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Hydrolytic Network Structure Degradation in Multi-Component Polycyanurate Networks

28 July 2016

Dr. Andrew Guenther¹

Mr. Neil Redeker¹

Dr. Giuseppe Palmese²

¹Aerospace Systems Directorate, Air Force
Research Laboratory

²Drexel University



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Outline



- **Background**
- **Quantitative Models**
- **New Data**



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- **Air Force Research Laboratory, Rocket Propulsion Division**
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- **Mr. Jason Lamb, optical microscopy**
- **Mr. Michael Ford, chemistry support**



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Cyanate Esters for Next-Generation Aerospace Systems



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

Resin Viscosity
Suitable for
Filament
Winding / RTM

Compatible with
Thermoplastic
Tougheners and
Nanoscale
Reinforcements

High T_g

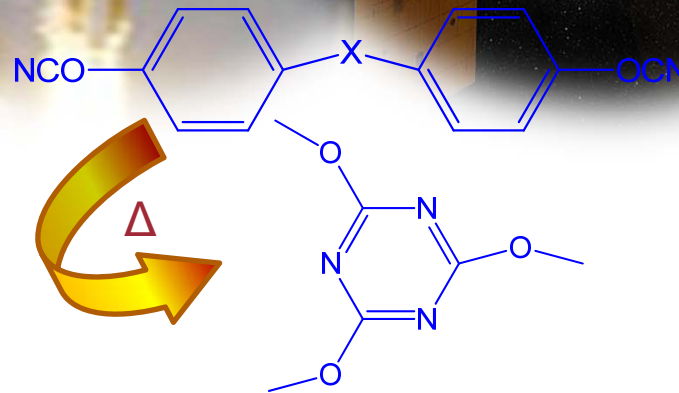
Onset of Weight Loss:
> 400 °C with High
Char Yield

Ease of
Processing

Resistance to
Harsh
Environments

Good Flame,
Smoke, &
Toxicity
Characteristics

Low Water Uptake
with Near Zero
Coefficient of
Hygroscopic
Expansion





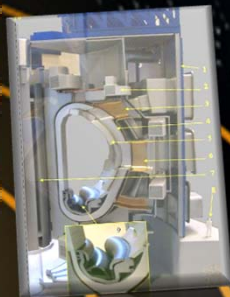
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Cyanate Esters Around the Solar System



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



Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons)

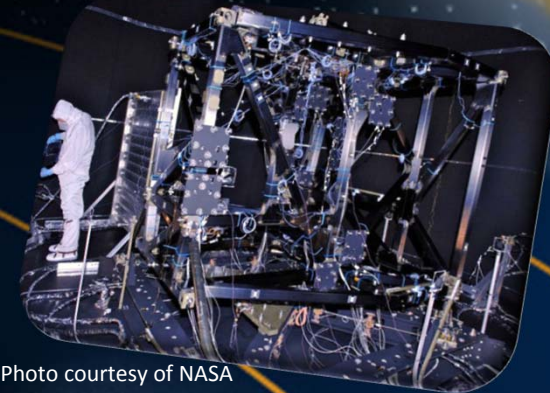


Photo courtesy of NASA

- 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



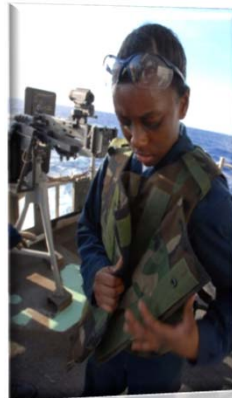
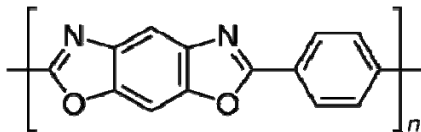
Photo by U.S. Navy photo by
Photographer's Mate 1st
Class Anibal Rivera (public
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- Water can add significantly to launch or take-off weight (3% water in composite resins = about 50 lbs of extra weight on an large SRM)
- Items with high water content 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



U.S. Navy photo by Photographer's Mate 3rd
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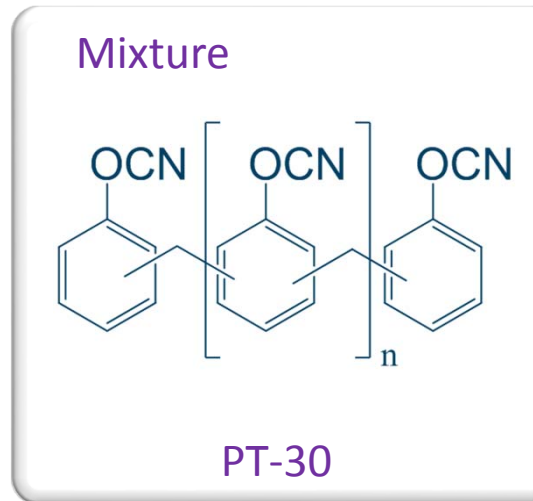
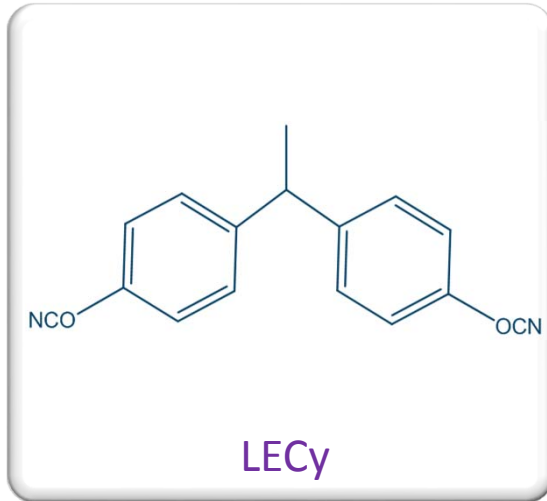


