Polyimide (PI) aerogels are highly porous solids having low density, high porosity and low thermal conductivity with good mechanical properties. They are ideal for various applications including use in antenna and insulation such as inflatable decelerators used in entry, decent and landing operations. Recently, attention has been focused on stimuli responsive materials such as cellulose nano crystals (CNCs). CNCs are environmentally friendly, bio-renewable, commonly found in plants and the dermis of sea tunicates, and potentially low cost. This study is to examine the effects of CNC on the polyimide aerogels. The CNC used in this project are extracted from mantle of a sea creature called tunicates. A series of polyimide cellulose nanocrystal composite aerogels has been fabricated having 0-13 wt of CNC. Results will be discussed.
Polyimide Cellulose Nanocrystal Composite Aerogels

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What are aerogels?

Sol
- Highly porous solids made by removing liquid portion of a wet gel
- Nanometer scale pore size (10 – 40 nm)
- High porosity (> 90%) and surface area (200 – 650 m²/g)
- Low density (< 0.3 g/cm³)

Gel

Aerogel

Cosmic dust collector
Stardust Mission

Rover battery insulation
Possible applications

- Cryotank Insulation
- Insulation for EVA suits, habitats and rovers
- Ultra-lightweight, multifunctional structures for habitats, rovers
- Inflatable Decelerator
Aromatic polyimide aerogels

- Low thermal conductivity
- High temperature stability (short term)
- Moisture resistance depending on backbone chemistry
- Improved mechanical properties
- Flexible and durable
- Easy to manufacture into thin film

Objective:
- Crosslinked polyimide aerogels
- Incorporation of a nano filler to further enhance physical and mechanical properties - cellulose nanocrystals (CNCs)
Cellulose nanocrystals (CNCs)

- Bio-renewable, potentially low cost
- Exist in most plants and can be found in dermis of some mammals
- Can easily be modified with different charge densities or functionalities
  - make them compatible with different solvents and polymers
- Possibility to gain further mechanical strength and/or stimuli responsive behaviors
  - Flexible in water, rigid in air, etc
- CNC extracted from the mantles of a sea creature called a tunicate (tw-CNC) with aspect ratio of 80:1
Monomers used

**Diamines**
- 2,2’-Dimethylbenzidine (DMBZ)
- 4,4’-Oxydianiline (ODA)

**Triamine**
- 1,3,5-Triaminophenoxy benzene (TAB)

**Dianhydride**
- 3,3’,4,4’-Diphenyl tetracarboxylic dianhydride (BPDA)

**Triamine**
- 1,3,5-Triaminophenoxy benzene (TAB)

**Solvent**
- N-methyl-2-pyrolidiinone (NMP)

**Water Scavenger**
- Acetic anhydride (AA)

**Nano filler**
- Acid functional cellulose nanocrystals (tw-CNC)

**Catalyst**
- Pyridine (Py)
Chemical imidization at room temperature

\[
\text{H}_2\text{N-R-NH}_2 \rightarrow \text{ TAB, AA, Py} \rightarrow \text{ Chemical Imidization}
\]
Compositions

Concentration of total solids in solution:
- Solid concentration = \( \frac{\text{g total solid}}{\text{g solution}} \) = 7.5 wt%
- Total solid weight = g polymer + g CNC
- Repeat units, \( n = 30 \)

Diamine variation on the backbone:
- 100 mol% DMBZ
- 100 mol% ODA

CNC loading:
- 0 – 13.33 wt% of total solid
- CNC concentration = \( \frac{\text{g CNC}}{\text{g CNC} + \text{g polyimide}} \)
NMRs and TGAs: Evidence of CNC in the matrix

- CNC can be detected using NMR
- Can be quantified by TGA
- Same wt. loss in both sets of aerogels
- Low calculated CNC wt loss than formulated → interaction between CNC and PIs
- Higher $T_d$s of CNC → effect of aromatic PIs
- Lower $T_d$s of PIs → effect of aliphatic CNC
Scanning Electron Micrographs (SEMs): No difference in pore structure

Aerogels with DMBZ in the backbone are more porous
Incorporation of CNC improves physical properties

At higher CNC loading and more rigid backbone:
- Lower % shrinkage
- Lower density
- Higher % porosity
Brunauer-Emmet-Teller (BET) surface area

At higher CNC loading:
• Lower BET surface area
• Larger pore diameter
• Wider pore diameter distribution

DMBZ vs. ODA:
• Higher pore volume
• Narrower pore diameter distribution

DMBZ series

ODA series
Improves mechanical properties at high CNC loading

Higher CNC loading:
- Slight decrease in compression modulus (density dependent)
- Higher tensile modulus
- Lower % elongation

More rigid backbone:
- Higher modulus (density independent)
- Lower % elongation
Aging Study: CNC diminishes at 200°C

- Aged at 150°C for 30 h and 200°C for 24 h
- CNC is stable at 150°C for 30 h → no wt. loss during the aging period
- CNC starts to decompose at 200°C
  → Slowly diminishes over 24 h of aging
  → Higher decomposition rate at higher CNC content (less PI in the matrix composite)
Aging study: higher CNC loading reduces shrinkage and lowers density

- At higher CNC content → lower shrinkage and density
- At elevated temperature
  → higher shrinkage and higher density
  → Higher shrinkage and density for DMBZ-base aerogels
Conclusion

With the incorporation of CNC:
• Good CNC-polyimide interaction
• Retained pore size and structural integrity
• Improved both physical and mechanical properties

At higher CNC loading:
• Lower shrinkage and density (both at RT and elevated temperatures)
• Higher porosity
• Lower BET surface area
• Little change in compression modulus
• Higher tensile modulus
• Lower % elongation

More rigid backbone, DMBZ vs. ODA:
• Better physical properties at room temperature
• Physical properties suffered more at elevated temperature
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