

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

NASA Glenn Research Center

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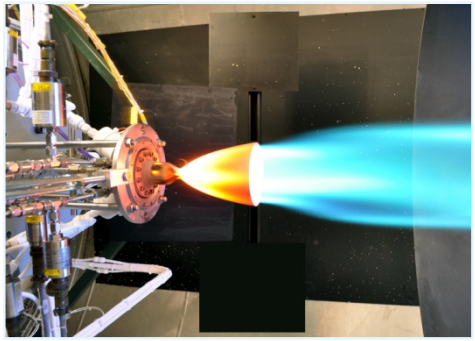
NASA Glenn Research Center



NASA GRC Core Competencies



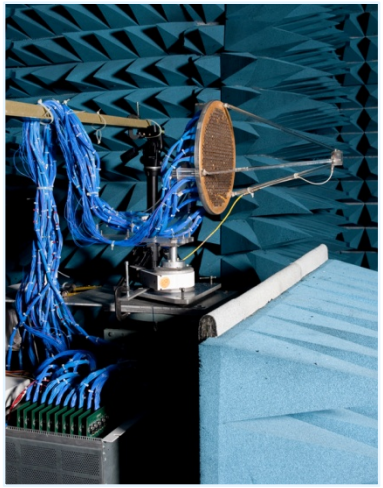
Aerospace Propulsion



In-Space Propulsion and Cryogenic Fluids Management



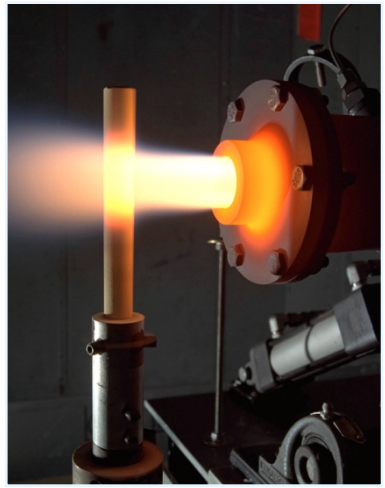
Physical Sciences and Biomedical Technologies in Space



Communications Technology and Development



Power, Energy Storage and Conversion

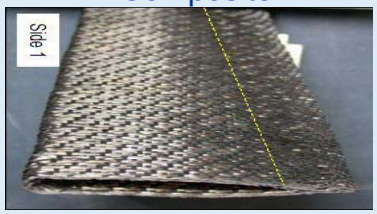


Materials and Structures for Extreme Environments

Materials and Structures Division

High Temperature Materials

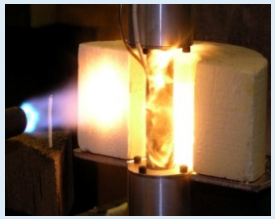
Ceramic Matrix Composite



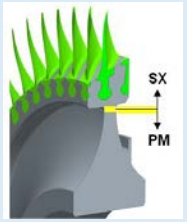
Protective Coatings



Thermal Protection Seal



Hybrid Disk

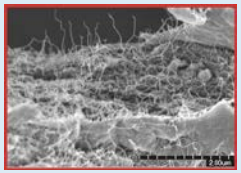


Lightweight Concepts

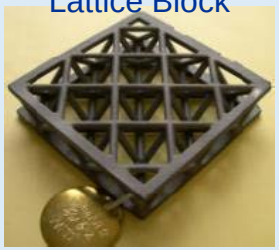
Hybrid Composite



Nanotube Yarn



Lattice Block



Flexible Aerogel



Electric Propulsion Materials

Materials for High Power Density Electric Motors

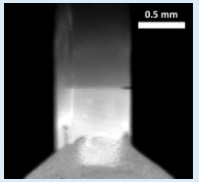




Lightweight Power Transmission Cable



Silicon Carbide Semiconductor

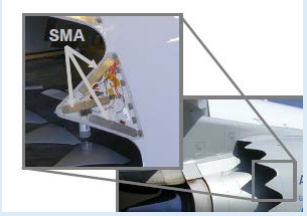


Mechanisms and Drive Systems

High Efficiency Gear



Shape Memory Alloy-Based Actuation



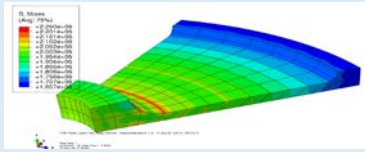
Superelastic Bearing



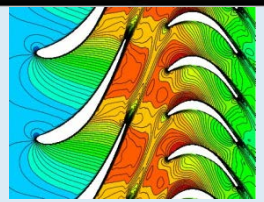
Spring Tire



Computational Modeling

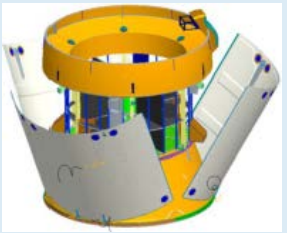






Flight Structures

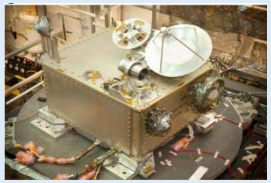
Orion Fairing Jettison



Low Impact Docking Seal



Vibration Testing



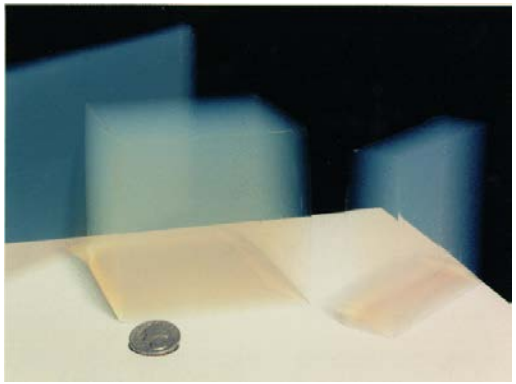
Large Composite Structures



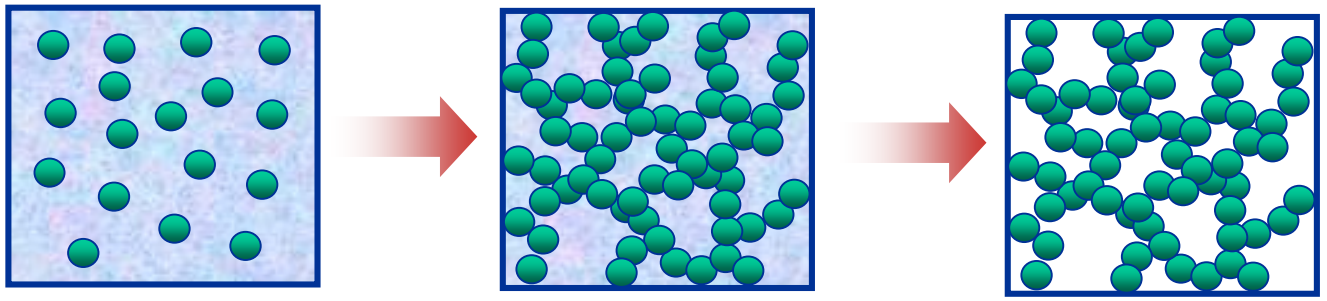
What are Aerogels?

