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## **New and Simple Ways to Minimize Water Uptake and Hydrolytic Degradation in Cyanate Esters**

27 January 2016

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# Outline



- Background
  - The Importance of Understanding Chemical Structure
- Ways to Mitigate Water Issues
  - Methylation
  - *ortho,para*-coupling
  - Silica



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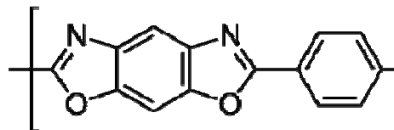
# Importance of Moisture Uptake in Composite Component Performance



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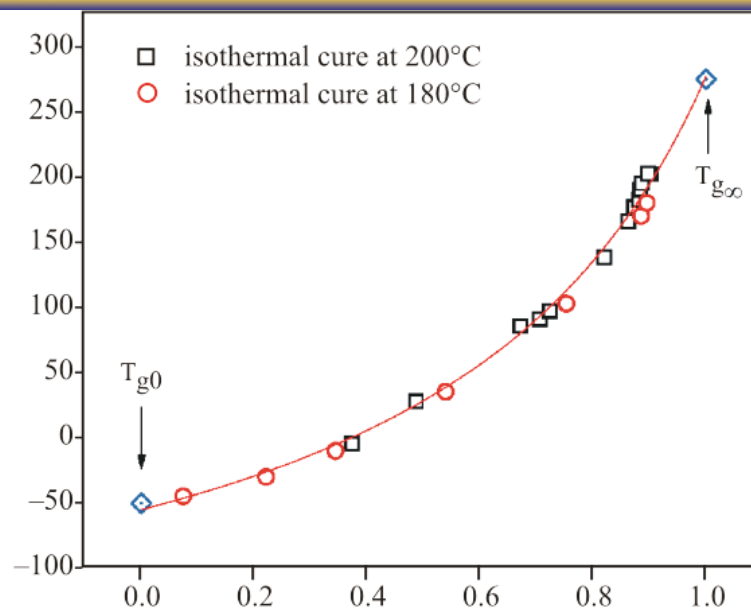
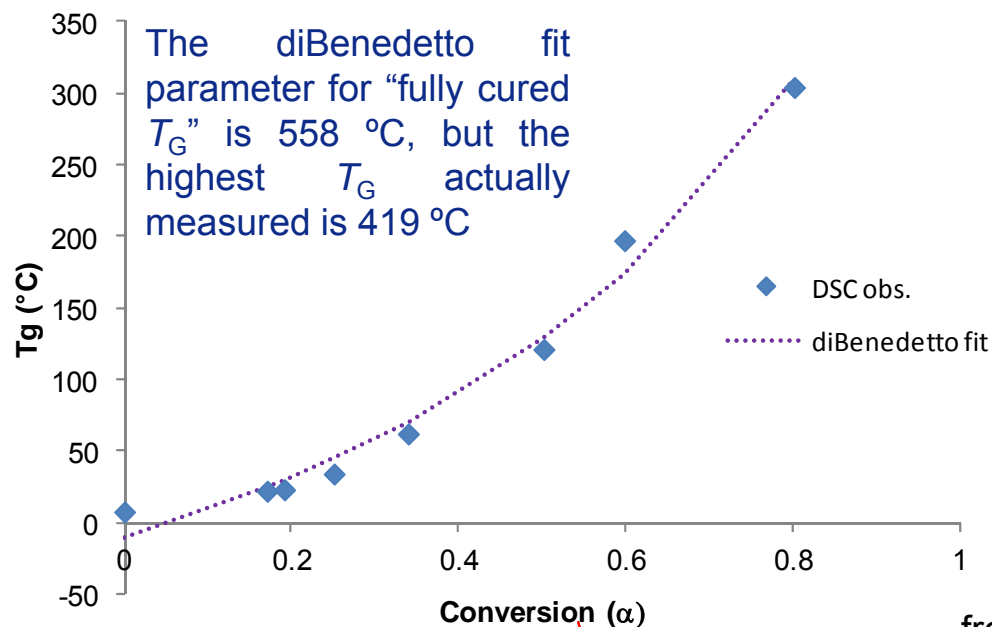


U.S. Navy photo by Mass Communication  
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- Water can add significantly to launch or take-off weight (3% water in composite resins = about 50 lbs of extra weight on a large SRM)
- Items with high water content can fail catastrophically when suddenly 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

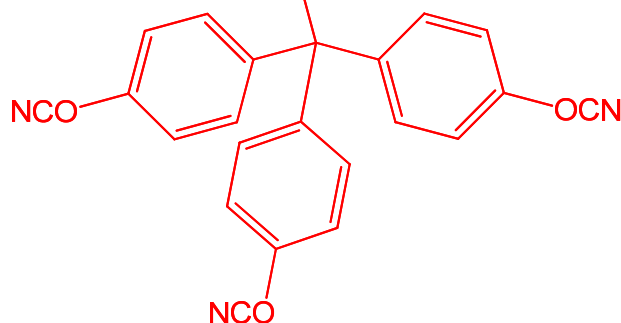


# Cyanate Ester Networks: Defined by Composition and Conversion

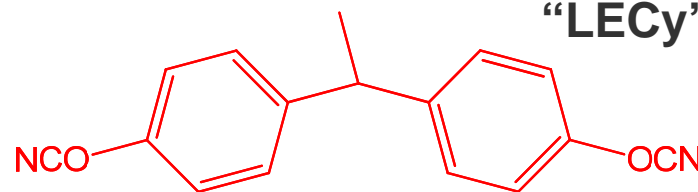


from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, 93, 77-85 for EX-1510

“ESR255”



“LECy”



