

Effect of Molecular Flexibility upon Ice Adhesion Shear Strength

Joseph G. Smith Jr.¹, Christopher J. Wohl¹, Richard E. Kreeger²,
Jose Palacios³, Taylor Knuth³, and Kevin R. Hadley⁴

¹NASA Langley Research Center, Hampton, VA 23681, United States of America

²NASA Glenn Research Center, Cleveland, OH 44135, United States of America

³The Pennsylvania State University, University Park, PA 16802, United States of America

⁴South Dakota School of Mines and Technology, Rapid City, SD 57701, United States of America

joseph.g.smith@nasa.gov

Introduction

Icing is a major safety concern for aircraft whether on the ground or in-flight since it degrades aerodynamic performance leading to the eventual loss of lift if not addressed. Both ground and in-flight icing events are the consequence of super-cooled water droplets (SCWD) impacting the vehicle surface. Ground icing typically occurs at airports that experience cold weather events such as freezing rain/drizzle. In-flight icing, however, can happen anytime throughout the year when an aircraft travels through a cloud that contains freezing precipitation or SCWD.¹ The type of ice formed when this event occurs can vary from clear/glaze, rime, and mixed; the type depending on a number of environmental factors including air temperature (-5 to -20°C), liquid water content (0.3-0.6 g/m³), and SCWD size (median volumetric diameter of 15-40 μm) prevalent at the time of impact.

Methods currently used to address aircraft icing involve mechanical (e.g. pneumatic boots, heated surfaces) and chemical (e.g. ethylene- and propylene-based glycols) means. Some concerns with these approaches are that they may increase vehicle weight, utilize large amounts of energy, provide benefit only when activated or applied, and/or have potential negative environmental effects. One desirable solution to aircraft icing is one based on an icephobic or anti-icing coating that could be used independently or in conjunction with one of the more traditional approaches.

Coatings based on superhydrophobic surfaces (SHS)² and slippery liquid-infused porous surfaces (SLIPS)³ have been investigated. Delays in icing have been reported with SHS; however, durability and icing in humid environments are potential issues.² SLIPS have shown very good results with respect to ground testing. However, fluid loss due to gravity, for instance, may result in increased ice adhesion strength. Anti-freeze proteins that were incorporated into a coating have also shown promising results.⁴ Durability, though, has been observed to be an issue.

The strategy used to develop polymeric coatings that are discussed herein was based upon results obtained under a NASA Aeronautics Research Institute (NARI) Seedling activity where the effect of end group functionality and chain length upon ice adhesion shear strength (IASS) was investigated.⁵ Simulated icing conditions were generated in the Adverse Environment Rotor Test Stand (AERTS)⁶

facility for the determination of IASS. To compare coating performance, an adhesion reduction factor (ARF) was calculated according to Equation 1.⁷

$$\text{ARF} = \frac{(\text{IASS of uncoated Al surface})}{(\text{IASS of coated Al surface})} \quad (1)$$

An ARF > 1 implies ice did not adhere as well to the coating relative to the uncoated Al surface, whereas values < 1 indicate greater adhesion. In general, non-hydrogen bonding and hydrogen bonding accepting groups and molecular flexibility provided by aliphatic chain moieties were found to be desirable. These results were related back to impacting SCWD that undergo a phase transition to ice. As this change happens, the dispersive and polar components of the surface energy are dramatically altered resulting in ice exhibiting a nonpolar characteristic.

Based on the NARI study results, aromatic diamine monomers were prepared and incorporated into epoxy resins used to coat aluminum (Al) substrates. ARF values were found to be larger when molecular flexibility was incorporated in the polymer chain as opposed to a chain pendant to the polymer backbone.

