### POST-VITRIFICATION CURE KINETICS OF HIGH TEMPERATURE COMPOSITE RESINS: IMPLICATIONS FOR CHARACTERIZATION AND PERFORMANCE

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**ABSTRACT**
Many high-temperature composite resins, such as cyanate esters, require high temperatures in order to achieve complete cure. In such situations, incomplete conversion often persists in completely solidified “cured” samples, leading to potentially significant degradation in performance. Moreover, the very steep dependence of the glass transition temperature of the composite resin on the extent of cure leads to unusual cure effects such as 1) significant cure below the glass transition temperature 2) cure kinetics that involve extremely strong temperature dependence coupled with very weak dependence on cure time, and 3) unexpected conversion-property relationships (e.g. a decrease in elastic modulus with increasing extent of cure). These effects not only complicate the prediction of composite performance, they also make the determination of even simple properties such as the extent of conversion or glass transition temperature prone to large, difficult-to-detect errors. This paper describes and demonstrates newly developed characterization methods that combine multiple techniques to overcome these difficulties, and allow for a more complete description of the evolving glass transition temperature of composite resins during part fabrication, testing, and performance. In addition, the paper describes how insights into the unusual phenomena associated with resins that cure at high temperature can lead to design strategies for high-temperature composite resins that provide optimal performance.

### SUBJECT TERMS
- Composite resins
- High-temperature cure
- Glass transition
- Characterization methods

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Outline

• Background: Cure Below $T_G$ and Its Effect on Structure-Property Relationships in Thermosetting Polymer Networks

• Tools: Differential Scanning Calorimetry

• Results:
  – Isothermal Cure Kinetics
    • Validity of $T_G$ Estimation by DSC
    • Results for Dicyanates (BADCy) and Tricyanates (ESR-255)
  – Non-Isothermal Cure Kinetics
    • Dimensionless Analysis

• Implications for Composite Process Development

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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

- Resistant to Harsh Environments

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

- Good Flame, Smoke, & Toxicity Characteristics

- Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

- Ease of Processing
  - Resin Viscosity Suitable for Filament Winding / RTM

- Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements

- Good Flame, Smoke, & Toxicity Characteristics

- Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

Legend:
- NCO
- OCN
- X
- N
- O
- Δ

Note: The structures shown are representations of cyanate esters.
Thermosetting Polymers Have a $T_G$ Envelope – Not Just a $T_G$

- The glass transition temperature of a thermoplastic such as PVC exhibits a nearly fixed value regardless of processing-induces changes to the system.
- In contrast, the glass transition temperature of a thermosetting polymer can vary over a wide range of temperatures depending on how the polymer is processed.
- For cyanate esters, the bounds of the $T_G$ envelope are typically well-defined because of the well-defined cure chemistry.

A. R. Berens and I. M. Hodges, *Macromolecules* 1982, 15, 756 (digitized data from Fig. 2)
The Envelope May Be Unknown – Some Monomers Can Not Cure Fully

- Essentially, ESR255 forms such a rigid macromolecular network that the molecular strain energy needed to connect all the loose ends is great enough to break the chemical bonds, so “full cure” simply is not geometrically possible
- Since achieving complete cure is critical for the long-term hydrolytic stability of cyanate esters, a monomer such as ESR255 is actually too rigid by itself
- Even if they can be fully cured, rigid cyanate esters often require very high temperatures and/or active catalysts (which hurt stability) to cure effectively

Conversion determined via combined DSC/IR

The diBenedetto fit parameter for “fully cured $T_G$” is 558 °C, but the highest $T_G$ actually measured is 419 °C

\begin{align*}
\text{Tg (°C)} & \quad \text{Conversion (α)} \\
0 & \quad 0 \\
50 & \quad 0.2 \\
100 & \quad 0.4 \\
150 & \quad 0.6 \\
200 & \quad 0.8 \\
250 & \quad 1 \\
300 & \quad \text{DSC obs.} \\
350 & \quad \text{diBenedetto fit}
\end{align*}
A Large diBenedetto Envelope Means \( T_G \) Exceeds \( T_{cure} \) at Late Stages of Cure

- Vitrification slows down conversion, but does not stop it completely.
- Under isothermal conditions, the rate of conversion will fall as conversion increases, but the sensitivity of \( T_G \) to conversion will rise, resulting in a fairly constant rise in \( T_G \).
- The greater the sensitivity, the further \( T_G \) can rise above \( T_{cure} \).

\( T_G (^\circ C) \) of Cyanate Esters Cured 12 h

<table>
<thead>
<tr>
<th>( T_{-Cure} (^\circ C) )</th>
<th>125</th>
<th>150</th>
<th>170</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>BADCy</td>
<td>134</td>
<td>168</td>
<td>--</td>
<td>246</td>
</tr>
<tr>
<td>LECy</td>
<td>142</td>
<td>183</td>
<td>213</td>
<td>--</td>
</tr>
<tr>
<td>SiMCy</td>
<td>152</td>
<td>186</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

\*catalyst consists of 160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol.

