Advances in Epoxy Technology as Matrix Materials for Wind Turbine Blade Composites

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The Dow Chemical Company

Acknowledgements
Prof. Frank Bates' group at University of Minnesota
Prof. H. J. Sue's group at Texas A&M
John F. Mandell's group at Montana State University

Outline

- Background on Epoxies
- Goal of current effort
- Introduction to block copolymer (BCP) technology
- Effects of BCP toughening on cured epoxy clear castings
- BCP Toughening mechanisms
- Effect of BCP toughening on cured epoxy composites
- 2nd generation toughening
- Summary and conclusions

Why are Epoxies Useful?

* Extremely good *corrosion resistance*

* Extremely good *chemical resistance*
  (acids, bases, solvents)

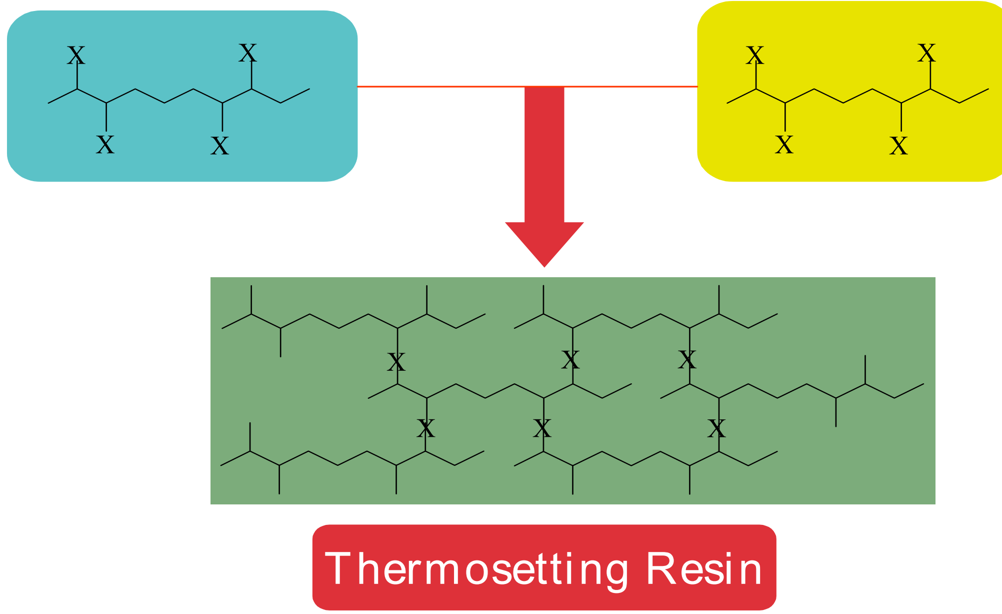
* Excellent *adhesion* to metals

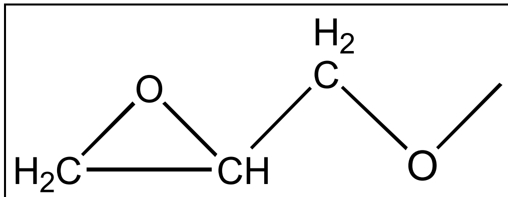
* Good *thermal* resistance

* Low shrinkage

* Dimensionally stable under wide range of conditions (e.g. temperature)

* Availability of versatile curing chemistries, to tune properties (flexibility, curing properties, waterborne formulations, etc.).

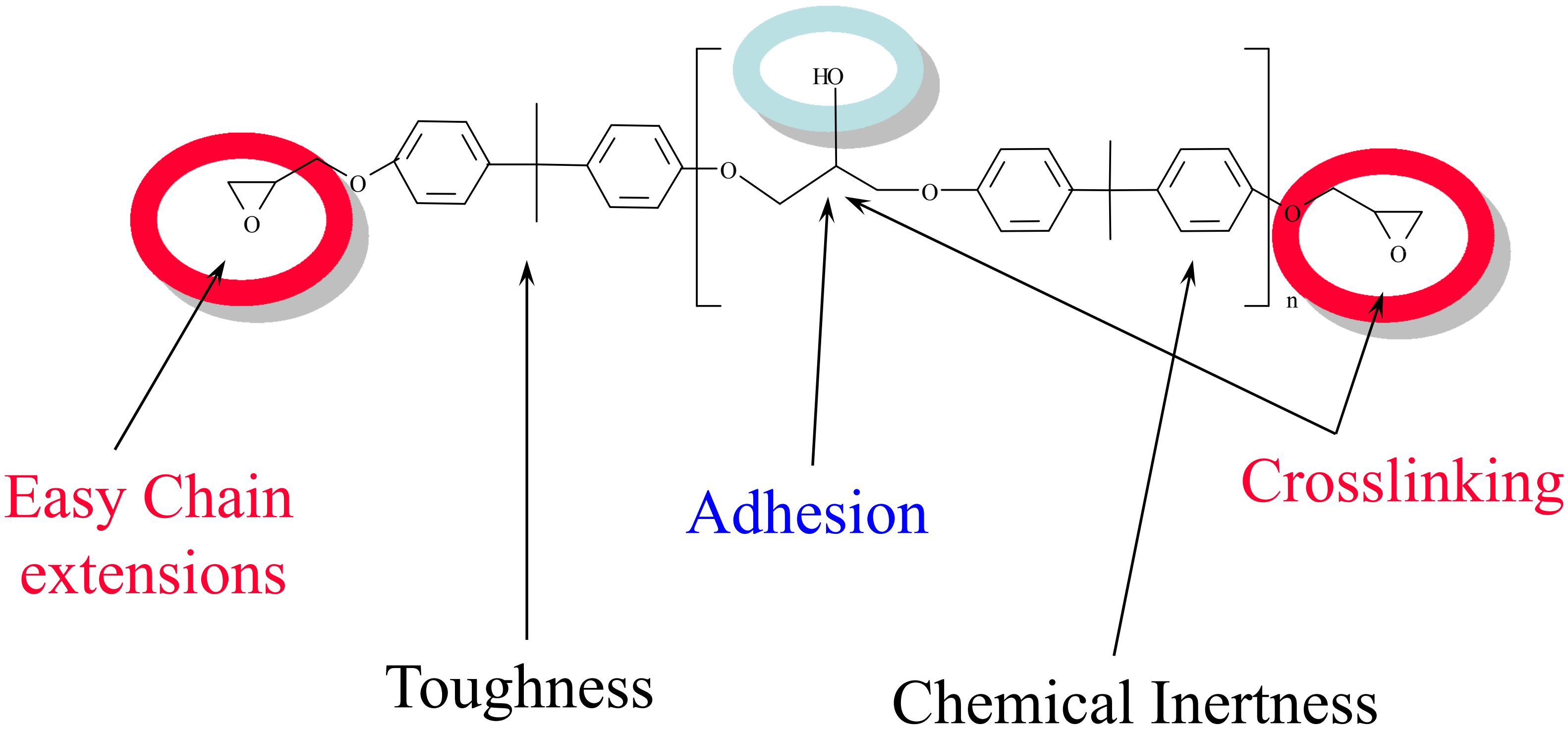




$C_4H_8O_2$
Exact Mass: 88.0524
Mol. Wt.: 88.1060
C, 54.53; H, 9.15; O, 36.32

Glycidyl Ether

Versatility of Epoxy Resins



Demands of the Market

Low exotherm

Longevity

Adjustable pot life

Fast cure response

Light Weight

Crack Resistance

Latency

Longer Pot Life

Fast Infusion

Fatigue

Stable viscosity

Controllable pot life

Low viscosity

Goal

- Provide toughness to epoxy thermosets but not at the **expense of processibility** and other **key performance attributes** for the applications of interest

Processibility: high viscosity, rate of cure, component compatibility, etc.