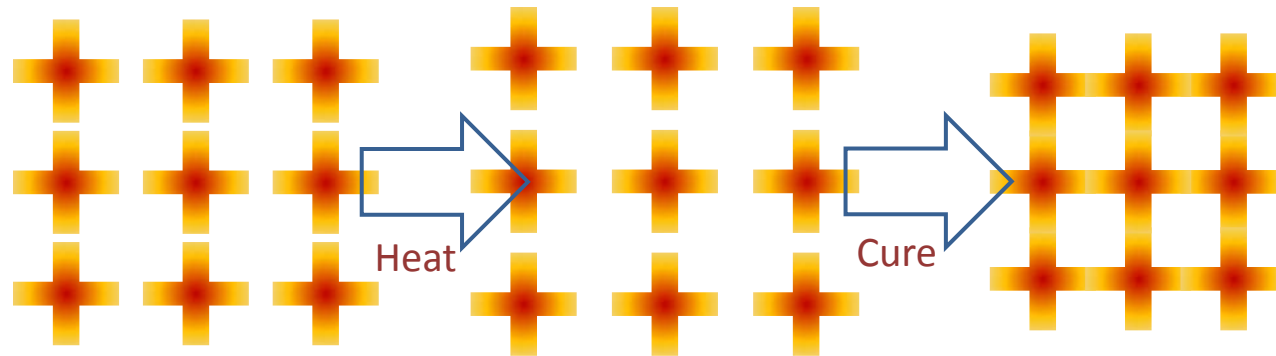
- The very good fit to the diBenedetto equation indicates that monomer conversion is highly correlated with “network conversion” – the former measured disappearance of monomer, the latter the successful formation of the network



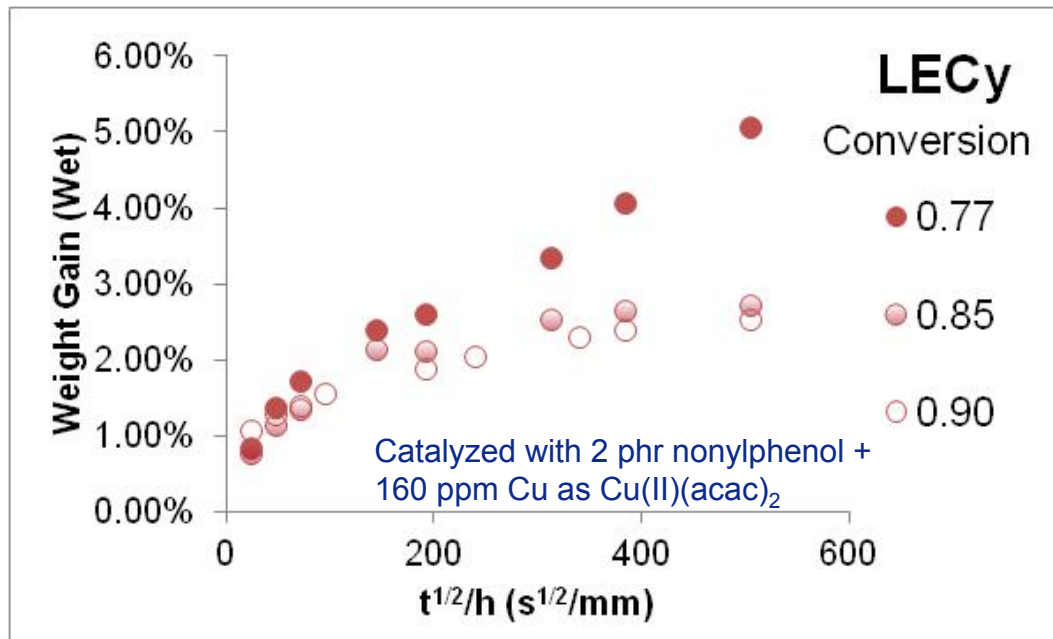
# Traditional Understanding of Moisture Uptake in Thermoset Resins



## Main Stage Thermal Cure



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



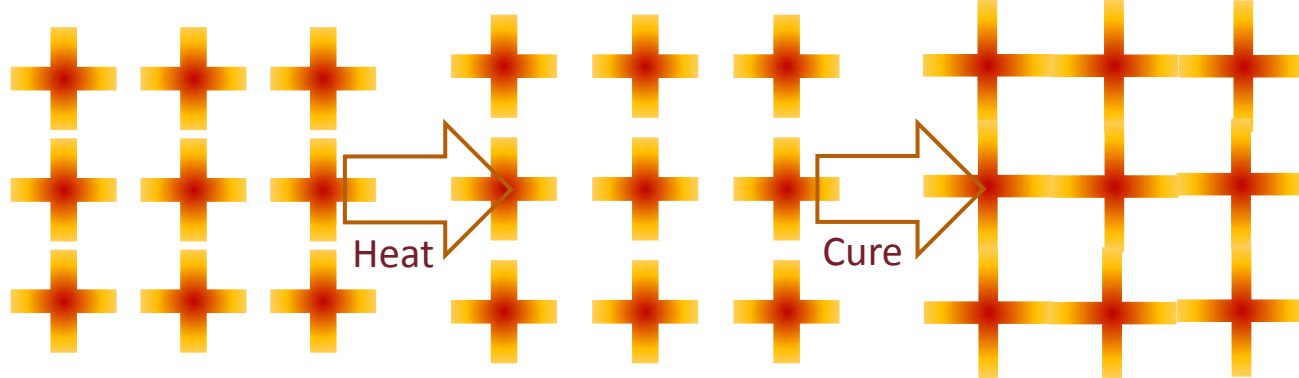
- Increasing conversion joins together more "loose ends" in the network, eliminating free space where water can be absorbed, therefore water uptake is expected to decrease with increasing conversion



# Proposed Role of Vitrification in Controlling Moisture Uptake

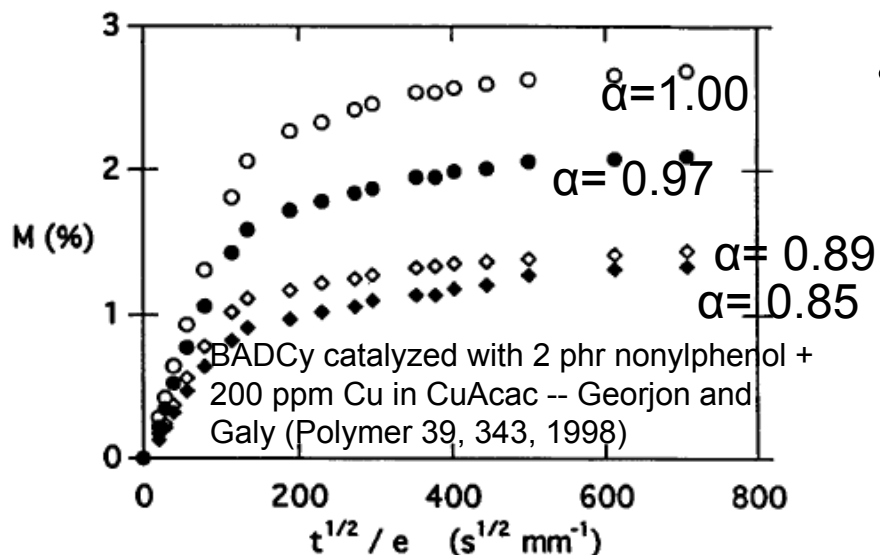


## "Vitreous Cure"



• Cure results in:

