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pilot. As seen in Figure 1, weather-related pilot errors account for 16% of all fatal airplane crashes. Pilots encounter unexpected icing conditions while flying which put them in these dangerous accidents. The introduction of the ice protection systems and de-icing equipment has helped to reduce the frequency of icing accidents, however, the best way to avoid icing accidents yet has been to avoid icing conditions, like freezing rain and very low temperatures. In 2016, over 800 million people in the United States alone traveled by plane, so avoiding these conditions would cost both time and money for everyone involved [4]. Meteorological forecasts are not always reliable, so pilots have to take into account many factors to effectively make a quick decision that can alter the path of the flight. If the de-icing agent doesn't get rid of ice fast enough, the pilot may have to lower the altitude of the plane, making the flight longer. The pilot then has to consider if it is worth adding time and using more fuel to get rid of the ice or take a chance that the problem will fix itself. According to the International Air Transport Association, if all flight times in 2016 were cut by one minute, airlines would have saved \$1.5 billion and reduced carbon dioxide emissions by 4.8 million tons. [boeing source] In the case of Continental Flight 3407, even with the most up-to-date de-icing system, there was too much ice to get rid of to safely land the plane. Steven Green, an expert in inflight icing accidents observed that "aircraft's scale is more significant to icing events than pilot training, pilot experience, icing equipment and icing certification," because different categories of aircraft react differently to ice accretion [5].

In most cases, when an aircraft encounters icing conditions, the performance of the plane is limited and pilots lose control of the plane. Depending on how severe the icing conditions are, the aircraft can experience loss of control or stall. When the plane loses lift force it will start to angle towards the ground, which results in fatal crashes [6].

As technology and economic growth are making air travel more accessible to people around the world, airplanes, now more than ever, have to be sustainable. Airplanes must be durable, fly efficient routes, while also being environmentally friendly. Today, traveling by air is more fuel efficient than most cars, trucks and trains. Jet fuel can be the most expensive part of flying a plane so by reducing the amount used, airlines reduce their costs and greenhouse gas emissions [7]. Today's airplanes are also made with recycled, composite materials that adds significantly to airplane performance. Even with the current de-icing systems, the used fluid is recycled and has uses in other commercial and consumer applications. There is an increased effort in making airplanes more efficient and leave a smaller carbon footprint, all techniques that lead to sustaining the aircraft and the Earth. Even though the current de-icing agents are environmentally friendly, the statistics on weather-related crashes show that these methods are ineffective, leading researchers to look for a more effective

way to get rid of ice buildup on flights in the air to lower the ice related fatalities.

### THE PROBLEM: ICING ON AIRCRAFT

#### Icing

When an aircraft flies through the air, temperatures can be as low as -15 to -20° Celsius, causing all water particles to freeze [8]. Ice molecules are highly cohesive, meaning that once attached to other ice molecules, the molecules bond tightly together and it takes a lot of energy to separate them [9]. This is why ice accumulation, the thin coating of ice, is so dangerous because it can increase the weight of objects by 30 times [10].

As an aircraft increases in altitude, it passes through air layers of decreasing temperatures and humidity, which increases the formation of ice. Aircraft icing is the accretion of supercooled liquid onto an airplane during flight [11]. There are three types of icing: rime, clear, and mixed.

Rime ice is brittle and opaque and forms as soon as water droplets come into contact with the aircraft, typically at temperatures between -15 and -20° Celsius [8]. Rime ice is the most common type of aircraft icing, but the least severe because it grows into the airstream on the leading edges, where de-icing equipment is typically installed [12]. Rime ice is also less dense than the other types of icing so it does not disturb the airflow, making it less likely to affect the flight of the aircraft. Rime ice can become dangerous if the aircraft does not have de-icing technology or if it is not activated when needed [13].

Another type of icing is clear ice. It has a translucent, glossy appearance that is smooth and it is more hazardous because it can spread over a part of the aircraft's surface that is not protected by de-icing or anti-icing equipment. This is the reason clear ice disrupts airflow more than rime ice. Even though clear ice can cover more area than rime ice, it can still almost always be completely removed by using de-icing devices as soon as it's needed. Mixed ice is a combination of rime and clear ice that can appear as layers of relatively clear and opaque ice when examined from the side. Like clear ice, mixed ice can also spread over a portion of the aircraft's surface not protected by de-icing or anti-icing equipment.

