National Aeronautics and Space Administration

Flexible polyimide aerogel cross-linked by poly(maleic anhydride-alt-alkylene)

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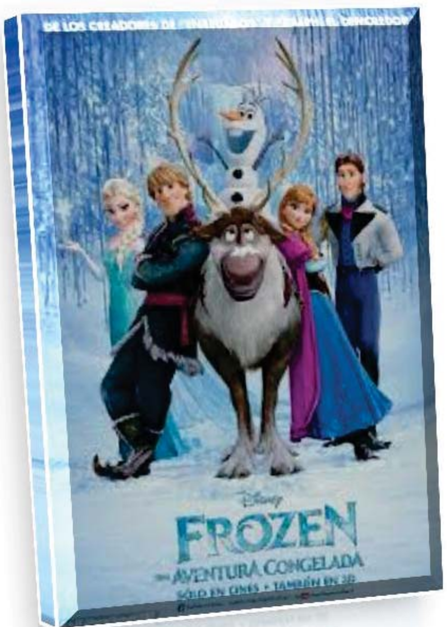
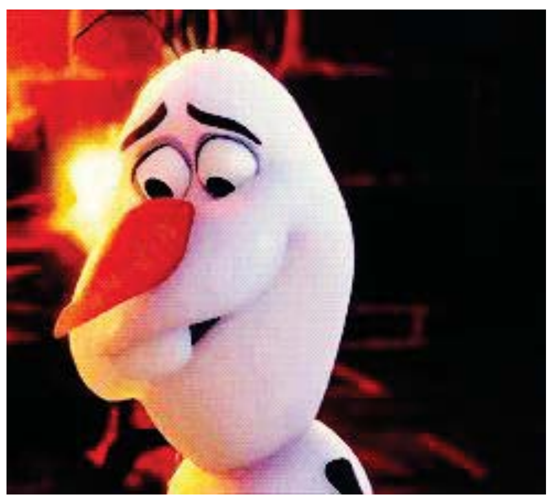
Mar-17-2014



http://disney.wikia.com

http://delicious-to-c.blogspot.com/2013/12/frozen-2013.html



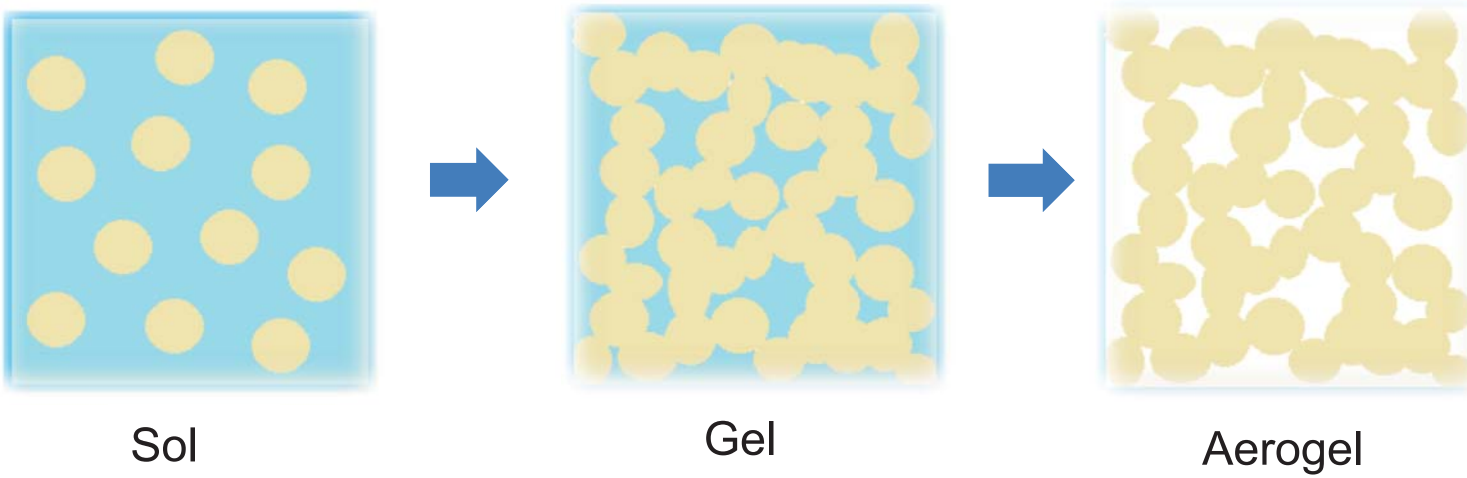
http://royal-tarts.deviantart.com/art/Olaf-GIF-4-Melting-Request-426015061

Some people are worth melting for...

Aerogel protection for Olaf

www.dynax-j.com

Why aerogels?



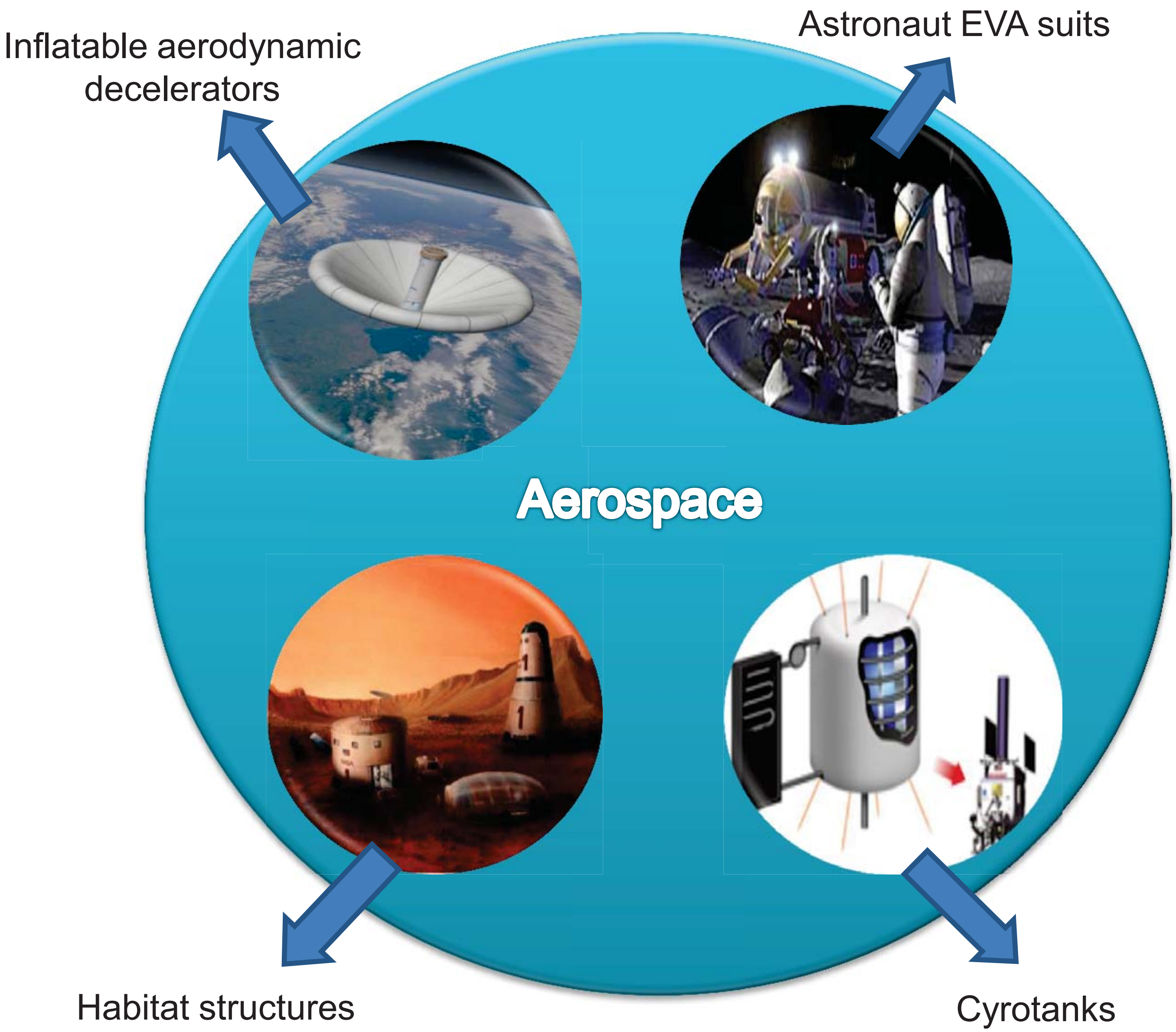
- Made by removing solvent from wet gels without collapsing the structure
- High porous solids
- Low density
- High surface area
- Good thermal insulation material
  - reduces heat transfer (convection, conduction, and radiation)

http://en.wikipedia.org/wiki/Aerogel

Potential applications of aerogels

http://spinoff.nasa.gov/spinoff2001/ch5.html

Potential applications of aerogels



http://spinoff.nasa.gov/spinoff2001/ch5.html

What should be considered for real application?

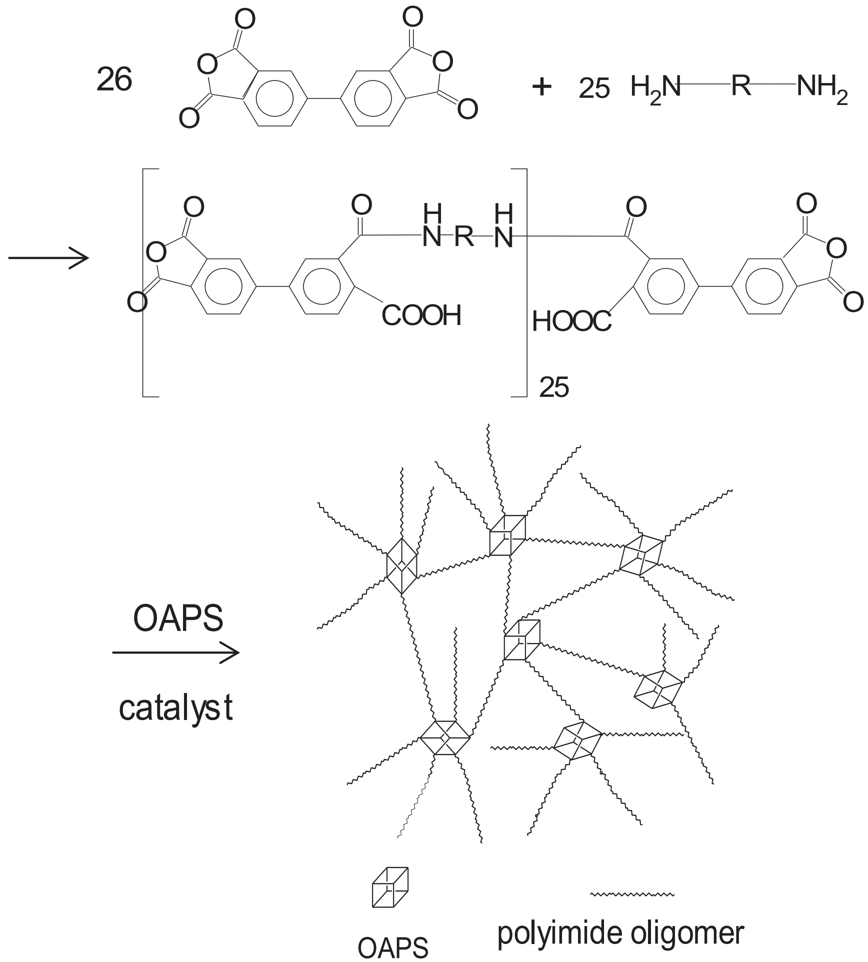
- Light weight
- High porous
- High surface area
- Low thermal conductivity

