

Synthesis and characterization of poly(maleic anhydride)s cross-linked polyimide aerogels

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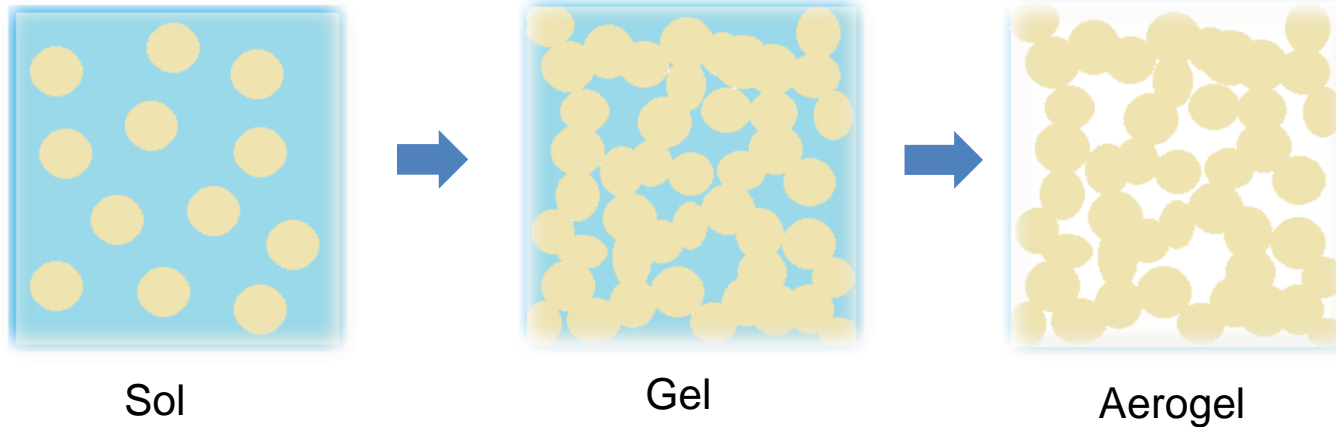
NASA Glenn Research Center



August-19-2015



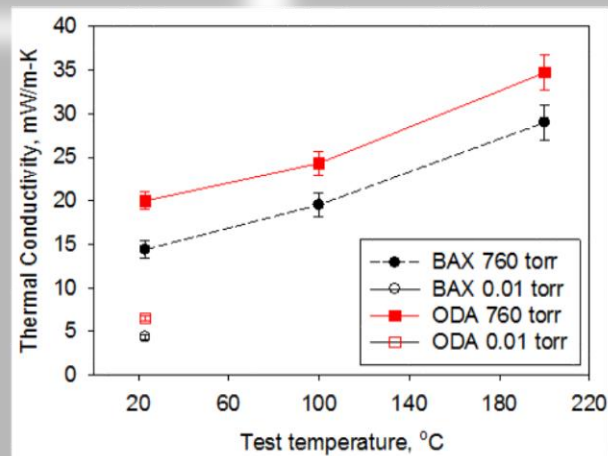
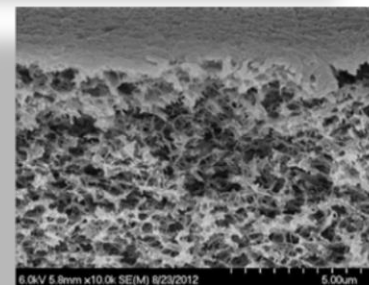
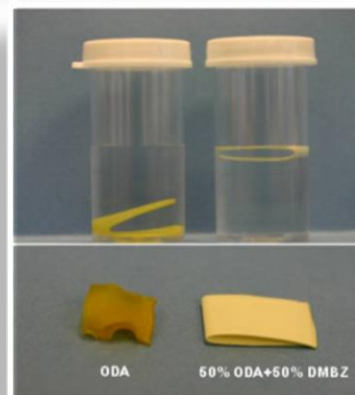
Why aerogels?



- Made by removing solvent from wet gels without collapsing the structure
- High porous solids with extremely small pore size (typically 10-40nm)
- Low density
- High surface area
- Good thermal insulation material
 - reduces heat transfer (convection, conduction, and radiation)

Cross-linked polyimide aerogels

- Low density and shrinkage
- High porosity, surface area, and modulus
- Moisture resistant
- Low dielectric constant
- Low thermal conductivity
- Can be metalized with gold
- Flexible thin film



M.A. B. Meador, et al. ACS Appl. Mater. Inter., 2012, 6346.

H. Guo, et al. ACS Appl. Mater. Inter., 2012, 4, 5422.

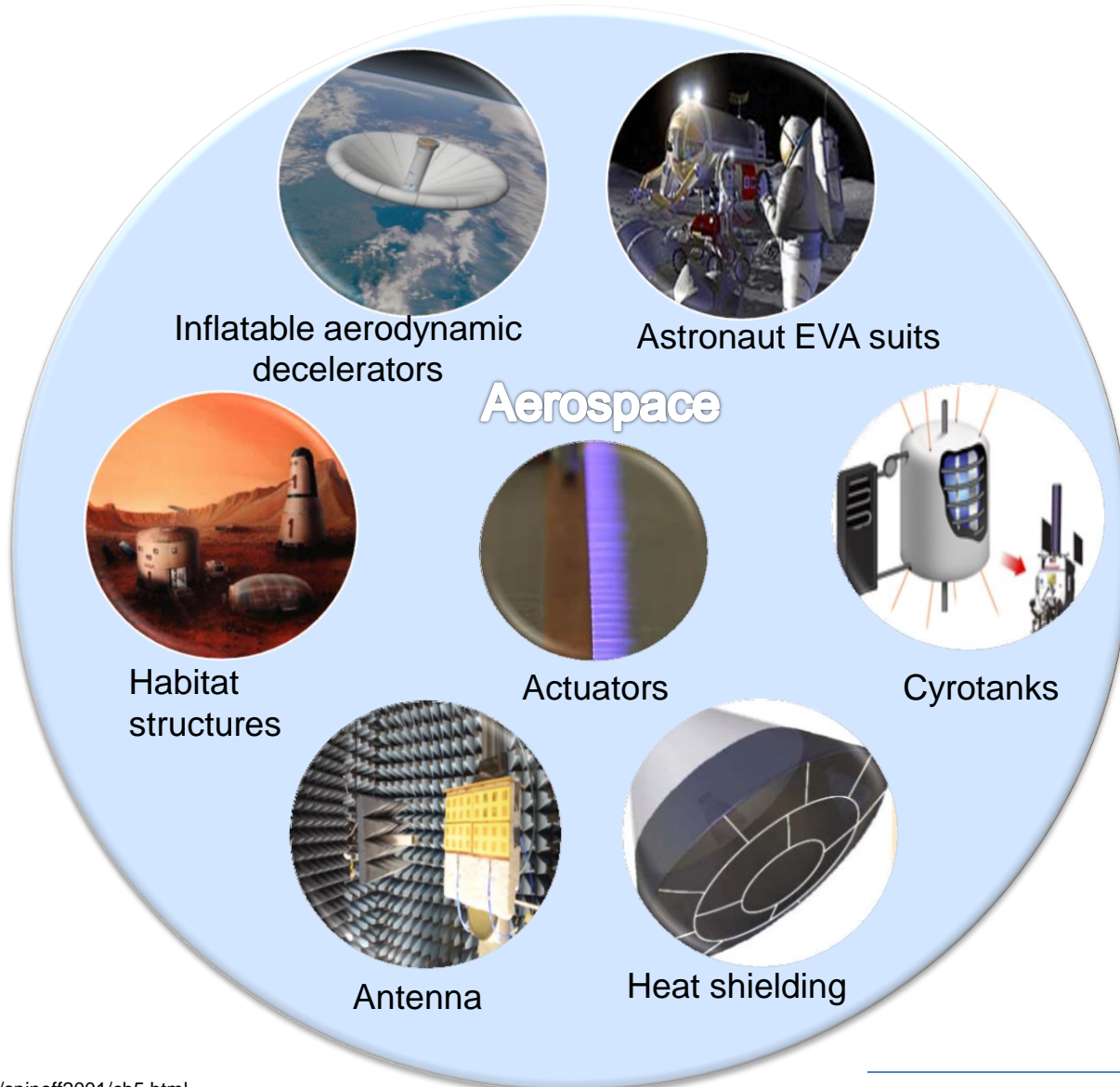
M. A. B. Meador, et al. ACS Appl. Mater. Inter., 2012, 4, 536.

