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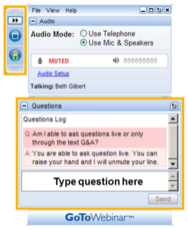

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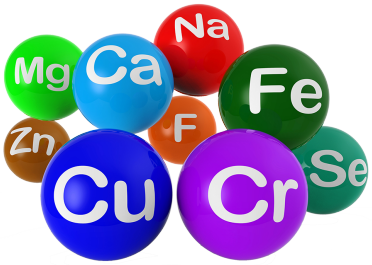

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Dr. Alicja Kluczyk
Faculty of Chemistry, University of Wroclaw
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Thursday, July 21, 2016

Chemistry and the Economy: The Brexit, Challenges of Over-Supply and the End of Bank Stimulus

Paul Hodges, Chairman of International eChem (IeC)

William Carroll, Past ACS President and ACS Chair of the Board

Thursday, July 28, 2016

Nucleic Acids Therapeutics: Making Sense of Antisense

Punit Seth, VP of Medicinal Chemistry, Ionis Pharmaceuticals

Richard Olson, Bristol-Myers Squib

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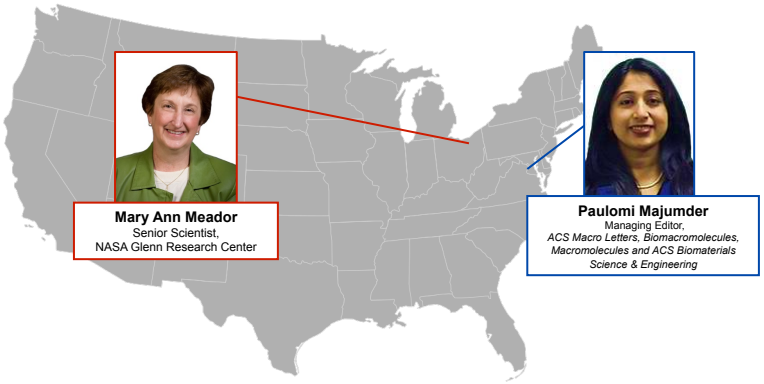
Insulation Chemistry on Earth and Beyond:
Polyimide and Polyamide Aerogels



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National Aeronautics and Space Administration

Insulation Chemistry on Earth and Beyond: Polyimide and Polyamide Aerogels

Mary Ann Meador
NASA Glenn Research Center
Cleveland, OH

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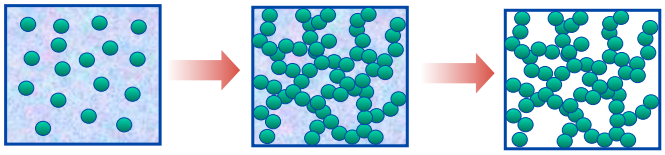
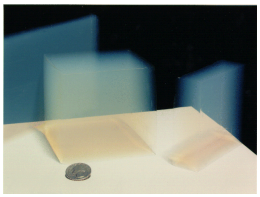
What are aerogels?



- Highly porous solids made by drying a wet gel without shrinking
- Pore sizes extremely small (typically 10-40 nm)—very good insulation
- 2-4 times better insulator than fiberglass under ambient pressure
- 10-15 times better in light vacuum
- Invented in 1930's by Prof. Samuel Kistler of the College of the Pacific



Typical monolithic silica aerogels

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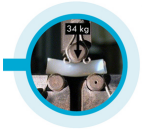
Current aerogel products and market

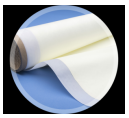
Cabot
Lumira Aerogel in skylights
Grand Rapids, Mi

