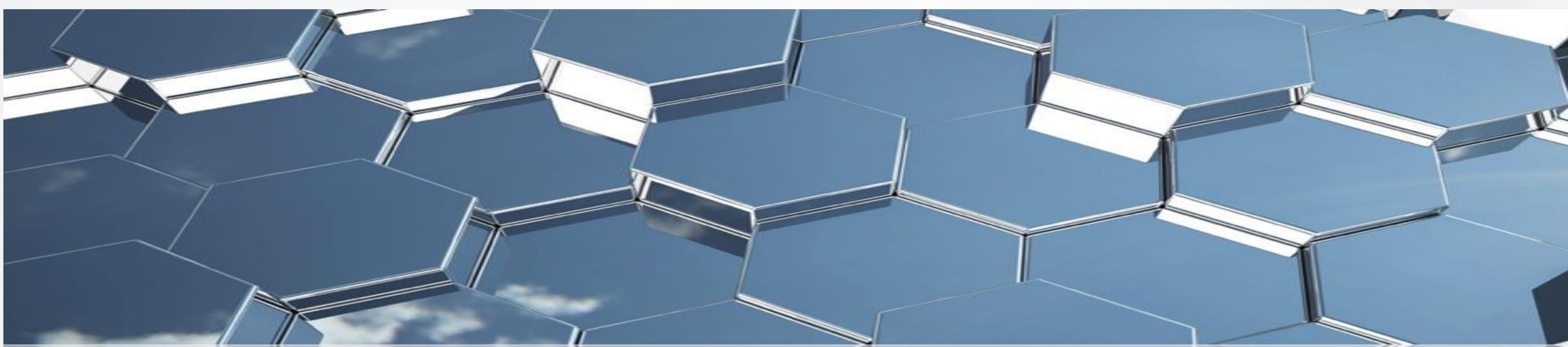
New Insights into Controlling Sub-micron Failure Mechanisms in Composites using Discrete Functionalized Multiwall Carbon Nanotubes, Molecular Rebar™

C.P. Bosnyak



Special Thanks

Organizing Committee for the Symposium celebrating the 75th Year of Prof. Alexander Chudnovsky.

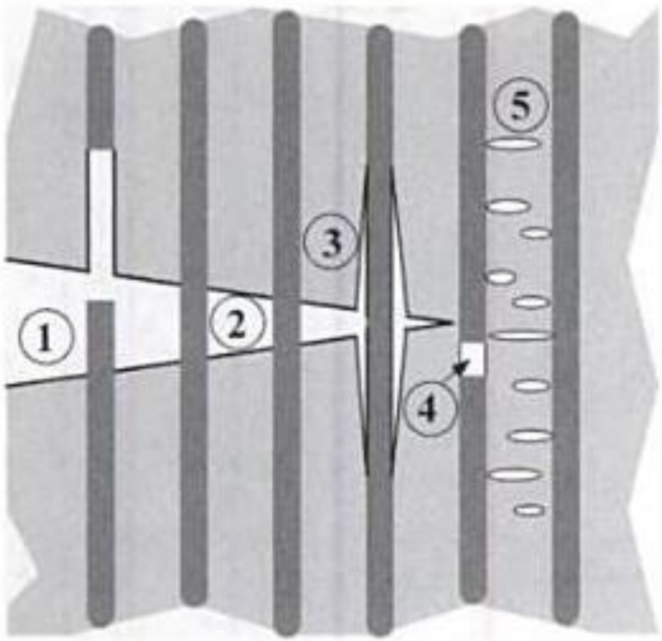
In particular : Victor Berdichevsky
Ephraim Suhir

Unmet Needs in the Composites Industry

- Mass Transportation – train, bus
  - Light weighting – fuel economy
  - Surface quality (out of the mold)
  - Flame retardant – all mass transport
- Wind
  - Increase turbine capacity using longer blades
  - Improved resistance to failure (especially seawater)
- Aerospace
  - Reliability
  - Lighter and larger parts at same stiffness
  - Corrosion resistance
  - Better static electricity management (lightning strikes)
  - Repair

Fiberglass → FG & carbon fiber hybrids → FG, CF, Nanotechnology hybrids

Basic failure mechanisms of epoxy-fiber composites



(a) In-plane damage.

1. Fiber Pull-Out.
2. Fiber Bridging.
3. Fiber/Matrix Debonding
4. Fiber Failure.
5. Matrix Cracking.

Initial scale of failure in epoxies on submicron scale – **aim of nanocomposites is to control failure at this scale**

Failure in composites often due to interlaminar cracking

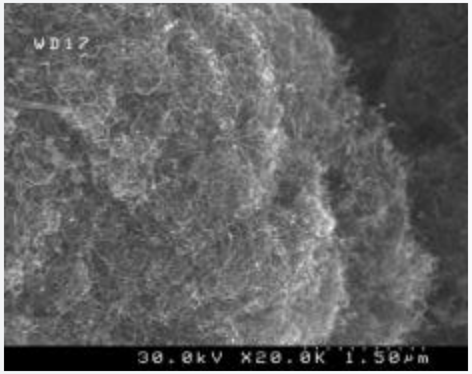
Literature

- Several studies on epoxy and carbon nanotubes since 1993.
- Almost all studies show MWNT agglomerates.
- Tubes typically contain 10-20% residual catalysts and soot.
- Mechanical properties show bonded tubes much better than non-bonded.
- Conductivity highly dependent on amount and dispersion state of tubes.
- For improved dispersions need to modify the thermodynamics of the tube surface and detangle
  - Highly dependent on epoxy-hardener type