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

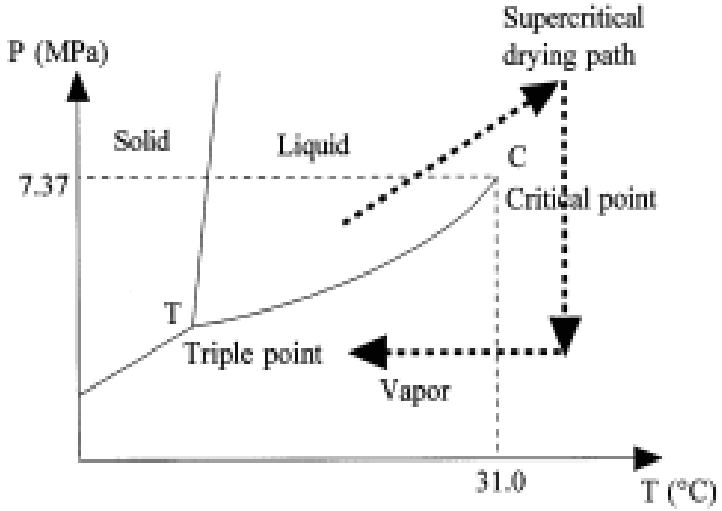


Silica Aerogel Monoliths



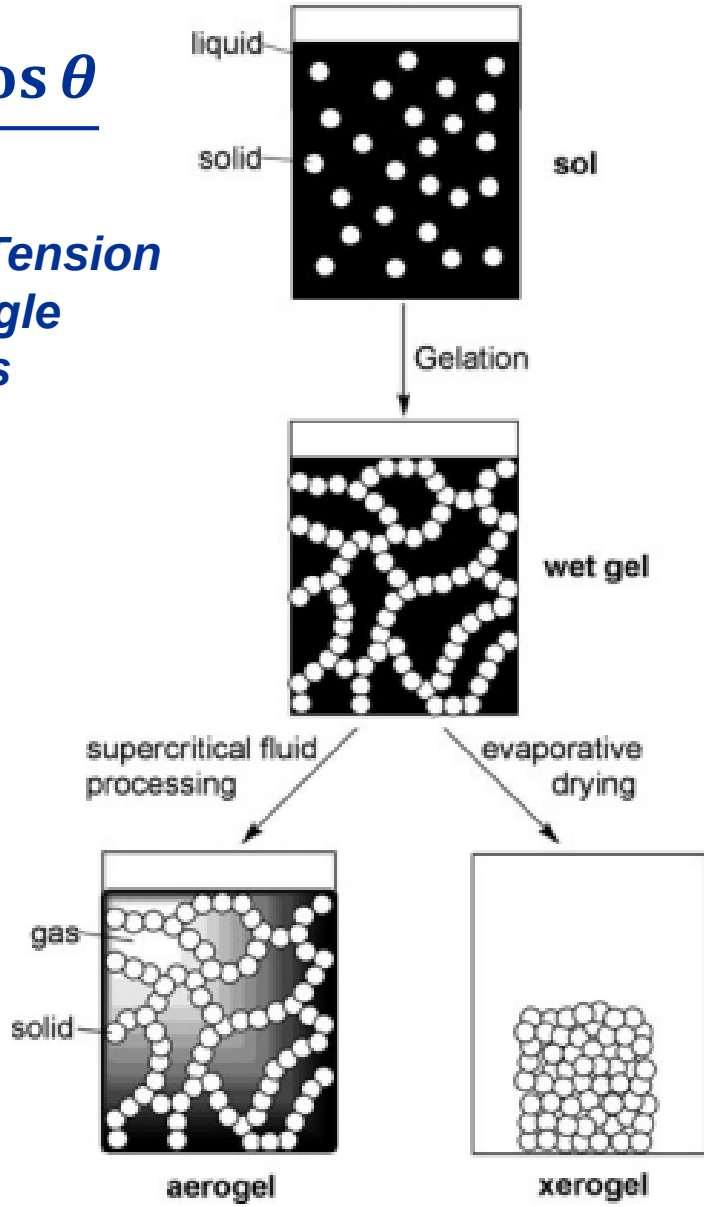
Sol Gel Aerogel

Aerogel Fabrication



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

γ = Interfacial Tension
θ = Wetting Angle
r = Pore Radius



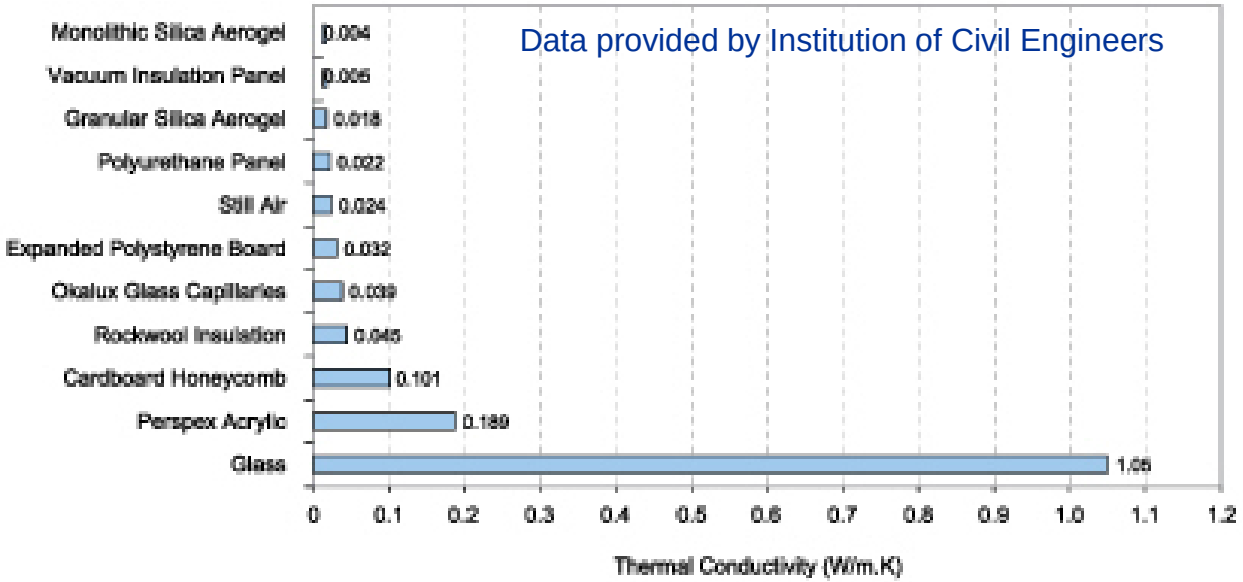
Aerogel Fabrication Steps:

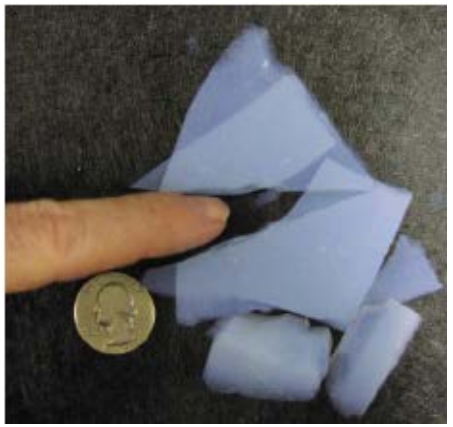
1. Dissolve monomeric precursors into solution (sol)
2. Gel network forms incorporating monomers into skeleton
3. Removal of solvent occurs either by sublimation or supercritical extraction

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

Monolithic silica aerogels provides superior insulation

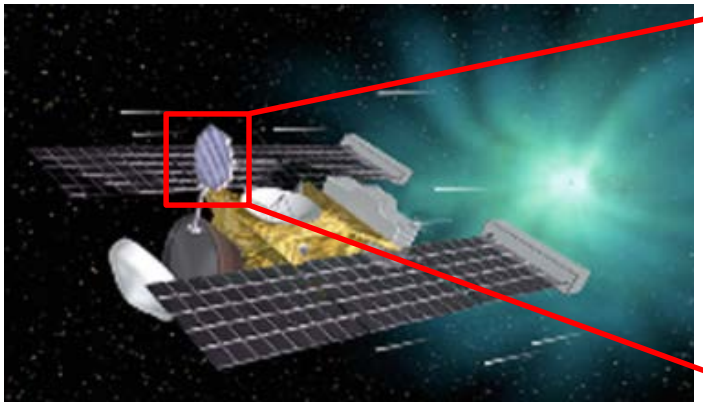


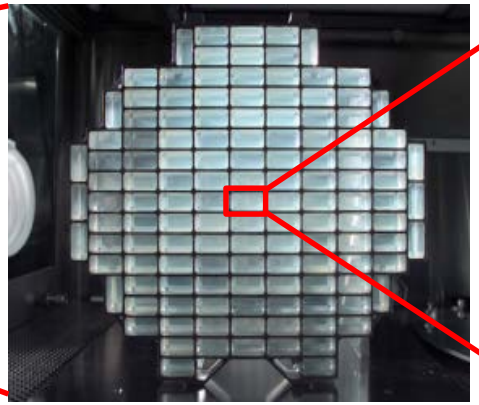




…but are extremely fragile and moisture sensitive

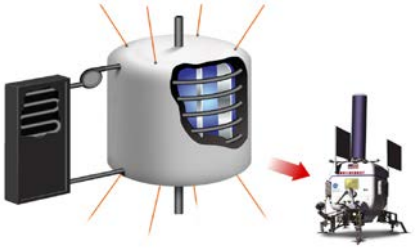
…and limited to a few exotic applications



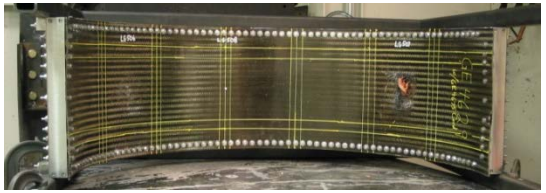




Potential applications for durable aerogels in aeronautics and space exploration



Cryotank Insulation



Fan engine containment (Ballistic protection)



Antenna substrates



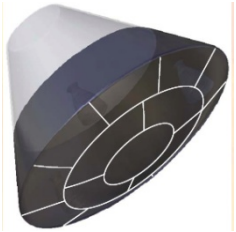
Ultra-lightweight, multifunctional structures for habitats, rovers