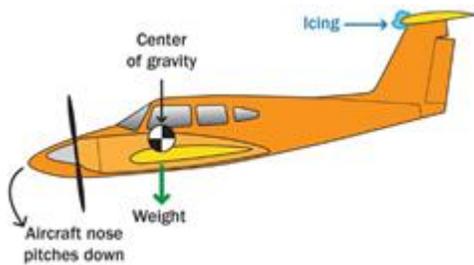
There are four different categories of icing that correlate to the damage it does on aircraft: trace, light, moderate, and severe. Trace icing is the least severe. On this level, the rate of accumulation is slightly greater than the rate of sublimation, the rate at which the ice goes from solid to gaseous state [8]. It is not dangerous even without using de-icing equipment as long as it does not stay in this stage for more than one hour [11]. When light icing occurs, de-icing equipment must be used within an hour or else the ice will

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become a problem for the aircraft. In this stage, de-icing equipment will fix any problem created by icing. In moderate icing conditions, the rate of accumulation is so high that even brief encounters in these conditions can be hazardous. A combination of de-icing equipment and a change in altitude must be used to remove and try to prevent further ice buildup [8]. In the case of severe icing, the rate of accumulation is so high that de-icing equipment cannot reduce the hazard created by the ice. The pilot will have to change the heading, the angle of the nose of the aircraft, or change altitude immediately to avoid crashing into the ground.

**Effect on Aerodynamics**

Aircraft are influenced by four forces: weight, lift, thrust, drag [14]. Icing creates a problem with most of these forces. One of the main reasons icing is especially dangerous during flights is because it increases the weight on the aircraft. Adding weight to a flight compromises the structural integrity of the aircraft and as a result, reduces the overall performance [15]. Excessive weight on an aircraft in flight would lower maximum altitude, reduce cruising speed, and reduce maneuverability are all examples of low aircraft performance. Additional weight would also change the location of the center of gravity. In very extreme cases, the added weight makes the center of gravity location move towards the front of the plane, which results in nose heaviness, making it difficult or impossible to flare for landing. As seen in figure 2, changing the center of gravity location on the aircraft would make it extremely difficult to control and create very violent stall moments.



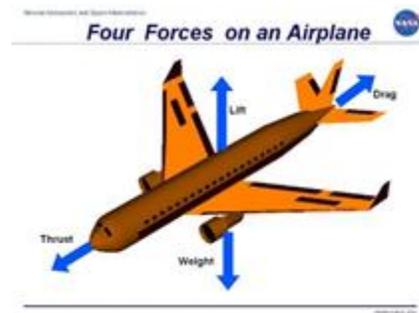
**FIGURE 2 [16]**

**Visual example of stalling**

Icing also decreases lift and thrust and increases drag [14]. The force of lift is the only force that counteracts weight and sustains an aircraft in flight. It is produced by the motion of the airplane through the air. Lift is generated by every part of the airplane, but most of the lift on a normal aircraft is generated by the wings. The amount of lift produced by an aircraft wing is determined by the design of the wing, speed of surrounding air, and air density [14]. Because lift force must oppose the force of weight, any added weight on an aircraft will throw this balance off and create problems. If the weight is greater than the lift force, the aircraft will have

trouble taking off. If the flight is already in the air, it may cause the aircraft to crash.

Drag is an aerodynamic force that opposes the aircraft's motion along the plane [15]. Every part of an aircraft generates drag force and it is caused by friction and differences in air pressure [17]. Thrust is the force that counteracts drag force that makes the aircraft accelerate in the desired direction. In order to have a successful takeoff, the thrust force must be larger than the drag force because the plane should accelerate in the direction of the thrust force. Once the aircraft reaches cruising altitude, thrust force must equal drag force because it is a constant velocity, resulting in no acceleration. In all commercial aircraft, the thrust force is provided by a propulsion system. Icing decreases thrust and increases drag on aircraft, and this combination could cause engine failure [18].



**FIGURE 3 [14]**

**Forces on an Aircraft**

**APPLICATIONS OF ANTI-ICING  
MATERIALS**

**Anti-Icing Agents**

Because icing on aircraft is so dangerous in how it affects the aerodynamics of aircraft, current researchers in the field are focusing on how to reduce this icing effect. A solution to ice accretion is the use of icephobic materials on the aircraft. An icephobic material is described as a material that has ice adhesion strength of less than 100 kilopascals [19]. An icephobic material has the ability to reduce the adhesion that is likely to occur between ice and the structure of an aircraft.

