Organic/Inorganic Nanocomposites with Completely Defined Interfacial Interactions From Cubic Silsesquioxane

Depts. of Materials Science & Eng., Chemistry and the Macromolecular Science and Eng. Center

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Outline

- Fundamentals
  - Nanocomposites
  - Organic/Inorganic Architectures
- Octahedral Silsesquioxanes
  - Synthesis
- Properties
  - Microporous
  - Mechanical
In Materials Science it is well known that

- Processing and intrinsic materials properties together dictate microstructure (nanostructure)
- Intrinsic materials properties and microstructure together dictate properties

Control at finest scales gives highest homogeneity

Which should give:

- Highest reproducibility, predictability, ability to tailor.
Fundamentals

- **Composite properties**
  - Combine properties of two (or more) materials and microstructures

- **Rule of mixtures predicts properties**
  - Weighted on volume fraction basis
  - Fails for nanocomposites

- **Nanocomposite properties**
  - Finer is better for reasons stated above and
  - Extensive interfacial interactions will significantly influence composite properties
  - At the nanometer scale interfacial interactions may act as a third phase—Interphase
Fundamentals

- Interphase materials
- How do you:
  - make them
  - model them
  - develop synthesis-processing-property relationships
- Nonlinear properties
  - Properties unavailable from either component
- Our objectives are to make such materials and prove how different they are.
Organic/Inorganic Nanocomposites

- Two definitions
  - At least one component has at least 1 dimension < 100 nm
  - Volumes of all components < 100 nm dia.

- Morphologies
  - Continuous
    - Several types
  - Discontinuous
    - Several types
Discontinuous Nanocomposites

Continuous Matrix

Both Phases Discontinuous
¿microporous materials?
Continuous Nanocomposites

Interpenetrating
gyroid

Interpenetrating
cubic
Lamellar Nanocomposites

Discontinuous
PS-PMMA diblock copolymers

Continuous

Construction of Architectures

- **Simultaneously**
  - sol-gel
  - block copolymers

- **Sequentially**
  - sol-gel (infiltration)
  - infiltration/exfoliation

- **Defined Hard Particle**
  - Cubic silsesquioxane (POSS)
  - Control architecture of organic segments used to link hard particles
    - Should allow complete definition of interphase
Choosing Hard Nanoparticles

Rice Hull Ash $\xrightarrow{+\text{8Me}_4\text{NOH/RT}}$ (90 % yield)

What’s to do with molecular hard particles?

Polymer Hybrid Nanocomposites

Nanocomposite Coatings

Nanoporous materials Low k dielectrics

Liquid Crystalline Materials

Photonic crystals

1-1.5 nm
What’s to do with Cubes?

- “Cubes” have eight reactive sites.
  - Functionalize sequentially or simultaneously

- In principle, can put eight different groups on

- First step in making nanocomposites is to introduce crosslinkable groups that provide
  - complete discontinuity
  - an organic continuous phase
  - an inorganic continuous phase
Crosslinkable Functionality

Viscosity = 100 cps

Crosslinkable Functionality

Crosslinkable Functionality

Viscosity = 300 cps

Crosslinkable Functionality

C. Zhang, L. Viculis, R.M. Laine, unpublished work

Tetra--m.p. 60 °C
Octa--m.p. 120°C
Crosslinkable Functionality

H. Cheng, R.M. Laine, unpublished work

High refractive index
What kind of properties do they have?

Octahydroxypropyl

What kind of properties do they have?

Temperature (°C)

230°C
99.5%

900°C
65.6% Exp.
63.4% Calc.
What kind of properties do they have?

1260  Exp.  \( M_n \)
1475  Calc.  \( M_n \)
1.02    PDI

**Temperature (°C)**
- 225°C  99.4%
- 900°C  63.9%  Exp.
  65.1%  Calc.

**Weight %**
- 225°C  99.4%
- 900°C  63.9%  Exp.
  65.1%  Calc.

**Time (minutes)**
- 30
- 31
- 32
- 33
- 34
- 35
- 36
- 37
- 38

**Response**
What kind of properties do they have?

Transparent to 157 nm
Nanolithography?

C. Zhang, L. Viculis, R.M. Laine, unpublished work
What kind of properties do they have?

Micro- and Meso-Porous Cubes

What kind of properties do they have?

Micro- and Meso-Porous Cubes

Pore Volume Distribution of Polymer D

SSA = 400 m²/g

What kind of properties do they have?

**Micro- and Meso-Porous Cubes**

What kind of properties do they have?