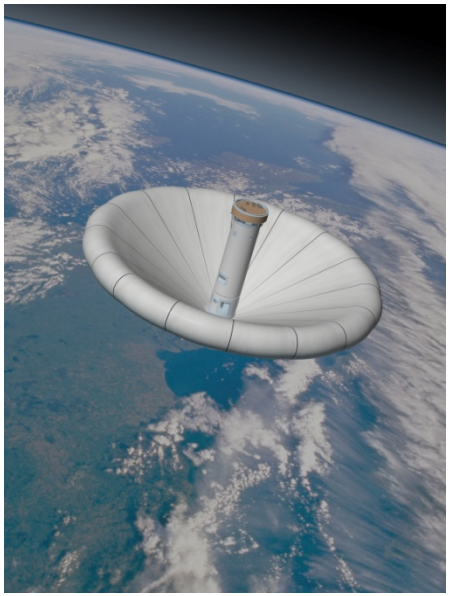
Sandwich structures



Propellant tanks



Heat shielding

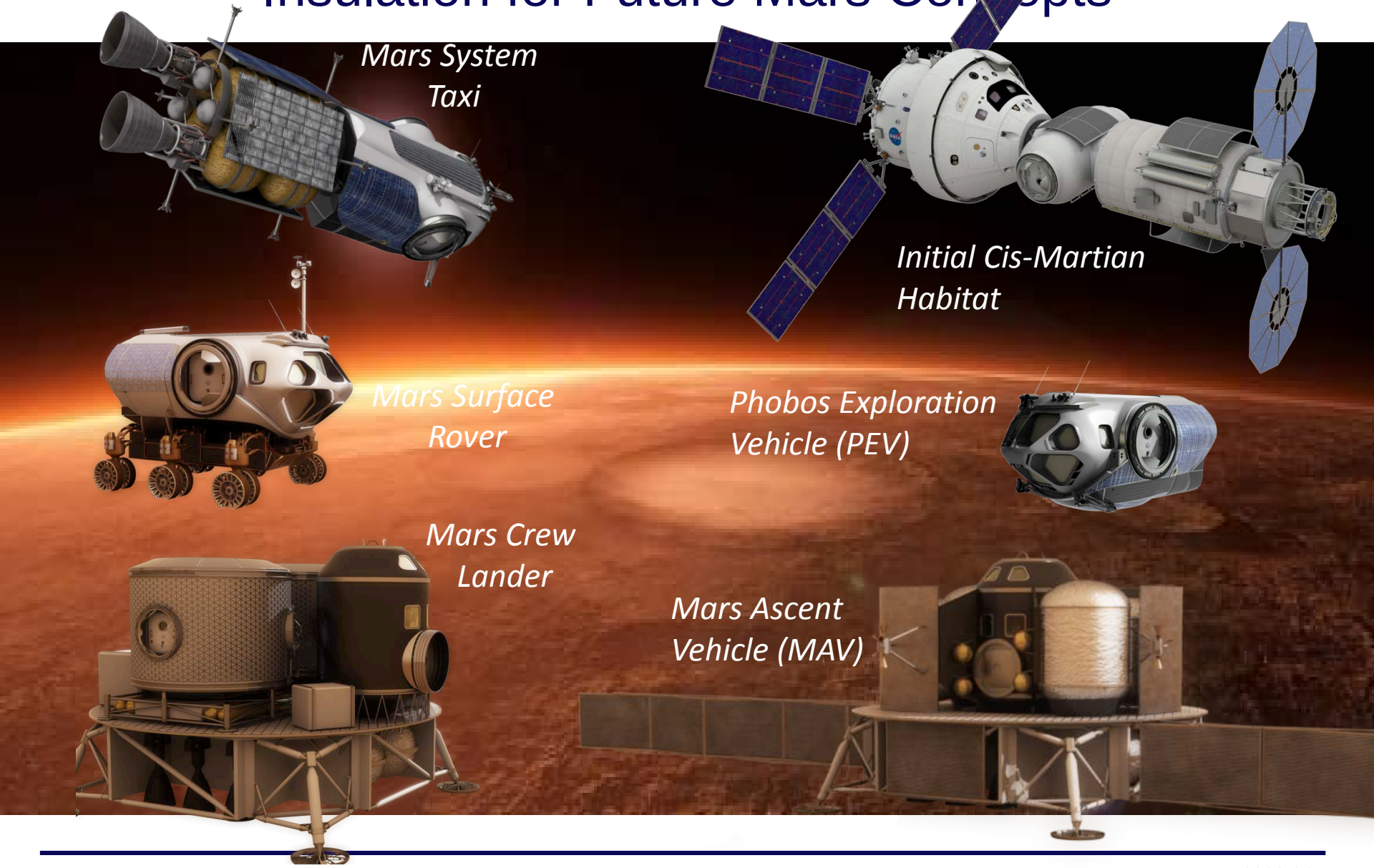


Inflatable aerodynamic decelerators



Insulation for EVA suits and habitats

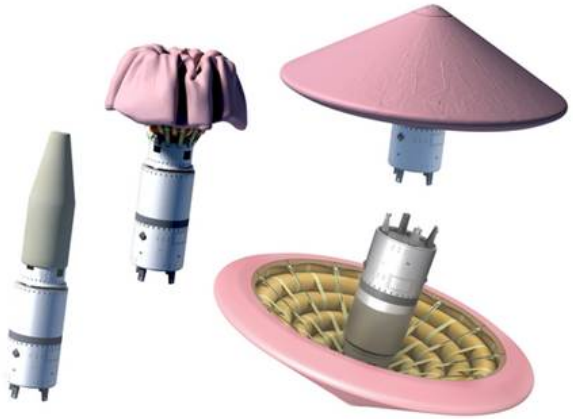
Insulation for Future Mars Concepts



Hypersonic inflatable aerodynamic decelerator concept

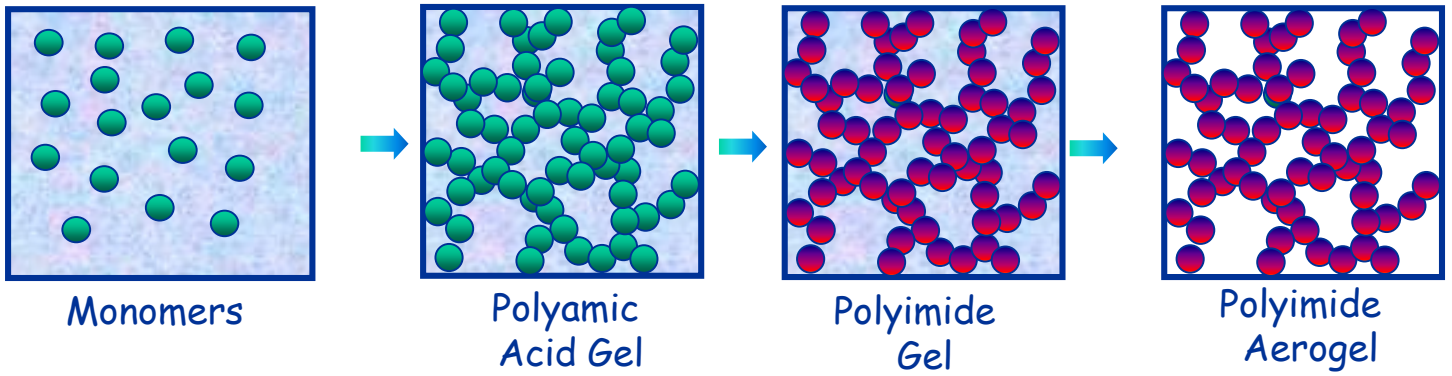
- Hard aeroshells used to land rovers on Mars limit size of payload
- Inflatable structure overcomes this limitation
- Concept is a series of stacked inflatable tori tied with a network of straps
- Flexible thermal protection system on fore body
- Baseline insulation was Aspen silica Aerogel composite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







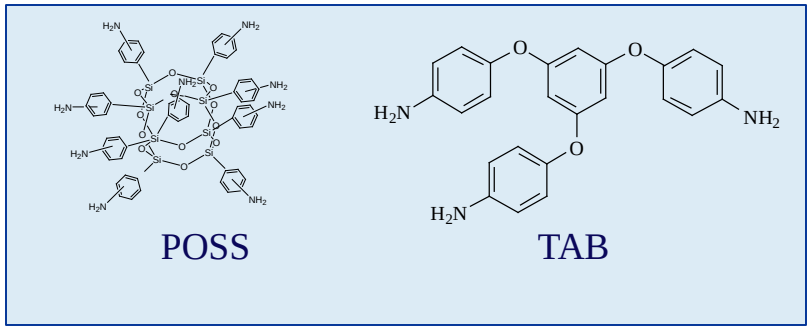
Polyimide aerogels



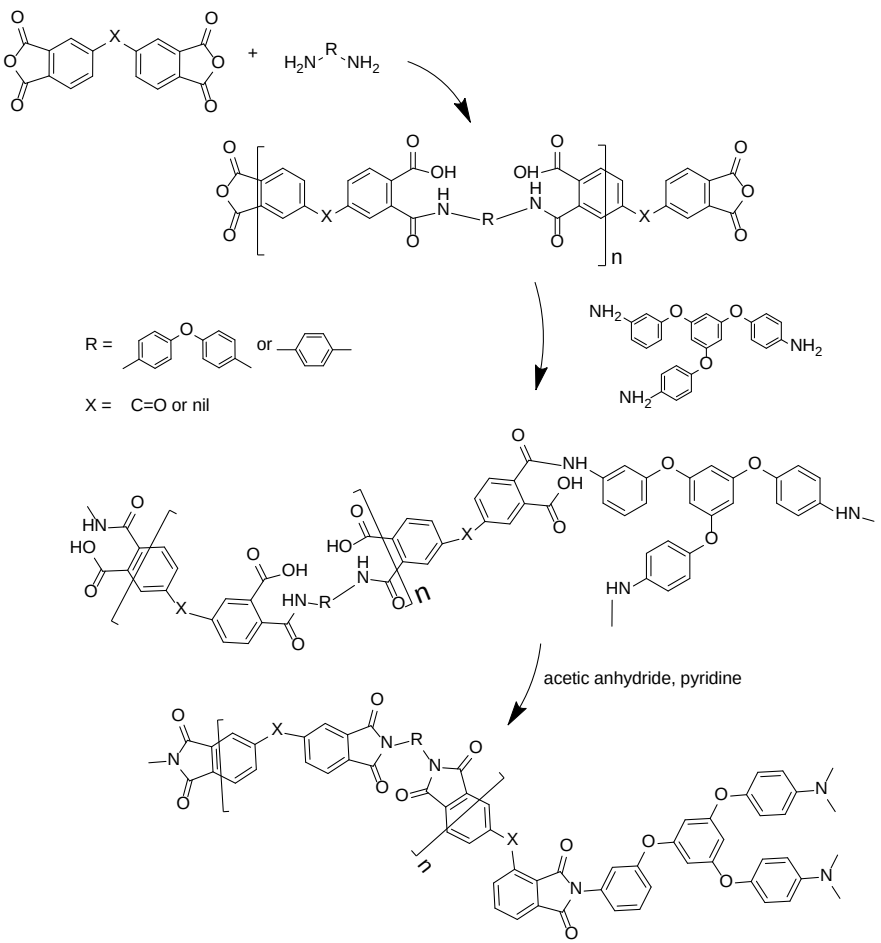
- Entire aerogel skeletal architecture synthesized from a polymer should be flexible as a thin film
- Polyimides are known for their high temperature stability
- Family of polymer aerogels made by cross-linking polyimide oligomers to form gel network
- Supercritical fluid extraction to remove liquid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

Meador, US Patent application filed 9-30-2009
Meador and Guo, US Patent application filed 2/4/2012

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



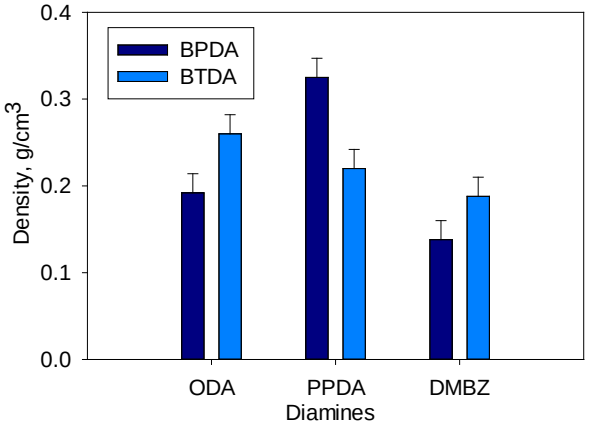
Meador, US Patent 9,309,369, April 12, 2016.
Meador and Guo, US Patent 9,109,088, August 18, 2015.
Nguyen and Meador, US Patent 8,974,903, March 10, 2015.

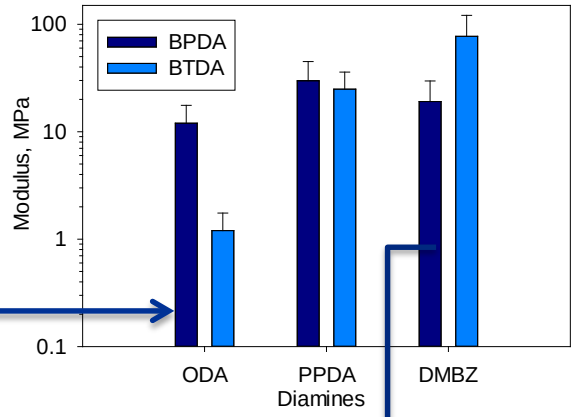
Polyimide Aerogels much stronger than silica aerogels at similar density



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

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





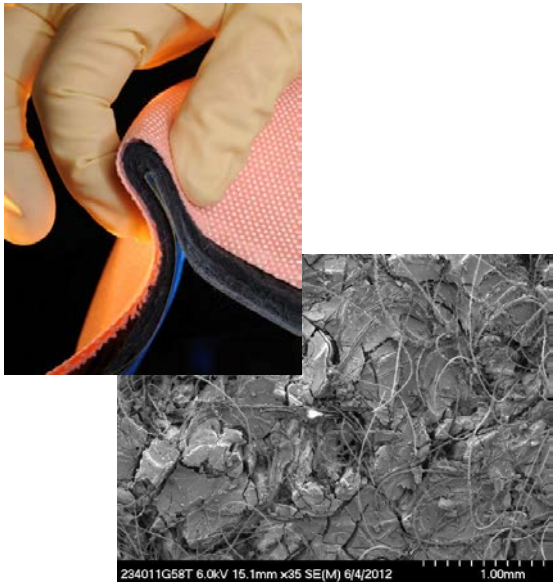
As-cast wet films

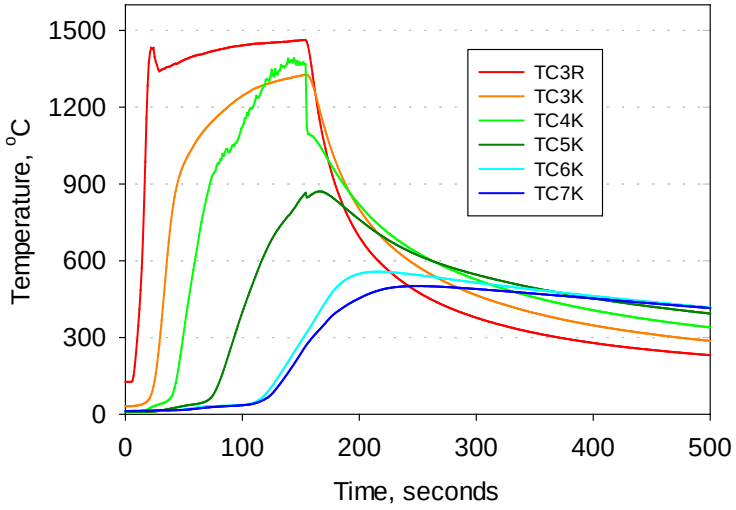


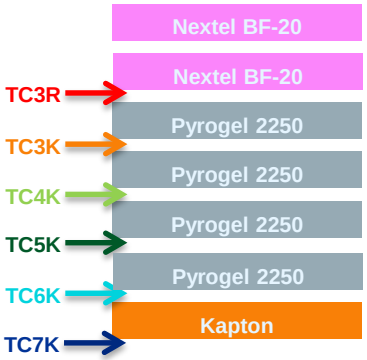
Dry aerogel

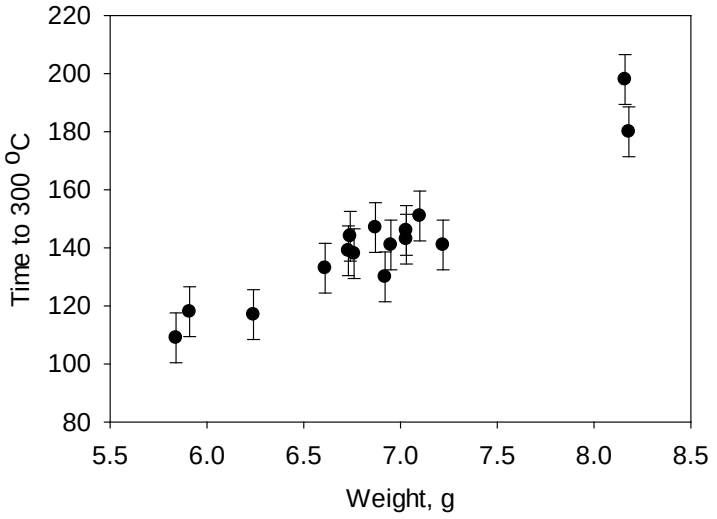
Baseline insulation for HIAD is Pyrogel-2250