Aspen Aerogels
Pyrogel pipe insulation

BASF
Slentite
panels

Aerogel
Technologies
Airloy





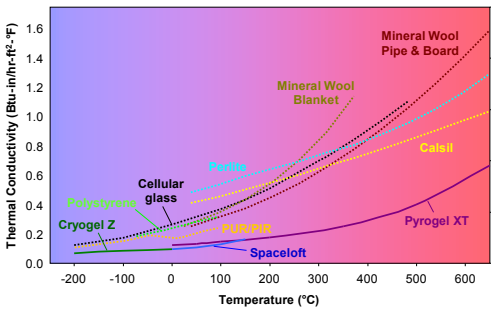
Blueshift
AeroZero

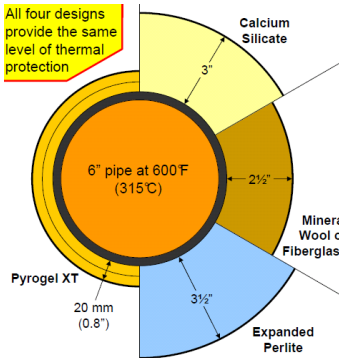
Main players—silica aerogels

Emerging players

National Aeronautics and Space Administration

Comparison of Aspen Aerogels blanket insulation with traditional insulation





Source: George Gould, Aspen Aerogels

www.nasa.gov

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

The current insulation market is worth about $44 billion.
About what percentage of that is currently aerogel?

- 0.01 percent
- 1 percent
- 10 percent
- 30 percent

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Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

The current insulation market is worth about $44 billion.
About what percentage of that is currently aerogel?

- 0.01 percent
- 1 percent
- 10 percent
- 30 percent

* Though aerogels are superior insulation, most current products are silica based which are limited to particulate or composite, which can be dusty. Emerging technologies are overcoming that but costs are still high compared to conventional insulation.

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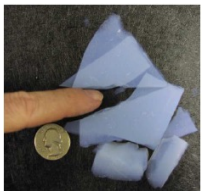
National Aeronautics and Space Administration

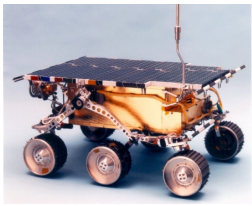
Monolithic silica aerogels out-perform particulate forms as insulation

However, silica aerogels are extremely fragile…



…and therefore limited to a few exotic NASA applications

Cosmic dust collector – Stardust Program



Insulation on rovers

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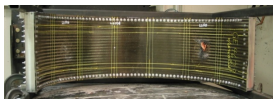
Potential applications for durable aerogels in aeronautics and space exploration

Cryotank Insulation

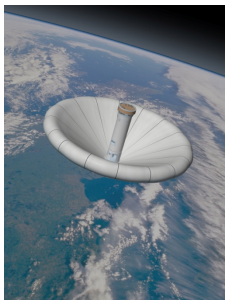


Fan engine containment
(Ballistic protection)

Antenna substrates

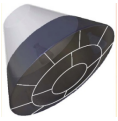
Ultra-lightweight, multifunctional structures for habitats, rovers

Sandwich structures



Inflatable aerodynamic decelerators

Propellant tanks

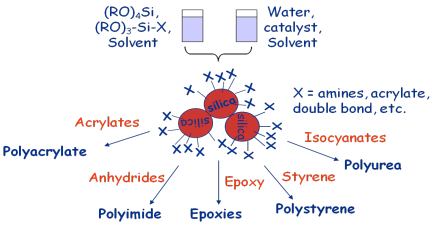


Heat shielding

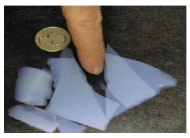
Insulation for EVA suits and habitats

National Aeronautics and Space Administration

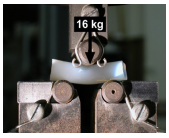
Durable aerogels by reinforcing silica aerogels with polymers



- Versatile: cross-linking with variety of polymers
- Collaboration with Aspen Aerogels to scale up streamlined process