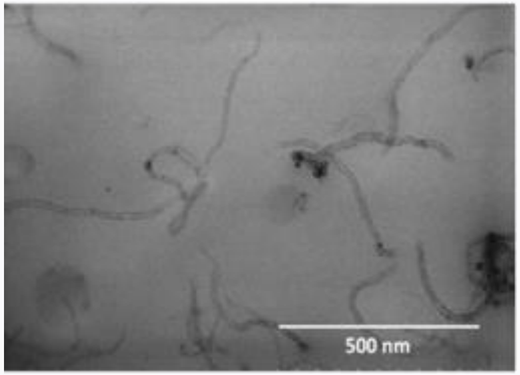
Molecular Rebar™ (MR)

Key Competitive Advantage

External Purchase of MWCNT's → Exfoliation/ Separation → Formulation - Dispersion → Master Batch - Concentrate → Customer Integration into end-product



Clumps of entangled CNT's

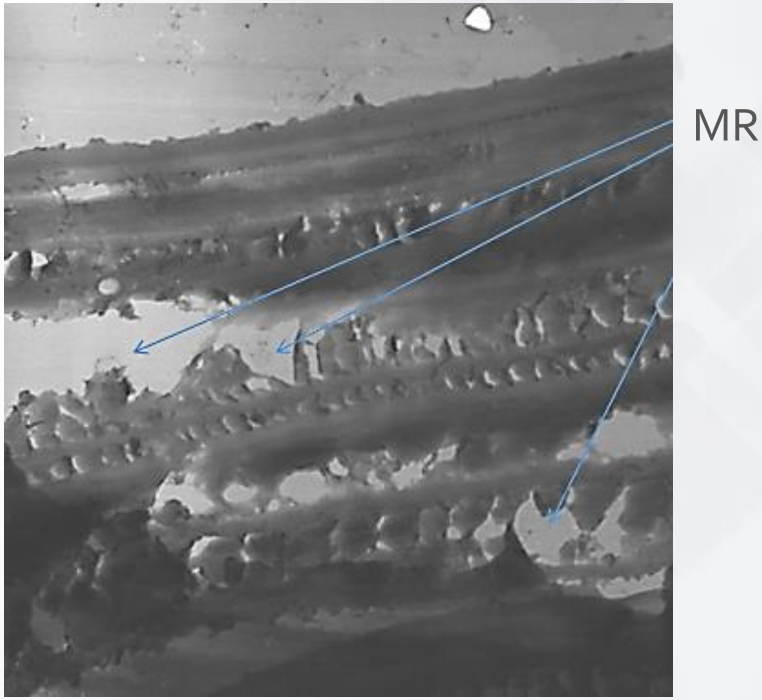


Clean, Discrete Tubes
10 walls
Aspect Ratio 60-100
13nm x 800nm
Surface modified for Dispersion & Bonding

Integration into parts

Advantages of MR

- Discrete, well-dispersed carbon nanotubes can move within plies without filtering
- Bonded to matrix to improve inter-laminar shear modulus and strength
  - Reduced mechanical stress gradients
  - Reduced thermal coefficient of expansion – reduced stress gradients (also cure)
  - Increased crack resistance



→ Increased durability, improved safety

Challenges for Nanotube Reinforcing Thermoset Composites

- Many varied performance requirements for a broad set of applications
- Many varieties of chemistries
- Impossible to test all variations…
- *so - Can we begin to develop a set of "Materials Design Rules for Durability" with MR?*

Chudnovsky Approach to Durability Assessment

- Consider the environment the material is to survive in
  - Stress state, Temperature, Time, Surrounding medium, etc.
- Quantify the initial material structure
  - Consider Homogeneity vs Heterogeneity relative to scale of measurement
- Identify & quantify the possible mechanisms of failure dependent on the external imposed variables
- Model – "Predict with Understanding"
  - Challenge is to predict Failure ***Initiation*** as well as Failure Propagation

Notch Sensitivity Index, K

X. Nui et al. “Notch Sensitivity of Pipe Grade Polyethylene and Polybutylene” ANTEC 2000 - Proceedings of 58th Annual Technical Conference & Exhibition, Vol. XLVI, Orlando Fl., May 7-11, Society of Plastics Engineers, p 3162-3106

Test Unnotched versus Notched

Impact Energy

$$K_e = \lim_{a \to 0} \frac{W}{W(a)} = 1 + \frac{W_{i.}}{W_{p.}}$$

Time to creep failure

$$K_t = \lim_{a \to 0} \frac{t}{t(a)} = 1 + \frac{t_{i.}}{t_{p.}}$$

Which part of this ratio do nanotubes influence?