Experimental

Aromatic diamines containing flexible aliphatic chains terminated with non-hydrogen bonding and hydrogen bonding accepting groups as a pendant group were prepared from the corresponding dinitro compound using known chemical reactions. In-chain flexibility was provided by the introduction of a linear aliphatic chain between the aromatic amine groups. These materials were characterized using ¹H and ¹³C nuclear magnetic resonance spectroscopy and attenuated total reflection Fourier-transform infrared spectroscopy. Coatings formulated from these diamines and a mixture of Bisphenol A and polyethylene glycol (PEG) epoxies in methylethyl ketone were spray coated onto Al 3003 panels. The coated panels were subsequently cured in flowing air at 125 and 177 °C for 2 and 4 h, respectively. Contact angle (CA) goniometry was performed on a First Ten Angstroms FTA 1000B goniometer at RT using an 8 μL drop of water. Surface roughness was determined 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 was collected over a 1.0 mm length at a resolution of 0.056 $\mu\text{m}/\text{point}$. Five single line scans at different locations were collected and processed using a two-point leveling subtraction. The resultant R_a (arithmetic roughness) and R_q (root mean square roughness) average values were calculated. IASS was determined on Al panels (10.16 cm x 15.24 cm, pristine and coated) in AERTS at -8, -12, and -16°C within the FAR Part 25/29 Appendix C icing envelope.⁸ The rotor was operated at 400 rpm in an icing cloud density (i.e. liquid water content) of 1.9 g/m^3 with a water droplet mean volumetric diameter of 20 μm . The same sample was tested in triplicate at all test temperatures commencing at -16°C and ending at -8°C. Two specimens of the same coating were evaluated during each test run due to the rotor configuration. As the rotor turned at speed, the accumulation and subsequent shedding of ice from the surface enabled IASS determination after data analysis and visual examination. Details of the test procedure are described in reference 6.

Results and Discussion

Small Compound Study

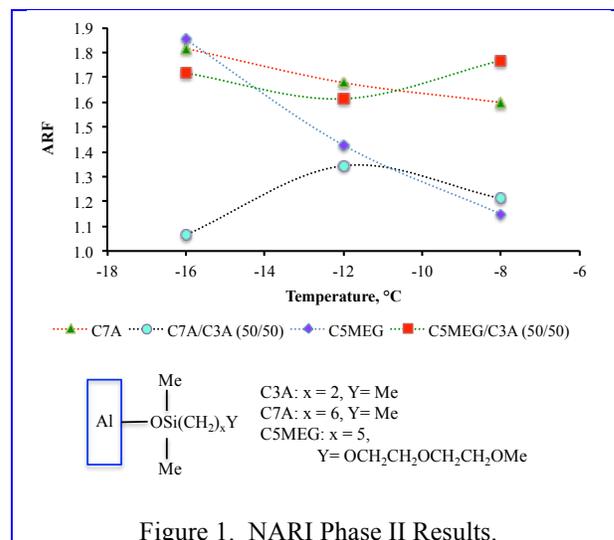
The best performing coatings from the NARI study displayed non-hydrogen bonding (C7A) and hydrogen bonding acceptor (C5MEG) effects with respect to water. The roughness of the samples listed in Table 1 suggested a smooth surface (ASTM A480 Finish #7).⁹ This allowed for comparison of IASS data based on calculated ARF values (Figure 1). The receding water CA for coated surfaces were greater than that observed for the control and followed the expected trend: non-hydrogen bonding > hydrogen bonding (acceptor). Incorporation of the neat moieties

Table 1: Small Compound Surface Characterization

Surface	R_a , μm	R_q , μm	Rec. Water CA, °
Aluminum Control	0.326 ± 0.048	0.388 ± 0.060	58
C7A	0.282 ± 0.105	0.354 ± 0.130	88
C7A/C3A (50/50)	0.430 ± 0.087	0.518 ± 0.097	87
C5MEG	0.390 ± 0.199	0.466 ± 0.217	79
C5MEG/C3A (50/50)	0.264 ± 0.022	0.344 ± 0.038	81

into a polymer matrix as a pendant group would afford a surface coverage less than 100%. To evaluate this dilution effect, mixed compositions with C3A were evaluated. Unexpectedly the receding water CAs for these mixed compositions were similar to that of the pure coating compositions (Table 1).