H. Guo, et al. ACS Appl. Mater. Inter., 2011, 3, 546.

Potential applications of aerogels

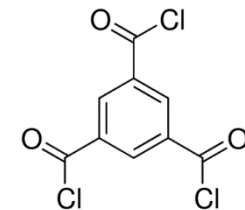
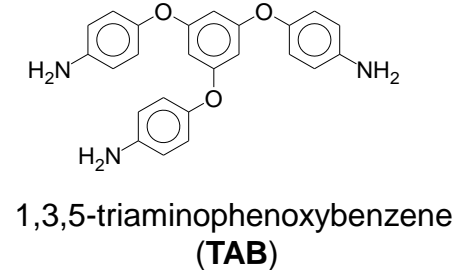
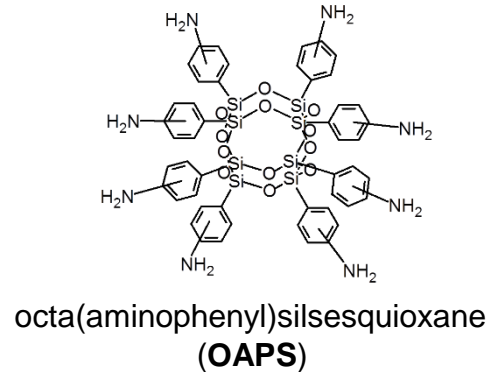
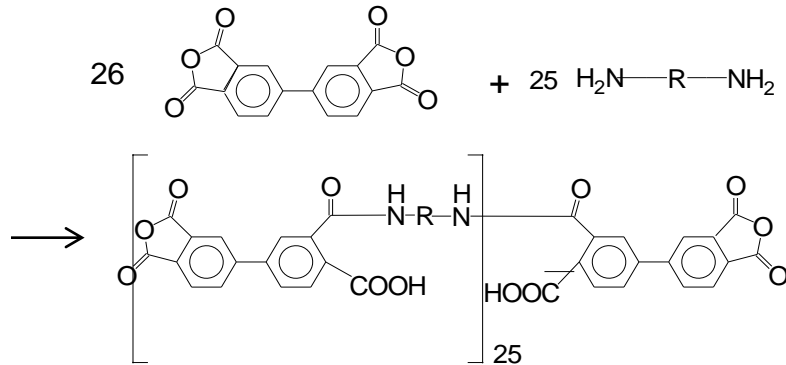


Potential applications of aerogels



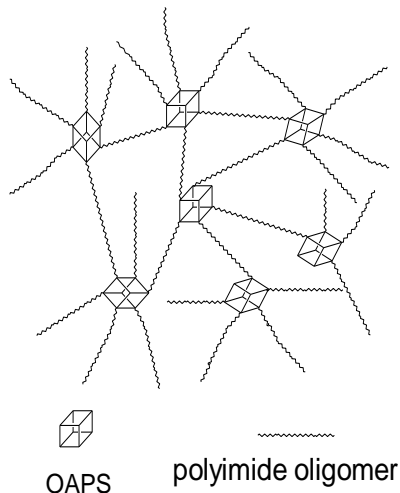
Cross-linked polyimide aerogels

Cross-linkers



1,3,5-Benzenetricarbonyl trichloride
(BTC)

- Various polyimide oligomer backbones using different dianhydrides and diamines
- Chemical imidization



M. A. B. Meador and H. Guo, LEW-18864-1, US patent application No. 61/594,657

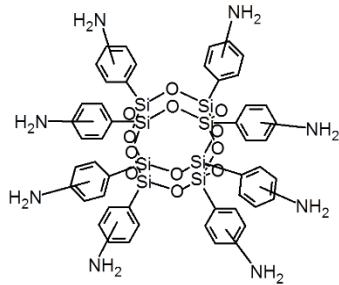
M.A. B. Meador et al, *ACS Appl. Mater. Interfaces*, **2015**, 7, 1240



Objectives

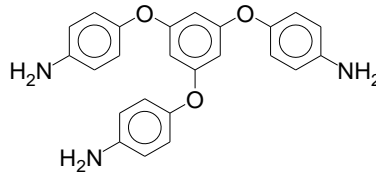
- Explore commercially available and less expensive cross-linkers
- The aerogels still maintain the similar properties

Cross-linker Cost Comparison



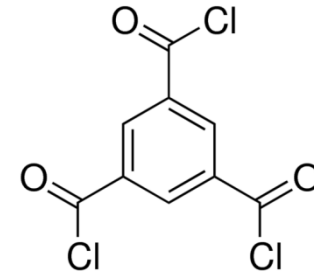
octa(aminophenyl)silsesquioxane
(OAPS)

77.11/g



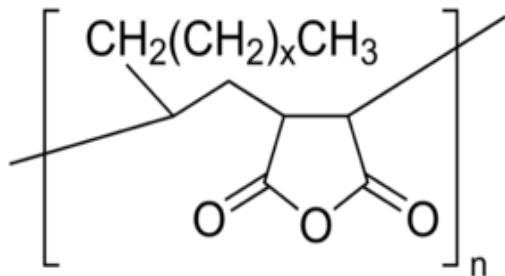
1,3,5-triaminophenoxybenzene
(TAB)

Custom made



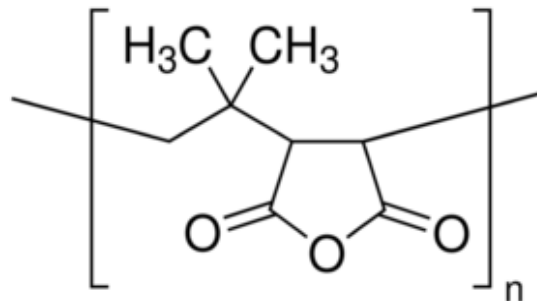
1,3,5-Benzenetricarbonyl trichloride
(BTC)

0.97/g



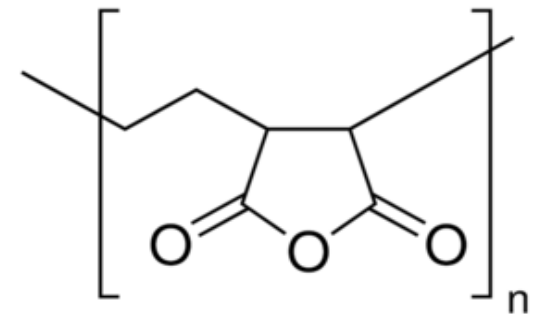
poly (maleic anhydride-alt-1-octadecene)
(PMA-O) Mn 30,000-50,000

\$0.145/g



poly (isobutylene-alt-maleic anhydride)
(PMA-D) Mw ~6000

\$0.04/g

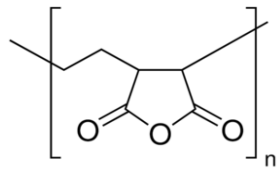


poly(ethylene-alt-maleic anhydride)
(PMA) Mw 100,000-500,000

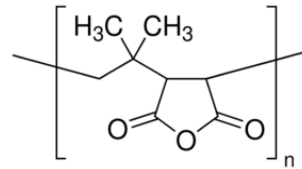
\$0.67/g

Design of Experiment

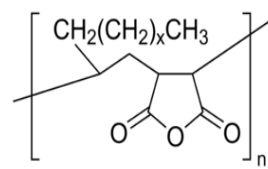
- Cross-linkers:



PMA



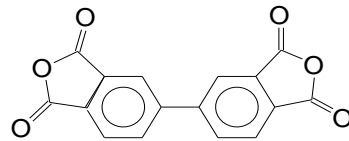
PMA-D



PMA-O

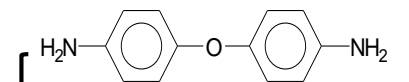
- 10 wt% polyimide oligomer

- Dianhydride:

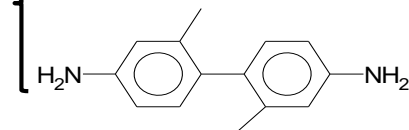


BPDA

- Diamine:

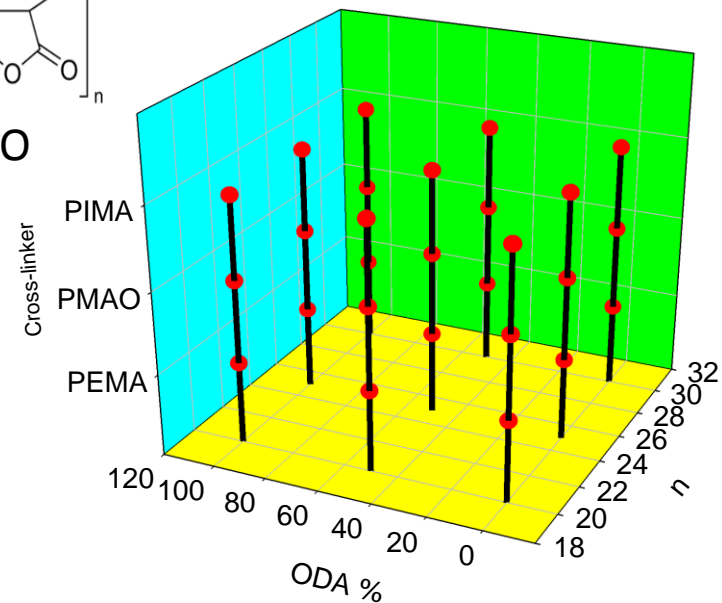


ODA 0-100%

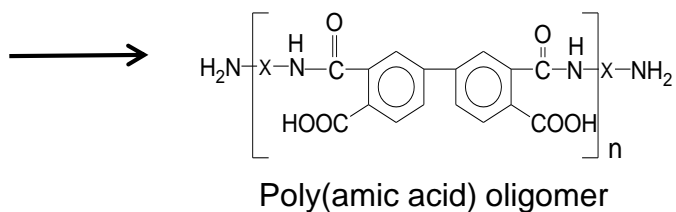
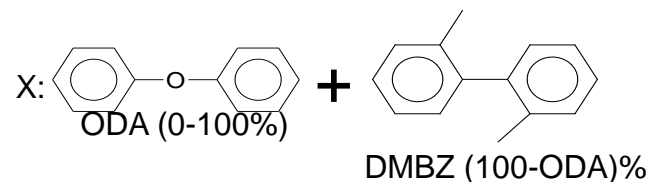
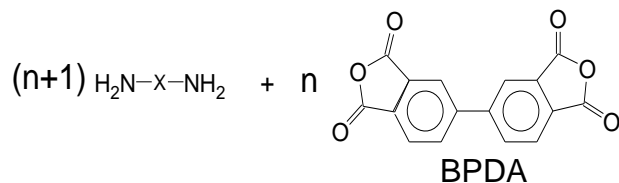