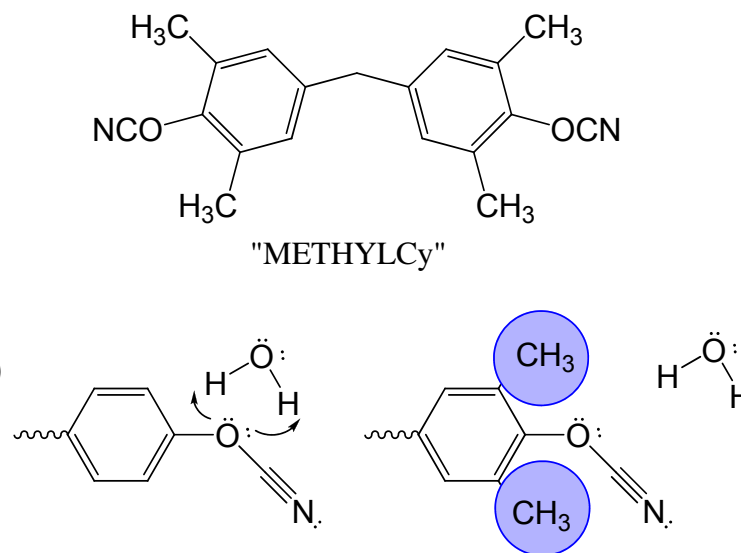
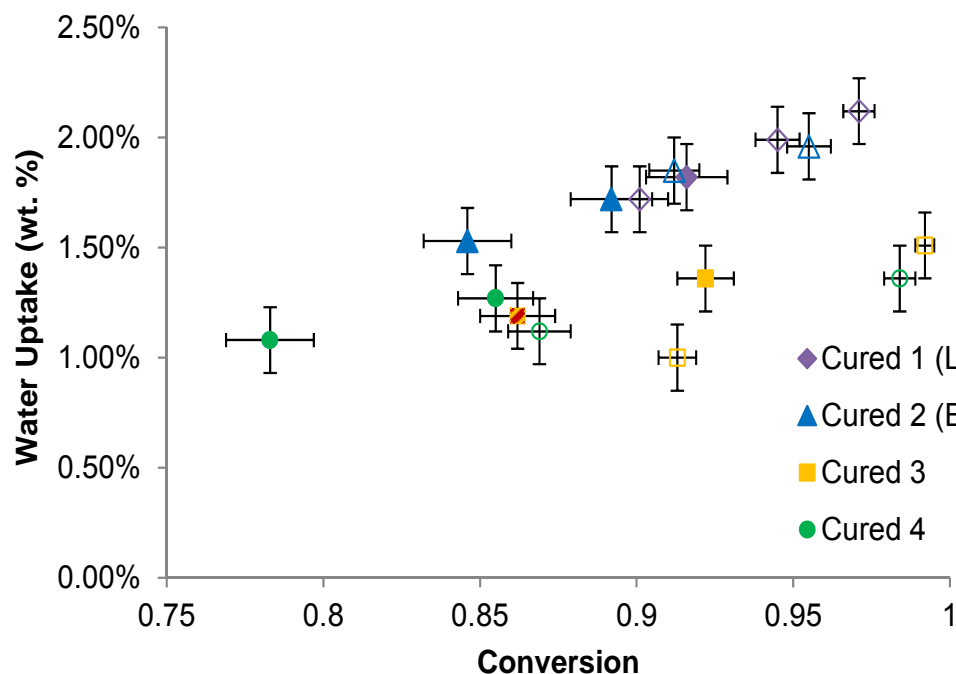
- *Net Expansion*
- *Higher permeability*
- *Lower modulus*
- *Toughness*



- Increasing conversions join "loose ends", but in the process they "freeze" the individual molecular centers-of-mass in place, resulting in exactly the opposite of the effects predicted by the traditional picture.



# Effect of Methylation on Moisture Uptake

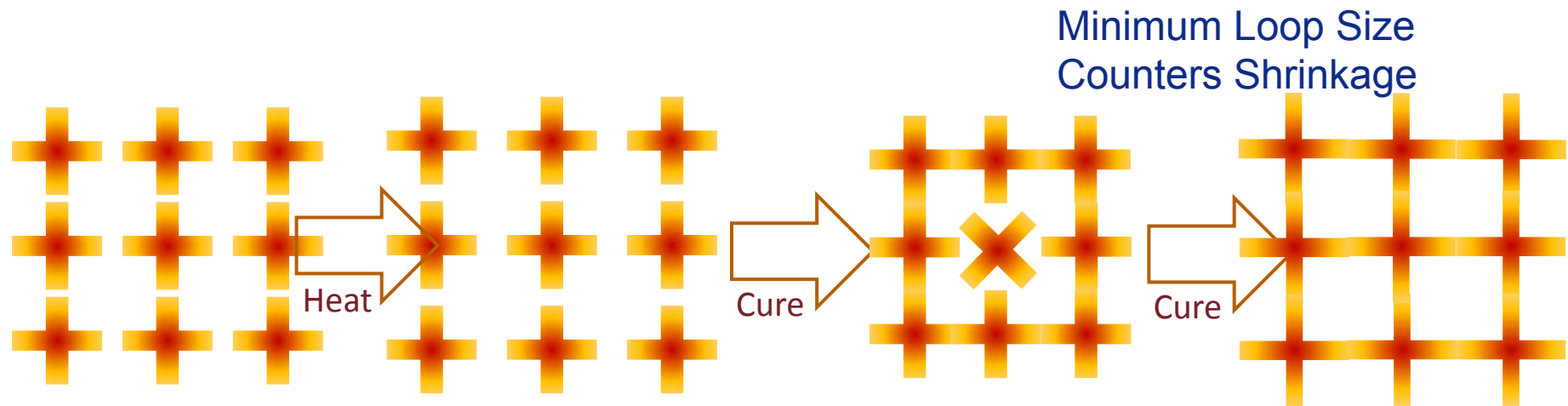


- Addition of a methyl group near the cyanurate oxygen causes a significant reduction in the tendency of moisture uptake to increase at high conversions
- Addition of a methyl group far from the cyanurate oxygen has no effect on water uptake as a function of conversion
- Methyl groups near the cyanurate oxygen block the favored sites for water uptake
- Vitrification appears not to influence the results. However, a 5% difference in conversion can change water uptake by 25%