Another property of hydrophobic materials is their high contact angle. A contact angle is the angle that a water droplet makes with the surface of a solid material, as seen in figure 4. For example, water spreads completely flat on a material that has a contact angle of 0°. To be considered at least “slightly hydrophobic,” the material must have a water contact angle greater than 90°. A superhydrophobic surface however has a contact angle greater than 150° [19].

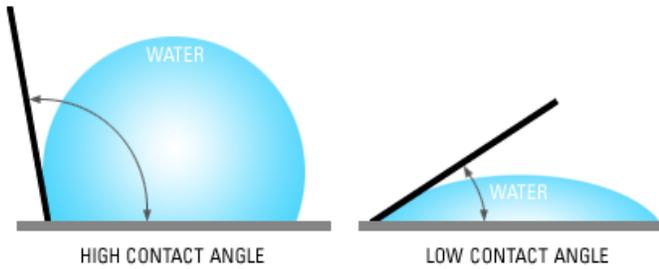


FIGURE 4 [19]

**Difference between high and low contact angles**

Superhydrophobic materials can be used as coatings in various industries just like hydrophobic materials. It was proven by chemist Robert N. Wenzel that enhancing the roughness of a hydrophobic surface will increase its hydrophobicity. “The phenomenon of roughness-induced superhydrophobicity,” is called the “lotus effect.” [20].

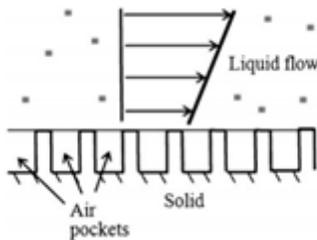


FIGURE 4 [20]

**Superhydrophobic surface interacting with liquids**

The figure above shows a liquid interacting with a superhydrophobic surface with enhanced roughness. The diagram shows the contact angle of the water as it meets the surface. The diagram also illustrates the “composite interface with air pockets” that can form due to the roughness of a superhydrophobic surface which helps reduce ice adhesion [21]. This reduced ice adhesion strength is very beneficial to the purpose of reducing ice buildup on aircraft, however in temperature conditions less than  $-8^{\circ}\text{C}$  and high humidity the sought-after effect of very low adhesion strength becomes much weaker, as the contact angle decreases [20]. Under these weather conditions in this experiment done by Shuqing Yang et. al, even the best superhydrophobic material, SNF-1 coating had a contact angle reduction of  $41^{\circ}$  [20]. What is happening is that the air pockets between the material and the surface area is being filled with the condensed water, reducing the superhydrophobicity. This is a problem when considering the sustainability of these materials for aircraft in harsh weather conditions.

Though superhydrophobic surfaces have this amazing ability to coat materials and decrease corrosion and ice adhesion, researchers have found that there are some other drawbacks

to superhydrophobic materials. In a study done by Dr. Kripa K. Varanasi, a mechanical engineering professor at the Massachusetts Institute of Technology, he concluded that as frost forms on its surface, icephobic properties are decreased, which may pose a problem if icephobic surfaces are used for both on-ground and in-flight applications [22]. This issue becomes a problem of sustainability and whether the superhydrophobic surface is durable enough to withstand harsh weather conditions and continue to provide protection even after enduring the loss of its hydrophobic properties due to some frosting.

**INTRODUCING FLUOROPOLYMERS**

Fluoropolymers are very stable fluorocarbon polymers that possess icephobic qualities, due to the strength of their intermolecular forces. Fluoropolymers are used in various industries beyond aerospace, including construction, electronics, and energy. What makes fluoropolymers so useful and applicable to so many industries, is the molecule’s durability and various properties such as “chemical inertness, excellent dielectric properties, non-flammability, self-lubricating, resistance to weathering, anti-stick, almost no moisture absorption [23].” Fluoropolymers are very durable and can withstand various hazardous and unwanted weather conditions. They can withstand corrosion and other weathering effects. In the industry of aerospace alone, fluoropolymers are used for different reasons, one being the use for wire insulation. In terms of applying them for de-icing aircraft, the property of icephobicity is most important [23]. Researcher, Myer Kutz, explains in his book the applications of fluoropolymers, and he describes the chemical properties of fluoropolymers that help give them these icephobic characteristics. Kutz also describes how the ability of fluoropolymers to possess this icephobic property lies in the molecular makeup of the molecule. He describes how due to the increase in fluorine content in fluoropolymers it increases chemical and solvent resistance, improves a polymer’s electrical potential, lowers the coefficient of friction, raises its melting point, increases its thermal stability, and weakens its mechanical properties [22].” The strong fluorine carbon bonds are the key to fluoropolymers.