DMBZ (100-ODA)%

- Polyimide oligomer repeat unit:
 $n=20-30$



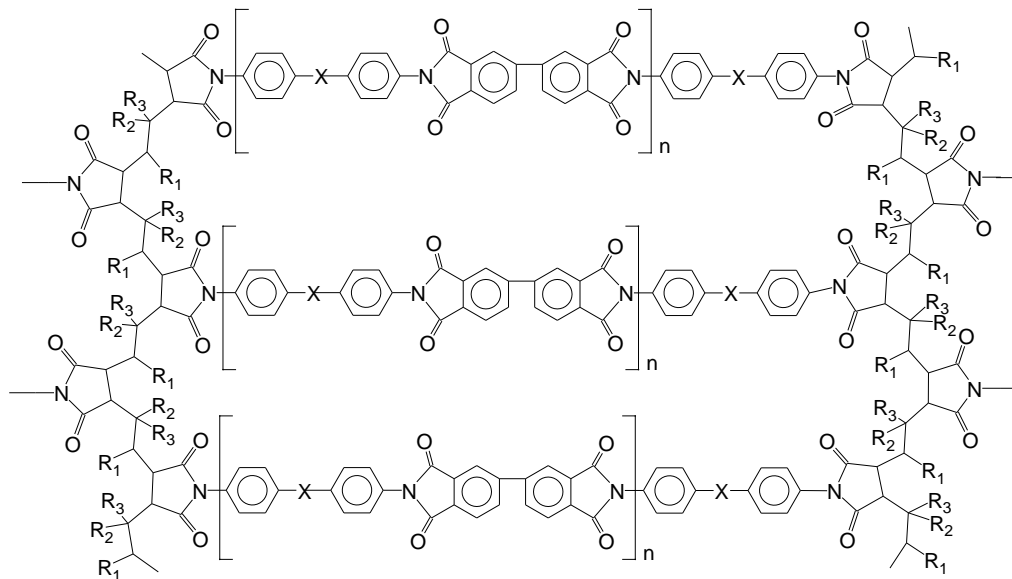
Network formation using poly(maleic anhydride)s as cross-linkers



Cross-linker	R ₁	R ₂	R ₃	Molecular weight
PMA	H	H	H	Mw 100,000-500,000
PMA-D	H	CH ₃	CH ₃	Mw 6000
PMA-O	C ₁₆ H ₃₃	H	H	Mn 30,000-50,000

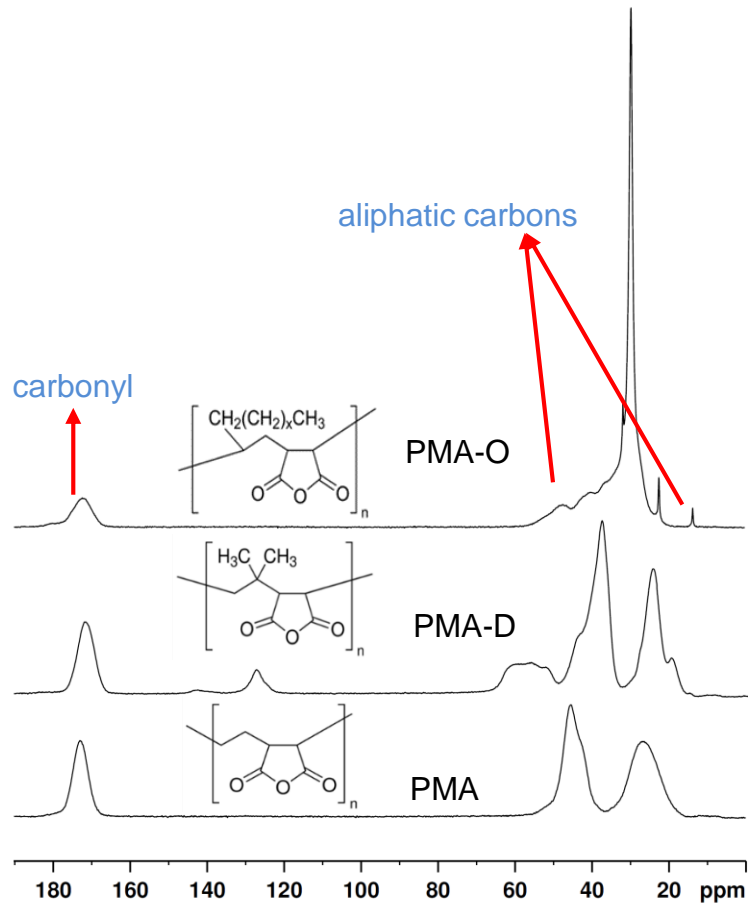
Poly(maleic anhydride)