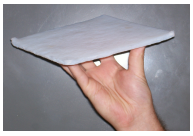


Native

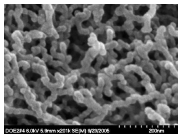


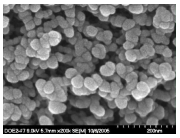
Cross-linked

- ***Two order of magnitude*** increase in strength at the same density
- Does not change pore structure



Polymer reinforced aerogels used to insulate cryotanks—collaboration with MSFC





Low density... to higher density, same aerogel pore structure

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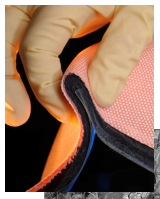
Hypersonic inflatable aerodynamic decelerator concept

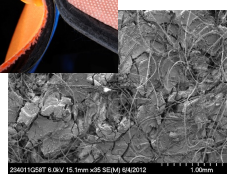
- Hard aeroshells used to land rovers on Mars limit size of payload
- Inflatable structure overcomes this limitation
- Concept shown constructed from a series of stacked inflatable tori tied with a network of straps
- Flexible thermal protection system on fore body
- More information about successful test launch: http://www.nasa.gov/centers/goddard/news/features/2012/IRVE3.html

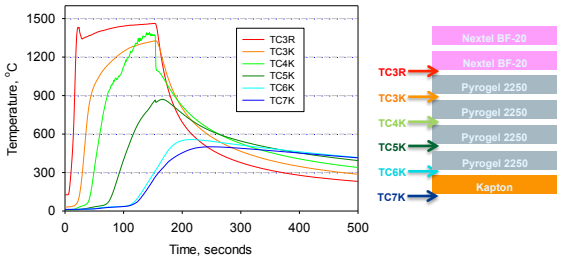
National Aeronautics and Space Administration

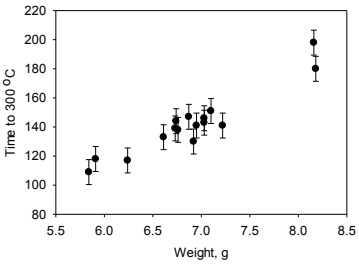
Baseline insulation for HIAD was Pyrogel-2250

- Composite insulation: silica aerogel in batting
- Flexible but sheds dust particles on handling
- Begins to out gas at 380 °C
- In high heat flux testing, time to 300 °C of bottom thermocouple related to weight of insulation
- Lost 20-34 % weight during test









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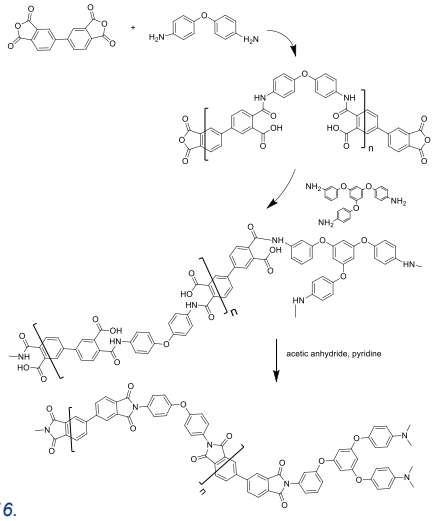
Polyimide aerogels

- Family of polymer aerogels made by cross-linking polyimide oligomers to form gel network
- Supercritical fluid extraction to remove liquid from gels



Meador, US Patent 9,309,369, April 12, 2016.
Meador and Guo, US Patent 9,109,088, August 18, 2015.
Nguyen and Meador, US Patent 8,974,903, March 10, 2015.

