

Improvements to the Synthesis of Polyimide Aerogels

Cross-linked polyimide aerogels are viable approach to higher temperature, flexible insulation for inflatable decelerators. Results indicate that the all-polyimide aerogels are as strong or stronger than polymer reinforced silica aerogels at the same density. Currently, examining use of carbon nanofiber and clay nanoparticles to improve performance. Flexible, polyimide aerogels have potential utility in other applications such as space suits, habitats, shelter applications, etc. where low dusting is desired.



Improvements to the synthesis of polyimide aerogels

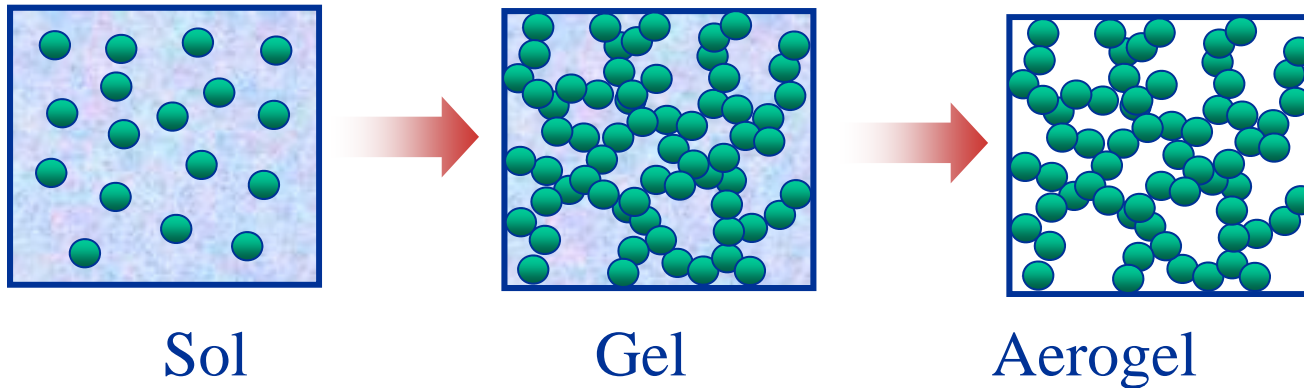
Mary Ann B. Meador, Baochau N. Nguyen,
Haiquan Guo, Stephanie Vivod, Zuhui He, Ericka
Malow and Rebecca Silva

NASA Glenn Research Center
Cleveland, OH 44135

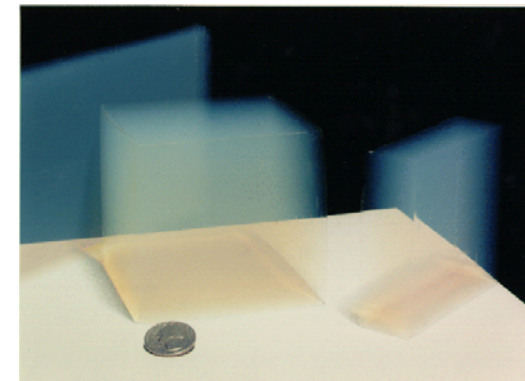
Maryann.meador@nasa.gov



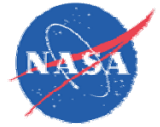
What are aerogels?



- 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 of the College of the Pacific



Typical monolithic silica aerogels



Examples of current commercial aerogel products

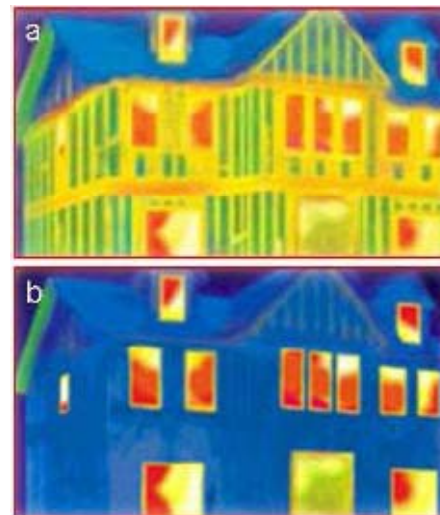
- Cabot
 - Pellets, composite
 - Oil and gas pipeline insulation
 - Cryo-insulation
 - Day-lighting applications
- Aspen Aerogels
 - Flexible blanket insulation
 - Oil and gas pipeline
 - Construction materials
 - Aerospace, apparel
- Nanopore
 - Vacuum insulation panels
 - Shipping containers
 - Refrigeration
 - Apparel



Expansion Pack™

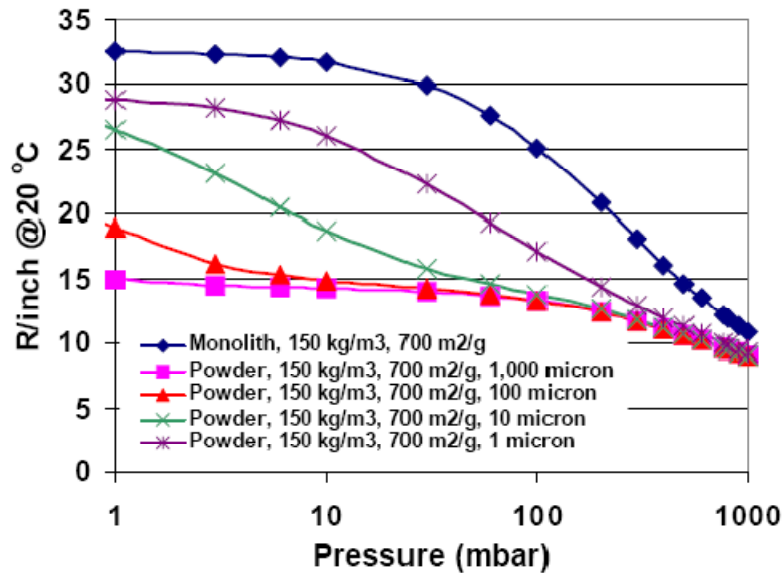


Particle Pack™





Monolithic silica aerogels out-perform particulate forms as insulation



...but are extremely fragile and moisture sensitive

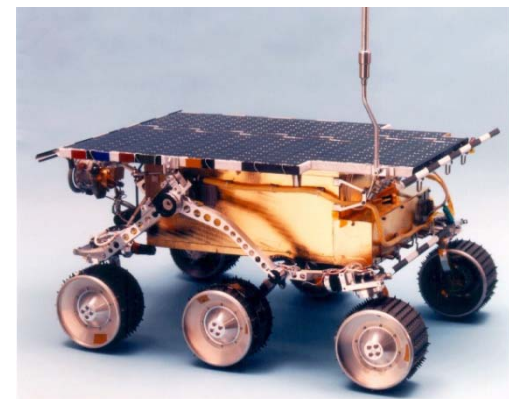


Doug Smith, Aerogel Conference, 2007

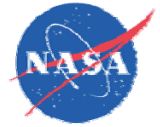
...and limited to a few exotic applications



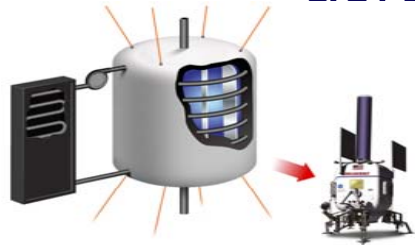
Cosmic dust collector - Stardust Program



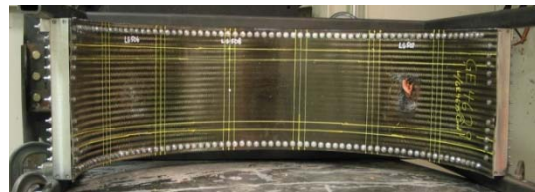
Insulation on rovers



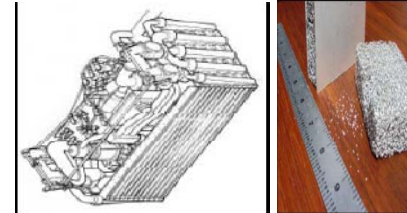
Potential applications for durable aerogels in aeronautics and space exploration