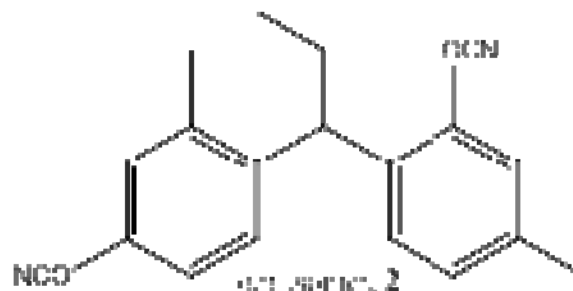
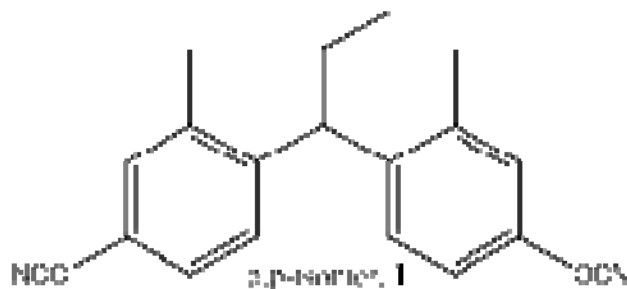
# Refined Moisture Model: Packing & Hydrophilic Regions



- If structural features control the network molar volume, then conversion / density and conversion / water uptake relationships should not depend on the cure path
- If hydrophilic regions are blocked, then increases in free volume will not lead to increases in water uptake.
- Similarly, if increased free volume is distributed away from hydrophilic regions, then increased free volume will not lead to increased water uptake.



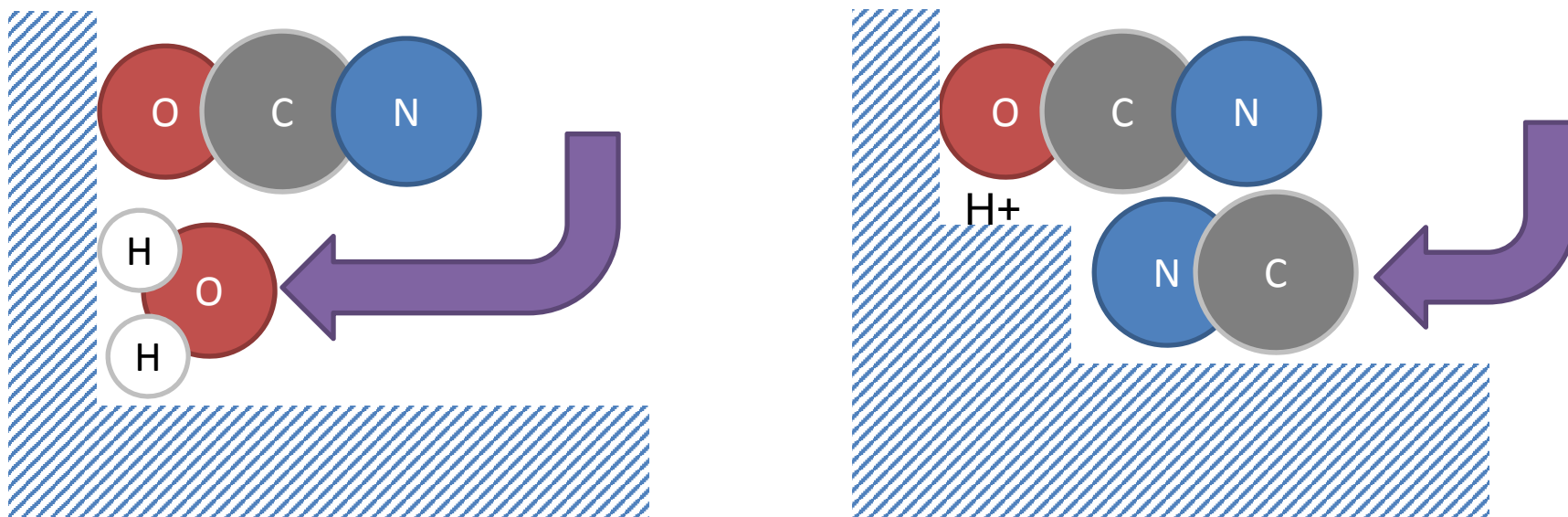
# Substitution Patterns on Bisphenol-Based Monomers



- Bisphenols are typically made by coupling of phenol with a carbonyl-containing bridge.
- Reactions are typically optimized to form only the *p,p*-coupled product (e.g., **1**) while minimizing the secondary *o,p*-coupled product (e.g. **2**).
- Often the *o,p*-product is separated and discarded.
- *o,p*-coupled products, however, offer steric hindrance of the phenolic oxygen due to the proximity to bridging groups, when these groups are sufficiently bulky



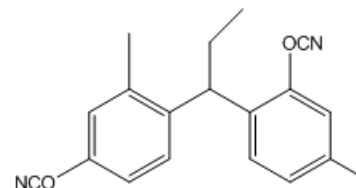
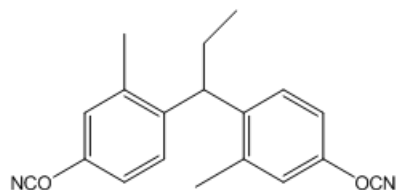
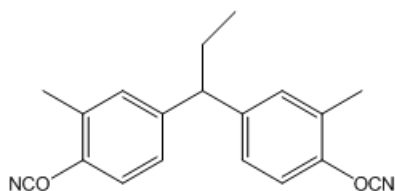
# Effect of Steric Hindrance on Cure and Hydrolysis of Cyanate Esters



- Water uptake (or hydrolysis) requires that a water molecule move near to the 3<sup>rd</sup> from terminal atom (O) in the cyanate ester atomic chain
- The typical proton-catalyzed cure of a cyanate ester requires that a proton reach the 3<sup>rd</sup> from terminal atom (O) while a terminal N atom must reach the 2<sup>nd</sup> from terminal C atom
- Water uptake / hydrolysis therefore requires a much larger “pocket” of free volume than does cure catalysis.



