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CURE CHARACTERISTICS OF TRICYANATE ESTER HIGH-TEMPERATURE COMPOSITE RESINS

24 May 2011

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Outline

• Background
• Cure of Flexible Core Tricyanate Esters
  – Effect of Molecular Structure
  – Effect of Monomer Purity
  – Comparison of Measurement Techniques
    • Activation Energy
    • Conversion

• Conclusions

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AFRL Propulsion Directorate
(AFRL/RZ)

Create and Transition Propulsion and Power Technology for Military Dominance of Air and Space

- Space & Missile Propulsion
- Hypersonics
- Energy, Power & Thermal
- Turbine Engines
Cyanate Esters: Universe of Applications

- Chip housings
- Capacitors
- Turbine brush seals
- Airframes
- Radomes
- Fusion reactors
- Interplanetary space probes

• Understanding cure kinetics is essential to fabricating items like these …

Photo credits: (clockwise from “chip housings” Antonio Pedreira, Omegatron (Wikimedia Commons), FAA, US Navy (Marvin E. Thompson), US Coast Guard, Gerritse (Wikimedia Commons). Background image: NASA. All images are public domain or freely distributed.
Tricyanate Ester with Enhanced Molecular Flexibility

**GOAL:** Explore the effect of a “flexible core” architecture in overcoming limitations such as incomplete cure, brittleness, and severe drop in $T_g$ under wet conditions associated with rigid high-$T_g$ tricyanate esters.

**AF/Navy Collaboration:**
Monomer synthesized by Dr. Matthew Davis at NAWCWD China Lake

**Publications:**

“FlexCy”

- Trifunctional architecture offers density of cyanate groups and aromatic content nearly equal to PT-30 for high dry $T_g$

- Flexible central branch point enhanced conformational degrees of freedom for more readily obtaining full cure

“Control” molecule: Primaset® PT-30
Types of Comparisons Performed

**Molecular Structure**
- FlexCy vs. Primaset® PT-30 (Lonza)

**Methods of Purification**
- Precipitated into ethanol (lower solubility results in higher yield but higher level of impurities)
- Precipitated into isopropanol (higher solubility lowers yield but is more effective at removing impurities)

**Methods of Measurement**
- Isothermal kinetics (rates and heat of reaction at one temperature; requires multiple experiments to measure activation energy)
- Non-isothermal kinetics (simpler, single experiment to measure activation energy and heat of reaction)
FlexCy and Primaset® PT-30: TGA Analysis

- FlexCy shows decreased thermal stability compared to Primaset® PT-30
- FlexCy thermal stability exceeds dicyanates for char yield and matches dicyanates for decomposition temperature.
- High char yields are a direct result of the high aromatic content in both FlexCy and PT-30
Dry Samples – PT-30 FlexCy

Wet Samples, Heating – PT-30 FlexCy

- PT-30 retains rigidity at higher temperatures when dry due to both thermochemical and thermomechanical effects.
- After exposure to 85 °C water for 96 hrs, both PT-30 and FlexCy have similar thermo-mechanical properties, with Tg ~ 240 °C.
- Bubble formation on rapid heating of wet samples is evident in both materials.
FlexCy and Primaset® PT-30: Initial DSC Analysis

- DSC shows both FlexCy and Primaset® PT-30 are of high purity (cure temperature exceeds 300°C).
- FlexCy has a slightly higher peak exotherm temperature and narrower exotherm due to lower impurity levels (not less favorable cure kinetics).
FlexCy and Primaset® PT-30: Isothermal Cure Kinetics

- Extent curves are calculated by integrating DSC isothermal heat flow data using constant baselines from post-cure (when available) or pre-cure isothermal holds.
- Note that extent of cure is based on measurement of residual exotherm by DSC on heating to 350 °C, thus the conversion numbers are not necessarily absolute.
- Heating and quench rates following 30 minute isothermal periods are approximately 100°C / min.
- Note that overall rates of cyanate ester cure are almost entirely the result of impurity levels; the temperature dependence is a more intrinsic feature.
FlexCy and Primaset® PT-30: Activation Energy for Cure

