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

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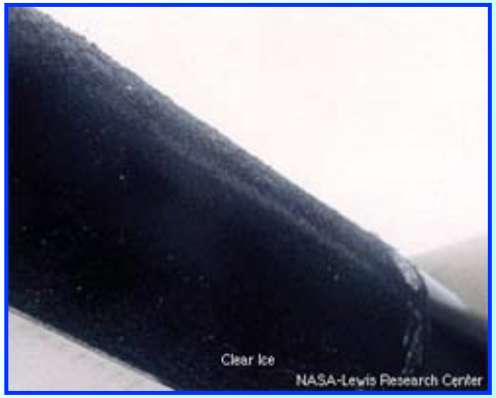
Background

- 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/m^3)
    - Droplet size (median volumetric diameter of 15-40 μm)

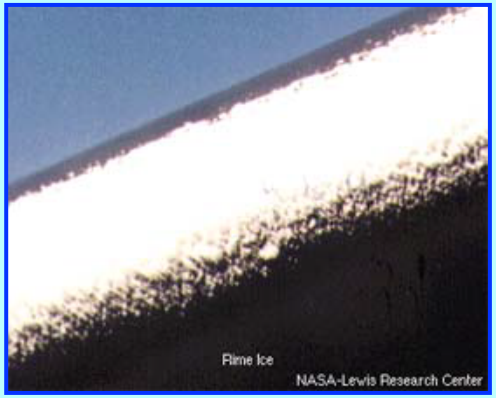
M.K. Politovich, “Aircraft Icing” in Encyclopedia of Atmospheric Sciences, Academic Press, Oxford, 2003, 68-75.
H.E Addy Jr., M.G. Potapczuk, and D.W. Sheldon, “Modern Airfoil Ice Accretions,” NASA TM 107423, 1997.

Background



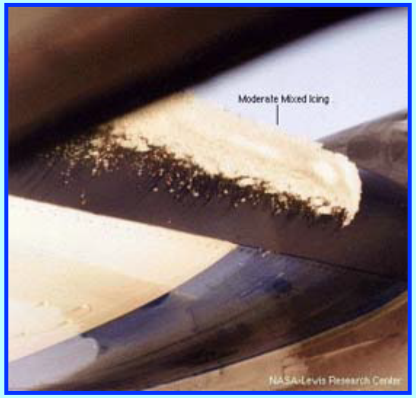
Glaze/Clear

- 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

M.K. Politovich, "Aircraft Icing" in Encyclopedia of Atmospheric Sciences, Academic Press, Oxford, 2003, 68-75.
H.E Addy Jr., M.G. Potapczuk, and D.W. Sheldon, "Modern Airfoil Ice Accretions," NASA TM 107423, 1997.

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 surfaces[1]
  - Surfaces containing anti-freeze proteins[2]
  - Slippery liquid-infused porous surfaces[3]
  - Aqueous lubricating layer[4]

1. S.A. Kulinich et. al., *Langmuir*, 27 (2011) 25-29.
2. Anitei, S. Fish 'Antifreeze' Against Icy Aeroplanes. Aug. 8, 2007; http://news.softpedia.com/news/Fish-Antifreeze-Against-Icy-Aeroplanes-62189.shtml
3. L. Mishchenko, et. al.,"Design of Ice-free Nanostructured Surfaces Based on Repulsion of Impacting Water Droplets," ACS Nano, 4 (2010) 7699-7707.
4. R. Dou et.al., "Anti-icing Coating with an Aqueous Lubricating Layer," ACS Appl. Mater. Interfaces (2014).

Objective

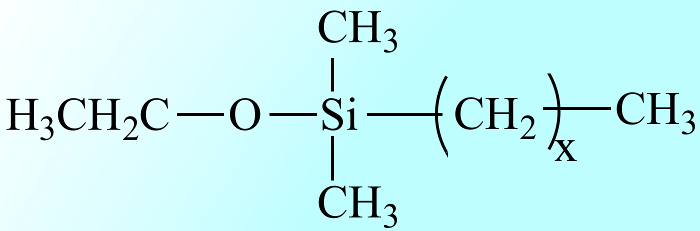
To assess the effect of surface chemical functionalization upon ice adhesion shear strength (IASS).

Approach

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

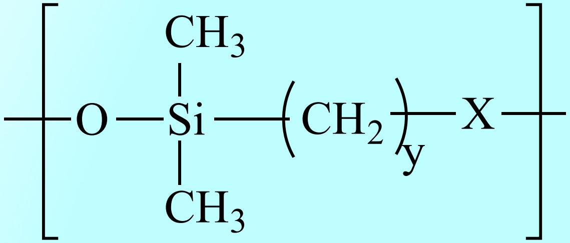
- Prepare and characterize substituted alkyldimethylalkoxysilanes containing Hydrogen Bonding (HB) and non-HB groups.
  - ATR-FTIR, NMR (^{1}H, ^{13}C, ^{29}Si)
- Prepare and characterize aluminum (Al) substrates coated with pure and mixtures of alkyldimethylalkoxysilanes containing HB and non-HB groups.
  - 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

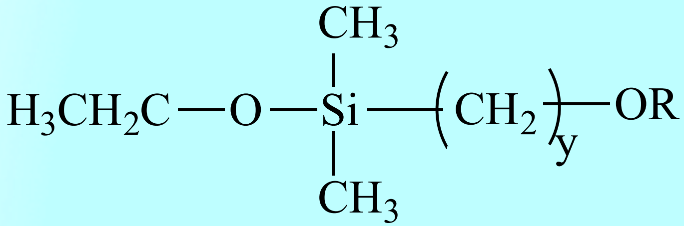
    x = 2 (C3A), 6 (C7A), 10 (C11A)



- Hydrogen-bonding (donor/acceptor)
  - Hydroxyl

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

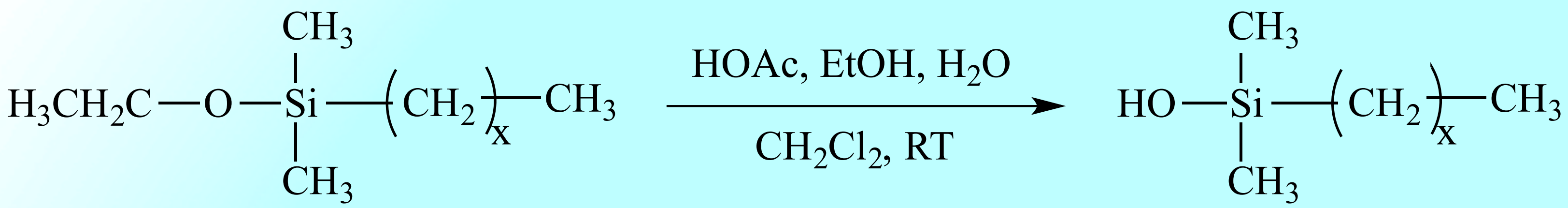
    X = $-OCH_2CH_2-$, y = 2 (EG)

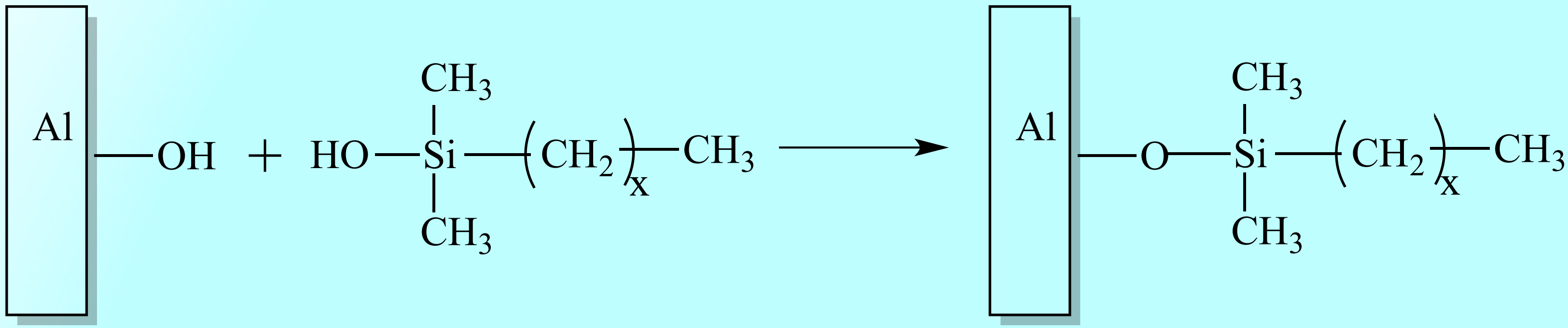


- Hydrogen-bonding (acceptor)
  - C5MEG

    R = $-CH_2CH_2OCH_3$, y = 5

Coating Al Substrate I





Non-hydrogen bonding

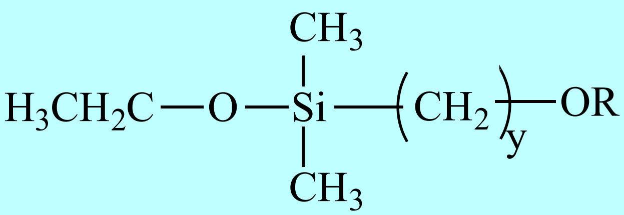
- Aliphatic

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

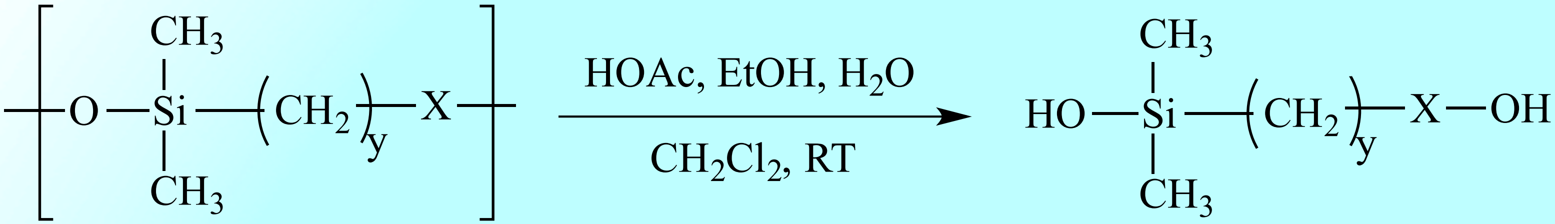
Same method for Hydrogen-bonding (acceptor)