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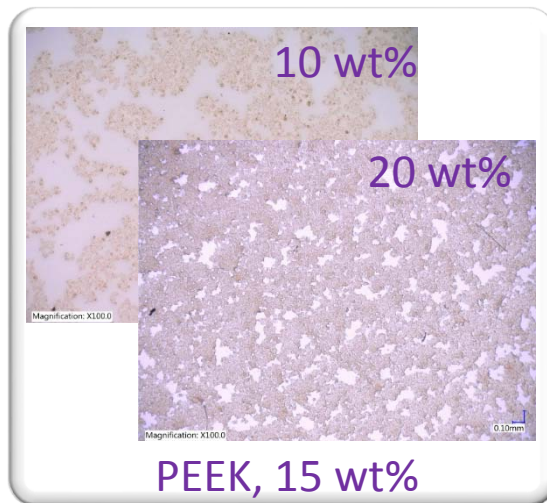
Materials Utilized

Monomers



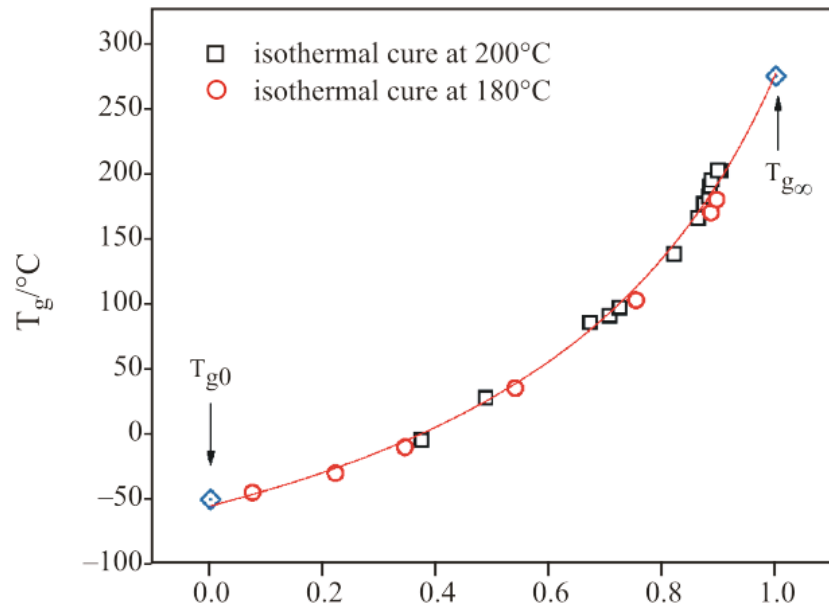
LECy/PT-30 (50/50 by weight) co-cured networks were cured at 170, 190, 210, and 240 C for 8 hrs to achieve a variety of conversion. Catalyst used was 160 ppm Cu as Cu-acac with 2 phr nonylphenol.

Additives





Models for Network Initial States



from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, 93, 77-85 for EX-1510

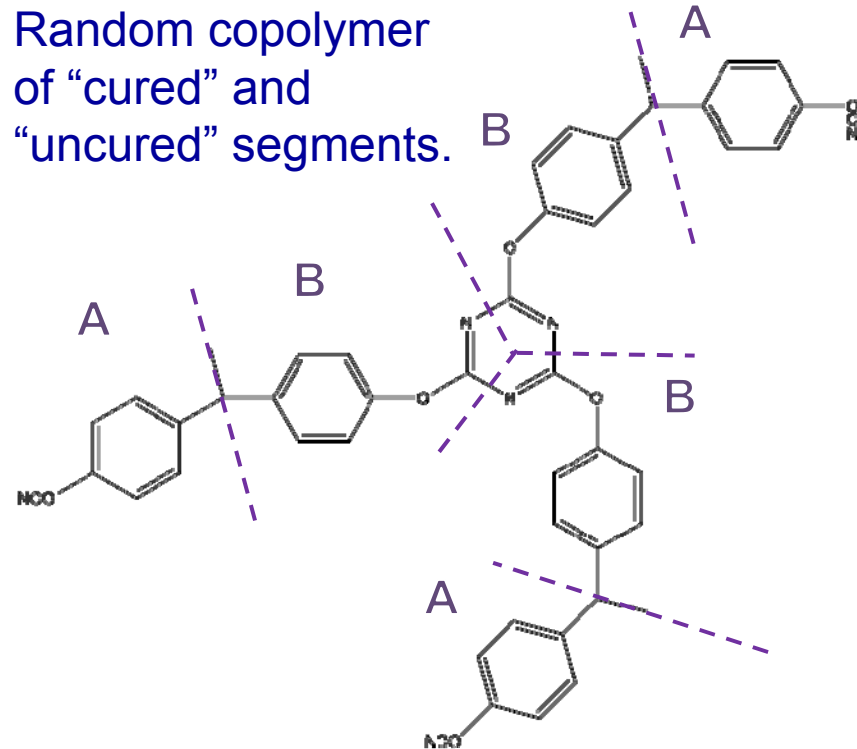
DiBenedetto equation is just Gordon-Taylor equation recast with $1-\alpha = \phi_1$, $\lambda = k$

Assumptions:

$$\Delta H_{mix} = 0; \Delta S_{mix} = 0, \Delta v_{mix} = 0,$$

$$S \text{ continuous at } T_G, dS/dP = 0$$

Random copolymer of "cured" and "uncured" segments.