imidization

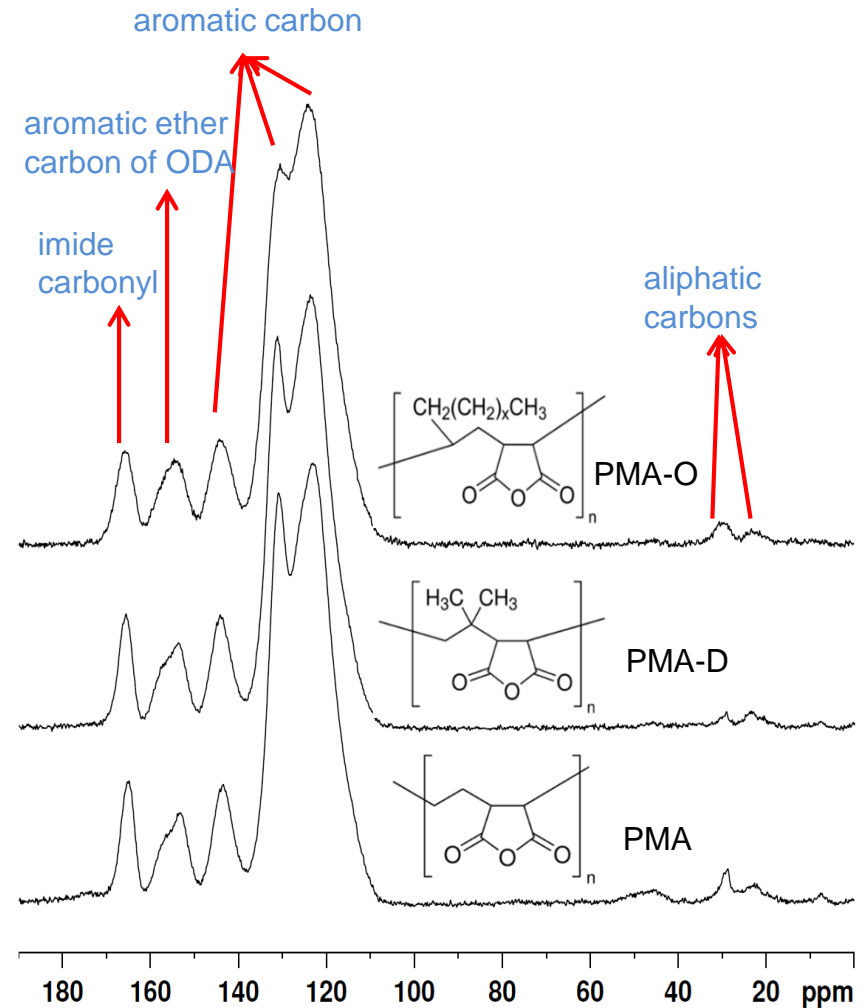


^{13}C NMR proves imidization was completed

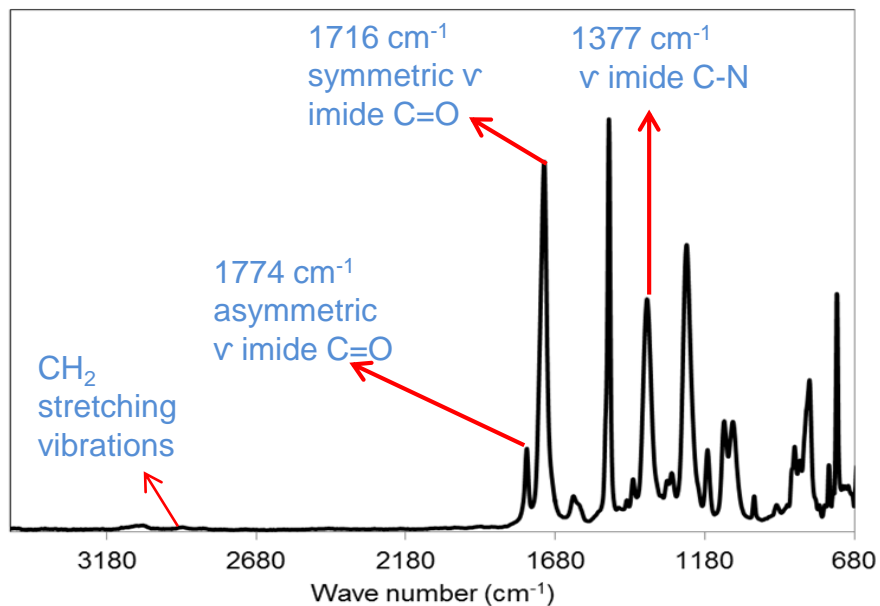
Cross-linker themselves



Cross-linked polyimide aerogels



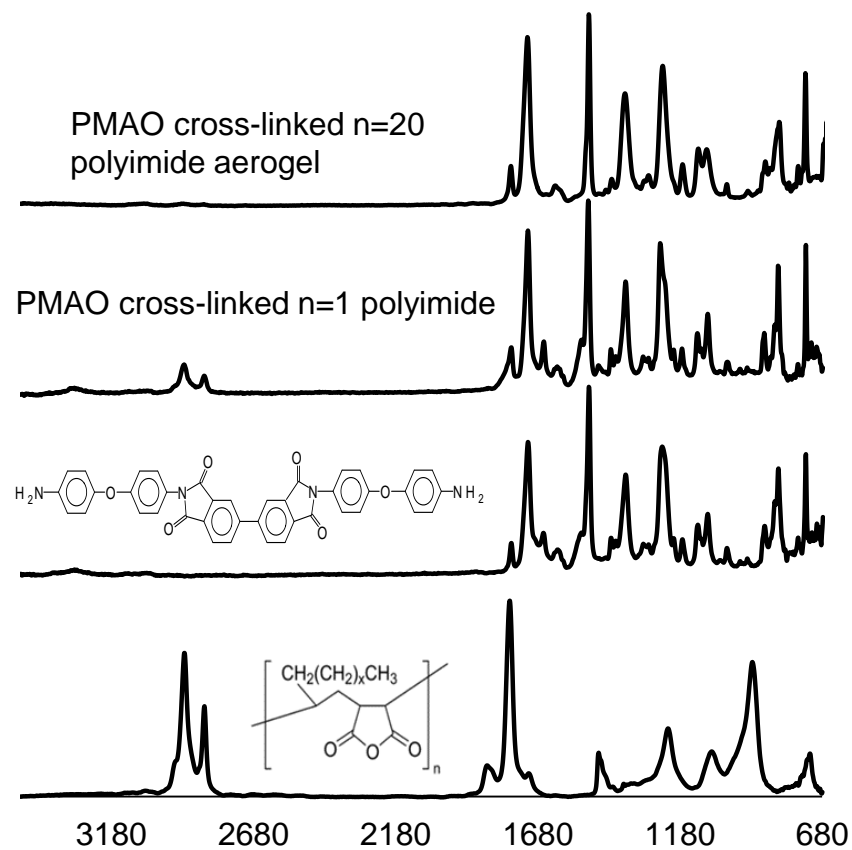
FTIR spectra



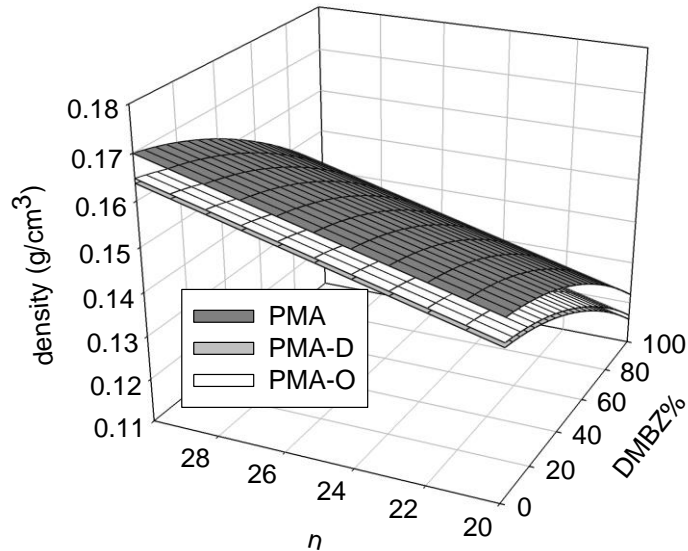
Typical Fourier transform infrared (FTIR) spectrum of aerogels

Absent

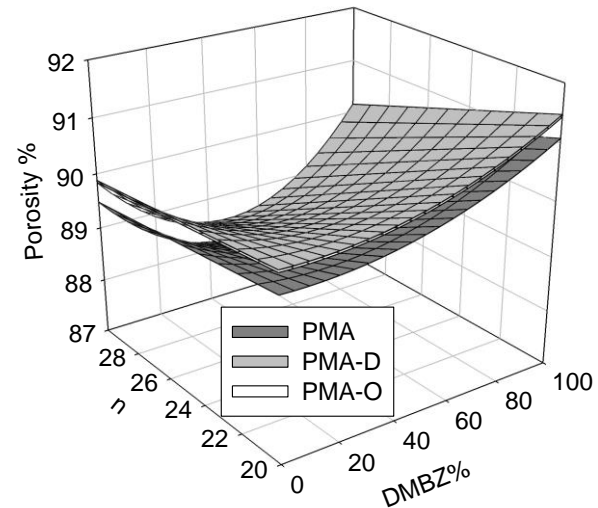
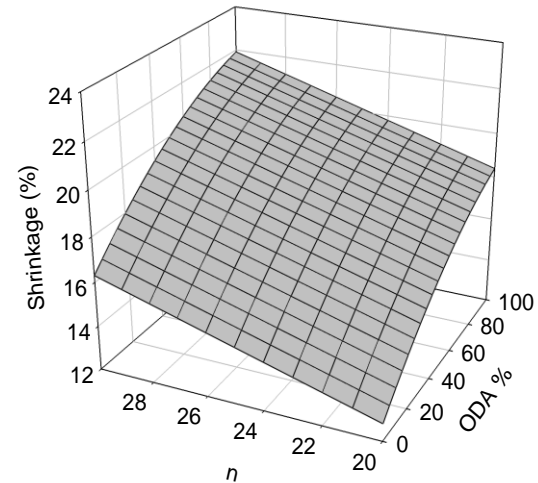
- 1860 cm^{-1} unreacted anhydride
- ~1807 & 980 cm^{-1} isoimide
- ~1660 cm^{-1} ν amic acid C=O
- ~1535 cm^{-1} ν amide C-N



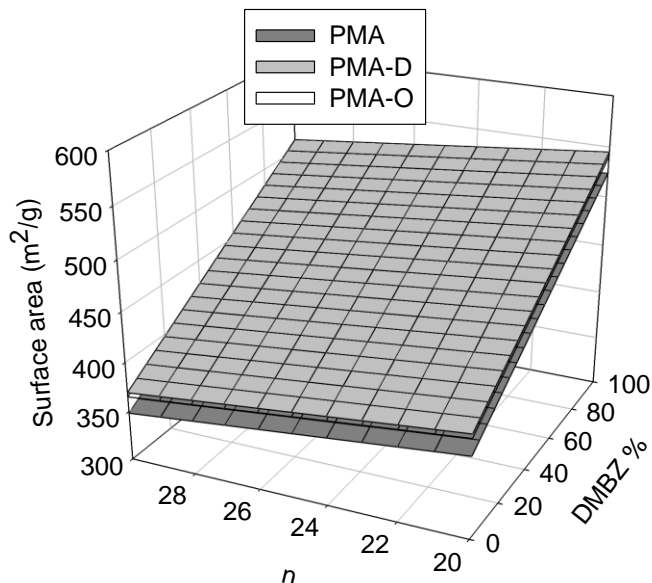
Density, shrinkage, and porosity



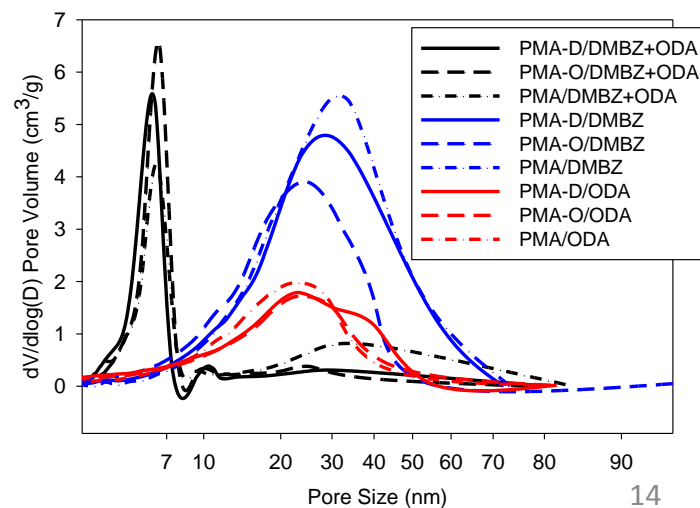
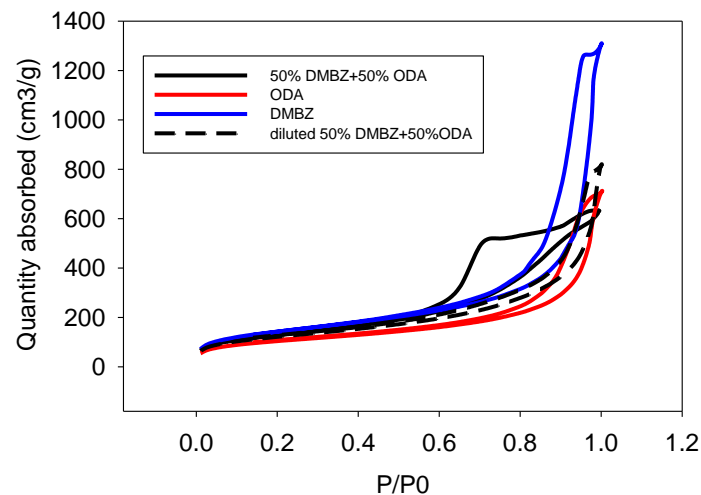
- PMA cross-linked aerogel has the highest density, and the lowest porosity
- Shrinkage is not affected by the cross-linkers



