Hydrolytic Network Structure Degradation in Multi-Component Polycyanurate Networks

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Viewgraph/Briefing Charts

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Hydrolytic Network Structure Degradation in Multi-Component Polycyanurate Networks

28 July 2016

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Outline

• Background
• Quantitative Models
• New Data

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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

Good Flame, Smoke, & Toxicity Characteristics

Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements

Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

Resistance to Harsh Environments

High $T_g$

Ease of Processing
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)
Importance of Moisture Uptake in Composite Component Performance

- Water can add significantly to launch or take-off weight (3% water in composite resins = about 50 lbs of extra weight on a large SRM)
- Items with high water content can fail catastrophically when suddenly heated
- Long-term exposure to water can facilitate many mechanisms of chemical degradation, necessitating substantial “knock down” factors in design allowables
- Though more stable than epoxy resins, cyanate esters can degrade on long-term exposure to hot water
Materials Utilized

Monomers

![LECy](image1.png)

LECy/PT-30 (50/50 by weight) co-cured networks were cured at 170, 190, 210, and 240°C for 8 hrs to achieve a variety of conversion. Catalyst used was 160 ppm Cu as Cu-acac with 2 phr nonylphenol.

Additives

![PEEK](image2.png)

PEEK, 15 wt%

![4-K Mica](image3.png)

4-K Mica, 10 wt%

![Suzorite 325-S Mica](image4.png)

Suzorite 325-S Mica, 10 wt%
Models for Network Initial States

Random copolymer of “cured” and “uncured” segments.

DiBenedetto equation is just Gordon-Taylor equation recast with $1-\alpha = \phi_1, \lambda = k$

Assumptions:
$\Delta H_{\text{mix}} = 0; \Delta S_{\text{mix}} = 0, \Delta v_{\text{mix}} = 0,$
$S$ continuous at $T_G, dS/dP = 0$

No volume change on cure, so $\alpha = \phi_{\text{cured}}$

Consequence
Initial state of network entirely described by one parameter - $\alpha$

Chemical Reaction Scheme

Network states:
\[ \phi_A, \ldots \phi_F, \phi_E \text{ and } \phi_F \text{ related by stoichiometry} \]
If networks are heated only to 350 °C, then only one of \( \phi_C \) or \( \phi_D \) may be non-zero.
Result: three parameters prior to heating: network conversion \( \alpha' \) based on \( \phi_B \), plus \( \phi_C \) and \( \phi_F \). Two parameters after heating, \( \phi_D \) and \( \phi_F \).
Chemical Reaction Models

Carbamate formation

\[ A \cdot C \]
Weight gain of \(0.14\phi_c\)
Loss of \(\Delta H_{\text{cure}}\), Loss of FT-IR signal at 2250 cm\(^{-1}\), gain in FT-IR signal at 1700 cm\(^{-1}\), no change in \(T_G\)

Carbamate decomposition

\[ C \cdot D \]
Heating to 350 °C will complete
Weight loss of \(0.34\phi_c\)
No change in \(\Delta H_{\text{cure}}\), Loss of FT-IR signal at 17000 cm\(^{-1}\), no change in \(T_G\)

Other decomposition

\[ E \rightarrow G, B \rightarrow H, A \rightarrow I \]
Assumed negligible below 350 °C

Residual Cure

\[ A \cdot B \]
Heating to 350 °C dry will complete
No weight change
Loss of \(\Delta H_{\text{cure}}\), Loss of FT-IR signal at 2250 cm\(^{-1}\), increase in \(T_G\)

Network Scission

\[ 3B \cdot 2E + F \]
Weight gain of \(0.14\phi_E\)
No change in \(\Delta H_{\text{cure}}\), only discernible readily via near-IR, decrease in \(T_G\)

More details:
Effective Conversion Reduction

Multi-Component Gordon-Taylor Equation:

\[ T_G = \left( T_{GA} \phi_A + k_{BA} T_{GB} \phi_B + \ldots + k_{EA} T_{GF} \phi_F \right) / \left( \phi_A + k_{BA} \phi_B + \ldots + k_{FA} \phi_F \right) \]

Can be simplified using an “effective conversion reduction factor” \( K \)

\[ \alpha^{'eff} = \alpha^{'0} - K\phi_F \]

\[ T_G = T_{G0} + \left( T_{G\infty} - T_{G0} \right) \lambda \alpha^{'eff} / \left[ 1 - (1-\lambda) \alpha^{'eff} \right] \]  (just the diBenedetto equation)

Test 1: Use \( K \) from \( \phi_F = 0.02; \) (Test 1) extrapolate to \( \phi_F = 0.2 \) with \( \alpha^{'0} = 0.8 \) and \( \phi_C / \phi_F = 1; \) Max error 8 °C

Test Parameters; \( k_{BA} = 0.4; \) \( T_{GB} = 300 \) °C; \( k_{CA} = 1.2; \) \( T_{GC} = 0 \) °C; \( k_{DA} = 0.9; \) \( T_{GD} = -30 \) °C; \( k_{EA} = 0.6; \) \( T_{GE} = 100 \) °C; \( k_{FA} = 0.8; \) \( T_{GF} = -20 \) °C;

Assumes: Same network physics throughout hydrolysis; \( \phi_C \) and \( \phi_F \) are correlated
Assumes diBenedetto parameters are known

Cure sample
- Measure dry weight
- Measure dry $T_G$
- Heat sample to 350°C
- Measure dry $T_{G\infty}$

Expose samples to water at 85 °C
- Measure wet weight
- Measure wet $T_G$
- Heat sample to 350°C
- Measure wet $T_{G\infty}$

Dry sample
- Measure weight
- Heat sample to 350°C
- Measure weight

FT-IR may be added for verification if possible. Dry sample glass transition best if measured by DSC; wet glass transition best if measured by TMA

Final “wet and dried” weights determine – $\phi_C$, $\phi_F$, $T_{G\infty}$ data cross-checks other degradation.
Weight Gain After Water Exposure (No Drying)

Slow hydrolysis evident; conversion dependence as expected
PEEK reduces water uptake as expected
Data from samples exposed and dried with mild heating; slight correlation with conversion; additives show little effect so far …
Mica appears to add water and inhibit diffusion. Diffusion appears to be faster at higher conversions.
Conversions are from DSC only and are preliminary
Rate constant is for all hydrolysis reactions – includes carbamate formation and network scission
Glass Transition Temperature

DSC data for dry samples is shown as open symbols; in-situ cure affects results at early times, even after exposure, proving –OCN groups are still present.
Summary

- The relative simplicity of the chemical structure of polycyanurate networks, in combination with ease of analysis, allows for quantitative modeling of hydrolytic degradation. These models link chemical structure, physical properties, and environmental conditions, while allowing for validation.

- Hydrolytic degradation processes have been quantified for Cu/nonylphenol-catalyzed, co-cured LECy/PT-30 networks, with and without additives for toughening, under exposure to hot water. The effects of conversion have been examined.

- Preliminary data shows rates of hydrolysis that are lower than for PT-30 alone. Overall hydrolysis rates appear to be slightly higher at higher conversions, suggesting that carbamate formation is not responsible for a large portion of weight gain.

- Glass transition temperatures decrease gradually as expected. Determination of the effective network conversion reduction parameter requires further work to distinguish carbamate formation from network scission.