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

Consequence

Initial state of network entirely described by one parameter - α

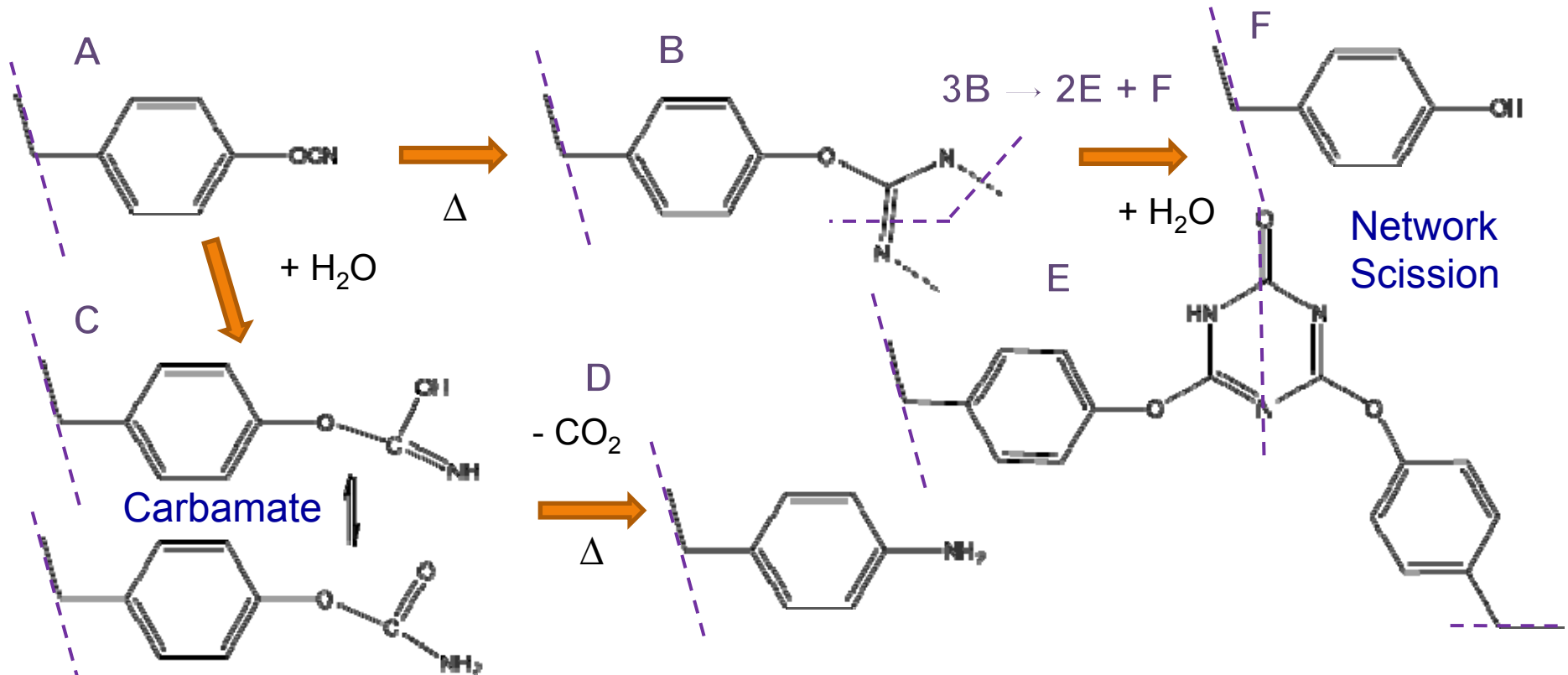




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Chemical Reaction Scheme



Network states:

ϕ_A, \dots, ϕ_F ϕ_E and ϕ_F related by stoichiometry

If networks are heated only to 350 °C, then only one of ϕ_C or ϕ_D may be non-zero.

Result: three parameters prior to heating: network conversion α' based on ϕ_B , plus ϕ_C and ϕ_F . Two parameters after heating, ϕ_D and ϕ_F .



Chemical Reaction Models

Carbamate formation



Weight gain of $0.14\phi_c$

Loss of ΔH_{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



Heating to $350 \text{ }^\circ\text{C}$ will complete

Weight loss of $0.34\phi_c$

No change in ΔH_{cure} , Loss of FT-IR signal at 17000 cm^{-1} , no change in T_G

Other decomposition



Assumed negligible below $350 \text{ }^\circ\text{C}$

Residual Cure



Heating to $350 \text{ }^\circ\text{C}$ dry will complete

No weight change

Loss of ΔH_{cure} , Loss of FT-IR signal at 2250 cm^{-1} , increase in T_G

Network Scission



Weight gain of $0.14\phi_E$

No change in ΔH_{cure} , only discernible readily via near-IR, decrease in T_G

More details:

Davis, M. C.; Guenther, A. J.; Sahagun, C. M.; Lamison, K. R.; Reams, J. T.; Mabry, J. M. "*Polymer* **2013**, *54*, 6902-6909.

Marella, V. V.; Throckmorton, J. A.; Palmese, G. R. *Polym. Degrad. Stabil.* **2014**, *104*, 104-111.



Effective Conversion Reduction

Multi-Component Gordon-Taylor Equation:

$$T_G = (T_{GA} \phi_A + k_{BA} T_{GB} \phi_B + \dots + k_{EA} T_{GF} \phi_F) / (\phi_A + k_{BA} \phi_B + \dots + k_{FA} \phi_F)$$

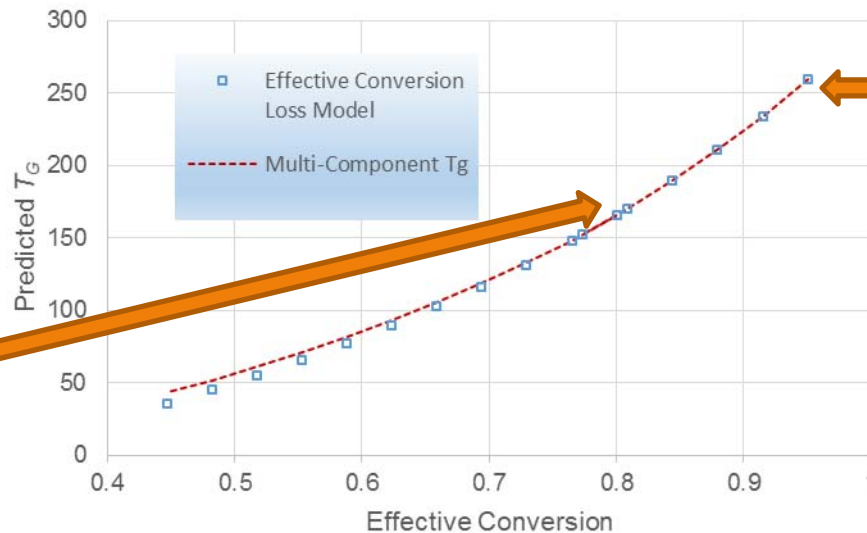
Can be simplified using an “effective conversion reduction factor” K

$$\alpha'_{eff} = \alpha'_0 - K\phi_F$$

$$T_G = T_{G0} + (T_{G\infty} - T_{G0}) \lambda \alpha'_{eff} / [1 - (1-\lambda) \alpha'_{eff}] \quad (\text{just the diBenedetto equation})$$