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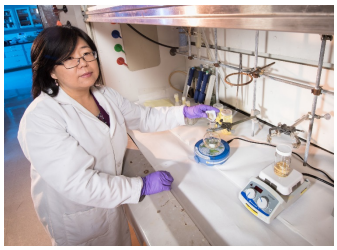
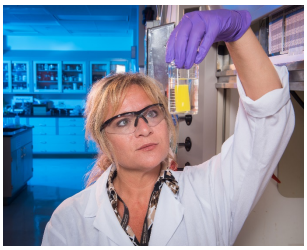
Typical PI Aerogel Process



Monomers mixed in NMP

Solution poured into mold

Extracted after gelation



Solvent exchange into acetone

Supercritical CO_2 extraction

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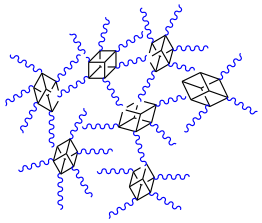
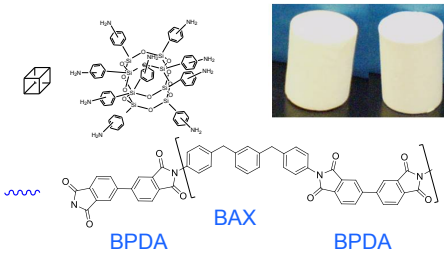
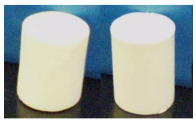
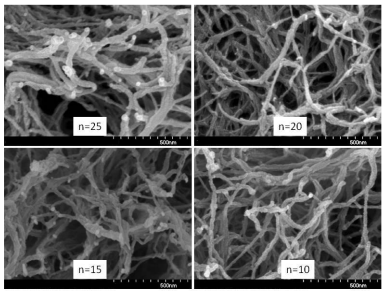
Polyimide 3D network using T8-POSS-first successful formulations







- PI cross-linked with POSS
- Chemically imidized with pyridine/ acetic anhydride
- BPDA-(BAX-BPDA)n; n = 10 to 25
- Low shrinkage (~10 %)
- Density: ~0.1 g/cm^3
- Porosity > 90 %



*Guo, et al, ACS Appl. Mater. Interfaces, **2011**, 3 (2),546-552*

National Aeronautics and Space Administration

Cross-linked polyimide aerogels cast as thin film are flexible

- Collaboration with Prof. Miko Cakmak, University of Akron
- Density of film is similar to molded cylinder
- Middle picture is 9” x 13” pan; film is folded multiple times
- Currently can cast up to 18” inches wide, 8 ft. long

As-cast wet films

Dry aerogel

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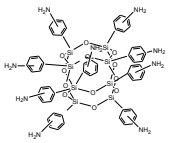
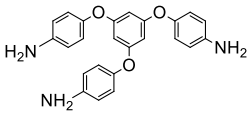
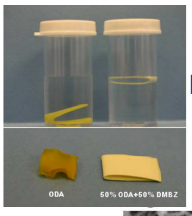
Polyimide Aerogel Development



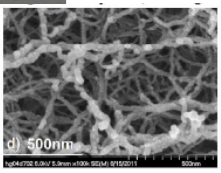


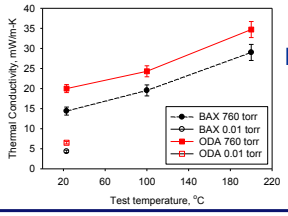


Moisture resistant

- Two cross-linking approaches evaluated
- Over thirty different combinations of backbone chemistry studied
- Formulations identified with
  - Best moisture resistance
  - Best mechanical properties at lowest density
  - Low thermal conductivity
  - Short term stability up to 400 °C
- 100s of enquiries from companies for commercial products