FlexCy Kinetic Data

- Kinetics fitted to Kamal model: \( \frac{d\alpha}{dt} = k_1 (1-\alpha)^n + k_2 \alpha^m (1-\alpha)^n \)
- As expected for highly pure systems, \( k_2 \) (auto-catalytic) >> \( k_1 \) (catalytic), allowing for the simplification \( \alpha \big|_{\frac{d\alpha}{dt}=\text{max}} = \frac{m}{m+n} \)
- Activation energy computed based on \( k_2 \) value obtained by forcing constant \( m, n \) for all temperatures
- Lower activation energy for FlexCy is robust toward analytical assumptions
- Measured activation energies are similar to those reported for other cyanate esters (e.g. Simon, S. L. ; Gillham, J. K., J. Appl. Polym. Sci. 1993, 47, 461).
Effect of Purity on Cure Kinetics of FlexCy

Precipitated into IPA (higher purity)

- Increased impurities lead to more rapid cure and higher overall rates of cure.
- The effect takes place mainly at low conversions, indicating the difference is primarily in the $k_1$ parameter (catalytic) in the Kamal model.
Effect of FlexCy Purity on Activation Energy

- Activation energy computed based on $k_2$ value obtained by forcing constant $m$, $n$ for all temperatures.
- Activation energies appear similar for all FlexCy samples above 230°C, but appears to drop to ~80 kJ/mol at lower temperatures.
- The lower apparent activation energy at low temperatures may be the result of spurious attribution of catalyzed cure (dominant at these low temperatures) to the auto-catalytic route in the Kamal model.
Non-isothermal Cure Kinetics for FlexCy-IPA

Kissinger’s method

\[ E_a = 101 \pm 8 \text{ kJ/mol} \]

Ozawa’s method

\[ E_a = 108 \pm 13 \text{ kJ/mol} \]

Friedman’s method

\[ E_a = 107 \pm 4 \text{ kJ/mol} \]

- The activation energies are all similar, and agree with the range of values (103 – 110 kJ/mol) found by four different versions of the isothermal method.
- Ozawa’s method showed the greatest non-linearity but also the greatest consistency across conversions.
Ozawa’s method shows higher activation energy for PT-30 across all conversions, whereas Friedman’s method shows significant differences only at low conversions due to an activation energy for PT-30 that is lower than all other methods.

Data at very low conversions is subject to large errors due to DSC baseline uncertainties and a low signal-to-noise ratio; the increase in activation energy at high conversions reflects gelation and vitrification.

In auto-catalytic systems, non-isothermal kinetic measurements are hampered by the confounding of thermal activation and increasing catalysis over time, but isothermal measurements are not hampered by a large initial transient.
FlexCy and Primaset® PT-30: FT-IR Cure Comparison

- FT-IR spectra are referenced to the phenyl peak at 1500 cm\(^{-1}\)
- Peaks near 2250 cm\(^{-1}\) signify uncured cyanate ester groups, those at 1360 cm\(^{-1}\) and 1550 cm\(^{-1}\) signify cyanurate rings (i.e., properly cured cyanate ester groups)
- FT-IR conversion estimates of 95% (FlexCy) and 80% (PT-30) are only approximate due to their dependence on the choice of reference peaks, baselines, and limits of integration, as well as the effects of changes in the solid-state structure during cure.
Measurements of Conversion in High-Temperature Thermosets

- **DSC**: High precision, but both full cure and maximum attainable cure give the same (lack of) signal
- **FT-IR**: Absolute bounds, but low quantitative accuracy and precision
- **Mechanical T_g** (DMA, etc.): Good precision, but samples can cure or degrade *in-situ*

Multiple techniques, when combined, can provide a reasonable estimate of conversion

