Incorporation of Functionalized Polyhedral Oligomeric Silsesquioxane Nanomaterials as Reinforcing Agents for Impact Ice Mitigating Coatings.

Devon M. Beck[1], Joseph G. Smith Jr.[2], Christopher J. Wohl[2]
[1]NASA Internships and Fellowships, NASA Langley Research Center, Hampton, VA 23681, United States of America
[2]NASA Langley Research Center, Hampton, VA 23681, United States of America
joseph.g.smith@nasa.gov, c.j.wohl@nasa.gov

Introduction

In-flight, aircraft are exposed to a wide range of environments. One commonly exposed environment are clouds containing super-cooled water droplets. These water droplets exist in a metastable state below the freezing point of water, in the range of 0 to -20°C. As the vehicle impacts the droplets, latent heat is released and within milliseconds the droplets convert to ice. This process is referred to as impact icing or in-flight icing.[1]

Impact icing is a major concern for aircraft since it can lead to degraded aerodynamic performance and, if left untreated, can lead to loss of the vehicle. Active approaches (i.e., pneumatic boots, heated air ducts) typically utilized in mitigating in-flight ice accretion significantly increases vehicle weight and cannot be applied to all aircraft.[1-3] A passive approach based on coatings is desired, but durability issues are a concern, especially on the wing leading edge.[3]

Nanomaterials have been shown to afford significant improvement in coating and composite physical properties at low loading levels.[4] In this study, Polyhedral Oligomeric Silsesquioxane (POSS) nanomaterials have been shown to increase coating durability. Also, with wide variety of functionalities present on the arm structure, POSS nanomaterials have been shown to readily alter coating surface chemistry to mitigate impact ice adhesion from -16 to -8°C in a simulated in-flight icing environment.

Experimental

POSS based coatings were fabricated by dissolving POSS 1 and 2 in N,N'-dimethylformamide and POSS 3 and 4 in 2-heptanone (*Fig 1*). Solutions of POSS were incorporated at 0.5 and 1 wt% loading into a resin mixture of 1,3-bis(4-aminophenoxy)benzene hardener and Bisphenol A based diglycidyl ether epoxy resin (Control Coating) after 1 hour of B-Stage heating. The mixture was heated for an additional hour to further increase viscosity and ensure dispersion of POSS nanomaterials.

(POSS 1) R = Hydrophilic
(POSS 2) R = Binder Reacting
(POSS 3) R = Hydrophobic 1
(POSS 4) R = Hydrophobic 2

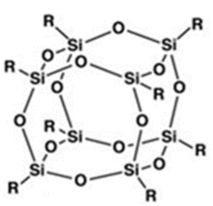

Figure 1: *POSS Cage Structure in T8 isomer form with varying R functionalities investigated in this study.*

Coating mixtures were then applied to treated aluminum (Al) substrates (i.e., disks and pucks). The surface treatment involved oxidizing the Al with Chemetall® and applying 3M's AC-131 sol-gel surface treatment. A controlled volume of coating was applied via a syringe to generate coatings of consistent thickness. The coated substrates were placed in a dry air box for 24 hours and subsequently cured at a 100°C for 2 hours and 177°C for 4 hours.

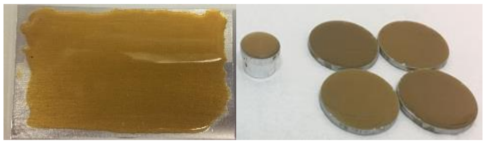

Figure 2: *Al substrates for coated samples.* ***On Left:*** *Panel for Stylus Profilometry and Contact Angle Goniometry.* ***Center:*** *Puck for Icing Testing.* ***Right:*** *Disks for Taber abrasion*

Coated pucks were analyzed for ice adhesion strength (IAS) on a custom-built laboratory-scale Adverse Environment Rotating Test Stand Jr (AERTS Jr).[5] AERTS Jr test parameters consisted of a liquid water content of 0.4-0.5g/m^3, a medium volume droplet size of 20µm, and a linear velocity of approximately 89 m/s. The samples were tested a minimum of three times at each of the test temperatures (-16, -12, and -8ºC). These test parameters were within the FAR Part 25/29 Appendix C guidelines for supercooled water droplet impact within the icing envelope.[6]