Porous aerogel structure



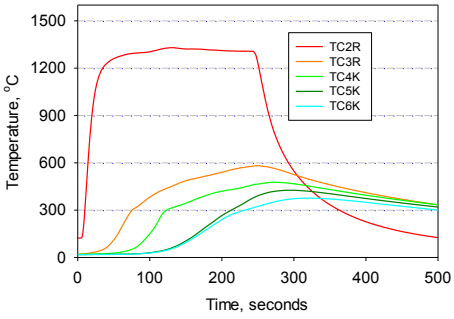


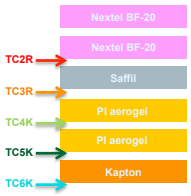
Low thermal conductivity

National Aeronautics and Space Administration

LCAT test—Saffil in combination with PI aerogel

- Layer of Saffil
- Two equivalent thicknesses PI aerogel
  - 50% DMBZ \ 50% ODA
- Test stopped after 247 s
  - Bottom TC reached 300 °C
- Top of PI stack ~590 °C max
- PI lost much less weight than Pyrogel





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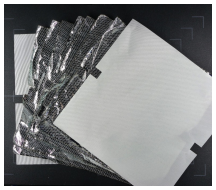
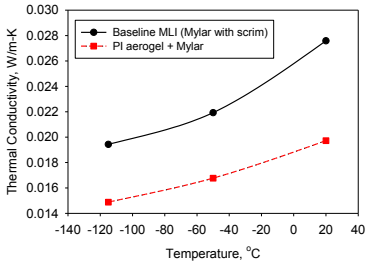
Multifunctional, Universal Thermal Insulation System

- Current multilayer insulation (MLI) only functions in vacuum
  - Layers of Mylar separated by scrim layers
- Aerogel is best insulation in gaseous environment
- MLI incorporating aerogel in place of scrim reduces TC by 23-37%
- Partnership with JSC and GRC



Baseline MLI (Mylar + scrim)

Pi aerogel + Mylar



MLI with and without aerogel tested under simulated Mars atmosphere (8 Torr Argon, -120 to 20 °C)

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Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

What properties do polyimide aerogels possess, besides being a great insulator that makes them important for aerospace applications?

- Good mechanical properties
- Low density
- High surface area
- Very low dielectric constant
- All of the above

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Audience Survey Question

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What properties do polyimide aerogels possess, besides being a great insulator that makes them important for aerospace applications?

- Good mechanical properties
- Low density
- High surface area
- Very low dielectric constant
- All of the above

* Good mechanical properties combined with low density means they can be used as lightweight structures. The high surface area, low dielectric constant and superior insulation capability allow for the introduction of other functionality in the structure (insulation, sensing, etc.)

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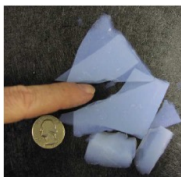
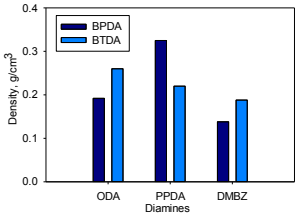
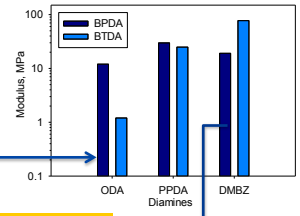
Polyimide Aerogels much stronger than silica aerogels at similar density



Silica aerogel is easily broken by light finger press while PI aerogel easily supports the weight of a car





This formulation is actually *stronger* and *lighter* than one shown in picture

www.nasa.gov

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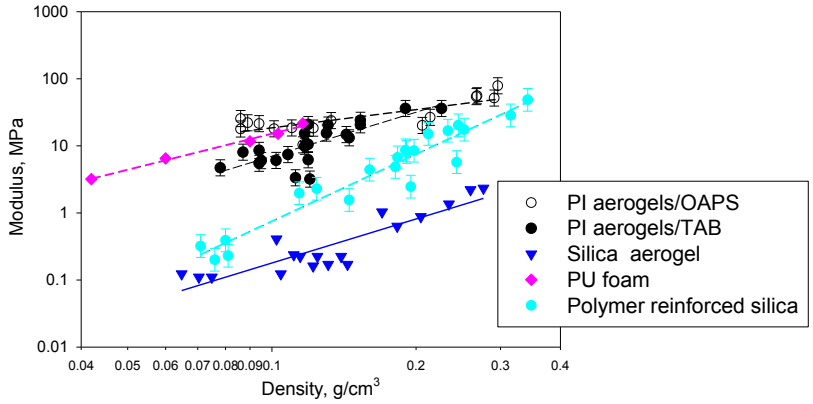
Polyimide aerogels are stronger than silica and polymer reinforced silica aerogels