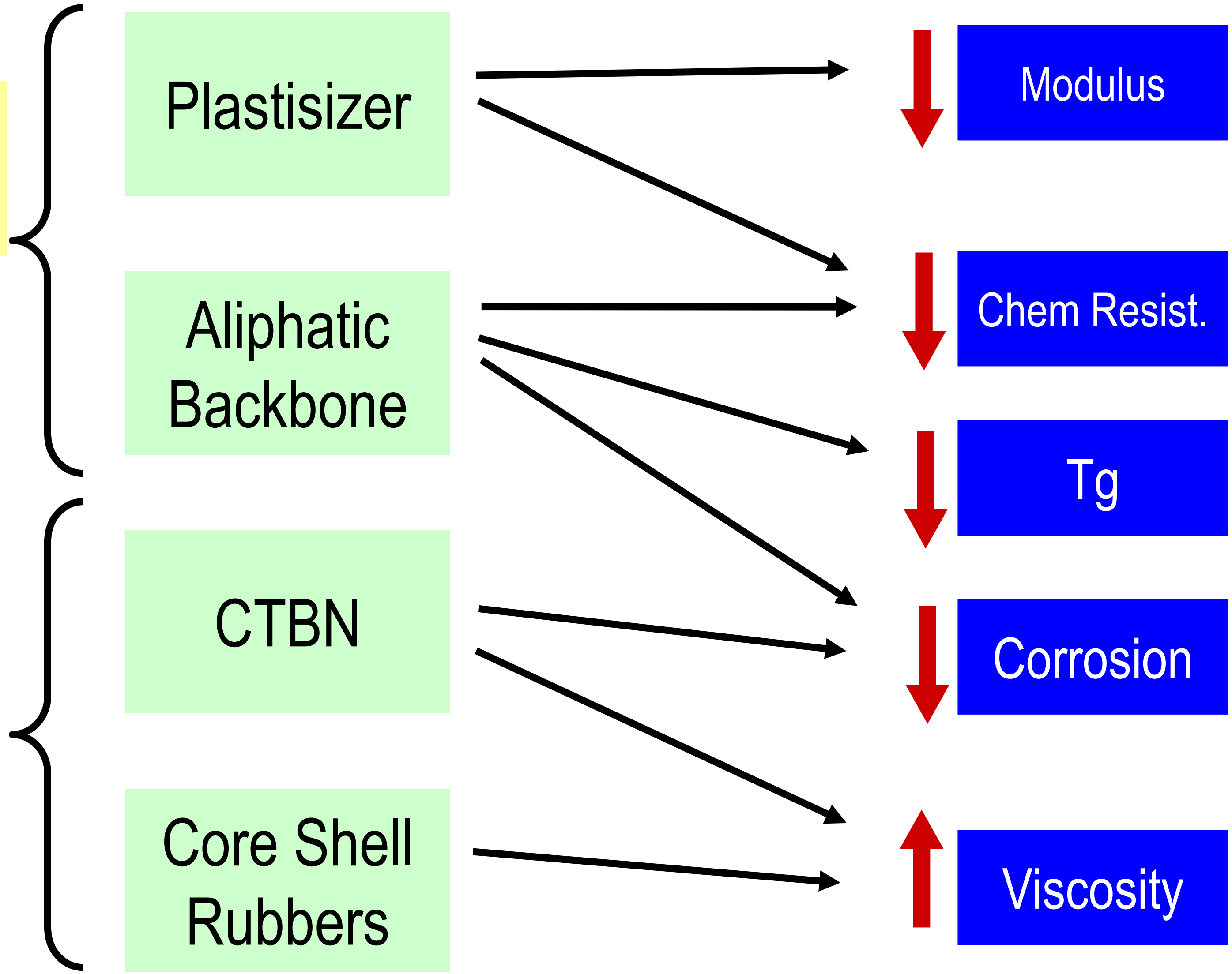
Performance attributes: Tg, modulus, adhesion, water uptake, solvent resistance, etc.

Applications: Protective coatings (liquid and powder), adhesives, composites including wind turbine blades

Overview of Toughening Approaches

Flexibilization
- Decrease in backbone stiffness
- Decrease in crosslink density
- Uses plasticizers and diluents

Toughening
- Properties of modifier
- Concentration
- Interfacial strength
- Particle size