Materials that have higher notch sensitivity are probably less reliable under load considering the presence of defects.

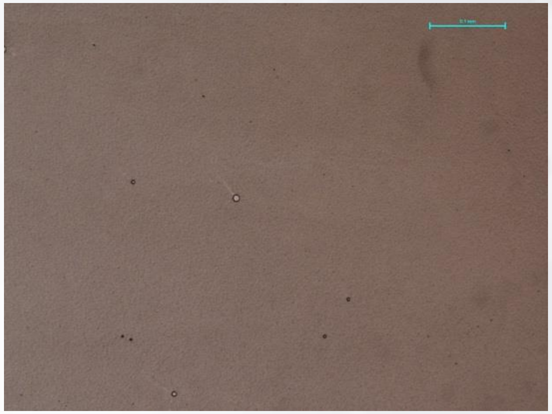
Thermoset Resin Systems

- Bisphenol A / Jeffamine D230
  - Cure profile: 2hr 100°C, 1hr 150°C; Tg 95°C
- Bisphenol F / TETA
  - Cure profile: 2 hr 100°C; Tg 105°C
- TGDDM / DDS
  - Cure profile: 2 hr 120°C, 1hr 150°C, 2hr 177°C, 4 hr 200°C;Tg 290°C

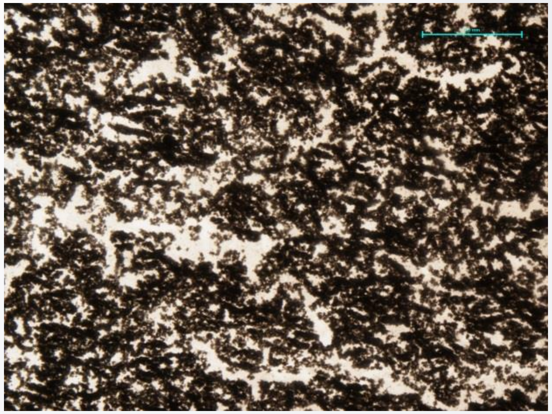
Challenge of nanotube dispersion

- High surface area of MR ~ 250 m^2/g means small changes in surface energy differences strongly affect degree of dispersion.
- Challenge is to keep the dispersion while the epoxy components are mixed and during curing.