As shown in Figure 1, C7A displayed larger ARF values at -8 and -12°C than C5MEG that may be due to the longer persistence of the polar nature of SCWD as it transitioned to ice. At -16°C these two surfaces exhibited similar behavior. The ARF values at -8 and -12°C for C5MEG/C3A increased relative to C5MEG with a minor decrease at -16°C. The better performance of this mixture can be related to the improved accessibility of SCWD to the methoxyglycol unit. The mixed C7A/C3A composition showed a decrease at all test temperatures compared to



C7A suggesting a mechanism for ice to adhere to the surface due to isolated chains (i.e. molecularly rough surface) being exposed to SCWD.

Epoxy Coatings: Functionality as a pendant group

Aromatic diamines incorporating non-hydrogen bonding and hydrogen bonding accepting groups based on m-phenylene diamine (mPDA, Figure 2) were synthesized and confirmed by spectral characterization. The heptyl (C7) chain pendant to the aromatic ring provided the non-hydrogen bonding characteristic, while the hydrogen bonding accepting characteristic was afforded by methoxyethoxy (OEtOMe) and methoxy(ethoxy)₂ [(OEt)₂OMe] pendant chains. Coating solutions prepared from one of these substituted diamines or m-phenylene diamine and a mixture of Bisphenol A and PEG epoxies were spray coated onto Al substrates and thermally cured. The receding water CA and roughness values are listed in Table 2. Similar to coatings prepared from the small compound study, the surface roughness values indicated a smooth finish (ASTM A480 Finish #7). The receding water CAs were less than that for uncoated Al (58°), which is attributed to the presence of the PEG epoxy.

Table 2: mPDA Derivative Surface Characterization

Surface	R_a , μm	R_q , μm	Rec. Water CA, °
mPDA	0.127 ± 0.015	0.150 ± 0.020	46
mPDA-OEtOMe	0.170 ± 0.129	0.222 ± 0.162	46
mPDA-(OEt) ₂ OMe	0.156 ± 0.107	0.180 ± 0.117	50
mPDA-C7	0.126 ± 0.033	0.148 ± 0.038	50

IASS were obtained on AERTS under the same conditions as employed for the small compound study, allowing for direct comparison of the results. The expected trend, as temperature increased IASS decreased, was observed (data not shown). The ARF values for the epoxy coatings and the two mixed coatings from the small compound study are shown in Figure 2. All the epoxy coatings

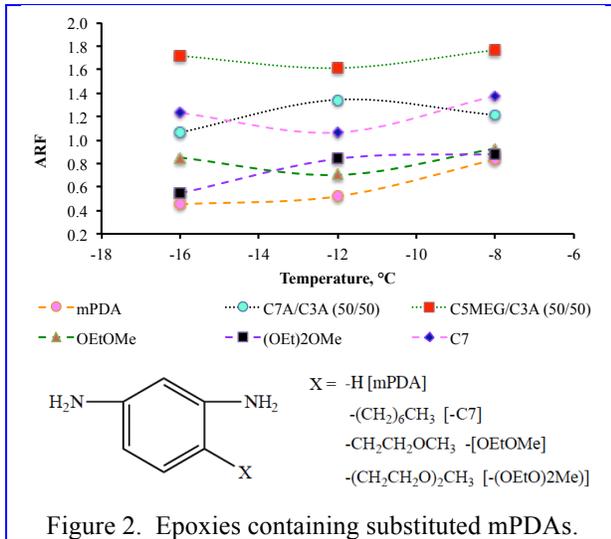


Figure 2. Epoxies containing substituted mPDAs.

with the exception of C7 exhibited greater adhesion to ice compared to bare Al as indicated by ARF < 1. The results for the hydrogen bonding acceptor coatings, OEtOMe and (OEt)2OMe, were similar except at -16°C. The greater adhesion displayed by (OEt)2OMe may be the result of the longer chain providing a clamping mechanism for ice. The ARFs for these two coatings were significantly lower than C5MEG/C3A. The difference in the connecting group between the aromatic ring and the silicon atom of the small compound (C5MEG) was a linear pentyl chain that may have provided molecular flexibility. The C7 epoxy had similar performance to C7A/C3A except at -12°C where the latter displayed lower ice adhesion.