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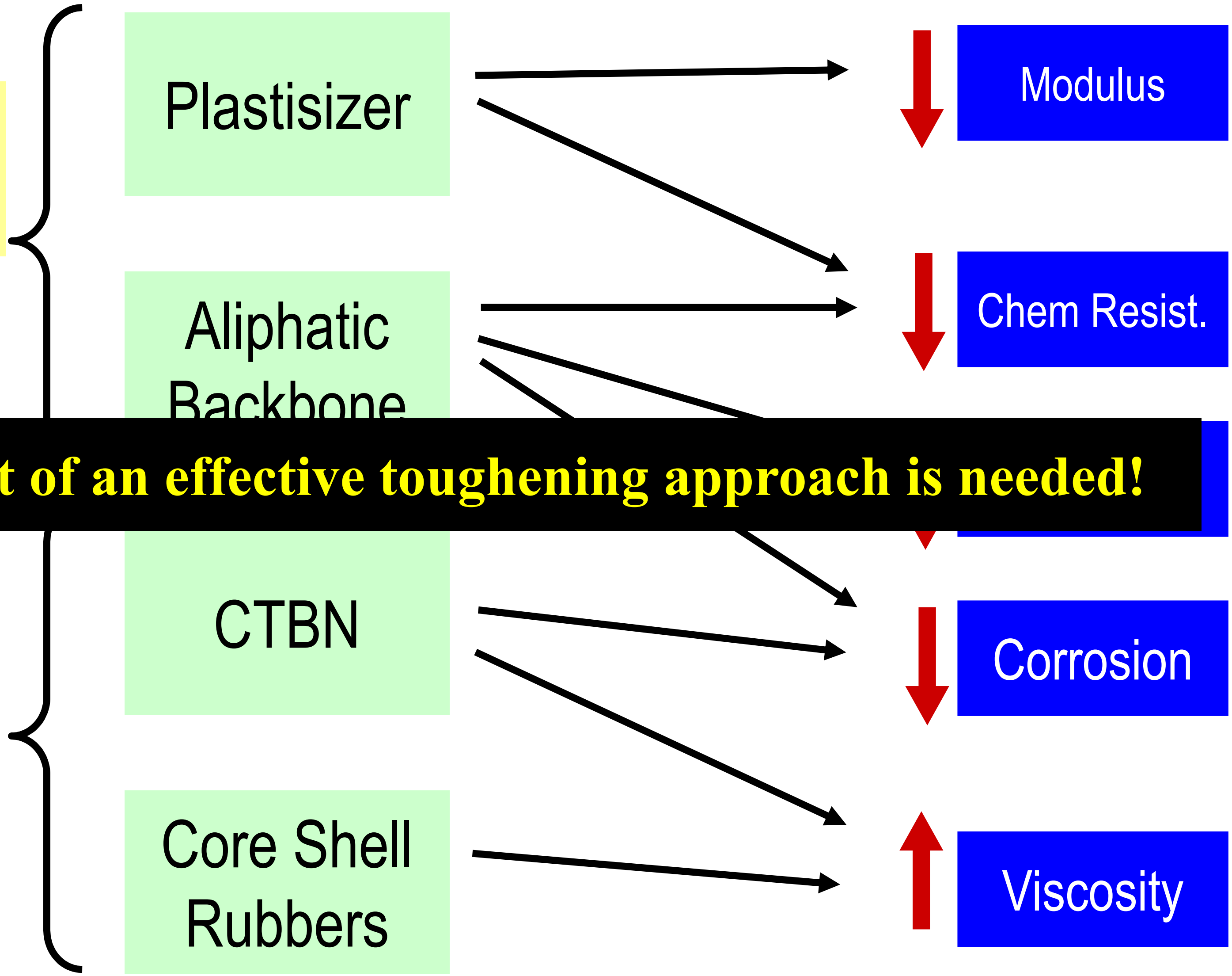
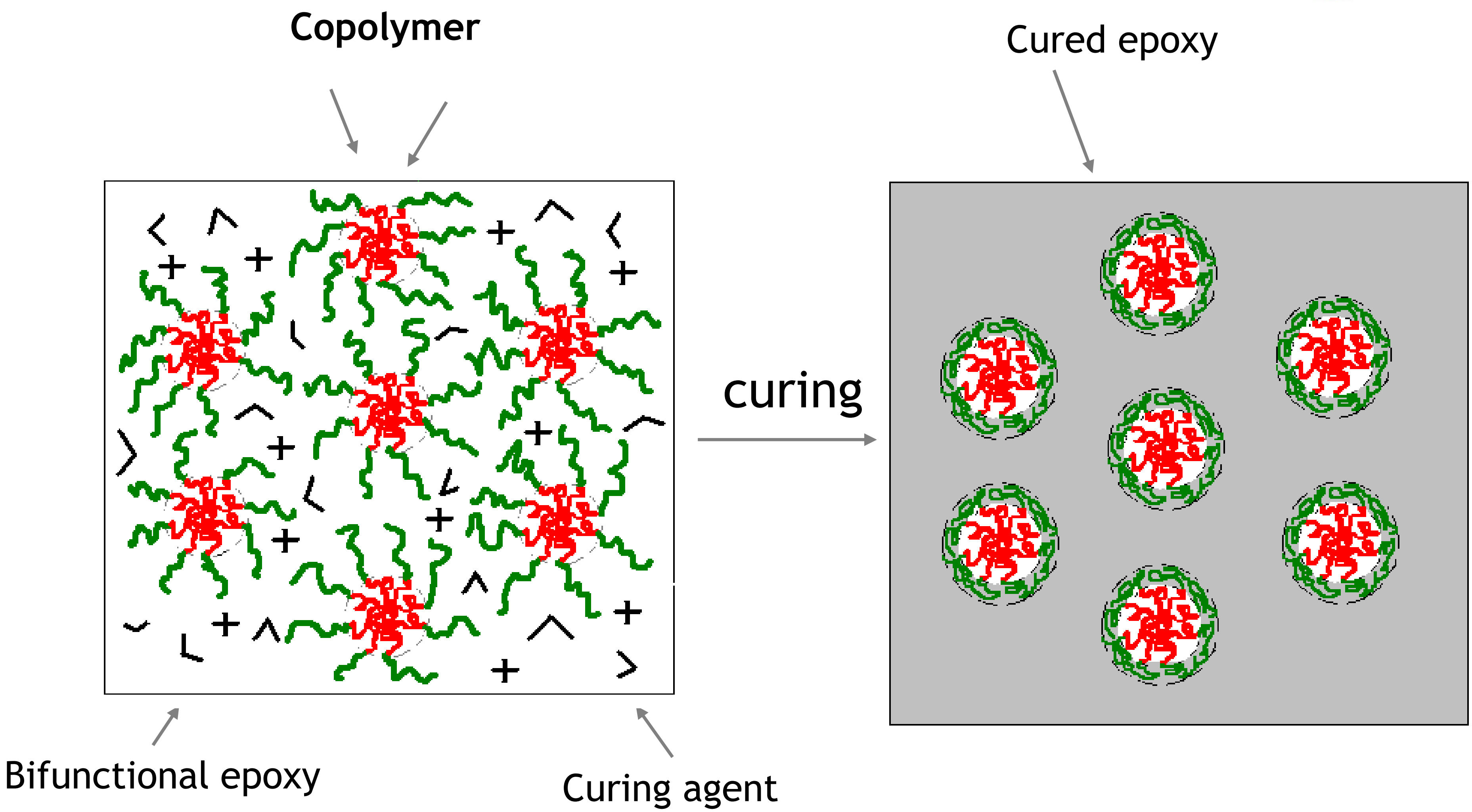


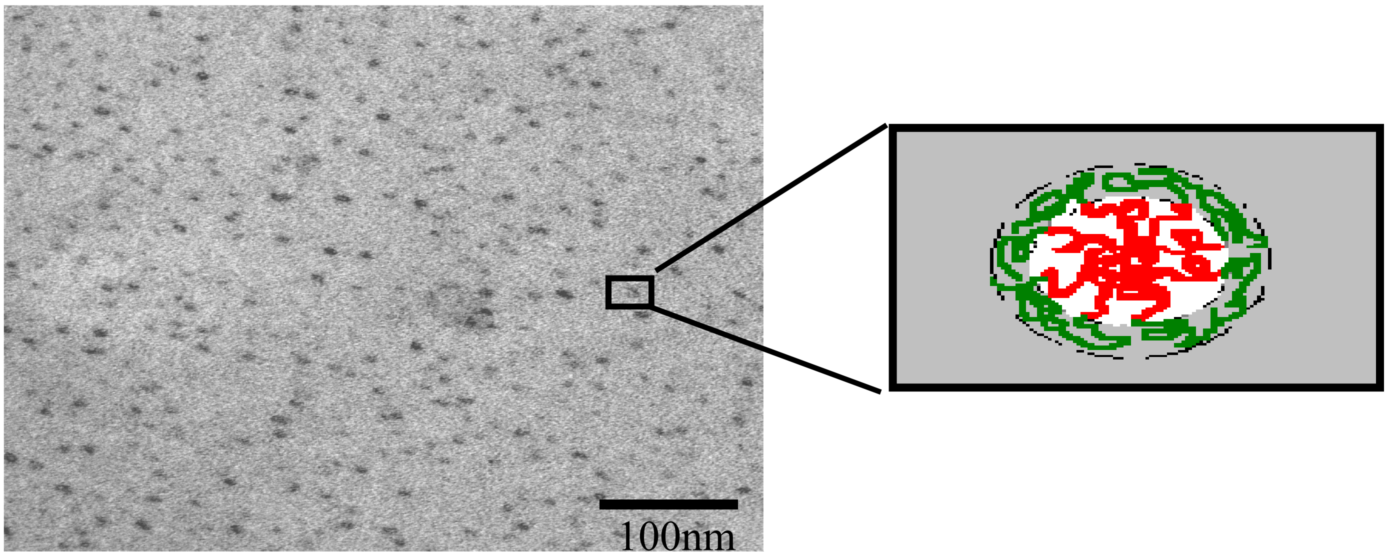
Development of an effective toughening approach is needed!