Cryotank Insulation



**Fan engine containment
(Ballistic protection)**



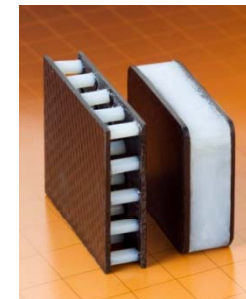
Air revitalization



Ultra-lightweight, multifunctional structures for habitats, rovers



Inflatable aerodynamic decelerators



Sandwich structures



Propellant tanks



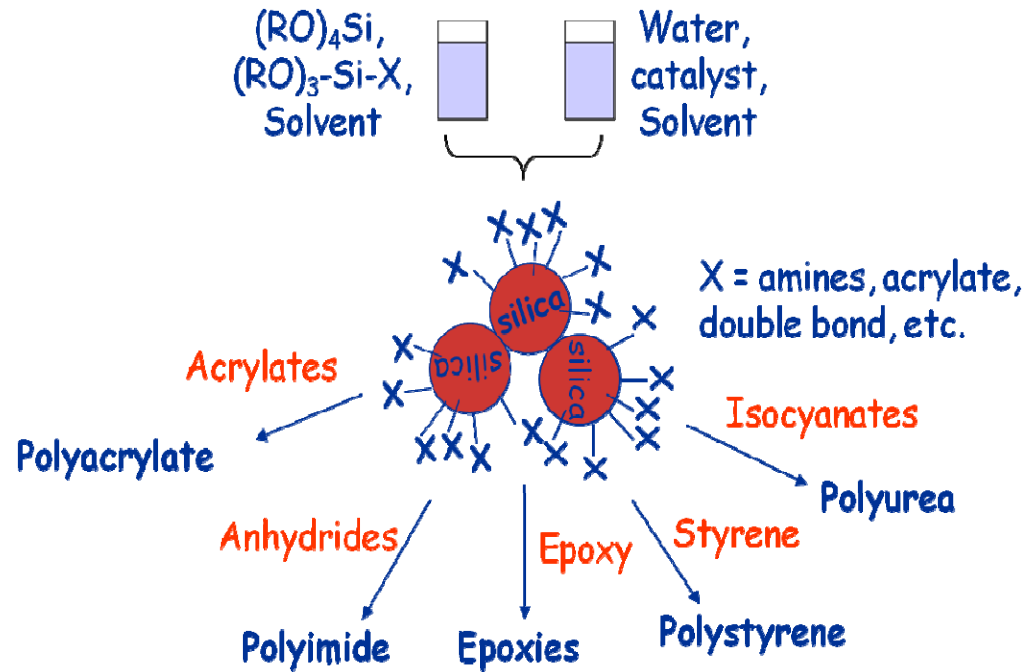
Heat shielding



Insulation for EVA suits, habitats and rovers



Durable aerogels by reinforcing with polymers



Native



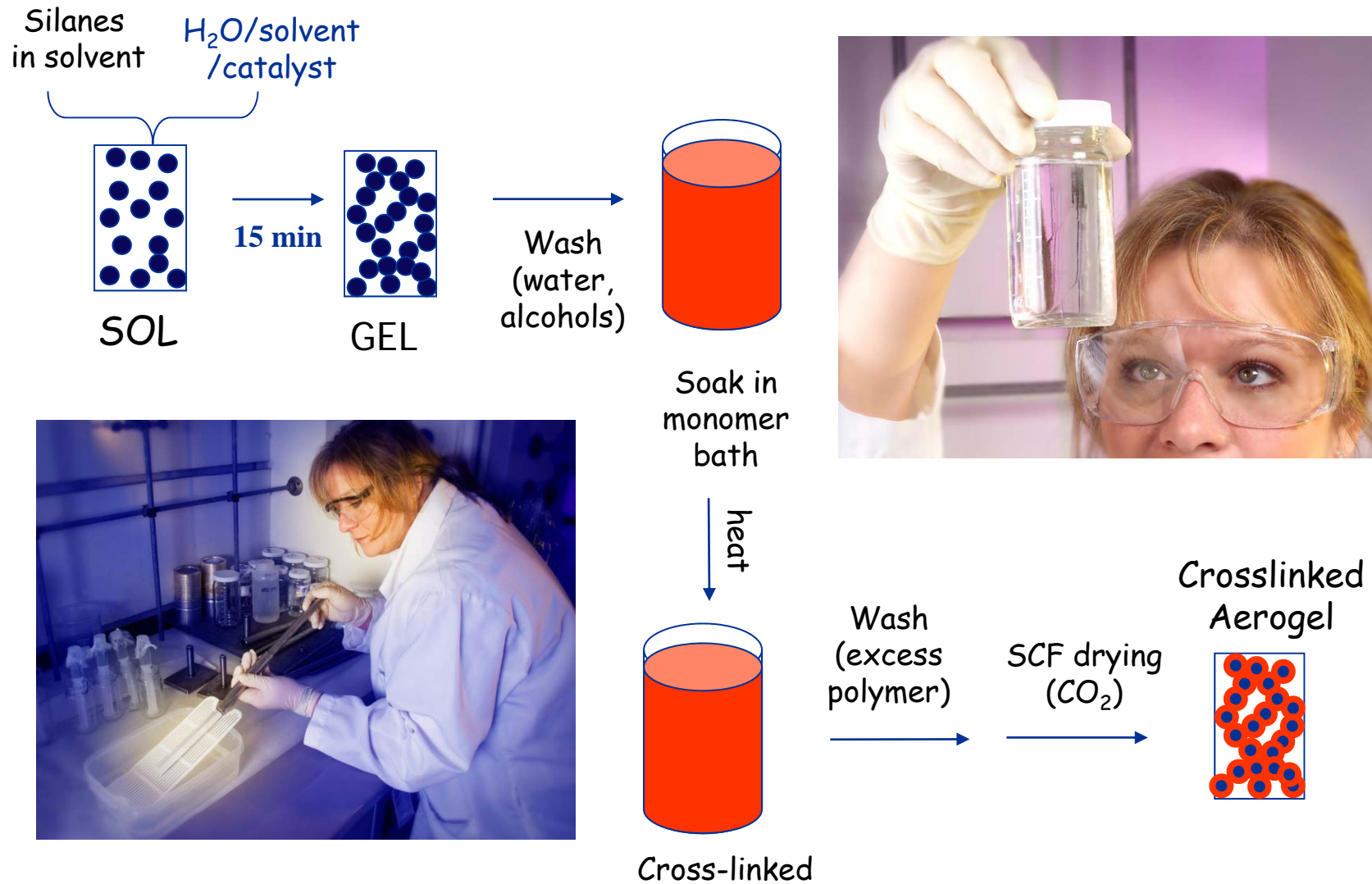
Cross-linked

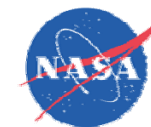
- Polymer reinforcement **doubles** the density
- Results in **two order of magnitude** increase in strength
- Reduces surface area by only 30-50%

- Leventis, Meador, Johnston, Fabrizio, and Ilhan, US Patent No. 7,732,496; June 8, 2010
- Jason P. Randall, Mary Ann B. Meador, and Sadhan C. Jana, *ACS Appl. Mater. Interfaces*, 2011, 3 (3), pp 613-626



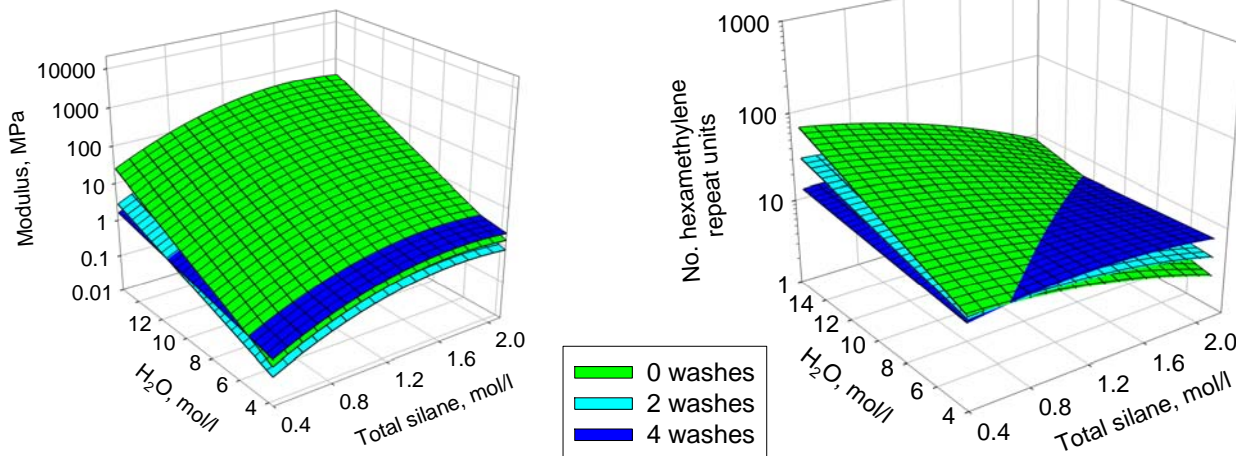
Typical Aerogel Cross-linking Process



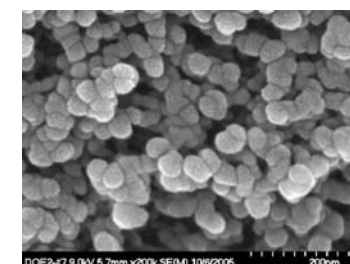
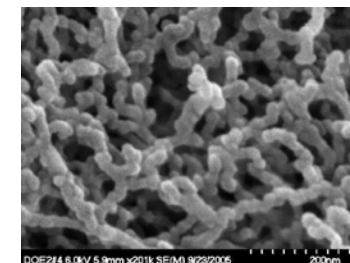


Process/property optimization of di-isocyanate cross-linked aerogels

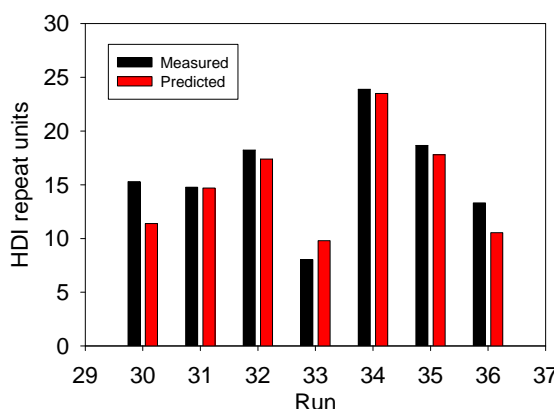
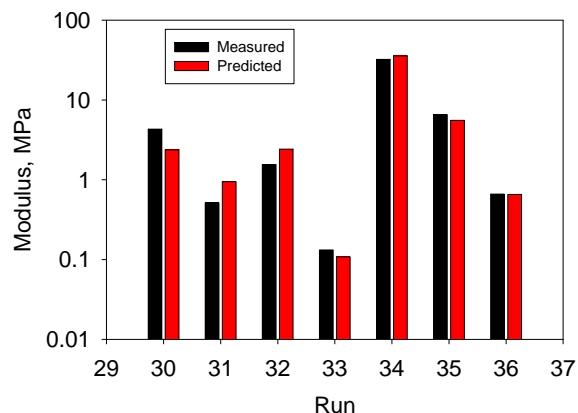
Empirical models...



Low density...

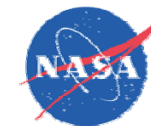


...used for predictions of optima

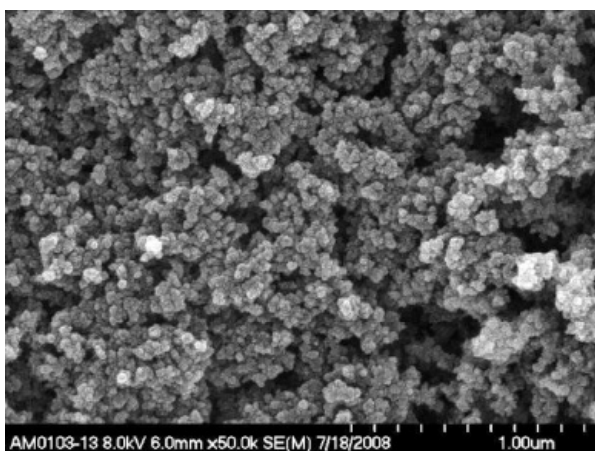


...to high density...
and everything
in-between

Meador et al, *Chemistry of Materials*, 2007, 19, 2247-2260

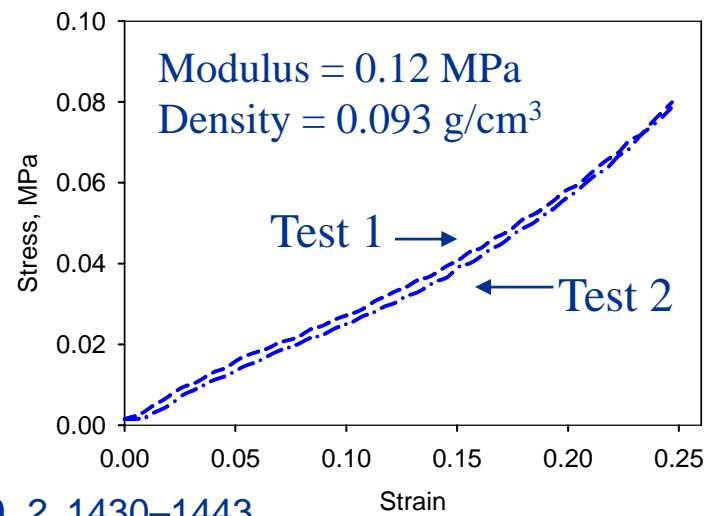
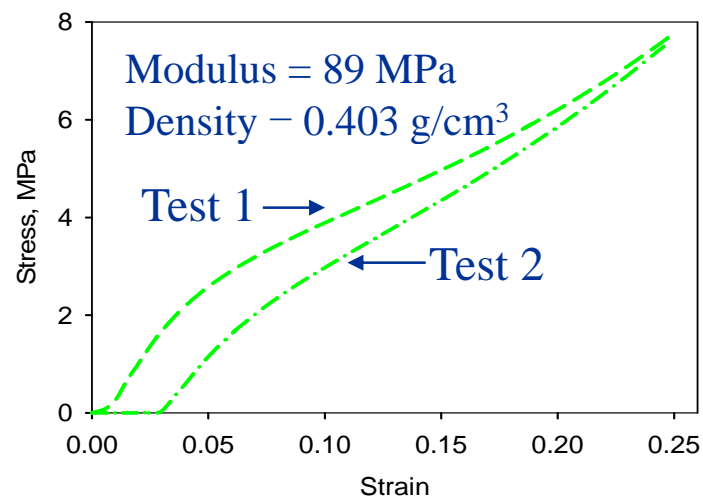


Reduced bonding in silica backbone leads to excellent elastic recovery over modulus range of 0.01 to 100 MPa