Epoxy Coatings: In-chain flexibility

Since the pendant side chain may afford an attachment point for ice, it was of interest to investigate the effect in-chain molecular flexibility had upon IASS. Two diamine monomers were prepared and the structures confirmed spectrally (Figure 3). RM2-3 incorporated a hydrogen bonding (donor/acceptor) group in the form of an amide substituent as well as a branched non-hydrogen bonding group. Epoxy coated Al panels were fabricated as described above with the surface roughness and receding water CA summarized in Table 3. A smooth surface finish

Table 3: Surface Characterization

Surface	Ra, μm	Rq, μm	Rec. Water CA, $^\circ$
CM2	0.116 \pm 0.044	0.136 \pm 0.047	36
RM2-3	0.052 \pm 0.015	0.074 \pm 0.040	47

was indicated (ASTM A480 Finish #7 and #8) thus allowing for comparison of ARF values. The receding water CAs were less than that of uncoated Al due to the presence of the PEG epoxy. The IASS followed the expected trend (data not shown) with the calculated ARF values shown in Figure 3. The ARF values from the non-hydrogen bonding small compound (C7A) and pendant to the polymer chain

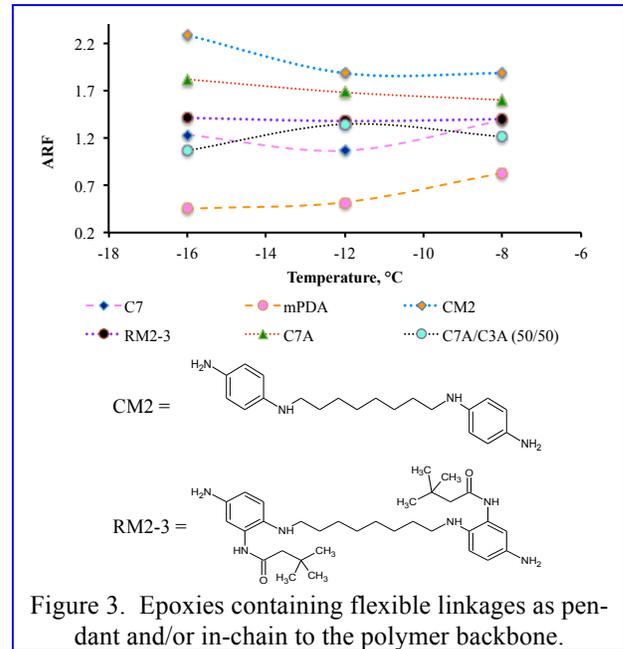


Figure 3. Epoxies containing flexible linkages as pendant and/or in-chain to the polymer backbone.

(C7) studies are included for comparison. The ARF values for CM2 were 1) comparable to the effect that C7A had in decreasing ice adhesion and 2) significantly greater than that for mPDA; both suggesting that in-chain flexibility was desirable. The addition of an amide pendant group (RM2-3) resulted in greater ice adhesion (i.e. decrease in the ARF values) compared to CM2 that may be due to the presence of the hydrogen bonding (donor/acceptor) characteristic of the amide functionality with regards to SCWD. The presence of the non-hydrogen bonding pendant heptyl aliphatic chain in C7 resulting in lower ice adhesion as compared to mPDA lends support to this observation.

Conclusions

ARF values of the epoxy coatings calculated from IASS data suggested that molecular flexibility of a non-hydrogen bonding functionality, located either pendant to or in the polymer backbone, was advantageous to reducing ice adhesion.

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