Also compares favorably with polymer foams

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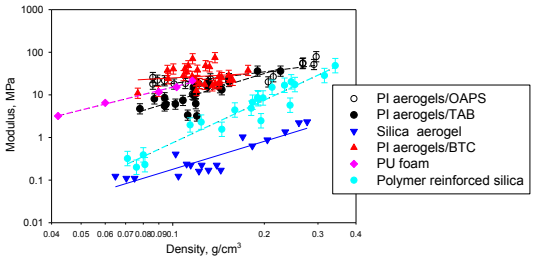
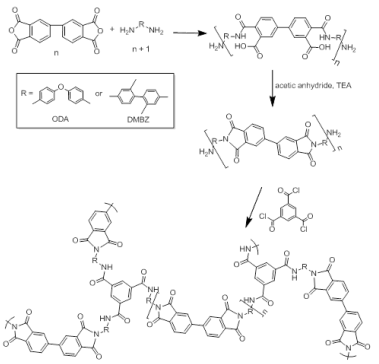
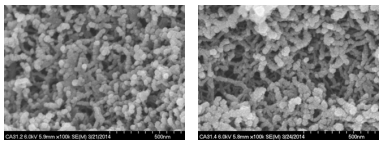
One issue with polyimide aerogels is cost

- Cross-linkers used either not commercially available or expensive
- Solution:
  - Triacid chloride cross-linker with amine capped oligomers
- Properties similar to other cross-linkers







DMBZ ODA

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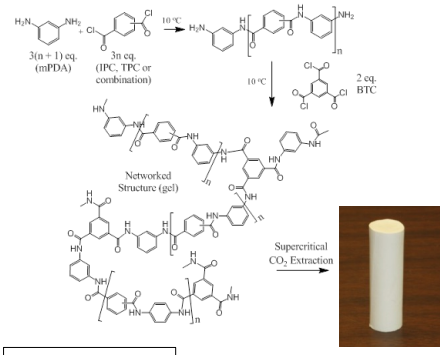
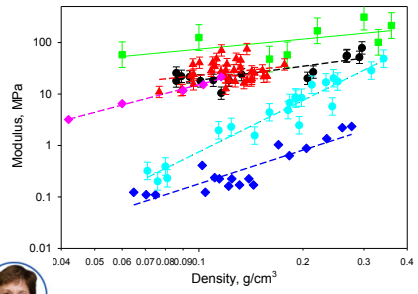
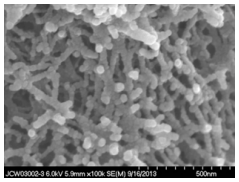
Polyamide aerogels

- Lower cost monomers and cross-linkers
- Slightly less thermally stable
- Stronger than PI aerogels at the same density







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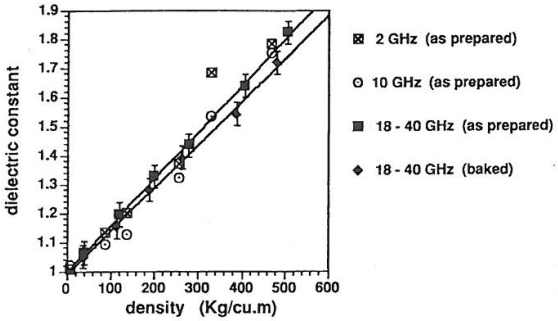
Aerogels also have low dielectric properties



Hrubesh, Keene and Latorre, *Journal of Materials Research*, **1995**, *8*, 1736-1741

- Dielectric properties of silica aerogels vary linearly with density
- Substrates with lower dielectric constants improve performance and reduce weight of antennas

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

How many antennas does a typical commercial aircraft have?