- Flexible
- Strong
- Less dusty
- Hydrophobic
- Low cost

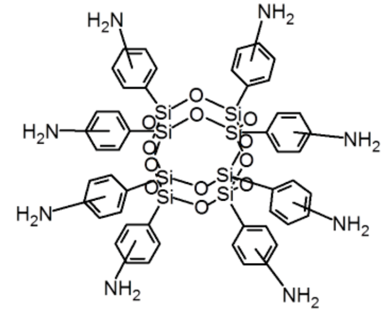
Silica aerogel is fragile

Better mechanical properties and environmental stability are needed…

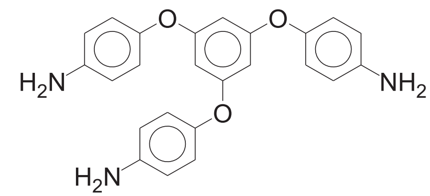
Cross-linked polyimide aerogels



Cross-linkers



octa(aminophenyl)silsesquioxane (**OAPS**)



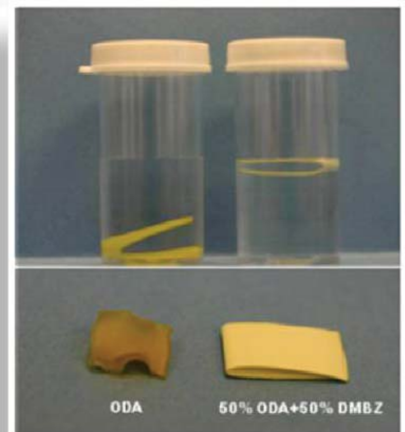
1,3,5-triaminophenoxybenzene (**TAB**)

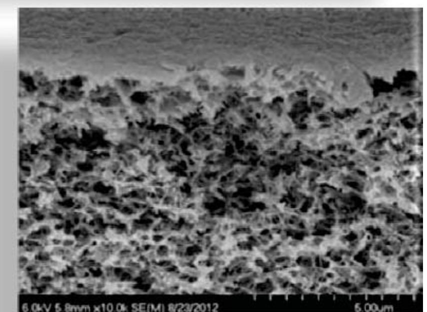
- Two cross-linkers with amine functional groups
- Various polyimide oligomer backbones using different dianhydrides and diamines
- Chemical imidization

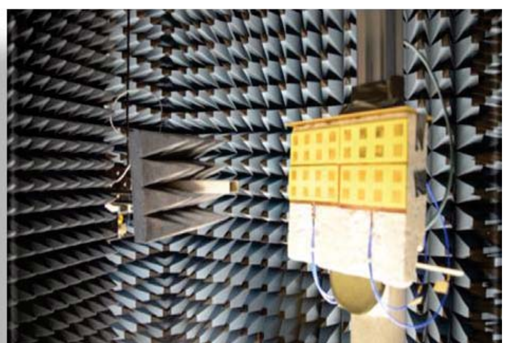
M. A. B. Meador and H. Guo, LEW-18864-1, US patent application No. 61/594,657

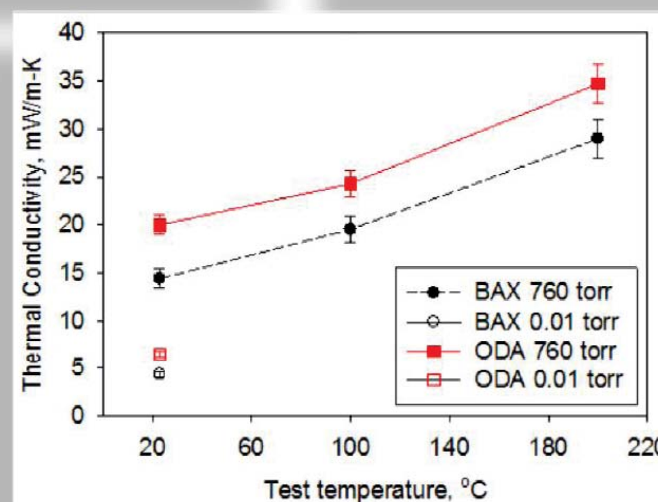
Cross-linked polyimide aerogels

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





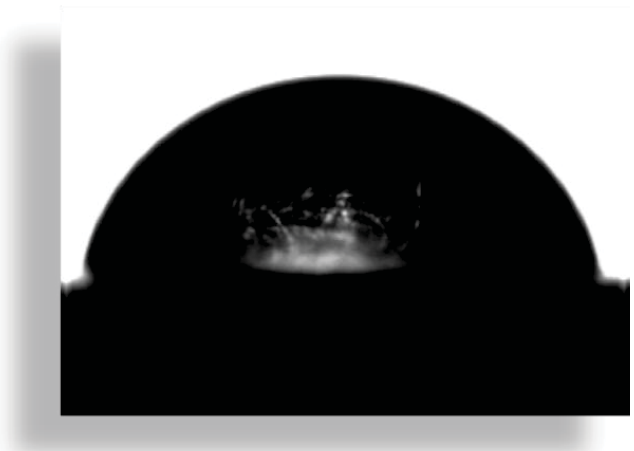




M.A. B. Meador, et al. ACS Appl. Mater. Inter., 2012, 6346.
H. Guo, et al. ACS Appl. Mater. Inter., 2012, 4, 5422.
M. A. B. Meador, et al. ACS Appl. Mater. Inter., 2012, 4, 536.
H. Guo, et al. ACS Appl. Mater. Inter., 2011, 3, 546.

Problems of previous cross-linked polyimide aerogels

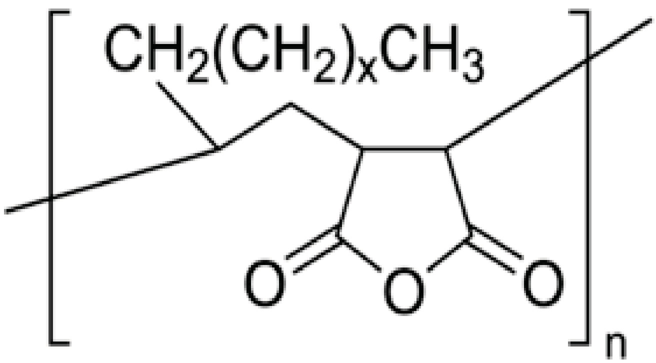
- OAPS cross-linker is expensive
- TAB cross-linker is not commercially available, requires custom synthesis
- Contact angle for the moisture resistant polyimide aerogel is 85-90^{o}



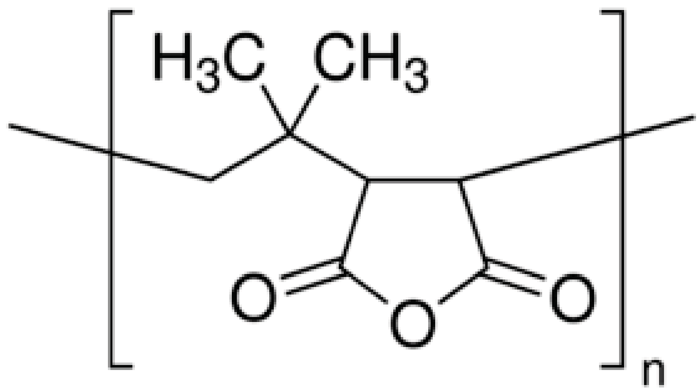
Objectives

- Explore commercially available and less expensive cross-linkers
- Look for less expensive monomers that might impart flexibility, hydrophobicity, etc.

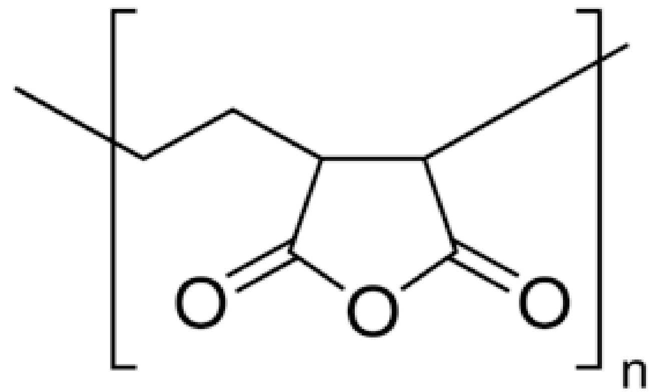
Commercially available poly(maleic anhydride)s as cross-linkers