**The Fluoropolymers Industry**

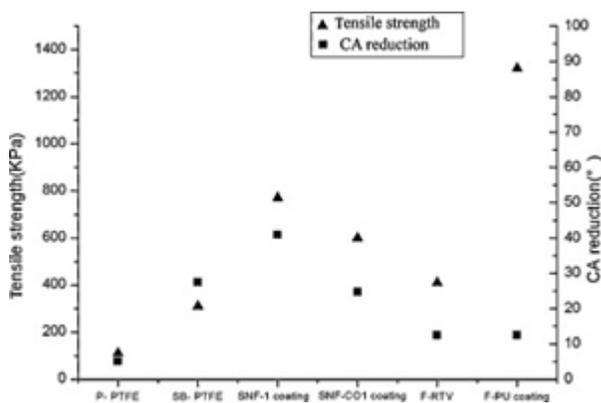
As discussed, fluoropolymers are used in various industries for various purposes including construction, automotive, and aerospace. Though they are widely used in these fields today, they came about by the accidental discovery of polytetrafluorethylene by American chemist Dr. Roy J. Plunkett in 1938 [23]. He discovered that this new-found chemical was very icephobic, and solvent resistant. At the time, however he did not know of a good use for the substance, but realized that its highly resistive properties could be utilized in various ways including anti-stick coatings, and wire insulation. This is how fluoropolymers

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became known and started being used in different industries. Fluoropolymers first came on the market scene in the 1940's when they were used as anti-corrosion protection for metal military equipment during World War II [23]. After this, fluoropolymer usage spread to various other industries for their anti-corrosive, and anti-ice adhesive properties.

Because of the globalization of fluoropolymer use in multiple industries, there is a concern, however, for whether its usage can be sustained for a long period of time. In this article published by the Royal Society of Chemistry, the global reserves of fluorspar, which is used for fluorination processes, is estimated at around  $5 \times 10^{11}$  kg [24]. This information along with the pattern of usage of fluorine for various purposes estimates that there is only "sufficient fluorspar available to meet fluorine chemistry requirements for little under 100 years" [24]. Though new methods of getting fluorine may be discovered, the use of fluorine will still continue to grow as there are more technological advancements which proposes a major concern of long term sustainability of fluorine chemistry.

There are various types of fluoropolymer coating examples. The two main groups are homopolymers, and copolymers sold commercially [21]. Within each group there are sub types of polymers that each differ with specific properties. Some homopolymers include polytetrafluoroethylene (PTFE), perfluoroalkoxy alkanes (PFA), fluorinated ethylene propylene (FEP), and ethylene-tetrafluoroethylene (ETFE). The most widely used fluoropolymer is PTFE because of its very low adhesion strength. PTFE was once known as the slipperiest material in the world [22]. Many industries utilize this particular fluoropolymer for these reasons, and "noticeably, PTFE still remains the largest type of fluoropolymer with about 70% of the total fluoropolymer market worldwide" [23].



**FIGURE 5 [19]**

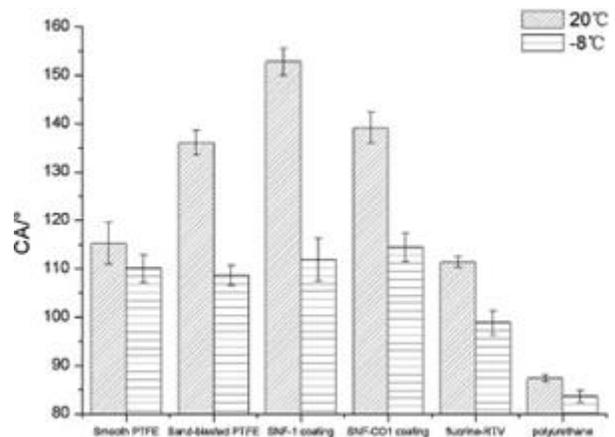
**Tensile strength and contact angles for different fluoropolymers**

As shown in the figure, a study was done testing the tensile strength and contact angle reduction of various fluoropolymers after decreasing the temperature from 20° to -8°C [19]. As discussed previously, the high contact angle is a property of a adhesion resistive materials. The icephobicity decreased for each material in lower temperatures, which is why the contact angles were reduced, however P-PTFE showed the lowest contact angle reduction of 5°.