- 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 ^{o}C
- High heat flux testing at Large Core Arc Tunnel (LCAT) facility at Boeing
- Time to 300 ^{o}C of bottom thermocouple measured
- Related to weight of insulation
- Pyrogel layers lose 20-34 % weight during test



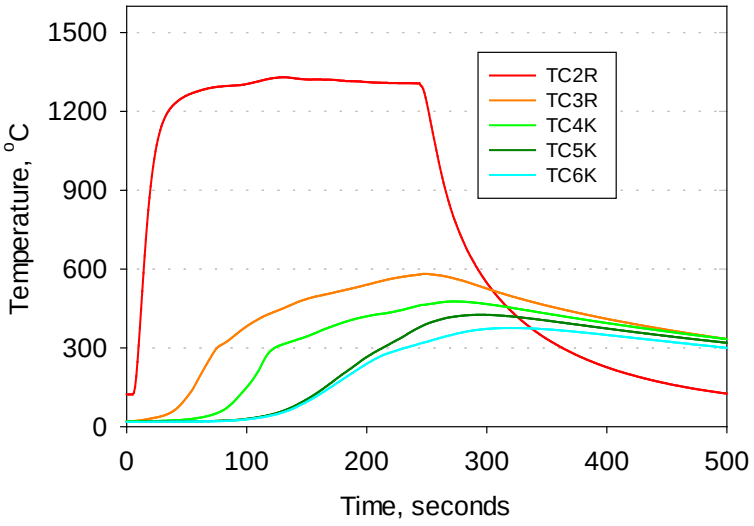


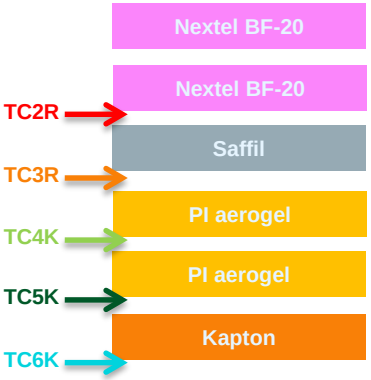


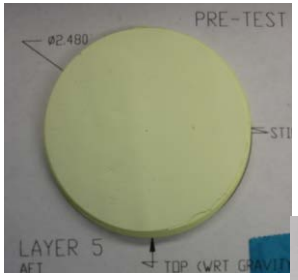


LCAT test—Saffil in combination with PI aerogel

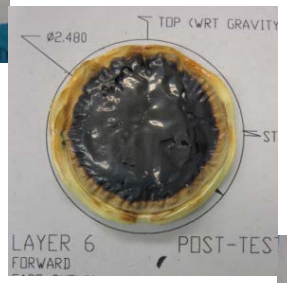
- Layer of Saffil backed by two equivalent thicknesses PI aerogel
  - 50% DMBZ \ 50% ODA
- Test stopped after 247 s when the bottom RC reached 300 °C
- Top of PI stack ~590 °C max
- PI lost much less weight than Pyrogel



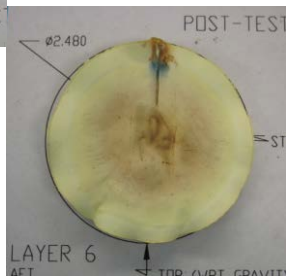




Before test



Top, after test



Bottom, after test

Multifunctional, Universal Thermal Insulation System

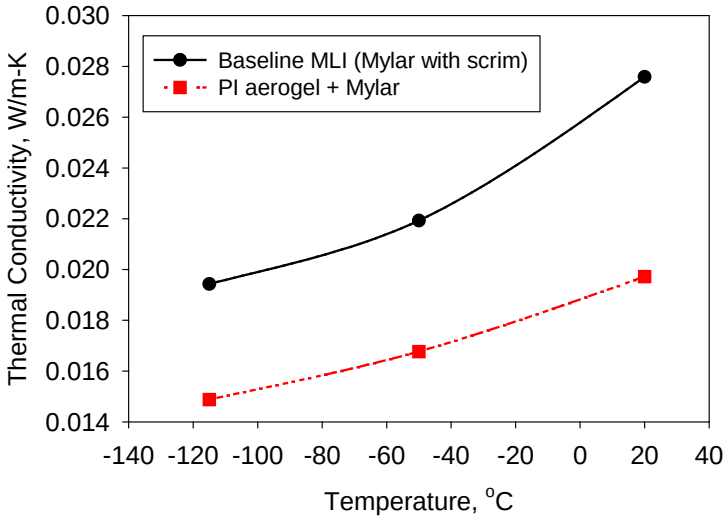
- Current multilayer insulation (MLI) only functions in vacuum
  - Layers of Mylar separated by scrim layers
- Aerogel is best insulation in gaseous environment
- MLI incorporating aerogel in place of scrim reduces TC by 23-37%
- Partnership with JSC and GRC



Baseline MLI (Mylar + scrim)



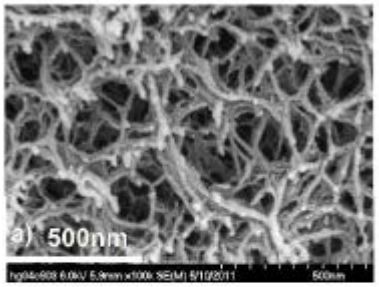
Pi aerogel + Mylar



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

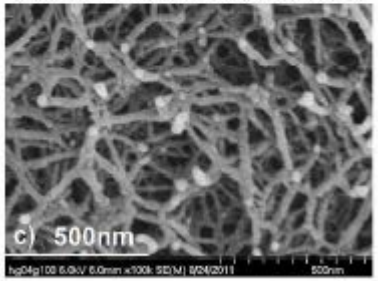
Mixtures of rigid and flexible diamines give better combination of properties

100 % DMBZ



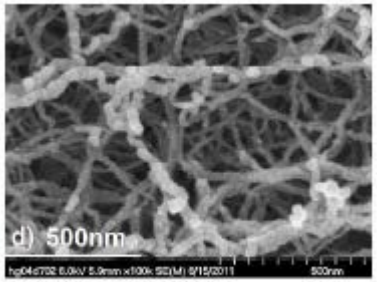
0.09g/cm^3, 94% porous, 498 m^2/g

100 % ODA



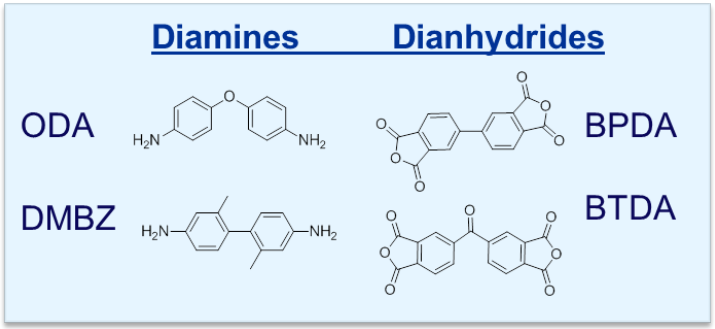
0.13g/cm^3, 91% porous, 295 m^2/g

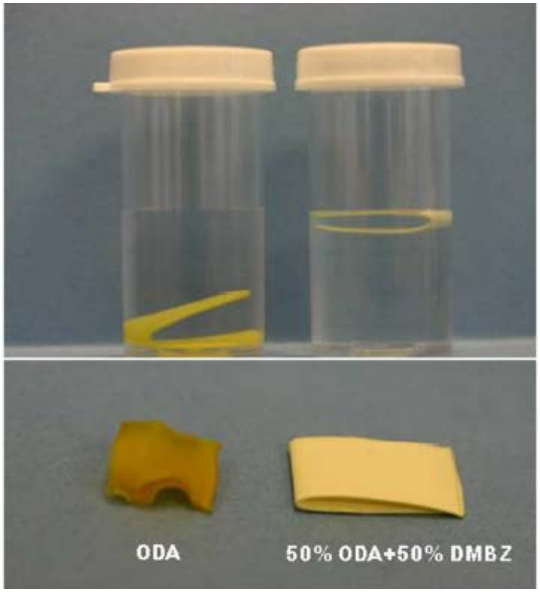
50 % ODA 50% DMBZ

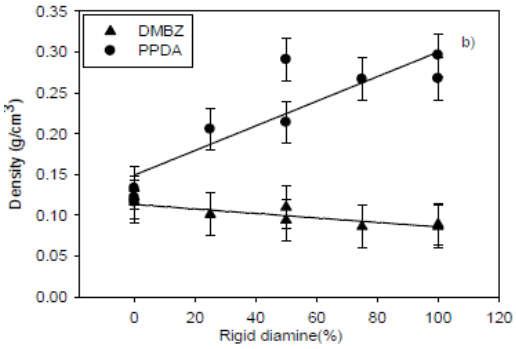


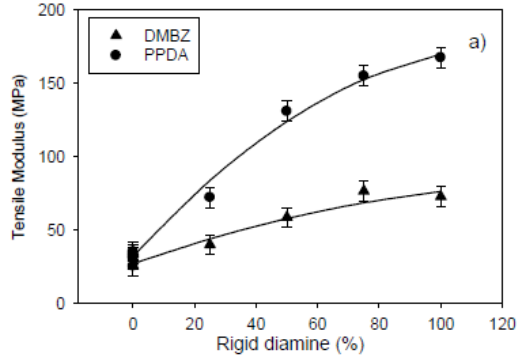
0.10g/cm^3, 93% porous, 392 m^2/g

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





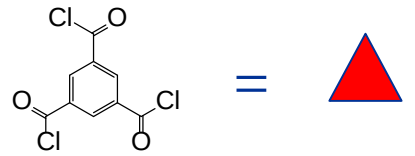


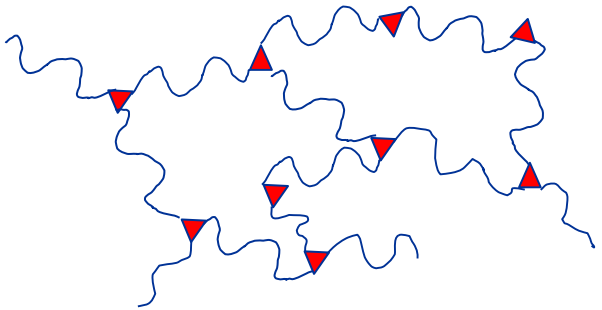


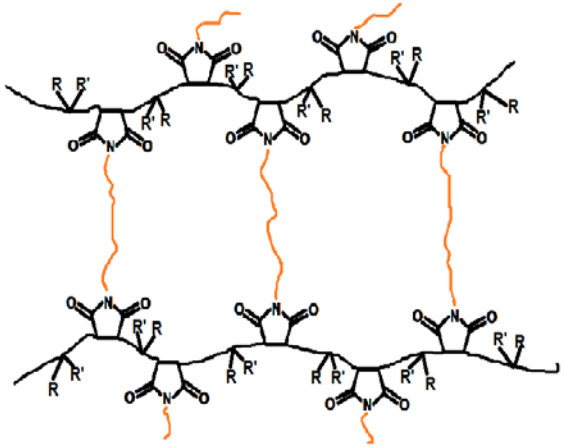
Guo et al, ACS Applied Materials and Interfaces, **2012**, ASAP