Pore structure
influenced by
bonding

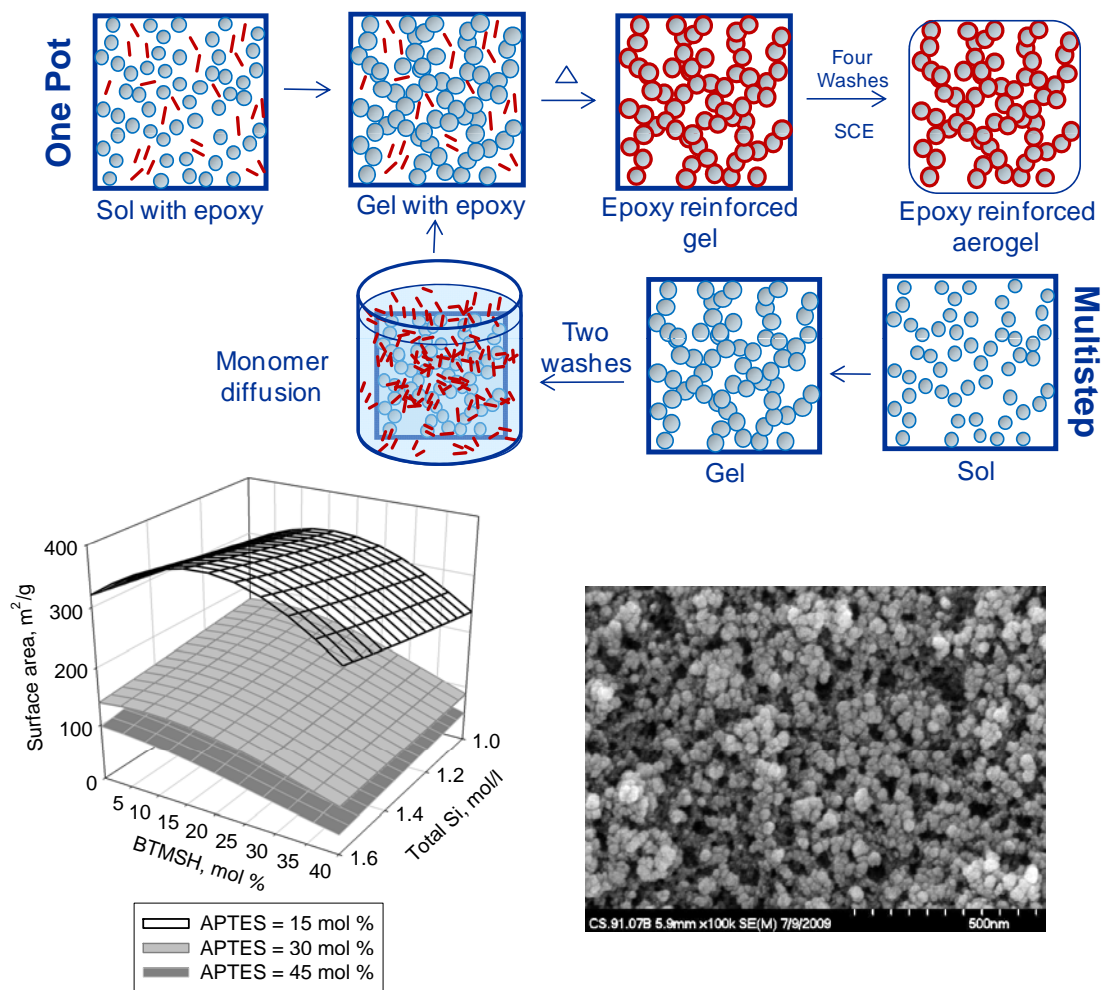
- Use of MTMS instead of TMOS gives 25 % reduction in Si-O-Si bonding
- Almost all length is recovered after two compressions to 25%
- Polymer cross-linking provides increased modulus/maximum stress at break



Nguyen et al, *ACS Applied Materials and Interfaces*, **2010**, 2, 1430–1443



One pot process streamlines aerogel fabrication



- Eliminating diffusion
 - Shortens process
 - Cross-linking more efficient
 - Aerogels are more uniform
- Properties are the same as multistep when 15 mol % APTES used
- Higher APTES leads to much higher density, lower surface area
 - Diffusion not a factor
 - Amount of polymer cross-linking much higher

Meador et al, *ACS Applied Materials and Interfaces*, **2010**, 2, 2162-2168

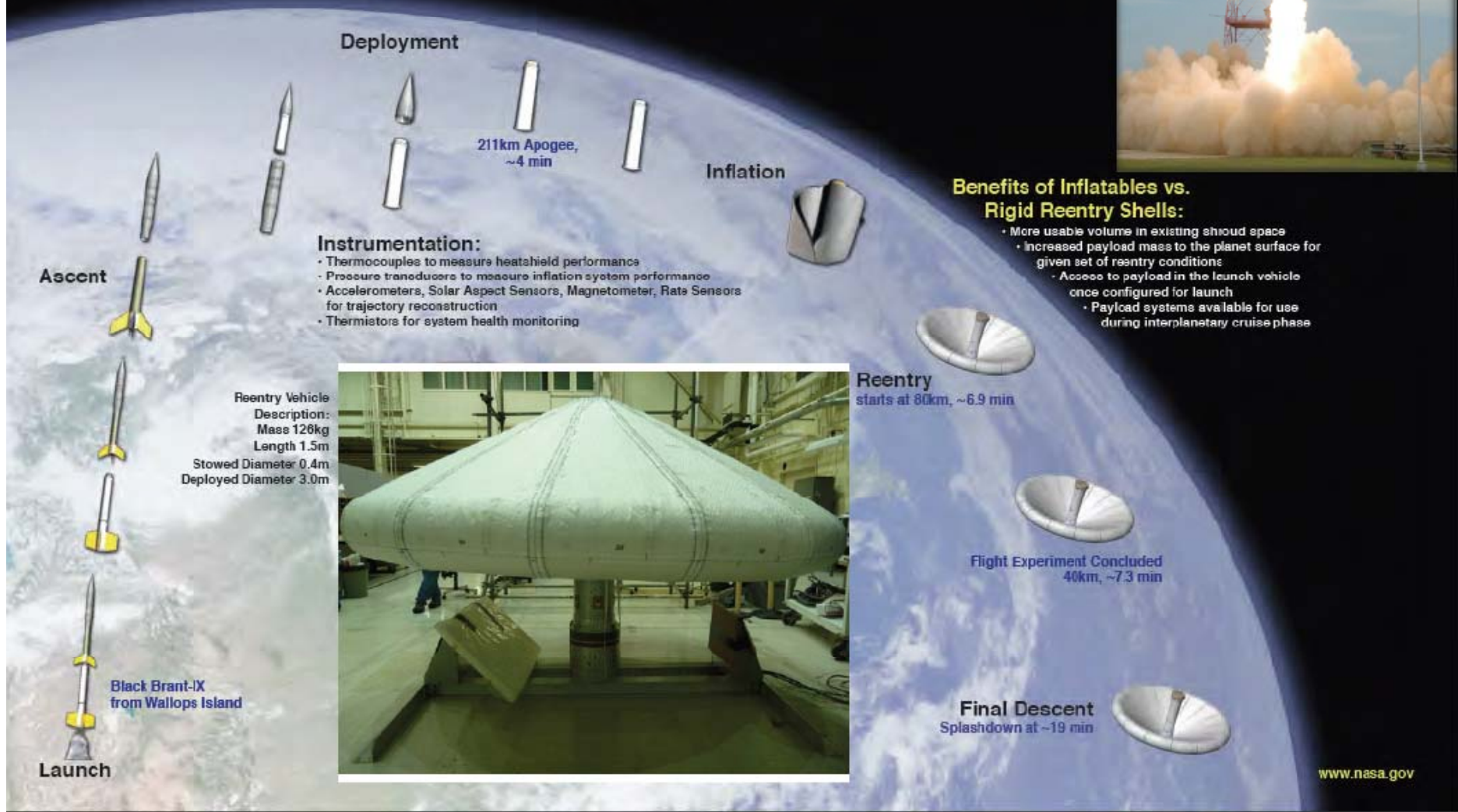


First Fully Successful Reentry HIAD Flight Demo



IRVE-II (Inflatable Reentry Vehicle Experiment) Mission

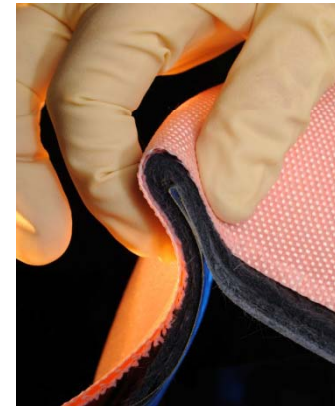
Developing Cutting Edge Technology for Atmospheric Reentry

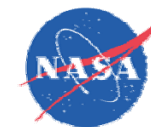




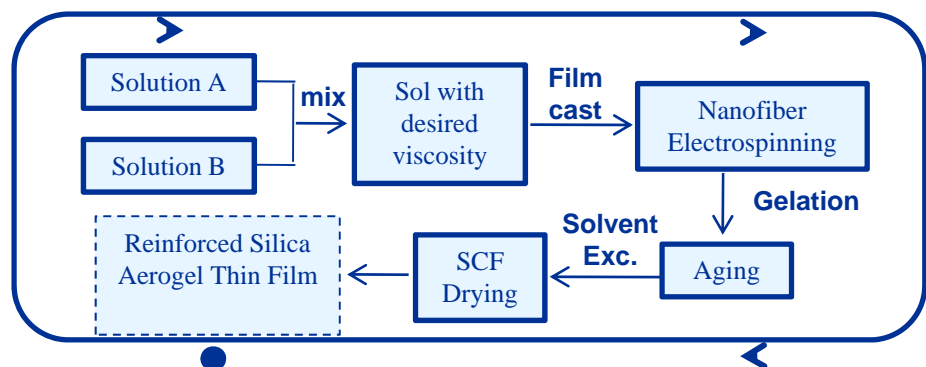
Improved insulation for inflatable re-entry vehicles

- Baseline insulation is Aspen Aerogels Pyrogel 3350
- Needs to be more flexible, foldable, less dusty, thermally stable
- Target: thin film aerogels with nanofiber reinforcement
 - Silica aerogels with PDMS flexible linking groups
 - Silica aerogels reinforced with polyimide
 - Cross-linked polyimide aerogels
 - Manufacture into thin film form
 - Electrospun fibers in film for added durability/flexibility

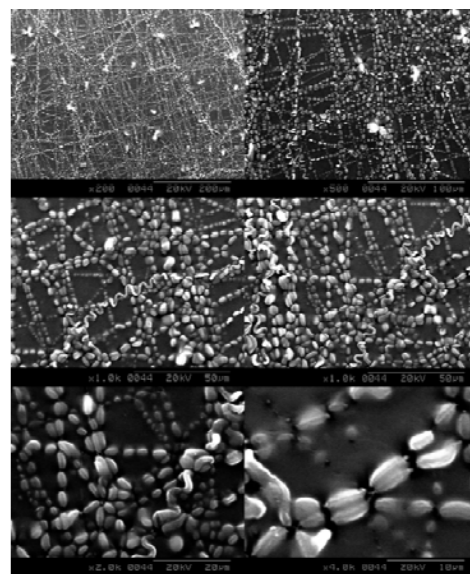
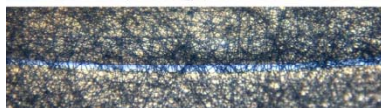
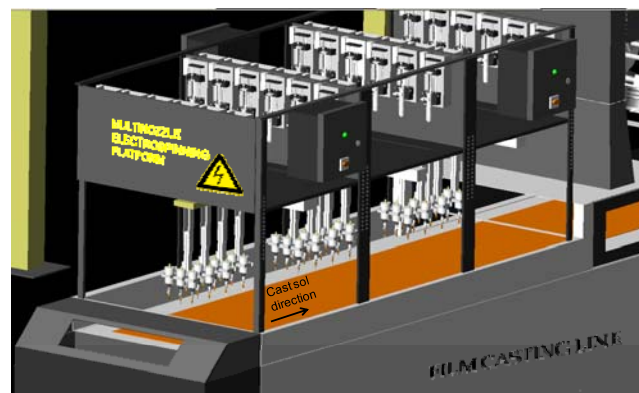
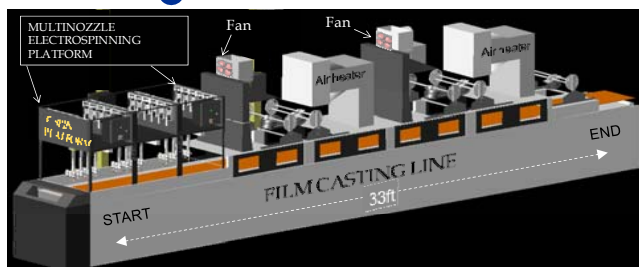




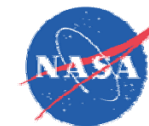
Collaboration with University of Akron—thin film aerogels reinforced with electrospun nanofiber