N_2 adsorption/desorption shows the aerogels have mesoporous structure

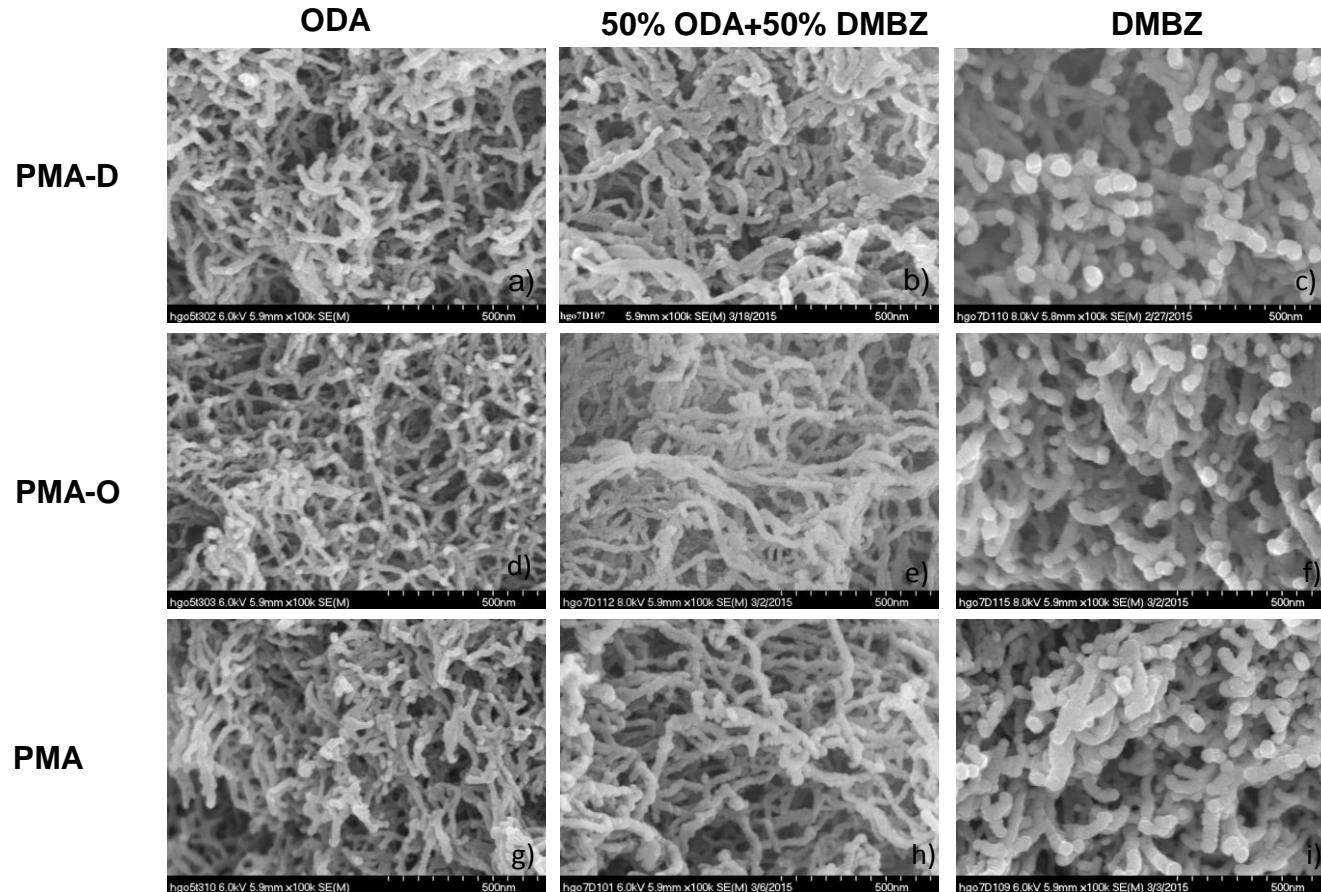


- PMA cross-linked aerogel has the least surface area.
- Increase DMBZ% and n value, surface areas increase
- DMBZ+ODA formulations have sharp peaks around 6nm.



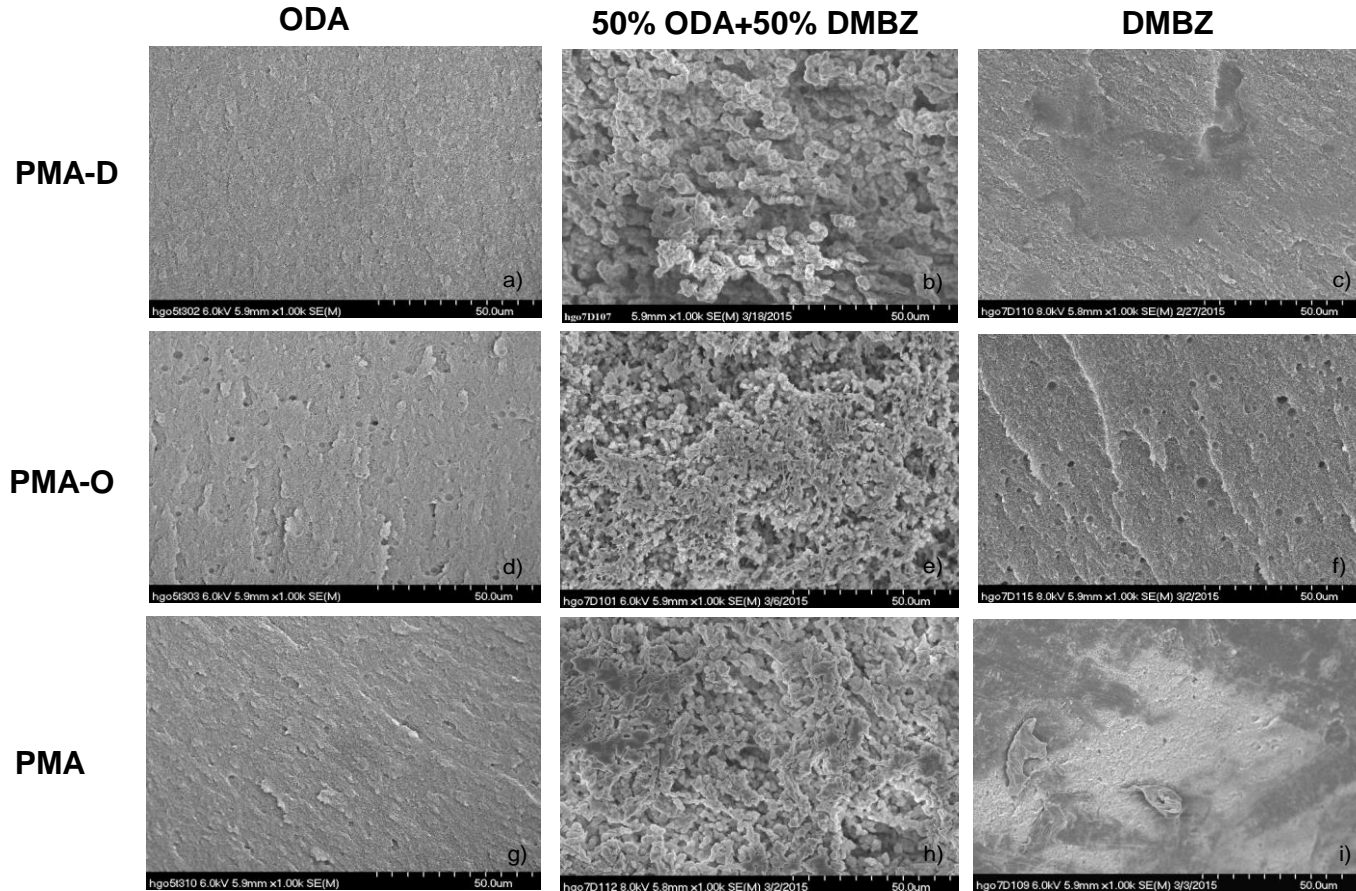


Scanning electron microscope (SEM) images

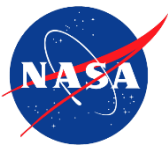


- DMBZ containing formulations had larger diameter strands than ODA alone formulations
- Aerogels have fibrous network structure