Introduction to Amphiphilic BCP Technology

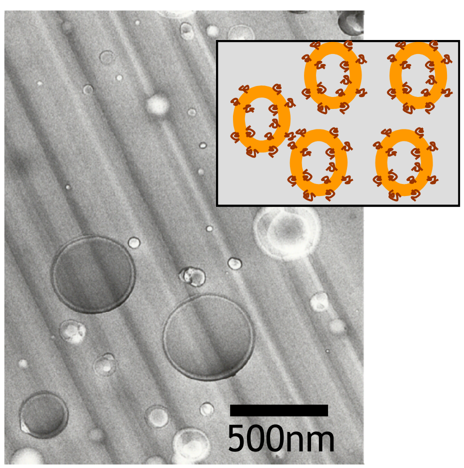


- Creation of rough spherical micelles before cure and refine structure duri
- Morphology at nano-meter length scale

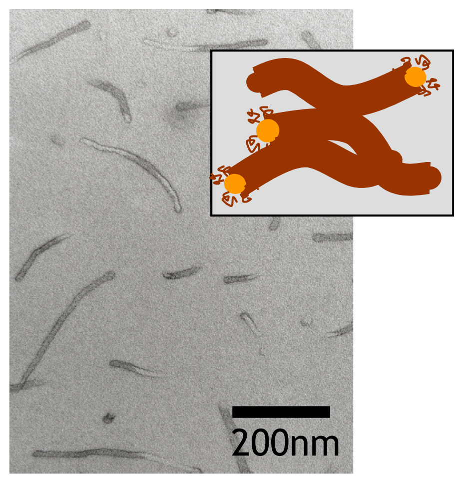
BCP in Epoxy



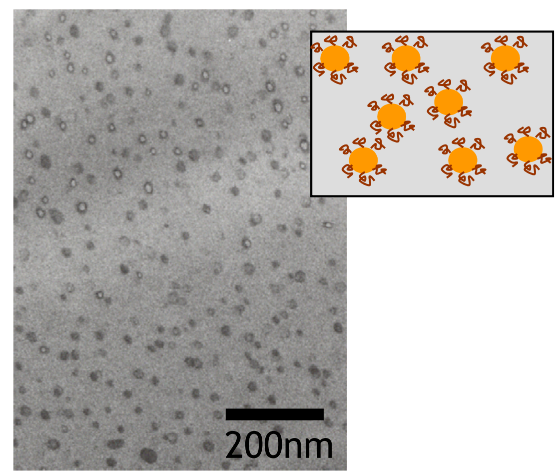
