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Polyurethane in Composites

Presentation at SANDIA

May 31, 2012

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DOE project Objectives

- Carbon Nanotube Reinforced Polyurethane Composites for Wind Turbine Blades
  DOE Award Number DE-EE0001361

  1. Determine if polyurethane based composites offer performance advantages over incumbent materials (epoxy, vinyl ester) used in the manufacture of wind turbine blades.
  2. Determine if carbon nanotubes can be used to strengthen both incumbent and experimental polyurethane systems.

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Challenges

- Polyurethane
  - Speed of Reaction
  - Viscosity
  - Moisture Sensitivity
- Carbon Nanotubes
  - Dispersion
  - Re-agglomeration
  - Viscosity

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Resins

- Epoxy
- Vinyl ester
- Polyester
- Polyurethane
    - PU RTM
    - PU/Soy

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PU Development

- Developed two PU systems specifically designed for Wind
  - Conventional
  - Soy based
- Low viscosity
- Long gel time >2 hours
- Infusion time >50 minutes
- Compared performance with Epoxy and Vinyl Ester Composites

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Soy based polyols

- Why Soy?
  - Adds renewable content to the PU
  - Reduces moisture sensitivity of the system
- Synthesized a new soy polyol
  - Viscosity; Reactivity

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Improve water sensitivity with soy

	PU	Soy PU
Initial sp. gr. g/cc	1.127	1.167
sp. gr. g/cc after 4 weeks	0.973	1.124
% reduction in sp. gr.	13	3.7

Soy Polyol shows improved water sensitivity vs. commercial polyol

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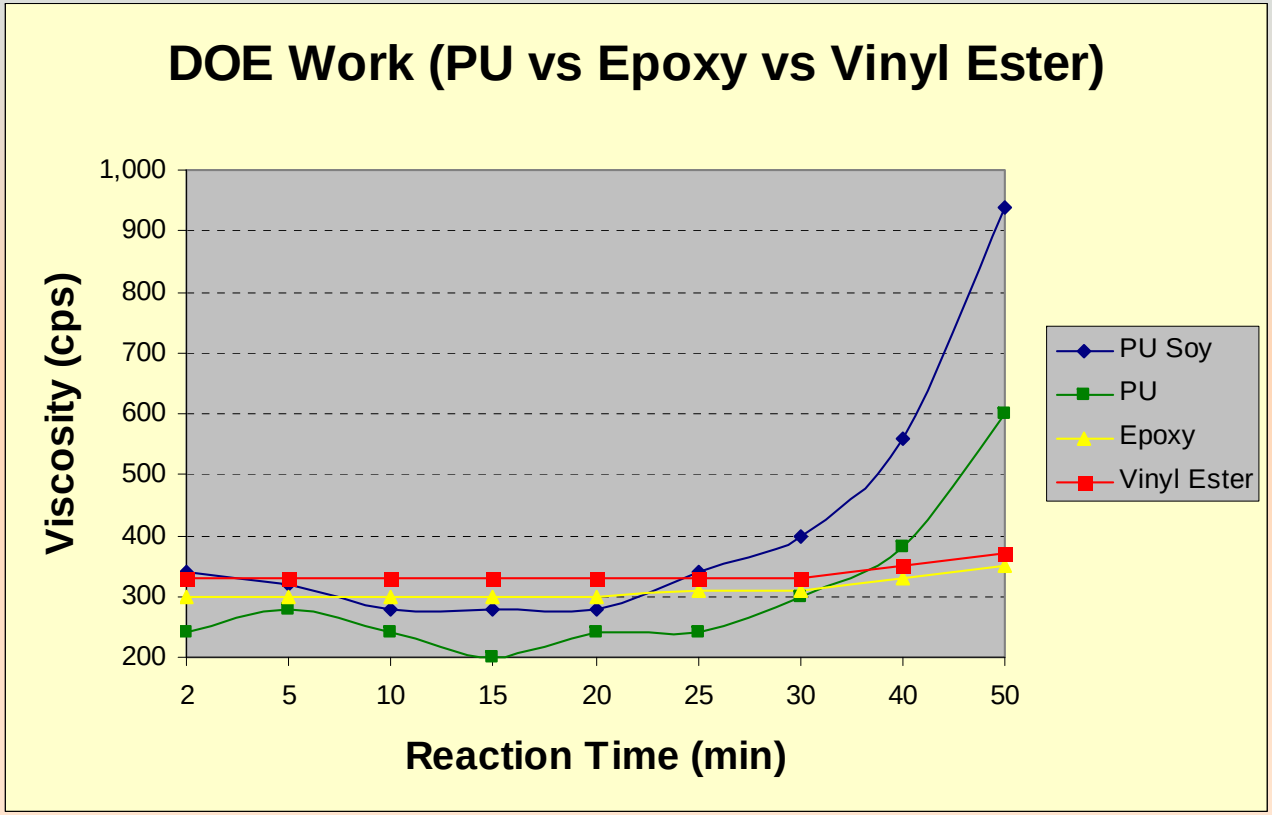
Viscosity rise over time PU RTM and PU Soy



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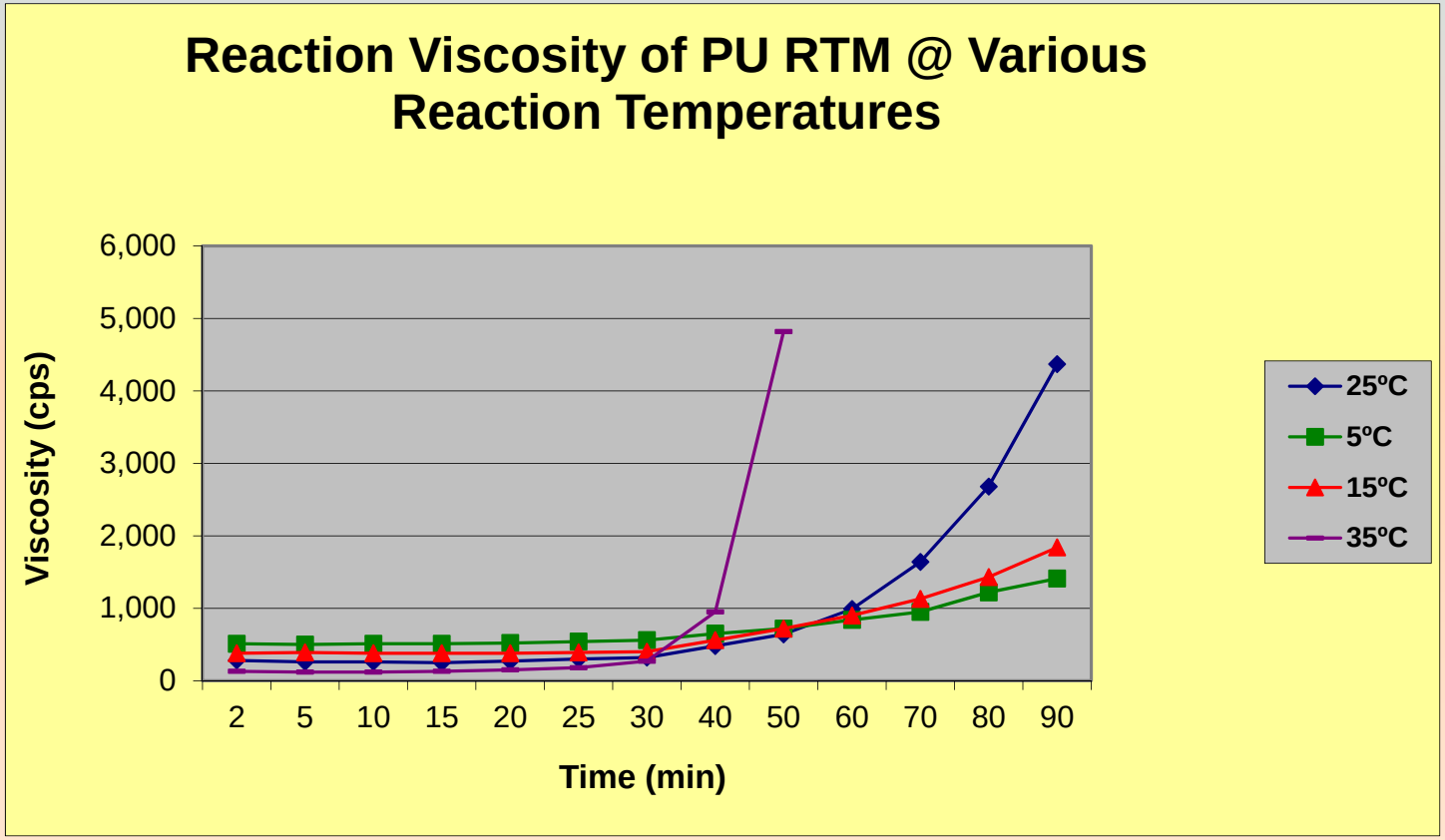
PU system and the effect of heat on cure