**Use of Fluoropolymers on Aircraft**

Now understanding the properties of fluoropolymers, the question becomes whether their application on critical parts of the aircraft such as the wings and tail will have the sought-after effect of reduced ice adhesion. To understand this application, it is important to first understand how the properties of fluoropolymers will mix with the material of current aircraft structures which are commonly made from aluminum, and sometimes steel. The addition of icephobic materials as a coating can reduce the ice adhesion strength of structures made of aluminum and steel. These materials typically have high ice adhesion strength around 1600 kPa for aluminum and 1400 kPa for steel [22]. This reduction of ice adhesion makes it much easier for an aircraft to lose the ice as it falls off due to wind, gravity, vibration, and other natural forces or with artificial assistant. Without the use of internal energy of the plane, the icephobic coating will help to bring back the original geometry of the plane restoring aerodynamic performance [22].

A study was conducted by researcher Shuqing Yang et al. and showed that there is a strong correlation between contact angle reduction and ice adhesion strength of fluoropolymers [19]. They showed that fluoropolymers can help reduce ice adhesion strength very well at 20° C but the icephobic ability decreased as the temperature decreases to -8°C [19].



**FIGURE 6 [19]**

**Contact angles of different fluoropolymers at different temperatures**

### The Problem with Fluoropolymers on Aircraft

After doing research related to the application of nanotechnology such as fluoropolymers on aircraft, a concern that has come up is the fluoropolymer's durability and resistivity to corrosion over time. In this study done by Asmatulu et al., various kinds of coatings were tested for their resistivity to corrosion over time. Because of this, they found that currently the lowest ice adhesion values have only been reported using lubricants with values of ice adhesion equal to 16 kilopascals or gels with ice adhesion strength of 0.4 kilopascals [23]. These lubricants have these low ice adhesion strength values because of their low surface energy and high contact angle with water. The problem with using these lubricants, is that they are not durable, and their lack of long-term durability leads to short-lived resistivity [24]. The study concluded that there were, "no reports of durable icephobic surfaces that maintain or even exhibit an ice adhesion strength less than 15 kPa," which would be needed to "passively remove ice with no external energy input [24]."

Another issue that arises with the use of fluoropolymers is the cost. Fluoropolymers are costlier to produce in comparison to many other plastics due to its high fluorine content [25]. Because of the amount of work it takes to process fluoropolymers, in 2015, sale prices ranged from approximately \$10–15 USD/kg for PTFE to more than \$100 USD/kg for specialty grades of PFA [26]. This is a crucial concern because the cost of applying fluoropolymer coatings can become very costly when trying to cover the crucial parts of an aircraft. The cost of fluoropolymers is important to know to determine whether fluoropolymers are sustainable economically for production.

### FUTURE OF FLUOROPOLYMER MATERIALS ON AIRCRAFT

While fluoropolymers applied to surfaces help to decrease adhesion strength in many conditions, they are not durable enough for application on an airplane. The problem of ice accretion on aircraft is a major concern to help reduce the amount of fatal airplane crashes due to harsh weather conditions. As discussed, fluoropolymers have an adhesion strength of about 100 kilopascals and a contact angle of more than 90°, which makes them a probable solution to the ice accretion problem. While the use of superhydrophobic fluoropolymers that have very low adhesion strength to water and ice molecules as a coating seems very favourable, these molecules become less icephobic under temperature of -8° C. While that does not seem like a major issue in the application of airplanes, they would not be able to sustain harsh weather conditions that aircraft are bound to encounter in flight. Another problem with the use of fluoropolymers stems from the lack of durability of the superhydrophobic materials. The most superhydrophobic materials that would have the desired criteria to work as an ice repellant are unstable and therefore

are not sustainable as a coating on an aircraft. Though the use of fluoropolymers as an anti-icing agent is not sustainable in terms of durability and cost efficiency, researchers in the field are still looking to improve fluoropolymers or find a better solution to reduce ice accretion on aircraft.

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