Synthesis and properties of cross-linked polyamide aerogels

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Overview

• Aerogel Basics/Applications
• Relevant prior work involving polyamides and polyimides
• Hurdles
  – The first step growth polyamide aerogel
• Optimization of completely aromatic systems
• Results
  – Density
  – Porosity
  – Surface area
  – Compressive strength
  – Dielectric measurements
• Conclusions/Acknowledgements
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
Potential applications

Flexible Insulation for spacesuits

Durable/Fire resistant structural insulation

Insulation for crucial mechanical components

Low dielectric antenna substrates

Optically transparent antennae for use with solar components
Basic polymer aerogel processing

4 STEPS
1. Polymer solution prepared
2. Cross-linking agent is added and the mixture is poured into a mold
3. The resulting gel is solvent exchanged with a SCF compatible solvent such as ethanol
4. The solvent is then removed using an SCF such as carbon dioxide
Recently developed polyurea and polyimide aerogels have Young’s moduli that are orders of magnitude larger than traditional silica aerogel.

The motivation behind investigating stepgrowth polyamide aerogels is to see if we can obtain species that are even stronger.
Early literature involving polyamide aerogels

- Made via non-conventional amide forming methodology
- No control over chain length
- Glove box conditions
- Long reaction times
- High temperature
- Attempts at polymer chain formation lead to precipitation

Leventis et. al. J. Mater. Chem., 2011, 21, 11981
Polyimides as a Model for Polyamide Aerogels

Comparable to polyimide aerogel processes.

**Similarities include:**

1. Analogous polymerization between diamines and diacid chlorides
2. Crosslinking through the use of a trifunctional monomer (higher degrees of functionality are also possible)
3. Quick reaction times
4. No glove box required
5. Low temperature reaction conditions
6. Polymer chains that stay in solution
Aromatic amines do not require a catalyst

Aliphatic amines do require a catalyst (Et₃N)

Polymer 41 (2000) 8487-8500
Niesten et. al.
Potential features of polyamide aerogels

- Wide range of properties
  - From flexible/soft to rigid/strong
  - Hydrophobic/Hydrophilic
  - Colorless (maybe translucent/clear)
  - Low cost (monomers, cross-linker)
Completely aromatic systems

**Advantages:**
1. No catalyst required (NMP complexes with HCl)
2. Amine end caps make mixture stable to moisture indefinitely.
3. Reaction mixtures remain homogenous
4. Reactions undergo reliable gelation (more user friendly than acid chloride endcaps)
5. Control over rigidity

One problem remained........
Optimized vs. Non-optimized Systems

Left two figures: Polyamide aerogels before procedure optimization.

Right two figures: Three different polyamide aerogels (and SEMs) made via and optimized procedure.
Optimization of Polyamide Aerogels

- To minimize distortion, the following reaction parameters were examined and optimized:
  - Reaction and Cross-linking temperature
  - Stirring time/Stirring speed
  - Concentration of solutions
  - Cross-link density
  - Order and manner of addition of the reactants
  - Monomer species
Samples From Optimized Procedure

**Isophthaloyl chloride**, 0.10g/cm$^3$, 93% porous, 192 m$^2$/g.

**Terephthaloyl chloride**, 0.33g/cm$^3$, 77% porous, 384 m$^2$/g.
Monomers

1,3,5-Benzenetricarbonyl trichloride (1,3,5-BTC)
Isophthaloyl chloride (IPC)
Terephthaloyl chloride (TPC)
m-phenylenediamine (mPDA)

100% IPC

50% IPC/50% TPC

100% TPC
Aerogel Synthesis

\[ \text{H}_2\text{N}-\text{NH}_2 + \text{Cl} \begin{array}{ccc} & \text{Cl} \end{array} \text{O} \rightarrow \text{H}_2\text{N}-\text{NH}_2 + \text{Cl} \begin{array}{ccc} & \text{Cl} \end{array} \text{O} \]

3(n + 1) eq. (mPDA)  
3n eq. (IPC, TPC or combination)

\[ 10^\circ \text{C} \]

\[ \text{H}_2\text{N} - \text{NH}_2 + \text{Cl} \begin{array}{ccc} & \text{Cl} \end{array} \text{O} \rightarrow \text{H}_2\text{N} - \text{NH}_2 + \text{Cl} \begin{array}{ccc} & \text{Cl} \end{array} \text{O} \]

10 eq.

BTC

2 eq.

Networked Structure (gel)

\[ 10^\circ \text{C} \]

\[ \text{H}_2\text{N} - \text{NH}_2 + \text{Cl} \begin{array}{ccc} & \text{Cl} \end{array} \text{O} \rightarrow \text{H}_2\text{N} - \text{NH}_2 + \text{Cl} \begin{array}{ccc} & \text{Cl} \end{array} \text{O} \]

Supercritical \( \text{CO}_2 \) Extraction

Aerogel
Experimental design study

- Face-centered central composite design
- 15 different data points to model full quadratic equation
- 4 repeats of the center point to assess error
Results: Density

- Density increases as the fraction of the para substituted acid chloride increases.
- Density increases as the concentration of solids in the gel increases.
- n-value or length of the polymer chains, is not a significant factor for density.
- Standard deviation=0.016
- $R^2=0.98$
Results: Porosity

- Porosity decreases as the fraction of the para substituted acid chloride increases.
- Porosity decreases as the concentration of solids in the gel increases.
- n-value of the polymer chains is not a significant factor for porosity.
- SD = 1.26
- $R^2 = 0.98$
Surface area

- All three variables significant
- Data was log transformed before fitting to normalize data
- S.D. = 36.64
- $R^2=0.88$
Dielectric and Loss Tangent

SD=0.042, $R^2=0.92$

SD=0.0017, $R^2=0.93$
Compressive Strength

**SD=0.16, R²=0.90**

**2D Graph 2**

- **Density, g/cm³**
  - 0.05 to 0.40
- **Stress at 10% strain, MPa**
  - 0.1 to 10

**2D Graph 1**

- **Polymer conc., w/w %**
  - 4 to 11
- **Stress at 10% strain, MPa**
  - 0.1 to 10

**3D Graph 2**

- **Polymer conc., %**
- **TPC conc., %**
- **Stress at 10% strain, MPa**

**Graph Legend**

- Red circles: 100% IPC
- Red triangles: 50% IPC/50% TPC
- Blue squares: 100% TPC

**2D Graph 3**

- **Strain, %**
  - 0 to 80
- **Stress, MPa**
  - 0 to 18

- Linear fit: Dashed line
- Curve fit: Solid line

**Notes**

- SD = Standard Deviation
- R² = Coefficient of Determination
Young’s Modulus

(\log \text{standard deviation}=0.25, \text{R}^2=0.79)

Conclusions/Summary

• A simple procedure for the fabrication of polyamide aerogels has been developed and optimized
• A series of polyamide aerogels were produced that having densities ranging from 0.06g/cm$^3$ to 0.3g/cm$^3$, high porosities (77-93% porous), and surface areas as high as 426m$^2$/g
• Diverse properties arise through controlling monomer types, stoichiometry and weight percent solids
• Remaining work
  – Examine new monomer species
  – Experiment with different crosslinking methodologies
  – N-alkylate for hydrophobicity
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