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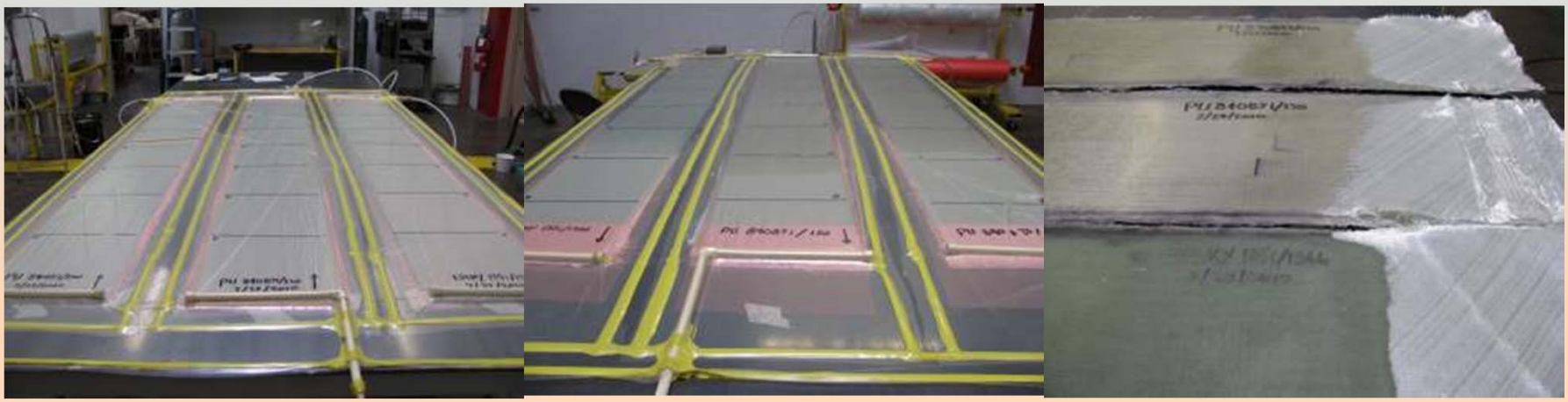
Thick Laminate, Long-Flow Infusion



Infusion flow distance (inches)	Epoxy infusion time (minutes)	PU infusion time, min	PU Soy infusion time, min
12	1	0.5	1
24	4	1	2
36	8	4	5
48	16	8	12
60	26	16	24

Epoxy, Vinyl ester, and PU 21 ply Root Ring Moldings

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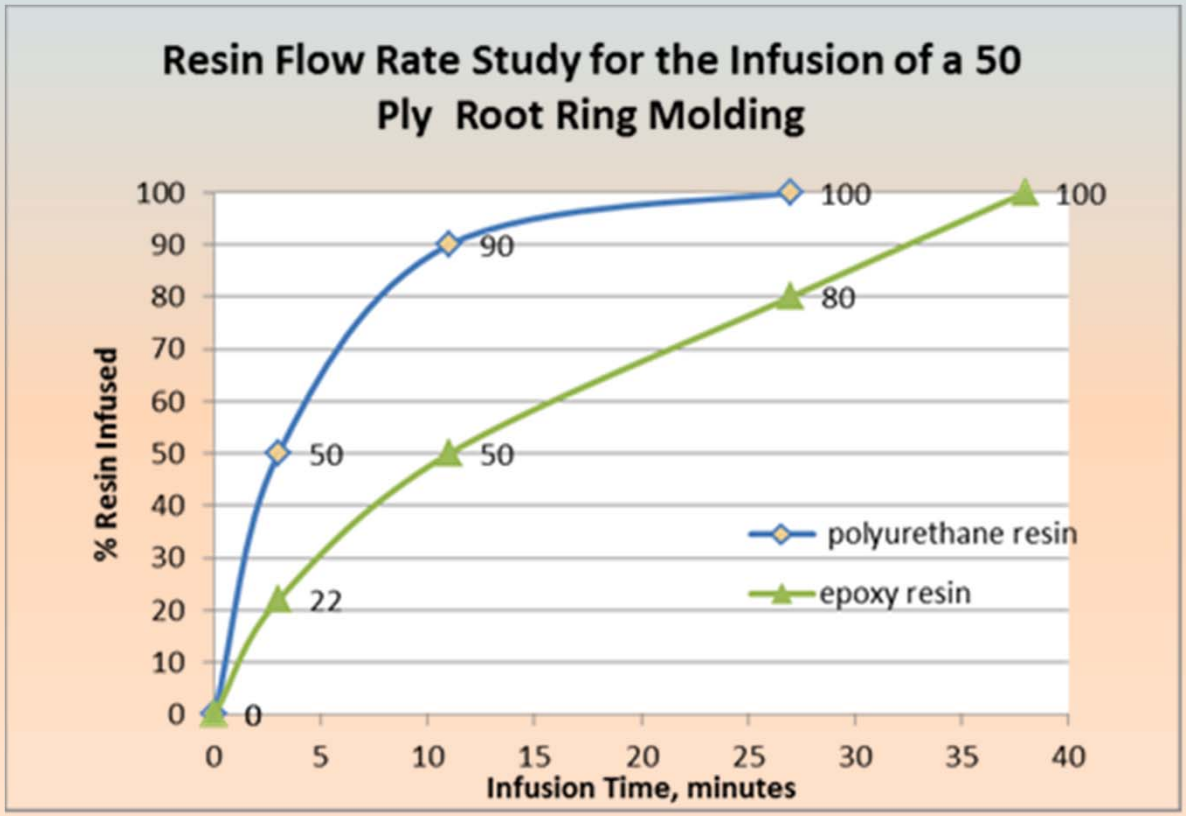
Faster Infusion



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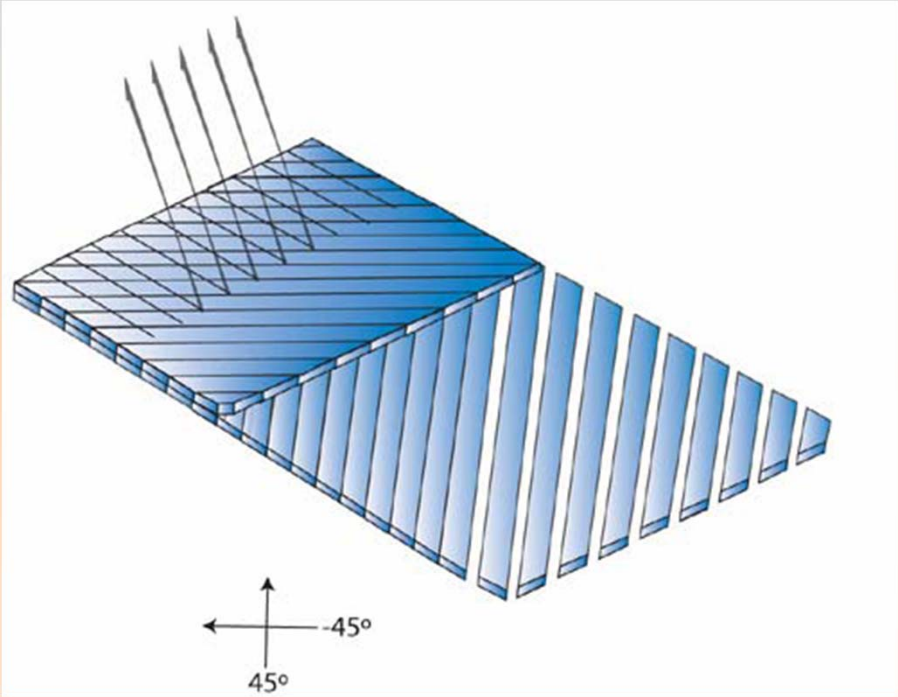
Reinforcements Used