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

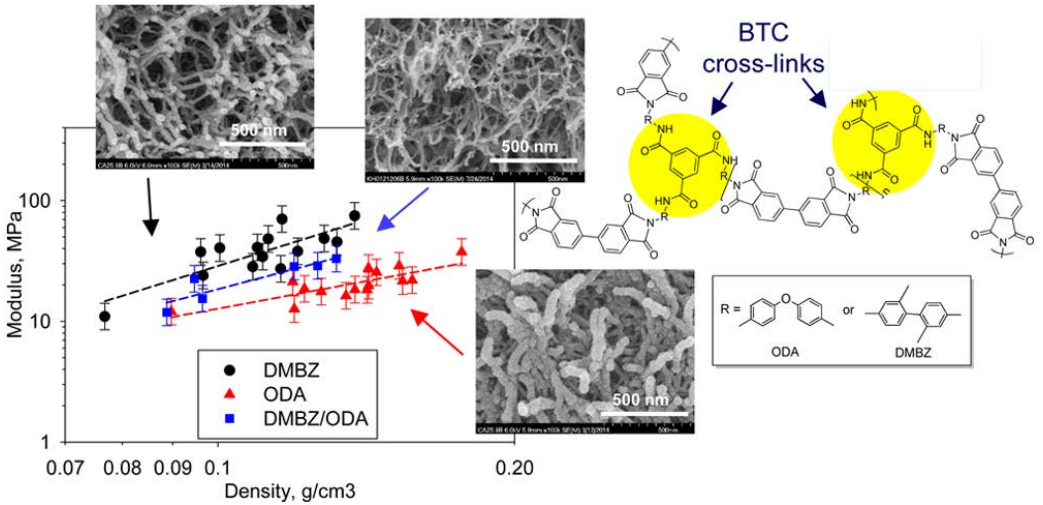


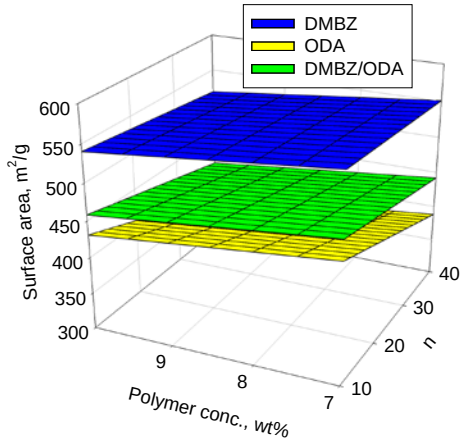


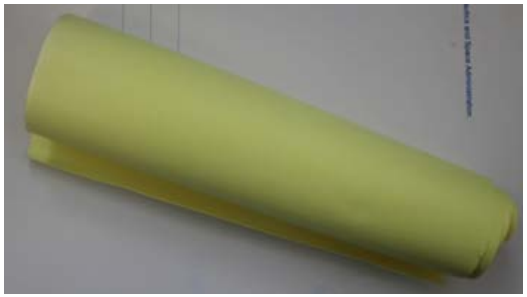


Polyimide aerogels with alternate commercially available cross-linker—BTC

- Used ODA or DMBZ in backbone to compare to other cross-linkers
- Modulus, morphology depend on backbone, not cross-linker
- Surface areas about 100 m^2/g higher with BTC



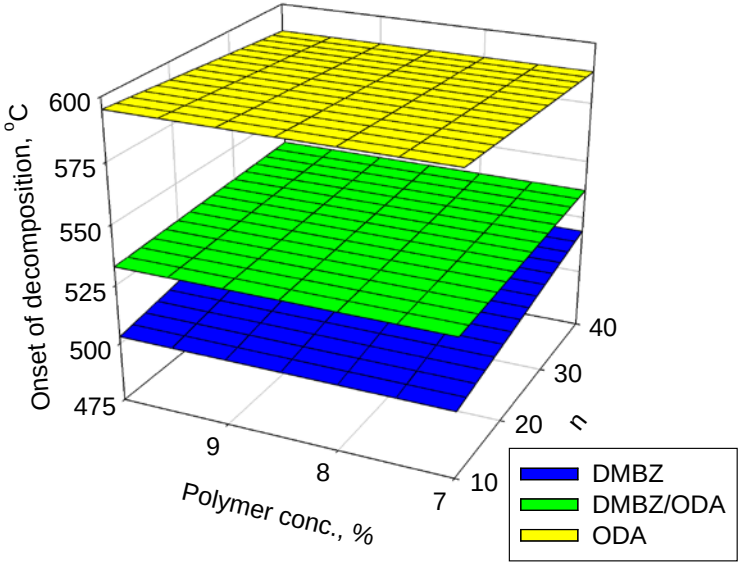


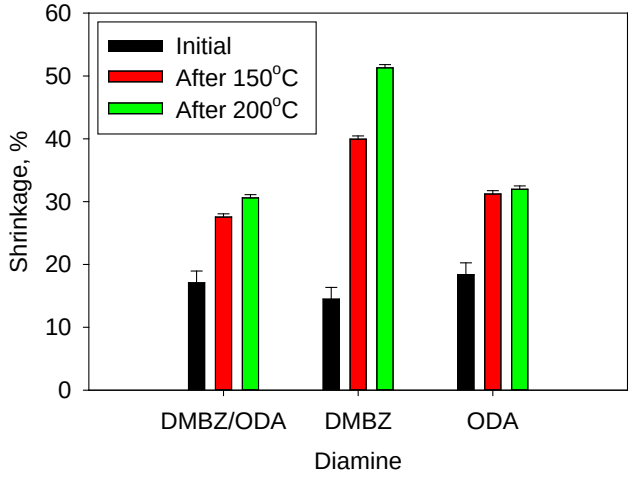


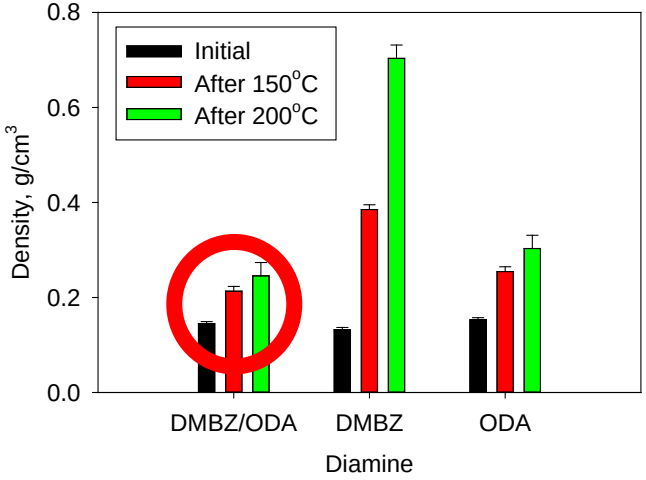
Meador et al, *ACS Appl. Mater. Interfaces* **2015**, *7* 1240-1249

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



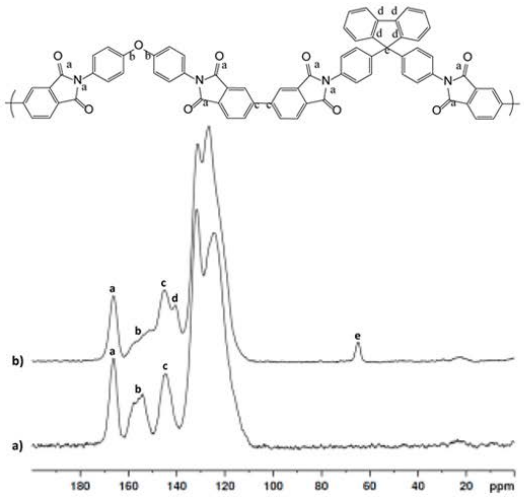


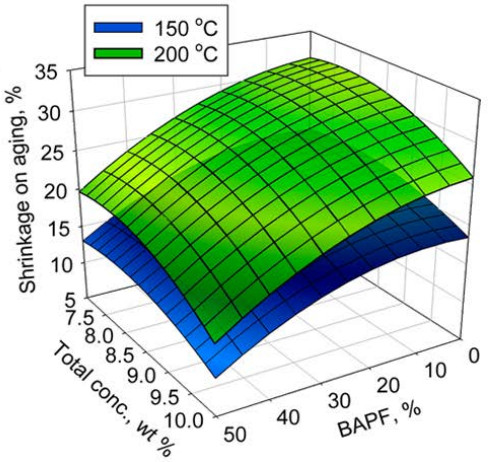


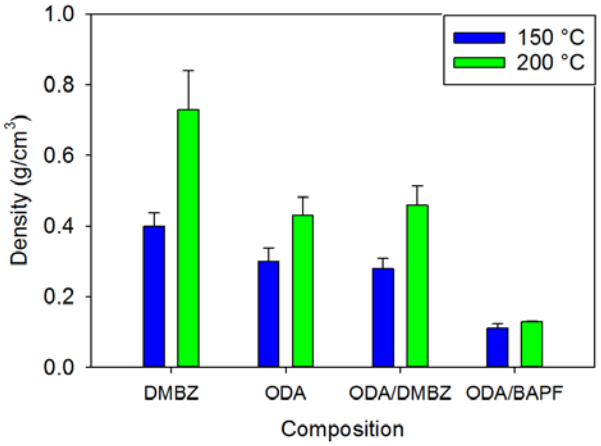
Meador et al, *ACS Appl. Mater. Interfaces* **2015**, *7* 1240-1249

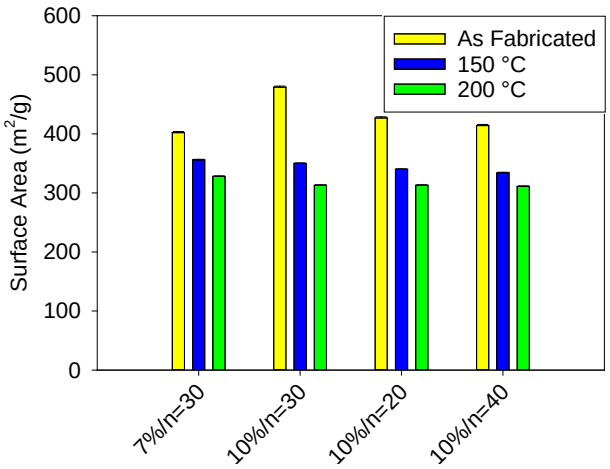
Use of bulky substituents in polymer chain reduces shrinkage after 500 hours aging