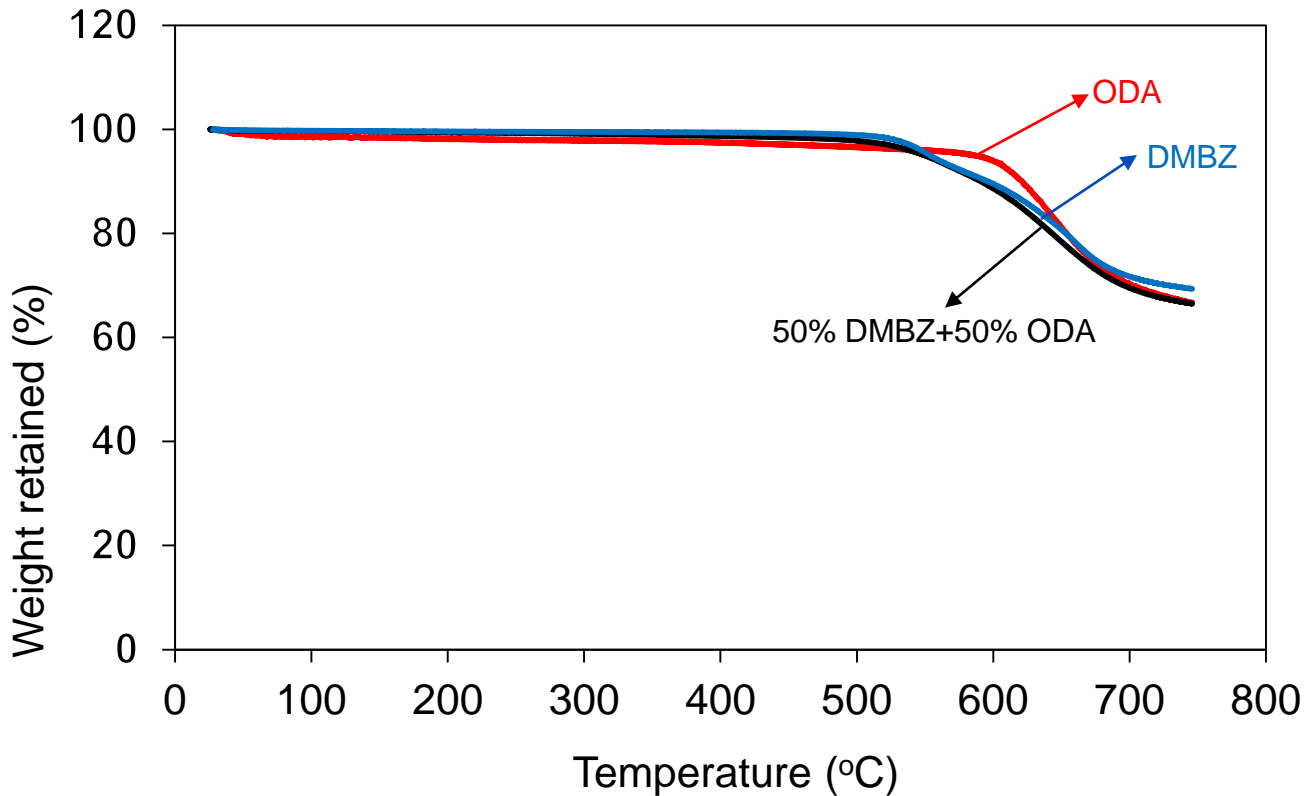
Lower Magnification SEM images



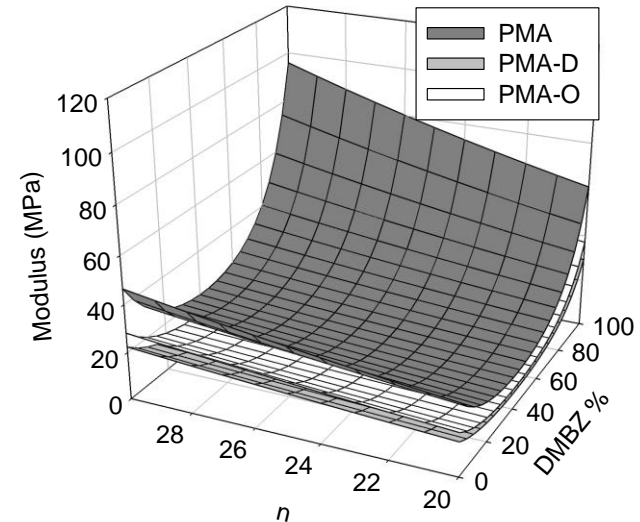
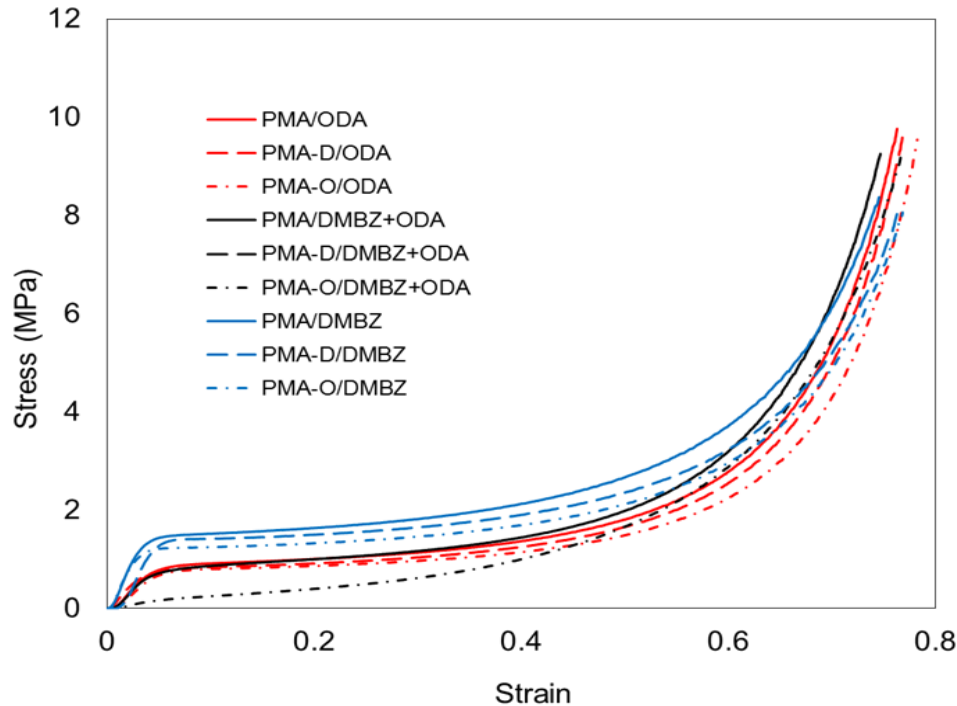
- PMA-O cross-linked aerogels show cavities in lower magnification SEM images
- 50%DMBZ+50% ODA formulations show spherical balls connecting together with polymer strands.



Td of the polyimide backbone is determined by the chemical components of the polyimide

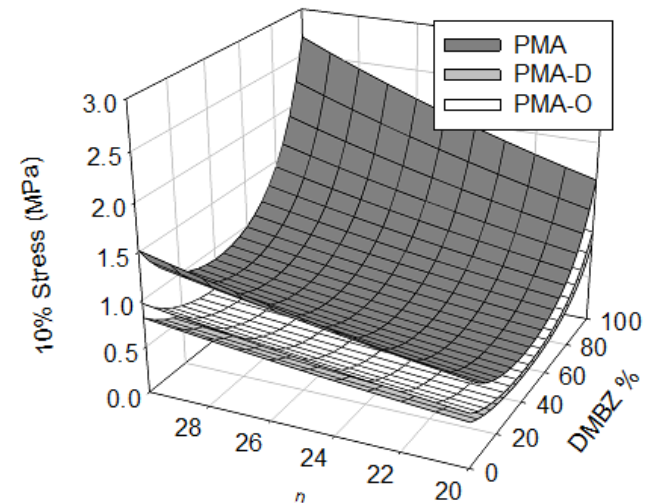
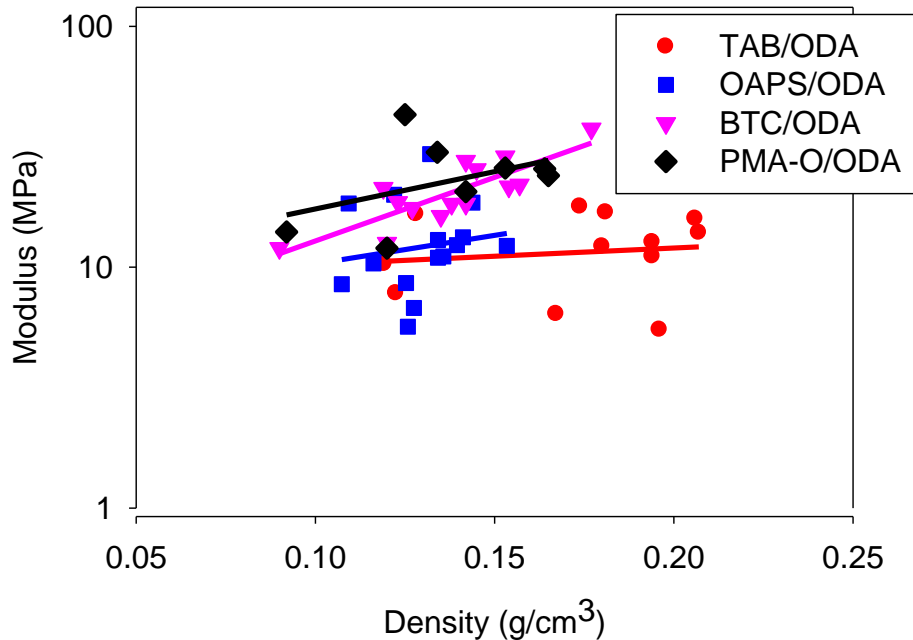


Compression tests were performed on the aerogels by compressing to 80%



- PMA cross-linked aerogels have higher modulus than PMA-O and PMA-O cross-linked aerogels
- 50% ODA+50% DMBZ formulations have lower modulus than DMBZ or ODA only formulations
- Increase n value, modulus increase slightly