- E-Glass
  - Vectorply E-BX 2400-5
  - 820 g/m^2 biax weave
  - Multi-compatible sizing
- Carbon Fiber
  - Vectorply C-BX 1800-5
  - 580 g/m^2 biax weave
- Carbon Fiber unidirectional
  - Toray
  - Toho



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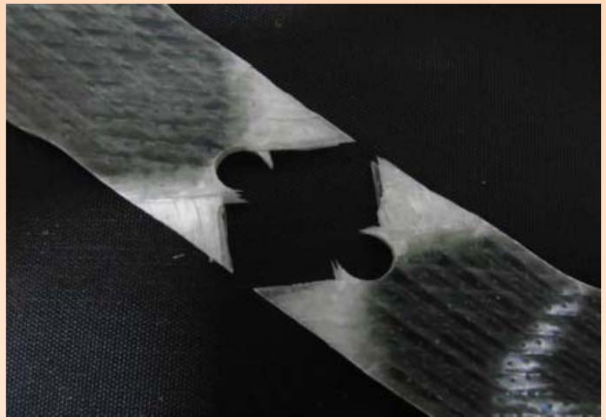
Composite Tensile
J Mater Sci (2008) 43:4487–4492

- 6 ply biax, tested at 45°
- Accutek testing labs

Sample	Ultimate Tensile Str. MPa
Epoxy	133.3
Vinyl Ester	129.5
Polyurethane	155.3



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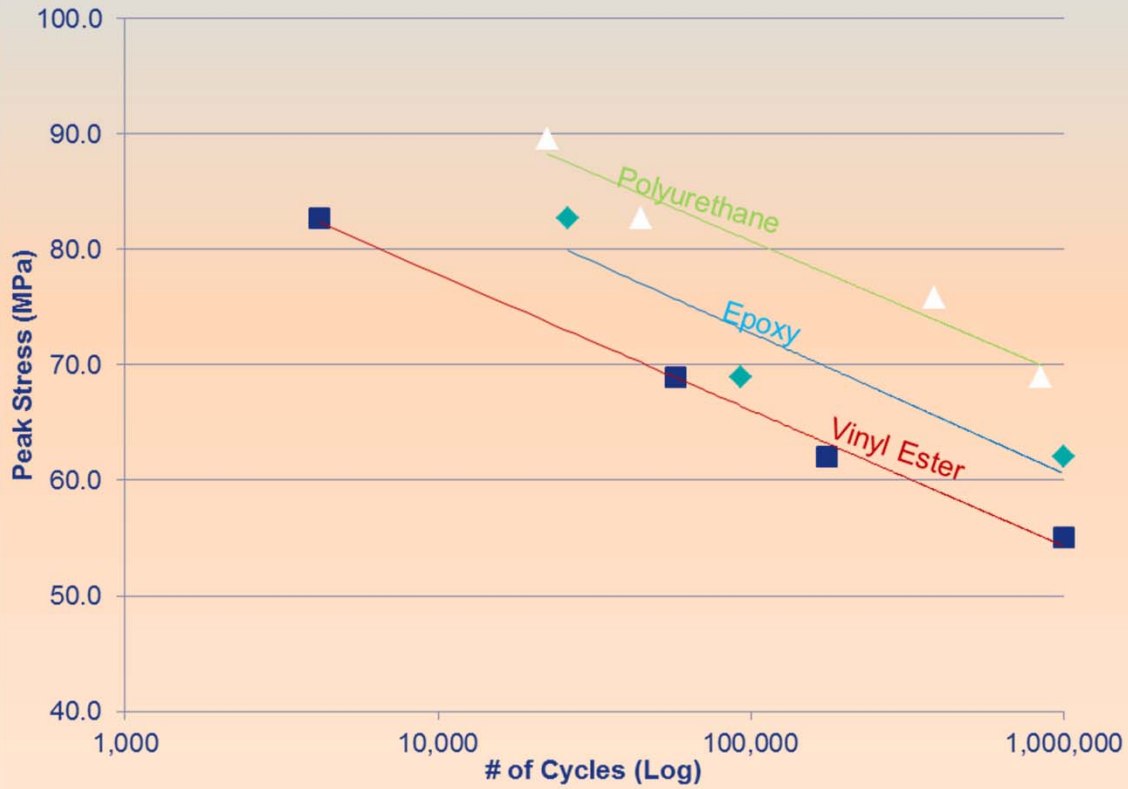
Tensile-Tensile Fatigue

- Tested 45° to fiber direction
- R Ratio = 0.15
- Frequency = 3 Hz



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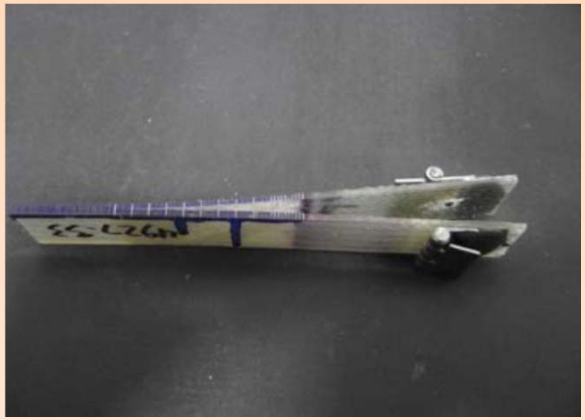
Interlaminar Fracture Toughness -G1C

- ASTM D5528
- Interlaminar fracture toughness
- 6 ply biax glass tested at 45° to fiber direction



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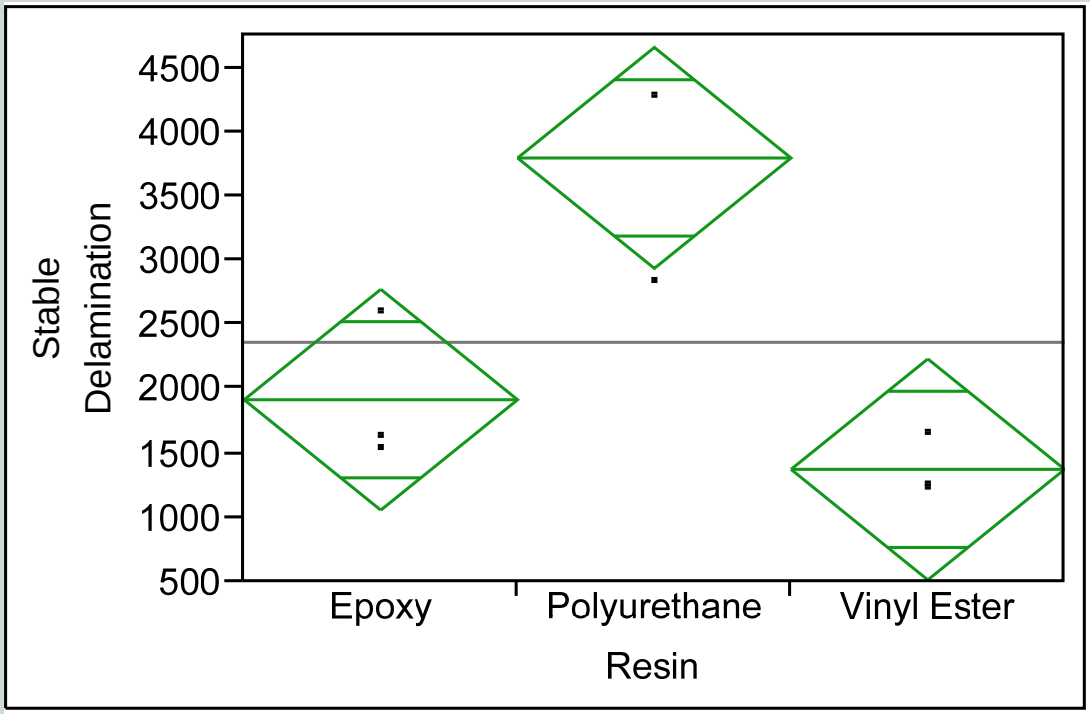
Superior Interlaminar Fracture Toughness