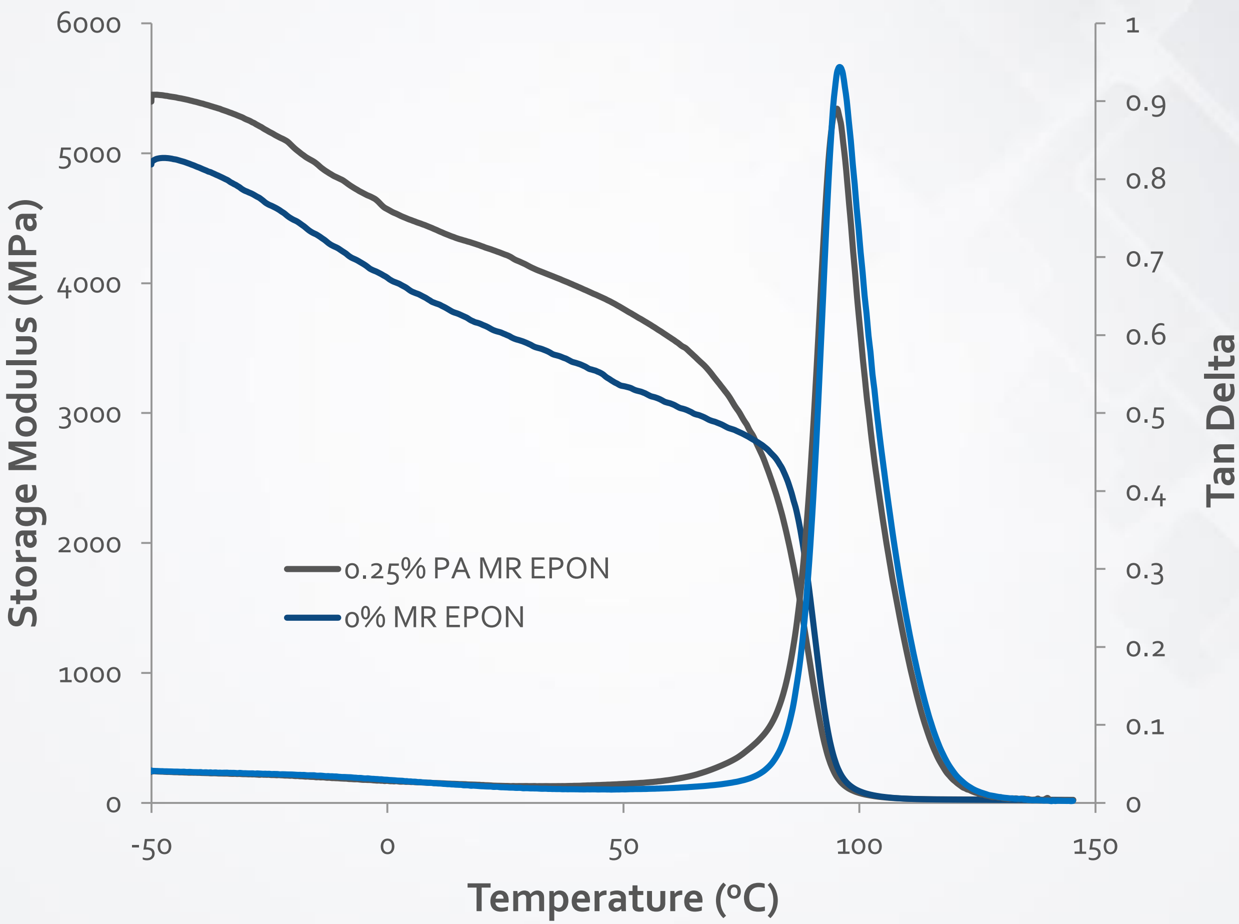
0.25% w/w MR treated



0.25% w/w MR not treated



Thermomechanical Characterization of Epon 828 + MR



No significant sub Tg transitions to -50°C

Testing Procedures

Single edge notched bending

- SENB - ASTM E1820, Test conditions: -78 to 60°C, 10mm/min.
- $K_{1c} = \frac{PS}{BW^{\frac{3}{2}}} f(x)$ s= span (4") , P = load

  Where $f(x) = 3x^{\frac{1}{2}}[\frac{1.99-x(1-x)(2.15-3.93x+2.7x^2)}{2(1+2x)(1-x)^{\frac{3}{2}}}]$ $x = a/w$

- Notched with a band-saw and crack initiated with a razor blade
- If crack moves faster to part failure than strain rate in SENB then $W_i > W_p$

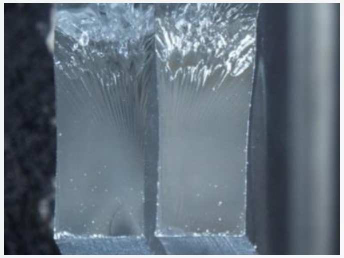
- Single edge notched tensile specimen for Bisphenol F epoxy
  - 1mm notch depth
  - $\sigma_{min}/\sigma_{max}$ 0.1
  - σ_{max} 16-17MPa
  - 1Hz, 25°C
  - Ramp test 0.25mm/min

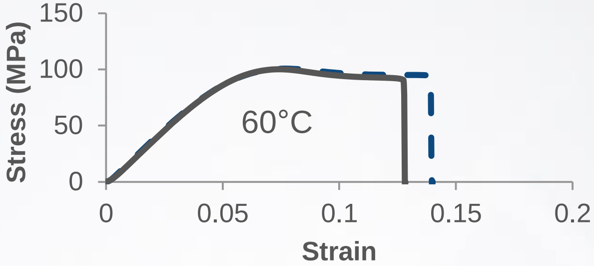
Unnotched Flexure w/wo MR

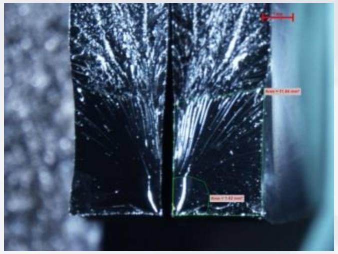
Control (Blue line)

0.25% MR type 1 (Black line)

