Coatings to Prevent Frost

Ricardo Losada Mateo*, Stefan Holberg*

*: Danish Technological Institute, Kongsvang Allé 29, 8000 Aarhus C, Denmark, rlm@teknologisk.dk

Abstract

Hydrophobic coatings were applied to decelerate the spreading of frost origination from ice nucleation spots. The application of these coatings to extend defrosting intervals for devices that are periodically defrosted, for example specific heat exchangers used for heating and ventilation, was evaluated with a novel ice test chamber. The probability of ice nucleation at low subzero temperatures, for example -4°C, is considerably low. However, in case of freezing, a bare aluminum surfaces freeze at once and completely. On hydrophobic coatings, the ice nucleation spot is isolated and growth slowly. At -4°C surface temperature in a +12°C/90% rel. humidity environment, on a surface providing advancing and receding water contact angles of 106° and 96°, a rate for the growth of the average radius of the frozen area of 4 µm/s was observed. Submitting the surface to an air flow of 1 m/s leads to faster frost spreading in flow direction.

Introduction

Frost affects various devices such as airfoils, electrical power lines or pipelines. The present work originated from two specific heating and ventilation problems. The first is air-to-refrigerant heat exchangers of heat pumps using outside air as heat source (evaporator in fig. 1). The heat exchanger fins are cooled below 0°C when the outside temperature is below about 7°C. The second is air-to-air heat exchangers of heat recovery ventilation (HRV in fig. 1). At outside temperatures below about -3°C, the more humid outgoing air is cooled to temperatures below 0°C. In both cases, ice accumulates on the respective surfaces, impairing the heat transfer and requiring periodic defrosting by heating, thus consuming energy. Periodic defrosting is also applied in other applications such as, for example, to deice wind turbine wings.

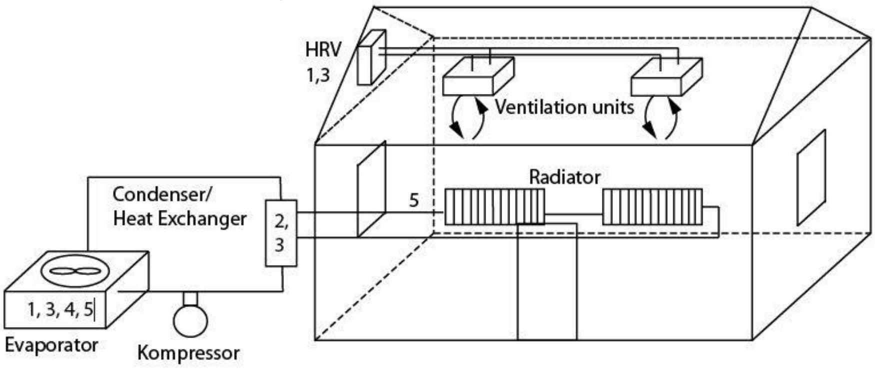


Figure 1: Schematic of a building with heat pump and heat recovery ventilation.

Scientists have put effort into anti-icing surfaces to reduce ice adhesion or retard the first ice nucleation on a wet surface [1] [2]. The efficiency of the frequently applied hydrophobic surfaces under conditions of high humidity, air flow or icing/deicing cycles has, however, been critically questioned [2] [3]. Especially on superhydrophobic surfaces, water can possibly condense inside a microstructure in a Wenzel-regime, void superhydrophobicity and increase ice adhesion due to a larger contact area.

Herein, we report a different approach for anti-ice coatings. Under realistic process conditions, the rate of ice nucleation is considerably low. Ice on certain spots can be tolerated, if the spreading is slow enough to significantly increase the time between two defrosting cycles.

Experimental

Materials: Aluminum: Al 8006, 0.2 mm. Steel: SAE grade 1008/1010; 0.5 mm. PP: Polypropylene, 50 µm film. PDMS: Nusil R 2180 silicone rubber. FEP: Fluorinated ethylene propylene, 25 µm foil. Coatings 1 to 3 are inorganic organic hybrid coatings applied to Al. Coatings 1 and 2 are previously described as examples 1 and 2 in [4].