- Biax Glass fabric
- Tested at 45º to fiber
- P value = 0.007

Resin	G1C J/m²
Bayer	3798
Epoxy	1918
Vinyl ester	1377



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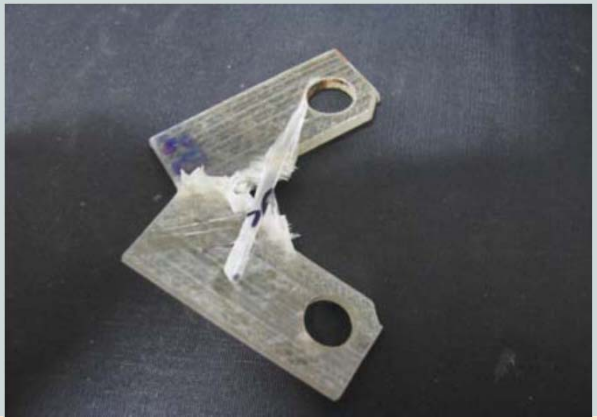
Fatigue crack growth

- ASTM E647
- R Ratio 0.1, 10 Hz
- Notch direction 45° to fiber direction
- Epoxy - At 24ksi/in stress crack growth Rate 2.4E-05 in/cycle
- Polyurethane - At 24ksi/in stress crack growth Rate 1.7E-06 in/cycle



Test coupon shown above

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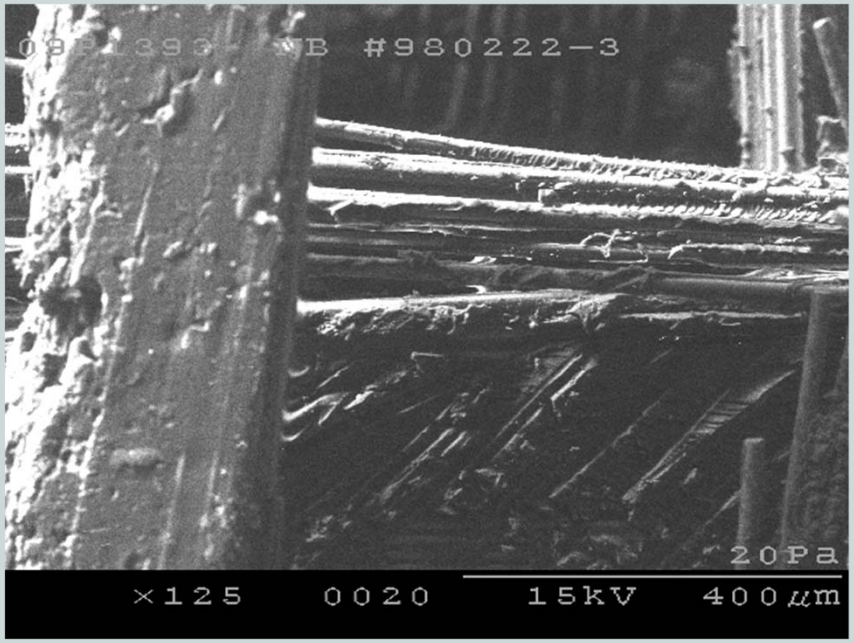
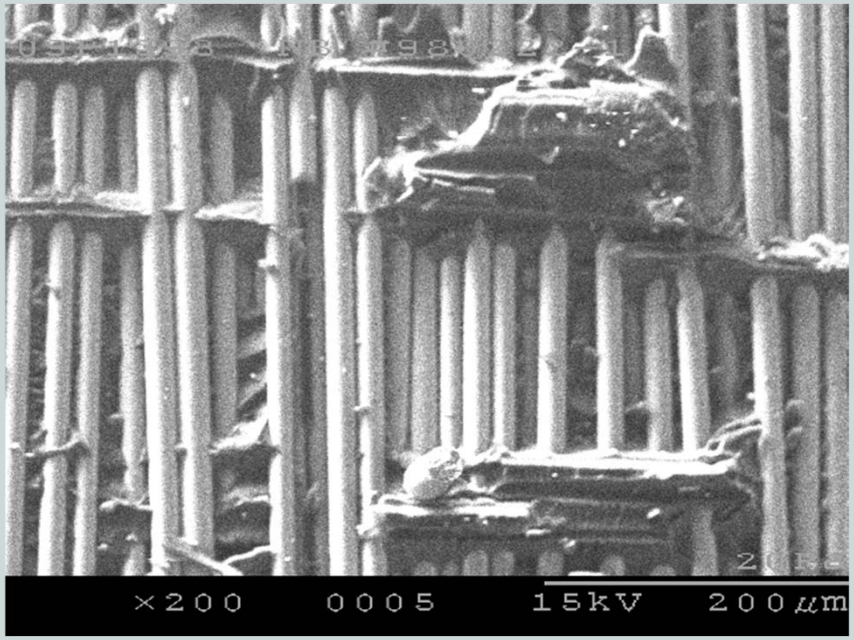
Better Adhesion to Glass Fiber

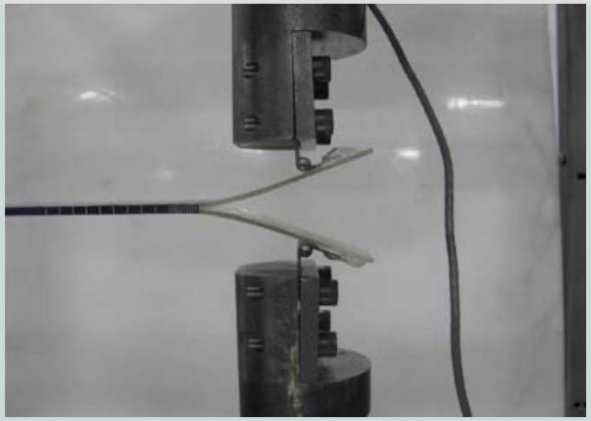
- Bayer PU Resin
- Epoxy Resin

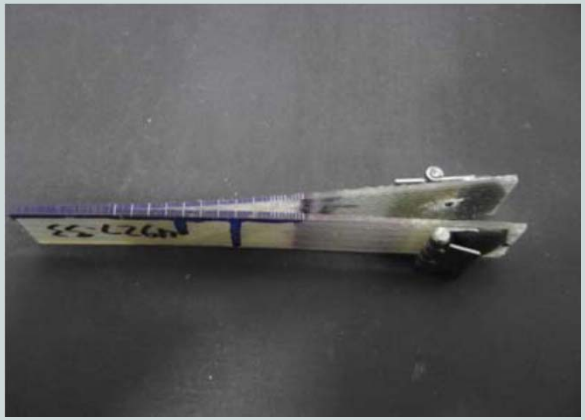




Polyurethane/carbon fiber composites

- ASTM D5528 Mode I
- Interlaminar fracture toughness with unidierctional carbon
- Epoxy 1512 J/m²
- Polyurethane 3116 J/m²