- Sol cast into thin film
- Electrospun fibers of PDMS/PU deposited into film
- Flexible nanofibers bridge cracks/hold structure together

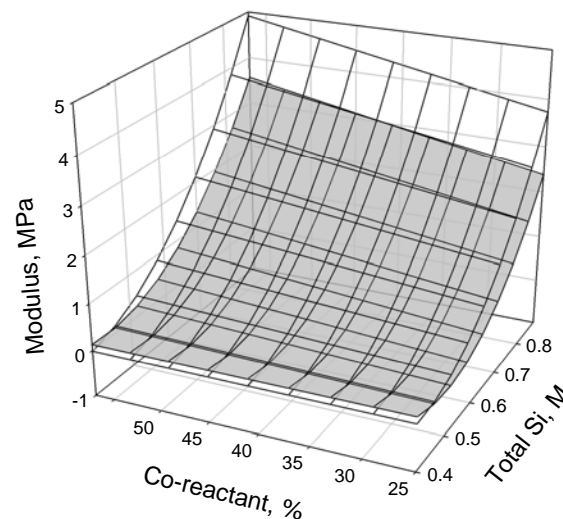
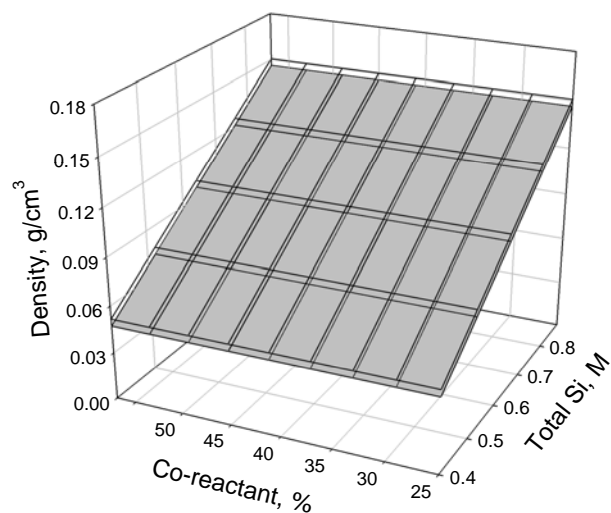
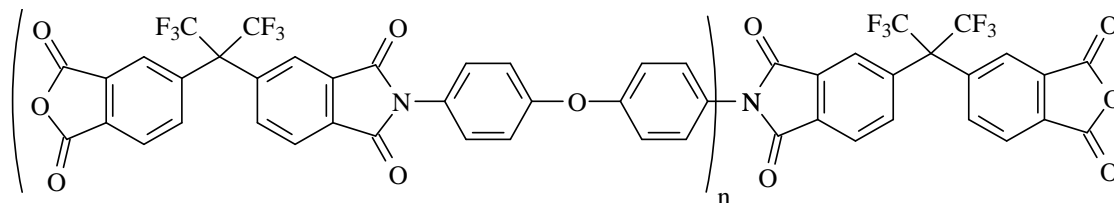


Li et al, *ACS Applied Materials and Interfaces*, 2009, 1, 2491-2501



Polyimide reinforced silica aerogels

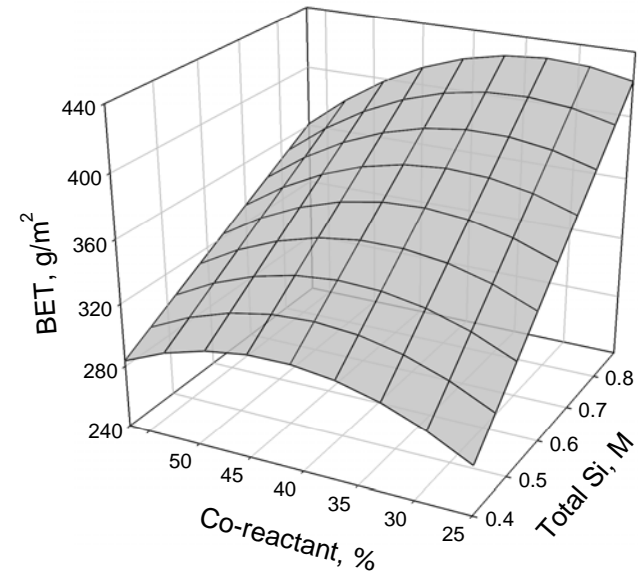
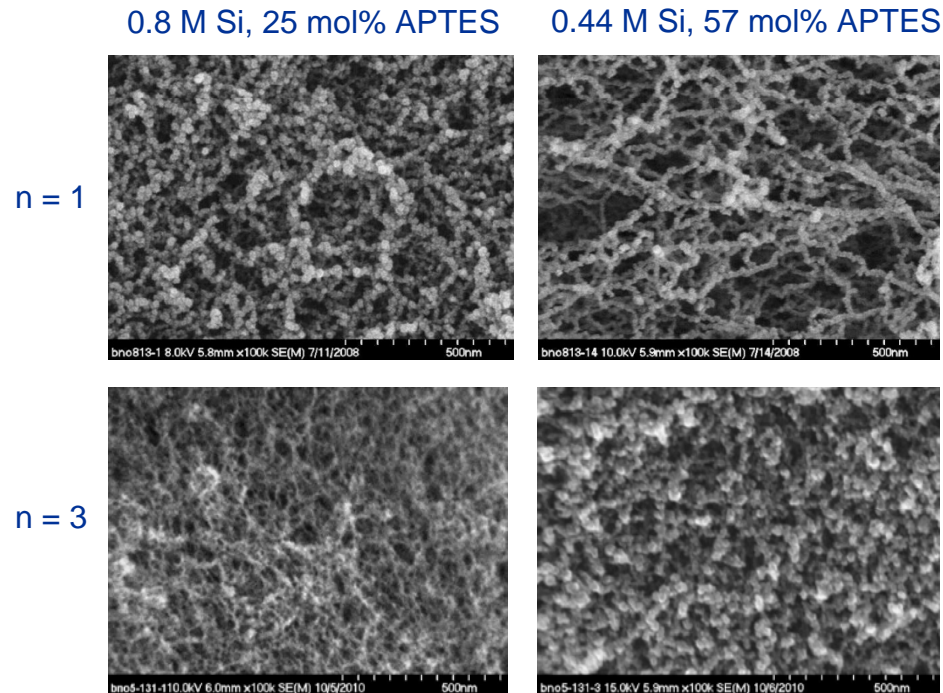
Polyimide cross-link reacted with APTES amine



- Low water to silane ratio (~3) used to make gels
- Gels prepared in acetonitrile
 - Solvent exchanged to NMP for cross-linking
 - Solvent exchanged to ethanol for drying
- Shrinkage <5%



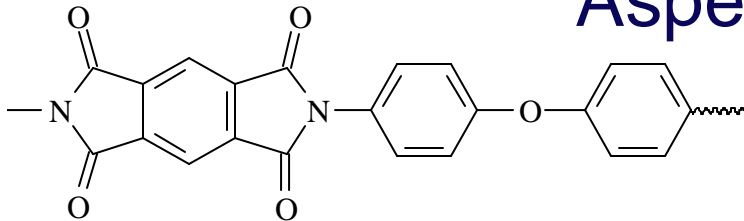
Surface areas, morphology of PI reinforced aerogels similar to other polymer reinforcement



- PI oligomers with $n = 3$ produced core-shell structures with gels at low silane concentration
- All $n = 1$ samples appear uniform
- Hence, diffusion into the gel was a problem for larger oligomers



Linear polyimide (PI) aerogels made by Aspen Aerogels



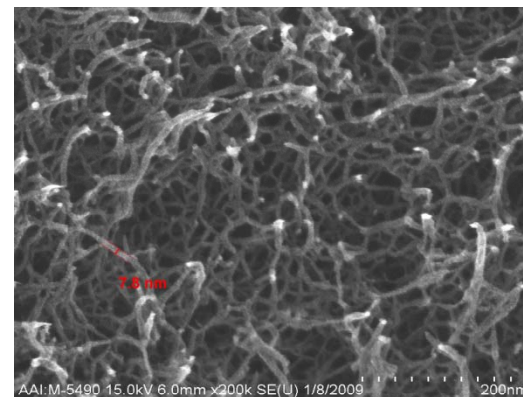
- High MW polyimide gels made from PMDA and ODA
- Supercritical drying produced aerogels
- Onset of decomposition >560 °C
- As strong or stronger than polymer reinforced silica aerogel
- But much shrinkage on preparation



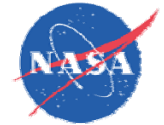
Wet gel



Aerogel

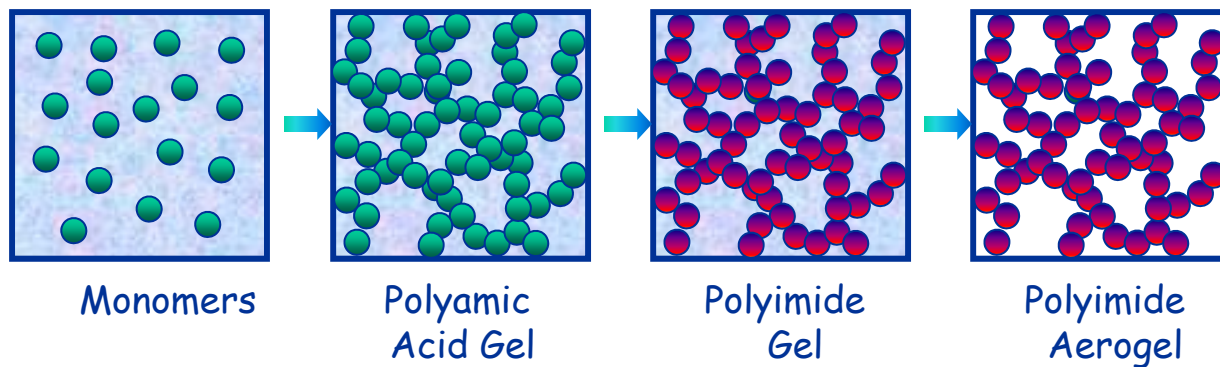
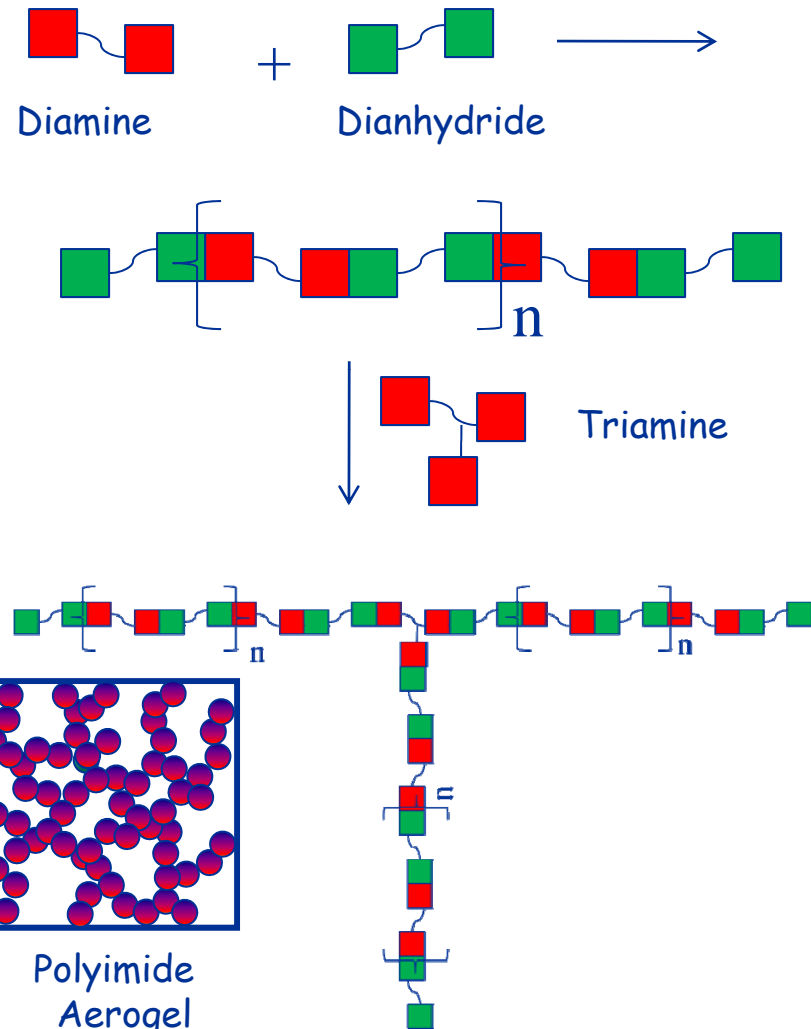


