Methodology for Characterizing Icephobicity of Hydrophobic Coatings

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ABSTRACT

The focus of this research is on investigating correlations in the properties which govern hydrophobicity and icephobicity, for the purpose of developing understanding of icephobic surfaces, moreover, how to tune surfaces for the function of delaying ice formation. An experimental set-up for characterizing icephobicity has been developed and is explained in this paper. The drop-deposition system controls the test environment conditions (constant -20℃ and low relative humidity (34%)) and has video recording capabilities, allowing for the visualization of a droplet's freezing process. In future experiments, this equipment will be used to collect data on surfaces' ability to delay or prevent ice formation by measuring the freezing delay times of a single droplet. This icephobicity data can then be analyzed in comparison to hydrophobicity (contact angle and roll-off angle) to reveal any correlations between surface energy and/or roughness.

KEY WORDS: Hydrophobicity, Icephobicity, Roughness, Surface Energy, Freezing Delay Time

INTRODUCTION

Challenges in Industry

Ice formation on aircraft vessels is a serious threat to both the safety of passengers as well as the financial interests of companies in the airline industry. While in flight, airplanes experience extremely low temperatures (reaching -20℃) and weather high moisture environments, especially upon descent; the aluminum body of the aircraft easily reaches subzero temperatures.[1] Hence, ideal circumstances are present for permitting water droplets in the atmosphere to freeze practically immediately upon contact with the vessel. The exterior of aircrafts are currently not fabricated of materials with capabilities to prevent or delay ice formation, therefore, once even the smallest ice crystal nucleates,

larger masses will begin to grow. Ice buildup has unfavorable consequences when it occurs on the wings, in the engine or within the air inlets of the pitot-static system; formation in these locations can cause engine failure, reduction of lift and aerodynamics, and errors in instrument readings.[2] These occurrences ultimately put the safety of the passengers in danger and cause costly damage to equipment.

Hydrophobicity

The term "hydrophobic" is used to describe a surface that lacks an affinity for water. This property is governed by a combination of two components: surface energy and roughness. Surface energy results from the chemical interactions on the surface of the coating.[3, 4] Coatings with high surface energy have high affinities for water, while coatings with low surface energy tend to be more hydrophobic. Hydrophobicity is also dependent upon a coating's surface roughness.[3, 4] Rougher surface textures result in the formation of air pockets between the water droplet and substrate and subsequently, a smaller liquid-substrate interface; because the contact area between water and substrate decreases with an increase in roughness, coatings with rougher surfaces tend to be more hydrophobic.

Hydrophobicity is characterized by contact angle, see "Figure 1," and roll-off angle. Roll-off angle is obtained by gradually increasing the incline of an initially horizontal substrate until the droplet can no longer remain attached to the substrate. Surfaces with large roll-off angles are considered hydrophilic, while those with low roll-off angles are more hydrophobic.

Figure 1

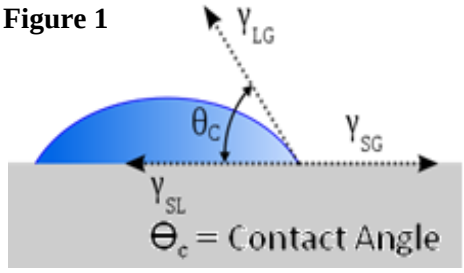

Figure 2

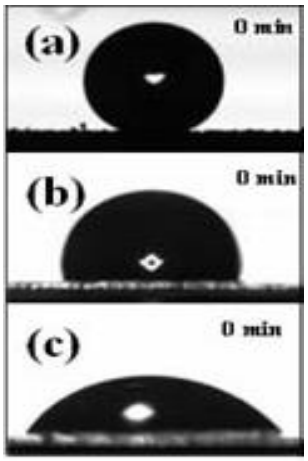

Figure 1 shows the contact angle of a droplet; this measurement characterizes hydrophobicity. When a contact angle is greater than 90, the surface is categorized as hydrophobic. Figure 2 shows how contact angle changes with hydrophobicity. Droplet "a" is most hydrophobic and has the largest contact angle; droplet "c" is least hydrophobic and has the smallest contact angle.

Recent Developments[5]

In years past, the question of whether icephobicity is synonymous with hydrophobicity has been a controversial topic of debate. Recently, Cao et al. performed investigations to develop answers to this question. Their experiments revealed correlations between median times in freezing-delay, surface roughness and contact angles. It was concluded that longer delays in the onset of freezing are associated with smoother surfaces. Additionally, it was concluded that the properties of hydrophobicity and icephobicity result from hierarchal surface texture created by a combination of particles on two different length scales. It was found that a surface can demonstrate hydrophobic properties if its surface particles are at most 10 μm; the coating will not exhibit icephobic properties until surface particles are 50 nm or smaller. Therefore, it was proposed that all icephobic coatings will demonstrate hydrophobic capabilities, but not all hydrophobic coatings can act icephobically. Their research has established groundwork for rational

design and tuning of icephobicity for hydrophobic coatings. See the "Supporting Information" section for a description of the coatings used in these experiments.