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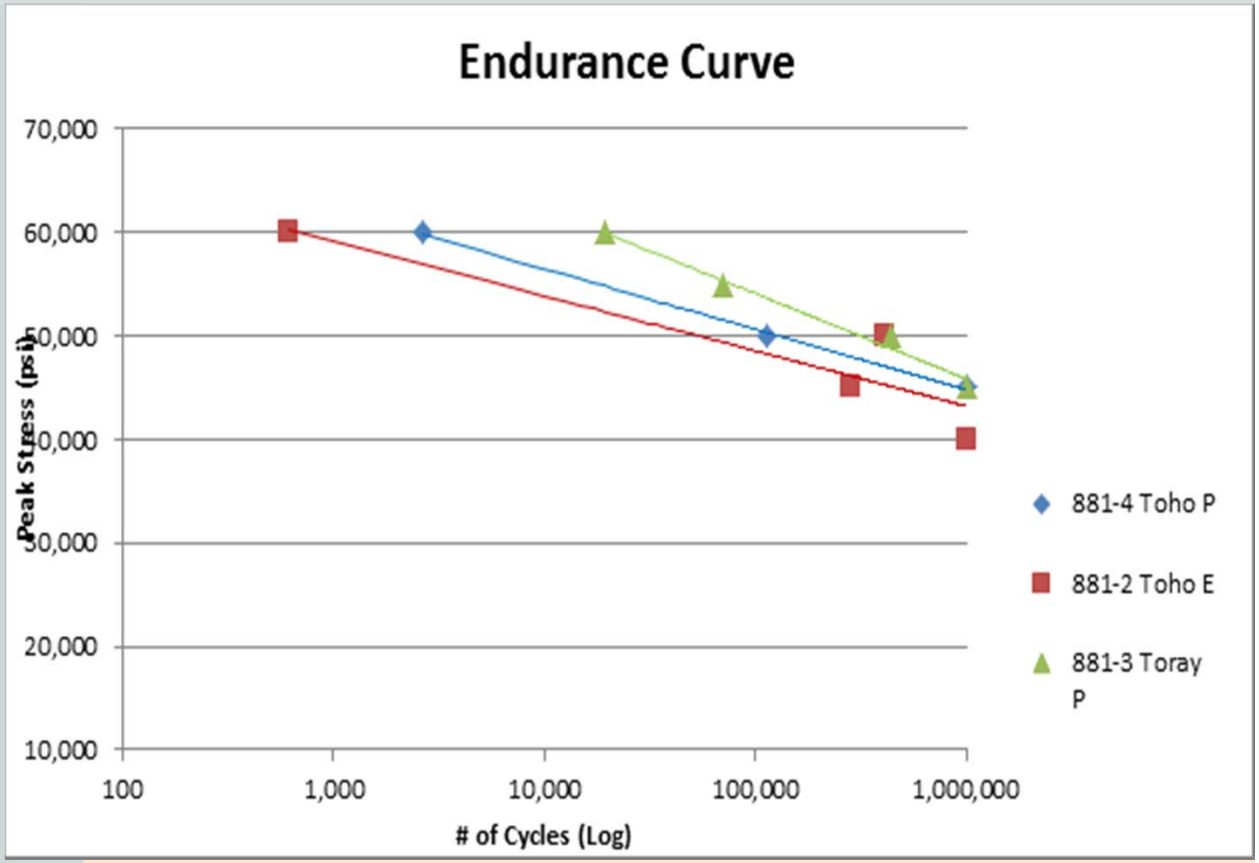
Tensile-Tensile Fatigue
Uni Carbon Fiber

- Tested 0° to fiber direction
- R Ratio = 0.15
- Frequency = 3 Hz



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Compressive Data

- Using uni- S glass
  - Comp str. PU = 840 MPa Epoxy 630 MPa
- Using E glass Unidirectional
  - In fiber direction
    - ❖ Comp Str. PU = 650 MPA E- Modulus= 45 kMPa
  - Perpendicular fiber
    - ❖ Comp Str. PU = 210 MPa, E-Modulus = 15 kMPa

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Results and Conclusions - Polyurethane

- Developed Two Polyurethane systems designed for vacuum infusion
  - Conventional polyether and Soy based polyols
- Glass and Carbon fiber reinforced Polyurethane composites are superior to epoxy , polyester, and vinyl ester composites
  - Fatigue resistance; Fracture toughness; Tensile strength; Fatigue crack growth resistance, Impact, and elongation.
  - Lower Shrinkage
  - 42 meter Blade Root Ring Molding Demonstrated
  - Faster Demold than Epoxy
  - Potentially a reduction in the cost of making a blade

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MWCNT Challenges

- Dispersion
- Re-agglomeration
- Viscosity limitations
- Performance advantages

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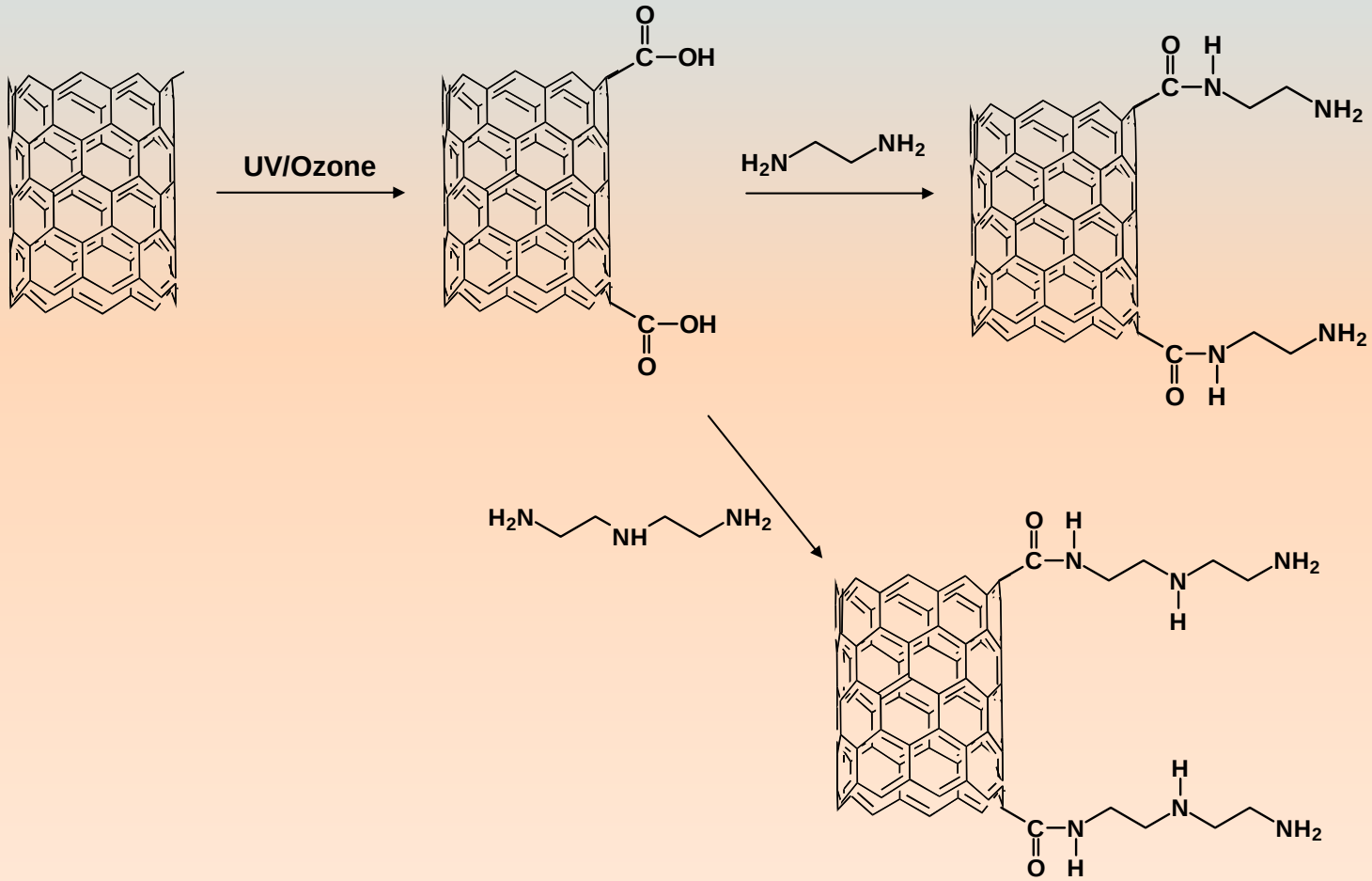
Non Functionalized and Functionalization CNT



