Aerogels: Overview and Outlook for Future Space and Terrestrial Applications at NASA

NASA Glenn Research Center

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Materials Chemistry and Physics Branch
NASA Glenn Research Center
NASA GRC Core Competencies

Aerospace Propulsion

In-Space Propulsion and Cryogenic Fluids Management

Physical Sciences and Biomedical Technologies in Space

Communications Technology and Development

Power, Energy Storage and Conversion

Materials and Structures for Extreme Environments
Materials and Structures Division

High Temperature Materials
- Ceramic Matrix Composite
- Protective Coatings
- Thermal Protection Seal
- Hybrid Disk

Lightweight Concepts
- Hybrid Composite
- Nanotube Yarn
- Lattice Block
- Flexible Aerogel

Electric Propulsion Materials
- Materials for High Power Density Electric Motors
- Silicon Carbide Semiconductor
- Lightweight Power Transmission Cable

Mechanisms and Drive Systems
- High Efficiency Gear
- Shape Memory Alloy-Based Actuation
- Superelastic Bearing
- Spring Tire

Computational Modeling
- Orion Fairing Jettison
- Vibration Testing

Flight Structures
- Low Impact Docking Seal
- Large Composite Structures
What are Aerogels?

Aerogels are a class of porous solids which exhibit many extreme properties which originate from a nanoporous skeletal architecture

- Highly porous solids made by drying a wet gel without shrinking
- Pore sizes extremely small (typically 10-40 nm)—makes for 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
Aerogel Fabrication

Aerogel Fabrication Steps:
1. Dissolve monomeric precursors into solution (sol)
2. Gel network forms incorporating monomers into skeleton
3. Removal of solvent occurs either by sublimation or supercritical extraction

Supercritical Extraction
1. Avoids liquid/vapor boundary by solvent removal above critical point
2. No liquid-vapor interface exists thus no capillary stresses
3. Based on capillary pressure equation, a small diameter ($r$), leads to a huge force resulting in compaction

$$P_{\text{cap}} = \frac{2\gamma \cos \theta}{r}$$

$\gamma$ = Interfacial Tension
$\theta$ = Wetting Angle
$r$ = Pore Radius
Monolithic silica aerogels provide superior insulation.

Data provided by Institution of Civil Engineers.

...but are extremely fragile and moisture sensitive... and limited to a few exotic applications.
Potential applications for durable aerogels in aeronautics and space exploration

- Cryotank Insulation
- Fan engine containment (Ballistic protection)
- Antenna substrates
- Sandwich structures
- Insulation for EVA suits and habitats
- Ultra-lightweight, multifunctional structures for habitats, rovers
- Heat shielding
- Inflatable aerodynamic decelerators
- Propellant tanks
Insulation for Future Mars Concepts

- Mars System Taxi
- Mars Surface Rover
- Mars Crew Lander
- Initial Cis-Martian Habitat
- Phobos Exploration Vehicle (PEV)
- Mars Ascent Vehicle (MAV)
Hypersonic inflatable aerodynamic decelerator concept

- Hard aeroshells used to land rovers on Mars limit size of payload
- Inflatable structure overcomes this limitation
- Concept is a series of stacked inflatable tori tied with a network of straps
- Flexible thermal protection system on fore body
- Baseline insulation was Aspen silica Aerogel composite blanket
- Loses fragile silica aerogel on handling
Polyimide aerogels

- Entire aerogel skeletal architecture synthesized from a polymer should be flexible as a thin film
- Polyimides are known for their high temperature stability
- Family of polymer aerogels made by cross-linking polyimide oligomers to form gel network
- Supercritical fluid extraction to remove liquid from gels

Two approaches to cross-linked PI aerogels developed

- Made by cross-linking polyimide oligomers to form gel network
- POSS decorated with eight aminophenyl groups or aromatic triamine (TAB)
- Supercritical fluid extraction same as silica aerogels

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.
Cross-linked polyimide aerogels cast as thin film are flexible

- 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, 33 feet long at a film casting line in the University of Akron
- Surface area, porosity and thermal conductivity similar to monolithic silica aerogels
Baseline insulation for HIAD is Pyrogel-2250

- Composite insulation made up of silica aerogel particles in O-PAN batting
- Flexible but sheds dust particles on handling
- Begins to out gas at 380 °C
- High heat flux testing at Large Core Arc Tunnel (LCAT) facility at Boeing
- Time to 300 °C of bottom thermocouple measured
- Related to weight of insulation
- Pyrogel layers lose 20-34 % weight during test
LCAT test—Saffil in combination with PI aerogel

- Layer of Saffil backed by two equivalent thicknesses PI aerogel
  - 50% DMBZ \ 50% ODA
- Test stopped after 247 s when the bottom RC reached 300 °C
- Top of PI stack ~590 °C max
- PI lost much less weight than Pyrogel
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

MLI with and without aerogel tested under simulated Mars atmosphere (8 Torr Argon, -120 to 20 °C)
Mixtures of rigid and flexible diamines give better combination of properties

- 100% DMBZ too stiff
- 100% ODA moisture sensitive
- 50-50 formulation is flexible, strong, moisture resistant

Guo et al, ACS Applied Materials and Interfaces, 2012, ASAP
Alternative lower cost, commercially available cross-linkers

• Much commercial interest in PI aerogel for insulation
  – Refrigeration, clothing, sporting goods, consumer electronics, building and construction, etc.