Contact Angles: Determination with a DSA 10 from Krüss, no recording of video sequences, thus, advancing and receding contact angle may be slightly lower and higher, respectively, as the actual values. All results are based on at least five measurements, standard deviation is between 1° and 3°.

Ice test chamber: A test box (fig 2, sample plate is mounted into the left wall) controls the environment. The temperature is hold at +12 °C, relative humidity at about 90%. There is a weak, undefined air flow downwards due to natural convection along the cold sample plate. In those experiments, where an air flow is specifically mentioned, a wing with an additional fan is mounted inside the box, parallel to the sample surface to enforces an upward air flow of about 1 m/s, reducing the humidity to about 60%.

The temperature of the sample plate surfaces is controlled by a cooling block (Cu-block with peltier element and thermo couple, see fig. 3, in fig. 2 eclipsed by the sample plate). The cooling block is connected to the sample plate by a thin ice film. Provided surface temperatures are cooling block temperatures. At the start of each experiment, the cooling block is placed outside the test box and is covered with water. The sample plates (101 x 152 mm) are with their backside placed on the cooling block and attached by freezing. The edge of the cooling block is throughout the whole experiments heated by a heating wire to temperatures above 0°C to prevent contact-freezing form the backside. By thawing tests performed at the end of each experiment, where we kept the ice covered plate at -0.5°C for 15 min, we could confirm, that only a stripe of about 1 cm from edges was warmer than 0°C, the rest of the sample surface was below 0°C. Thus, we expect a maximum error of 0.5°C for the whole sample surface except the area close to the edges. A camera inside the test box continuously monitors the sample plate surface.

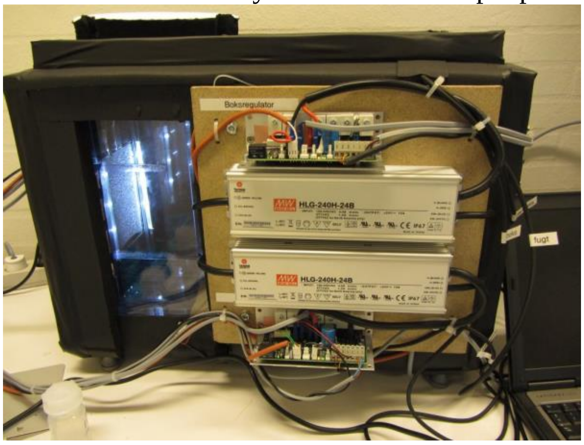


Figure 2: Ice test chamber.

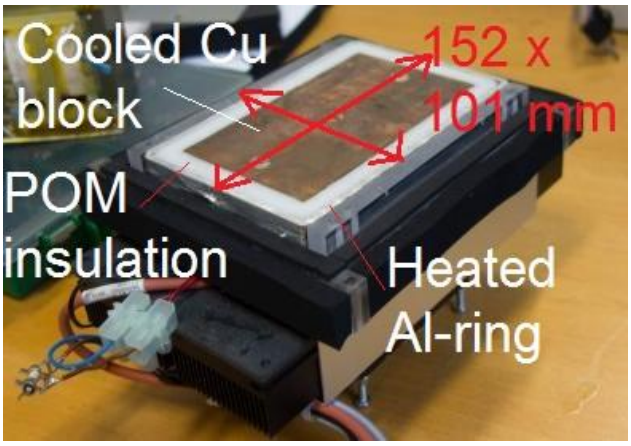


Figure 3: Cooling block for the ice test chamber.

The cooling block with the sample plate is mounted into an opening in the wall of the box, with the sample plate in vertical position. For all experiments, the sample plates are hold at -2°C until enough water has condensed on the plate to start running down in drops. Thereafter, the actual experiments starts. All experiments are carried out while water continuously condenses and drops run down.

