Hydrogen-Bonding Surfaces for Ice Mitigation: The Effect of Surface Chemical Functionality Upon Ice Adhesion

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Icing

- Ground problem during cold months
  - Freezing drizzle/rain
- In-flight problem year round
  - Results from super-cooled water droplets impacting the aircraft surface while flying through a cloud
  - Most occurrences are between 0 and -20°C

Icing types encountered in-flight

- Glaze/Clear, Rime, Mixed
- Dependent upon
  - Air temperature (0 to -20°C)
  - Liquid water content (0.3-0.6 g/m³)
  - Droplet size (median volumetric diameter of 15-40 µm)

Background

Glaze/Clear
- Large droplets
- Clear, nearly transparent, smooth, waxy thus hard to see
- Gradual freezing after droplet impact can result in runback along surface generating raised edges (i.e. horns)
- Difficult to remove

Rime
- Small droplets
- Brittle and opaque, milky appearance
- Rapid freezing after droplet impact with growth into the airstream
- Easier to remove than glaze

Mixed
- Variable droplet size
- Combination of glaze and rime ice

Background

❄ Current alleviation strategies

- Pneumatic boots
- Heated surfaces
- De-icing fluids (i.e., ethylene- and propylene-based glycols)

❄ A passive approach mitigating ice adhesion during the entire aircraft flight profile is desirable.

- Superhydrophobic surfaces¹
- Surfaces containing anti-freeze proteins²
- Slippery liquid-infused porous surfaces³
- Aqueous lubricating layer⁴

Objective

To assess the effect of surface chemical functionalization upon ice adhesion shear strength (IASS).

Approach

Investigate coated surfaces having controlled chemical functionality and carbon chain length between the substrate surface and the chemical functionality.

- Prepare and characterize substituted alkyldimethylalkoxysilanes containing Hydrogen Bonding (HB) and non-HB groups.
  - ATR-FTIR, NMR (\textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{29}Si)
- Prepare and characterize aluminum (Al) substrates coated with pure and mixtures of alkyldimethylalkoxysilanes containing HB and non-HB groups.
  - Contact Angle Goniometry
- Determine IASS of coated Al substrates in a simulated environment with comparison to uncoated Al.
  - Adverse Environment Rotor Test Stand
Substituted Dimethylalkoxysilanes

- Non-hydrogen bonding
  - Aliphatic
    - \( x = 2 \) (C3A), 6 (C7A), 10 (C11A)

- Hydrogen-bonding (donor/acceptor)
  - Hydroxyl
    - \( X = -, \ y = 7 \) (C7H), 10 (C10H), 11 (C11H)
  - EG
    - \( X = -\text{OCH}_2\text{CH}_2-, \ y = 2 \) (EG)

- Hydrogen-bonding (acceptor)
  - C5MEG
    - \( R = -\text{CH}_2\text{CH}_2\text{OCH}_3, \ y = 5 \)

\[
\begin{align*}
\text{H}_3\text{CH}_2\text{C} & \quad \text{O} \quad \text{Si} \quad \left( \text{CH}_2 \right)_x \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\left[ \text{CH}_3 & \quad \text{Si} \quad \left( \text{CH}_2 \right)_y \quad \text{X} \\
\text{O} & \quad \text{Si} \quad \left( \text{CH}_2 \right)_y \quad \text{X} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{CH}_2\text{C} & \quad \text{O} \quad \text{Si} \quad \left( \text{CH}_2 \right)_y \quad \text{OR} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]
Coating Al Substrate I

\[
\begin{align*}
\text{H}_3\text{CH}_2\text{C} & \text{O} \text{Si} \left(\text{CH}_2\right)_x \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3
\end{align*}
\]

\[
\text{HOAc, EtOH, H}_2\text{O} \quad \text{CH}_2\text{Cl}_2, \text{RT}
\]

\[
\begin{align*}
\text{HO} & \text{Si} \left(\text{CH}_2\right)_x \text{CH}_3 \\
\text{CH}_3 & \text{CH}_3
\end{align*}
\]

Al
\[
\text{OH} + \text{HO} \text{Si} \left(\text{CH}_2\right)_x \text{CH}_3
\]

Non-hydrogen bonding
- Aliphatic
  - \( x = 2 \) (C3A), 6 (C7A), 10 (C11A)

Same method for Hydrogen-bonding (acceptor)
- C5MEG
  - \( R = -\text{CH}_2\text{CH}_2\text{OCH}_3, \ y = 5 \)

Coating Al Substrate II

$$\text{HOAc, EtOH, H}_2\text{O} \xrightarrow{\text{CH}_2\text{Cl}_2, \text{RT}} \text{HO-Si-(CH}_2)_y\text{X-OH}$$

Al\(\text{OH} + \text{HO-Si-(CH}_2)_y\text{X-OH} \rightarrow \text{Al-O-Si-(CH}_2)_y\text{X-OH}\)

Hydrogen-bonding (donor/acceptor)
- Hydroxyl
  - \(X = -, y = 7 \text{ (C7H)}, 10 \text{ (C10H)}, 11 \text{ (C11H)}\)
- EG
  - \(X = -\text{OCH}_2\text{CH}_2-, y = 2 \text{ (EG)}\)
Receding Water Contact Angle

Water Receding Contact Angle, °

Lower Ice Adhesion Strength
Al Control
Higher Ice Adhesion Strength

Pennsylvania State University

Testing performed under simulated icing conditions.