# Synthesis of Cyanate Ester Isomers with Varied Substitution Patterns

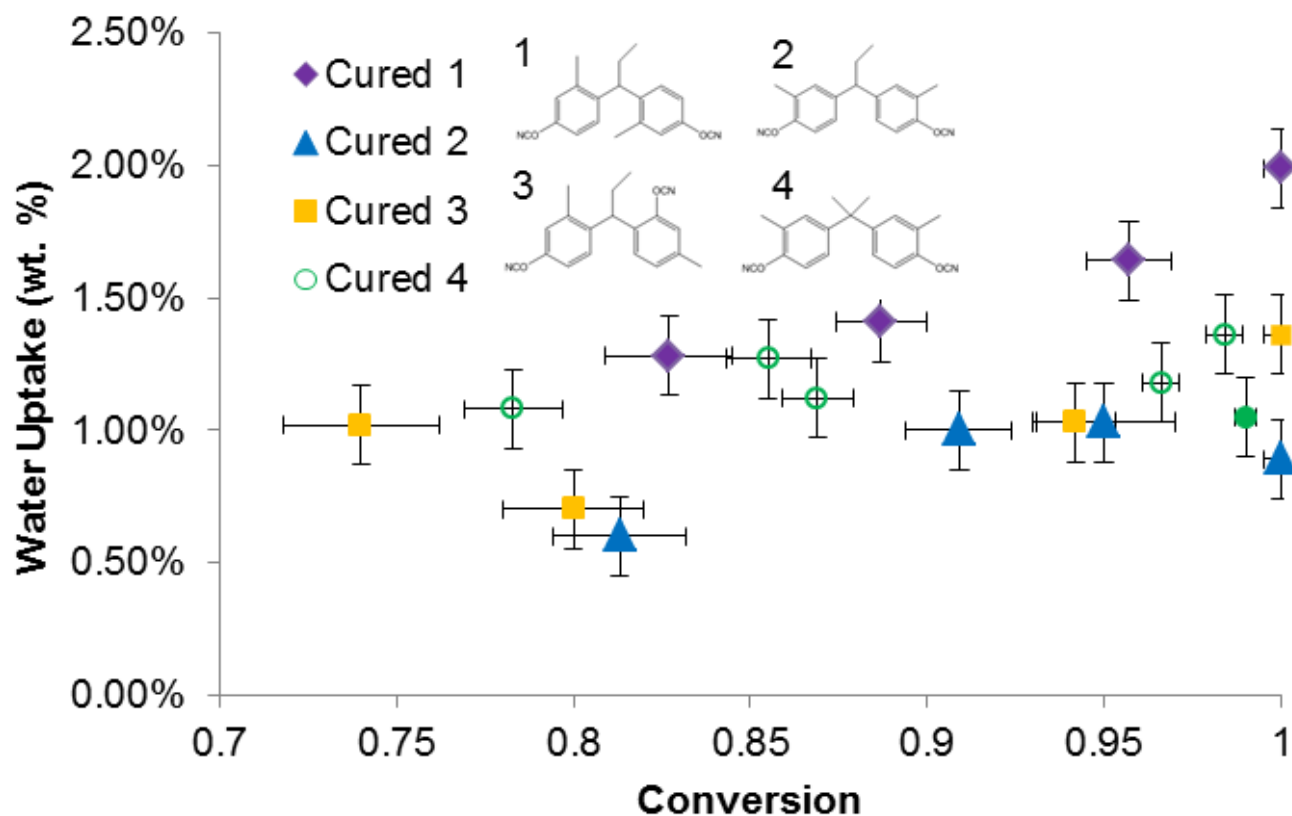


NAV  AIR

- Synthesis carried out at NAWCWD China Lake
- Methylation location (*meta* vs. *ortho*) relative to cyanate ester group varied
- Bis-phenyl linkage pattern (*o,p*) vs (*p,p*) also varied



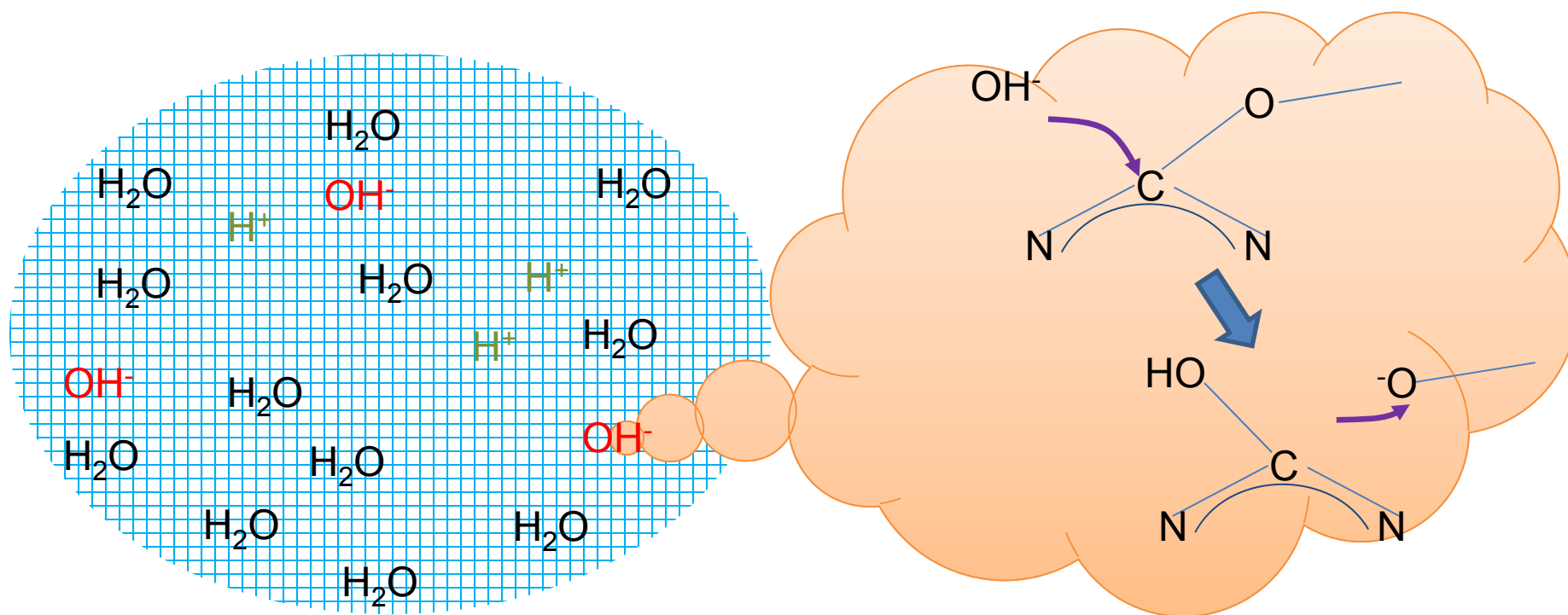
# Effect of Methylation and Substitution Pattern on Water Uptake