60°C

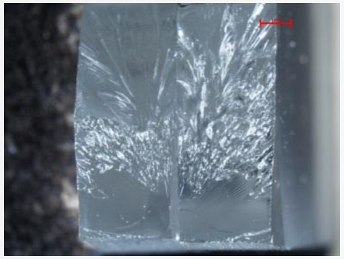


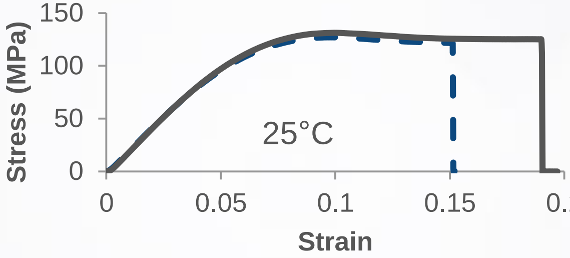


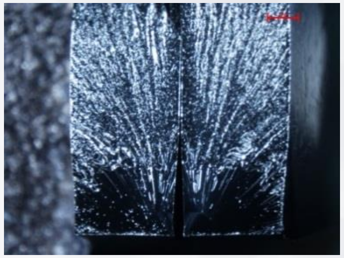


60°C

25°C

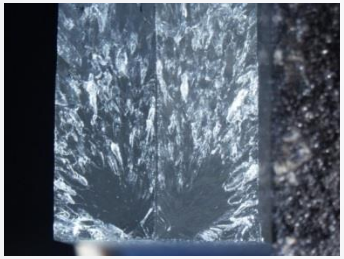


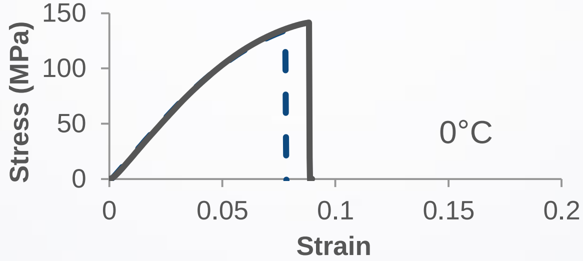


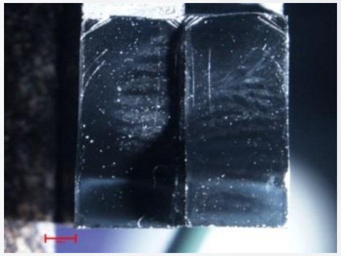


25°C

0°C

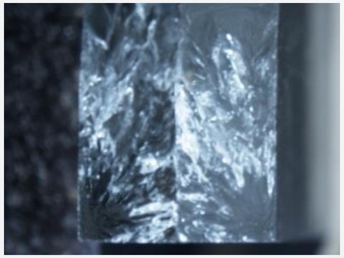


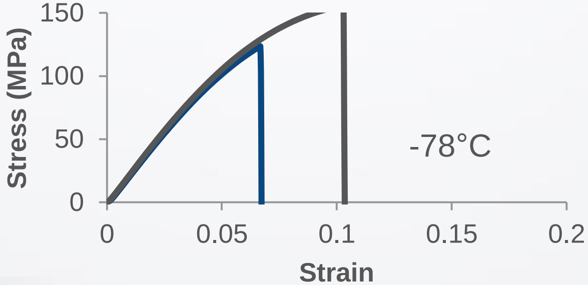


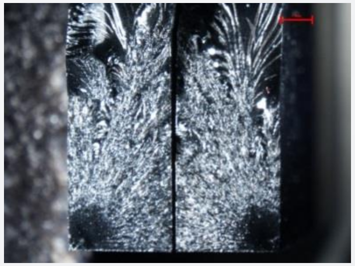


0°C

-78°C







-78°C

SENB, a/w ~ 0.5; w/wo MR

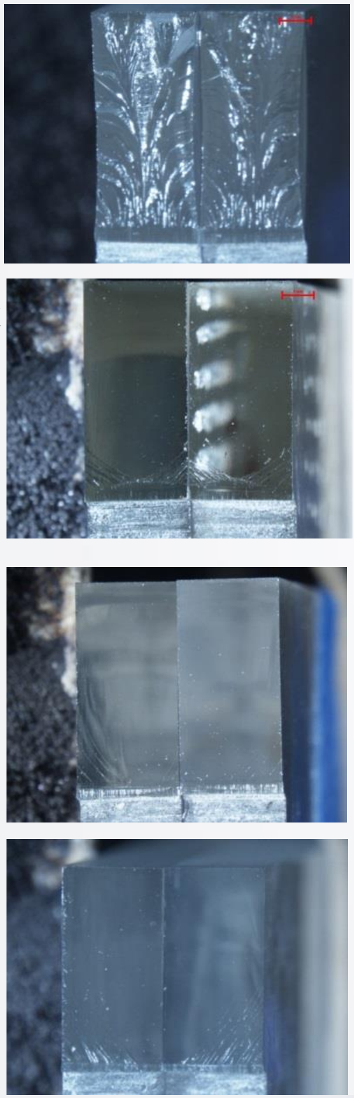
Control (Blue symbol)