poly (maleic anhydride-alt-1-octadecene) (**PAMO**)
Mn 30,000-50,000

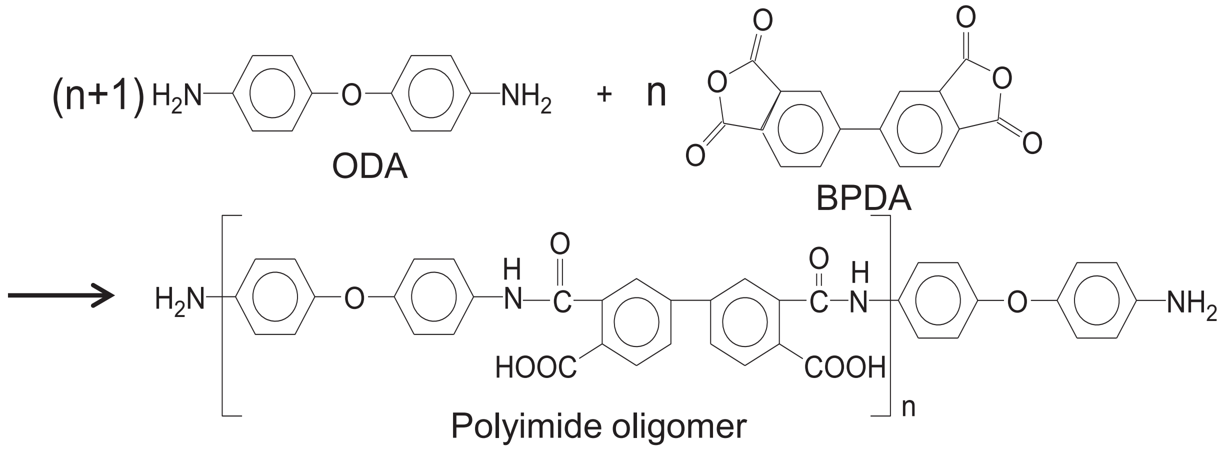


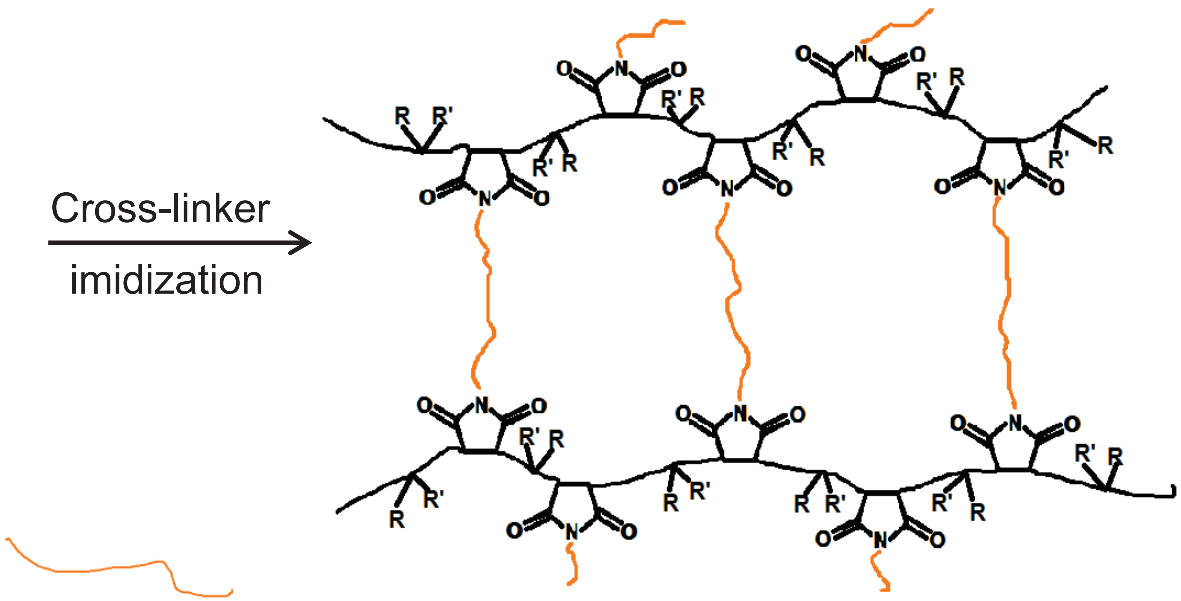
poly (isobutylene-alt-maleic anhydride) (**PIMA**)
Mw ~6000



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

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

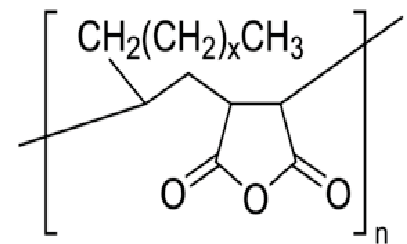




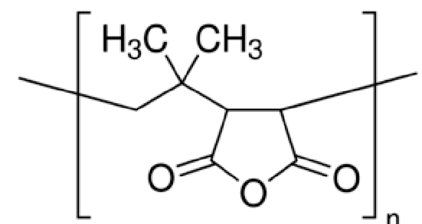
polyimide oligomer

R: H, CH_3, $CH_2(CH_2)xCH_3$ R': H, CH_3

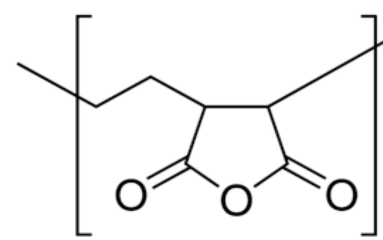
- n=20,10 w/w%
- Polyimide oligomers
- ODA+BPDA
- three cross-linkers



PMAO



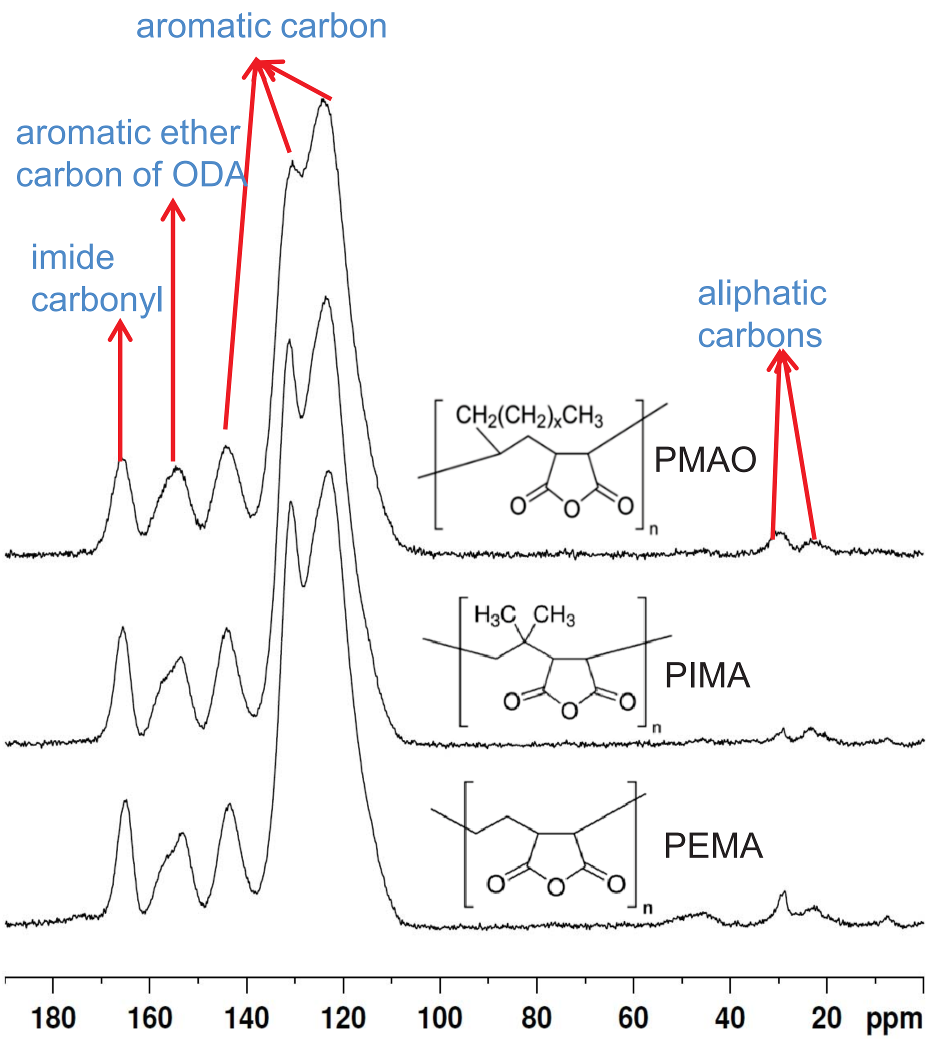
PIMA



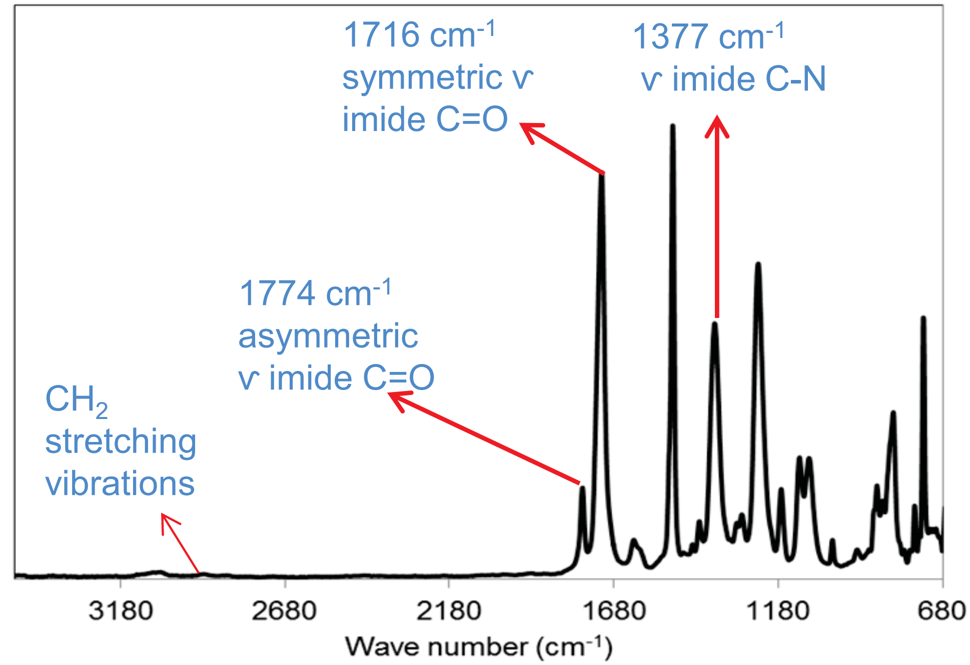
PEMA

H. Guo and M. A. B. Meador LEW-19108-1

NMR and FTIR spectra prove imidization was completed



^{13}C nuclear magnetic resonance (NMR)