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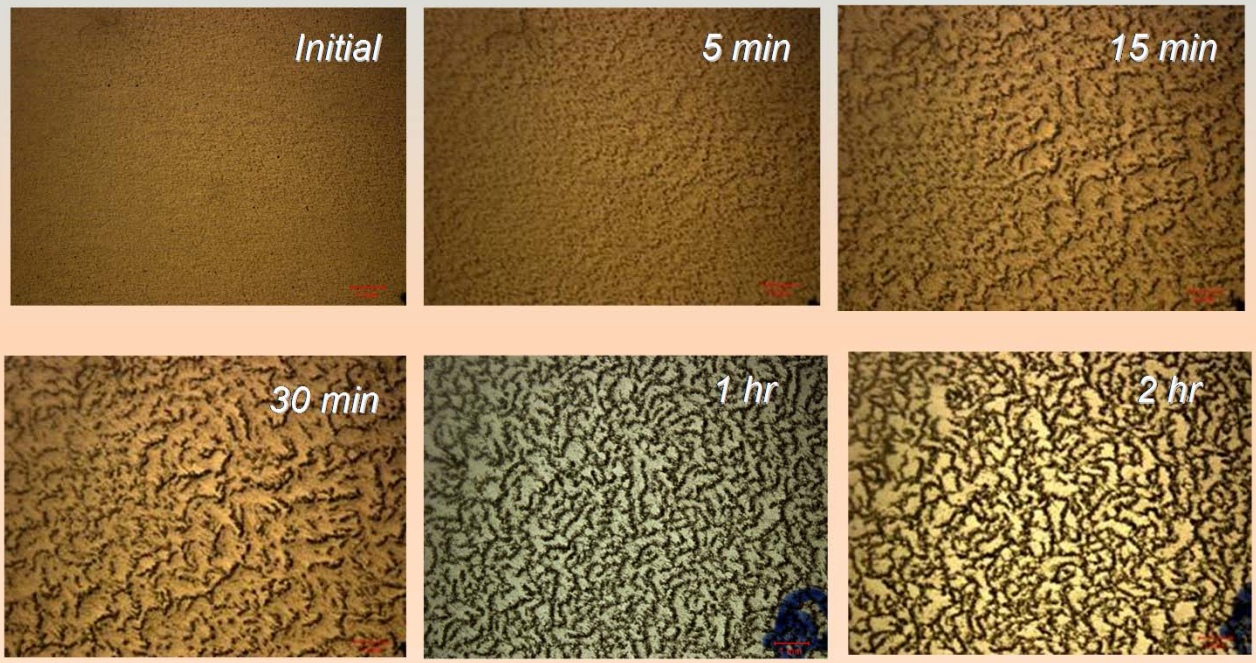
Re-agglomeration on CNT in Polyurethane



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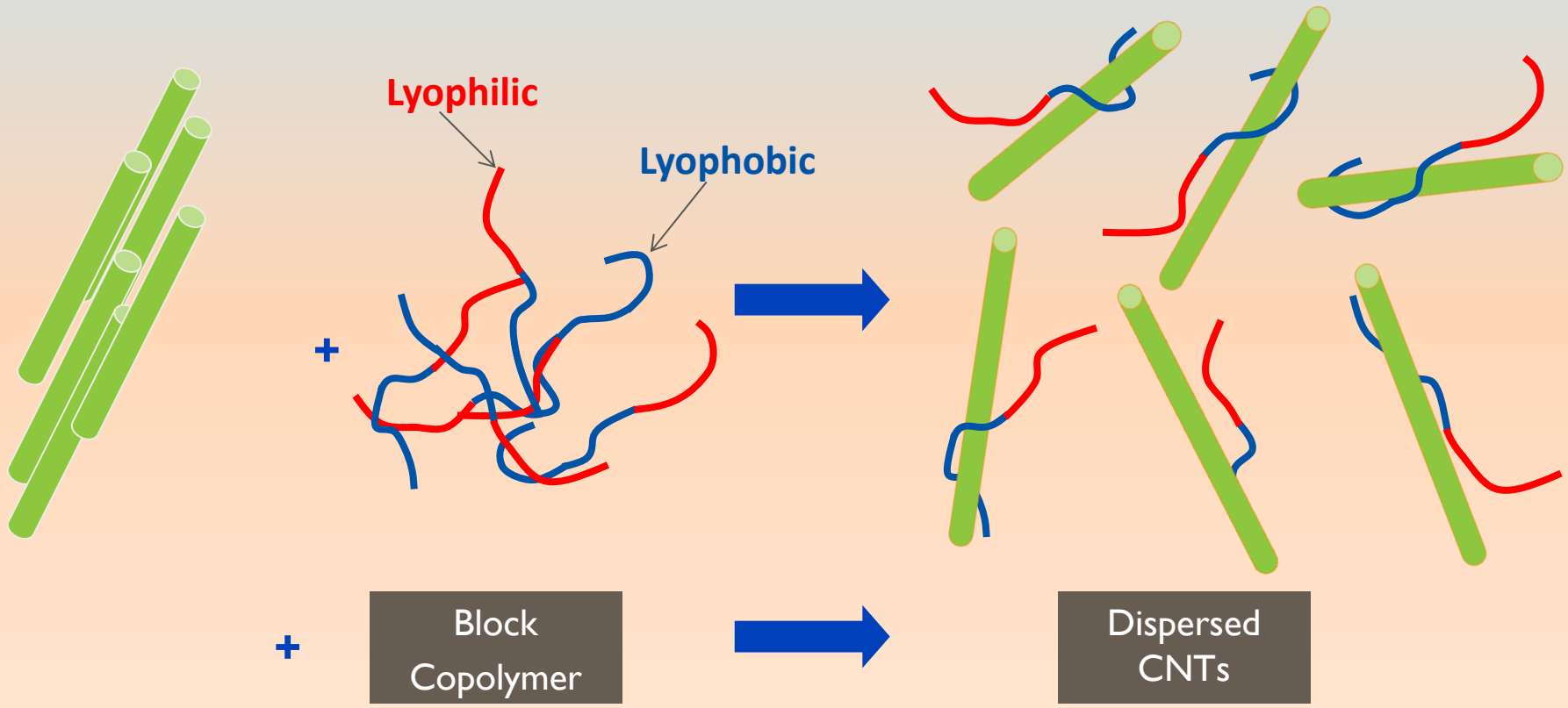
Block Copolymers as Dispersing Agents



J. Cho, I. M. Daniel / Scripta Materialia 58 (2008) 533–536

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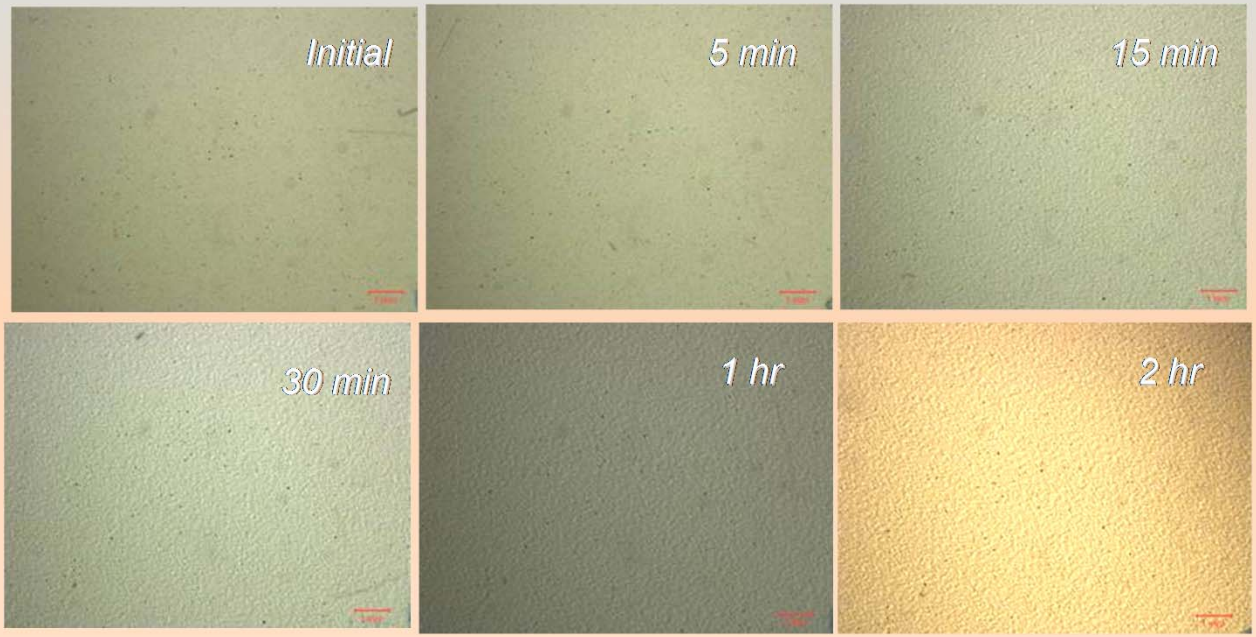
Effect of additives on Re-agglomeration on Carbon nanotubes in polyurethane