in epoxy



vesicle



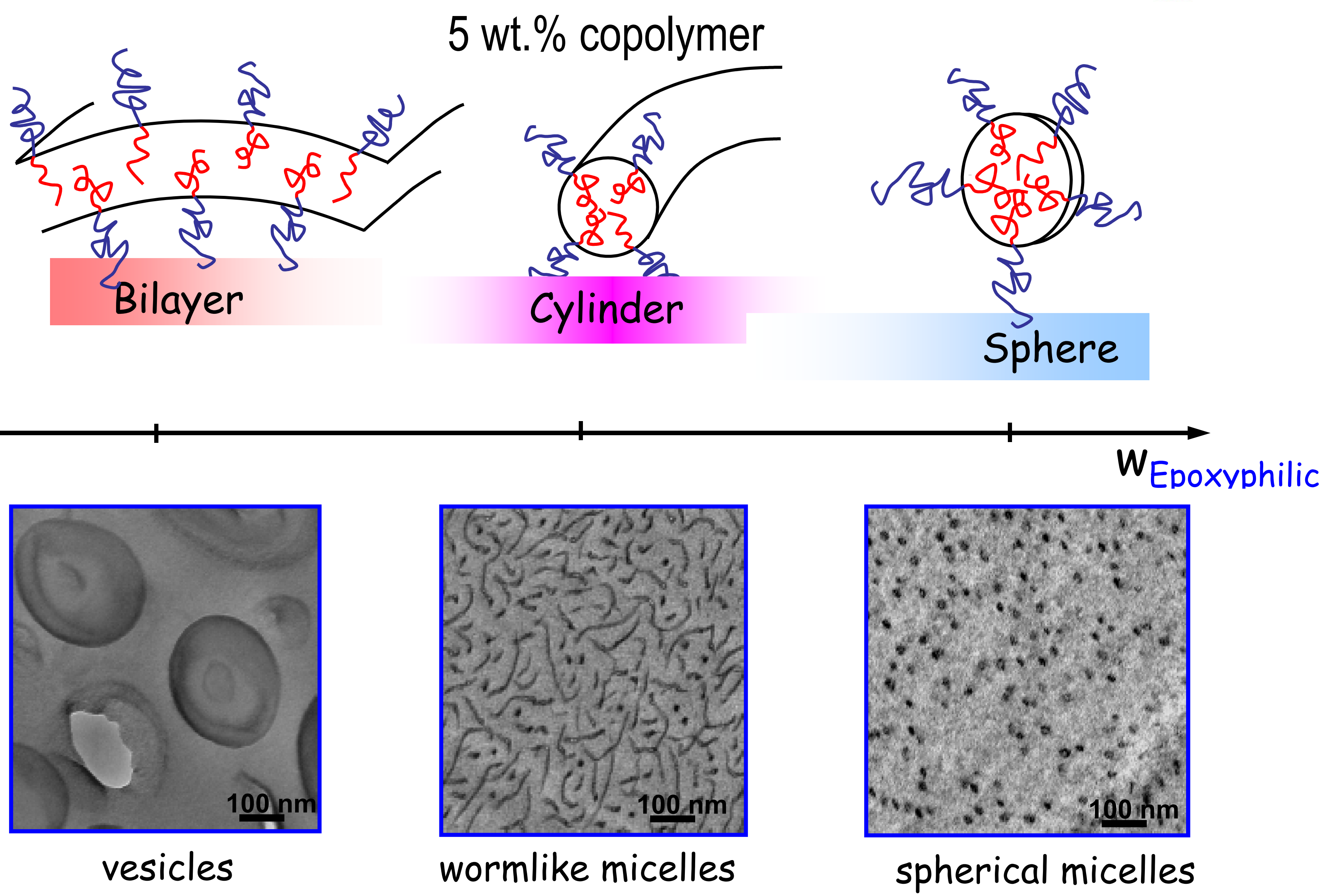
wormlike micelle



spherical micelle

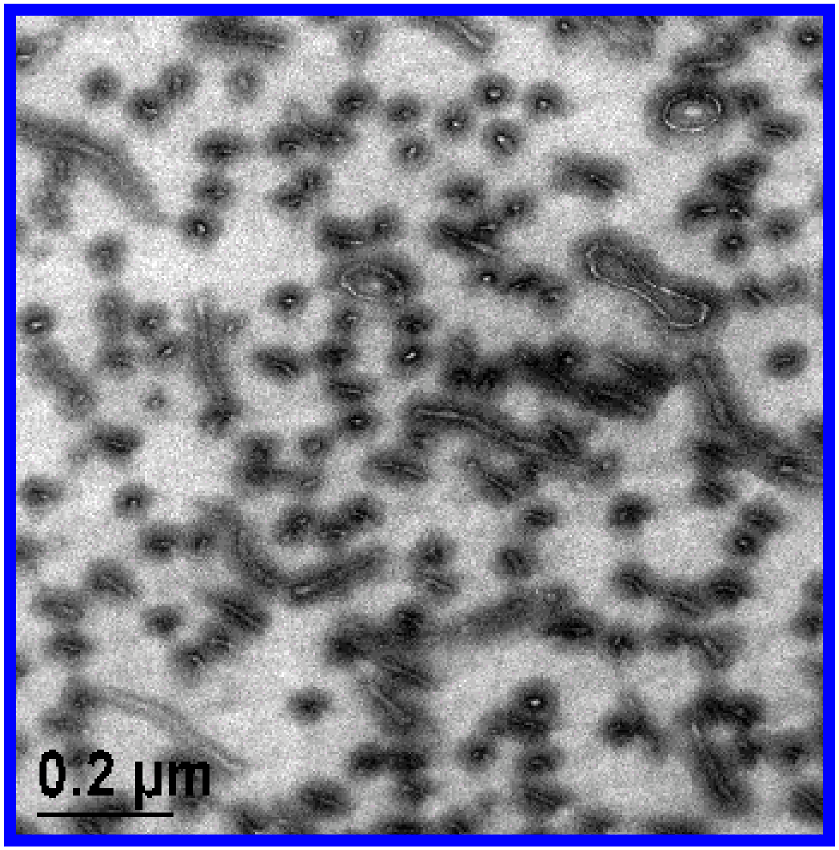
Dean, PhD thesis, 2002

Morphologies Accessed in the Dilute Limit

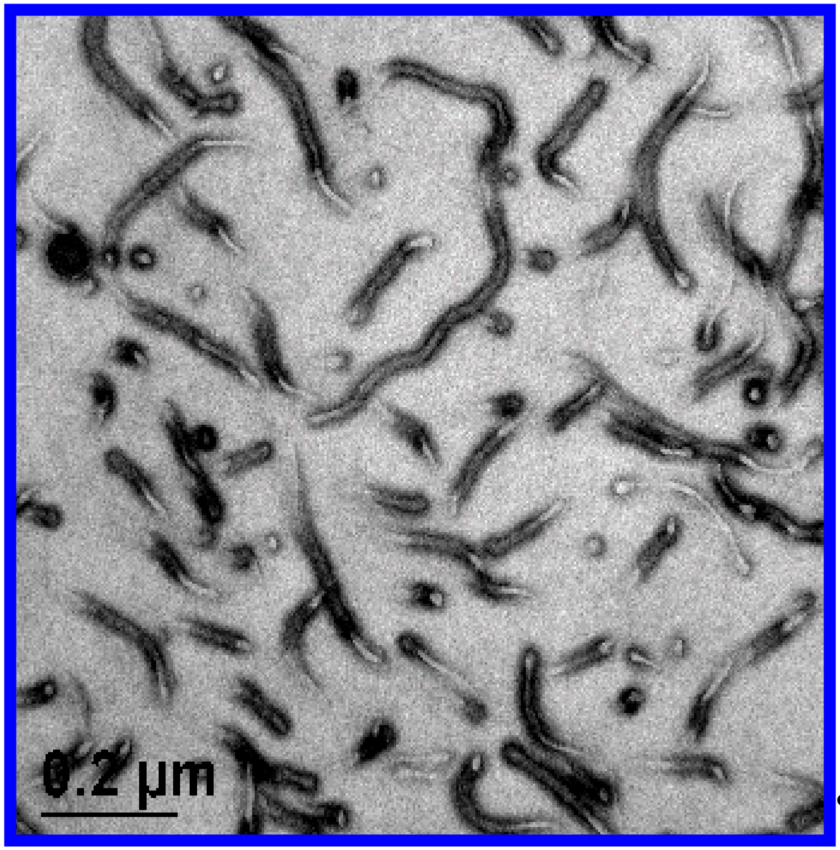


Morphology Refinement During Cure

Uncured