Assumes:
Same network physics throughout hydrolysis; ϕ_C and ϕ_F are correlated

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



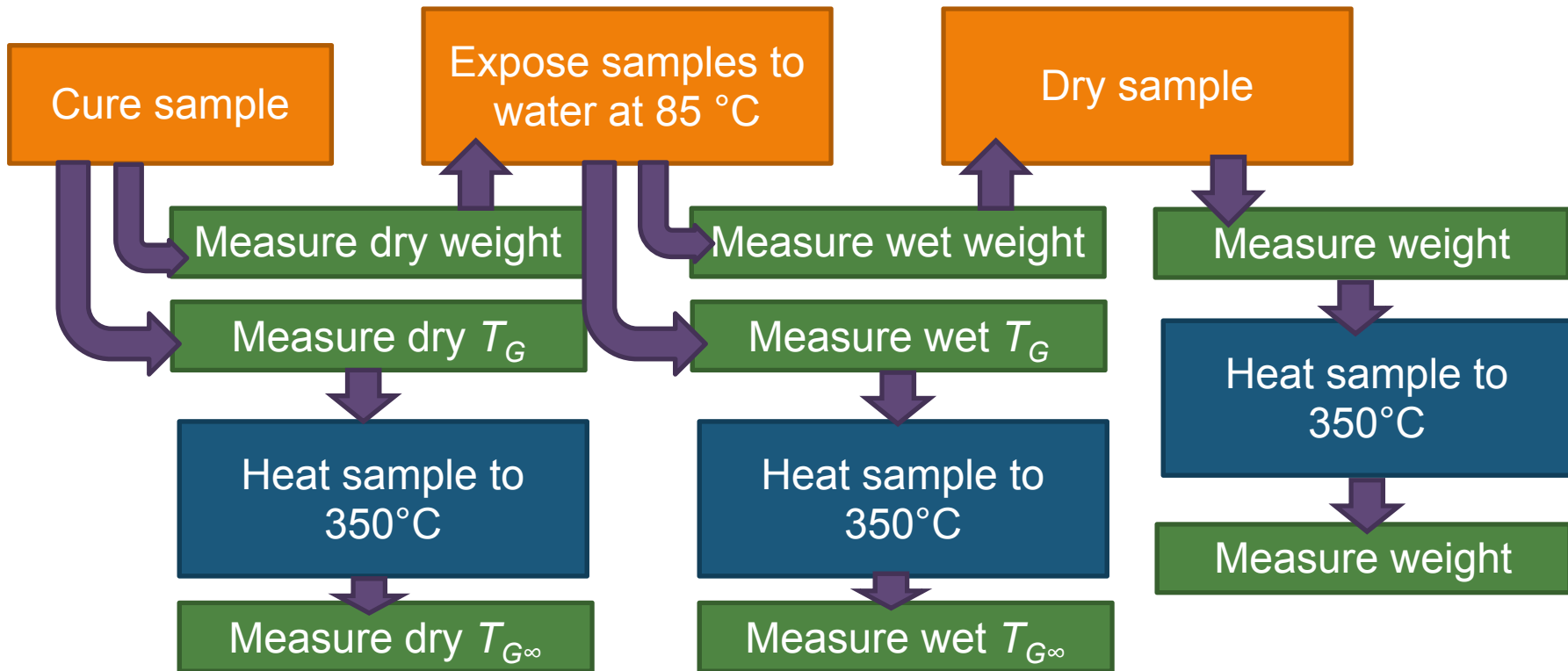
Test 1: Use K from $\phi_F = 0.02$; $\alpha'_0 = 0.95$, $\phi_C / \phi_F = 0.5$; extrapolate to $\phi_F = 0.1$. Max error 1 °C

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;