It is proposed that coatings with the ability to exhibit both hydrophobic and icephobic properties will have great value to the airline industry. Further developments of hydrophobic coatings which demonstrate icephobicity, based on the correlation found by Cao et al., must be pursued. Because the study of icephobicity is a rather new area of experimentation, methods of testing have been developed and are described here. With this equipment, icephobicity will be characterized by their ability to delay the onset of freezing ("freezing delay time"), measured in seconds.

METHODOLOGY

Parameters

Substrates will be tested at -20°C, simulating atmospheric conditions during flight. An environment with minimal humidity is established (34% relative humidity), as to reduce variability from the thermodynamic effects of moisture content on the behavior of the droplet during the freezing process; eliminating all moisture will ensure that freezing delays are based solely on surface characteristics. The setup also offers video recording capabilities for capturing the freezing process of a single droplet on the given substrate so that freezing delay time (the time from the point at which the droplet is deposited and the onset of freezing occurs) may be analyzed. Additionally, measures must be taken to reduce vibration and to ensure that the substrate's surface is level.

Design Features of the Experimental Setup

Figure 3

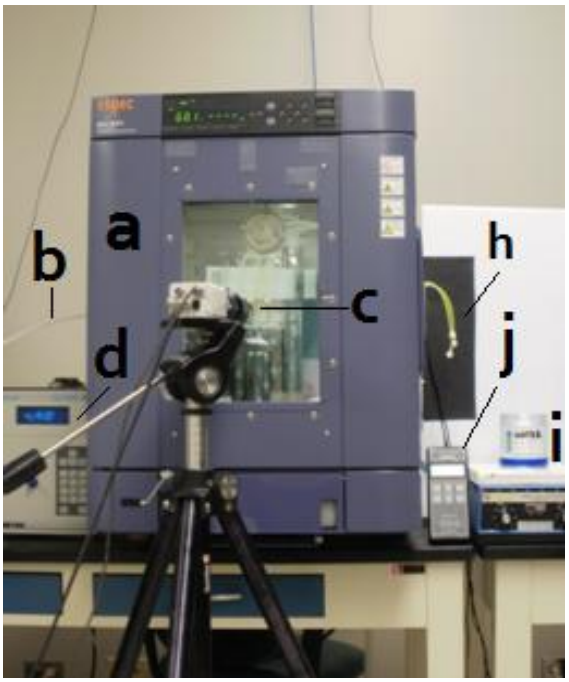

Figure 4

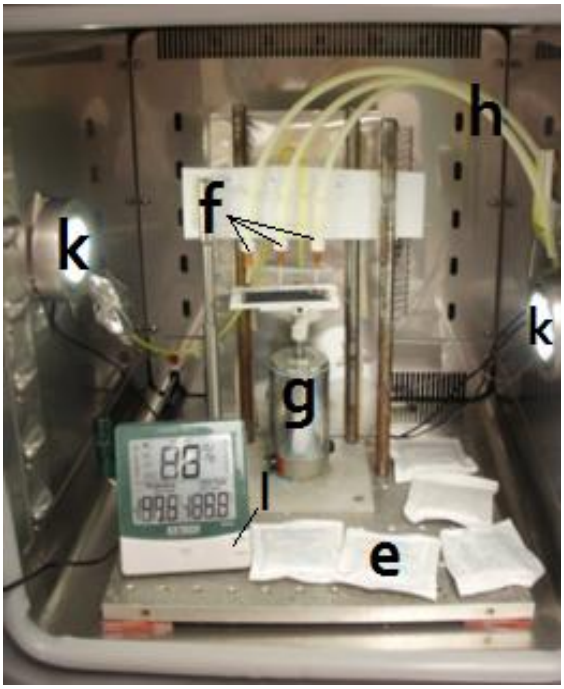

Figure 3 shows the experimental setup. Figure 4 displays the inside of the experimental setup.

A SH-641 ESPEC Bench-Top Type Temperature and Humidity Chamber (a) is used to control the temperature of the testing environment. Additionally, on the left side port, tubing (b) is attached to apply Nitrogen gas for pushing out moisture and maintaining low humidity. A CCD camera (c) is set up on the outside of the camber to visualize and record the freezing process of the droplet through the glass window on the front of the chamber. A Thermox CG-1000 Oxygen Analyzer (d) is used to monitor the chambers gas atmosphere. This device allows for monitoring the effectiveness of pumping in Nitrogen. During operation initial Oxygen content, prior to pumping Nitrogen is noted; significant decrease in Oxygen content also means significant decrease in moisture content (molar mass of $H_2O < O_2$). Additionally, desiccating packs (e) are placed in the chamber to

absorb any excess moisture. Three droplet-deposition needles (f) are placed above substrate stage (g); each needle has its own tubing (h) (two layers of Teflon tubes) which extends to the outside of the chamber, through the right side port, for application of droplet water. A hot plate (i) is used for heating the water before it is deposited (in order to prevent freezing in the tube during deposition). Thermocouples are placed within each needle for recording the temperature of the droplet before it meets the substrate. An additional thermocouple is placed on the substrate to confirm -20°C surface temperature. The thermocouple monitor is placed on the outside of the chamber (j). Because they do not produce heat, LED lights (k) are used to enhance the video resolution. A thermometer/humidity monitor (l) is placed inside the chamber for confirming a -20°C and 34% relative humidity atmosphere. De-ionized water should be used for the experiments and replaced daily.