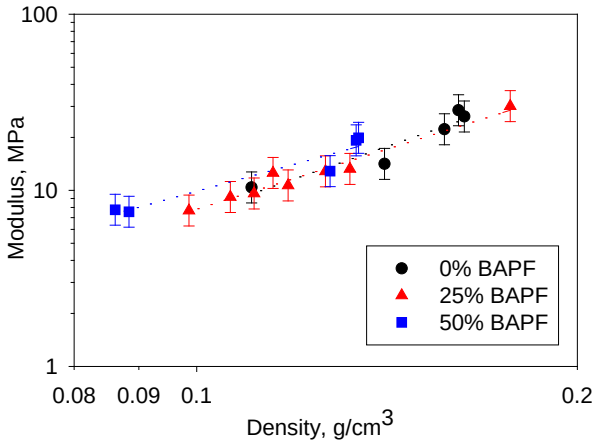
- Replacing 50 mol % of ODA with BAPF reduces shrinkage by up to half
- Surface area still above 300 m^2/g after aging











Viggiano et al, *ACS Appl. Mater. Interfaces* **2017**, *9*, 8287−8296

Multifunctional Energy Storage to Improve Efficiency

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

Challenges

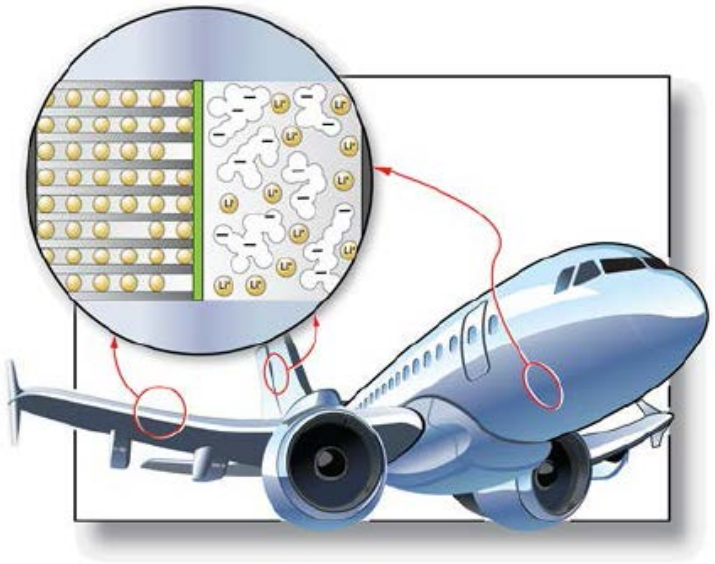
- Producing a structure capable of bearing weight and resisting forces associated with flight

Risks

- Current Li-Ion battery technology utilizes flammable components

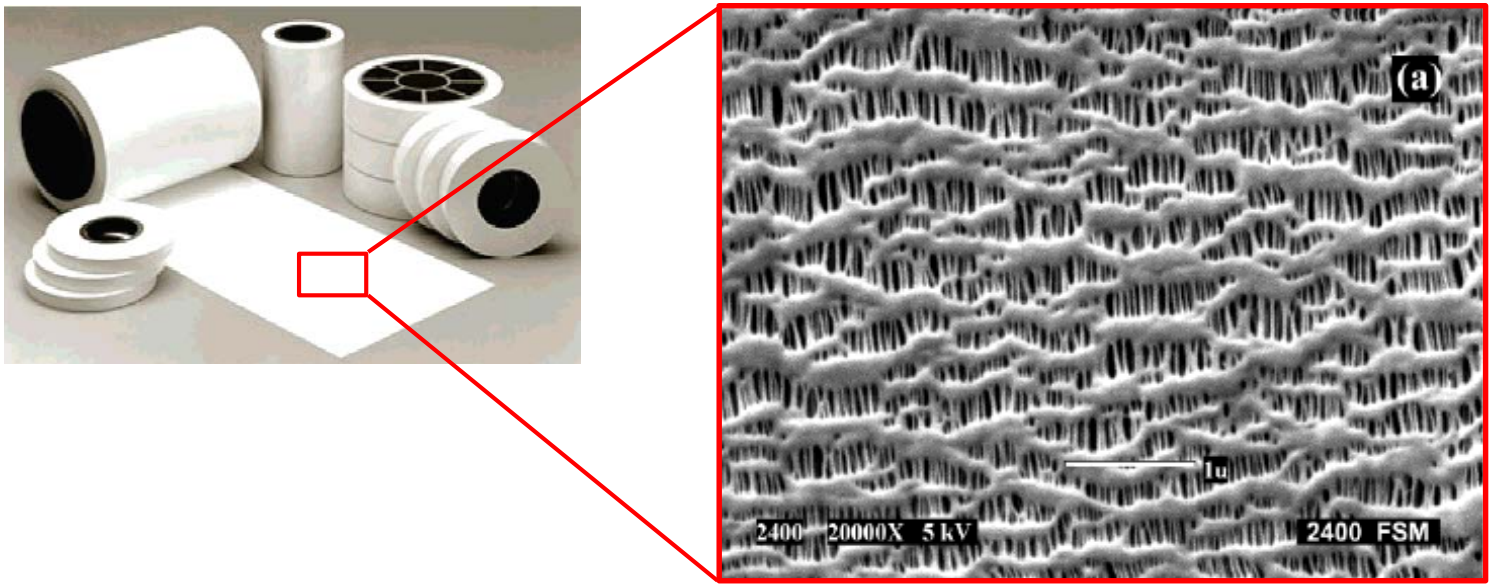
Goals

- 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%

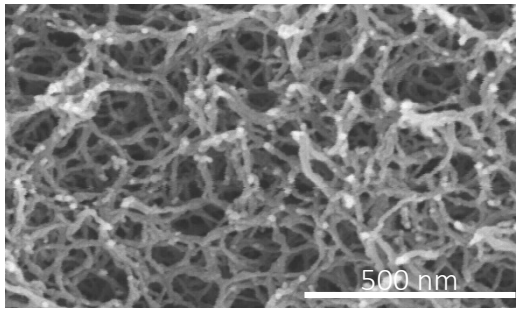
Polyolefin Separators used in Li-Ion Batteries



Separator/Properties	Celgard 2730	Celgard 2400	Celgard 2325	Asahi Hipore	Tonen Setela
Structure	Single Layer	Single Layer	Trilayer	Single Layer	Single Layer
Composition	PE	PP	PP/PE/PP	PE	PE
Thickness (µm)	20	25	25	25	25
Porosity (%)	43	40	42	40	41
Melt Temp. (°C)	135	165	135/165	138	137

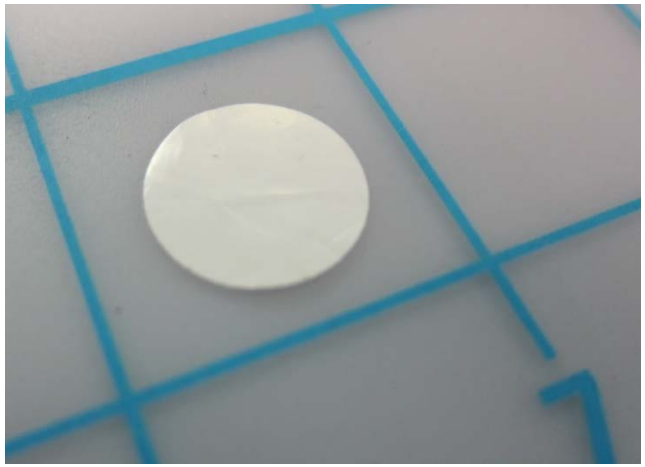
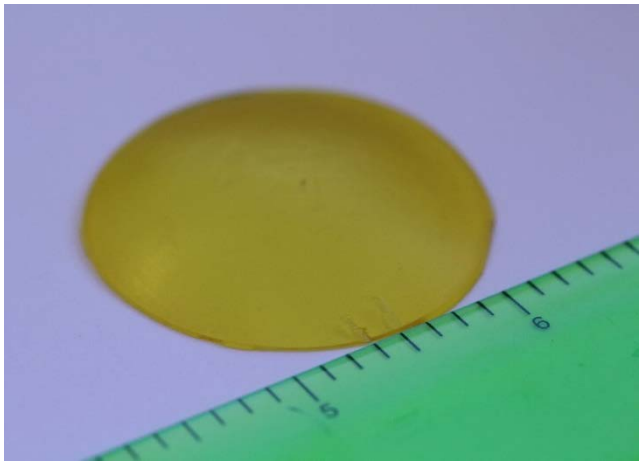
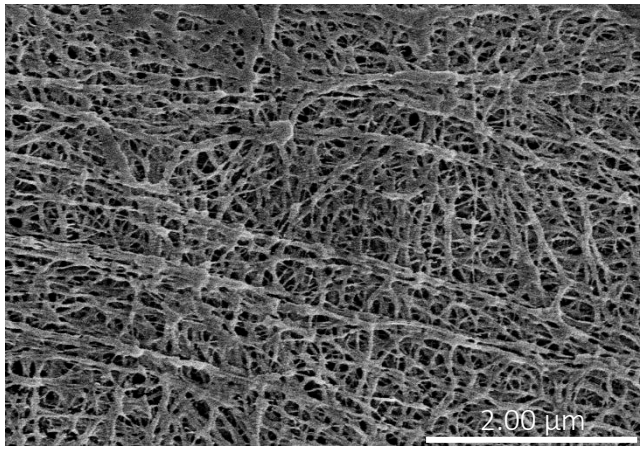
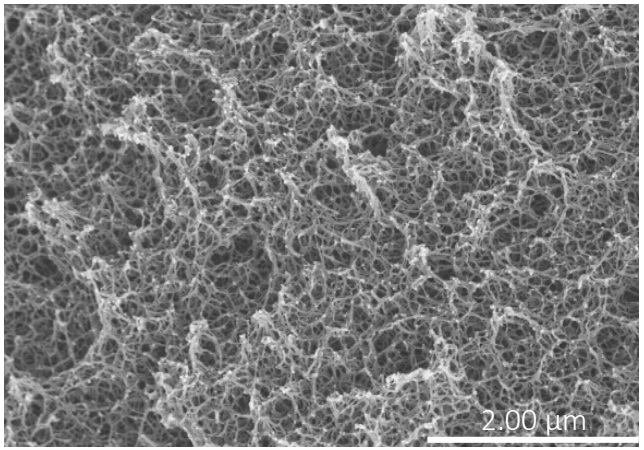
- Polyethylene and polypropylene are among the most flammable polymers
- Limited number of electrolytes wet the polyolefins