Analysis Procedure

Assumes diBenedetto parameters are known



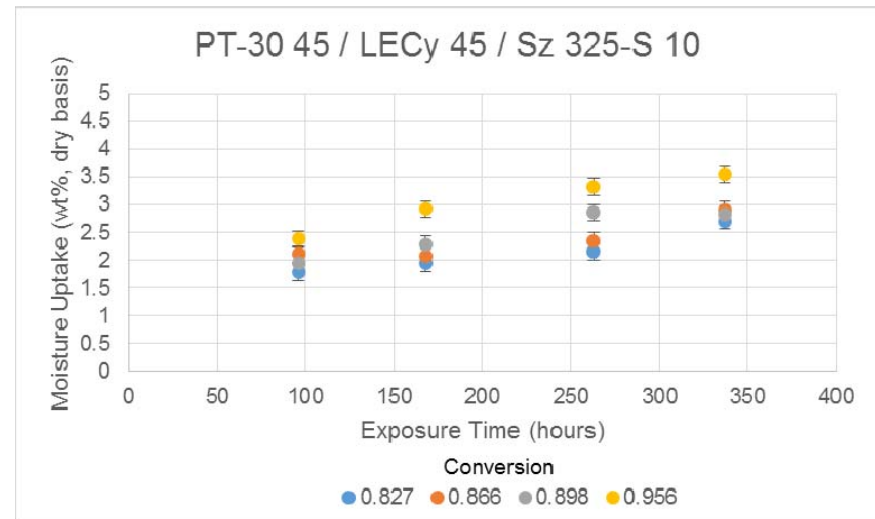
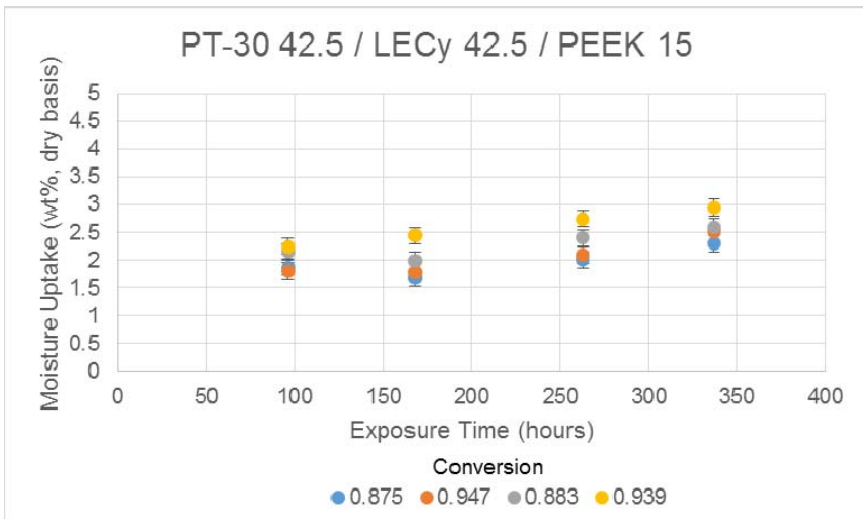
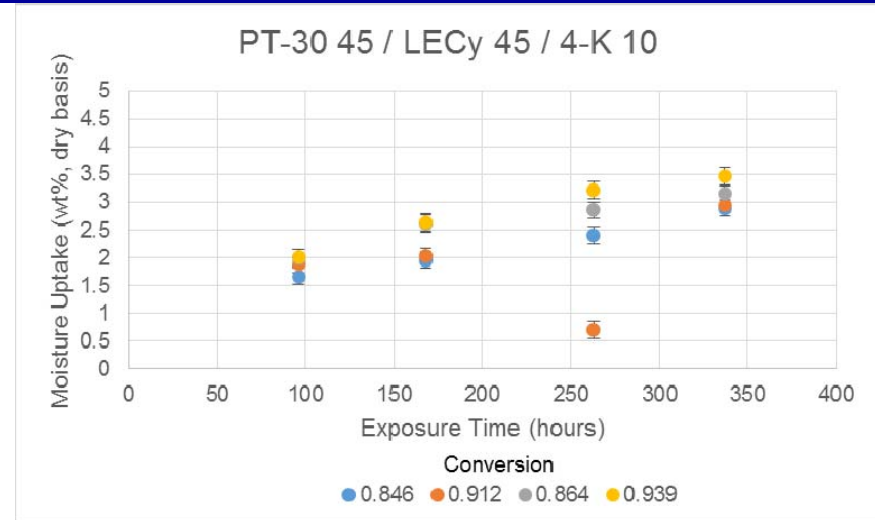
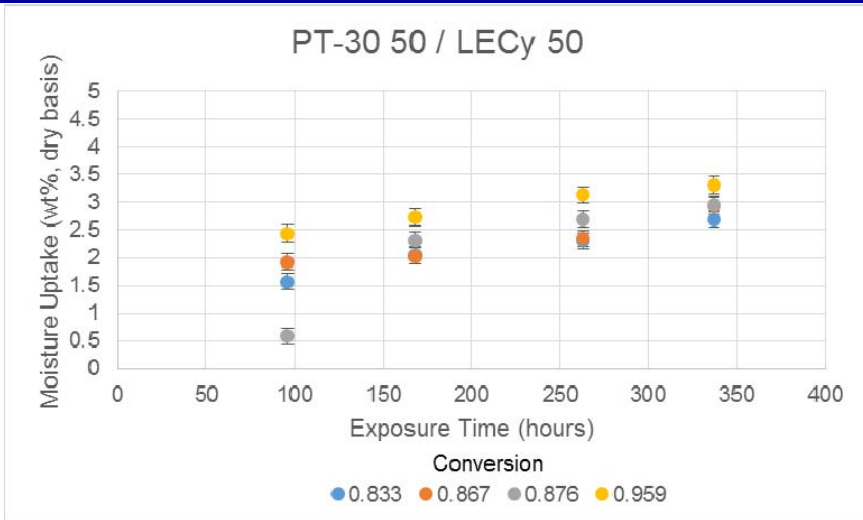
FT-IR may be added for verification if possible. Dry sample glass transition best if measured by DSC; wet glass transition best if measured by TMA

Final “wet and dried” weights determine ϕ_C, ϕ_F . $T_{G\infty}$ data cross-checks other degradation.



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Weight Gain After Water Exposure (No Drying)