Size of “gap” scales with diBenedetto envelope.
“Vitreous Cure” Differs Markedly from Main Stage Cure

Main Stage Thermal Cure

Cure results in:
- Net Shrinkage
- Less permeability
- Higher modulus
- Brittleness

“Vitreous Cure”

Cure results in:
- Net Expansion
- Higher permeability
- Lower modulus
- Toughness

- “Vitreous Cure” is promoted by rigid network segments with well-distributed extensibility, and by cure temperatures that are low in comparison to $T_G$
- Both types of cure can happen sequentially, simultaneously, or in mixed form
Indirect Measurement of $T_G$ via DSC and diBenedetto Equation

- Conversion computed via:
  \[ \alpha(t) = \frac{\Delta H(t)}{\Delta H(t_{\text{max}}) + \Delta H_r} \]
- $T_G$ computed via:
  \[ \frac{T_G(t) - T_{G0}}{T_{G\infty} - T_{G0}} = \frac{\lambda \alpha}{1 - (1 - \lambda) \alpha} \]

**Data is for uncatalyzed ESR-255**

- For any time (t), cumulative integration of the signal provides a heat flow $\Delta H(t)$
- The signals near the baseline are critical for post-vitrification kinetics
Cyanate Ester Monomers Used in DSC Cure Study

- BADCy was the first-commercialized cyanate ester; it is least expensive and has the largest property database.
- ESR-255 was originally synthesized and characterized by Shimp; it has the one of the highest “$T_G^{\infty}$” values known (note that chemical degradation takes place well below $T_G^{\infty}$, thus the parameter is meaningful only as an estimate of the sensitivity of $T_G$ to conversion.

<table>
<thead>
<tr>
<th>Name</th>
<th>$T_{G0}(^\circ C)$*</th>
<th>$T_G^{\infty}(^\circ C)$*</th>
<th>$\lambda$</th>
<th>Catalyst Added?</th>
</tr>
</thead>
<tbody>
<tr>
<td>BADCy</td>
<td>-38 ± 1</td>
<td>300 ± 3</td>
<td>0.38 ± 0.04</td>
<td>Yes</td>
</tr>
<tr>
<td>ESR-255</td>
<td>-9 ± 10</td>
<td>558 ± 40</td>
<td>0.32 ± 0.04</td>
<td>No</td>
</tr>
</tbody>
</table>

* catalyst consists of 160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol
Indirect Measurement of $T_G$ via DSC: Measurement Uncertainties

If DSC measurements were used to generate diBenedetto parameters, then there is a canonical relation for the error in $T_G$ measurement due to all parameters combined.

- Even though the error in $T_G$ estimation is large in this case, it is clear that ESR-255 will cure to a $T_G$ substantially higher than the cure temperature, and that the change in $T_G$ with time is substantial even during the post-vitrification period.
- Baseline effects become more important than diBenedetto parameter uncertainties after 1-2 hours of isothermal cure.
- Sensitivity analysis is the easiest way to determine effect of baseline uncertainties.

Data is for uncatalyzed ESR-255

Effect of baseline errors grows linearly with time

Initial error due to uncertainty in measurement of $T_{G0}$
# Comparison of Indirect and Direct $T_G$ Measurements via DSC

*Data for catalyzed BADCy*

<table>
<thead>
<tr>
<th>Source (Pred. from iso. DSC run, or “observed”)</th>
<th>$T_G$ after curing for temp. (°C) / time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150/60</td>
</tr>
<tr>
<td>Pred. 150 °C / 60 min.</td>
<td>107 ± 9</td>
</tr>
<tr>
<td>Pred. 150 °C / 1200 min.</td>
<td>114 ± 9</td>
</tr>
<tr>
<td>Pred. 150 °C / 720 min.</td>
<td>90 ± 22</td>
</tr>
<tr>
<td>Pred. 200°C / 30 min.*</td>
<td>113 ± 9</td>
</tr>
<tr>
<td>Pred. 200°C / 720 min.*</td>
<td>120 ± 22</td>
</tr>
<tr>
<td>Observed $T_G$</td>
<td>110</td>
</tr>
</tbody>
</table>

* Two step cure in which step 1 is 150 °C for 60 minutes

- “Hind-casting” $T_G$ values becomes uncertain when the ratio of elapsed time at the point of “hind-cast” to the total time used to measure cure becomes small, due to baseline uncertainty effects that tend to cancel one another at longer relative times
- When uncertainties are properly considered, there is no major discrepancy with observed values, although all large errors were under-predictions
The most common forms of kinetic analysis involve tracking key parameters with respect to conversion ($\alpha$).

Reaction rate (most models indicate proportionality to $(\alpha - \alpha_0)^2$, combined with nonlinear increase in $T_G$ with $\alpha$, results in a nearly linear change in $dT_G/dt$ with $\alpha$, and an intercept at a conversion of 0.75 ($T_G = 142 ^\circ C$).