Rhine, Wang and Begag, *US Patent 7,074,880 B2*, July 11, 2006



Cross-linked PI aerogels using branching

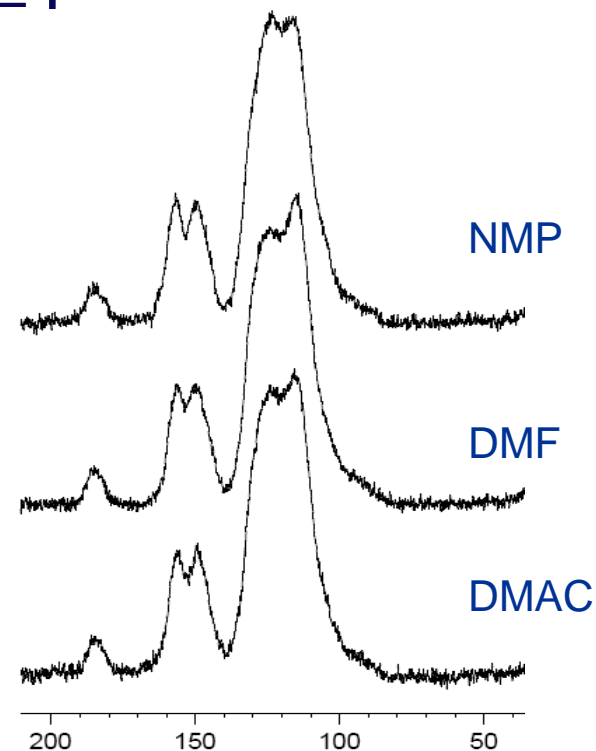
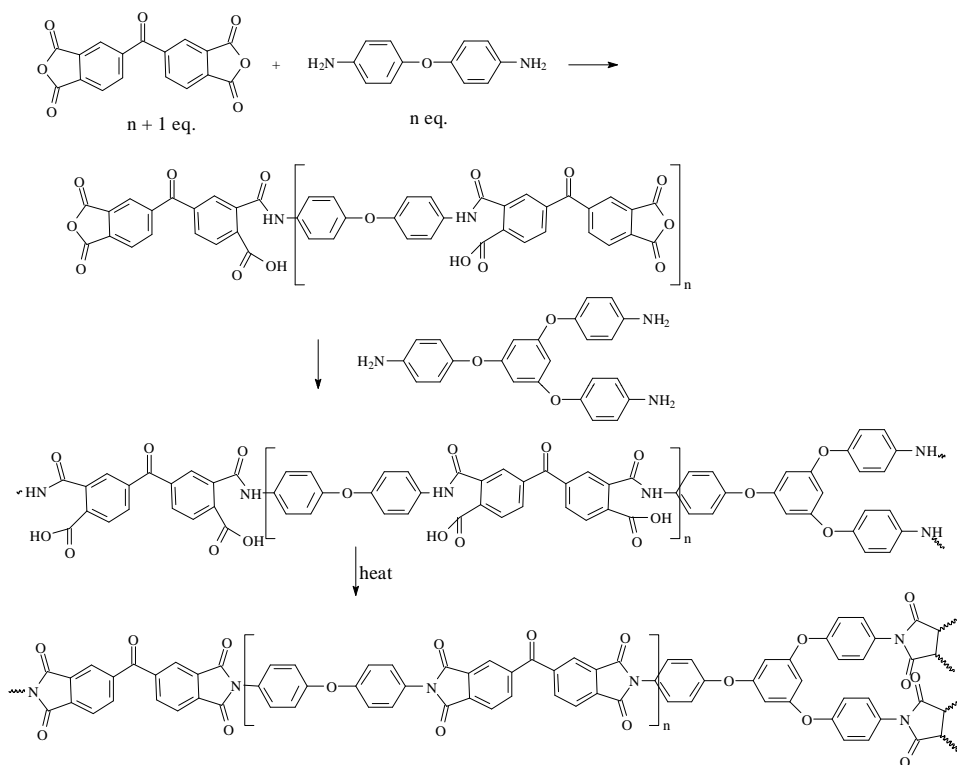
- Use of triamines, or other multifunctional groups to form network structure
- Gelled polyamic acid network is imidized
- Solvent exchange to acetone then supercritical drying to produce aerogel



Meador, US Patent application filed 9-30-2009



First example of PI aerogels from TAB/BTDA/ODA, $n=1$



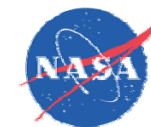
- Three solvents tried; gelation very fast
- Thermally imidized
- Gels liquefied during heating, re-gelled on cooling



DMAC

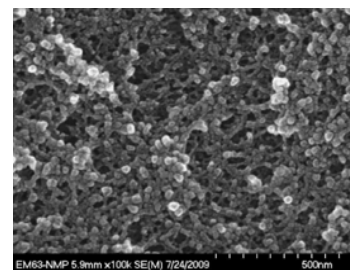
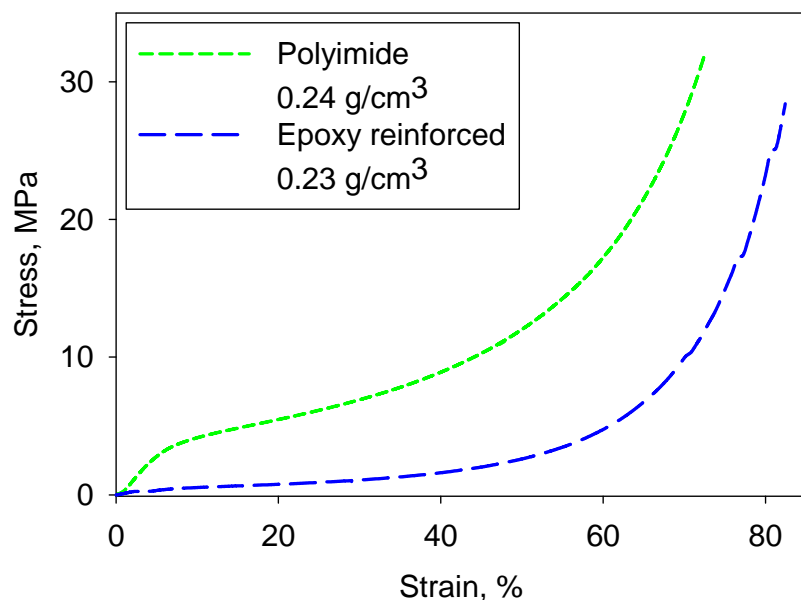
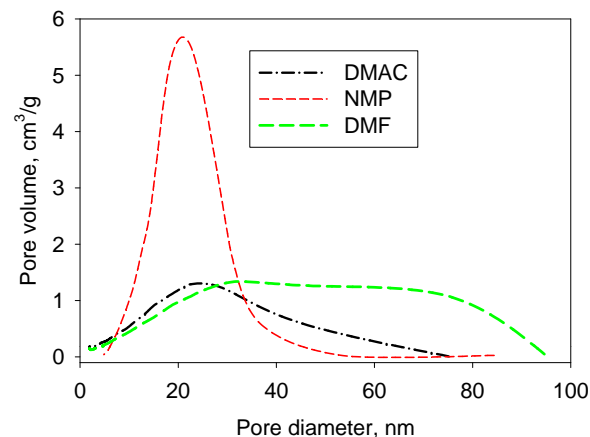


NMP

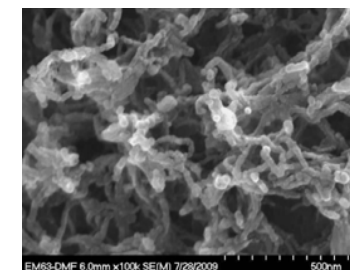


Properties of thermally imidized PI aerogels with TAB, n=1 oligomers

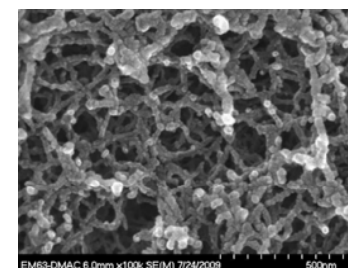
- Aerogels made in NMP shrink about 30 %
- Low shrinkage from DMF and DMAC
- 5 times stronger than epoxy reinforced aerogels of similar density



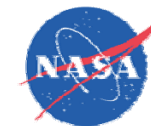
NMP: 0.27 g/cm³; 410 m²/g



DMF: 0.07 g/cm³; 356 m²/g

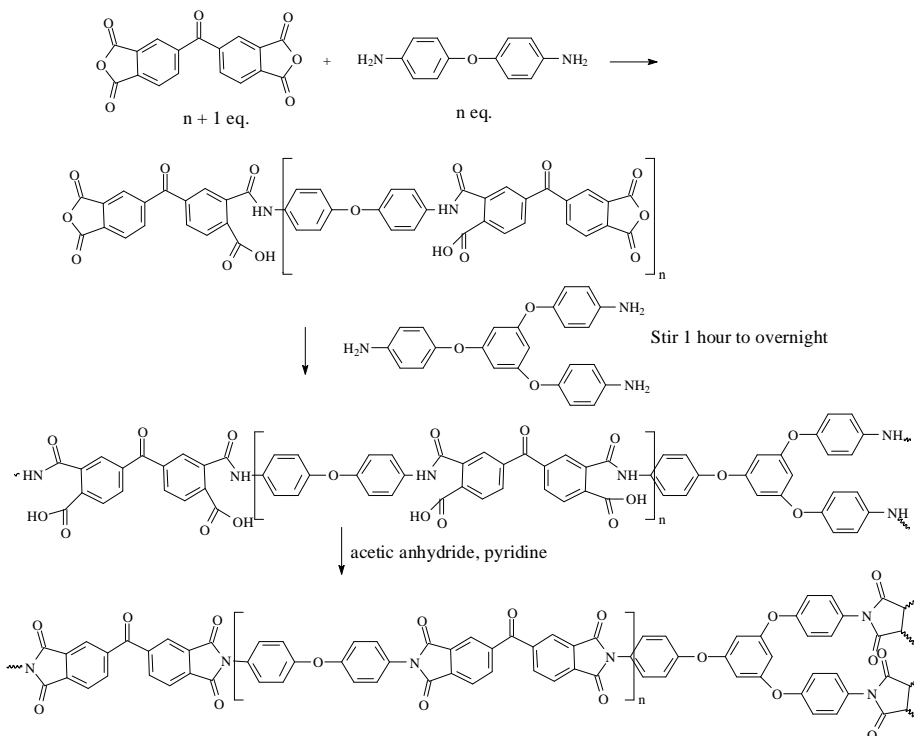


DMAC: 0.09 g/cm³; 410 m²/g

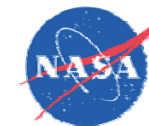


A better approach: chemical imidization with pyridine and acetic anhydride

- Pyridine catalyzes imidization
- Acetic anhydride reacts with water by-product
 - Prevents hydrolysis of amic acid
- Gel forms within 30 minutes; aged for 24 hours for $n = 15$ or greater, 5-10 wt % solids
- Imidization proceeds almost completely at room temperature