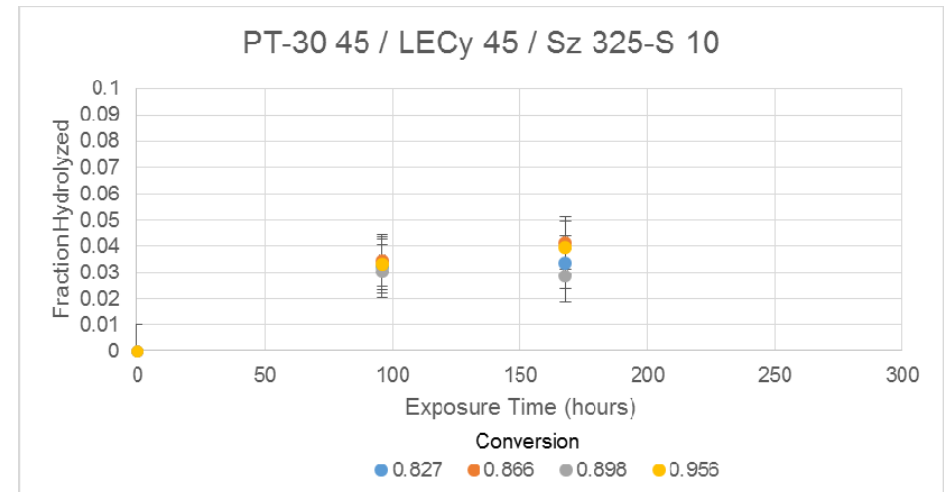
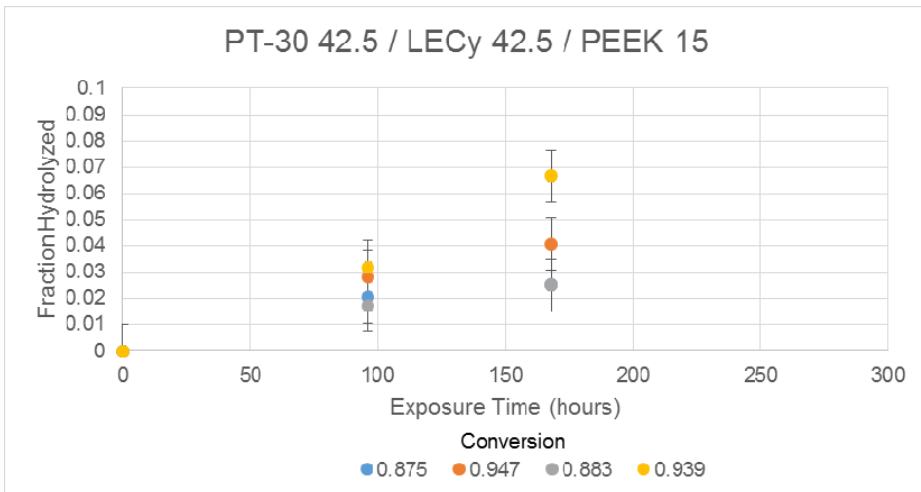
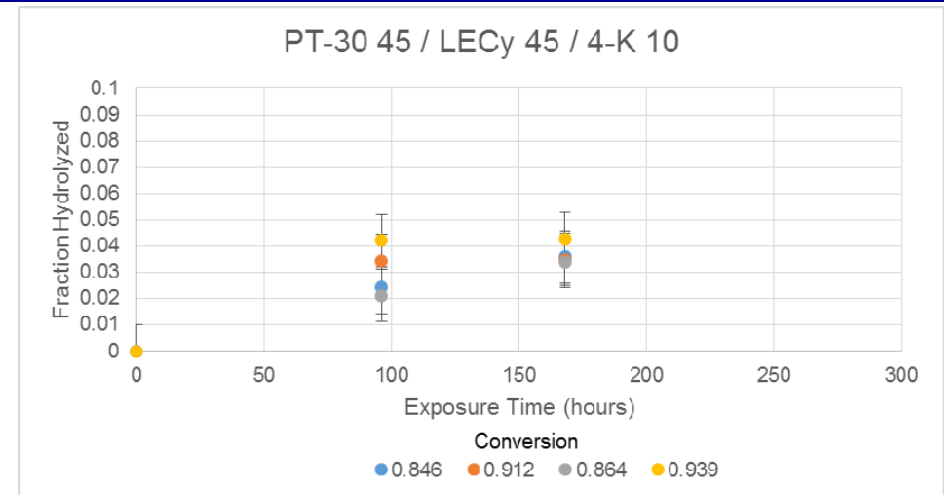
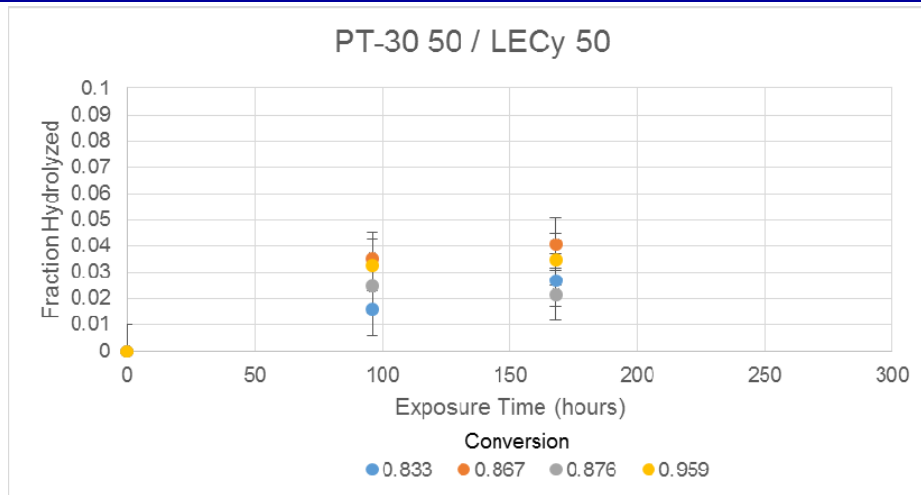
Slow hydrolysis evident; conversion dependence as expected
PEEK reduces water uptake as expected





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Hydrolysis Extent After Water Exposure



Data from samples exposed and dried with mild heating; slight correlation with conversion; additives show little effect so far ...