Down Selection to ODA-BPDA-N3300A

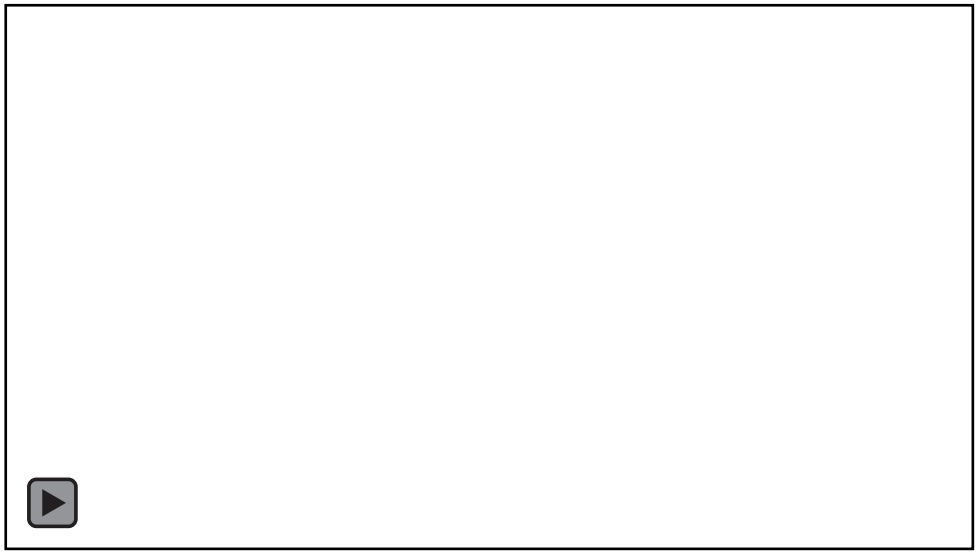


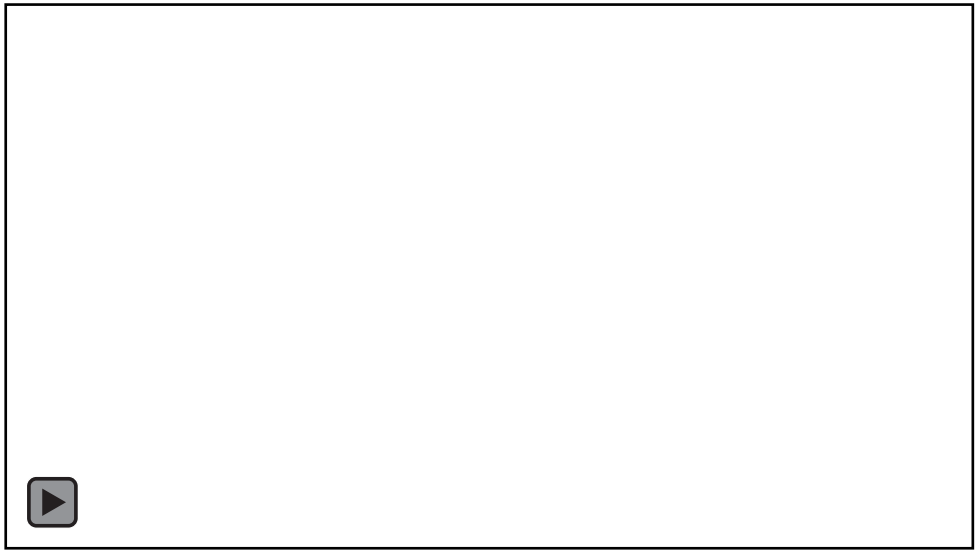
- Many polyimide backbone chemistries were synthesized and characterized
- Several factors were considered in down selection: film forming, mechanical strength, porosity
- ODA-BPDA-N3300A formed thin, mechanically robust films, with porosities of 93%

Comparison of Commercial Separator and PI Aerogel

Celgard© PE Separator	Polyimide Aerogel
	
	

PI/EMIM Gel Separator is Nonflammable Under Direct Contact with Flame





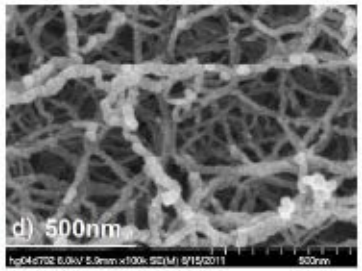
Polyimide Aerogel Development

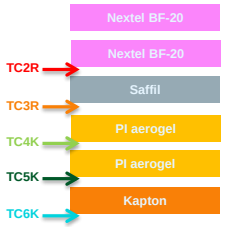
- Over fifty different combinations of backbone chemistry studied
- Multiple cross-linkers evaluated
- Properties more dependent on backbone
- Formulations identified with
  - Best moisture resistance
  - Best mechanical properties/density
  - Low thermal conductivity
  - More optical clarity

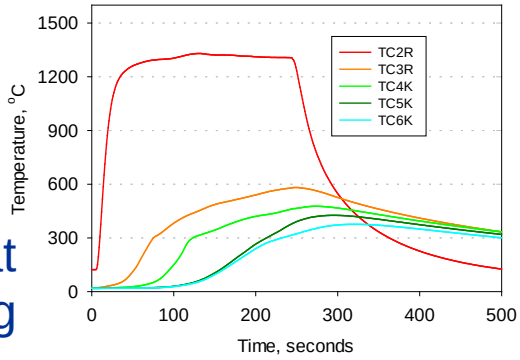


Clear to opaque

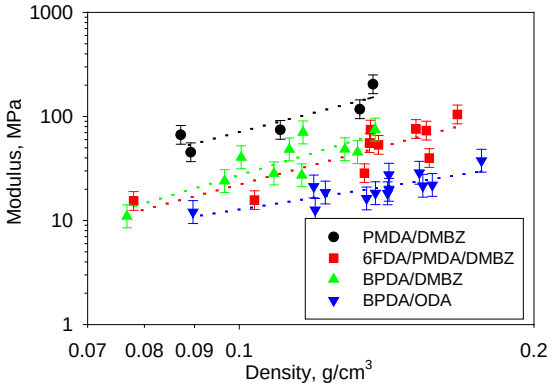
Pore structure





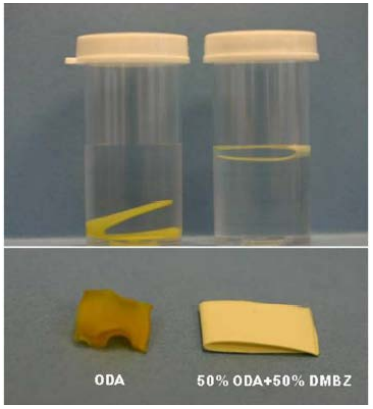


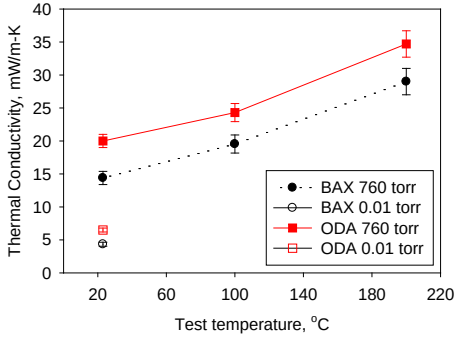
High heat flux testing



Mechanical properties related to density

Moisture resistant

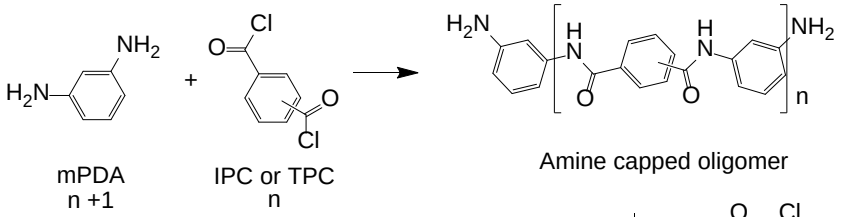


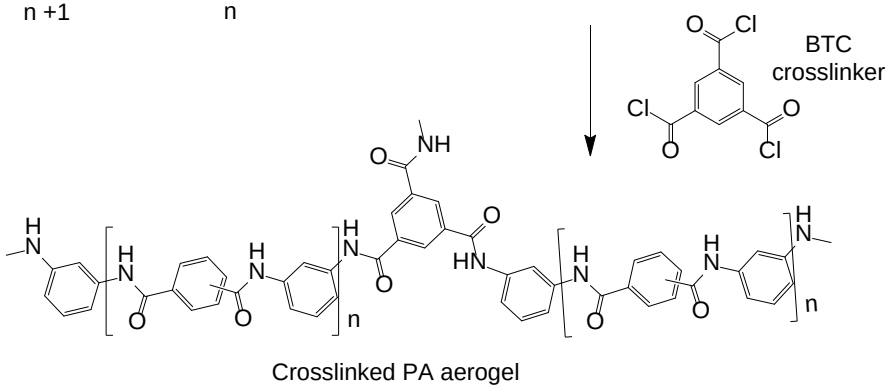


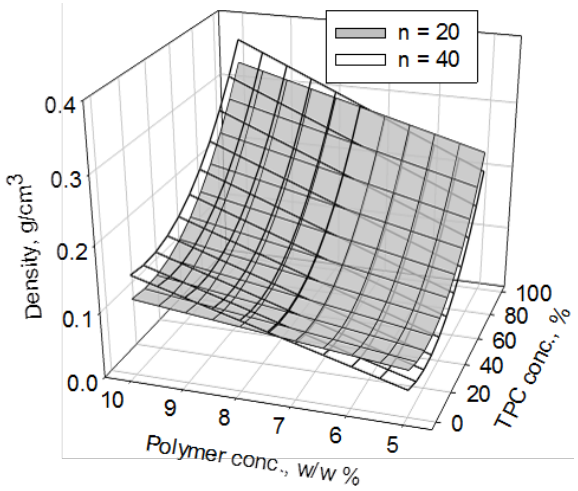
Low thermal conductivity

Polyamide aerogels

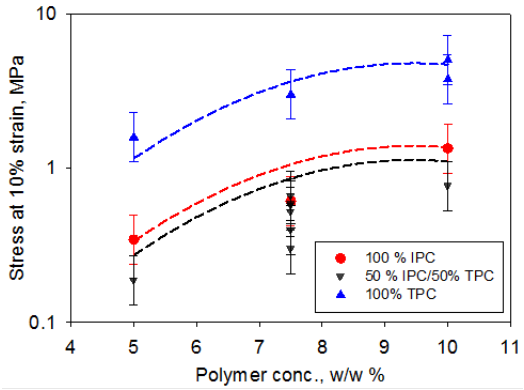
- Lower cost monomers and cross-linkers
- No catalyst needed
- Slightly less thermally stable