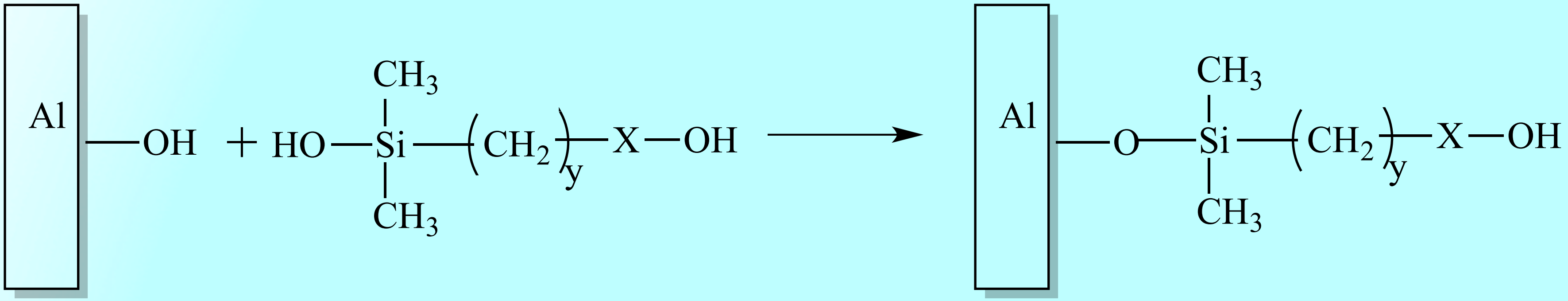
- C5MEG

  $R = -CH_2CH_2OCH_3$, $y = 5$



Coating Al Substrate II

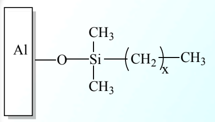




Hydrogen-bonding (donor/acceptor)

- Hydroxyl
  X = -, y = 7 (C7H), 10 (C10H), 11 (C11H)
- EG
  X = $-OCH_2CH_2-$, y = 2 (EG)

Receding Water Contact Angle



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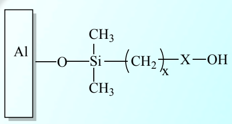
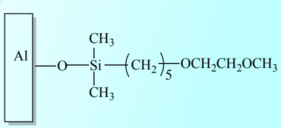
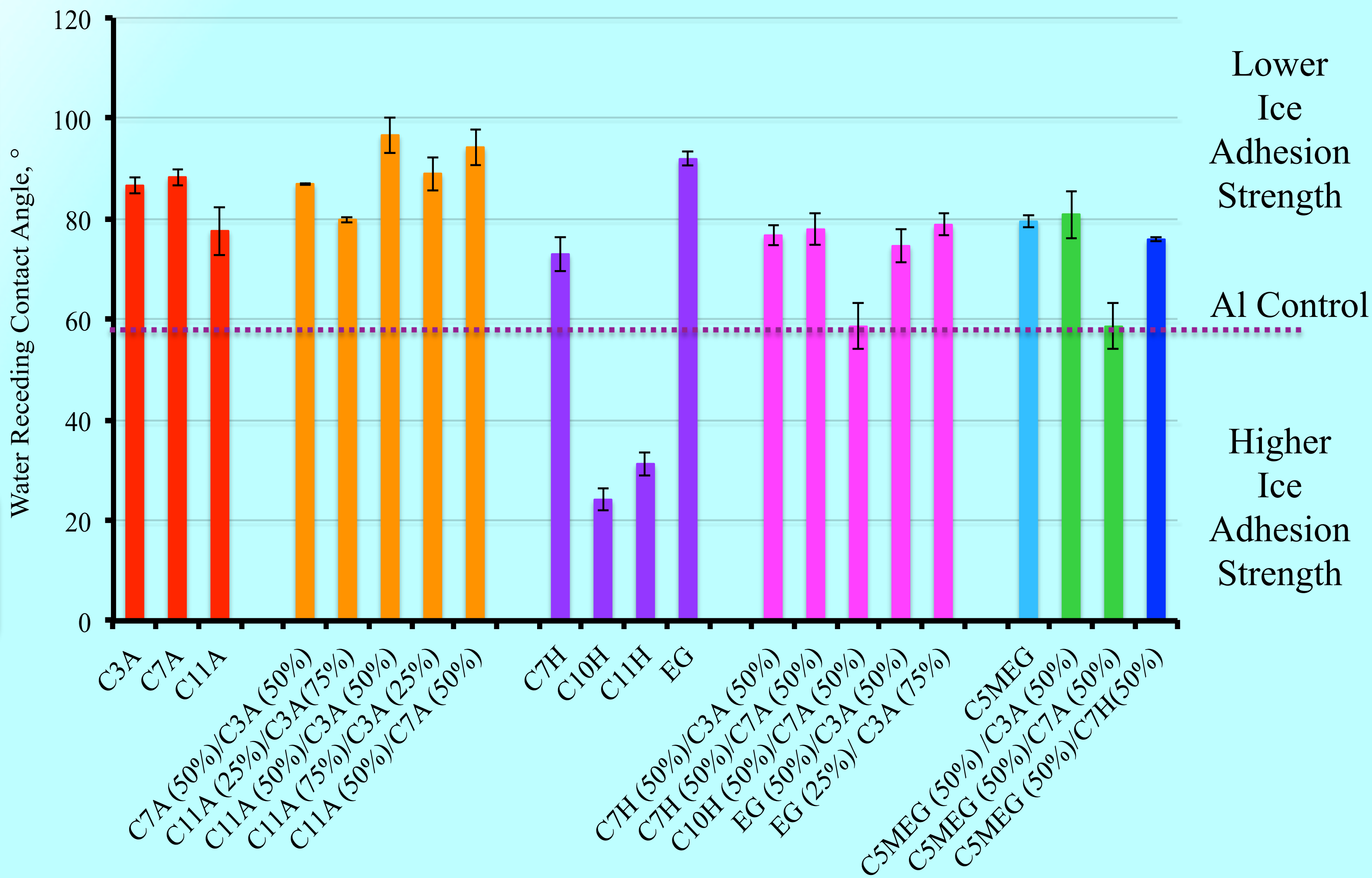


- X = --, y = 7 (C7H), 10 (C10H), 11 (C11H)
- X = $-OCH_2CH_2-$, y = 2 (EG)

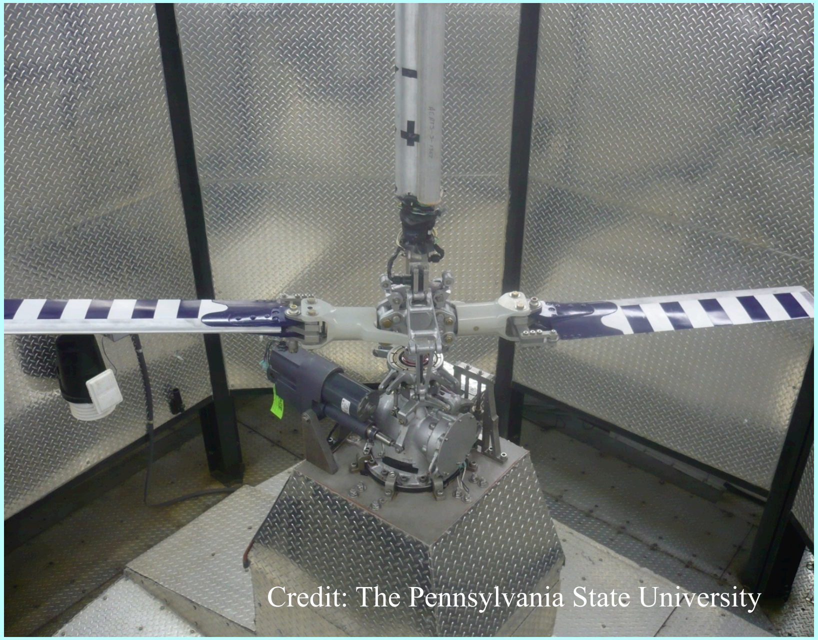


- C5MEG



Adverse Environment Rotor Test Stand

- 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/m^3
  - Water droplet mean volumetric diameter of 20 μm