- Less than 10
- About 20
- About 50
- As many as 100

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Audience Survey Question

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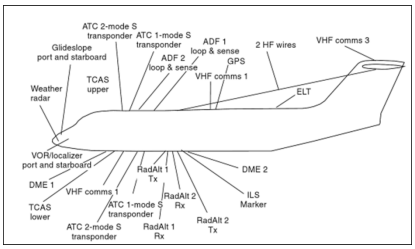

* Commercial and military aircraft can have up to 100 antennas for everything from ground communication to in-flight entertainment, taking up a large amount of room in the fuselage and weight of the aircraft.

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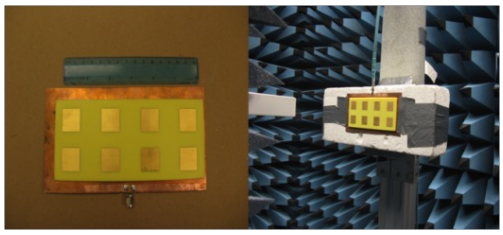
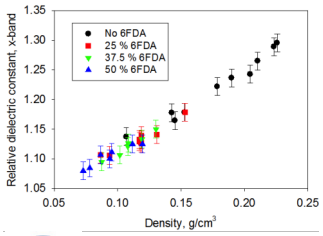
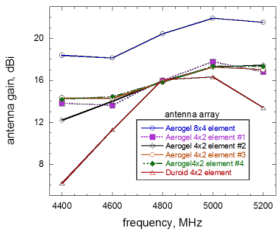
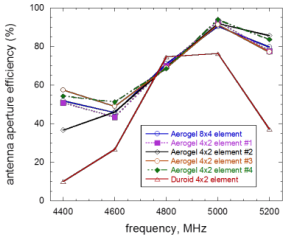
Low dielectric properties of PI aerogel lead to lightweight antennas

- Relative dielectric constants of aerogels scale with density
- Better antenna performance than Duroid
- 77 % lighter weight









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Summary

- PI aerogels produced as thin flexible films for use as insulation for inflatable decelerators or space suits
- Same aerogels as thicker parts are stiff and strong
- Lower cost options: new cross-linkers and other polymer chemistries (polyamide)
- Improved antenna performance with 77% lower mass
- Commercially available from Aerogel Technologies, LLC (molded shapes) and Blueshift (roll-to-roll films)

Aerogel Technologies Airloy

Blueshift AeroZero

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Acknowledgments

- **Polymer aerogel fabrication and characterization**
  - Erica Malow, Rebecca Silva, Brittany Chalfont, Alex Schwanz, Sarah Wright, Anna Sandberg, Elizabeth Barrios, Emily McMillon, Marika Agnello, Christian Aleman, Katrina Hanson, Nakaira Ramirez, Caitlyn Sullivan, Melissa Wilkosz, Jessica Cashman, Jose Maldonado (interns)
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  - Prof. Stuart Rowan, CWRU
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  - Dr. Félix A. Miranda
  - Nicholas Varaljay (GRC)
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  - Dr. Carl H. Mueller
  - Prof. Rafael Rodríguez-Solís (University of Puerto Rico)
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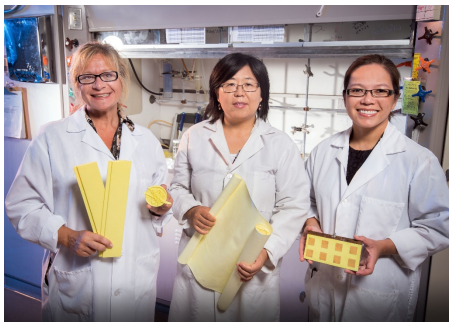
  - ARMD Seedling Proposal Program
  - STMD Game Changing Program
  - Director's Discretionary Fund