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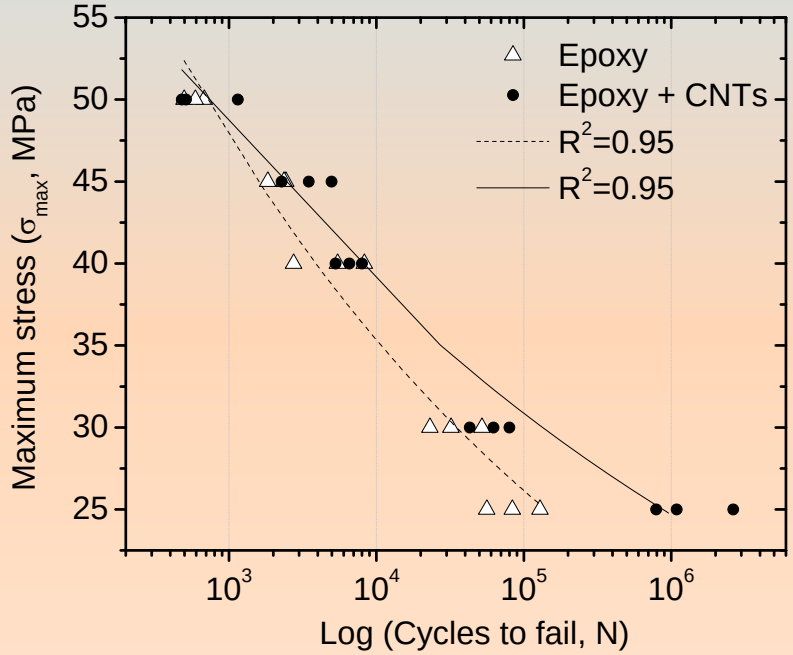
Fatigue of Neat Epoxy nanotubes measured at CASE



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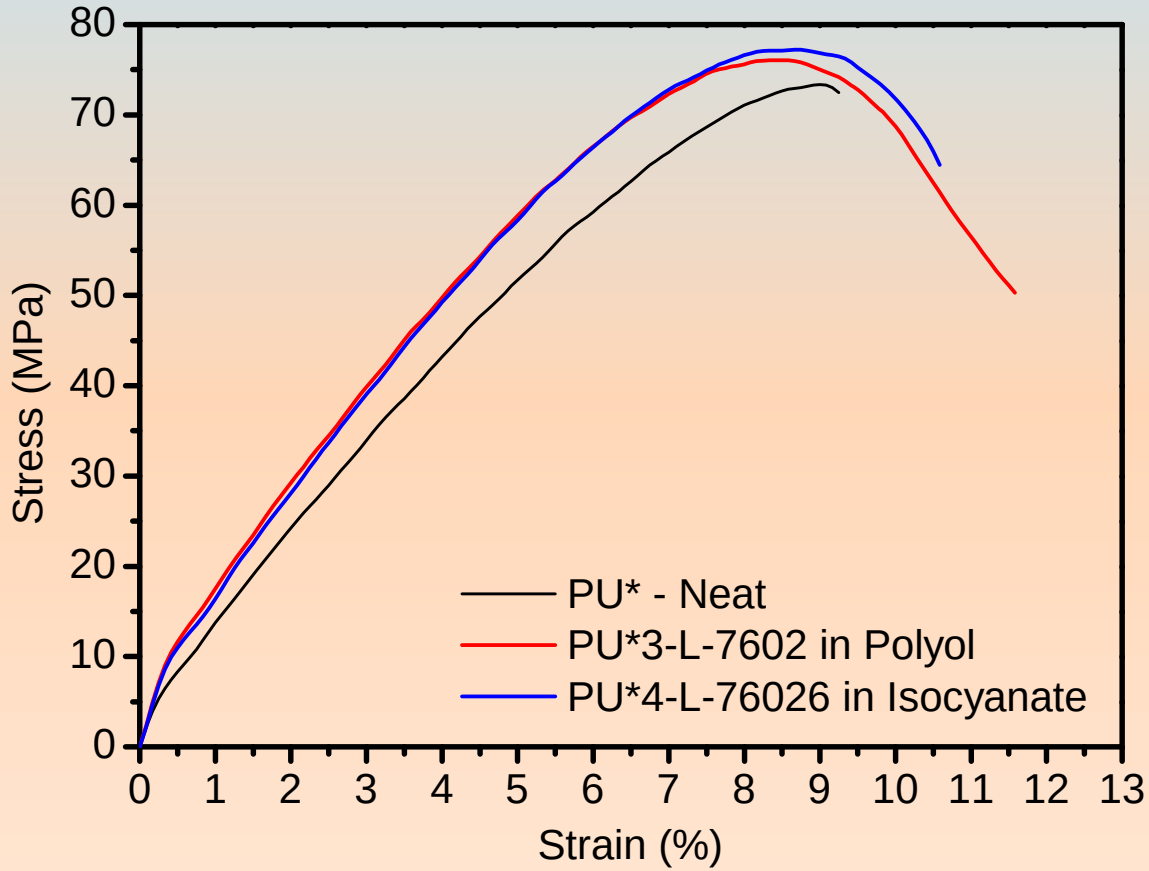
CASE Tensile Neat PU and PU/CNT



Representative stress-strain curves for the polyurethane based nano-composites. The CNTs amount is 0.1 wt.% in relation to polyol whereas the dispersing agent amount is 10X the amount of CNTs.

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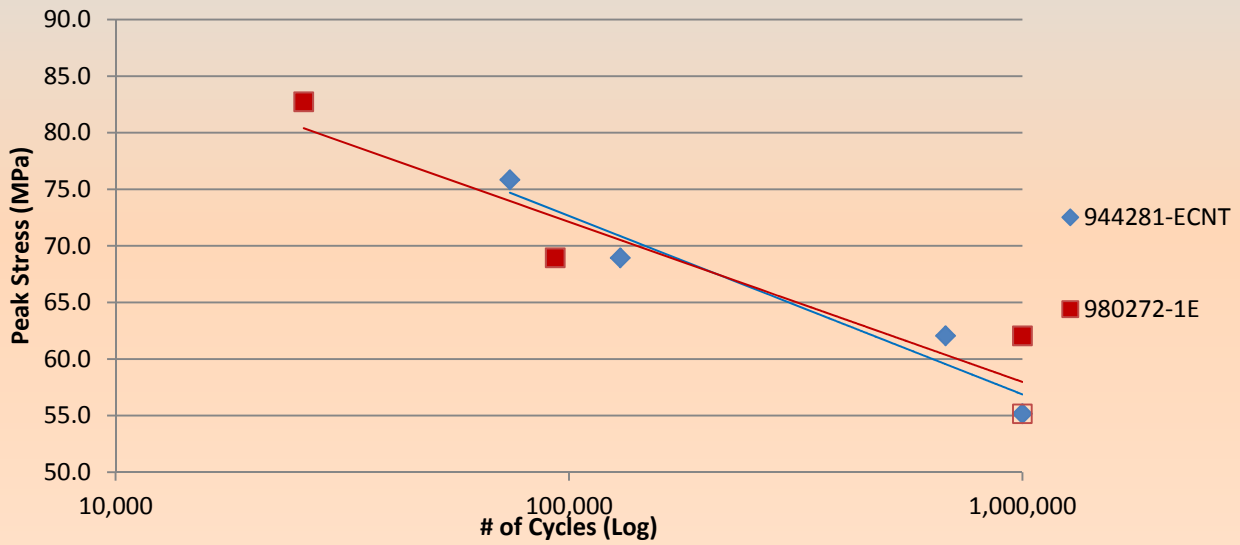
Tension-Tension Fatigue of glass reinforced Epoxy Resins with and without MWCNT