Coated disks were analyzed for abrasion resilience on a modified four mount Taber abrasion apparatus. Taber abrasion resistance was evaluated following ASTM D4060 using H18 wheels at 60 rpm over 1200 cycles.[9] Wear indexes were generated based on the mass loss calculation stated in the ASTM method. Surface roughness was measured before impact icing using a Bruker Dektak XT Stylus Profilometer. Measurements were conducted using a 12.5 µm tip at a vertical range of 65.5 µm with an applied force of 3 mg. Data were collected over a 1.0 mm length at a resolution of 0.056 µm/point. Five single line scans at different locations were collected and processed using a two-point leveling subtraction. The resultant arithmetic roughness (R_a) values were calculated. A First Ten Angstroms FTA 1000B goniometer was used to obtain contact angle data at ambient temperature using an 8 µL droplet of water deposited on the sample surface. Tilting axis measurement was utilized to determine receding and advancing contact angles. Interfacial tension measurements were made on a suspended droplet prior to testing to verify liquid purity and precision of the focused image. Contact angles were determined by droplet shape analysis.

Results and Discussion

In this work, epoxy based coatings containing POSS nanomaterials as fillers or as a reactive component to improve abrasion resistance were investigated. Functionalities on the POSS cage (*Fig. 1*) imparted either hydrophobic or hydrophilic characteristics to the coatings.

Ideal icephobic coatings have low surface roughness.[6] The small diameter of POSS nanomaterials (typically 1-3 nm) was anticipated to afford a minimal contribution to coating surface roughness. A minimal effect of POSS incorporation on R_a was shown. The most significant increase in roughness was observed for the 1.0wt% POSS 4 coating that increased by 31 nm in comparison to the control (*Table 1*).

Table 1: *Surface Roughness of POSS Coatings on AERTS Jr Pucks*

Sample	R_a (nm)	Sample	R_a (nm)
Control Coating	16 ± 14.1	0.5wt% POSS 3	29.4 ± 10
0.5wt% POSS 1	8.8 ± 4.2	1.0wt% POSS 3	33.6 ± 2.5
1.0wt% POSS 1	17.3 ± 14.6	0.5wt% POSS 4	8.8 ± 2.0
0.5wt% POSS 2	6.0 ± 2.0	1.0wt% POSS 4	47.4 ± 61.24
1.0wt% POSS 2	4.6 ± 1.2		

The effect of the various POSS nanomaterial incorporation upon advancing and receding water contact angles was investigated. As seen in *Fig. 3*, coatings incorporating hydrophilic and binder reacting POSS significantly decreased the advancing and receding water contact angles in comparison to the control coating. The opposite effect was observed by loadings of hydrophobic POSS which increased the advancing and receding contact angle. These results followed the expected trend with regards to hydrophilic and hydrophobic materials. In addition, it demonstrated that by changing the POSS functional arms the water contact angle can be altered, implying changes in surface chemistry in comparison to the control.

