 2010.
[14] V. Hejazi, K. Sobolev, M. Nosonovsky, From superhydrophobicity to icephobicity: forces and interaction analysis, Sci Rep 3 (1) (2013) 2194, https://doi.org/10.1038/srep02194.
[15] P. Kim, T.-S. Wong, J. Alvarenga, M.J. Kreder, W.E. Adorno-Martinez, J. Aizenberg, Liquid-infused nanostructured surfaces with extreme anti-ice and anti-frost performance, ACS Nano 6 (8) (2012) 6569–6577, https://doi.org/10.1021/nn302310q.
[16] M.J. Kreder, J. Alvarenga, P. Kim, J. Aizenberg, Design of anti-icing surfaces: smooth, textured or slippery? Nat Rev Mater 1 (1) (2016) https://doi.org/10.1038/natrevmats.2015.3.
[17] S. Yang, Q. Xia, L. Zhu, J. Xue, Q. Wang, Q. Chen, Research on the icephobic properties of fluoropolymer-based materials, Appl. Surf. Sci. 257 (11) (2011) 4956–4962, https://doi.org/10.1016/j.apsusc.2011.01.003.
[18] Ma. Research on asphalt concrete pavement deicing technology. Journal of Southeast University (English Edition) 2014;30(3):336.
[19] S. Han, T. Yao, X. Yang, Preparation and anti-icing properties of a hydrophobic emulsified asphalt coating, Constr. Build. Mater. 220 (2019) 214–227, https://doi.org/10.1016/j.conbuildmat.2019.06.021.
[20] Y. Meng, Q. Zhao, J. Lei, M. Mao, Y. Qin, C. Xi, Z. Lu, X. Yang, H. Rong, Preparation of biological antifreeze protein-modified emulsified asphalt coating and research on its anti-icing performance, Constr. Build. Mater. 294 (2021) 123473.
[21] H. Xia, X.u. Zhao, Y. Wu, T. Yuan, L. Song, M. Yan, F. Wang, H. Chen, Preparation and performance of antifreeze adhesive materials for asphalt pavement, Constr. Build. Mater. 258 (2020) 119554.
[22] Gao. Anti-icing design and model test of super hydrophobic and bionic cement pavement. Bulletin of the Chinese Ceramic Society 2016;35(10):3288.
[23] Gao. Anti-icing technology and effectiveness evaluation of super-hydrophobic bionic cement concrete pavement. Materials Review 2017;31(14):132.
[24] F. Sanchez, K. Sobolev, Nanotechnology in concrete – A review, Constr. Build. Mater. 24 (11) (2010) 2060–2071, https://doi.org/10.1016/j.conbuildmat.2010.03.014.
[25] K. Sobolev, Modern developments related to nanotechnology and nanoengineering of concrete, Front. Struct. Civ. Eng. 10 (2) (2016) 131–141, https://doi.org/10.1007/s11709-016-0343-0.
[26] I. Flores-Vivian, V. Hejazi, M.I. Kozhukhova, M. Nosonovsky, K. Sobolev, Self-assembling particle-siloxane coatings for superhydrophobic concrete, ACS Appl. Mater. Interfaces 5 (24) (2013) 13284–13294, https://doi.org/10.1021/am404272v.
[27] I. Flores-Vivian, R.G.K. Pradoto, M. Moini, M. Kozhukhova, V. Potapov, K. Sobolev, The effect of SiO2 nanoparticles derived from hydrothermal solutions on the performance of portland cement based materials, Front. Struct. Civ. Eng. 11 (4) (2017) 436–445, https://doi.org/10.1007/s11709-017-0438-2.
[28] Sobolev K, Nosonovsky M, Krupenkin T, Flores-Vivian I, Rao S, Kozhukhova M et al. Anti-icing and de-icing superhydrophobic concrete to improve the safety on critical elements on roadway pavements; 2013.
[29] W. Huang, Z. Li, H. Han, Q. Jia, Limit resistive forces from ice frozen to concrete-revetment interface of an inclined dam wall, Cold Reg. Sci. Technol. 141 (2017) 181–187, https://doi.org/10.1016/j.coldregions.2017.06.012.
[30] Q. Jia, W. Tian, Y.C. Lu, X.M. Peng, J.R. Yu, Experimental Study on Adhesion Strength of Freshwater Ice Frozen to Concrete Slab, Adv. Mat. Res. 243–249 (2011) 4587–4591, https://doi.org/10.4028/www.scientific.net/AMR.243-249.4587.
[31] R. Al-Rashed, M. Jabari, Dual-crystallization waterproofing technology for topical treatment of concrete, Case Stud. Constr. Mater. 13 (2020) e00408.
[32] R. Al-Rashed, M. Al-Jabari, Concrete protection by combined hygroscopic and hydrophilic crystallization waterproofing applied to fresh concrete, Case Stud. Constr. Mater. 15 (2021) e00635.
[33] R. Al-Rashed, M. Al-Jabari, Multi-crystallization enhancer for concrete waterproofing by pore blocking, Constr. Build. Mater. 272 (2021), 121668, https://doi.org/10.1016/j.conbuildmat.2020.121668.
[34] Al-Rashed R. Aqueous chemical mixture to mitigate water associated problems in concrete pavements: Google Patents; 2008.
[35] Kasaai M. R. 23rd International Conference on Offshore Mechanics and Arctic Engineering; 2004.
[36] Schulz M, Sinapius M. Evaluation of different ice adhesion tests for mechanical deicing systems; 2015.
[37] C. Wang, W. Zhang, A. Siva, D. Tiea, K.J. Wynne, Laboratory test for ice adhesion strength using commercial instrumentation, Langmuir 30 (2) (2014) 540–547, https://doi.org/10.1021/la4044254.
[38] G. Fortin, J. Perron, Ice Adhesion Models to Predict Shear Stress at Shedding, J. Adhes. Sci. Technol. 26 (4–5) (2012) 523–553, https://doi.org/10.1163/016942411X574835.
[39] M. Javan-Mashmool, C. Volat, M. Farzaneh, A new method for measuring ice adhesion strength at an ice–substrate interface, Hydrol. Process. 20 (4) (2006) 645–655, https://doi.org/10.1002/hyp.6110.