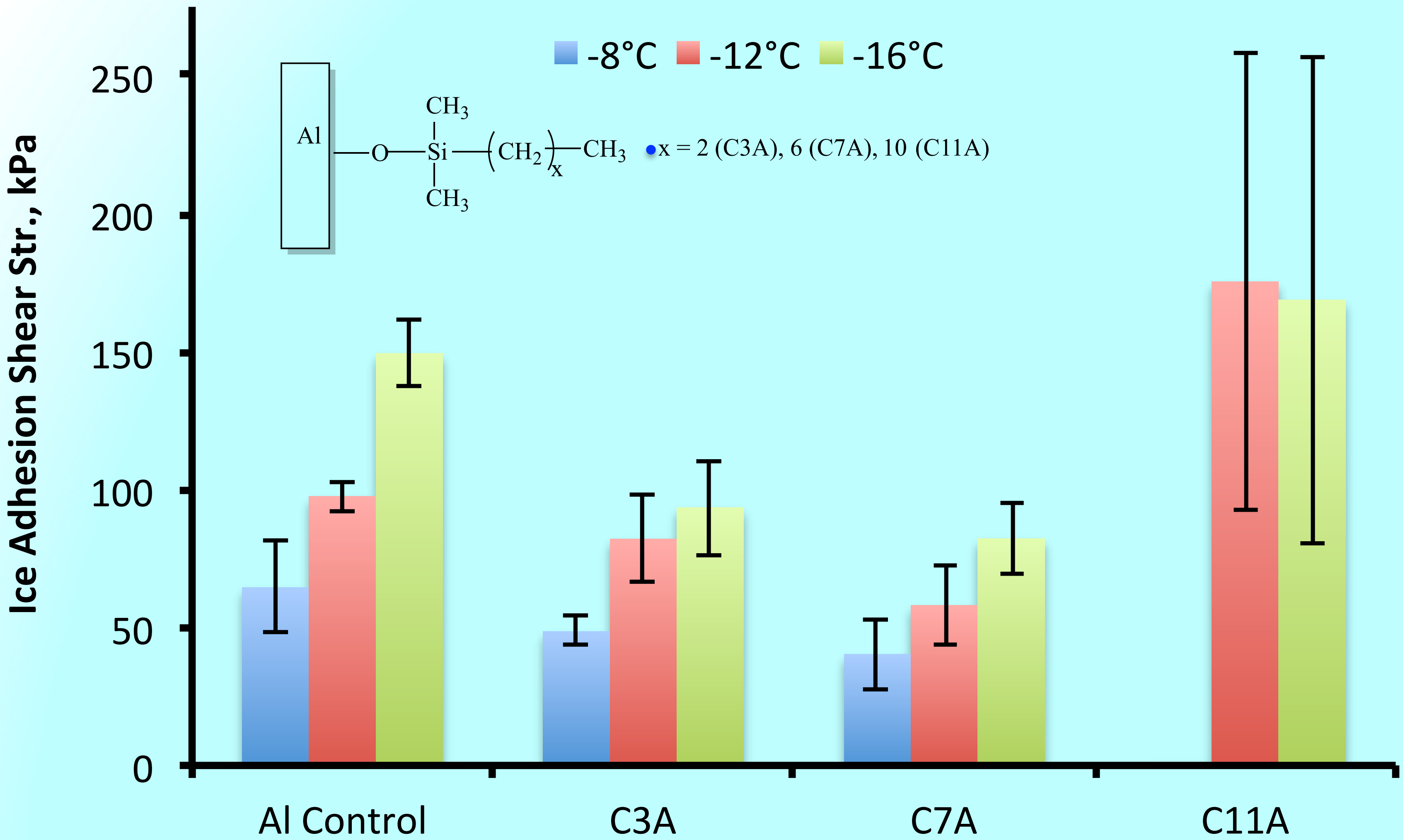


Credit: The Pennsylvania State University

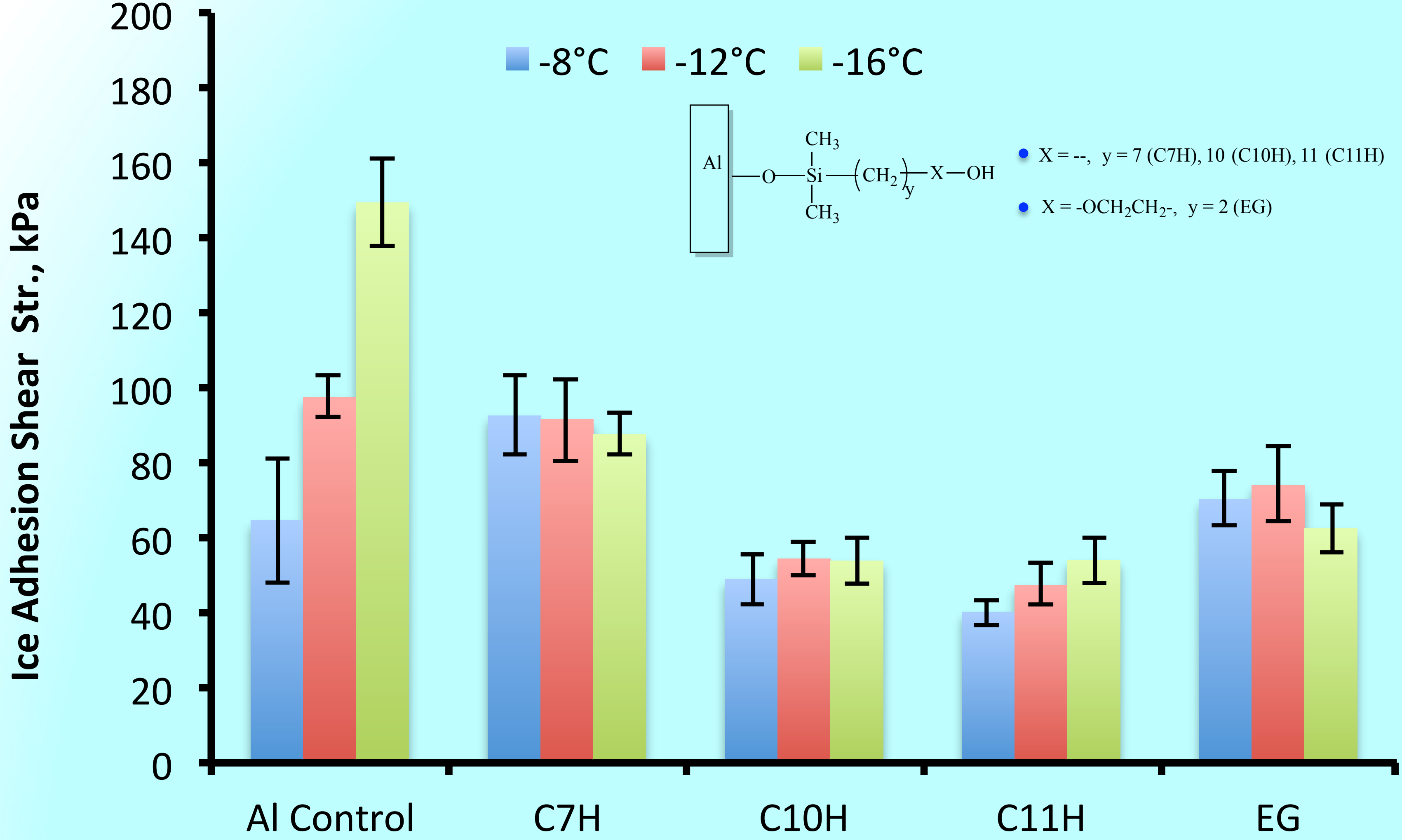
- Ice accumulation and subsequent shedding enabled determination of Ice Adhesion Shear Strength after data analysis and visual assessment.
- Experimental details discussed in J. Soltis, J. Palacious T. Eden, and D. Wolfe, "Evaluation of Ice Adhesion Strength on Erosion Resistant Materials," 54th AIAA/ ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, April 8-11, 2013, Boston, MA, AIAA 2013-1509.