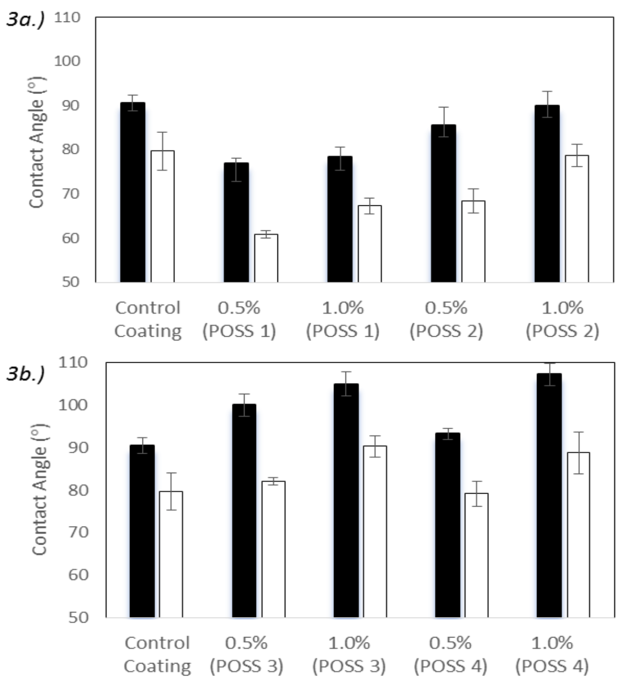

Figure 3: *Advancing (Filled) and Receding (Unfilled) water contact angles at a 60° Tilt.* ***A.)*** *Coatings containing hydrophilic (POSS 1) or binder reacting POSS (POSS 2).* ***B.)*** *Coatings containing hydrophobic POSS (POSS 3 or POSS 4).*

Modifications to the surface characteristics of the base resin with the various POSS functionalities provided significant changes in IAS performance that depended upon loading (*Fig. 4a - 4c)*. For hydrophobic POSS based coatings (POSS 3 and 4), the results were mixed where POSS 3 provided lower IAS compared to the control resin at -8°C whereas POSS 4 afforded little to an antagonistic performance. At -12°C, both hydrophobic POSS coatings afforded no benefit or increased IAS with respect to the control. POSS 4 showed an approximate 100% increase in IAS with respect to the base resin at a 1wt% loading which was unexpected. Hydrophilic POSS 1 afforded a similar loading dependency upon IAS relative to the base resin. In contrast to the hydrophobic POSS, the hydrophilic POSS performed better at -16°C (*Fig. 4a*) with minor a performance increase at -8°C that was not as dramatic as POSS 3 at a loading level of 0.5wt%.

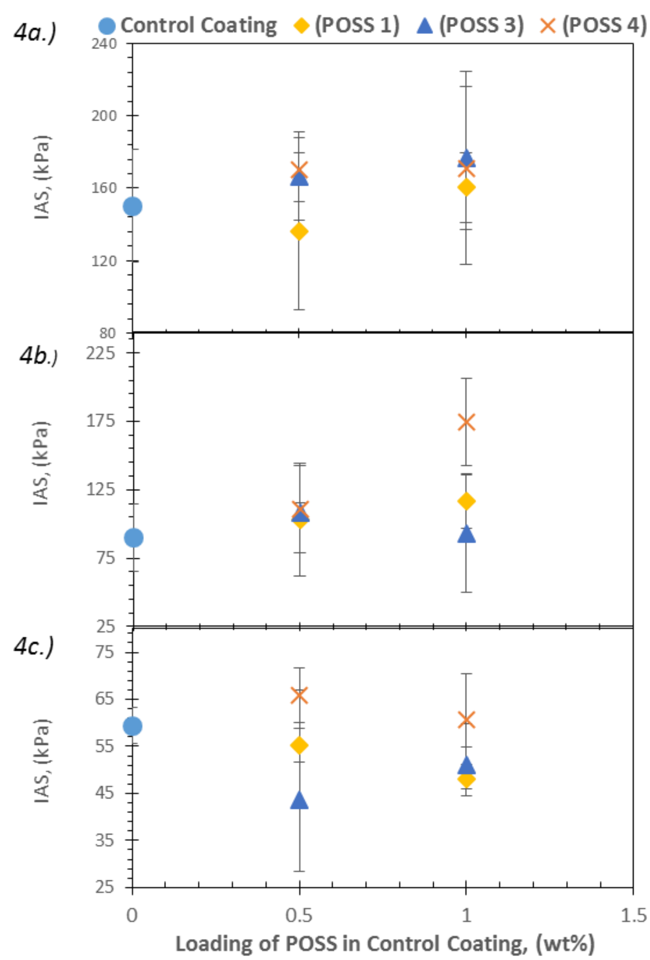

Figure 4: *Figure 4a, 4b, and 4c show results of AERTS Jr Testing of POSS based coatings at -16, -12, and -8°C, respectively.*