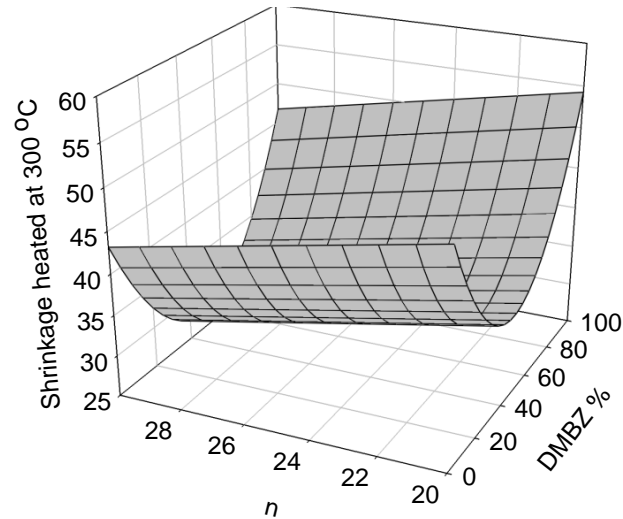
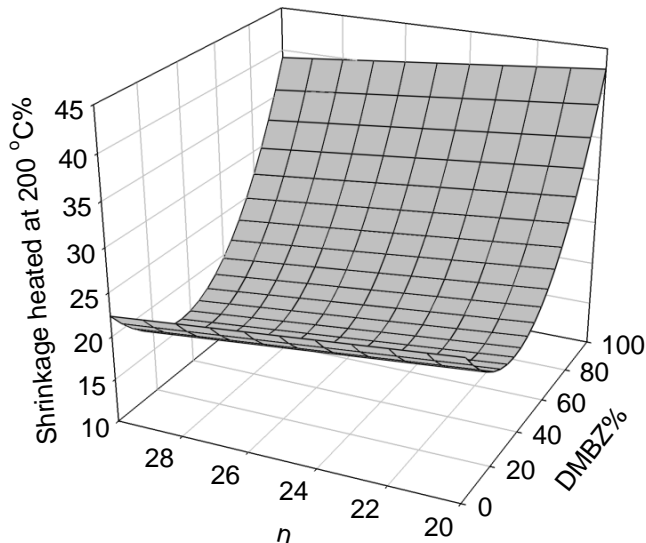
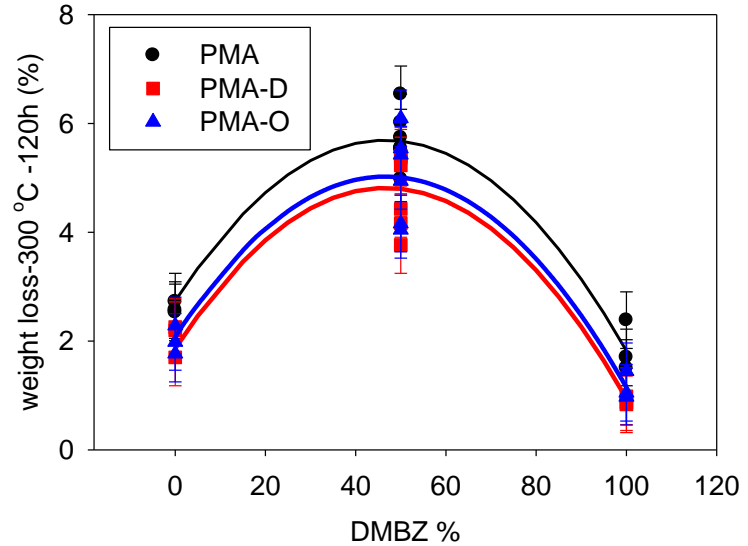
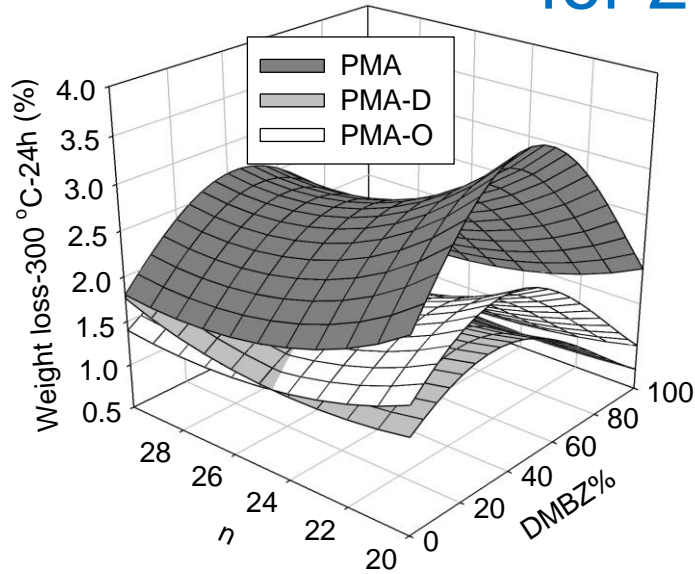
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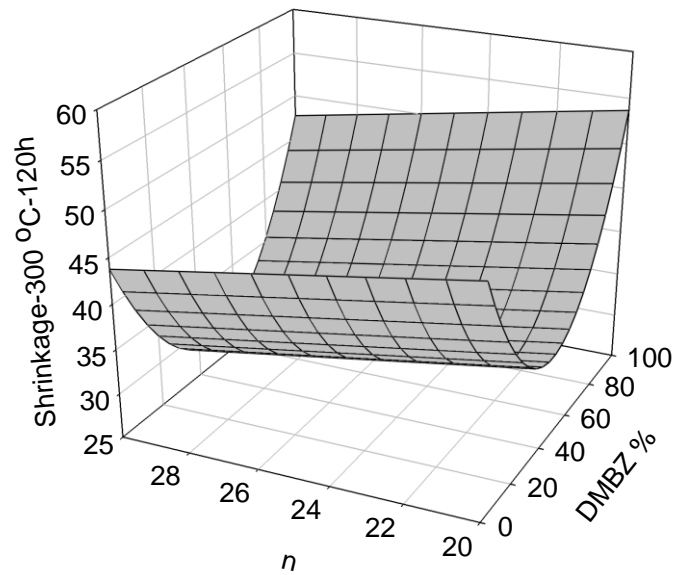
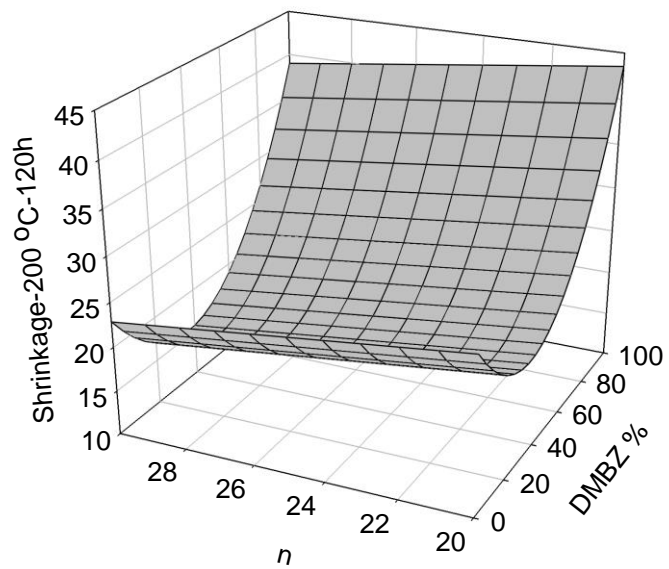
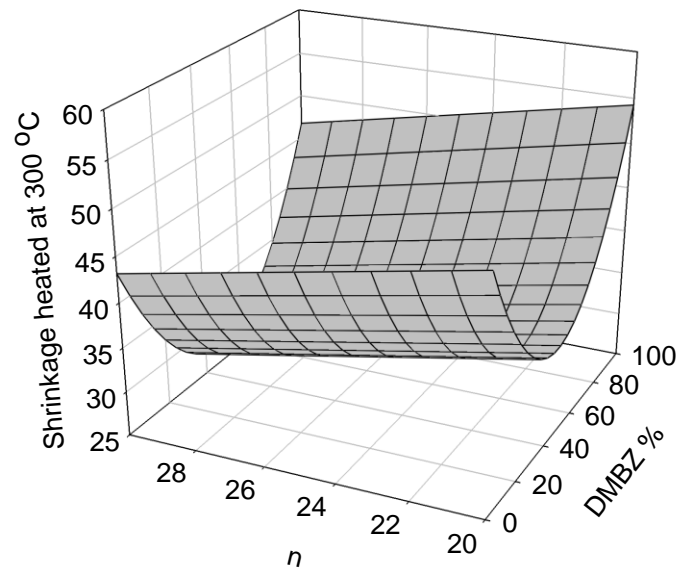
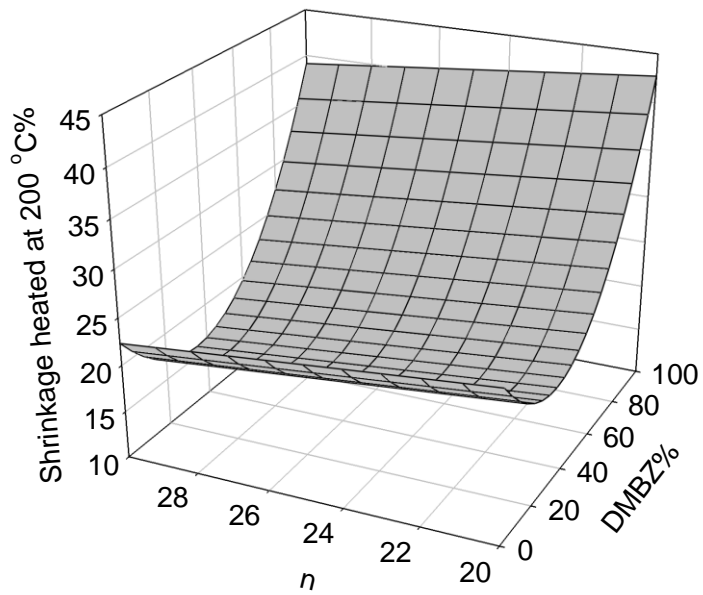


- Higher or similar modulus compared to TAB, OAPS or BTC cross-linked polyimide aerogels made with BPDA and ODA
- The higher n, the higher the 10% stress
- PMA cross-linked polyimide aerogels have the highest 10% stress