- Unfilled data points indicate systems catalyzed with 2 phr nonylphenol / 160 ppm Cu (as Cu-Acac)
- *o,p*-substitution is just as effective at reducing water uptake, and decreases conversion only modestly under typical cure conditions



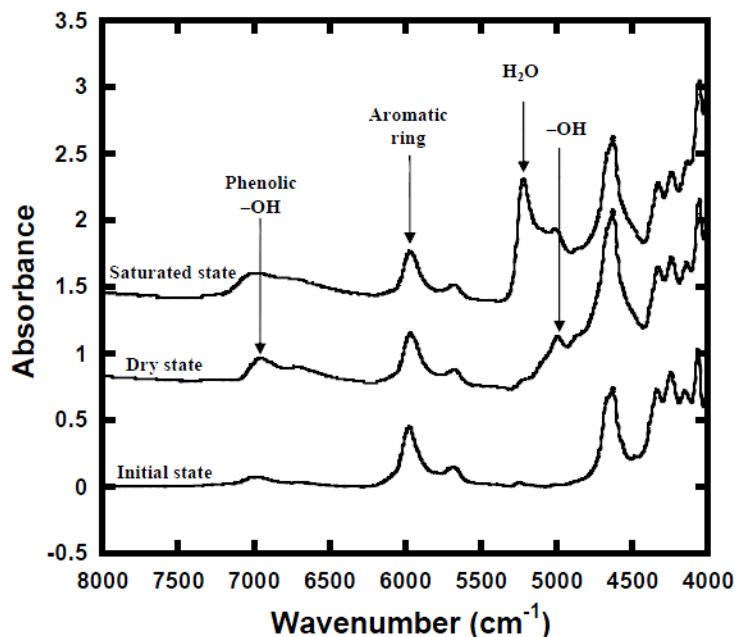
# Hydrolysis Reactions of Cyanate Esters



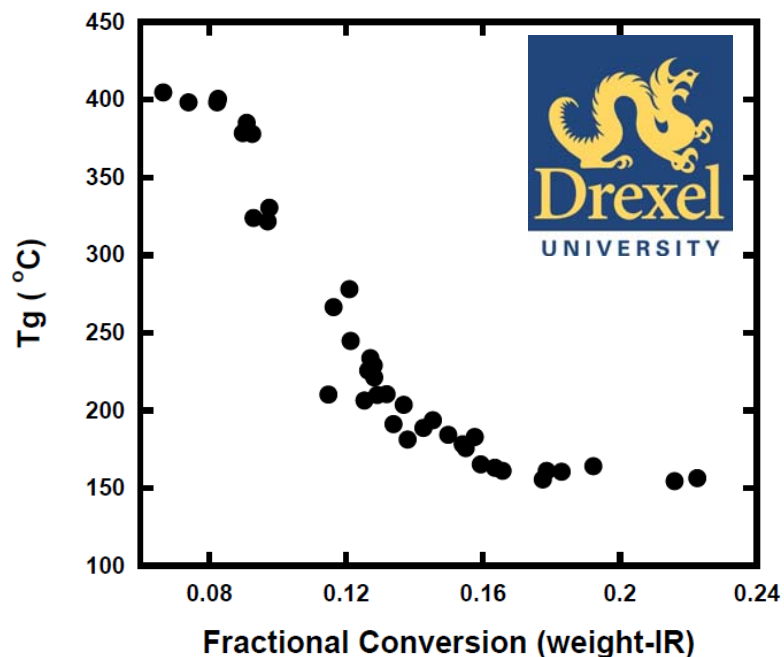
- Cyanate esters are especially vulnerable to base-catalyzed hydrolysis, in which a hydroxyl ion displaces a C-O bond to make a more stable anion, facilitated by attraction to electropositive carbon atoms.