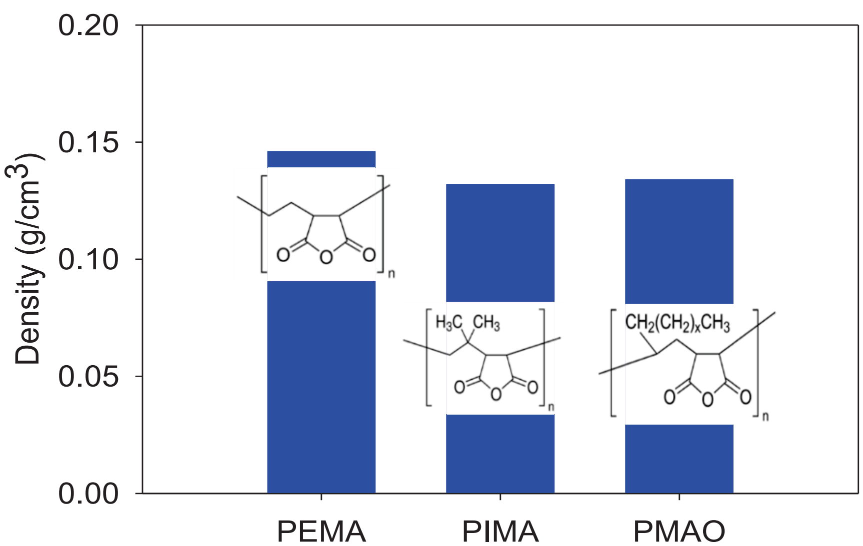


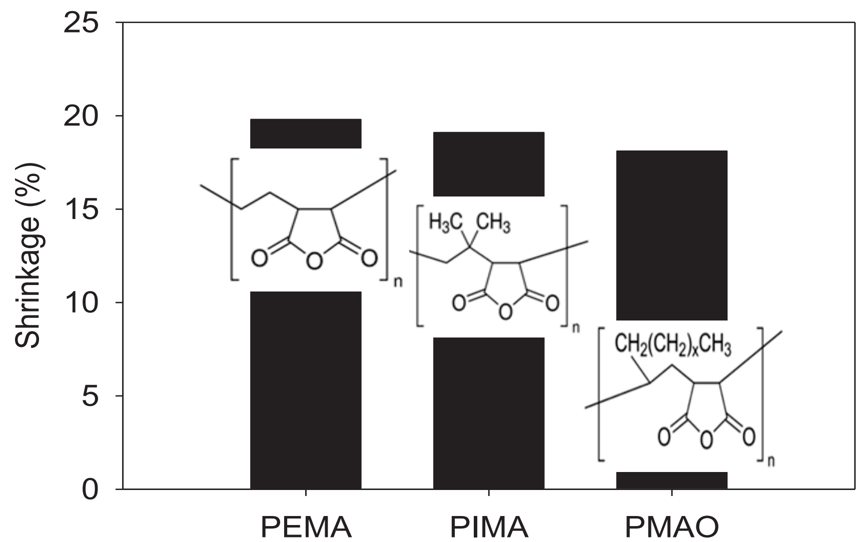
Typical Fourier transform infrared (FTIR) spectrum of aerogels

Absent

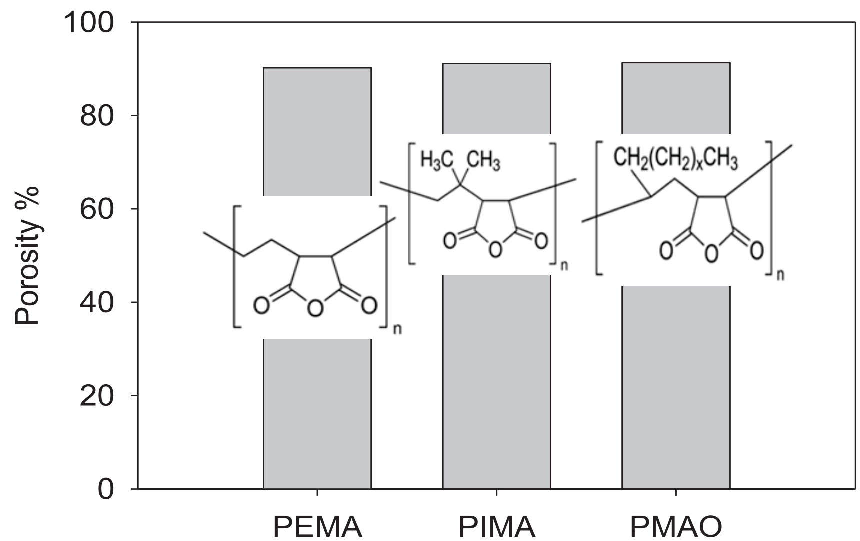
• $1860\ cm^{-1}$	unreacted anhydride
• ~ 1807 & $980\ cm^{-1}$	isoimide
• $\sim 1660\ cm^{-1}$	ν amic acid C=O
• $\sim 1535\ cm^{-1}$	ν amide C-N

Density, shrinkage, and porosity

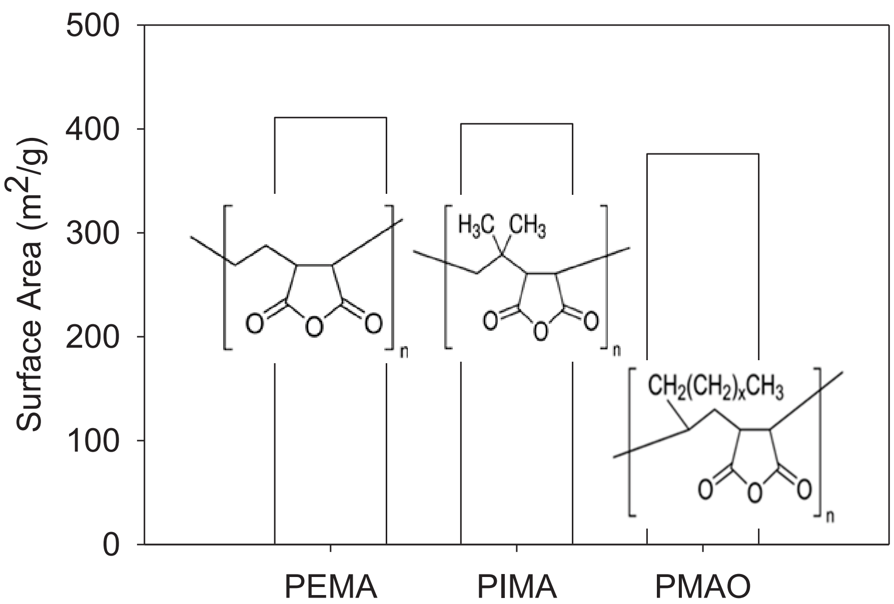


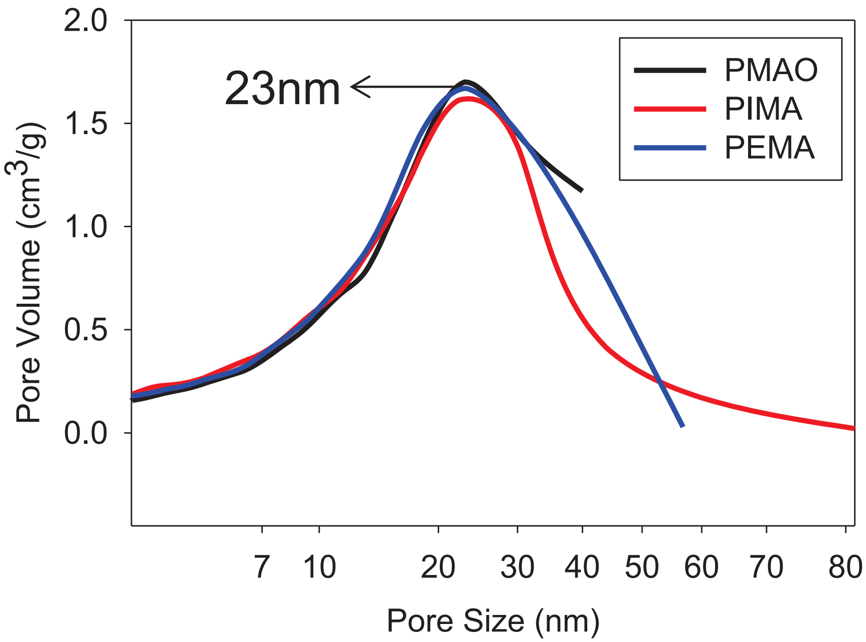


- PMAO cross-linked aerogel has the lowest shrinkage
- PEMA cross-linked aerogel has the highest density, the highest shrinkage, and the lowest porosity



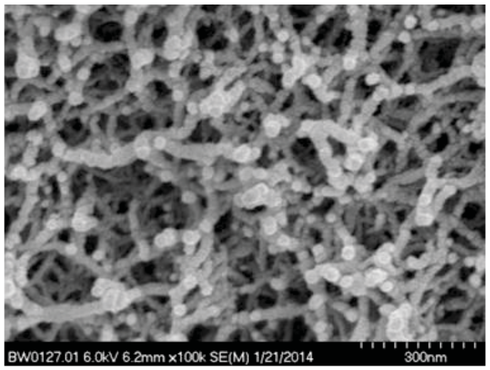
N_2 adsorption/desorption shows the aerogels have mesoporous structure



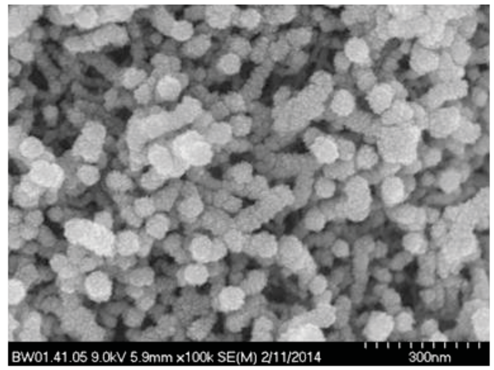


- PMAO cross-linked aerogels have no pores larger than 40nm

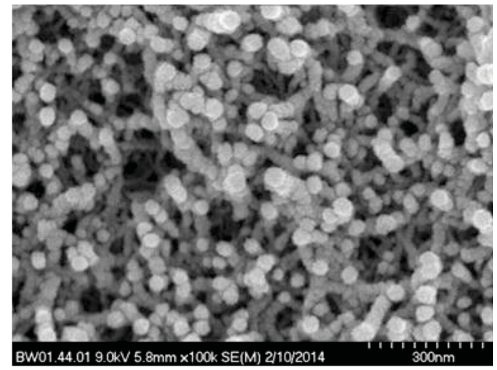
Scanning electron microscope (SEM) images