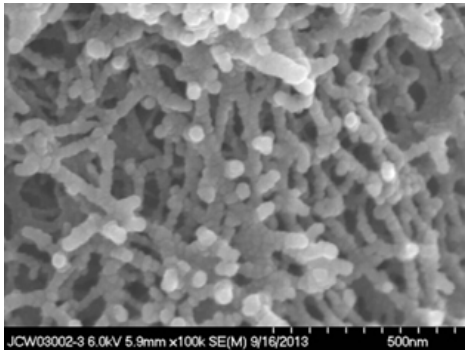








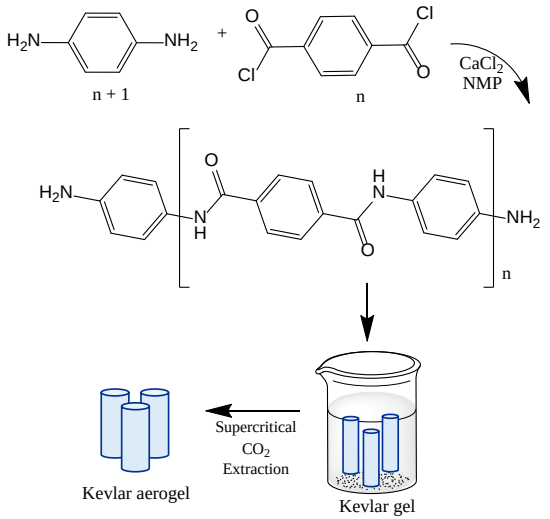


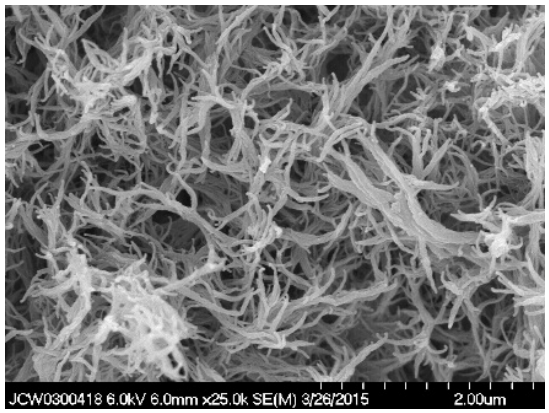


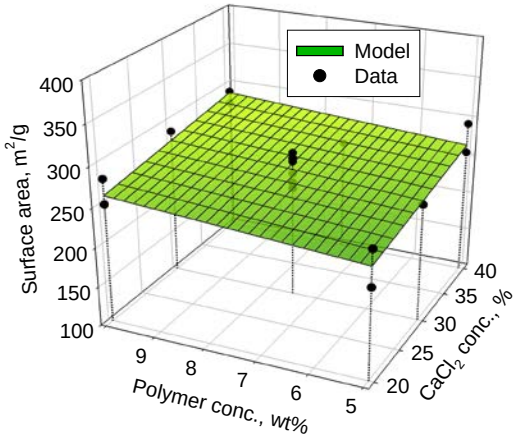
Williams *et al*, *Chem. Mater.*, **2014**, *26(14)*, 4163-4171

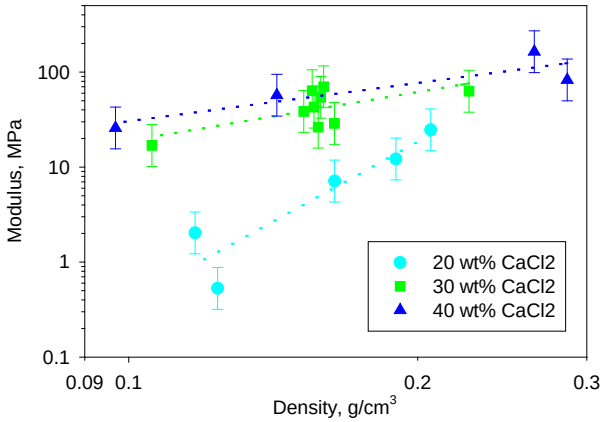
Polyamide aerogels—Kevlar based

- Low cost monomers
- All para substitution kept in solution by use of $CaCl_2$
- Salt also gets rid of distortion problem of PA gels during solvent exchange
- Different morphology, but still high surface area, strong

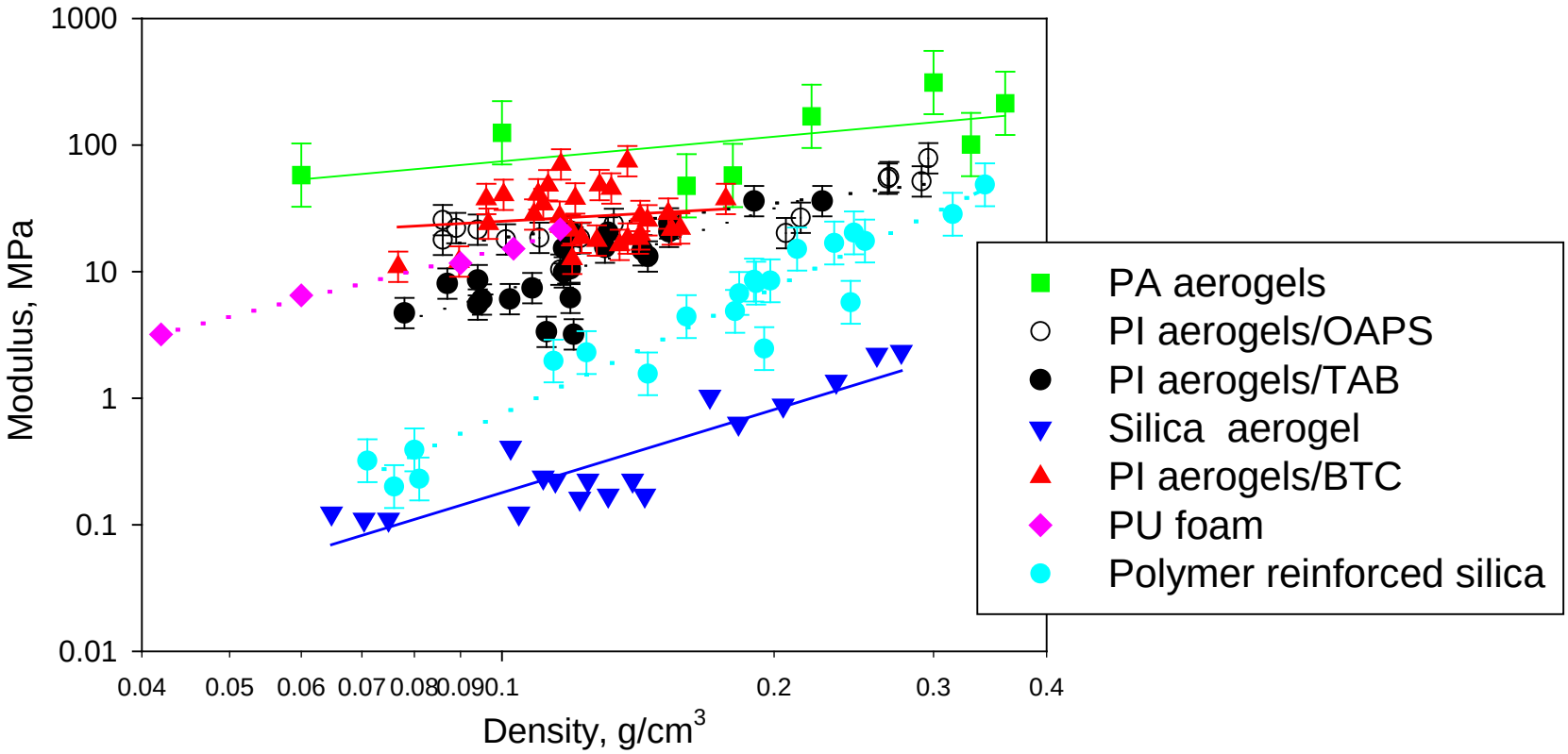








PI aerogels are stronger than silica aerogels but PA aerogels stronger yet on a density basis



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

Aerogel Technologies Airloy





Blueshift AeroZero

NASA Opportunities

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

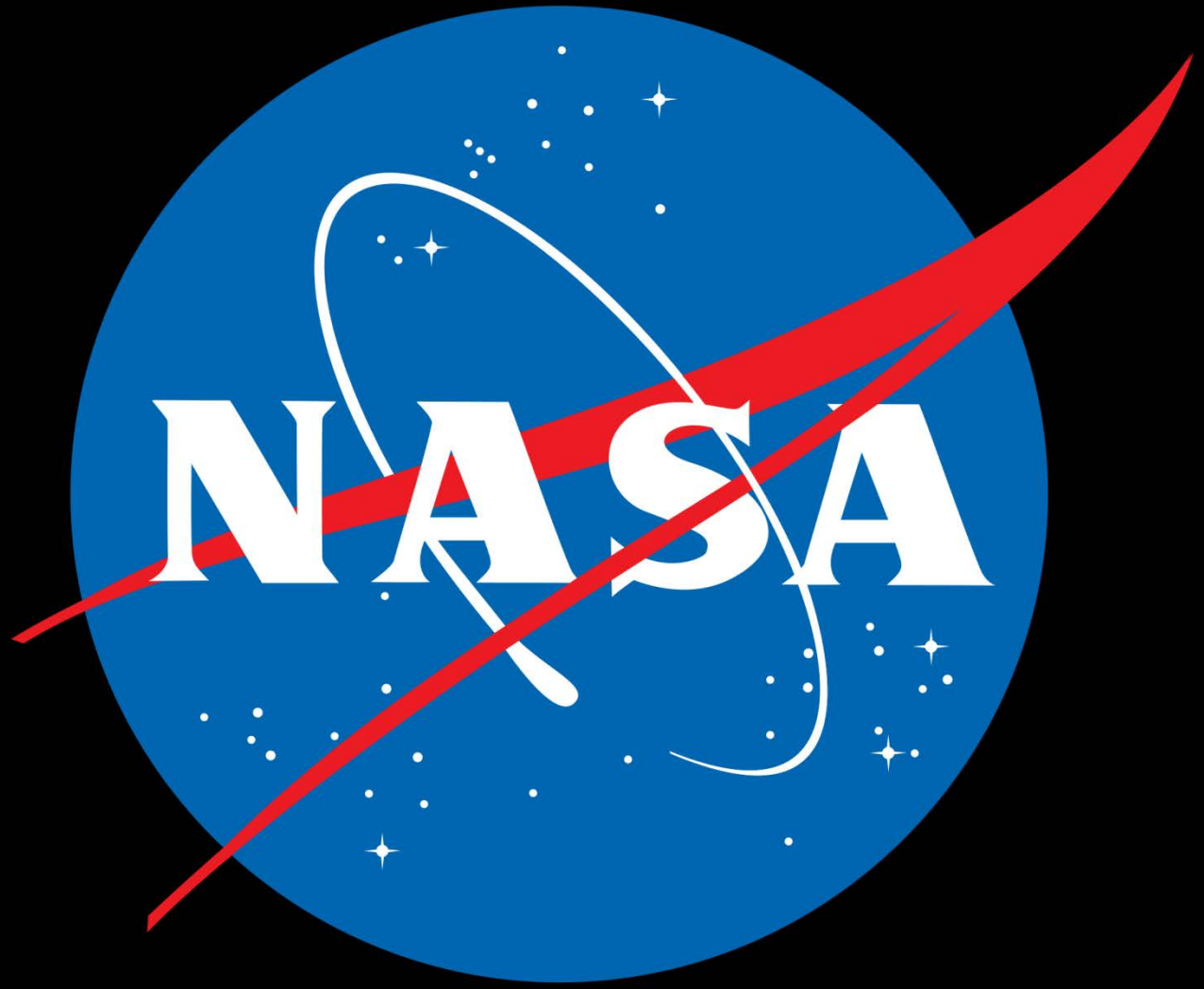
- Pathways Intern and Recent Graduate Positions:
  - www.usajobs.gov
  - Example-Search “glenn pathways”
  - For PMF-STEM visit www.pmf.gov

- Regular Full-Time Positions:
  - www.usajobs.gov
  - Search “glenn research center”

- Other Student Opportunities:
  - https://intern.nasa.gov
  - Search Opportunities
  - Limited opportunities for international students

NASA Glenn Research Center, Cleveland, OH

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