One Component Coatings

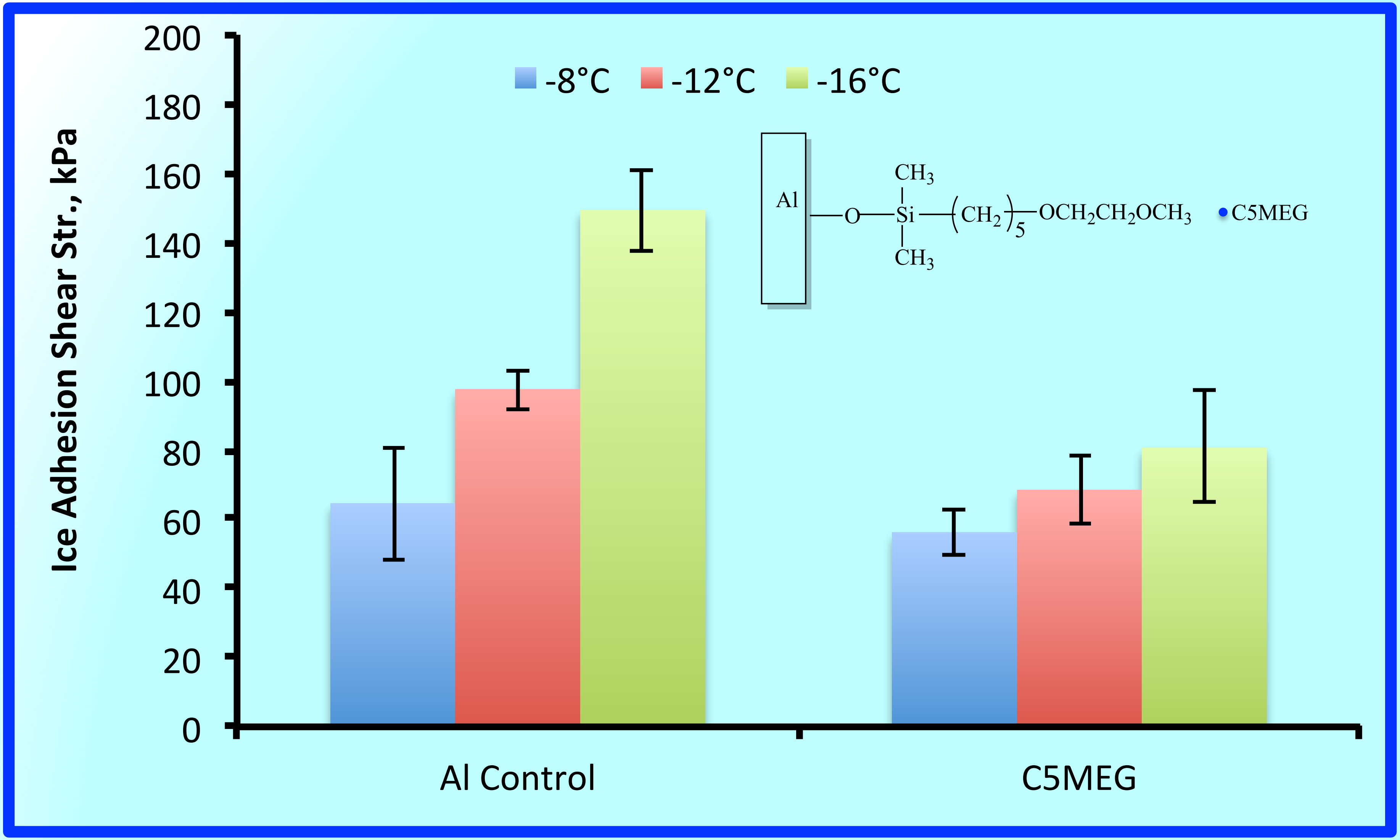
Non-HB: Chain Length Effect



HB (donor/acceptor): Chain Length Effect

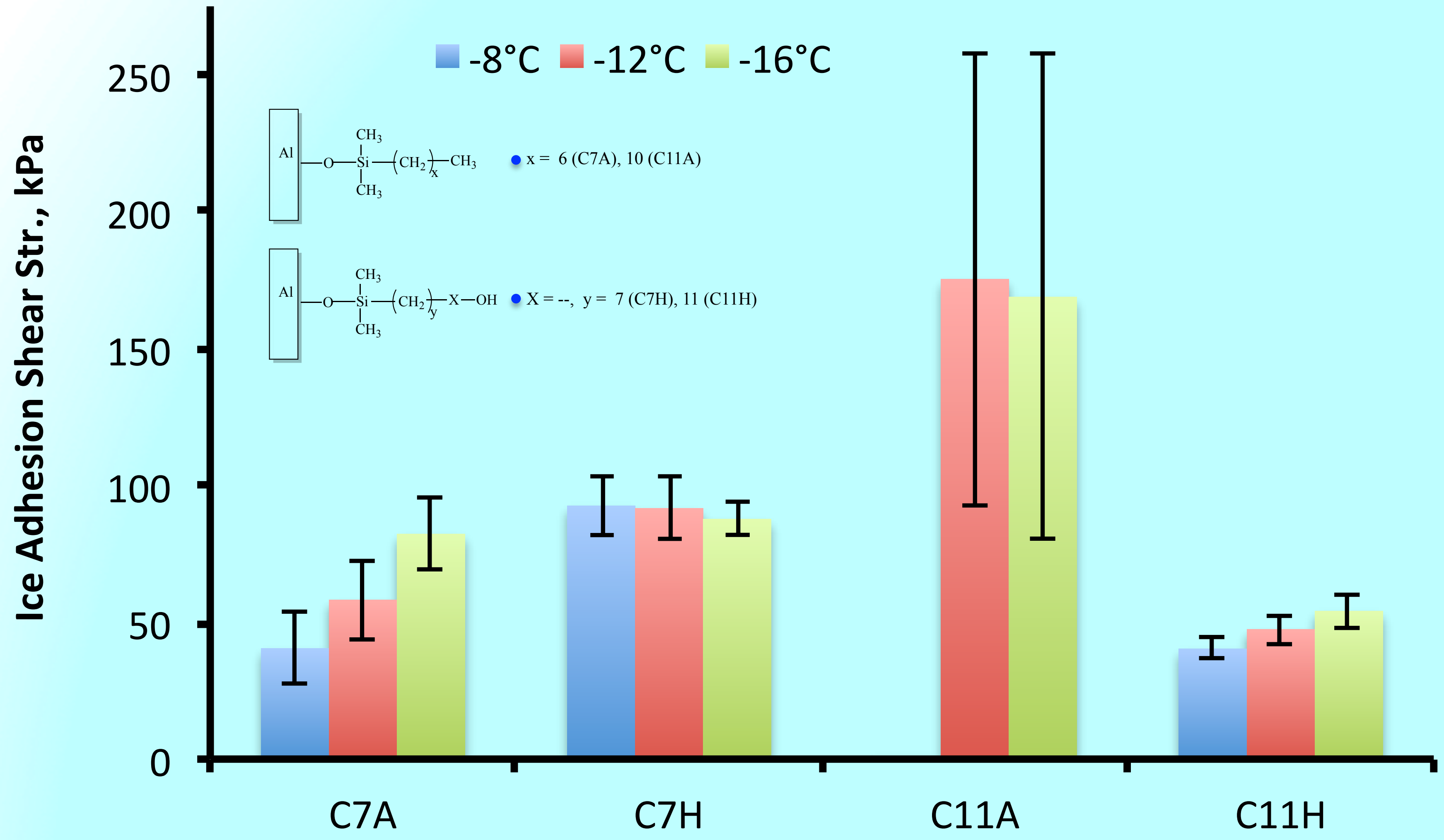


HB (acceptor)

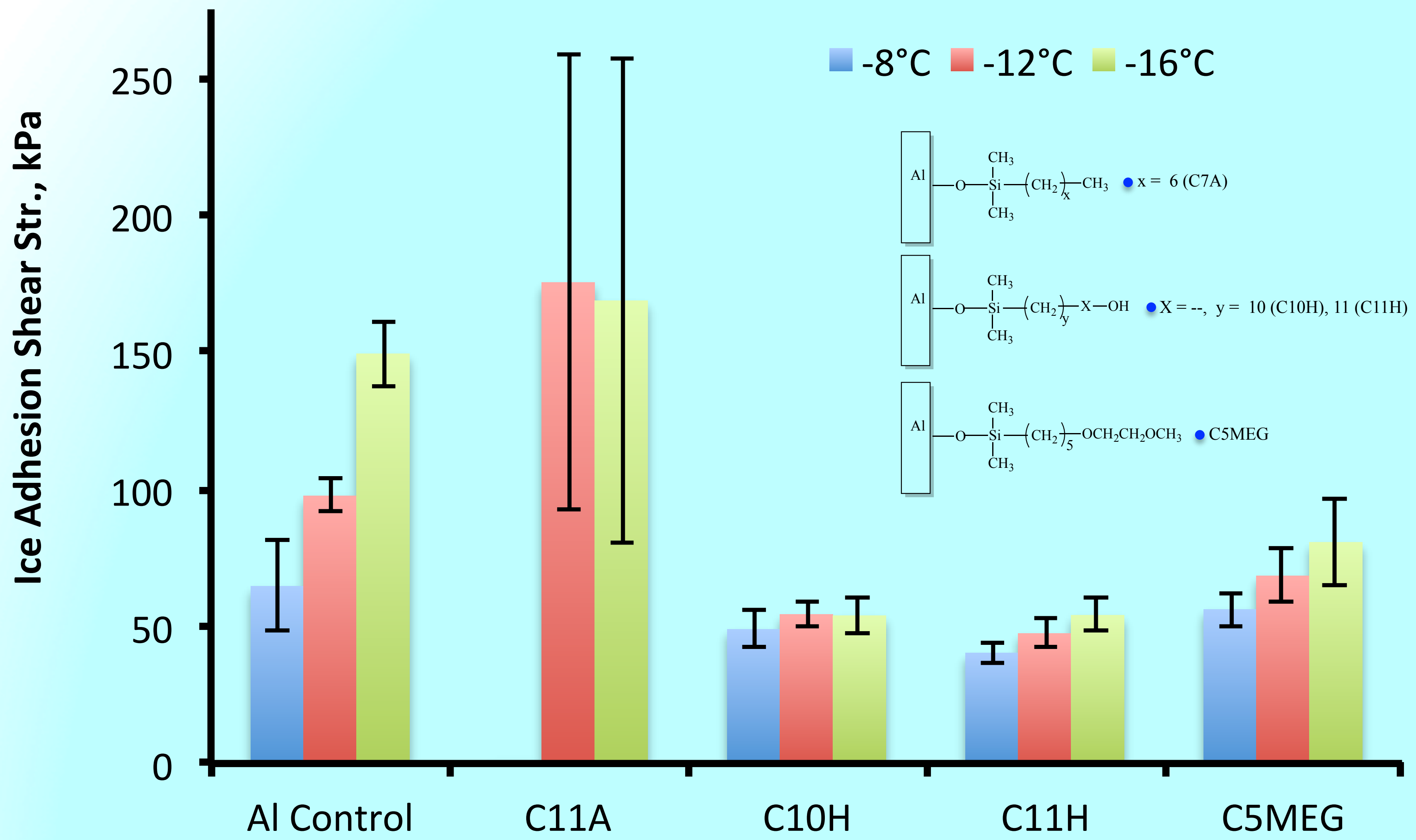


-8°C
-12°C
-16°C
Ice Adhesion Shear Str., kPa
0
20
40
60
80
100
120
140
160
180
200
Al Control
C5MEG
Al
O
Si
CH3
CH3
(CH2)5
OCH2CH2OCH3
C5MEG