- Super-cooled water injected into test chamber.
- Tests conducted from -8 to -16°C; commenced at -16°C
- Icing cloud density (i.e. liquid water content) of 1.9 g/m³
- Water droplet mean volumetric diameter of 20 µm

Ice accumulation and subsequent shedding enabled determination of Ice Adhesion Shear Strength after data analysis and visual assessment.

One Component Coatings
Non-HB: Chain Length Effect

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

Al

CH₃

Si

(CH₂)xCH₃

CH₃

x = 2 (C3A), 6 (C7A), 10 (C11A)

HB (donor/acceptor): Chain Length Effect

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

Al Control  C7H  C10H  C11H  EG

X = --,  y = 7 (C7H), 10 (C10H), 11 (C11H)
X = -OCH₂CH₂-,  y = 2 (EG)

HB (acceptor)

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

Al

CH₃

CH₂

OCH₂CH₂OCH₃

C5MEG

Functional Group and Chain Length

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

C7A  C7H  C11A  C11H

Functional Group: Similar Chain Length

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

Al Control  C11A  C10H  C11H  C5MEG

Aliphatic (non-HB)
- Minimum chain length (C7A) needed to decrease interaction of ice with the substrate (C3A)
- Long chain length (C11A) resulted in coating degradation
- Performance compared to HB series dependent on chain length

Hydroxy1 and EG (HB donor/acceptor)
- Not much difference in IASS between test temperatures
- Long chain (C10H, C11H) performed better
- EG performance similar to C7H

C5MEG (HB acceptor)
- Functional group performance similar to C7A
- Comparable chain length performance
  - HB donor/acceptor (C10H, C11H) resulted in lower IASS
  - C11A (non-HB) degraded
- In general, performed better than EG
Two Component Coatings
Non-HB: Different Chain Lengths

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

Al Control  0  50  100

C7A in C3A/C7A coatings, %

C3A and C7A are represented by their chemical structures with varying chain lengths.

Increasing HB Content: Different Chain Lengths


Ice Adhesion Shear Str., kPa

C7H in C3A/C7H coatings, %
Increasing HB Content: Similar Chain Lengths

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

C7H in C7A/C7H coatings, %

Increasing HB Content: Different Chain Lengths

![Graph showing ice adhesion shear strength at different temperatures and C10H content in C7A/C10H coatings.](image)

-8°C  -12°C  -16°C

C10H in C7A/C10H coatings, %

Increasing HB Content: Different Chain Lengths

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

EG in EG/C3A coatings, %

Al Control  0  25  50  100

Increasing HB (acceptor) Content: Different Chain Lengths

Ice Adhesion Shear Str., kPa

Al Control
0
50
100
C5MEG in C3A/C5MEG coatings, %

-8°C -12°C -16°C

Increasing HB (acceptor) Content: Different Chain Lengths

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

C5MEG in C7A/C5MEG coatings, %

Increasing HB (acceptor) Content: Different Chain Lengths

Ice Adhesion Shear Str., kPa

-8°C  -12°C  -16°C

C5MEG in C7H/C5MEG coatings, %

Two Component Coating Summary

❄ **Aliphatic (non-HB)**
  - IASS increased with increasing short chain (C3A) component.

❄ **HB (donor/acceptor) and Aliphatic (non-HB)**
  - General - Increasing HB component (Hydroxyl) increased IASS
    - Exception -16°C where IASS comparable
    - C7A/C10H suggested degradation, base components exhibited no degradation

❄ **EG/C3A**
  - 25% EG inclusion exhibited comparable performance to C3A
  - 50% EG inclusion
    - Better performance than C3A at -8 and -12°C
    - Worse performance at -16°C
Two Component Coating Summary

- HB (acceptor) and Aliphatic (non-HB)
  - Performance dependent upon non-HB chain length
    - C3A afforded lower IASS compared to C7A
      - Presumably due to better accessibility of in-chain ether group to water
    - C5MEG/C3A overall performance better than EG/3A 50/50

- HB (acceptor) and HB (acceptor/donor)
  - In general - performance not as good as HB (acceptor) alone
  - Data suggested coating degradation
Receding Water Contact Angle

Lower Ice Adhesion Strength
Al Control
Higher Ice Adhesion Strength

Conclusions

❄ Effect of coating composition on IASS is complex
  • One component coatings
    • Chain length effect upon IASS is functional group dependent
    • No clear trend observed between functional groups
  • Two component coatings
    • More relevant when incorporating functionalities into polymeric systems
    • General – increasing HB content (HB donor/acceptor) increased IASS
    • Mixed chain length effect upon IASS is composition-functional group dependent
Future Work

- Develop monomers with pendant groups based on non-HB and HB (acceptor) effects
- Prepare epoxies based on the developed monomers
- Test epoxy coated Al samples in AERTS to determine IASS

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