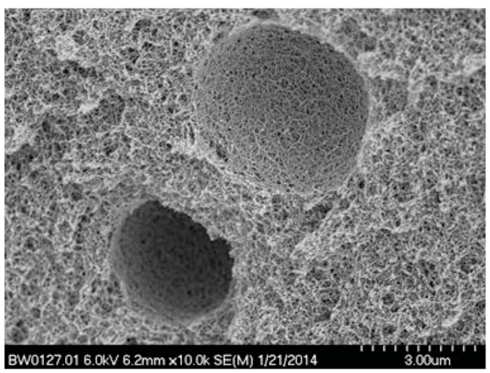
PMAO, 384 m^2/g, 0.134 g/cm^3



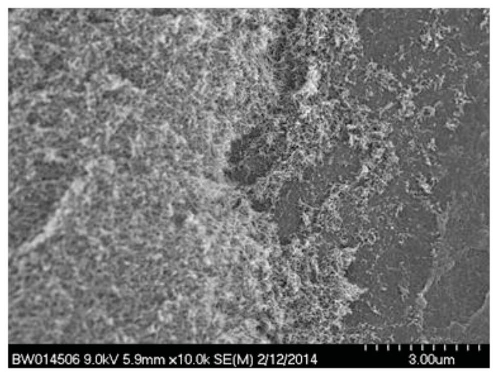
PIMA, 421 m^2/g, 0.139 g/cm^3



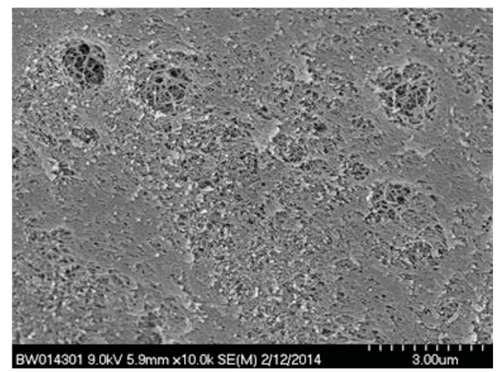
PEMA, 402 m^2/g, 0.144 g/cm^3



PMAO, lower magnification



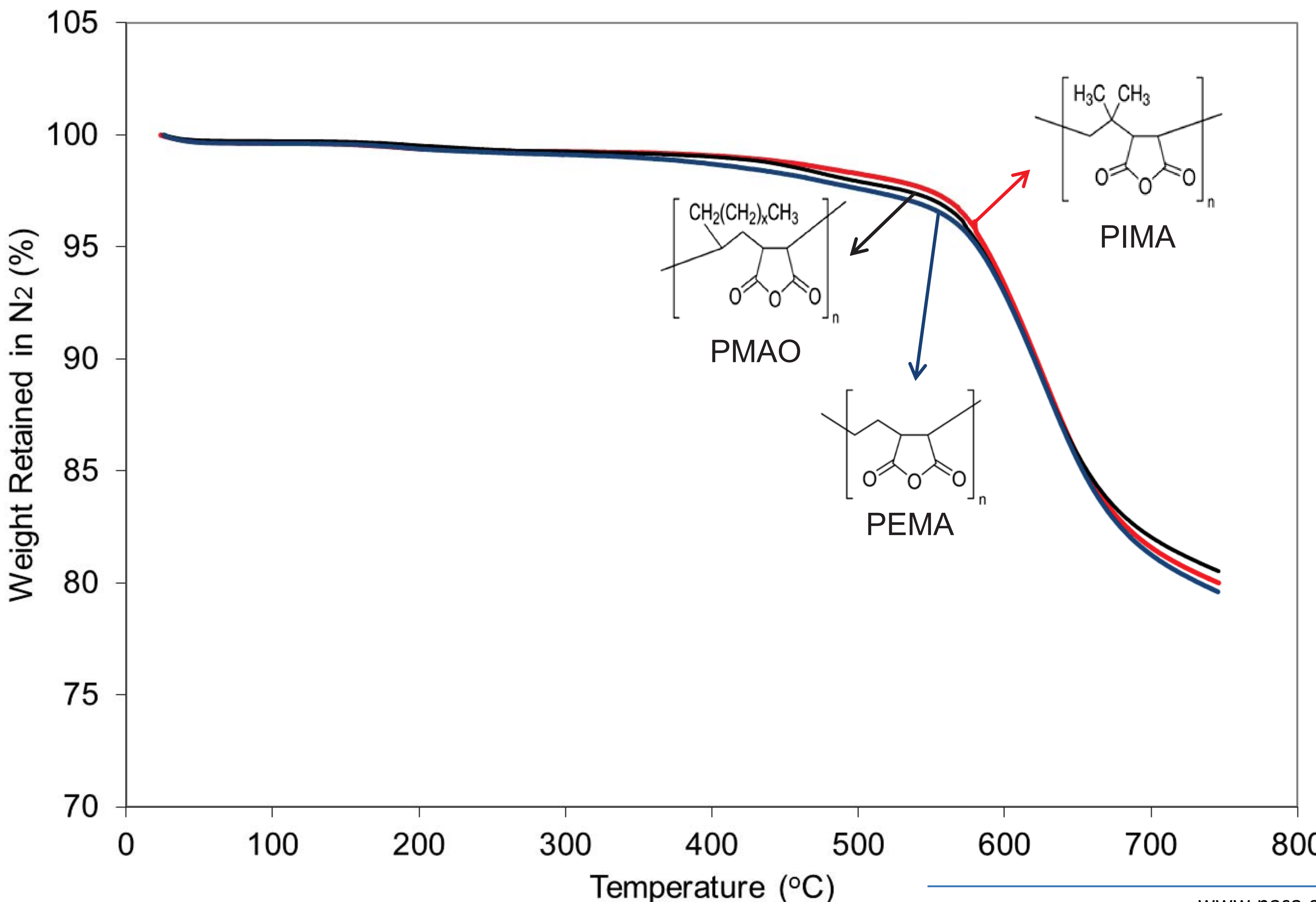
PIMA, lower magnification



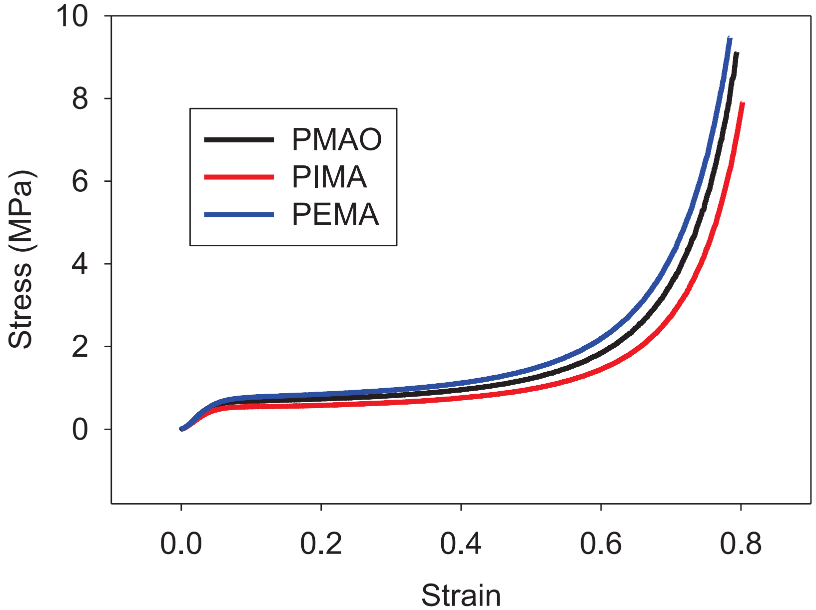
PEMA, lower magnification

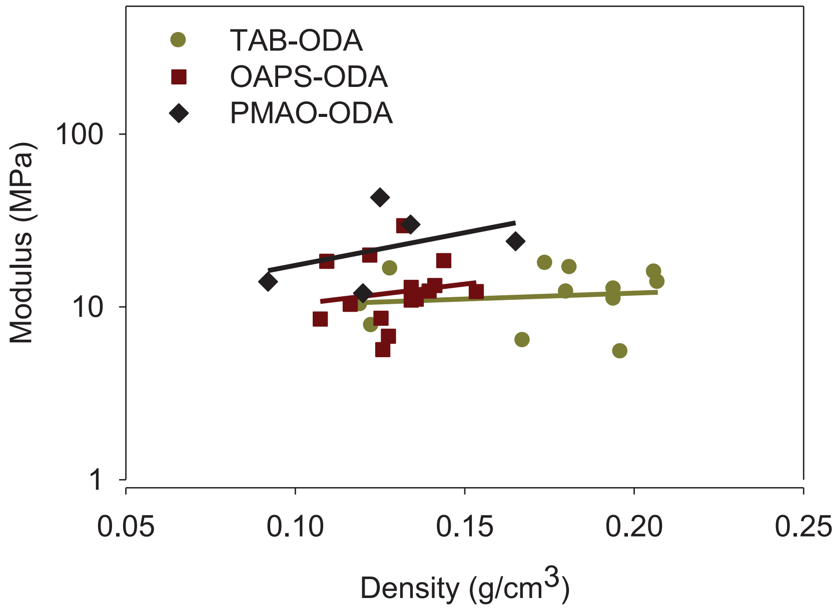
- PMAO and PEMA cross-linked aerogels have μm size cavities
- The polymer fibers in the cavities are much longer than the polymer fibers outside of the cavities
- PIMA cross-linked aerogels have more densely packed structure

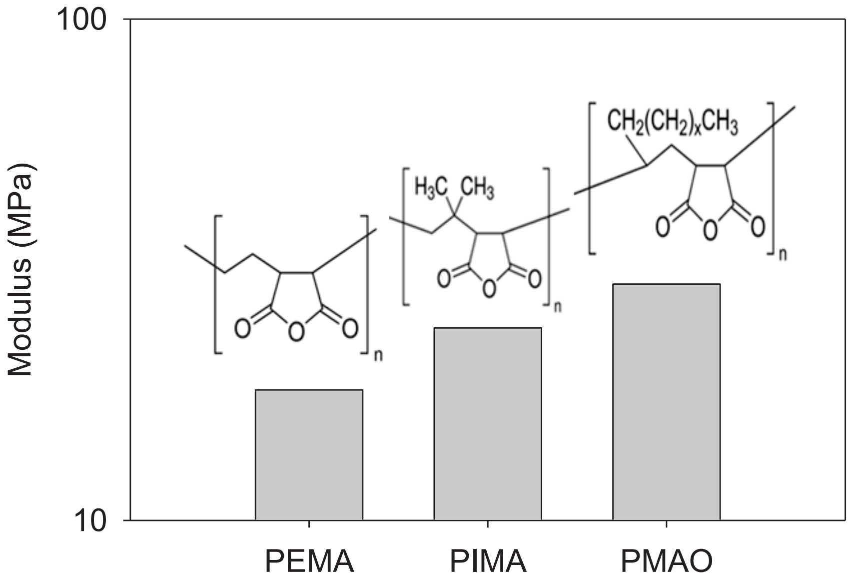
Small weight loss before decomposition of polyimide backbone is due to cross-linker



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



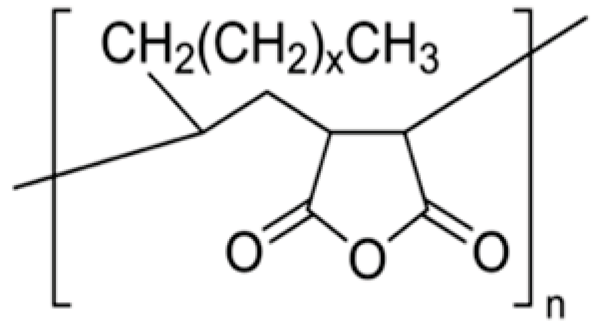




- Higher or similar modulus compared to TAB or OAPS cross-linked polyimide aerogels made with BPDA and ODA

PMAO was down selected as the cross-linker for the following study

- Lower density
- Higher porosity
- Lowest shrinkage
- Highest modulus

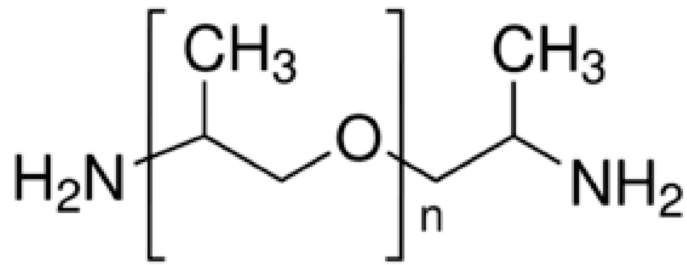


PMAO

OAI

Replacing ODA by PPG-230 or PPG-400 in polyimide oligomers

- Same or even higher flexibility
- Further reduce cost
- Increase hydrophobicity



poly(propylene glycol) bis(2-aminopropyl ether) Mn 230 or 400

(PPG-230 or PPG-400)