• Two cross-linkers either not commercially available (TAB) or expensive (OAPS)

• Some alternatives:
  – Benzenetricarbonyl chloride (BTC)—amide cross-links
  – Polymaleic anhydride (PMA)—aliphatic cross-links
  – Tri-isocyanates—urea cross-links
Polyimide aerogels with alternate commercially available cross-linker—BTC

- Used ODA or DMBZ in backbone to compare to other cross-linkers
- Modulus, morphology depend on backbone, not cross-linker
- Surface areas about 100 m²/g higher with BTC

Meador et al, ACS Appl. Mater. Interfaces 2015, 7 1240-1249
Shrinkage of the aerogel is limiting factor for higher temperature use

- High onset of decomposition temperature
- Varies based on diamine used
- Shrinkage is lowest for DMBZ/ODA aerogels
- Preconditioning at use temperature stabilizes shrinkage

Use of bulky substituents in polymer chain reduces shrinkage after 500 hours aging

- Replacing 50 mol % of ODA with BAPF reduces shrinkage by up to half
- Surface area still above 300 m²/g after aging

Multifunctional Energy Storage to Improve Efficiency

Enable hybrid electric propulsion for commercial aircraft by coupling load-bearing structure with energy storage

Challenges

• Producing a structure capable of bearing weight and resisting forces associated with flight

Risks

• Current Li-Ion battery technology utilizes flammable components

Goals

• Develop a separator/electrolyte system which possesses sufficient ionic conductivity with non-flammability

Hybrid electric aircraft with multifunctional storage could reduce emissions by 80% and fuel consumption by 60%
Polyolefin Separators used in Li-Ion Batteries

- Polyethylene and polypropylene are among the most flammable polymers
- Limited number of electrolytes wet the polyolefins

<table>
<thead>
<tr>
<th>Separator/Properties</th>
<th>Celgard 2730</th>
<th>Celgard 2400</th>
<th>Celgard 2325</th>
<th>Asahi Hipore</th>
<th>Tonen Setela</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Single Layer</td>
<td>Single Layer</td>
<td>Trilayer</td>
<td>Single Layer</td>
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<tr>
<td>Composition</td>
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<td>PP</td>
<td>PP/PE/PP</td>
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<tr>
<td>Thickness (μm)</td>
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<td>25</td>
<td>25</td>
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<tr>
<td>Porosity (%)</td>
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<td>42</td>
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<td>41</td>
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<tr>
<td>Melt Temp. (°C)</td>
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<td>165</td>
<td>135/165</td>
<td>138</td>
<td>137</td>
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</tbody>
</table>
Many polyimide backbone chemistries were synthesized and characterized
Several factors were considered in down selection: film forming, mechanical strength, porosity
ODA-BPDA-N3300A formed thin, mechanically robust films, with porosities of 93%
Comparison of Commercial Separator and PI Aerogel

<table>
<thead>
<tr>
<th>Celgard© PE Separator</th>
<th>Polyimide Aerogel</th>
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<tbody>
<tr>
<td><img src="image1" alt="Celgard image" /></td>
<td><img src="image2" alt="Polyimide image" /></td>
</tr>
<tr>
<td><img src="image3" alt="Microscopic image" /></td>
<td><img src="image4" alt="Microscopic image" /></td>
</tr>
</tbody>
</table>

- **Celgard© PE Separator**
  - Size: 2.00 μm

- **Polyimide Aerogel**
  - Size: 2.00 μm
PI/EMIM Gel Separator is Nonflammable Under Direct Contact with Flame
Polyimide Aerogel Development

- Over fifty different combinations of backbone chemistry studied
- Multiple cross-linkers evaluated
- Properties more dependent on backbone
- Formulations identified with
  - Best moisture resistance
  - Best mechanical properties/density
  - Low thermal conductivity
  - More optical clarity

Clear to opaque
Pore structure

Moisture resistant
High heat flux testing

Low thermal conductivity

Mechanical properties related to density

![Graphs and images showing properties of polyimide aerogels](image-url)
Polyamide aerogels

- Lower cost monomers and cross-linkers
- No catalyst needed
- Slightly less thermally stable

Polyamide aerogels—Kevlar based

- Low cost monomers
- All para substitution kept in solution by use of CaCl₂
- Salt also gets rid of distortion problem of PA gels during solvent exchange
- Different morphology, but still high surface area, strong
PI aerogels are stronger than silica aerogels but PA aerogels stronger yet on a density basis.
Summary

- PI aerogels were originally produced for use as thin flexible films for use as insulation for inflatable decelerators or space suits.
- Same aerogels as thicker parts are stiff and strong.
- Development of lower cost options: new cross-linkers and other polymer chemistries (polyamide) have led to commercialization.
- Commercially available from Aerogel Technologies, LLC (molded shapes) and Blueshift (roll-to-roll films).
- Due to their porous architecture and flexibility, PI aerogels can be used as non-flammable battery separators.
NASA Opportunities

• Pathways Program
  o Prepares students for careers by providing related work experience
  o Rotates scheduled work sessions with school

• Pathways Intern and Recent Graduate Positions:
  o [www.usajobs.gov](http://www.usajobs.gov)
  o Example-Search “glenn pathways”
  o For PMF-STEM visit [www.pmf.gov](http://www.pmf.gov)

• Regular Full-Time Positions:
  o [www.usajobs.gov](http://www.usajobs.gov)
  o Search “glenn research center”

• Other Student Opportunities:
  o [https://intern.nasa.gov](https://intern.nasa.gov)
  o Search Opportunities
  o Limited opportunities for international students
NASA Glenn Research Center, Cleveland, OH