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

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Some people are worth melting for...

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

http://royal-tarts.deviantart.com/art/Olaf-GIF-4-Melting-Request-426015061
Aerogel protection for Olaf
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
Potential applications of aerogels

- Inflatable aerodynamic decelerators
- Astronaut EVA suits
- Habitat structures
- Cyrotanks
What should be considered for real application?

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

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

Better mechanical properties and environmental stability are needed...

Silica aerogel is fragile
Cross-linked polyimide aerogels

Cross-linkers

- 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

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°
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

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

Polyimide oligomer

Polyimide oligomer

Cross-linker

imidization

polyimide oligomer

R: H, CH₃, CH₂(CH₂)xCH₃

R': H, CH₃

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

www.nasa.gov
NMR and FTIR spectra prove imidization was completed

13C nuclear magnetic resonance (NMR)

Typical Fourier transform infrared (FTIR) spectrum of aerogels

Absent
- 1860 cm\(^{-1}\) unreacted anhydride
- ~1807 & 980 cm\(^{-1}\) isoimide
- ~1660 cm\(^{-1}\) \(\nu\) amic acid C=O
- ~1535 cm\(^{-1}\) \(\nu\) amide C-N

1716 cm\(^{-1}\) symmetric \(\nu\) imide C=O
1377 cm\(^{-1}\) \(\nu\) imide C-N
1774 cm\(^{-1}\) asymmetric \(\nu\) imide C=O
CH\(_2\) stretching vibrations
• PMAO cross-linked aerogel has the lowest shrinkage
• PEMA cross-linked aerogel has the highest density, the highest shrinkage, and the lowest porosity
N\textsubscript{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 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
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)
Polyimide oligomers made with combination of PPG/ODA and BPDA

\[(n+1) H_2N-X-NH_2 + n \quad (n+1) H_2N-\text{ODA} \rightarrow \text{Polyimide oligomer}\]

- \(n = 20, 10 \text{ w/w}\%
- Polyimide oligomers: ODA + BPDA
- 10 w/w%
- PMAO as cross-linker
- Polyimide oligomers: ODA + BPDA
- Three cross-linkers
- Cross-linker
- Imidization
- Polyimide oligomers: R, H, CH\(_2\)(CH\(_2\)\(_x\))CH\(_3\), R': H, CH\(_3\)
- Polyimide oligomers: R, H, CH\(_2\)(CH\(_2\)\(_x\))CH\(_3\), 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
The higher the PPG-230 %, the larger the pore sizes
The higher the PPG-400 %, the lower the pore volume
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.

- 30% PPG-400, 121°
- 30% PPG-230, 99°
- 60% PPG-230, 124°
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°

• Aerogels shrink the most with 60% PPG-400, resulting in the highest density, lowest porosity, and lowest surface area
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