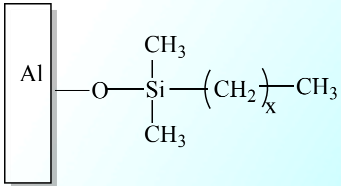
Functional Group and Chain Length



Functional Group: Similar Chain Length

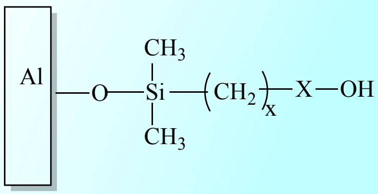


One Component Coating Summary



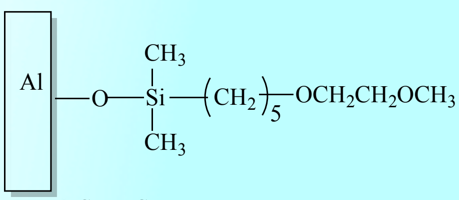
- x = 2 (C3A), 6 (C7A), 10 (C11A)

- 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



- X = --, y = 7 (C7H), 10 (C10H), 11 (C11H)
- X = $-OCH_2CH_2-$, y = 2 (EG)

- 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

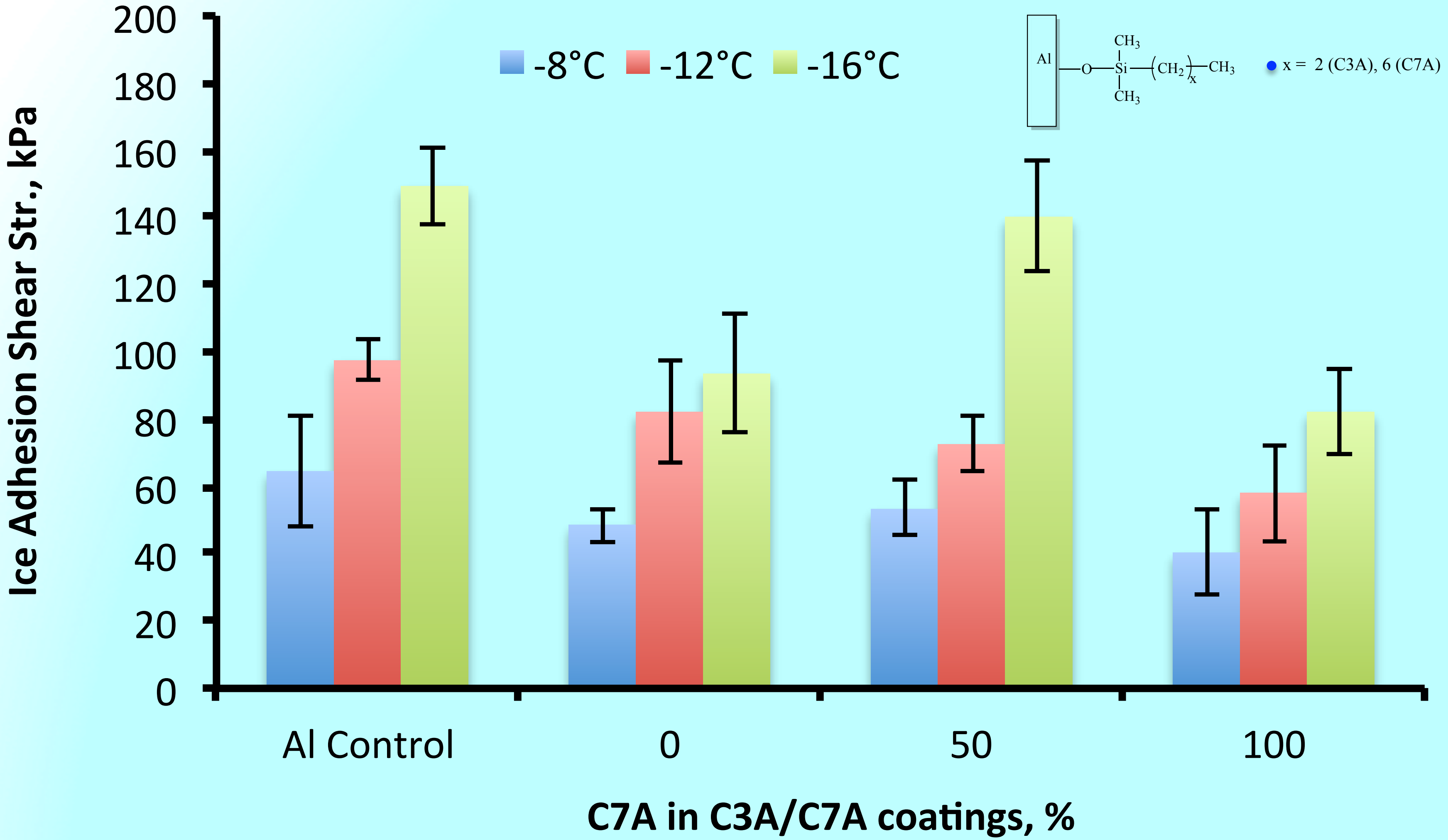


- C5MEG

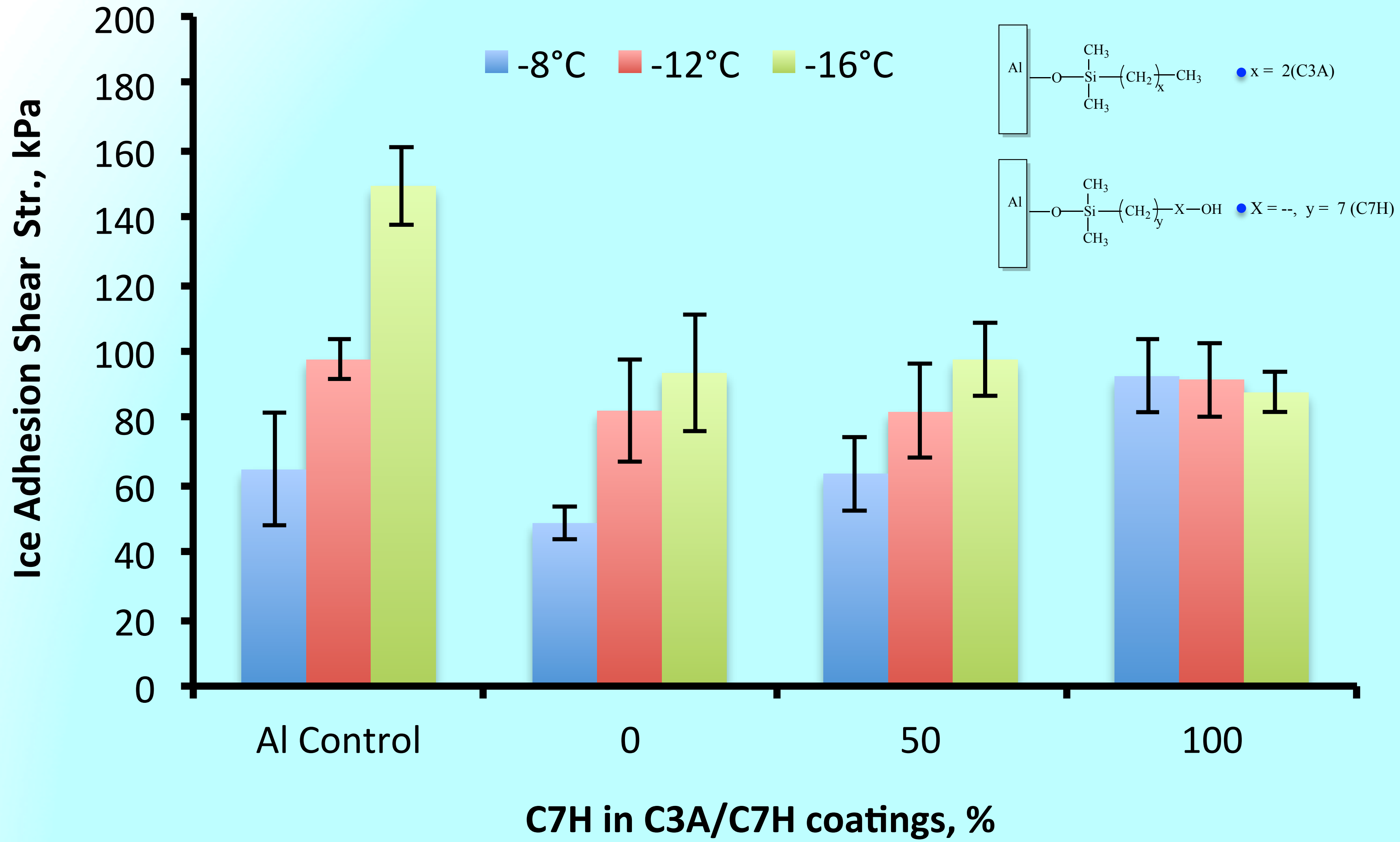
- C5MEG (HB acceptor)
  - Functional group performance similar to C7A
  - Comparable chain length performance
    - HB donor/acceptor (C10H, C11H) resulted in lower IASS
    - C11A (non-HB) degraded
  - In general, performed better than EG