An example of how T_g values can be converted to conversion values based on the diBenedetto equation (from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* 2008, 93, 77-85.) for EX-1510 dicyanate ester resin, for which T_g << T_{decomp}
Conversion Measurements for FlexCy and PT-30

<table>
<thead>
<tr>
<th>Material</th>
<th>Cure Temp. (°C)</th>
<th>Cure Time (hrs)</th>
<th>Tg via OTMA CTE (°C)</th>
<th>Tg via OTMA Loss Peak (°C)</th>
<th>Conversion via OTMA CTE</th>
<th>Conversion via OTMA Loss Peak</th>
<th>Conversion via FT-IR</th>
<th>Conversion via DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>FlexCy-IPA</td>
<td>210</td>
<td>24</td>
<td>310</td>
<td>338</td>
<td>0.91</td>
<td>0.92</td>
<td>0.83</td>
<td>n/a</td>
</tr>
<tr>
<td>FlexCy-IPA</td>
<td>250</td>
<td>2</td>
<td>307</td>
<td>&gt;352(^a)</td>
<td>0.90</td>
<td>&gt;0.94</td>
<td>0.82</td>
<td>n/a</td>
</tr>
<tr>
<td>FlexCy-IPA</td>
<td>290</td>
<td>0.5</td>
<td>&gt;349(^a)</td>
<td>&gt;349(^a)</td>
<td>&gt;0.95</td>
<td>&gt;0.94</td>
<td>0.94</td>
<td>&lt;0.98</td>
</tr>
<tr>
<td>FlexCy-IPA(^c)</td>
<td>210 / 290</td>
<td>24 / 0.5</td>
<td>302</td>
<td>351</td>
<td>0.89</td>
<td>0.94</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>FlexCy-EtOH</td>
<td>210</td>
<td>24</td>
<td>301</td>
<td>317</td>
<td>0.89</td>
<td>0.88</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>FlexCy-EtOH</td>
<td>250</td>
<td>2</td>
<td>327</td>
<td>&gt;354(^a)</td>
<td>0.93</td>
<td>&gt;0.94</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>FlexCy-EtOH</td>
<td>290</td>
<td>0.5</td>
<td>301</td>
<td>&gt;352(^a)</td>
<td>0.89</td>
<td>&gt;0.94</td>
<td>n/a</td>
<td>&lt;0.98</td>
</tr>
<tr>
<td>PT-30</td>
<td>210</td>
<td>24</td>
<td>274</td>
<td>309</td>
<td>0.82</td>
<td>0.85</td>
<td>0.80</td>
<td>n/a</td>
</tr>
<tr>
<td>PT-30</td>
<td>250</td>
<td>2</td>
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<td>0.91</td>
<td>&gt;0.92</td>
<td>0.80</td>
<td>&lt;0.99</td>
</tr>
<tr>
<td>PT-30(^c)</td>
<td>210 / 290</td>
<td>24 / 0.5</td>
<td>314</td>
<td>&gt;389(^a)</td>
<td>0.89</td>
<td>&gt;0.98</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

a. Run terminated due to sample decomposition prior to measurement of loss peak

- Under some cure conditions, FlexCy exhibits a higher T\(_g\) than PT-30, indicating a higher extent of cure was achieved
- Although all samples show >80% conversion, quantitative comparisons are difficult
- Loss modulus is more reliable than CTE for conversion determination via TMA
Conclusions

• The inclusion of a flexible core chemistry in cyanate esters confers benefits including lower activation energy, greater extent of cure under many cure conditions, and even higher maximum use temperatures in environments involving long-term water and short-term thermo-oxidative exposure.

• For auto-catalytic cyanate esters, isothermal methods for measuring kinetics appear to offer fewer difficulties, in contrast to most non-autocatalytic systems for which non-isothermal kinetic measurements are often simpler.

• Despite the difficulties, in general non-isothermal kinetic methods produced similar activation energy values for the cyanate esters studied.

• Conversion tracking is best handled by a combination of methods, even so, achieving a precise quantitative estimate can be more difficult than expected.
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