At 150 °C, cure rates are so slow that, after vitrification, the cure kinetics cannot be resolved, with uncertainty of around 3-5 x, and even slight baseline shifts overwhelming the signal (Note: error bars generated by sensitivity analysis, and are systematic within series).
Evolution of $T_G$ During Isothermal Cure of BADCy at 200 °C

Data is for catalyzed BADCy

- Again, roughly linear change in $dT_G/dt$ with conversion with an intercept at a conversion of 0.87 ($T_G = 203$ °C), but note that the final $T_G$ is in fact much higher, at 246 °C
- At 200 °C, cure rates are high enough that, even with a systematic 5-10 x uncertainty, there appears to be a significant slowing of cure (but not a complete stop) due to vitrification, which can be described by a simple “activated mode” Arrhenius model
- A ~0.1 °C / min. increase in $T_G$ after vitrification, with a 10x rate reduction for every ~25 °C increase in $T_G$, is consistent with observed behavior
Thermosets Have a $T_G$ Envelope – So $T_G$ Can Change as You Measure It!

- Isothermal steps help to smooth spatial variations and ensure conversion targets are reached
- Complete conversion is desired but often not achieved as $T_G > T_{cure}$
- $T_G$ usually measured after the fact

- Continuous ramp used to complete wide scan of possible temperature values in a short time; heating rate still limited by thermal gradients
- No change in conversion is desired during heating, but *in-situ* cure happens anyway
- Measured $T_G$ may not be accurate

* Data is for catalyzed BADCy

A simplified industrial process (multi-step cure)

Typical $T_G$ measurement
**$T_G$ Evolution in BADCy During Residual Cure**

Data is for catalyzed BADCy

- Only when the scan temperature and $T_G$ coincide is a signal generated. For thermoplastics, with a $T_G$ that does not change, this fact is trivial, but for incompletely cured thermosets, it matters a great deal!
- Note how the $T_G$ increases almost as fast as the scan temperature during residual cure.
$T_G$ Evolution in ESR-255 During Residual Cure

- No clear signal corresponding to a $T_G$ is observed in DSC traces, either during, or after, residual cure.
- Note how the $T_G$ increases fast enough that it never coincides with the scan temperature over the given range.
- The “moving target” nature of the $T_G$ means that the uncertainty in the “as cured” value remains, although the model indicates that the onset of heat flow is a reasonable guess for the “as cured” value.

Data is for uncatalyzed ESR-255

\[ T_G = T_{\text{scan}} \]
Dimensionless Analysis of $T_G$ Evolution During Residual Cure

$d\alpha/dt = \text{reaction rate (variable with conversion, generally } \sim 2\% / \text{minute or less after vitrification)}$

$T_{G0} = \text{monomer glass transition temperature (-50 to 0 °C typical for cyanate esters)}$

$T_{G\infty} = \text{glass transition temperature of fully cured network (may not be physically meaningful, typically 250 – 550 °C for cyanate esters)}$

$\lambda = \text{diBenedetto parameter (typically 0.3 for cyanate esters, dimensionless)}$

$dT/dt = \text{heating rate}$

Key dimensionless group:

$$\left(\frac{d\alpha/dt}{\lambda(dT/dt)}\right) \left( T_{G\infty} - T_{G0} \right)$$

- The dimensionless group represents the ratio of the rate at which $T_G$ increases to the rate at which sample temperature increases during residual cure.
- When the value of this group is larger than one, the $T_G$ can “outrun” the sample heating, leading to large measurement errors.
- As the value of this group approaches zero, the $T_G$ becomes stable over the time scale of the heating experiment and is accurately recorded.
- Using typical values for $d\alpha/dt$ and $\lambda$, the heating rate needed to avoid significant risk of in-situ cure (in °C / min.) is roughly $0.07 \times (T_{G\infty} - T_{G0})$, or roughly 25 °C / min. for BADCy, and roughly 40 °C / min for ESR-255. These are roughly consistent with experience.
Example: $T_G$ Measurements for ESR-255 Cured 24 hrs at 210 °C

- Using a heating rate that is too slow causes a very significant over-estimate of $T_G$
- Note that the effects of residual cure are clearly visible in the TMA traces, and include
  - Overly broad tan delta peak with noticeable low-temperature shoulder
  - Increase in storage after $T_G$ (circled)
- Using DSC in combination with TMA, it is clear that the “as cured” $T_G$ cannot be 300 °C
Implications for Composite Resin Development

- A key feature of cure schedules for high-temperature resins such as cyanate esters is passage through the vitrification point
  - Cure of vitrified samples often has the opposite of the intended effect (e.g. water uptake increases with further conversion, rather than decreases)
  - Because many high-temperature resins will cure significantly after vitrification, the assumption that industrial cure schedules always avoid it may need to be checked
  - Cure below the glass transition temperature is a significant issue for characterization of high-temperature composite resins, and can lead to significant over-estimates of thermo-mechanical performance
  - Hot / wet performance is often the limiting factor for many thermosetting resin systems; both “knockdowns” and “wet” property values may be affected by in situ cure (this issue needs more attention).
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