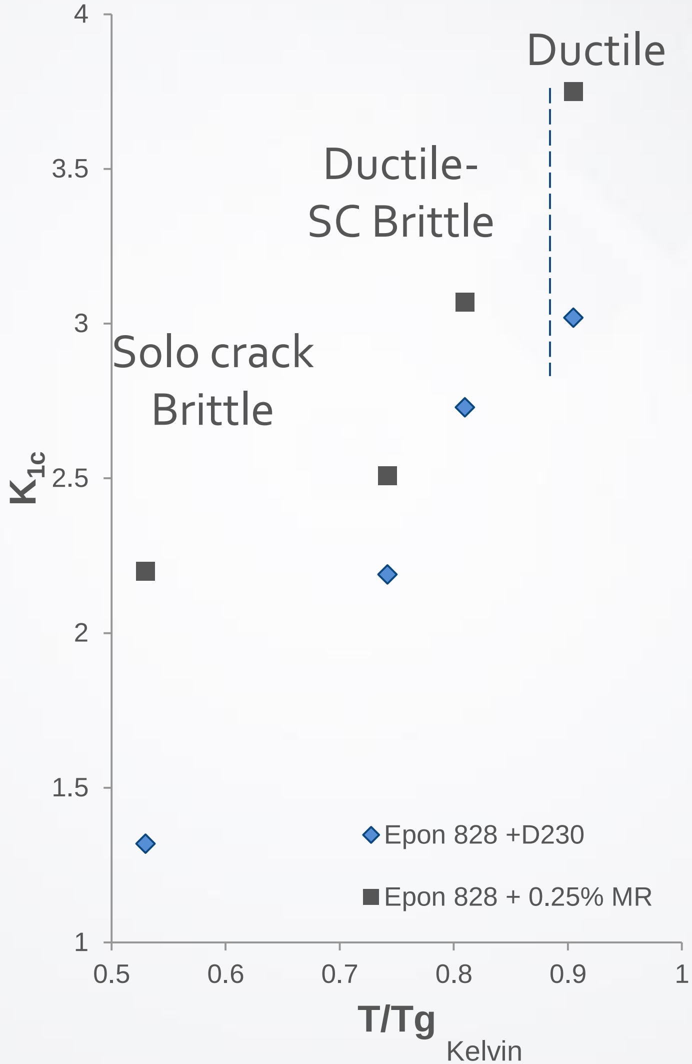
60°C

25°C

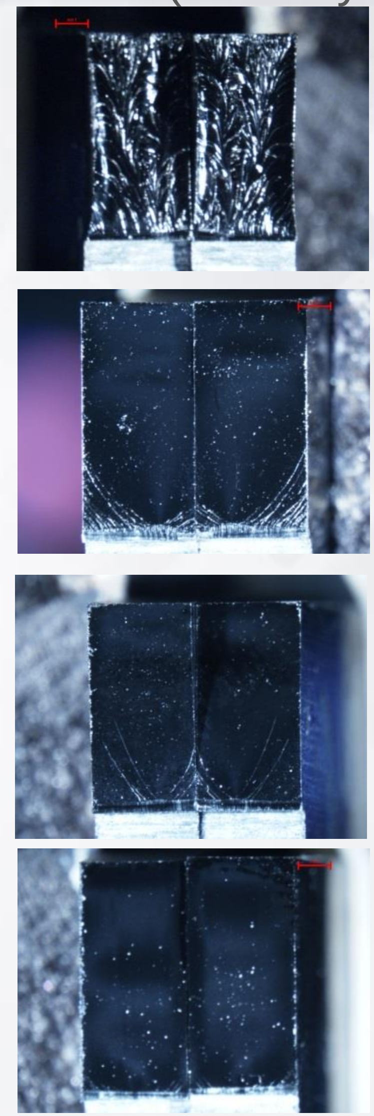
0°C

-78°C





0.25% MR (Black symbol)



60°C

25°C

0°C

-78°C

Notch Sensitivity Index values

Bisphenol A epoxy with Jeffamine

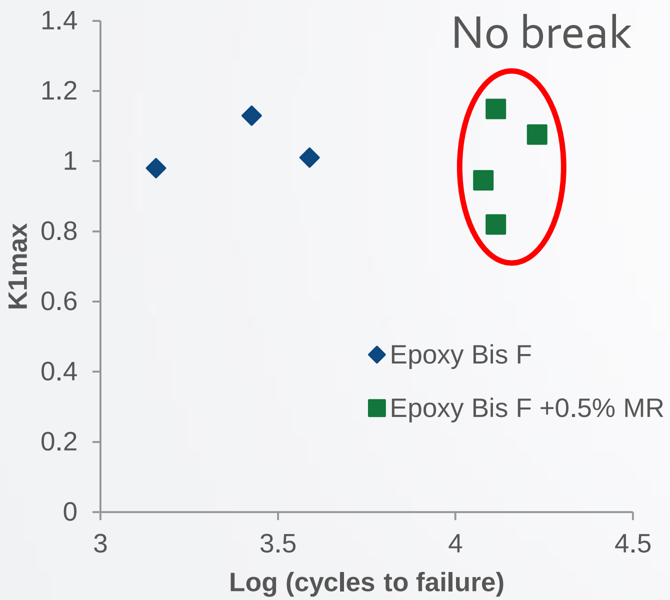
Epoxy + %MR	Temp °C	K_{1c}	NSI
0	-78	1.3	11
0	0	2.2	19.2
0	25	2.73	18
0.25%	-78	2.2	4.6
0.25%	0	2.5	14.2
0.25%	25	3.1	9.6

The values of K_{1c} and NSI, taken together with observations of the fractured surfaces are consistent with both W_i as well as W_p increasing with MR addition, but W_p is increasing relatively more than W_i on MR addition based on reduced NSI values.

