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SILICON-CONTAINING MOIETIES AS ENHANCERS OF SEGMENT AND JUNCTION FLEXIBILITY IN HIGH-TEMPERATURE THERMOSETTING POLYMER NETWORKS

11 December 2012

Andrew Guenthner\textsuperscript{1*}, Josiah T. Reams\textsuperscript{2}, Christopher M. Sahagun\textsuperscript{3}, Suresh C. Suri\textsuperscript{1}, Vandana Vij\textsuperscript{2}, Kevin R. Lamison\textsuperscript{2}, Gregory R. Yandek\textsuperscript{1}, Timothy S. Haddad\textsuperscript{2}, Joseph M. Mabry\textsuperscript{1}

\textsuperscript{1}Propulsion Directorate, Air Force Research Laboratory
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Outline

• Background / Motivation
  – Cyanate esters
  – Reasons for incorporating silicon into thermosetting resins
• Cyanate esters with Si substituted for C
  – Effect of Si Substitution on Crystal / Volumetric Properties
  – Effect of Si Substitution on Water Uptake
  – Effect of Si Substitution on Processing and Cure
• Cyanate esters containing siloxane segments

Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; PWG team members (AFRL/RZSM); Dr. Sean Ramirez (X-ray crystallography)
Leading the discovery, development, and integration of affordable warfighting technologies for our air, space, and cyberspace force.
Cyanate Esters for Next-Generation Aerospace Systems

- **Glass Transition Temperature**
  - 200 – 400 °C (dry)
  - 150 – 300 °C (wet)

- **Onset of Weight Loss**
  - > 400 °C with High Char Yield

- **Resin Viscosity**
  - Suitable for Filament Winding / RTM

- **Compatibility**
  - With Thermoplastic Tougheners and Nanoscale Reinforcements

- **Ease of Processing**

- **Resistance to Harsh Environments**
  - Good Flame, Smoke, & Toxicity Characteristics
  - Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

**High Tg**

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Cyanate Esters Around the Solar System

Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope

- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites

- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

Images: courtesy NASA (public release)
The Use of Si in Thermosetting Polymers

Silicon has mainly been used as a rigid reinforcement to promote improved mechanical and thermo-oxidative performance. Some examples of the use of silicon at a molecular level, in flexible rather than rigid form, are known (e.g. Wright et al., Polymer Preprints, 2004, 45(2), 294).

- In addition to the expected increase in short-term thermo-oxidative stability; the substitution of Si also results in lower melting temperatures and lower water uptake.

DSC scan of 2,2-cyanatophenylpropane (BADCy) and bis- (4-cyanatophenyl)dimethylsilane 3 (SiMCy) near the melting point.

TGA in Air (heating rate 10 °C / min.)

Weight Gain in Boiling Water
Si-Containing Cyanate Ester Monomers

Catalyzed systems use: 160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol, All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N₂, cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.
General Synthesis for Si-Containing Monomers

- SiMCy is the n=2 case (Si in network segment), n=3 or n=4 produces Si at network junctions
Si-Containing Cyanate Esters: Crystal / Volumetric Properties

<table>
<thead>
<tr>
<th>Compound / Property</th>
<th>BADCy</th>
<th>SiMCy</th>
<th>ESR255</th>
<th>STT3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point, °C (monomer)</td>
<td>83</td>
<td>55</td>
<td>115</td>
<td>118</td>
</tr>
<tr>
<td>Heat of fusion (J/g, monomer)</td>
<td>105</td>
<td>93</td>
<td>76</td>
<td>75</td>
</tr>
<tr>
<td>Density, g/cc @ 20 °C</td>
<td>1.201</td>
<td>1.171</td>
<td>1.270</td>
<td>1.245</td>
</tr>
<tr>
<td>Packing Fraction @ 20 °C</td>
<td>0.620</td>
<td>0.610</td>
<td>0.633</td>
<td>0.626</td>
</tr>
<tr>
<td>CTE, ppm / °C @ 150 °C</td>
<td>59</td>
<td>70</td>
<td>60</td>
<td>62</td>
</tr>
</tbody>
</table>

Unless indicated otherwise, properties are for as-cured networks with 85-100% conversion. BADCy and SiMCy cured networks were catalyzed.

- Incorporation of Si can improve processing characteristics by lowering the melting point of some crystalline monomers through packing effects.
- Incorporation of Si appears to create free volume and lower network junction density consistently, with a lower fully-cured Tg and higher CTE being the likely result.
- Note that differences in cure can confound these effects to some extent.
Correlation Between Water Uptake and Cyanurate Density

<table>
<thead>
<tr>
<th>Cyanate Ester - mmol cyanurate/ cc</th>
<th>mmol H₂O / cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>BADCY /2.9</td>
<td>1.7</td>
</tr>
<tr>
<td>LECY/ 3.1</td>
<td>1.6</td>
</tr>
<tr>
<td>SIMCY / 2.7</td>
<td>1.1</td>
</tr>
<tr>
<td>THIOCY / 3.9</td>
<td>1.2</td>
</tr>
<tr>
<td>METHYLNCY / 2.6</td>
<td>0.9</td>
</tr>
<tr>
<td>AroCy F / 2.6</td>
<td>1.5</td>
</tr>
<tr>
<td>REX-371 / 3.3</td>
<td>2.6</td>
</tr>
<tr>
<td>RTX366 / 1.9</td>
<td>0.4</td>
</tr>
</tbody>
</table>

- Based on data in Appendix a-3 of Hamerton, I (ed)., Chemistry and Technology of Cyanate Ester Resins (Blackie Academic, 1994) (uses monomer density)

- Maintaining a low density of cyanurate groups appears to limit water uptake
Si-Containing Cyanate Esters: Effect of Exposure to Water

The lower packing fraction of Si-containing cyanate esters results in fewer cyanurate groups per unit volume, which is expected to lead to reduced water uptake.