Results and Discussion

Freeze depressing / Probability of first ice nucleation

We screened various metal, bulk-polymer and coating surfaces. We do not question, that the probability of freezing differs depending on surface properties. However, our results from screening various metal and coating surfaces were not decisive to make any statements. In a DSC test, water drops were placed either in bare Aluminum pans, d~6 mm or in pans coated with the smooth hydrophobic coating 1. The pans were sealed with a cap (optionally coated) and cooled by a rate of -1°C/min, tests were repeated 9 times with different sample pans. For bare Al, freezing occurred between -17 and -27°C. For coating 1, freezing occurred between -18 and -24°C. In two tests runs, silver iodide powder was added; freezing occurred at

-2°C. This is the only decisive result due to the well known fact that silver iodide and ice have similar lattice spacing.

Using the ice test chamber described above, the water contact surface is with about 100 cm^2 about 3000 times larger than for the DSC pans with ~3 mm^2. Freezing tests should thus correspond with the worst result out of 3000 DSC tests. A real heat exchanger would have a 4000 times larger surface than the samples for the ice test chamber. Furthermore, there is continuous condensation in the ice test chamber and minor vibrations due to fans. Applying a cooling rate of 0.1°C/min, freezing for all samples occurred scattered between -4 and -12°C. For isothermal tests, the distribution of freezing times should theoretically follow first order decay kinetics. At present, we did at not perform a sufficient number of test runs to prove that. Eight test runs at -7°C with plates coated with coating 3 (also smooth hydrophobic) showed freezing times from 0 (before test start) to 11 h.

Frost spreading

We reproducibly observed significant differences for the behavior of the surfaces after occurrence of the first ice nucleation. While bare metal plates almost instantly freeze completely, the frozen area growth slowly on hydrophobic surfaces. When carrying out above described experiments to determine the freezing temperature, the sample plates were hold at their respective freezing temperature for 20 min to roughly estimate the rate of frost growth. These tests were for bare metals and for coating 1 repeated three times. The results are shown in table 1 and fig. 5.

According to previous investigations, frost spreads from a frozen drop to neighboring liquid drop [5], [6]. Water condenses faster on the frozen drop due to a lower vapor pressure than for the liquid drop. The frozen drop growth and finally touches a liquid drop. Due to the different vapor pressure, neighboring liquid drops may even evaporate and contract. A connection with the critical diameter d_{crit} for a water droplet to be big enough to start sliding down a vertical surface was proposed. The smaller d_{crit}, the slower the ice spreading, though no equation for this connection was established. d_{crit} can be calculated from advancing and receding contact angles, see fig. 4. Simplified, the optimal surface has a low contact angle hysteresis, and, for a given hysteresis, a high contact angle. The results of table 1 support the proposed trend, the contact angle data alone seems, however, not to be sufficient. Spreading on Aluminum was significantly faster than on PP, despite a similar d_{crit}.

$$Critical\ diameter = \sqrt{\left(\frac{24\, sin^3\theta adv\, \gamma(cos\theta rec - cos\theta adv)}{\pi\rho(1-cos\theta adv)^2(2+cos\theta adv)g sin\alpha}\right)}$$

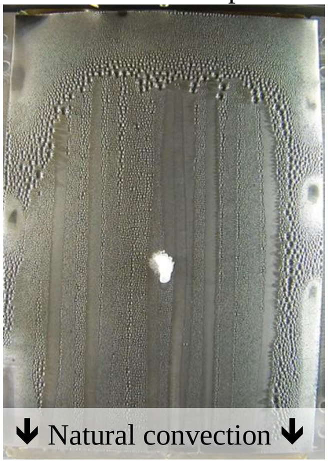
Figure 4: Critical diameter d_{crit} at which a drop starts to slide down according to [6]. α: surface tilt angle (90°.in our experiments), ρ: density of the liquid, γ: surface tension of the liquid, θadv and θrec are the respective contact angles, g: gravity acceleration.