Two Component Coatings

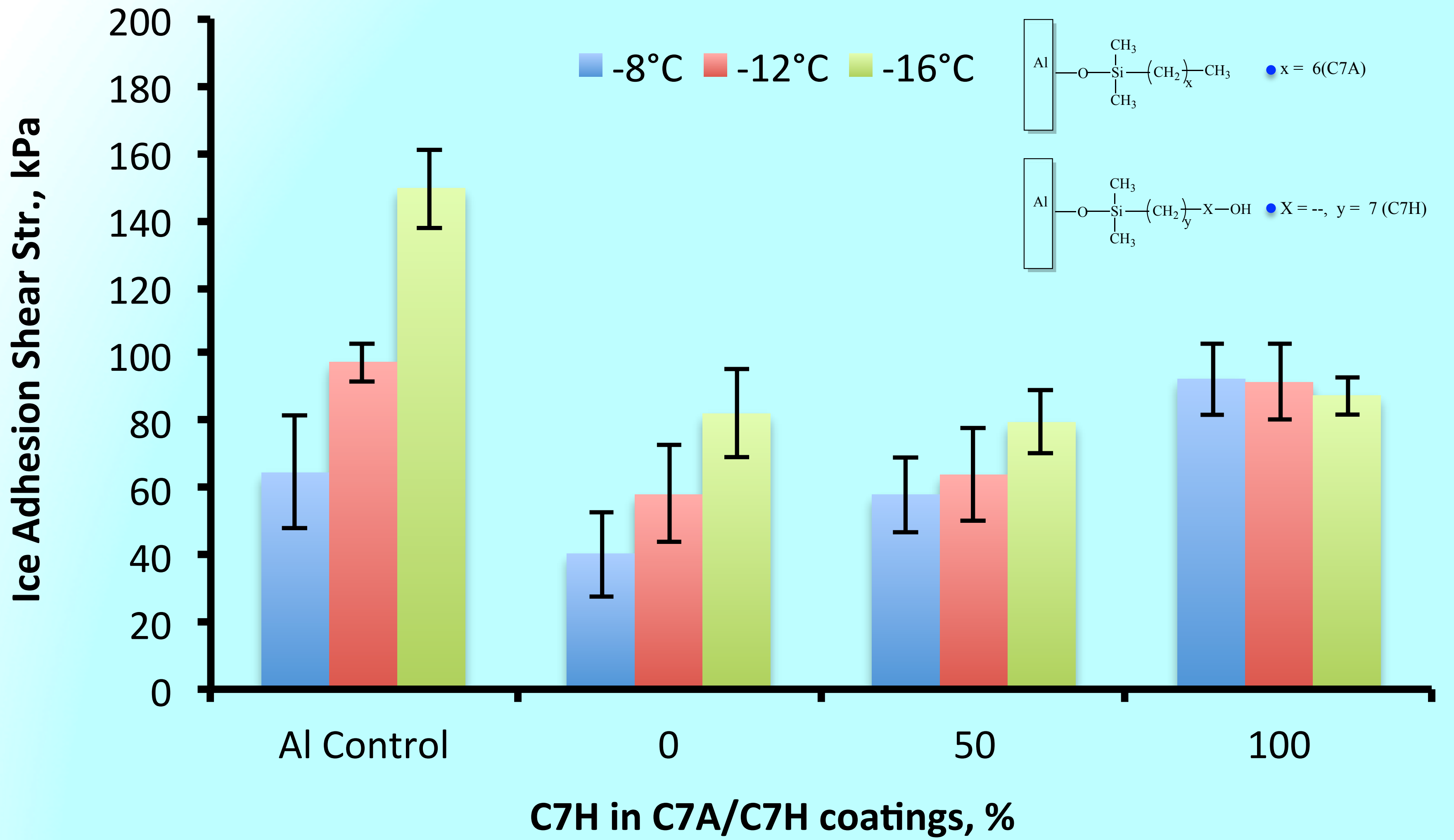
Non-HB: Different Chain Lengths



Increasing HB Content: Different Chain Lengths



Increasing HB Content: Similar Chain Lengths



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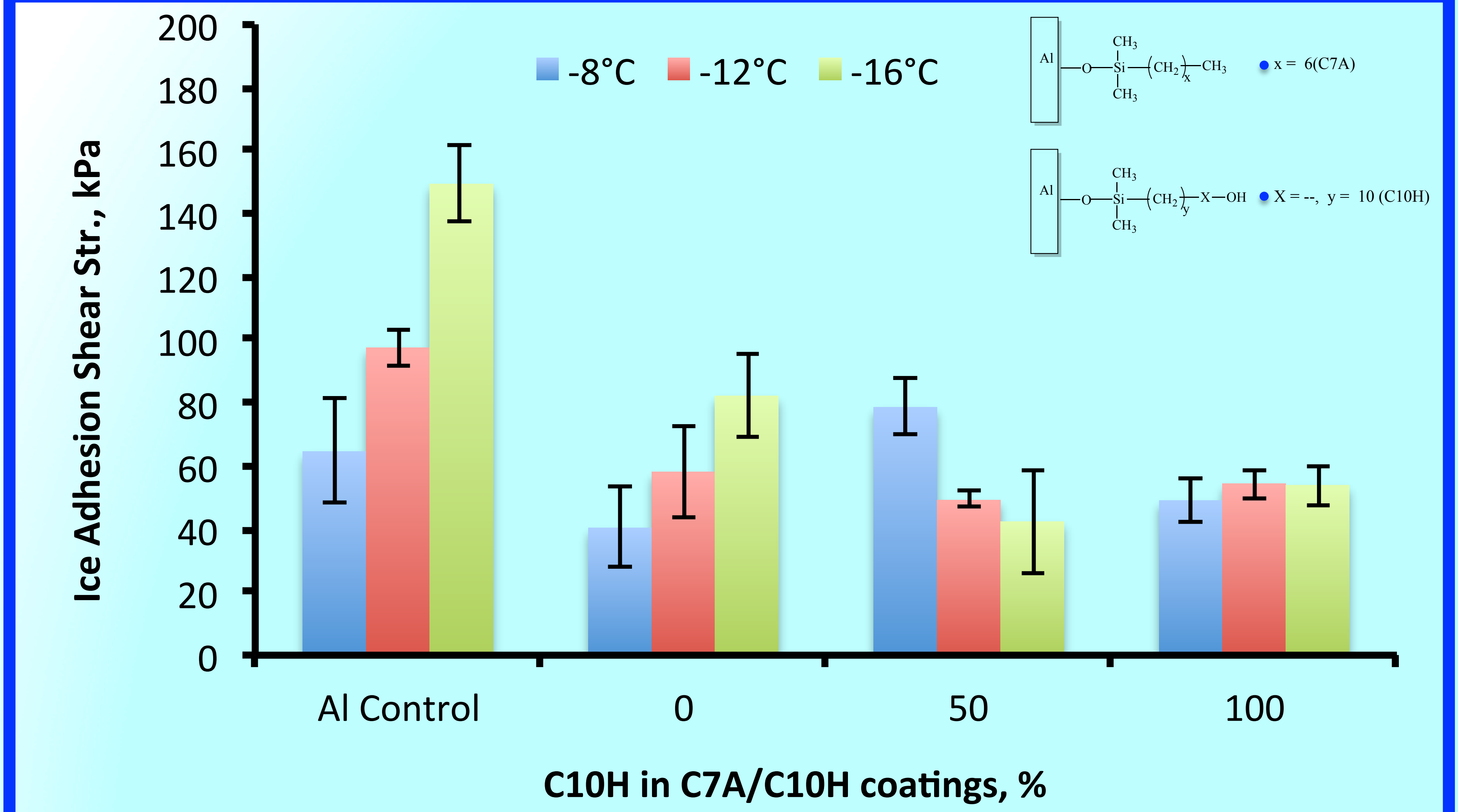