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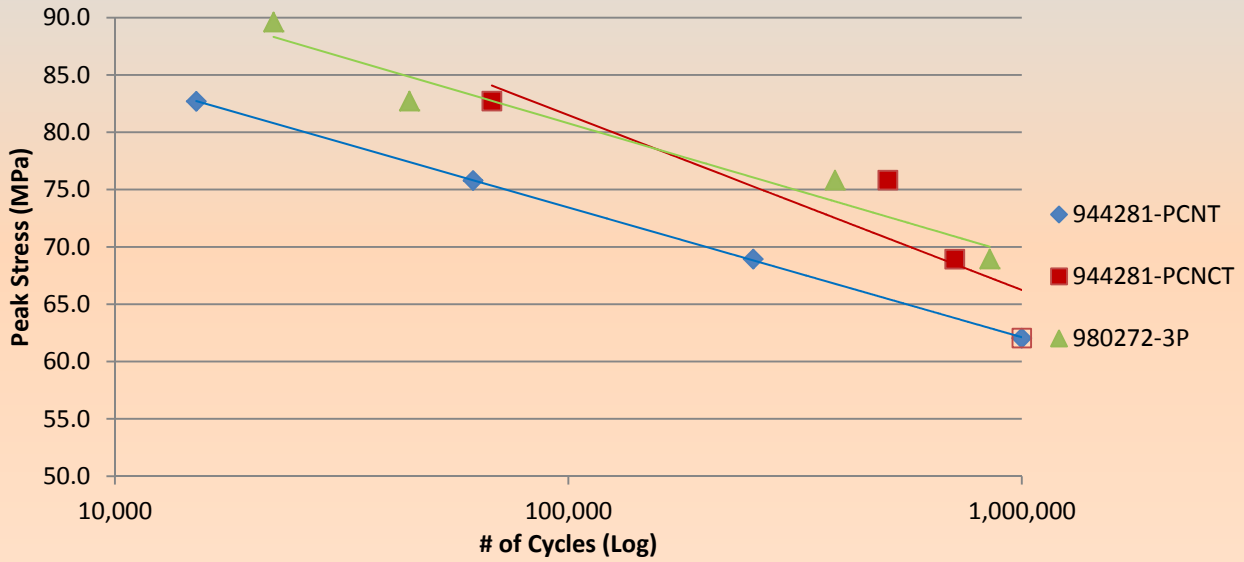
Tension-Tension Fatigue of Polyurethane Composites with and without MWCNT



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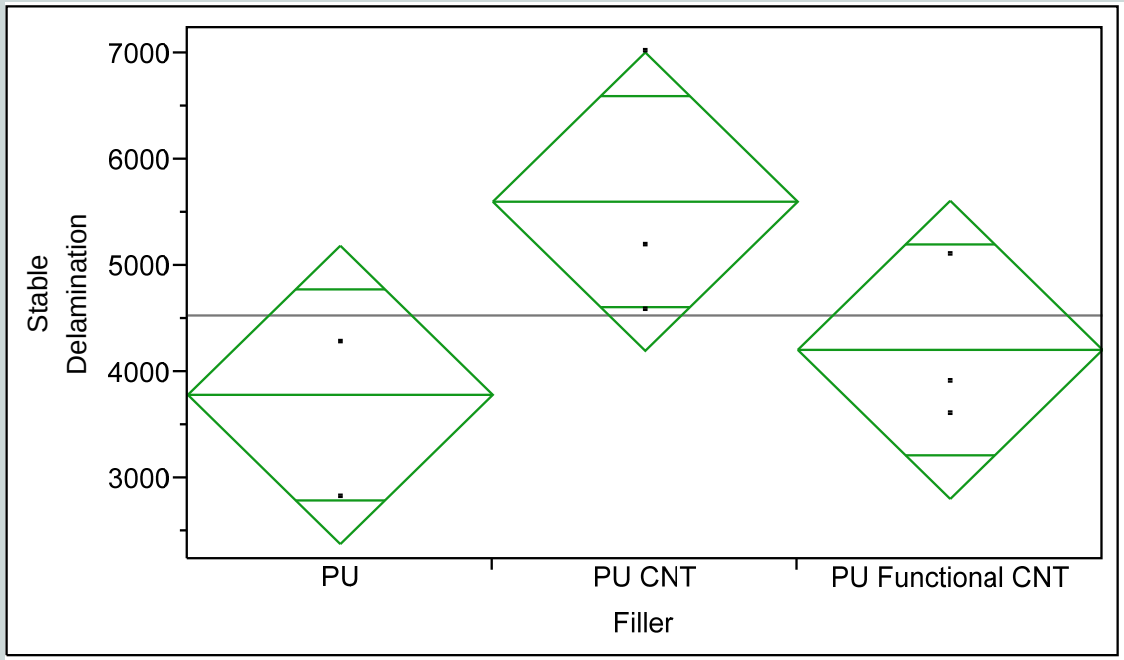
MWCNT further improves Interlaminar Fracture Toughness in PU

- Biax Glass fabric
- Tested at 45º to fiber
- P value = 0.142
- Resin + 0.38% MWCNT

Resin	G1C J/m²
Bayer	3798
Bayer + MWCNT	5617
Bayer + FMWCNT	4222



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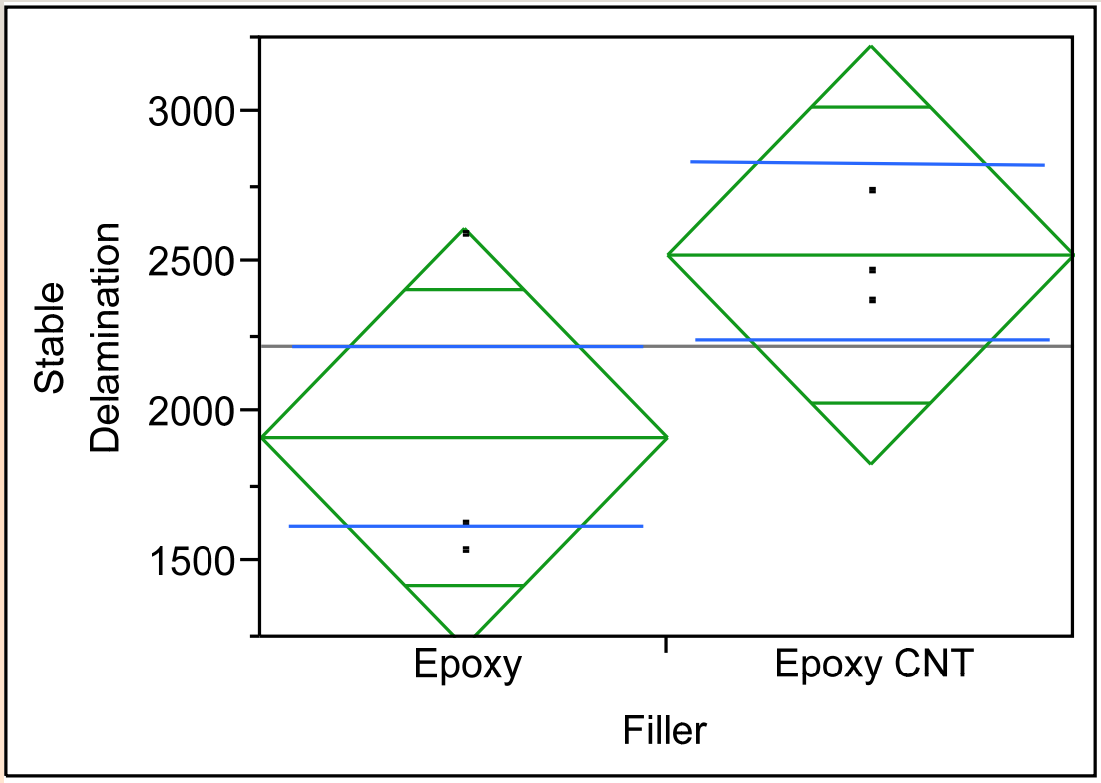
Interlaminar Fracture Toughness in Epoxy
ANOVA, P value = 0.162



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Results and Conclusions Carbon Nanotubes

- Carbon nanotubes dispersion stability is dependent on dispersing aids
- Carbon nanotubes reinforces the neat resin properties of polyurethane, epoxy and vinyl ester
  - Improved Tensile and Fatigue
- Carbon nanotubes reinforced glass fiber reinforced composites
  - Improves fracture toughness (G1C) both in epoxy and polyurethane systems
  - Improvement in fiber reinforced composites is largely dependent on what dominates properties Fiber or Resin
  - Improves electric and thermal conductivity of composites

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The Technical Collaboration Team

- Bayer MaterialScience
  - Usama Younes, Eric Giles, Robert Gastinger, Mike Wellman, Stephen Bailey, Al Magnotta, Tom Sekelek.
  - Serkan Unal, Robert Hunt, Jennifer Nau.
- Case Western Reserve University
  - Marcio Loos, Jingting Yang, Donald L. Feke, Ica Manas-Zloczower.
- Molded Fiber Glass
  - Frank Bradish, Peter Emrich, Richard Sesco

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