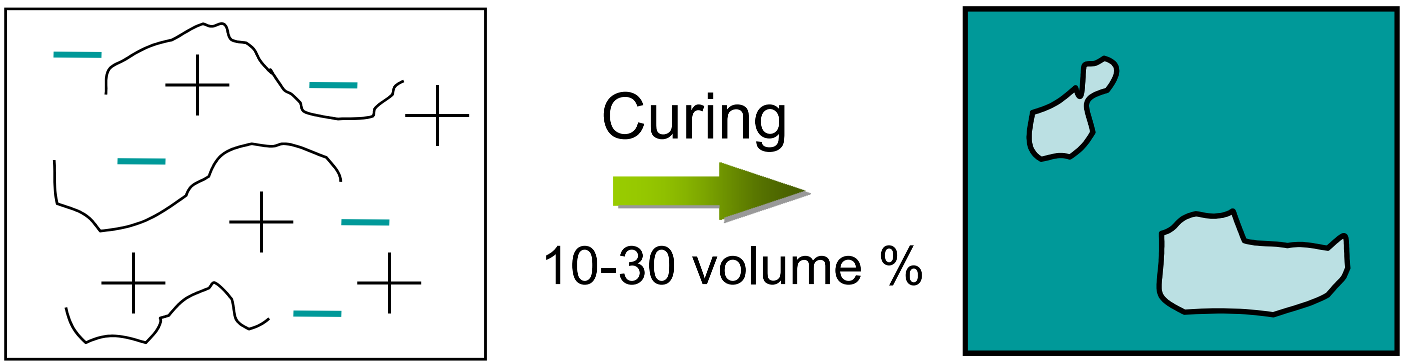


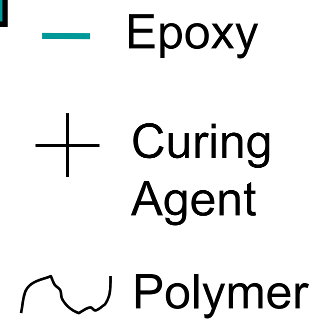
Cured



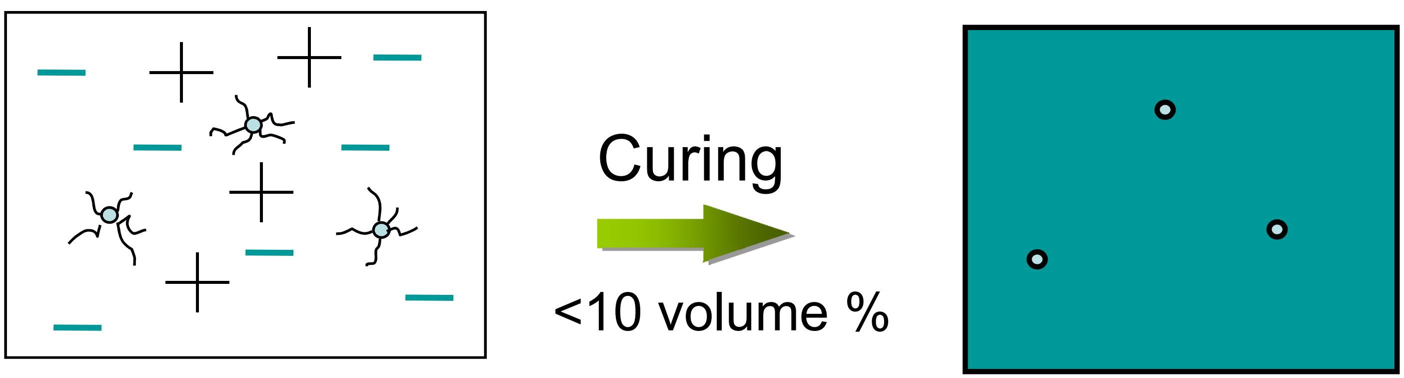
Self Assembly vs. Conventional Macro-Phase Separation

Conventional Toughening (Example: CTBN Technology)



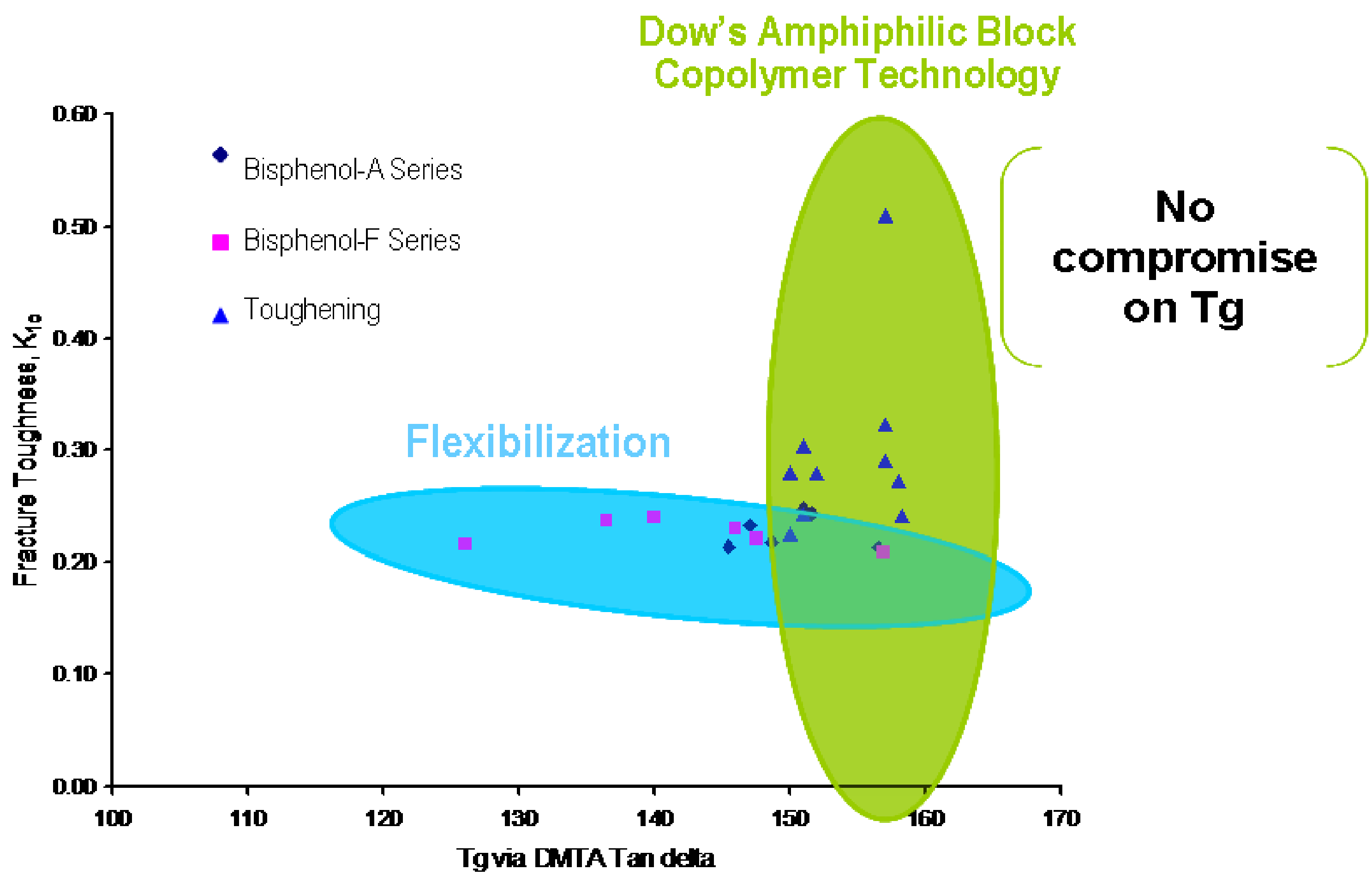


Self Assembly (BCP Technology)