Vivod, et al, POLY Poster 334, Wed 9:30



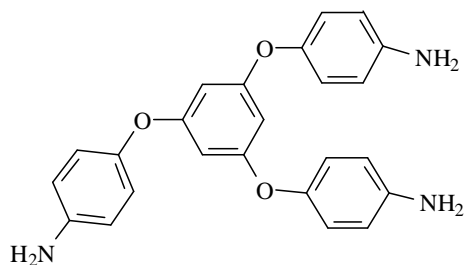
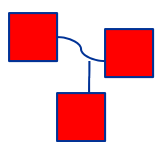
Approaches to PI aerogels

- Varying structure (connecting groups) of diamine and dianhydrides provide means to tailor properties

- Flexibility
- Thermal oxidative stability
- Mechanical properties
- Thermal conductivity

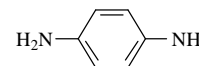
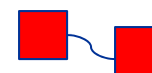
- Longer chains between cross-links

Triamine

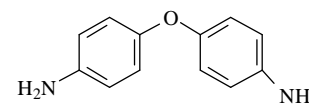


TAB

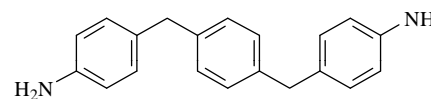
Diamines



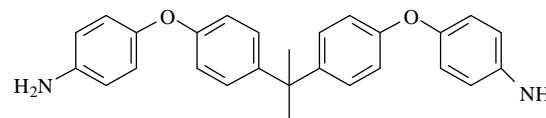
PPDA



ODA

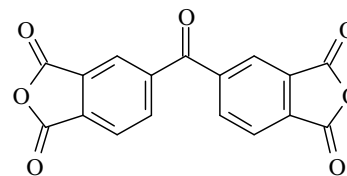


BAX

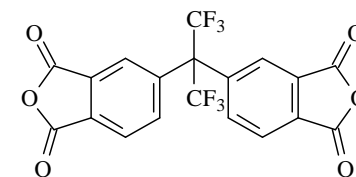


BAPP

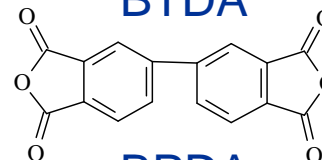
Dianhydrides



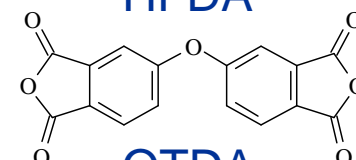
BTDA



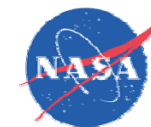
HFDA



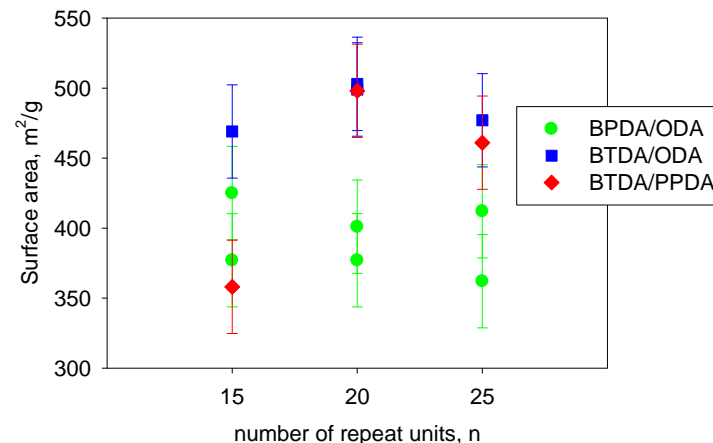
BPDA



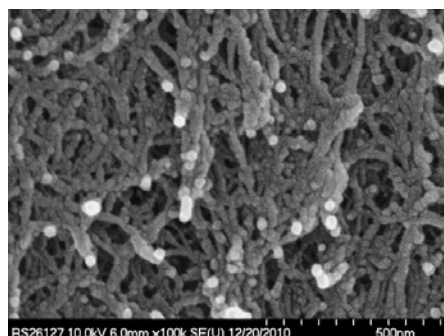
OTDA



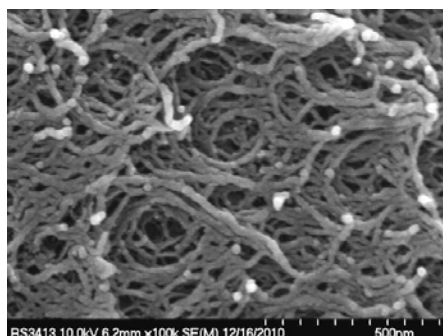
TAB cross-linked aerogels have different pore structure depending on monomers used



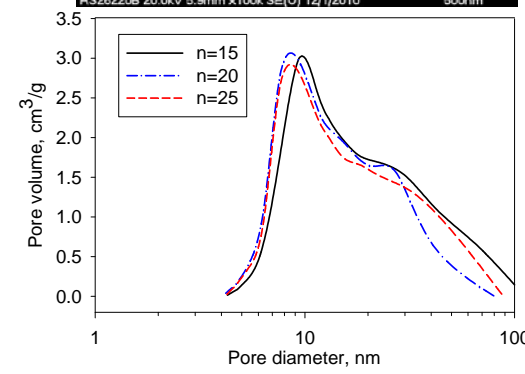
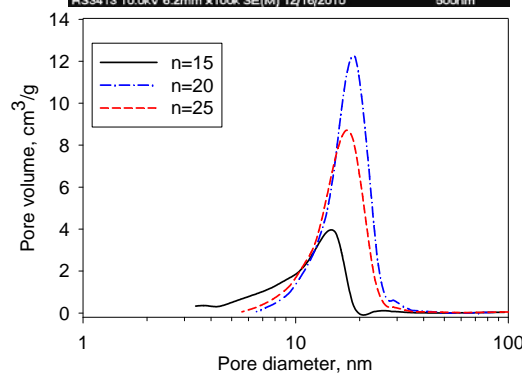
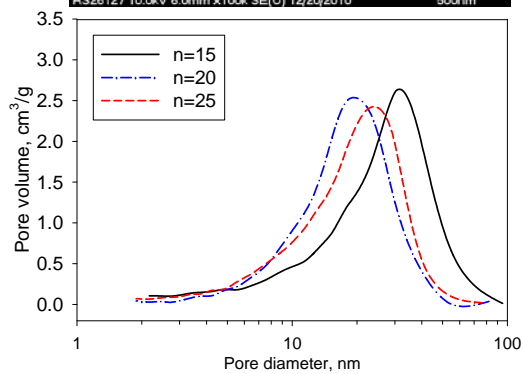
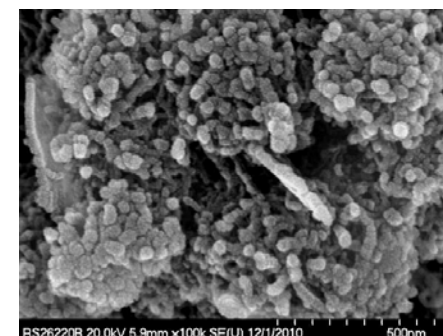
BPDA/ODA



BTDA/PPDA

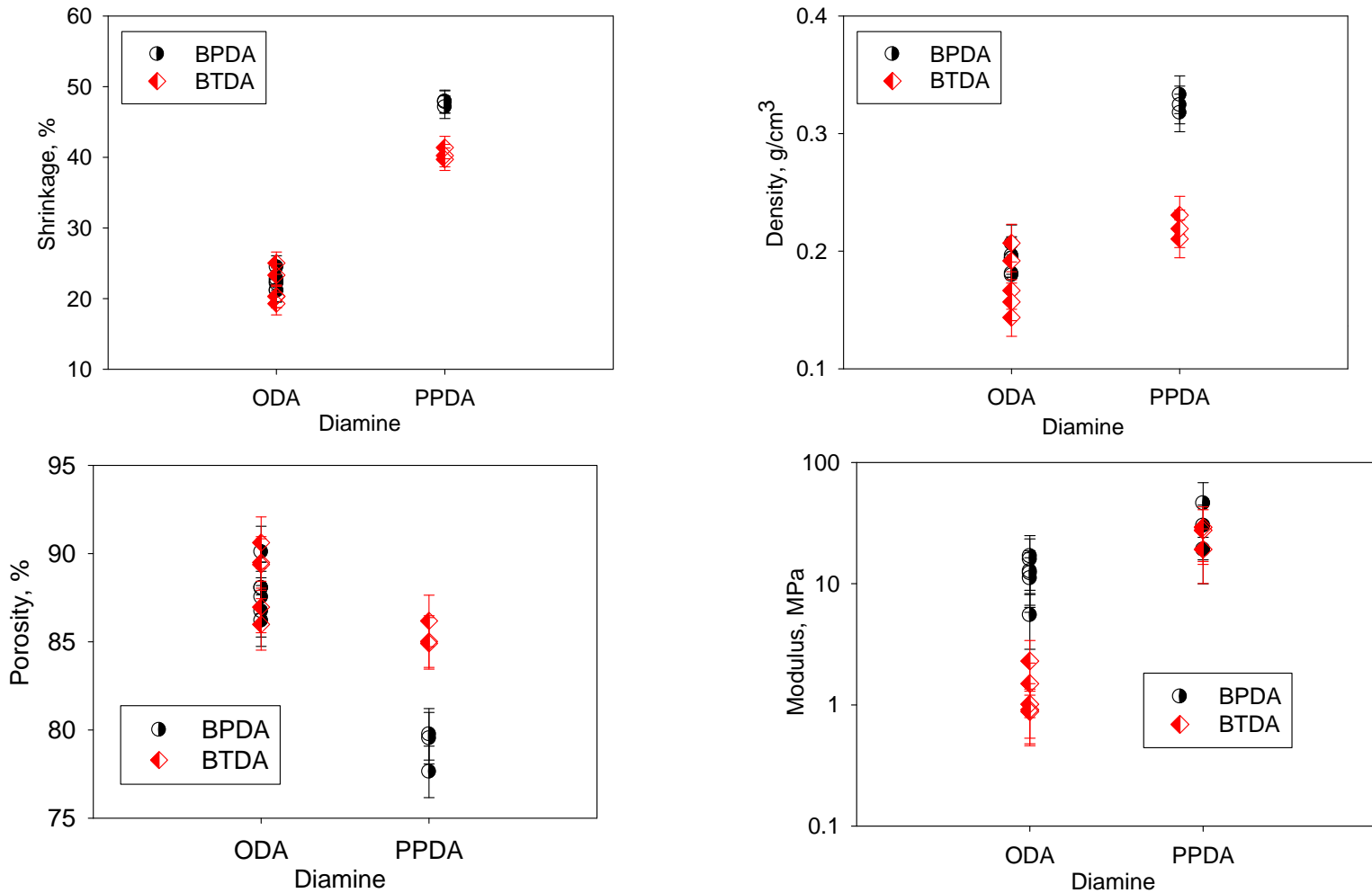


BTDA/ODA





Properties of the aerogels depend mostly on shrinkage during processing

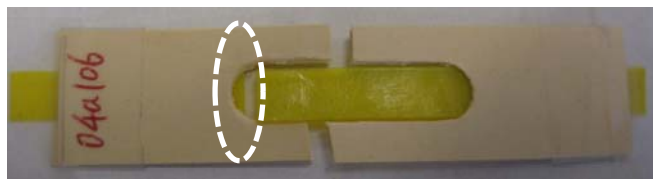


Number of repeat units between TAB cross-links had no effect on any of the properties