Although water uptake in SiMCy is lower than in BADCy, as expected, for the tricyanate analog, the water uptake is about twice as large as expected.

The differences in water uptake are not enough to outweigh the differences in segment flexibility in determining the “wet” $T_G$.

<table>
<thead>
<tr>
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<th>BADCy</th>
<th>SiMCy</th>
<th>ESR255</th>
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<tbody>
<tr>
<td>Cyanurate Density at Full Cure (mmol/cc)</td>
<td>2.9</td>
<td>2.7</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>“As Cured” Dry $T_G$ (°C)</td>
<td>278</td>
<td>254</td>
<td>245</td>
<td>&gt;350</td>
</tr>
<tr>
<td>“Fully Cured” Dry $T_G$ (°C)</td>
<td>309</td>
<td>266</td>
<td>&gt;420</td>
<td>&gt;350</td>
</tr>
<tr>
<td>Water Uptake (96 hrs / 85 °C)</td>
<td>2.3%</td>
<td>1.8%</td>
<td>3.5%</td>
<td>5.5%</td>
</tr>
<tr>
<td>“Wet” $T_G$ (°C)</td>
<td>206</td>
<td>186</td>
<td>224</td>
<td>194</td>
</tr>
</tbody>
</table>

Unless indicated otherwise, properties are for as-cured networks with 85-100% conversion. BADCy and SiMCy cured networks were catalyzed.
Si-Containing Cyanate Esters: Non-isothermal DSC

**BADCy**
- 114 kJ/mol
- Post-cure $T_g$: 305 °C
- Incomplete Cure

**ESR-255**
- 95 kJ/mol
- Incomplete Cure

**SiMCy**
- 117 kJ/mol
- Post-cure $T_g$: 250°C
- Slight Degradation

**STT3**
- 90 kJ/mol
- Incomplete Cure

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Si-Containing Dicyanates: Cure Kinetics

- Although the dependence of cure rate on temperature appears more drastic in BADCy, the most rigorous kinetic-based model data for high purity compounds does not indicate a significant difference in activation energy.
- Both BADCy and SiMCy achieve near complete conversion readily.

\[
E_a = 127 \text{ kJ/mol}
\]

\[
E_a = 131 \text{ kJ/mol}
\]
Si-Containing Tricyanates: Cure Kinetics

- Like the dicyanates, the tricyanates show no effect of silicon substitution on the auto-catalytic activation energy.
- Both ESR-255 and STT3 do not achieve full conversion even when cured at high temperatures, in accord with the shape of the non-isothermal DSC curves.
Si-Containing Cyanate Esters
Late Stage (Vitreous) Cure

- SiMCy cures faster and to a greater extent at lower temperatures when catalyzed.
- The relative ease of vitreous cure enables SiMCy to attain a higher $T_g$ for a given cure temperature, despite having the lowest $T_g$ for a given conversion.
- These effects likely caused by flexible core systems catalyzed with 160 ppm Cu (AcAc) + 2 phr nonylphenol.
Siloxane-Containing Cyanate Esters

- Higher inorganic content expected to result in better char yields at temperatures over 600 °C
- Balance of siloxane units for flexibility and branch points for elevated glass transition temperature
Siloxy-Containing Cyanate Esters: Non-isothermal DSC

- Exotherm behavior is typical of high purity cyanate ester monomers
- Both monomers are room-temperature liquids and cure to strong solids, DSC indicates a wide processing window
- Enthalpies of cyclotrimerization are typical of highly flexible cyanate esters but may include some heat from minor side reactions
- Symmetrical exotherm shapes are typical of highly flexible cyanate ester monomers; the monomer glass transition temperatures near -70 °C also indicate a high level of segmental flexibility
- Post-cure glass transition temperatures were not readily detected via DSC
- In summary: these are indeed highly flexible, easy to process cyanate ester monomers
**Siloxy-Containing Cyanate Esters: Glass Transition Temperature**

- **T(DM)3-Cy**
  - \( T_g = 56 \, ^\circ\text{C} \) (as-cured and fully-cured)

- **Q(DM)4-Cy**
  - \( T_g = 102 \, ^\circ\text{C} \) (as-cured)
  - \( T_g = 115 \, ^\circ\text{C} \) (fully-cured)

- Both cyanate esters showed a relatively low glass transition temperature for cyanate esters.
- The cyanurate density for these resins is roughly half that of typical cyanate esters.
- The branch point adds some stiffness, but not enough to make up for the long distance between network junctions.
- Further optimization of the cross-link and junction density will be needed to produce cyanate esters with both flexible core regions and high glass transition temperatures.
Summary

• Incorporation of silicon into thermosetting materials provides an important means of improving segment and junction flexibility, in addition to improving thermo-oxidative stability.

• It appears that silicon substitution does result in increased free volume, a lower fully cured $T_g$, and, when compared at the same degree of conversion, lower density, lower packing fraction, and higher coefficient of thermal expansion.

• The effect of silicon substitution on properties such as crystal melting point and water uptake appear to depend strongly on the specific architecture used.

• As seen in previous studies, the use of siloxane segments in cyanate esters provides for high levels of flexibility and ease of processing. Though branch points may moderate the decrease in $T_g$, both the cross-link and branch point densities must be carefully optimized to provide both flexibility and a desirable $T_g$. 
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