Better defined structures, reduced volume%, reduced viscosities

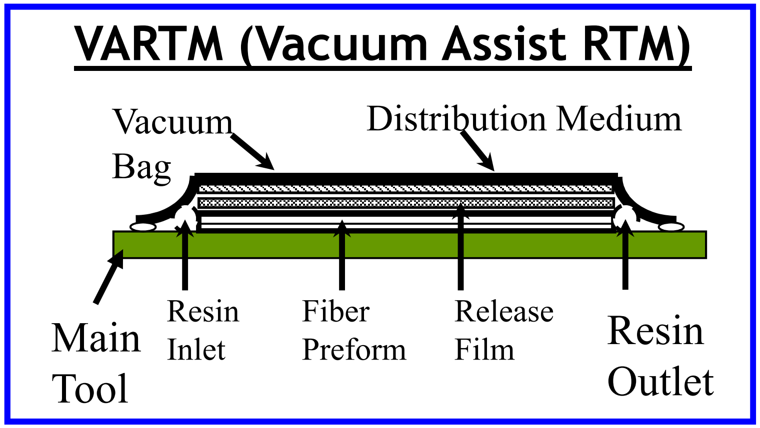
Flexibilizers vs Tougheners

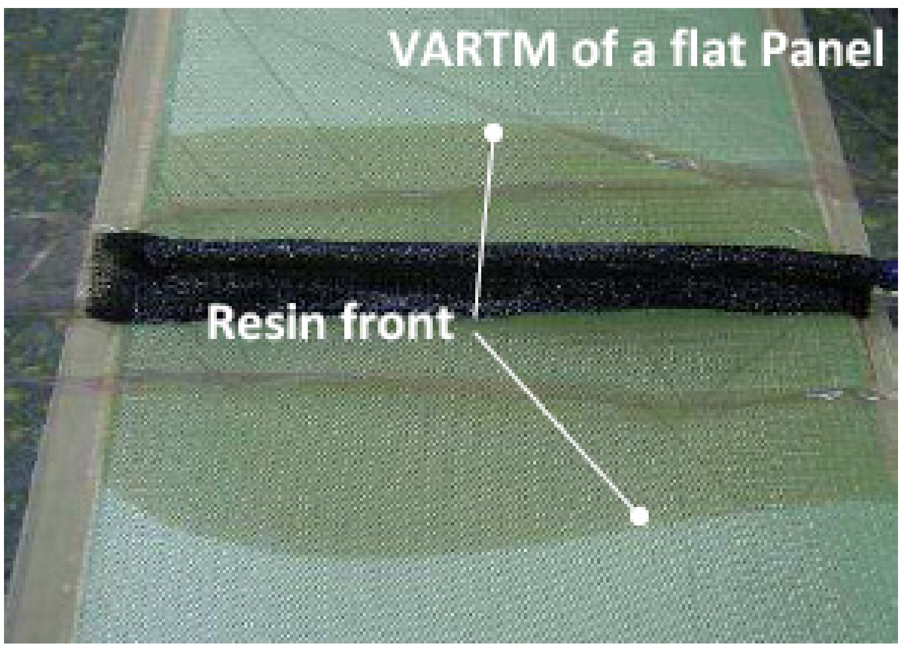


Increased level of flexiblizers or tougheners

Fracture toughness is represented in units of MPa $m^{0.5}$

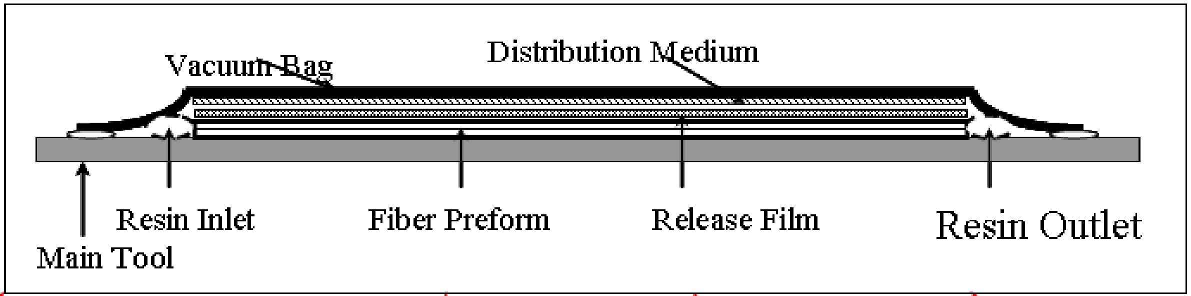
Composite Fabrication – Resin Infusion Process





Guide to Suitability of Toughening Technology

Infusion Resin Needs in Composite Parts



Cost – Must be affordable

Thermal (T_g)

Processing - Must be able to be infused

Most of the properties of the composite like stiffness and strength dominated by the fiber – Key composite properties dominated by the Matrix

Good Resistance to Delamination between plies

Measured by Interlaminar Fracture Resistance or Toughness (G_{IC} and G_{IIC})

Good Bonding to the fiber

Measured by higher strength in off axis direction

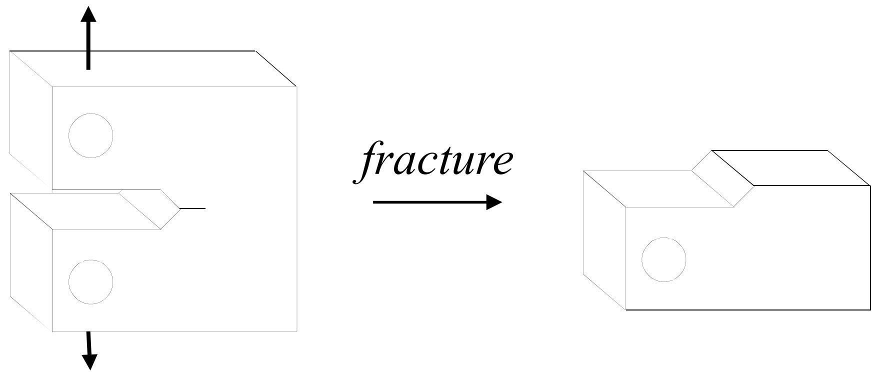
High Compressive Strength

Elastic Moduli (Low values will lead to fiber buckling)

Measured using tensile test

Performance in Clear Castings

Compact Tension Testing of Epoxies (ASTM D5045)



(plane strain)

Stress intensity factor

$$K_{1c} = \frac{P_{max}}{BW^{1/2}} f(a/W)$$

P_{nax} = load at failure
B = sample thickness
W = length
a = crack length
f(a/w) is geometry dependent

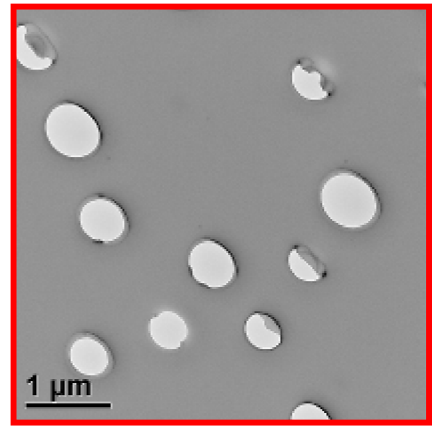
Strain energy release rate

$$G_{1c} = \frac{K_{1c}^2}{E}(1-\nu^2)$$

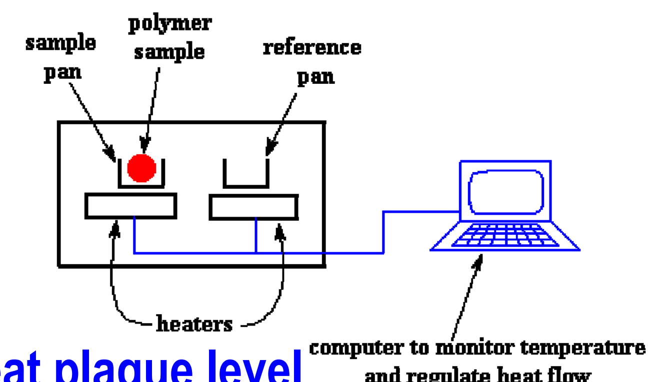
proportional to fracture toughness (J/m^2)