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Additional Resources

- http://technology.grc.nasa.gov/
  - Information about technology available to license from NASA Glenn
- http://www.aerogel.org/
  - Learn more about aerogels
- http://pubs.acs.org/doi/abs/10.1021/am507268c
  - Polyimide Aerogels with Amide Cross-Links: A Low Cost Alternative for Mechanically Strong Polymer Aerogels
- http://pubs.acs.org/doi/abs/10.1021/cm5012313
  - Synthesis and Properties of Step-Growth Polyamide Aerogels Cross-linked with Triacid Chlorides
- http://pubs.acs.org/doi/abs/10.1021/acs.chemmater.6b00474
  - Thermoresponsive Shape-Memory Aerogels from Thiol−Ene Networks
- http://pubs.acs.org/doi/abs/10.1021/am405106h
  - Dielectric and Other Properties of Polyimide Aerogels Containing Fluorinated Blocks
- http://pubs.acs.org/doi/abs/10.1021/am301985s
  - Low Dielectric Polyimide Aerogels As Substrates for Lightweight Patch Antennas
- http://pubs.acs.org/doi/abs/10.1021/am301347a
  - Tailoring Properties of Cross-Linked Polyimide Aerogels for Better Moisture Resistance, Flexibility, and Strength
- http://pubs.acs.org/doi/abs/10.1021/am2014635
  - Mechanically Strong, Flexible Polyimide Aerogels Cross-Linked with Aromatic Triamine
- http://pubs.acs.org/doi/abs/10.1021/am200007n
  - Tailoring Mechanical Properties of Aerogels for Aerospace Applications
- http://pubs.acs.org/doi/abs/10.1021/am101123h
  - Polyimide Aerogels Cross-Linked through Amine Functionalized Polyoligomeric Silsesquioxane

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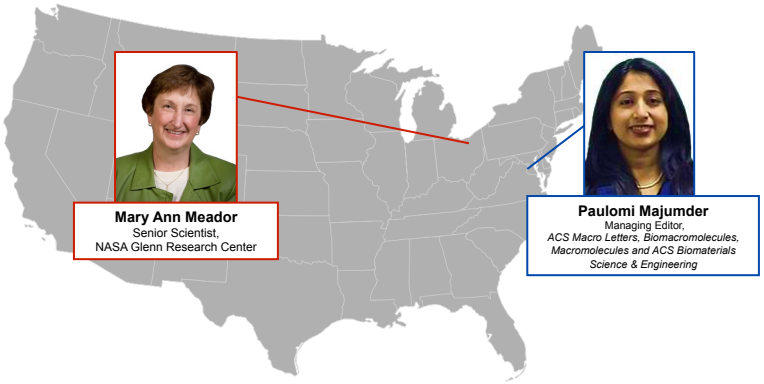

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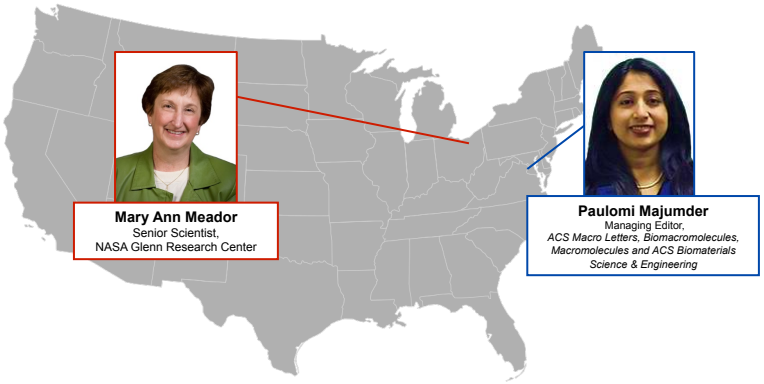

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