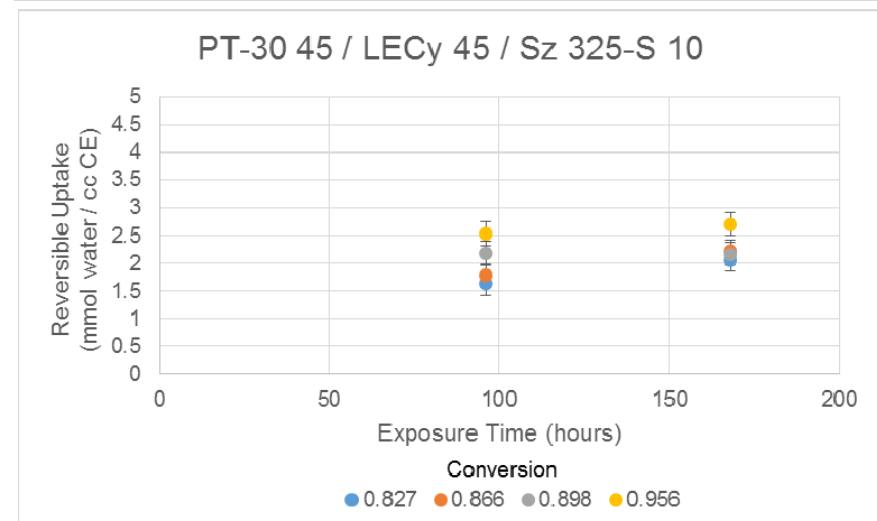
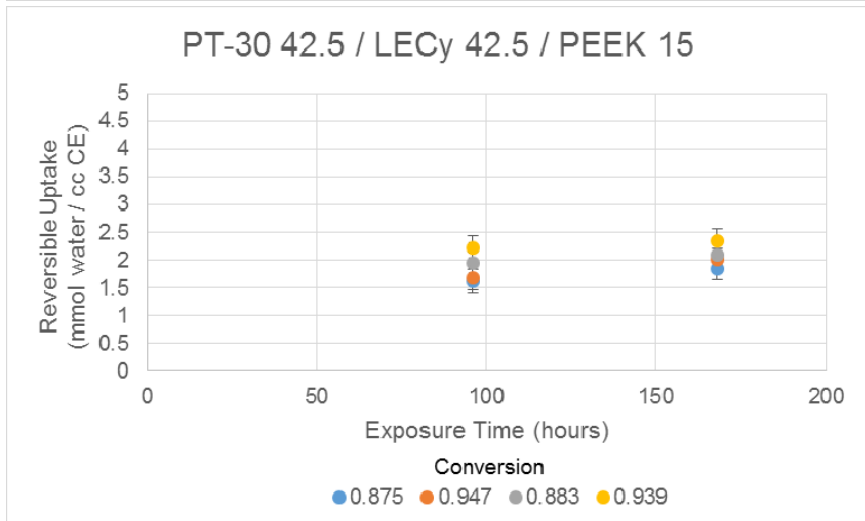
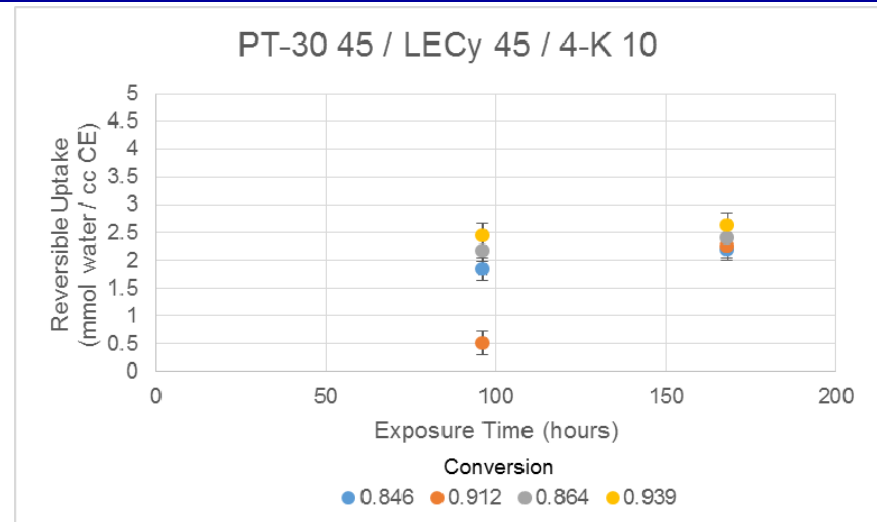
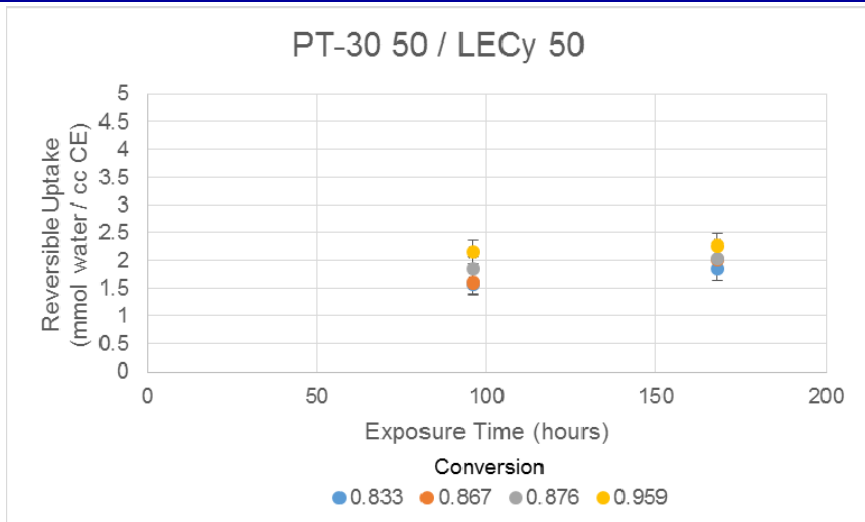




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Estimated Water Concentration



Mica appears to add water and inhibit diffusion. Diffusion appears to be faster at higher conversions.