[40] A. Barker, S. Bruneau, B. Colbourne, Bulk Adhesion of Ice to Concrete: Review of Test Programs, J. Cold Reg. Eng. 35 (3) (2021) 3121001.

[41] Itoh Y. Proc., 7th Int. Conf. on Port and Ocean Engineering under Arctic Conditions: Itoh, Y., A. Yoshida, Y. Asai, K. Sasaki, and H. Saeki. 1988. "Testing methods on sea ice-concrete sliding abrasion." In Vol. 3 of Proc., 7th Int. Conf. on Port and Ocean Engineering under Arctic Conditions, edited by W. M. Sackinger and M. O. Jeffries, 89–96. Fairbanks, AK: Univ. of Alaska Fairbanks, Geophysical Institute; 1988.

[42] Saeki H. Proc., of the IAHR Int. Symp. on Ice: Saeki, H., T. Ono, and A. Ozaki. 1981. "Mechanical properties of adhesion strength to pile structures." In Vol. 2 of Proc., of the IAHR Int. Symp. on Ice, 641–649. Quebec City, Canada: Laval Univ; 1981.

[43] J. Liu, P. Lv, Y. Cui, J. Liu, Experimental study on direct shear behavior of frozen soil-concrete interface, Cold Reg. Sci. Technol. 104-105 (2014) 1–6.

[44] L. Makkonen, Ice adhesionÔÇötheory, measurements and countermeasures, J. Adhes. Sci. Technol. 26 (4–5) (2012) 413–445.

[45] T. Pramanik, An experimental investigation of ice-concrete adhesion and corresponding abrasion, Memorial University of Newfoundland, 2021.

[46] R. Di Mundo, C. Labianca, G. Carbone, M. Notarnicola, Recent Advances in Hydrophobic and Icephobic Surface Treatments of Concrete, Coatings 10 (5) (2020) 449, https://doi.org/10.3390/coatings10050449.

[47] W.D. Bascom, R.L. Cottington, C.R. Singleterry, Ice Adhesion to Hydrophilic and Hydrophobic Surfaces, J. Adhes. 1 (4) (1969) 246–263, https://doi.org/10.1080/00218466908072188.

[48] T. Bharathidasan, S.V. Kumar, M.S. Bobji, R. Chakradhar, B.J. Basu, Effect of wettability and surface roughness on ice-adhesion strength of hydrophilic, hydrophobic and superhydrophobic surfaces, Applied Surface Science 314 (2014) 241–250, https://doi.org/10.1016/j.apsusc.2014.06.101.

[49] P.S.R. Beeram, Characterization of ice adhesion strength over different surfaces pertinent to aircraft anti-/de-icing, Iowa State University, 2017.

[50] Ashworth T. Proc., 2nd Int. Symp. on Snow Removal and Ice Control Research: Ashworth, T., B. Tollefsen, and J. A. Weyland. 1979. "Adhesion of ice to concrete surfaces: Preliminary results." In Proc., 2nd Int. Symp. on Snow Removal and Ice Control Research, 23–29. Hanover, NH: Np; 1979.

[51] Y. Zhang, E. Anim-Danso, S. Bekele, A. Dhinojwala, Effect of surface energy on freezing temperature of water, ACS Appl. Mater. Interfaces 8 (27) (2016) 17583–17590.