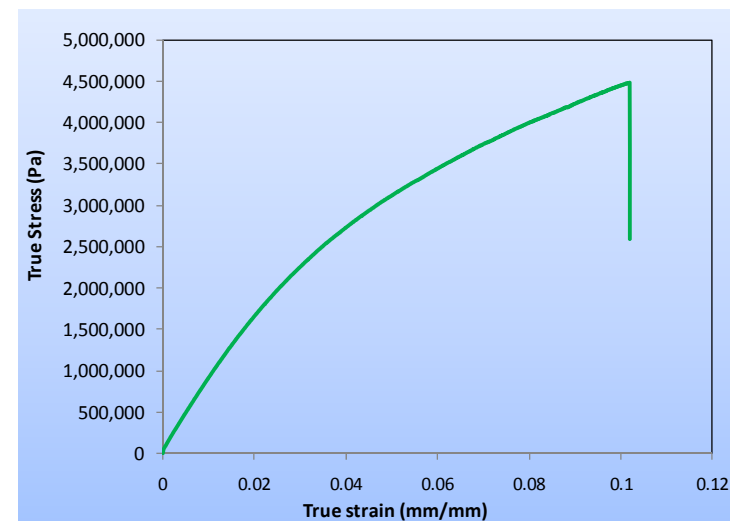


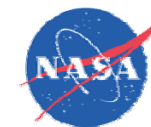
Thin films cast from TAB cross-linked PI aerogels

- Collaboration with Prof. Miko Cakmak, University of Akron
- TAB/ODA/BPDA, $n = 30$
 - $n = 25$ too viscous to cast
- Density of film: 0.17 g/cm^3 (shrinks a little more than thick part)
- Tensile testing:
 - 79 MPa modulus
 - Tensile stress at break = 4.5 MPa

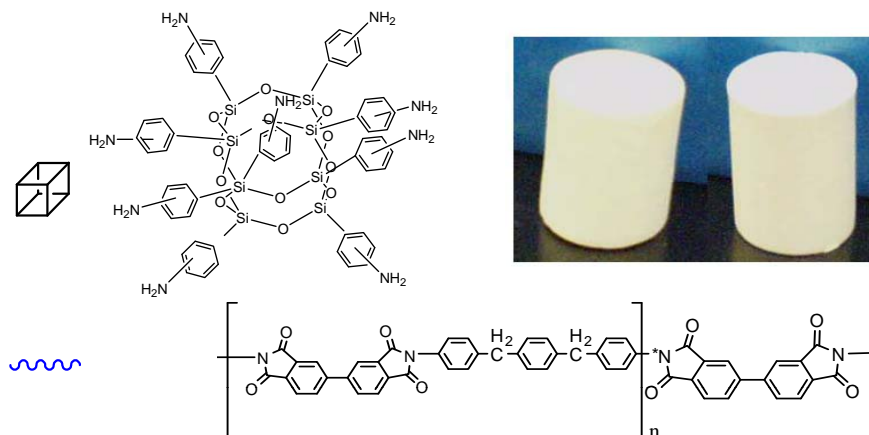
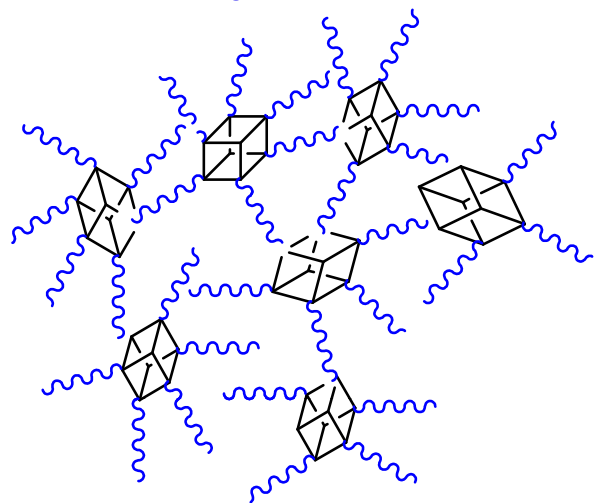


Tensile specimen

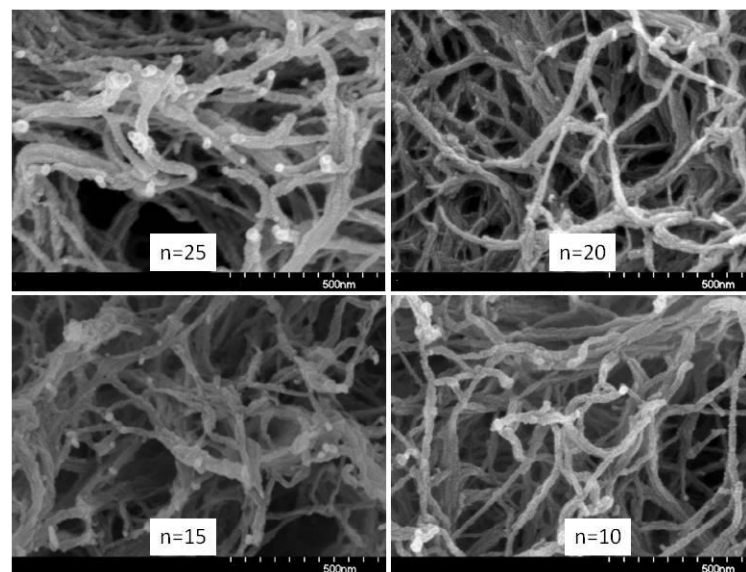




Polyimide 3D network using T8-POSS



- PI cross-linked with POSS
- BPDA-(BAX-BPDA)_n; n = 10 to 25
- Low shrinkage (~10 %)
- Density: ~0.1 g/cm³
- Porosity > 90 %

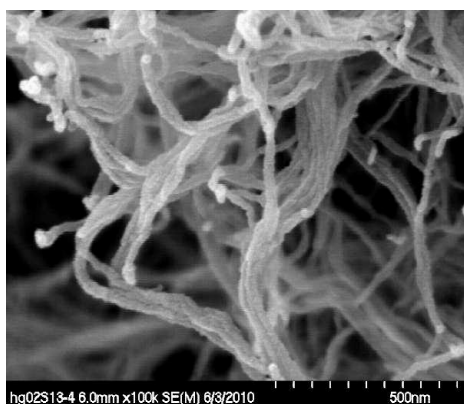
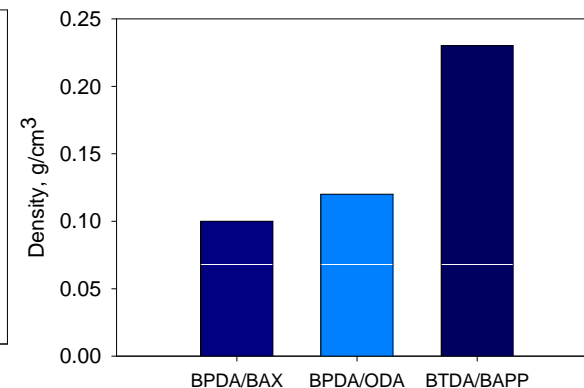
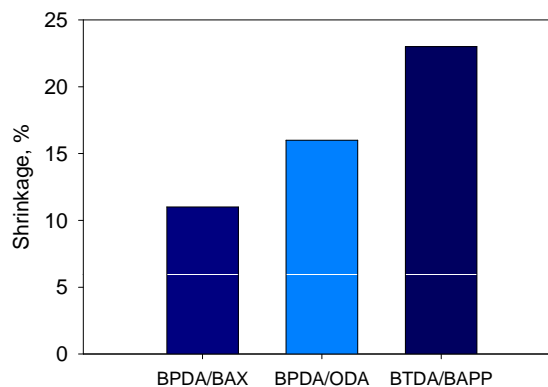


Guo, et al, *ACS Appl. Mater. Interfaces*, 2011, 3(2), 546-552
POLY Poster 327, Wed 9:30

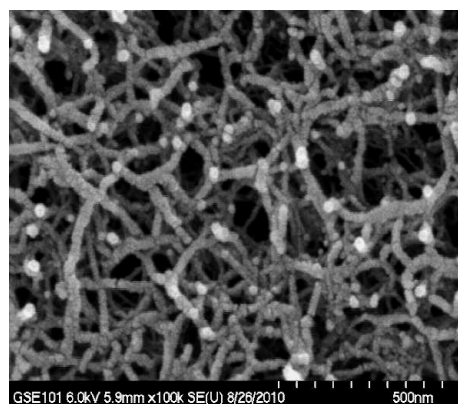


Formulation study of PI-POSS aerogels with different dianhydrides and diamines

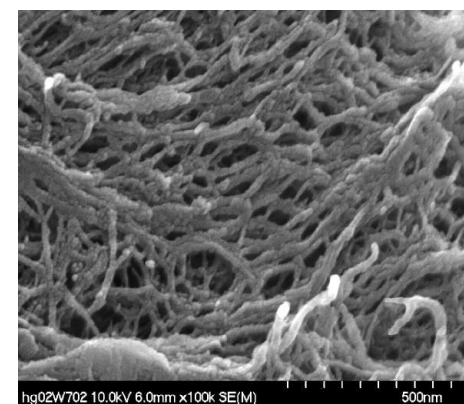
- Differences in shrinkage between different monomers affects density, other properties



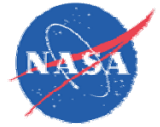
BPDA/BAX



BPDA/ODA



BTDA/BAPP

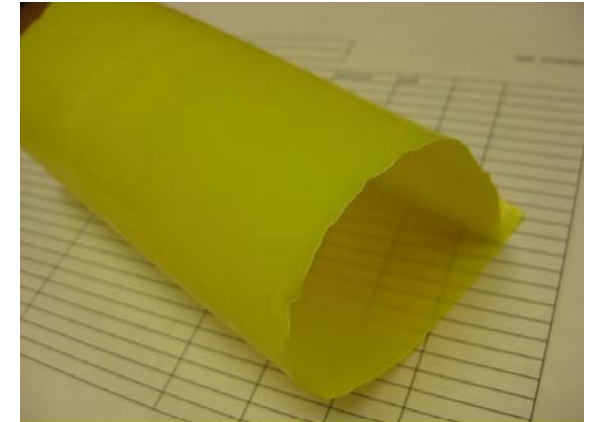


POSS/PI cast as thin film is flexible both before and after supercritical drying

- Collaboration with Miko Cakmak, University of Akron
- Density of film is similar to molded cylinder
 - 0.12 g/cm³
 - 90 % porous
- Middle picture is 9" x 13" pan; film is folded multiple times



As-cast wet films

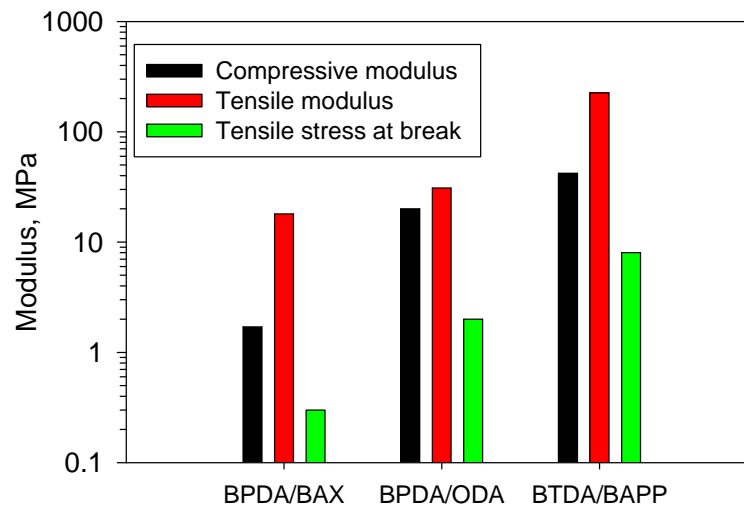
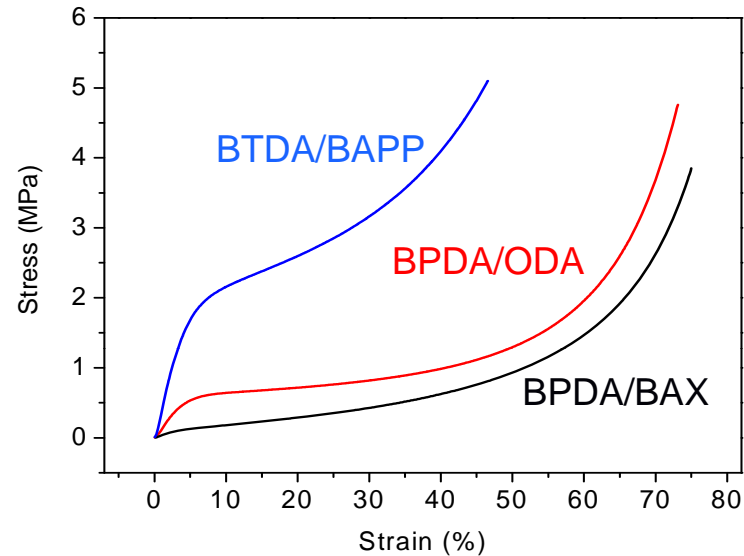