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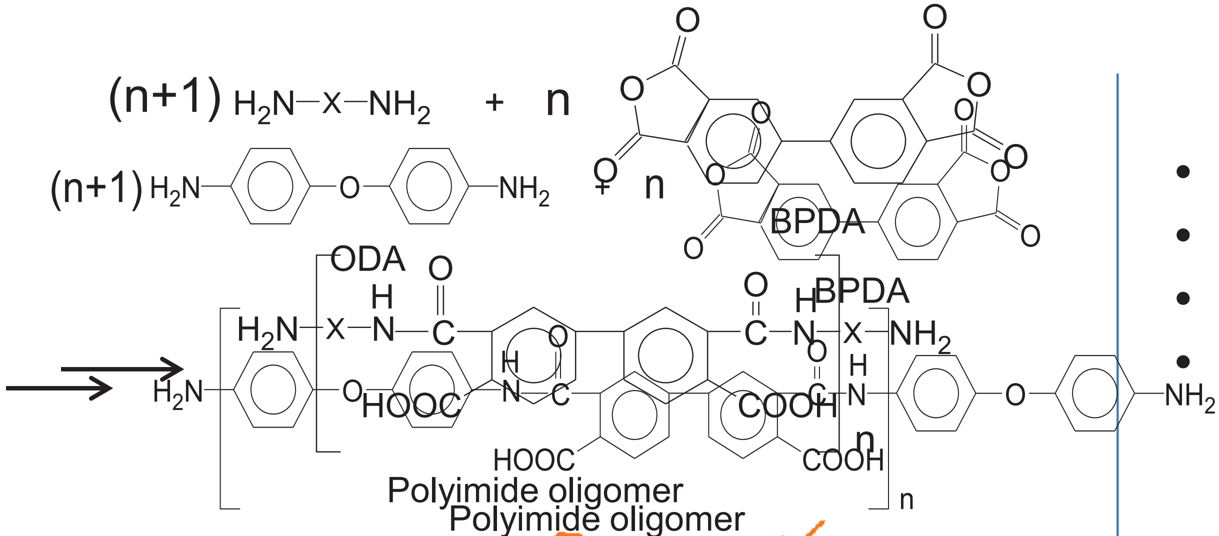
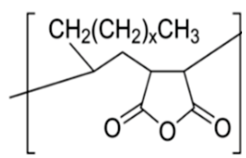
Polyimide oligomers made with combination of PPG/ODA and BPDA



- n=20,10 w/w%
- Polyimide oligomers
- ODA+BPDA
- three cross-linkers

- n : 10-30
- 10 w/w%
- PMAO as cross-linker
- Polyi
PPG/

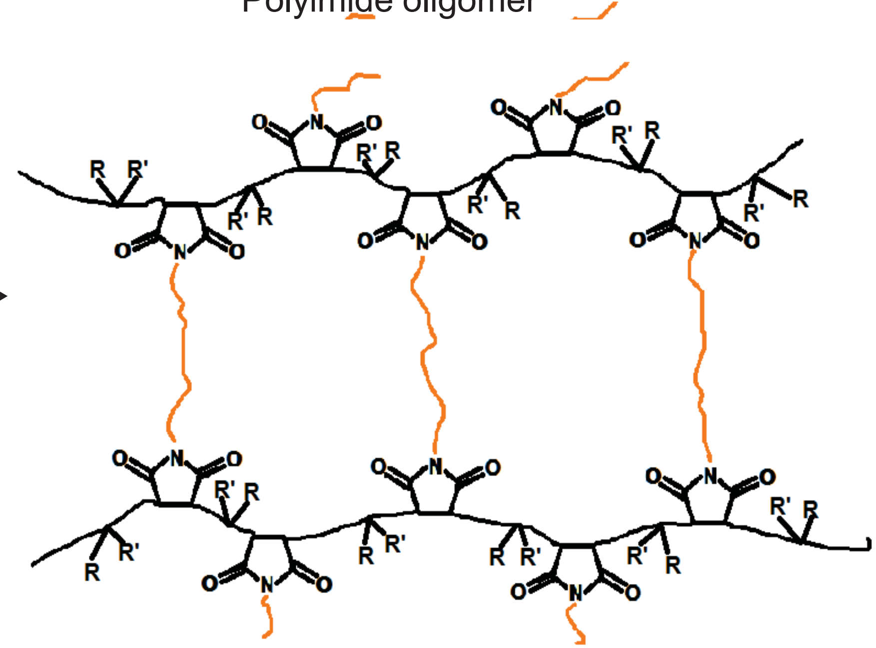
PPG-230



Cross-linker

imidization

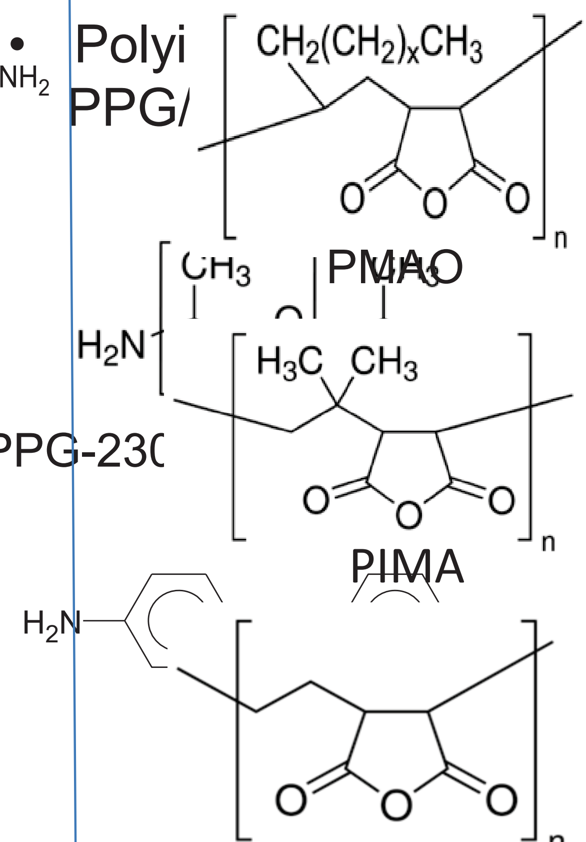
imidization



Polyimide oligomer

oligomers

R: H, CH_3, $CH_2(CH_2)xCH_3$ R': H R': H, CH_3



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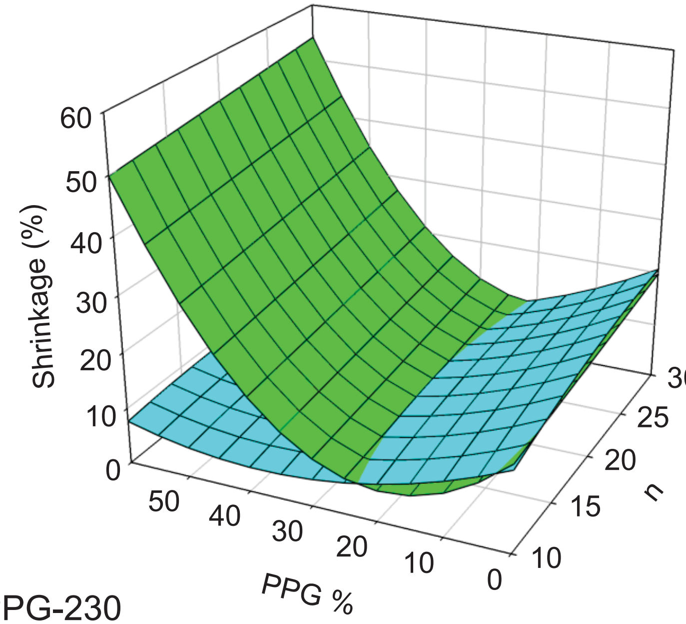
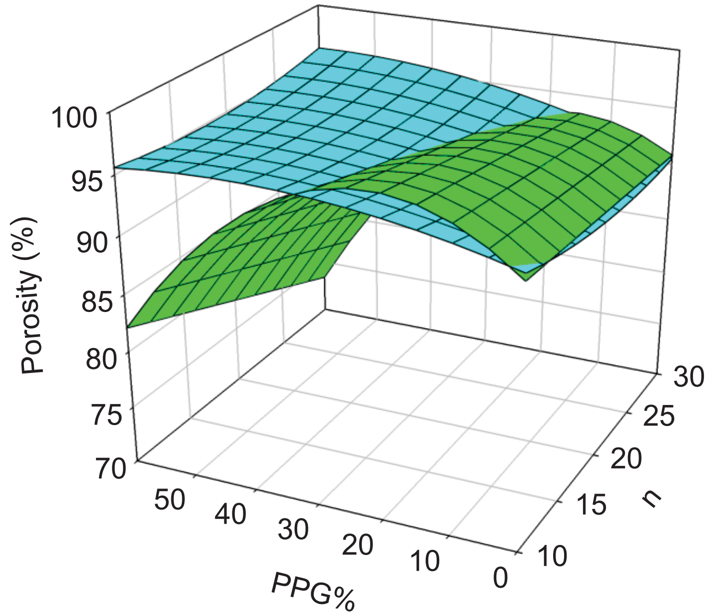
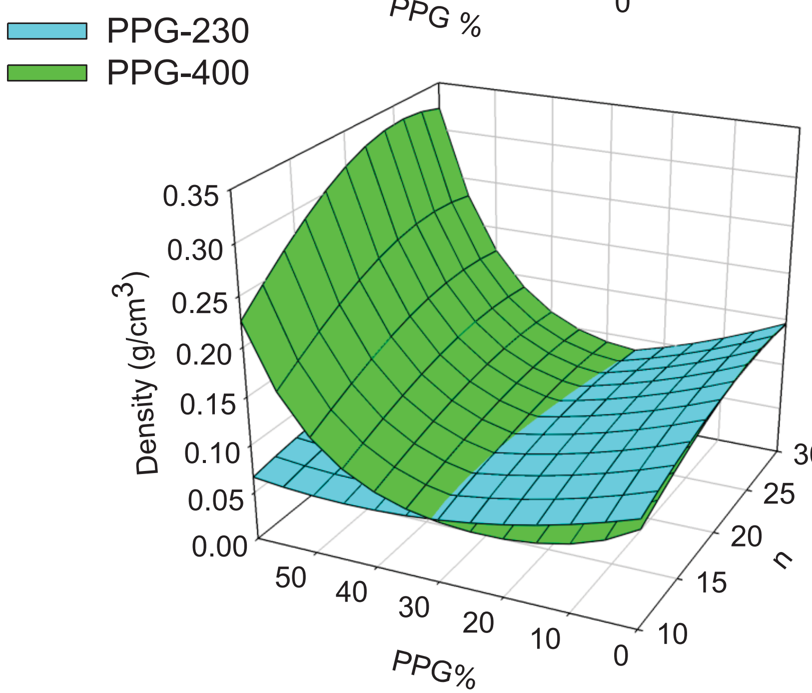
Density, Shrinkage, and Porosity