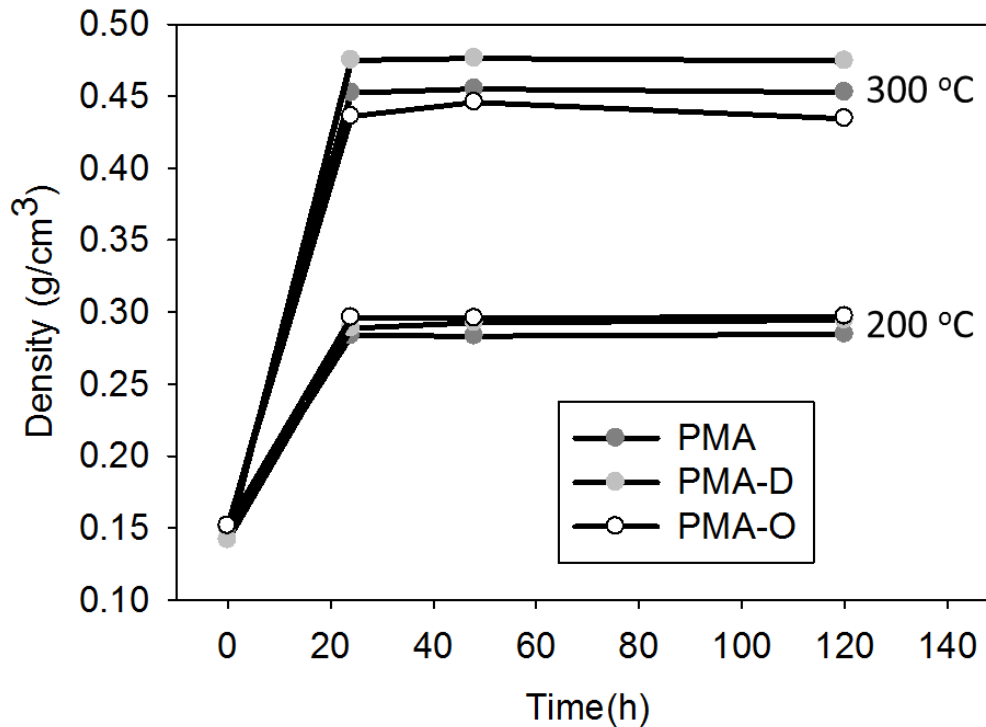


Weight loss after heated at 300 °C for 24h and 120h

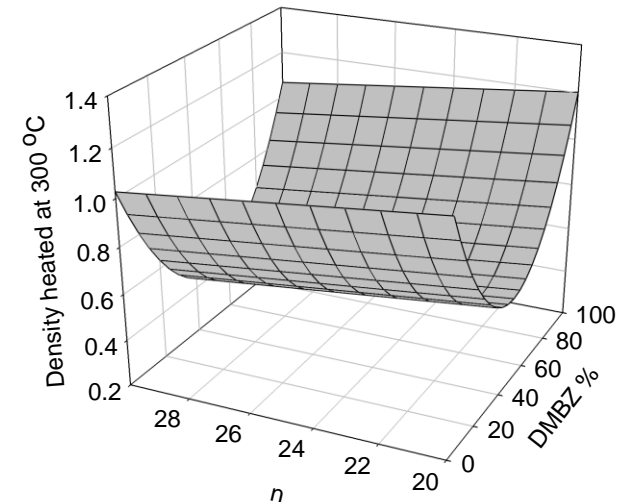
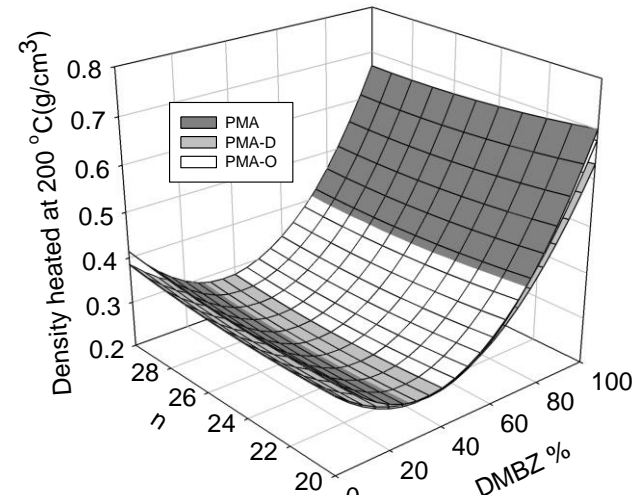


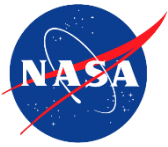


Density change after heated at 200°C and 300°C

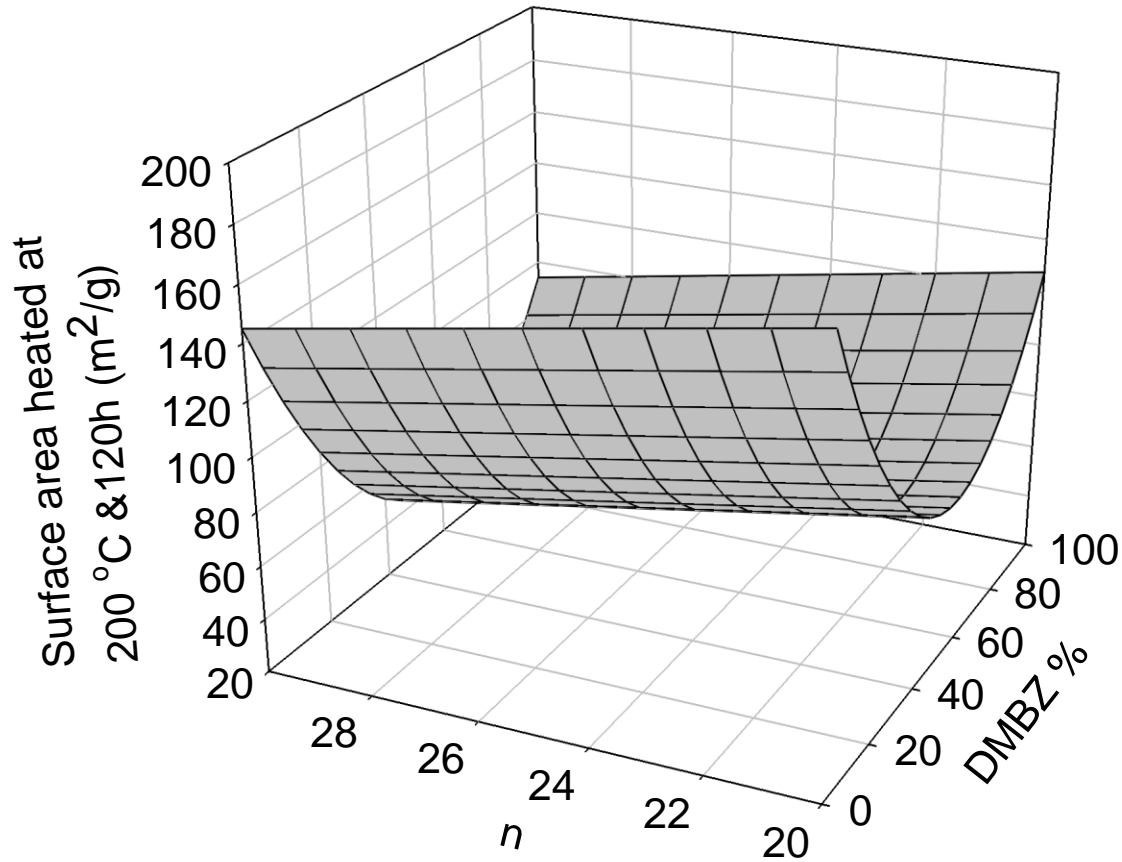


- 50% DMBZ+50% ODA formulation heated at 200°C and 300°C for 24h, 48h, and 120hour: Major density changes occur before 24h



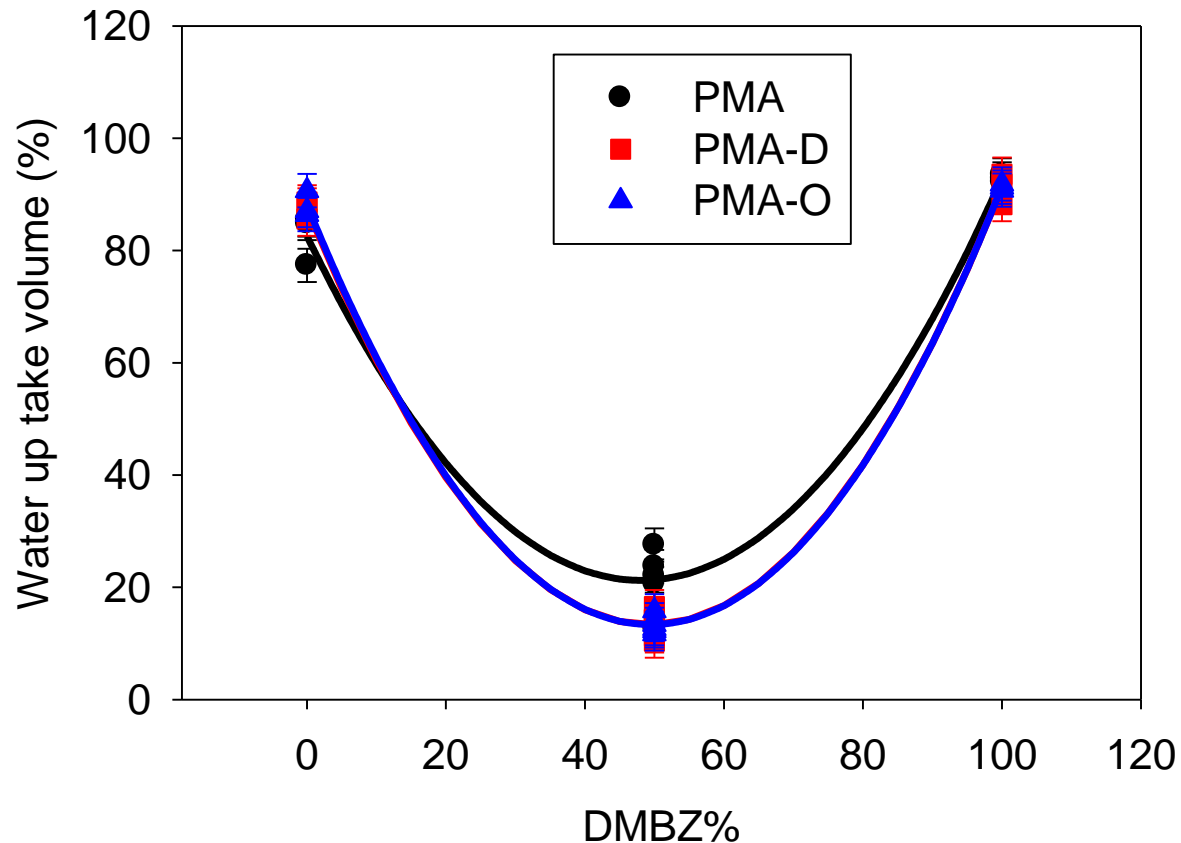


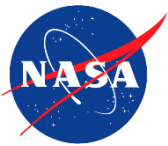
Surface area after heated at 200°C and 120h





Water uptake after 48h show 50% DMBZ+50% ODA absorb less water





Summary

- New aerogels made with amine capped polyimide oligomers and cross-linked by poly(maleic anhydride)s were synthesized
- PMA-O and PMA-D cross-linked aerogels have lower density, higher porosity and higher surface area
- PMA cross-linked aerogels have higher density and higher modulus
- The poly(maleic anhydride) cross-linked ODA capped aerogels have higher or similar modulus values compared to TAB, OAPS or BTC cross-linked ODA aerogels
- Density and shrinkage change when heated at 200°C and 300°C occur before 24 hour
- Cross-linkers have no effect on the shrinkage of the aerogels when heated at 200°C
- PMA-D cross-linked aerogels derived from DMBZ or ODA only have lower density than PMA-O and PMA cross-linked aerogels after heated at 200°C for 24h
- Cross-linkers have no effect on the density and shrinkage of the aerogels when heated at 300 °C



Acknowledgement

Aerogel team members

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Rocco P. Viggiano



Mary Ann



Baochau



Stephanie



Jarrod

Drying & characterization

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Linda S. McCorkle
Daniel A. Scheiman
Nathan G. Wilmoth



Dan H.



Linda



Dan S.



Brittany

Summer Intern

Brittany Wilkewitz
Shelley Hanes



Shelley

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Thank you!