# Effect of Hydrolysis on $T_g$



*Near-infrared spectra of Primaset® PT-30*

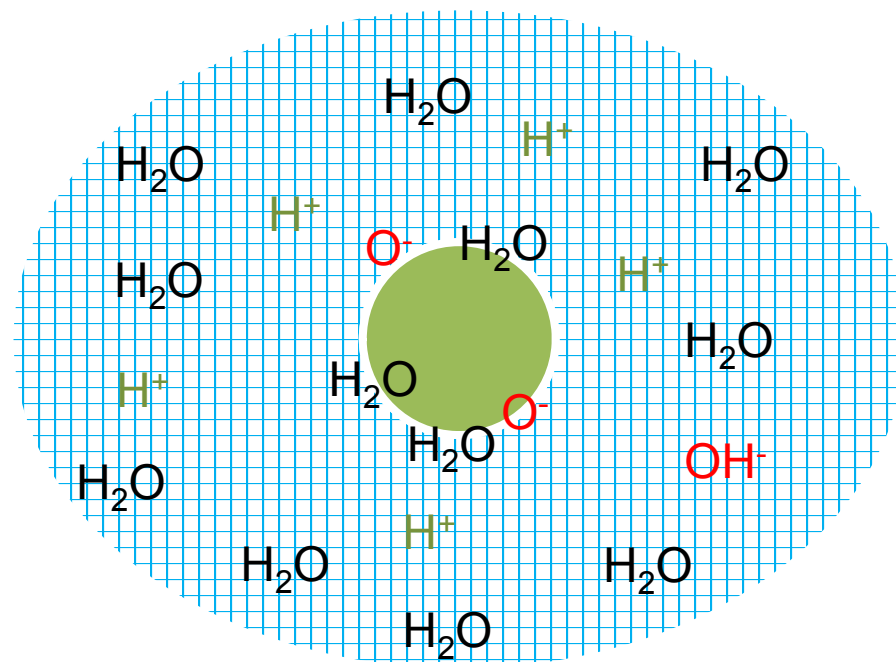
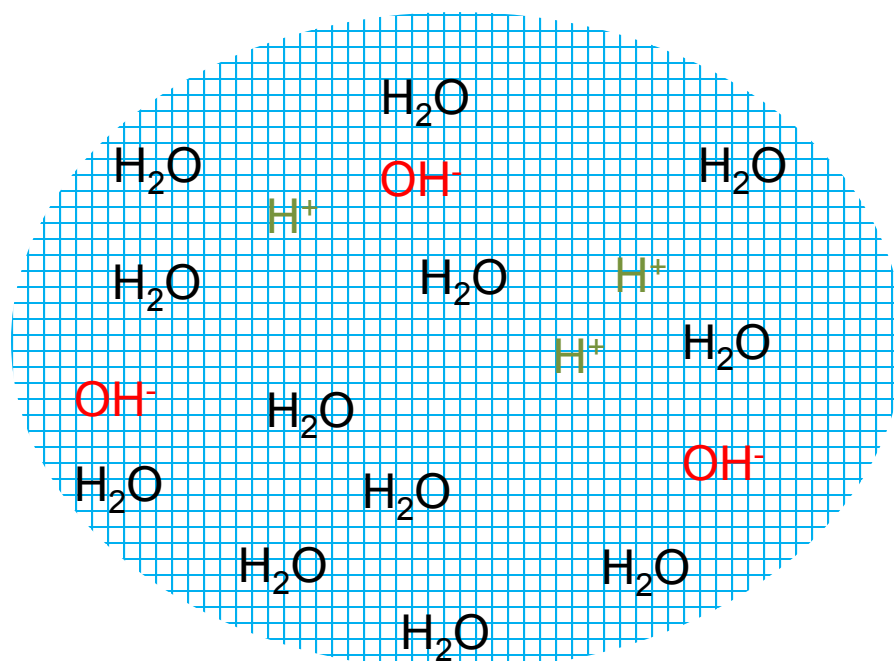


*$T_g$  of Primaset® PT-30 as a function of extent of degradation.*

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



# A “Negative Ion Trap” Will Curtail Cyanate Ester Hydrolysis



- Even in dense polymer networks, equilibration of ions takes place. Consequently, a stable surface that pins negative ions will lower the pH of the network as a whole, and will slow down hydrolysis