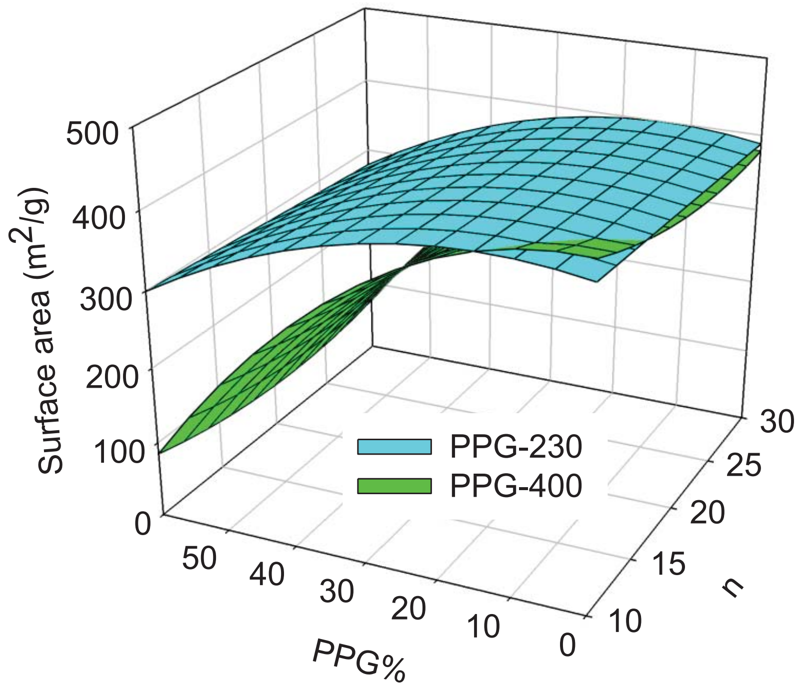


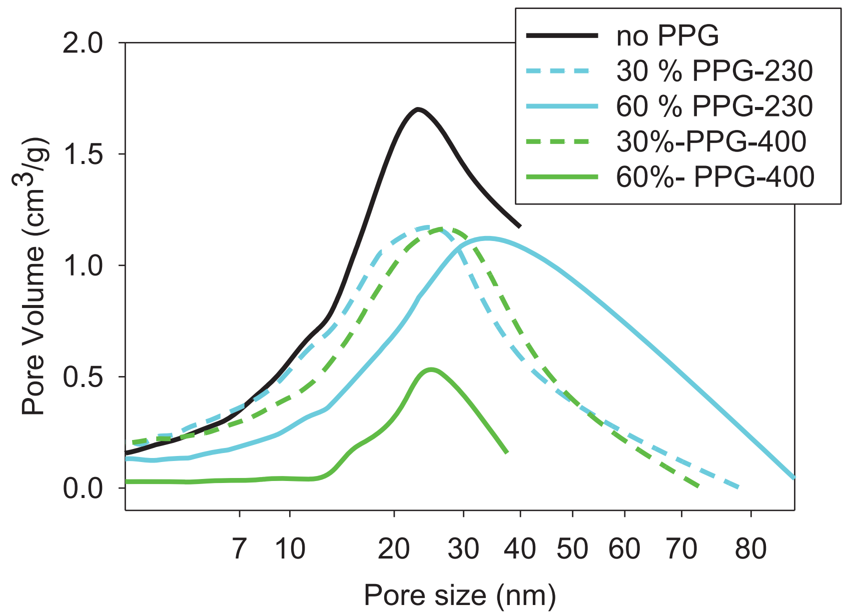




- Type and percentage of PPG affect the density, shrinkage and porosity
- At 60% PPG-400, the aerogels shrink the most, resulting in high density and low porosity

Increment of % and molecular weight of PPG decrease the surface area





- The higher the PPG-230 %, the larger the pore sizes
- The higher the PPG-400 %, the lower the pore volume

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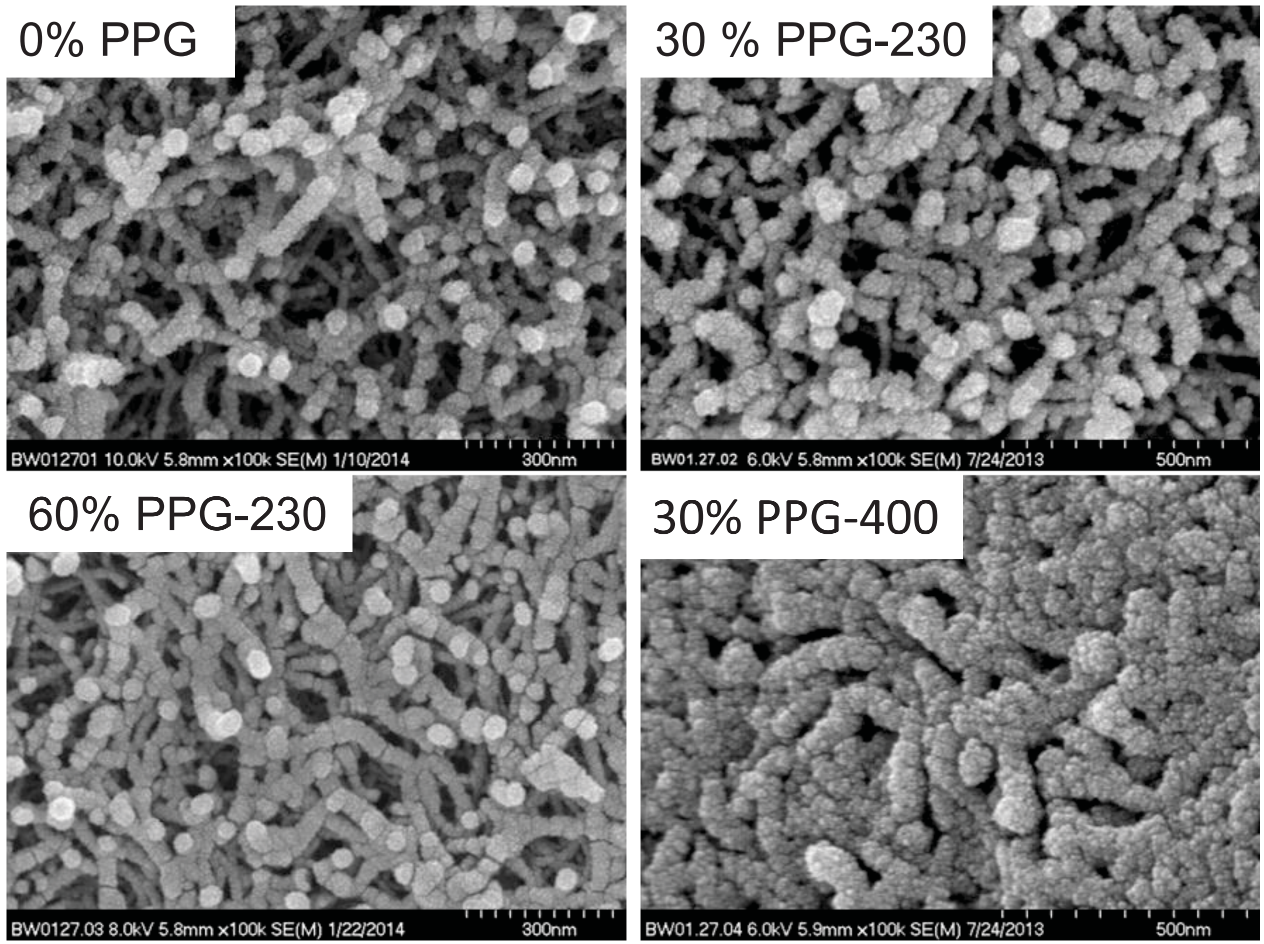
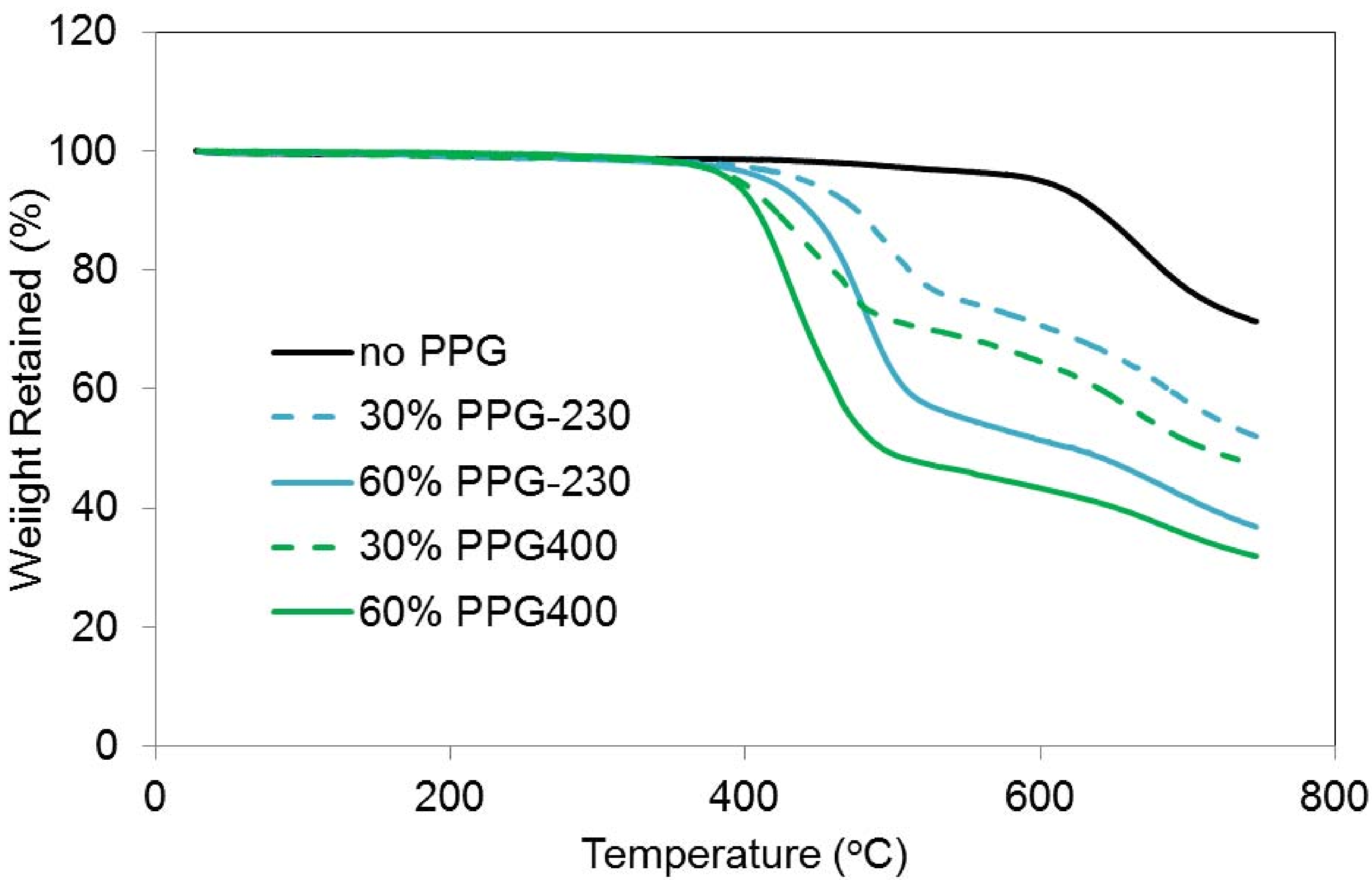
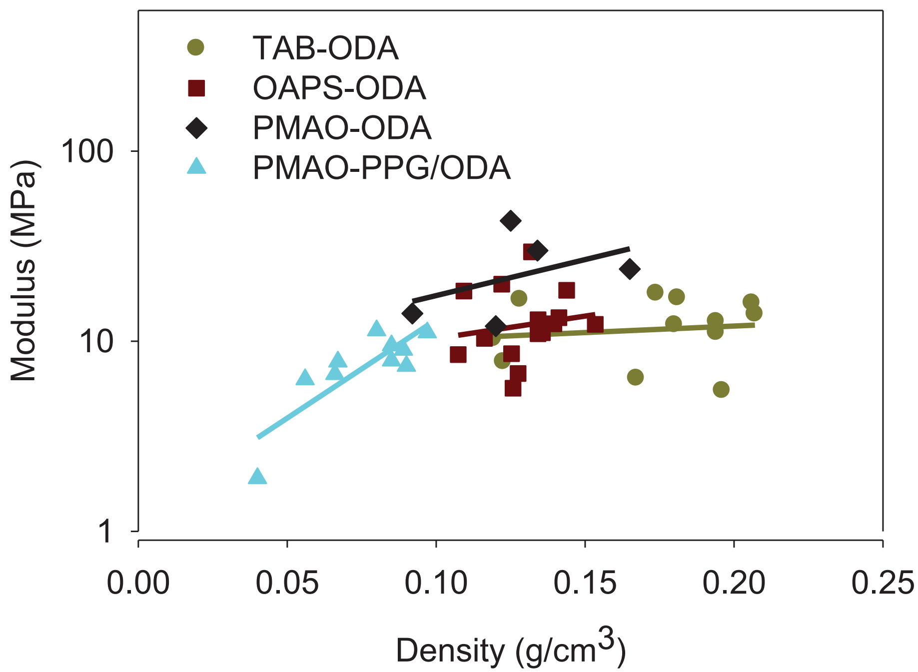
Increasing % or molecular weight of PPG causes densely packed fiber structures