Bisphenol F Epoxy cured with TETA

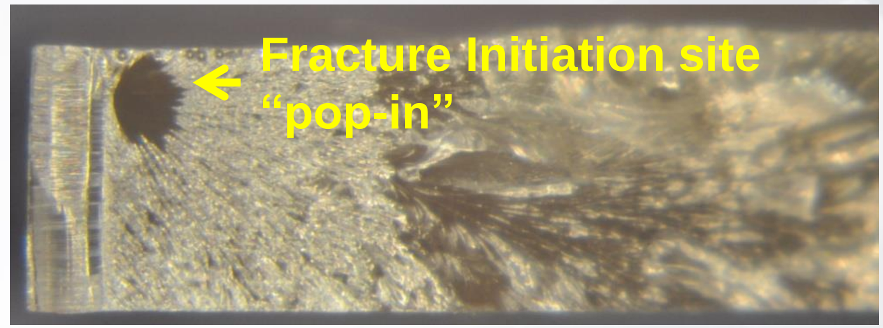
Tg = 105 °C; MR fully exfoliated in Bis-F Epoxy

0% wt MR K_{1c} (25°C) = 2.3 $MPa.m^{0.5}$
0.25% wt MR K_{1c} (25°C) = 2.7 $MPa.m^{0.5}$
0.5% wt MR K_{1c} (25°C) = 3.3 $MPa.m^{0.5}$