Table 1: Estimation of the frost spreading rate.

Surface	Water contact angle		Calc. crit. drop	Frost spreading rate	
	adv.	rec.	diam. d_{crit}	Rough estimation	Precise (-4 °C)
Bare carbon steel	69°	26°	5.1 mm	instantly, > 10 mm/s	
Bare aluminum	96°	50°	4.2 mm	instantly, > 10 mm/s	
PP	96°	69°	3.9 mm	1 mm/s to 50 µm/s	
Coating 2	89°	73°	2.8 mm	1 mm/s to 50 µm/s	
Bulk PDMS	113°	88°	2.5 mm	slow, <50 µm/s	
FEP	114°	95°	2.1 mm	slow, <50 µm/s	
Coating 1	106°	96°	1.8 mm	slow, <50 µm/s	~4 µm/s
Coating 3	104°	95°	1.8 mm	slow, <50 µm/s	~2 µm/s

For two selected smooth hydrophobic coatings, we investigated the frost growth rate more precisely. The sample plates were hold at -4 °C. A small ice lump was placed in the middle of the plates. The frozen area growth in all directions. After about 5, 10 15 and 20 min, the frozen area was evaluated. While the growth rate based on area per s accelerates, the linear rate of the growth of the average radius of the frozen area was constant.

Frost growth is further affected by drops sliding down. Drops touching the frozen area freeze, drops sliding close by remove other drops and decrease frost growth. Tests were also run, and repeated with five5 different plates, with forced convection at 1 m/s, as is typical for heat exchangers. After a short induction period, ice spreads fast in direction along the flow (see fig 6). In the other directions, spreading on hydrophobic surfaces is still slow. Thereby, growth is fastest in direction of the lowest humidity. Thus, this phenomenon cannot be explained by the model outlined above. Frost starts even to grow several cm away from the point of initiation, with liquid water in between. Even though no flying ice crystals were observed, a plausible explanation is, that lose frost forms on top of the droplets and is detached and transported by the flow.



Figures 5 (left) and 6 (right): 10 x 15 cm Al plates coated with coating 3, hold at -4 °C for 20 min after placing ice in the middle. Environment +12°C, ~90% (fig, 5) and ~60% (fig. 6) rel. humidity

Conclusions

- Realistic test methods are crucial in the development of coatings to prevent frost.
- Hydrophobic coatings can provide an anti-ice effect for devices that are periodically de-frosted. Basis is not the actual delay of the first ice nucleation, but the strong delay of frost spreading. Tests on real devices are required to evaluate drawbacks caused by airflow.
- The aim for the coating developer is hydrophobic coatings with low contact angle hysteresis and possibly high contact angles. For practical applications, coatings need to be durable in contact with water. In this work, smooth surfaces were applied. Theoretically, these should be outperformed by structured superhydrophobic surfaces, if long-term superhydrophobicity under condensation conditions would be provided.

Acknowledgements

The authors would like to thank the EU-commission for financial support through the EnE-HVAC project.

References

[1] A.J. Meuler, G.H. McKinley, R.E. Cohen; ACS Nano 2010, 4 (12), 7048-7052.
[2] V. Stenzel, N. Rehfeld; Functional Coatings, Vincentz Network, Hannover, 2011, p. 91 - 106.
[3] S. Jung, M.K. Tiwari, N.V. Doan, D. Poulikakos, Nat. Commun. 2012, 3, article no. 615.
[4] C. Bischoff, S. Holberg, WO 2012/083970 A1 (2012).
[5] a) J.B. Boreyko, C.P. Collier; ACS Nano 2013, 7, 1618.
b) X.M. Chen, R. Ma, H. Zhou, X. Zhou, L. Che, S. Yao, Z. Wang; Sci. Rep. 2013, 3, 2515.
[6] P. Kim, T-S. Wong, J. Alvarenga, M.J. Kreder, W.E. Adorno-Martinez, J. Aizenberg; ACSNano 2012, 6(8), 6569.