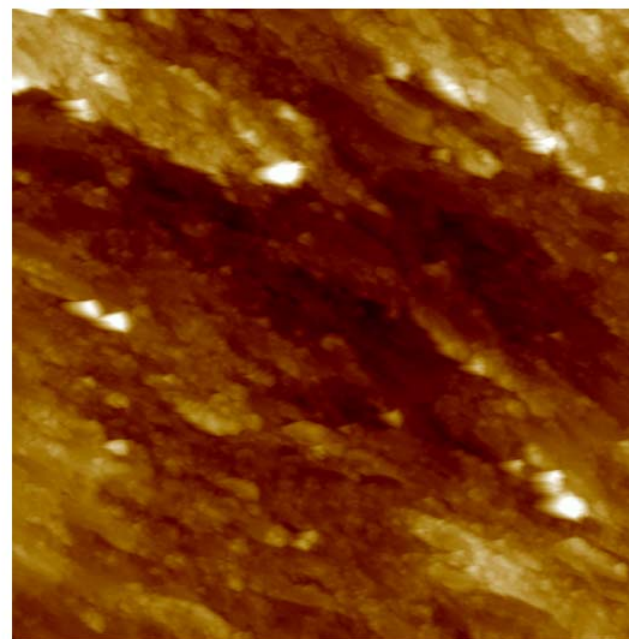
# Nanosilica Dispersed in LECy



Height

2.0 μm

**Neat LECy w/ catalyst (2 phr nonylphenol + 160 ppm Cu as Cu-Acac, cured 210 °C, 6 hrs**



Height

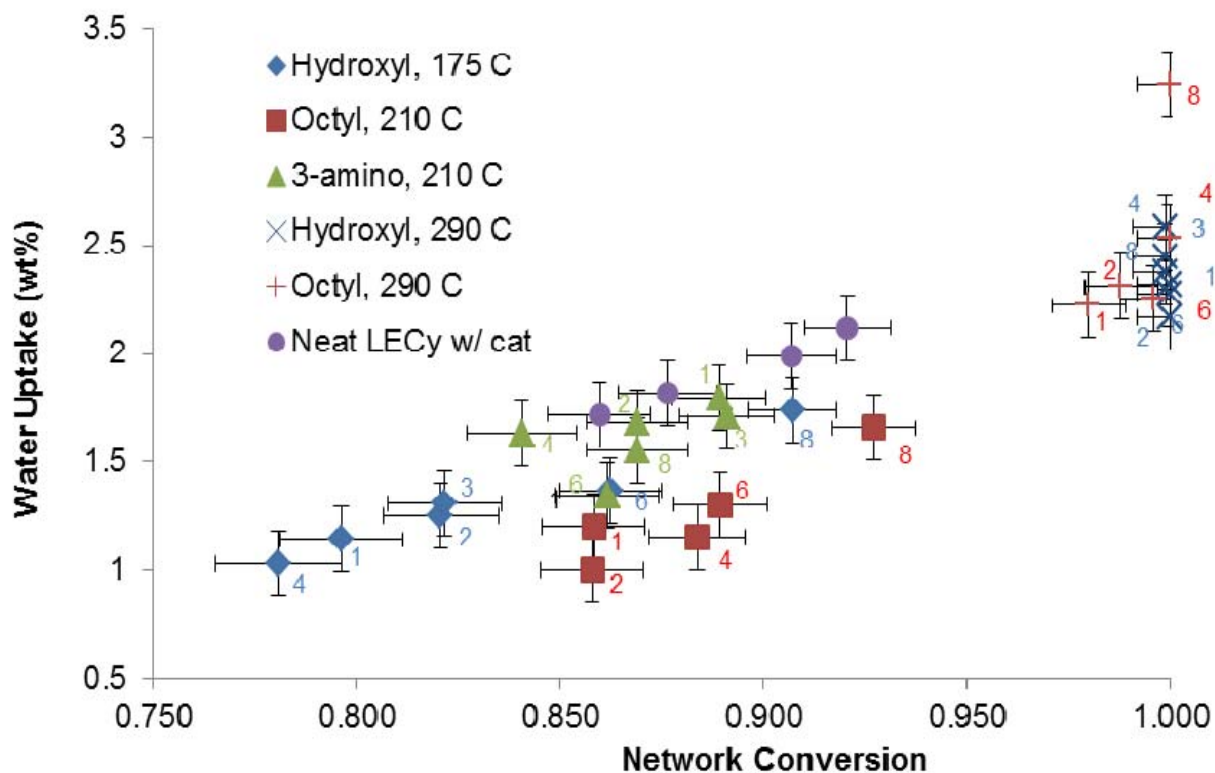
2.0 μm

**Neat LECy w/ catalyst (2 phr nonylphenol + 160 ppm Cu as Cu-Acac + 5 phr Aerosil® 200, cured 175 °C, 10 hrs**

- Unlike epoxy resins, neat LECy networks are featureless down to the nanoscale
- The surface of Aerosil® 200 is rich in silanol groups, which induce a low pH in the surrounding medium



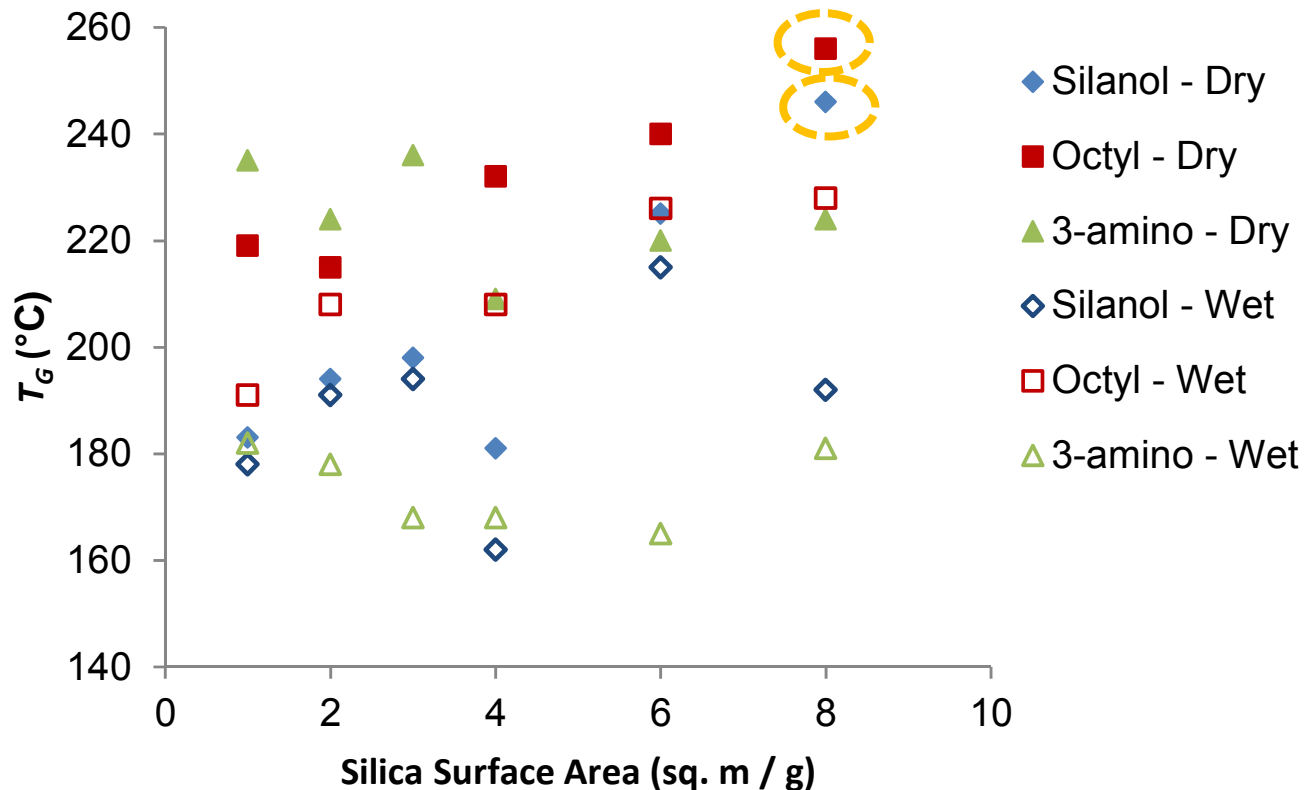
# Water Uptake of LECy Nanocomposites



- “Network conversion” is based on the resin  $T_G$  rather than on DSC data; it indicates the extent of network formation, as opposed to monomer reaction
- Numbers indicate surface areas of embedded particles in m<sup>2</sup>/g
- Three different surface types are shown: hydroxyl (low pH); octyl (closer to neutral pH), and 3-amino (higher pH).



# Hydrolytic Stability of LECy Nanocomposites



- “Network conversion” is based on the resin  $T_G$  as measured by dynamic TMA before and after 96 hrs immersion in water at 85 °C. Circled data points indicate dry TG is artificially high due to *in-situ* cure.
- Catalyzed neat LECy cured at 210 °C: ~250 °C (dry) / 190 °C (wet)



# Summary

- The physical behavior of cyanate ester networks is captured by just two factors: monomer composition and “network conversion”
- The water uptake of a cyanate ester network formed from a given monomer is often highly sensitive to conversion
- As the conversion of a cyanate ester network increases, more free volume is created around the hydrophilic cyanurate oxygen atoms, facilitating greater water uptake, unless these atoms are sterically hindered
- *Ortho*-methylation (one per –OCN) and *ortho,para*-substitution patterns appear to be equally effective at hindering the cyanurate oxygen.
- Because of differences in chemical mechanisms, it is possible to hinder access to water substantially while only modestly impacting cure rates
- Hydrolysis of cyanate ester networks is typically catalyzed under basic conditions. The addition of silica particles at low levels adjusts the network pH so as to effectively slow down the rate of hydrolysis