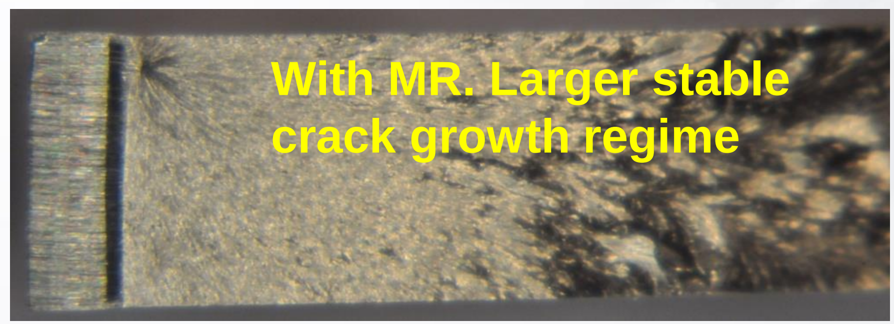


Ramp test

Fracture Surface of Bis F Epoxy



Bis F Epoxy and 0.5% wt MR

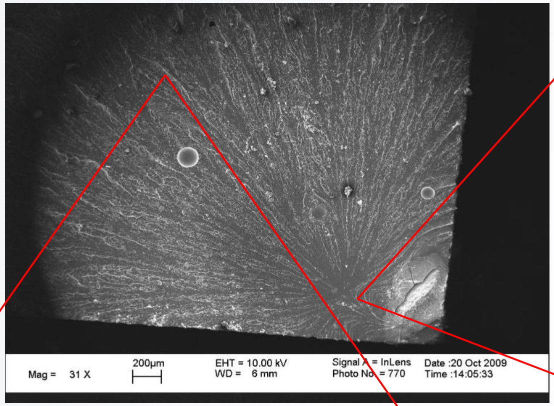


- **Increased fatigue fracture resistance at least 5X**

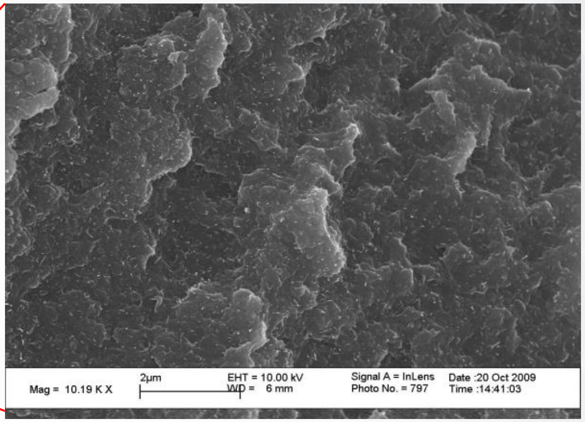
Electron Microscopy Gold sputtered

Fracture surface of unnotched tensile bar of 1% wt MR Bisphenol F epoxy

31X



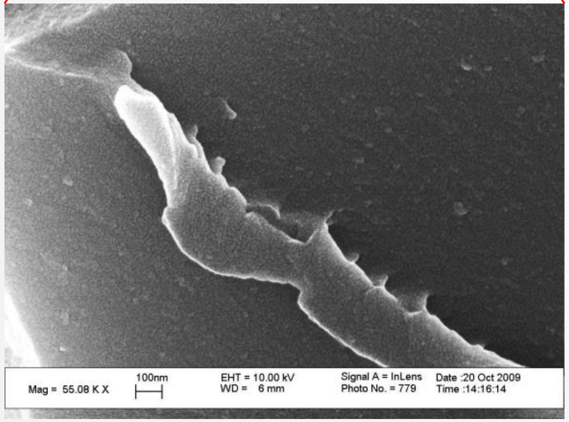
10KX



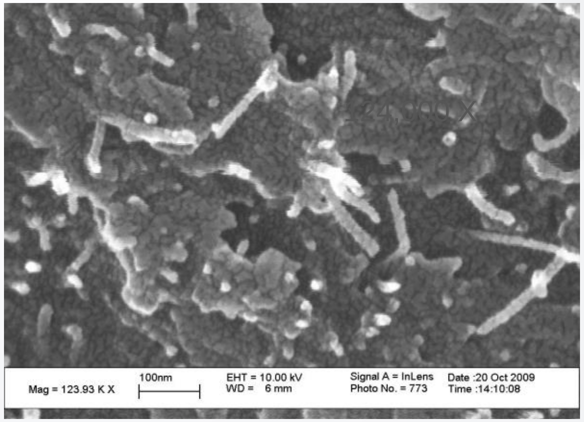
Fast Fracture Zone

Crack Initiation Zone

55KX

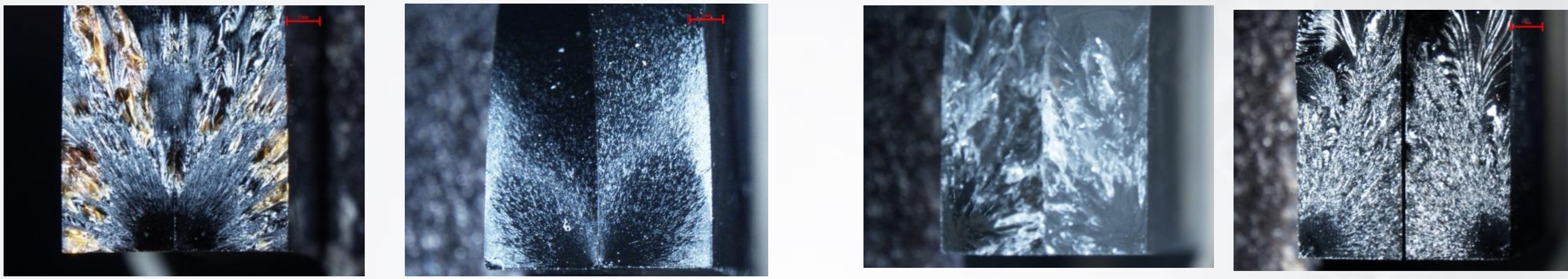


124KX

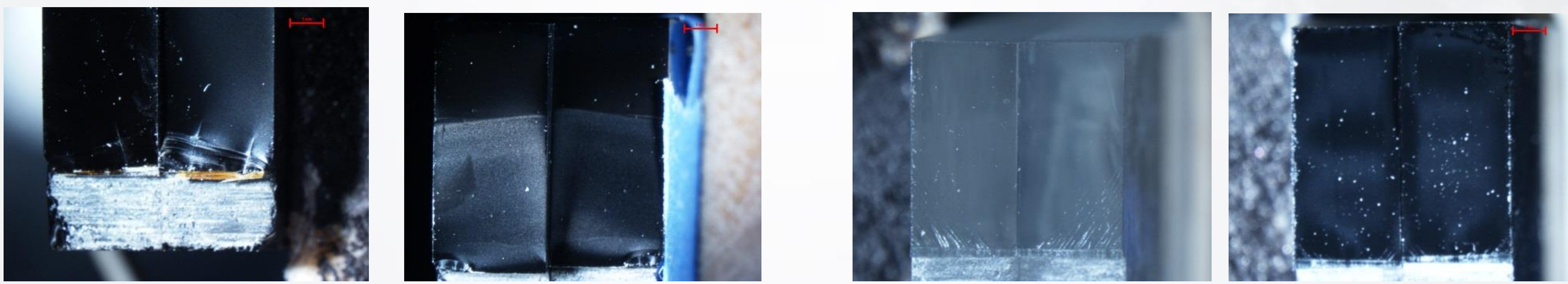


MY 721-DDS Tetra glycidyl, High Tg (290°C) Aircraft composites

MY 721 134°C unnotched Epon 828 -78°C



notched



- Difficult to get NSI and K_{1c} values => MY721 has very low W_i and low W_p even at 134°C.
- MR improves fracture resistance as seen by fracture surfaces. Should translate to improved fatigue or creep failure resistance.
- Scaling of fracture mechanism does not scale simply to T/Tg. Must also include understanding of molecular crosslink structure.

Conclusions

- Addition of MR to epoxy provides a microcrack bridging mechanism that:
  - Improves resistance to crack initiation and has greater crack dissipation energy, particularly for slow crack growth.
    - Smaller "pop-in" zone even though higher potential energy
    - Observed many more sub-micron scale fracture events (deltoids)
    - When a crack is moving fast the localized energy at the crack tip cleaves the carbon nanotubes at the crack surface)
    - Provides less sensitivity to material defects, lower NSI values
    - **Greatly improved material fatigue lifetime (and presumably creep fracture resistance) as well as impact toughness.**

Conclusions, cont.

- The higher the epoxy Tg and greater the crosslink density the more sensitive the material is to fracture via defects.
  - Nanotube dispersion quality has to be excellent.
- Can place MR (discrete, bonded tubes) between fiber plies to better manage interlaminar fatigue or creep failure events.
- Demonstrated a systematic approach to understanding failure initiation and propagation events provides much insight into proper design and expectations of performance for carbon nanotubes in epoxy systems.

Acknowledgements

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A. Chudnovsky for over 33 years of wisdom and guidance in the selection and design of materials for durability

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M. Gauthier, MRD for some sample preparation

Materials

Bisphenol F from the Dow Chemical Company

Bisphenol A from 3M Corporation

MY721 from Huntsman and recommendations for curing.