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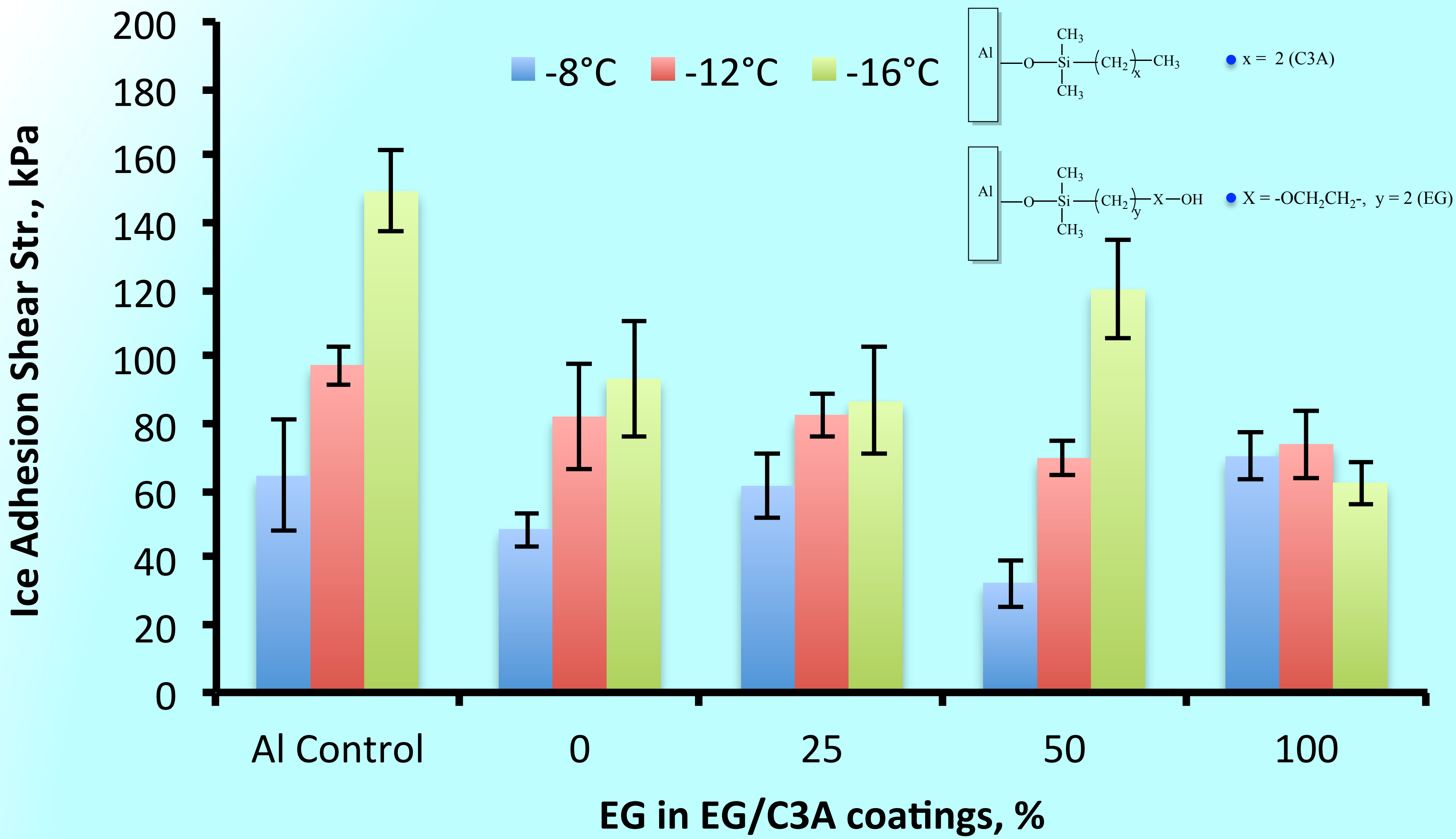
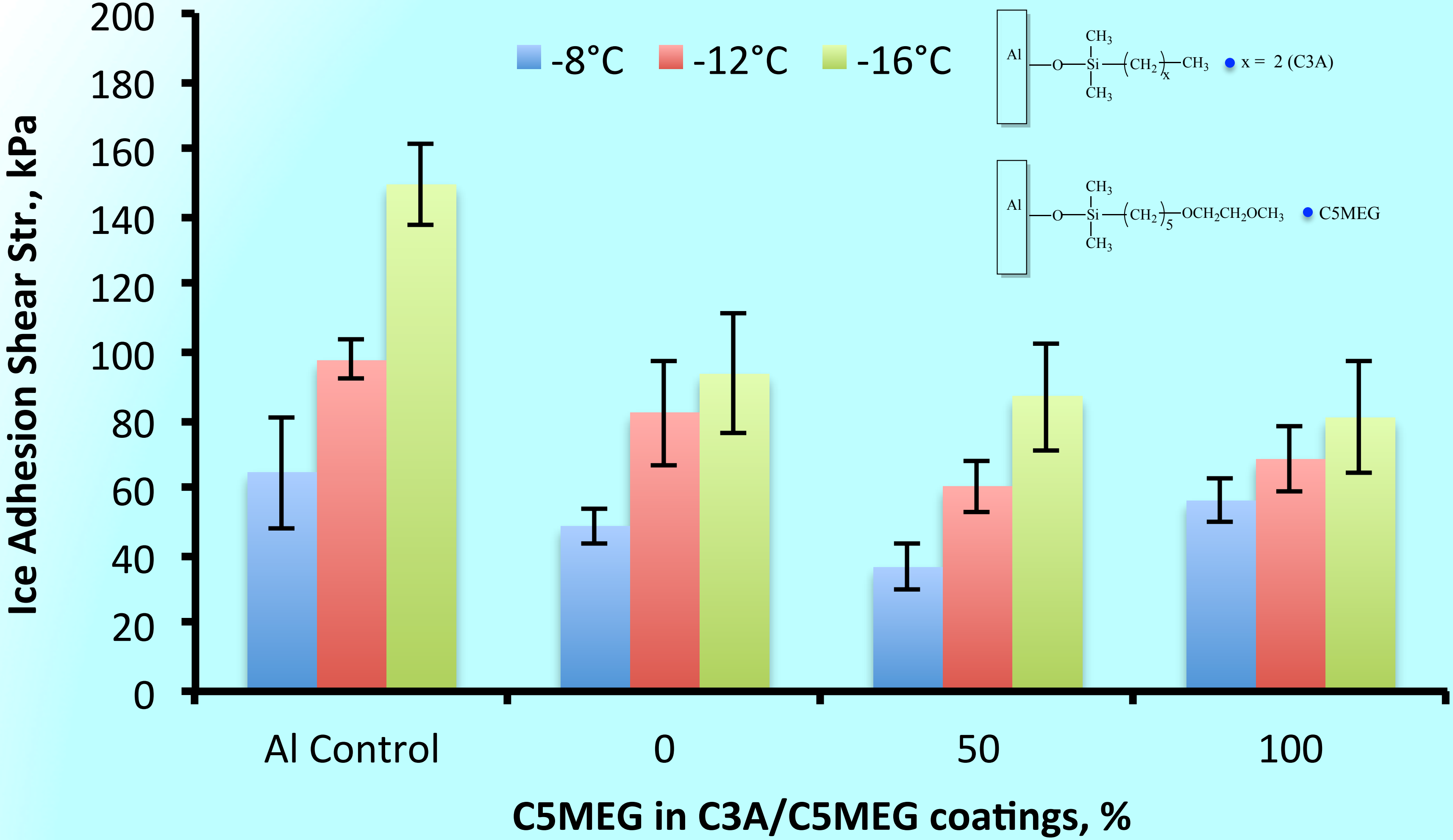
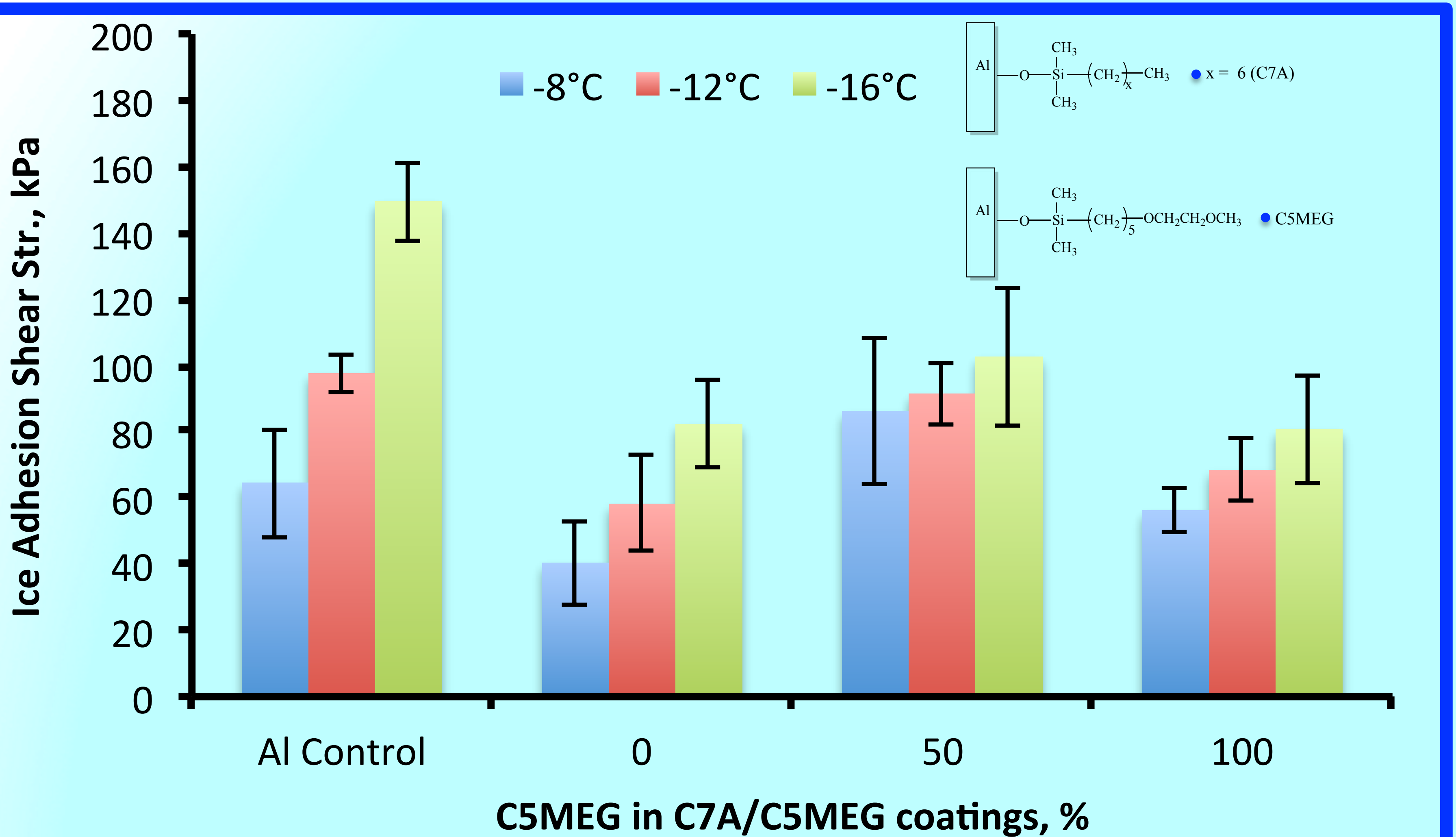


