How contact angle measurements can help develop anti-icing coatings



Over the past years, research on anti-icing surfaces has gained tremendous importance for many applications. Ice-formation on surfaces, especially on outdoor infrastructures (wind turbines, aircrafts, optical sensors, ships etc.) can results in huge economic loss and serious accidents. For instance, the de-icing of airplanes with glycol-based fluids, which is currently the most widely used method, costs airlines billions of dollars per year. If anti-icing coatings can delay ice formation on a surface for long enough to cover the airplane's waiting time for taking-off a very useful environmentally friendly and financially important solution could be at hand. Until now a manifold of different anti-icing strategies have been developed, but most of them are not really practical for harsh and high humidity environments. Akhtar et al. recently reported a new robust, extremely lightweight and potentially transparent anti-icing coating based on fluorinated graphene, which has an enormous potential for outdoor facilities in severe environments.

In order to develop an anti-icing coating it is necessary to closely measure and understand the factors that influence the icing process. Akhtar and his team found that the following factors lead to a suppression of the ice nucleation on the surface:

- 1. A minimum contact area between water and the coated substrate
- 2. A higher nucleation activation energy
- 3. A robust liquid layer

In addition to these, the surface roughness, surface wettability and interfacial water layer properties have critical influences on ice nucleation.

Graphene structures were chosen as the basis of the new coating due to their light weight and robustness, optical transmission and smooth surface with poor wettability. By fluorinating the graphene the interface to the water layer could further be improved due to the high electronegativity of fluorine.

Based on the above analysis, they made a row of different sapphire windows coated with fluorinated graphene. Firstly, they studied water droplets at room temperature on different sapphire windows: bare sapphire window (as-received); graphene coated sapphire window; fluorinated graphene coated sapphire windows (different fluorine contents). The surface of as-received sapphire window is hydrophilic (contact angle (CA) < 90 °) while all coated ones were hydrophobic. The results furthermore show that increasing fluorine contents will lead to higher CAs, because the highly polar C-F bond can lower the surface energy and more C-F bonds can reduce the surface energy further. During the research they also noticed that the temperature of freezing onset varies enormously between the as-received sapphire window (-15 °C) and fluorinated samples (-23 °C).

Furthermore, the freezing delay measurements of the water droplets on these four sapphire windows were carried out at subzero temperatures (-5 to -15 °C) with 5 °C/min cooling rate. As Figure 1 shows, the ice formation is significantly delayed for the fluorinated sample, and the anti-icing performance is obviously improved further with higher fluorine contents. Moreover, the fluorinated graphene coatings could keep very good anti-icing properties even after the durability test, which was exposed to the ambient environment 90 days with 15 icing/de-icing cycles.

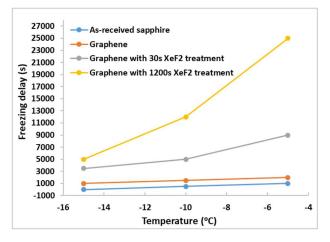
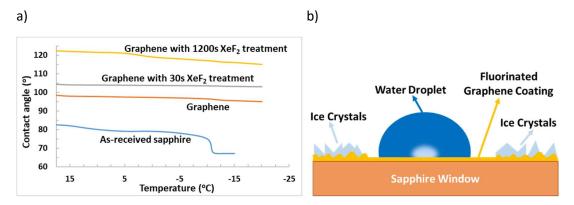


Figure 1: Measurements of the freezing delay.

In addition, the water contact angle as a function of the sample surface temperature was studied (Figure 2a). While the water contact angle on a bare sapphire surface has a sudden drop around -10 °C, graphene and fluorinated graphene coated surfaces showed and almost constant water contact angle during the whole test. For bare sapphire surface, the sudden drop is caused by an increased hydrophilic surface wettability since the onset of ice formation around -10 °C strongly changes the wetting behaviour. These results also indicate that the low surface energy was mainly induced by the chemical composition of the (fluorinated) graphene coating and could stay the same even in harsh environment.

To get a deeper understanding of the anti-icing mechanism, the authors made a side-view image of a water droplet on a fluorinated graphene sample. As Figure 2b illustrates, many small ice crystals appear at the sample edge while the drop is still liquid, where the

inhomogeneous coating and defect centres could give nucleation sites. It is very interesting to observe that even though these defect centres supply ice nucleation sites, the ice crystals prefer an "off-surface" growth mode on the hydrophobic surfaces. As recently reported, an "off-surface" growth mode provides much less ice-surface contact area, so that the adhesion of ice on hydrophobic surface is much lower than that on hydrophilic surface. This difference can dramatically increase the freezing delay time.



**Figure 2**: a) Static water contact angles as a function of substrate surface temperature. b) Side-view illustration of a water droplet on a fluorinated graphene sample.

In conclusion, this work introduced a new anti-icing coating based on fluorinated graphene which shows a very high application potential due to it's great durability and robustness as well as an excellent best anti-icing performance in high humidity environments. Besides, the authors also studied the water contact angels on these coatings as a function of sample surface temperature and shed light on the anti-icing mechanism on hydrophobic surfaces. Due to it's outstanding material characteristics these coatings have the potential to be applied to wind turbines, aircrafts, etc. in the near future.

An OCA 20 Contact Angle Analyser with Peltier temperature control chamber from DataPhysics Instruments GmbH, Germany was used in this research.

For more information, please refer to the following article:

**Fluorinated graphene provides long lasting ice inhibition in high humidity**; Naureen Akhtar, Gloria Anemone, Daniel Farias, Bodil Holst; *Carbon* **2019**, 141, 451–456