Micro- and Meso-Porous Cubes

Sublimation

$E_A = 124 \text{ kJ/M}$
What kind of properties do they have?

Micro- and Meso-Porous Cubes

Surface Area/Pore Size

<table>
<thead>
<tr>
<th>Ox. Temp.</th>
<th>220°C</th>
<th>250°C</th>
<th>280°C</th>
<th>325°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET m²/g</td>
<td>1.8</td>
<td>60</td>
<td>190</td>
<td>185</td>
<td>110</td>
<td>36</td>
</tr>
<tr>
<td>Ave. Pore</td>
<td>9 Å</td>
<td>29 Å</td>
<td>19 Å</td>
<td>16 Å</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
What kind of properties do they have?

Mechanical

"Interphase" Nanocomposites

- Append crosslinkable organic tether to the cubes
- Cure the structure
- Characterize the composite
What kind of properties do they have?

Mechanical  Epoxy Resins

Octaglycidylether cube (OG)

Octaethylcyclohexenyl-epoxide cube (OC)

Diglycidyl ether of bisphenol A (DGEBA)

Diaminodiphenylmethane (DDM)
What kind of properties do they have?

**Curing the Cube**

Variable \( N = \) No. of \( \text{NH}_2 \) groups (DDM): No. of epoxy rings (Cubes)

Curing: 6~10 hrs at 150 °C
What kind of properties do they have?

**Thermal Stability of Cubes under Nitrogen**

Temperature at 95%:
- OC: 413°C
- OG: 344°C
- DGEBA: 338°C

OC thermal stability 70°C > than OG
What kind of properties do they have?

**Storage Modulus of DGEBA cured with DDM**

- **Frequency**: 1 Hz
- **Temperature (°C)**: -50 to 250
- **Storage Modulus (MPa)**: 10^0 to 10^4

**Storage Modulus of OG cured with DDM**

- **Frequency**: 1 Hz
- **Temperature (°C)**: -50 to 250
- **Storage Modulus (MPa)**: 10^0 to 10^4

**Storage Modulus of OC cured with DDM**

- **Frequency**: 1 Hz
- **Temperature (°C)**: -50 to 250
- **Storage Modulus (MPa)**: 10^0 to 10^4

**OC** Tg > 60°C than **OG**, N = 1

**OG** high crosslink density at N = 0.5
What kind of properties do they have?

**Dynamic Mechanical Analysis**

- **Possible Network Structure of the Cube Composites**

  - **Possible Structure of OG at N~0.5**
  - Very high rubbery state modulus & Tg

  - **Possible Structure of OG at N~1.0**

  - **Possible Structure of OC**
What kind of properties do they have?

Mechanical  Tensile Strength

What kind of properties do they have?
What kind of properties do they have?

Mechanical Fracture Toughness

\[ K_{IC} = MPa \cdot m^{0.5} \]

Moles of Amine:Moles of Epoxy

- OC
- OG
- DEGBA

Diagram showing the relationship between Moles of Amine:Moles of Epoxy and Fracture Toughness.
What kind of properties do they have?

Epoxy Resins

1.7~3.0 nm

J. Choi, R.M. Laine, submitted
What kind of properties do they have?

Epoxy Resins

1.3~1.9 nm
What kind of properties do they have?

Mechanical Epoxy Resins

\[ K_{1c} = MPa \cdot m^{0.5} \]

- Moles of Amine:Moles of Epoxy
  - 0.5
  - 1.0
  - 1.5
  - 2.0

Graph showing the variation of \( K_{1c} \) with the ratio of moles of amine to moles of epoxy for different types of epoxy resins.
What kind of properties do they have?

Mechanical Epoxy Resins

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>N (No. of amine groups / No. of epoxy rings)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>OC</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>N</td>
</tr>
</tbody>
</table>

N (No. of amine groups / No. of epoxy rings)
Conclusions

- Numerous cubic silsesquioxanes with various functional groups easily prepared in high yields.
  - Can tailor functionality, reactivity and stability.
  - Flexibility of functional group controls xlink density

- Simple xlinking reactions provide access to materials with discontinuous and continuous nanocomposites

- Discontinuous epoxy resins can give
  - Improved thermal stability
  - Higher Tgs
  - Elastic moduli pure organics.
  - Fracture toughness that is pure organics.
Conclusions

- Simple changes in organic tether structure lead to dramatic changes in materials properties.

- Can be explained by Nanoarchitecture

- **Implication is:**
  - We can probe interphase behavior
  - Nanotailoring possible
  - allows unusual improvements in performance
- talmaterials.com
- Silsesquioxanes