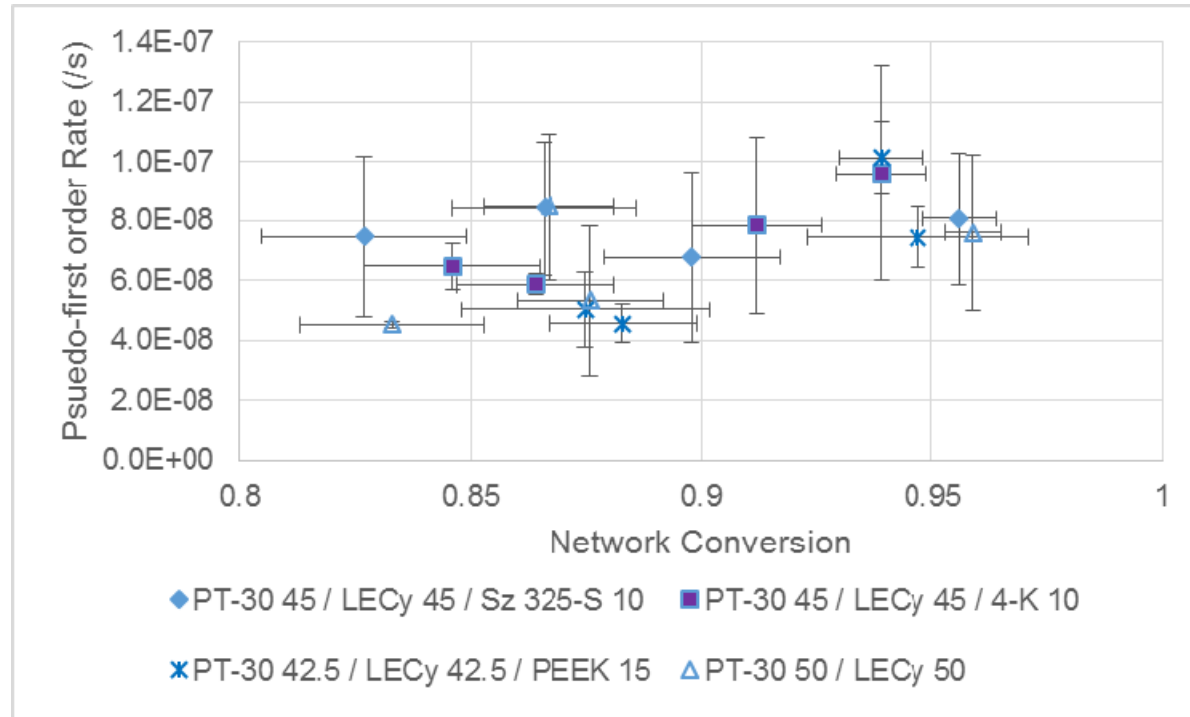




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Preliminary Kinetic Data



Conversions are from DSC only and are preliminary

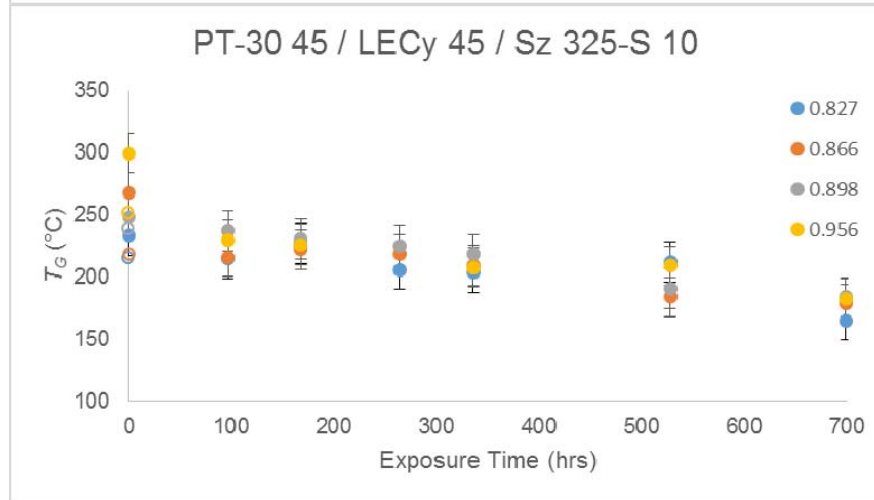
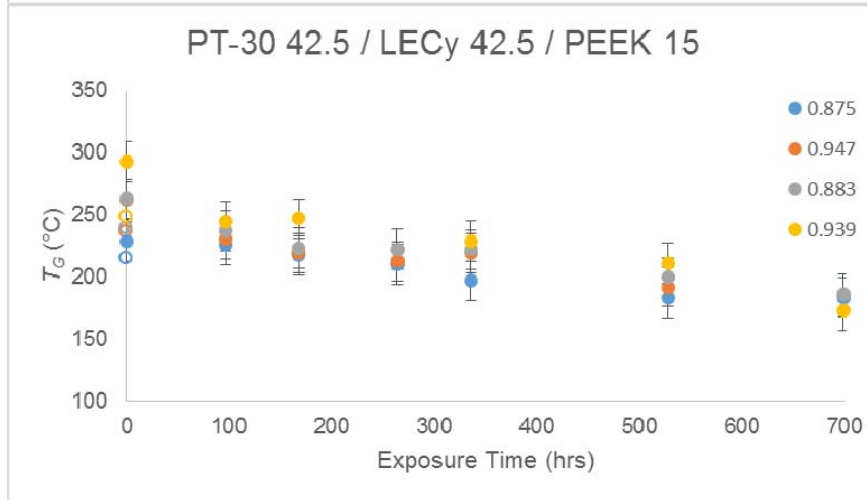
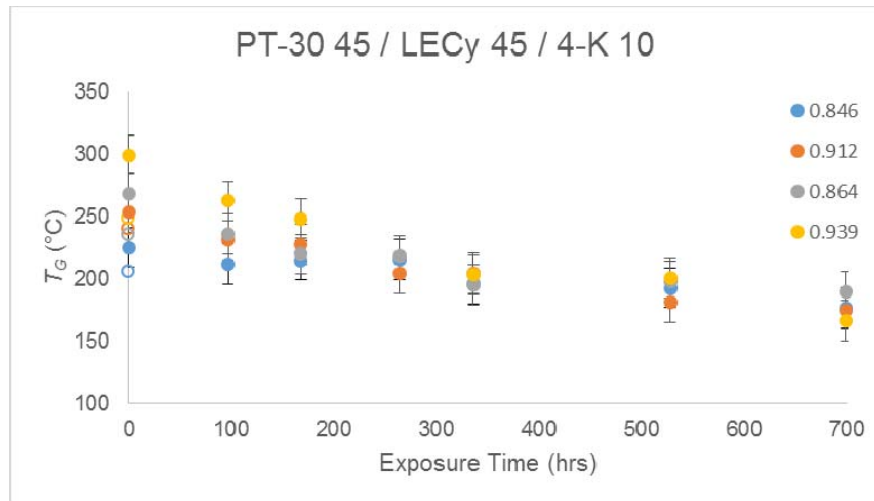
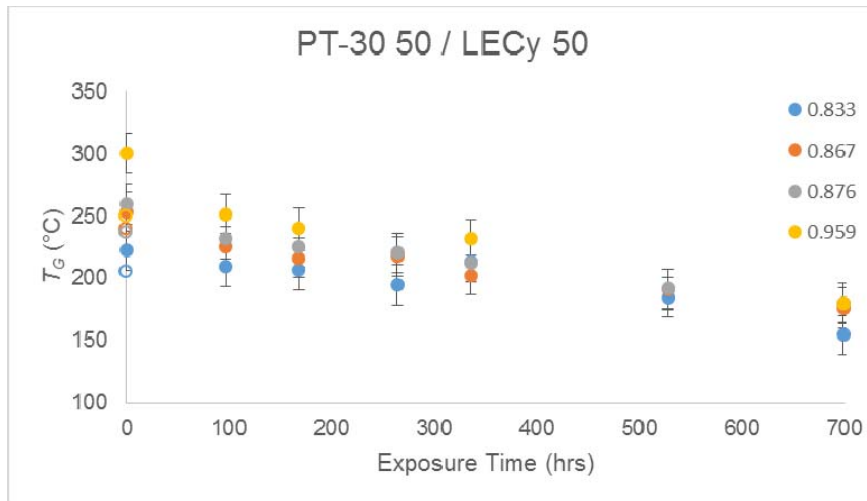
Rate constant is for all hydrolysis reactions – includes carbamate formation and network scission



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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





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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.**