Experimental Procedure

Heat the SH-641 chamber to 65°C in order to evaporate moisture (chamber understood to have leaks in sealing). Maintain 65°C temperature in chamber for ten minutes, then begin pumping in N_2 gas. Allow N_2 to run at 65°C for at least five minutes, then reset chamber's target temperature to decrease to -22°C (set the chamber two degrees less than the necessary -20°C, due to error in chamber's temperature monitor control; in practice, this will allow for substrate and chamber's internal atmosphere to establish -20°C, as confirmed by the substrate thermocouple and secondary thermometer/humidity monitor, respectively). Note that N_2 should be on throughout the rest of the operation from this point forward. Once -22°C reached, allow ten minutes for equilibrium to establish. Then turn off room lights and start "record" on camera. Turn off chamber to eliminate its

vibration. Confirm that the chamber temperature, substrate temperature, percent oxygen and relative humidity are appropriate for the trial. Apply the heated de-ionized water through the tubing, from the exterior. Right before the droplet falls from the tip of the needle, record the water's temperature from the thermocouple monitor. Deposit droplet. Allow video to run until onset of freezing occurs. Save video. Then re-cool chamber to make sure substrate and atmosphere are back at -20°C; allow five minutes to re-establish equilibrium. Then repeat deposition-recording process for the next two needles and substrates.

Characterization of Icephobicity

Icephobicity of coatings will be characterized by analyzing the freezing process from the video recordings. The time (in seconds) from the point at which the droplet meets the substrate until the onset of freezing occurs will be called the "freezing delay time;" this time will be used to compare the coatings' icephobicity. Longer freezing delay times will be associated with higher icephobicity.

PRELIMINARY RESULTS AND DISCUSSION

Now that the lab has a means to characterize icephobicity, experiments will be carried out in order to develop an understanding of the surface properties which govern the delay or prevention of ice formation. The freezing delay times for varying levels of roughness will be compared, as well as for varying levels of surface energy. Once these experiments are performed, coatings for airplanes, as well as power lines, windshields, boats, etc. can be intelligently developed.

Four successful experiments have been carried out already. Two of the experiments yield initial data for comparisons among varying degrees of roughness for a metal (aluminum); in these

experiments, two trials per degree of roughness (one with a brushed satin, grade 4 finish and the other with a mirror, grade 8 finish) were done, all of which resulted in instantaneous onset of freezing (zero delay time). Additionally, two in-house developed coatings, with chemical make-ups of the same material in differing ratios and with varying contact angles, were tested (see the "Supporting Information" section for a description of these coating's chemistry). The coating with a contact angle between 130-140° and a more "sticky" surface exhibited a ten second freezing delay. The other coating, which had a contact angle greater than 150° and a rougher surface than the former, exhibited instantaneous freezing. At this time, due to limited data, no conclusions can be made about the effect of roughness, surface energy, contact angle or roll-off angle on freezing delay. However, the effectiveness of the assembled apparatus to quantify freezing delay for different surfaces has been demonstrated successfully.

SUPPORTING INFORMATION

The coatings in the experiments of Cao et al. used an acrylic polymer binder with silica surface particles, which varied in size according to desired surface roughness. The size of the silica particles ranged from 20 nm to 20 mm. The resin was composed of a consistent formula of styrene, butyl methacrylate and glycidyl methacrylate in toluene, using azodiisobutyronitrile (AIBN) as the initiator. It was stated that correlation between icephobicity and roughness will exist for any binder, particles or resin.

The in-house developed coatings used in the preliminary experiments discussed in the "Preliminary Results and Discussion" section of this paper consisted of PVDF 0.15 gm (0.75 gm 20% solution in DMF) with PMMA 0.10 gm (1.0 gm 10% solution in Acetone) and 0.38 wt% CNF dispersion (in DMF:Acetone = 40:60; where amount wt% CNF varied, per coating). The

coating which exhibited a ten second freezing delay had 8 wt% of CNF; the other, with instantaneous onset of freezing had 14 wt% of CNF. Both of the coatings were dried at 90°C for three hours; additionally, 1.08 gm of PTFE particle (~ 200 nm) in 9 gm of acetone was added in the final dispersion. CNF may also be referred to as PR24_XT_HHT.

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