Table 2: *IAS values of 2024 T3 Clad Aluminum Alloy*

Test Temperature (°C)	-16	-12	-8
Average Ice Adhesion Strength, (kPa) 2024 T3 Clad Aluminum Alloy	397.46 ± 40.37	339.56 ± 48.18	140.43 ± 20.79

Adhesion Reduction Factors (ARF) were generated based on average IAS values obtained for uncoated 2024 T3 clad Al Alloy (*Table 2)* divided by the average IAS values from the best performing coatings with the results shown in *Fig. 5*. An ARF value of 1 describes the performance of the clad Al. Higher ARF values signify a performance improvement with respect to uncoated Al. As seen in *Fig. 5*, the hydrophobic and hydrophilic characteristic of the POSS additive showed opposing performance at the two test temperature extremes. At -16°C, the 0.5wt% loading of hydrophilic POSS 1 showed an approximate three-fold performance improvement while the 0.5wt% of hydrophobic POSS 3 also showed an approximate three-fold improvement at -8°C. Similar performance behavior was observed for functionalized monoalkoxysilanes.[8]

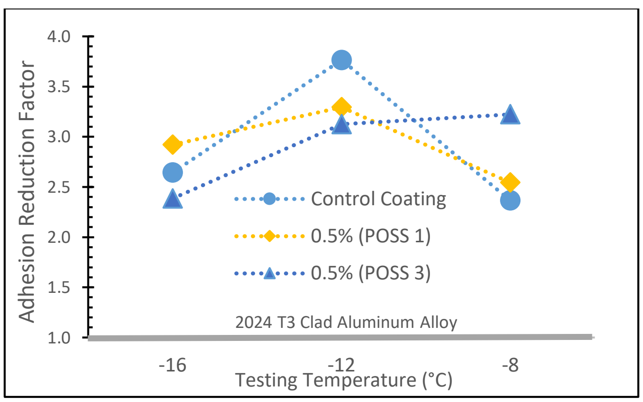

Figure 5: *Adhesion Reduction Factors of best performing POSS coatings for ice adhesion reduction.*

As previously stated, coatings for the wing leading edge need to be resilient to abrasion forces. Lower wear indexes show reduction in mass loss, implying improvements in coating resistance to shear force, according to the ASTM method. As shown in *Fig. 6*, freely dispersed POSS 1,3, and 4 reinforced coatings showed up to a 25% improvement in wear resistance than the control resin, while binder reacting POSS 2 showed no improvement in durability consequently they were not tested for IAS.

Conclusion

The addition of POSS nanomaterials into an epoxy based coating readily altered surface chemistry while not significantly affecting surface roughness. The effect the POSS additives had upon IAS depended on the functionality, loading percentage, and test temperature. POSS fillers improved abrasion resilience of the coating by up to 25% whereas

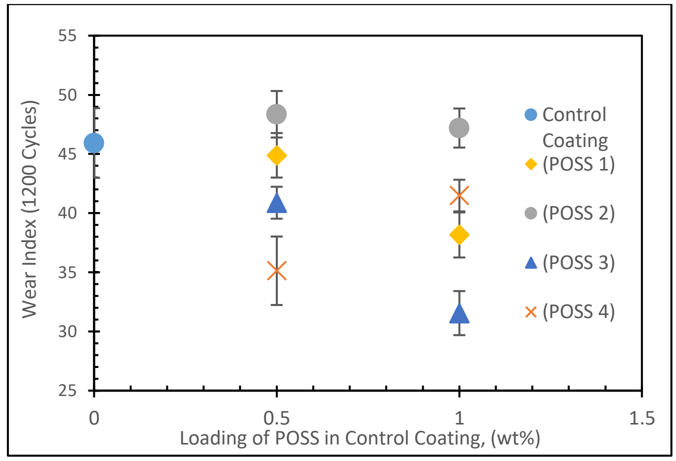

Figure 6: *Wear Index from Taber Abrasion Testing of 1200 Cycles.*

POSS that was incorporated within the matrix architecture showed no durability improvement. Overall, POSS fillers show promise for future low IAS coatings for aircraft.

Acknowledgements

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