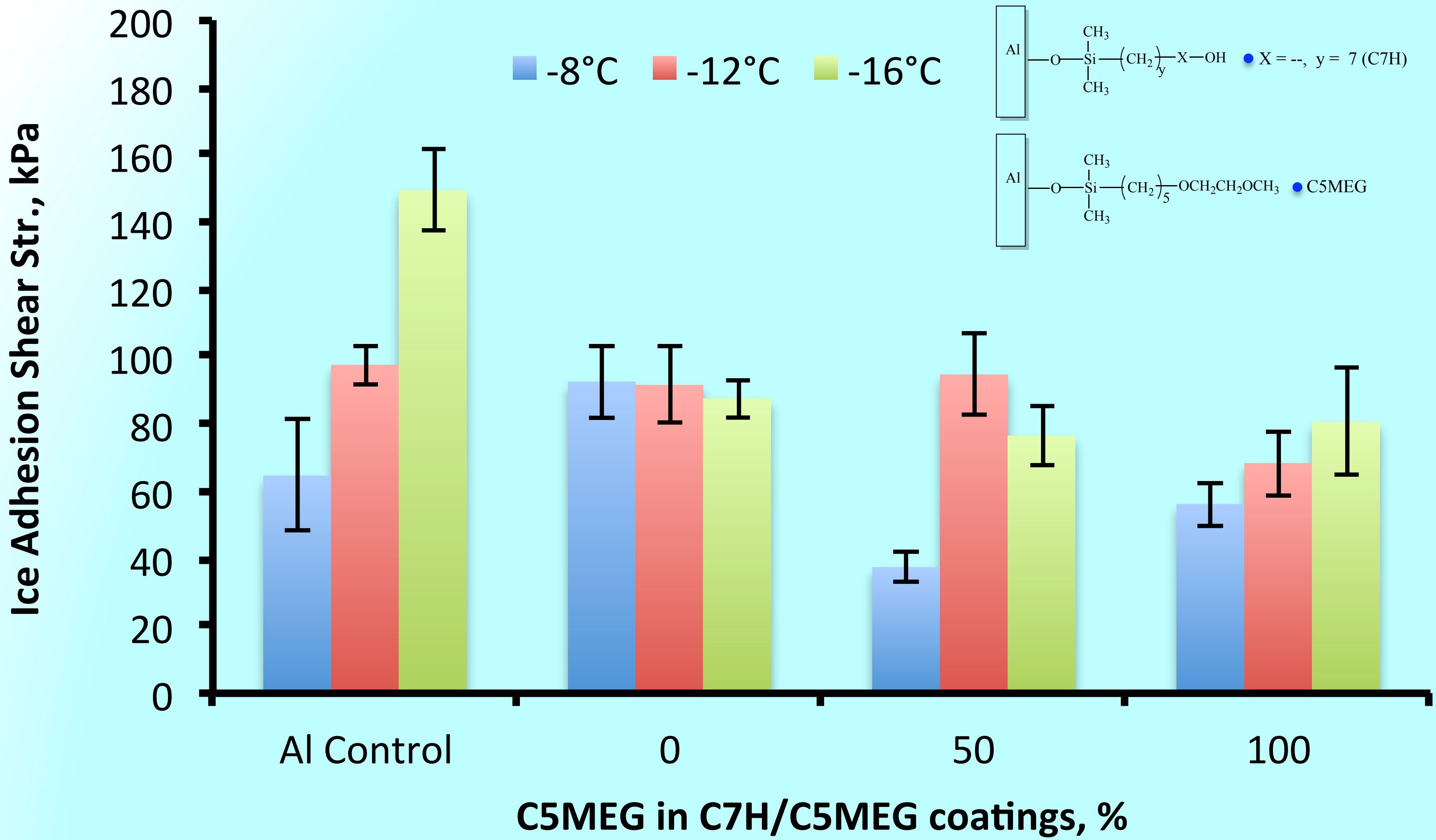
Increasing HB (acceptor) Content: Different Chain Lengths



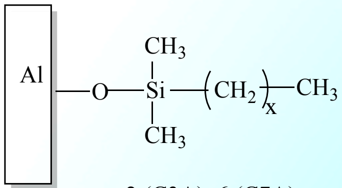
Increasing HB (acceptor) Content: Different Chain Lengths



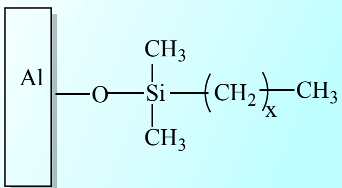
Increasing HB (acceptor) Content: Different Chain Lengths



Two Component Coating Summary



- x = 2 (C3A), 6 (C7A)



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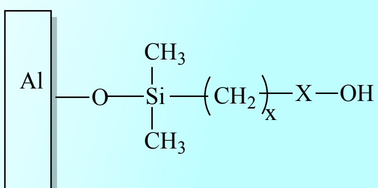
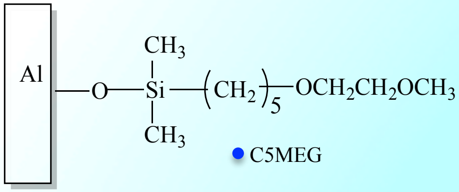


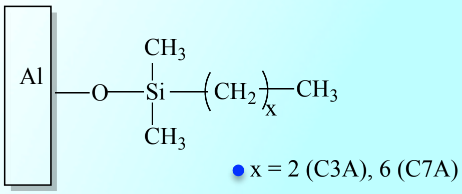
- X = --, y = 7 (C7H), 10 (C10H)
- X = $-OCH_2CH_2-$, y = 2 (EG)

- 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



- C5MEG



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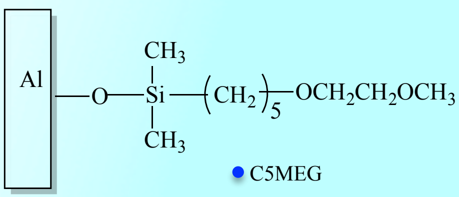
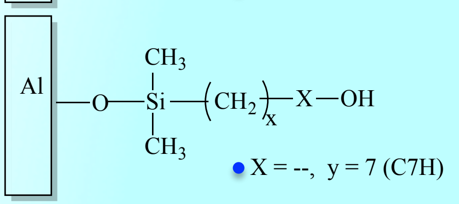


- C5MEG

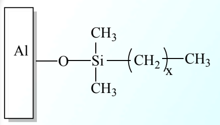


- X = --, y = 7 (C7H)

- 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



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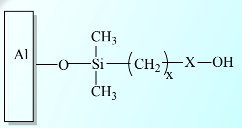

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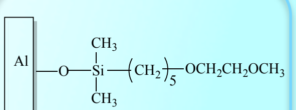
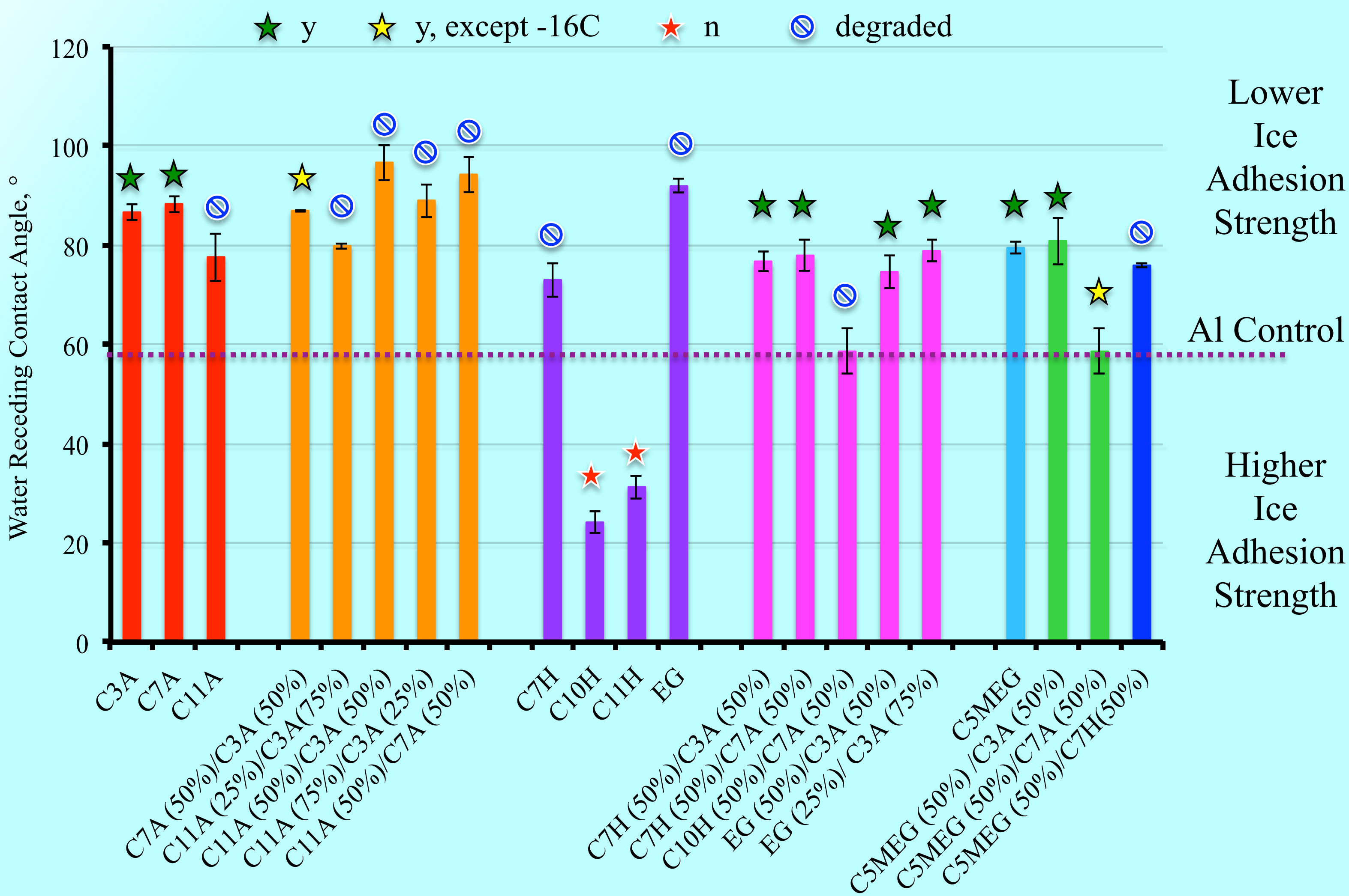


- C5MEG



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

Acknowledgements

- Ronald Penner (Science Technology Corporation)
- Dennis Working (NASA)