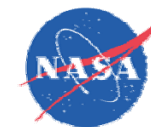
Dry aerogel



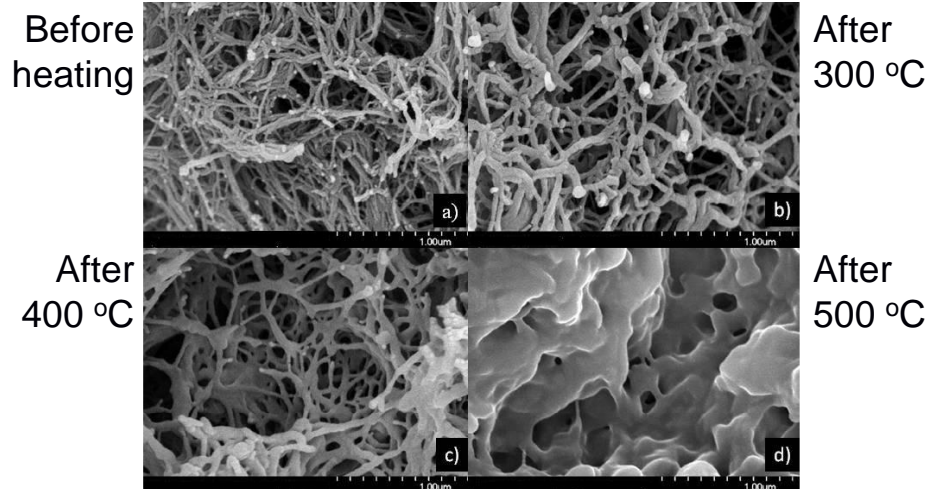
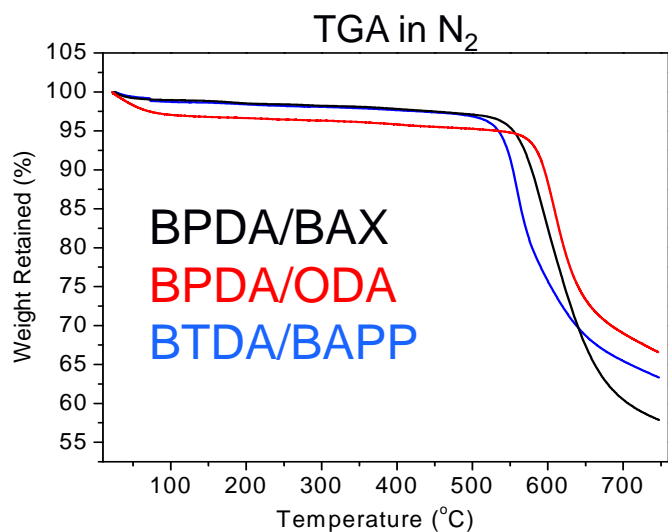
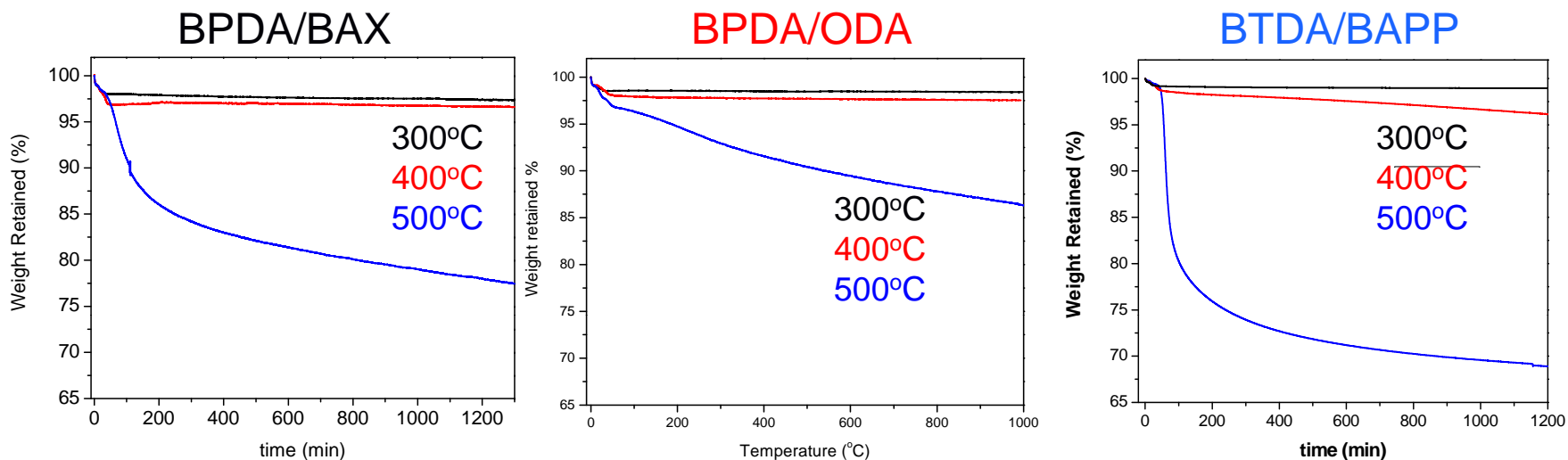
Mechanical properties: Tensile and compression

- Slight decrease in compressive modulus with increasing n
- Differences in modulus/stress at break probably mostly due to shrinkage
- Formulations which shrink the most have the highest density
- Mechanical properties track with density





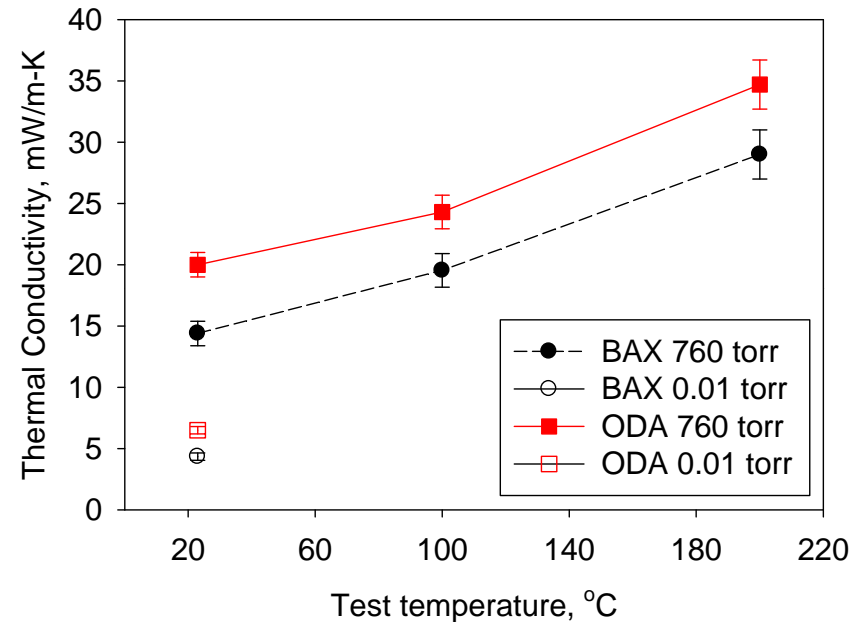
Aging up to 500 °C in N₂ for 24 hours





PI-POSS aerogels—thermal conductivity

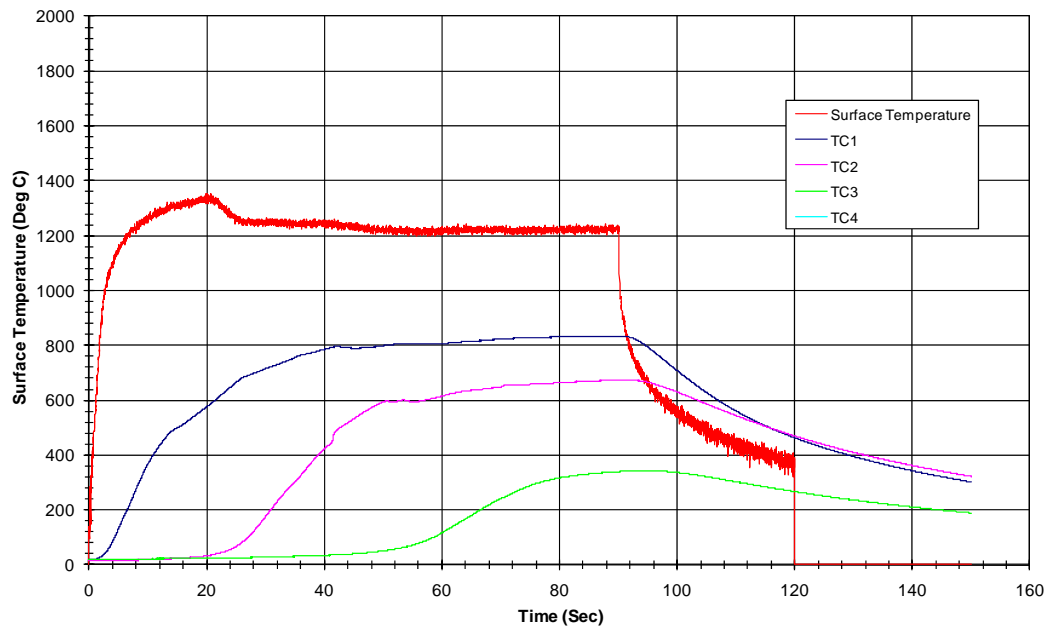
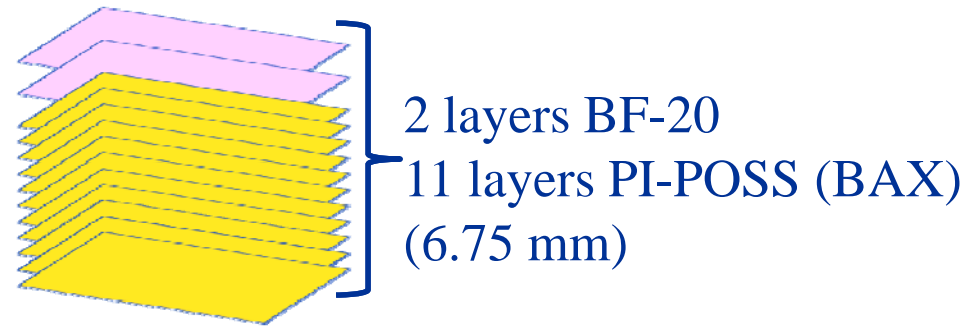
- n = 20 formulation measured at TPRL
- Multiple layers 0.6 mm thick measured
- Comparable to baseline insulation for inflatable decelerator (Pyrogel 3350) in both thermal conductivity and density
- About 5-6 layers equals one layer of Pyrogel 3350
- Much more flexible, foldable





Testing of PI-POSS aerogels under high heat flux

- Laser Hardened Materials Experimental Lab, Wright Pat
- Heat flux 20 W/cm², 8 torr N₂
- 90 sec duration
- Bottom layer only darkened, no hole, no cracks





Conclusions

- Cross-linked polyimide aerogels are viable approach to higher temperature, flexible insulation for inflatable decelerators
- Results indicate that the all-polyimide aerogels are as strong or stronger than polymer reinforced silica aerogels at the same density
- Currently, examining use of carbon nanofiber (Poster 334) and clay nanoparticles to improve performance
- Flexible, polyimide aerogels have potential utility in other applications such as space suits, habitats, shelter applications, etc. where low dusting is desired



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ARSC: Dan Schieman

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Guilhermo Sprowl, Sarah Ercegovic**

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Dr. Jiao Guo**

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Thank you!