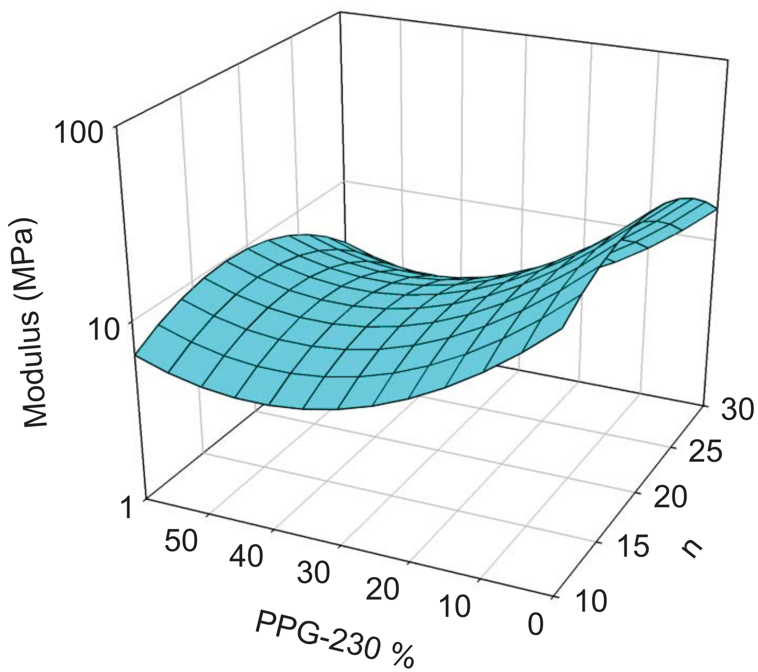


TGA curves show Td and char yield decrease with increasing aliphatic groups



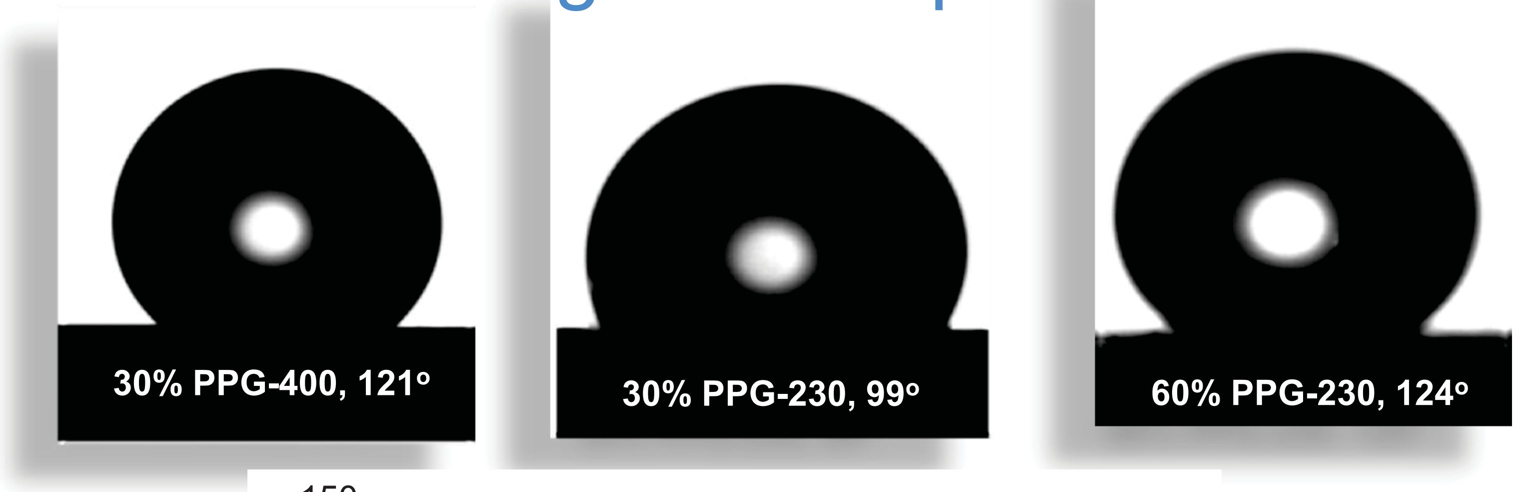
Compression tests show aerogels with n=20 have a higher modulus

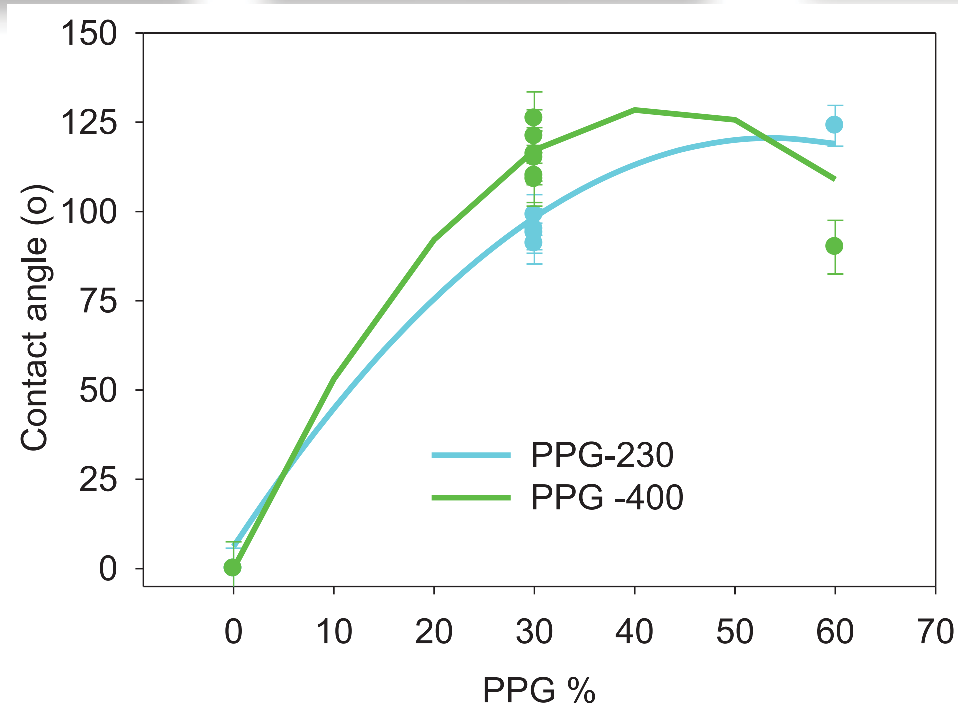




- The higher the density, the higher the modulus
- The aerogels with PPG-230 have lower modulus than the aerogels without PPG-230

Contact angle testing shows more hydrophobic aerogels were produced





Summary

- New aerogels made with amine capped polyimide oligomers and cross-linked by poly(maleic anhydride)s were synthesized
- The poly(maleic anhydride) cross-linked ODA capped aerogels have higher or similar modulus values compared to TAB or OAPS cross-linked ODA aerogels
- PMAO cross-linked aerogels have lower density and higher porosity, the lowest shrinkage and the highest modulus
- Addition of PPG alters the properties of the aerogels, such as density, shrinkage, porosity, and modulus
- Aerogels with more than 30% PPG are hydrophobic with contact angles 90-124^{o}
- Aerogels shrink the most with 60% PPG-400, resulting in the highest density, lowest porosity, and lowest surface area

OAI

Acknowledgement

Aerogel team members

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Nathan G. Wilmoth

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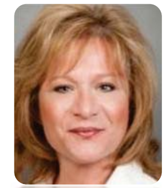
Stephanie


Jarrod


Dan H.


Linda


Dan S.


Brittany

Thank you!