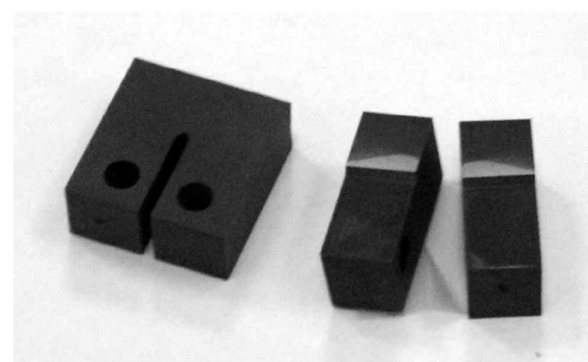
Typical Epoxy Composite Infusion Formulation – Low Tg System

Property	Untoughened System	Toughened System
DSC T_{g1} (°C)	88	85
DSC T_{g2} (°C)	99	97
Tensile Yield Strength, MPa	68 (stdev = 0.6)	63 (stdev = 1.0)
Tensile Modulus, GPa	3.5 (stdev = 0.2)	3.1 (stdev = 0.04)
Tensile Strain @ Yield, %	4.3 (stdev = 0)	4.3 (stdev = 0.4)
Tensile Strain @ Break, %	5.8 (stdev = 0.7)	8.5 (stdev = 0.3)
Fracture Toughness (MPa m^0.5)	0.96 (stdev = 0.07)	2.59 to 2.80



- Significant improvement in Toughness (>150%)
- No change in cured T_g
- Increase in elongation at break

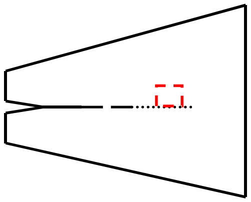




Properties measured at the neat plaque level

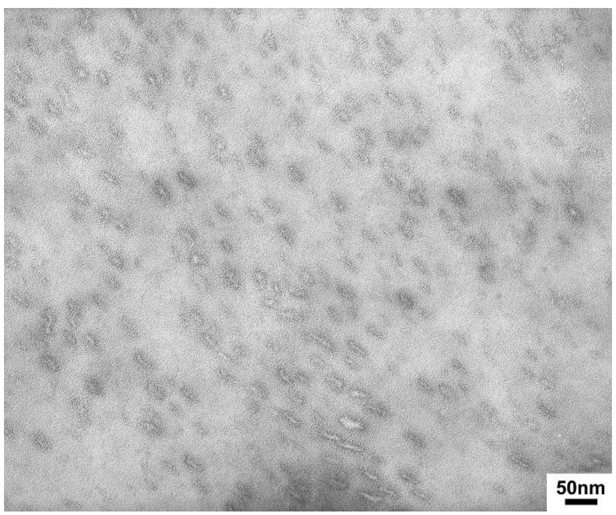
Toughening Mechanism

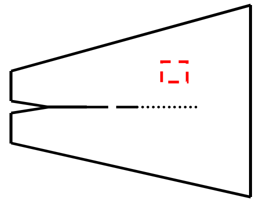
TEM Micrographs



Adjacent to crack wake

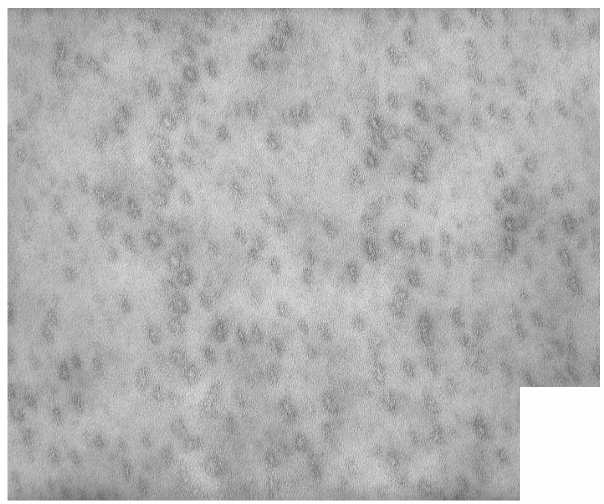
- Elongated copolymer particles
- Orientation of copolymer particles
- Cavitation

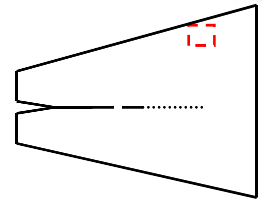




Some distance from crack wake

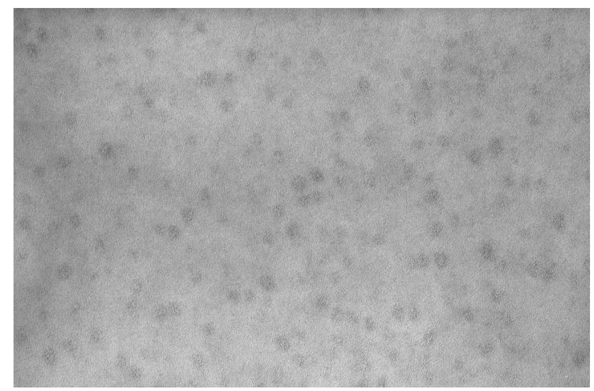
- Less or no elongation of copolymer particles
- No orientation of copolymer particles
- Cavitation

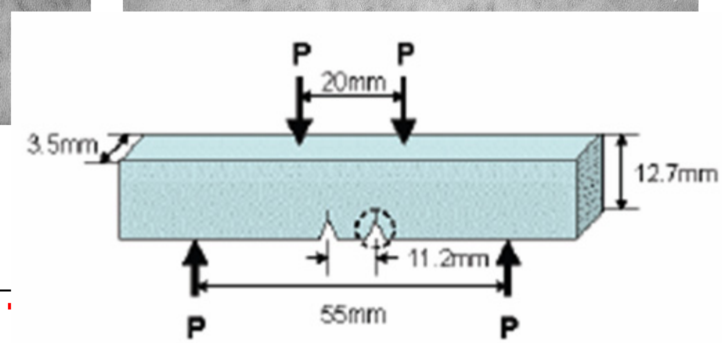




Some distance from crack wake

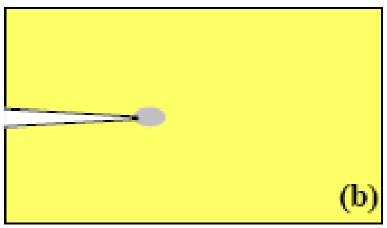
- No elongation or orientation of copolymer particles
- No cavitation



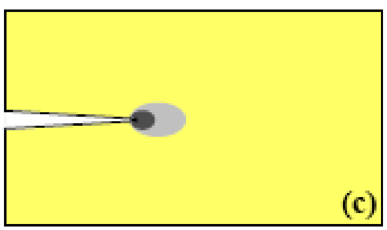


Cavitation-Induced Matrix Shear Banding

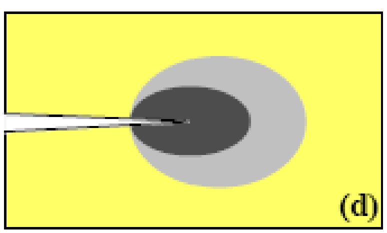
(a) initiation of a starting crack



(b) formation of a block copolymer cavitation zone at the crack tip when the specimen is loaded



(c) expansion of the cavitation zone and initiation of a matrix shear banding zone at the crack tip when the hydrostatic stress is relieved by the cavitation

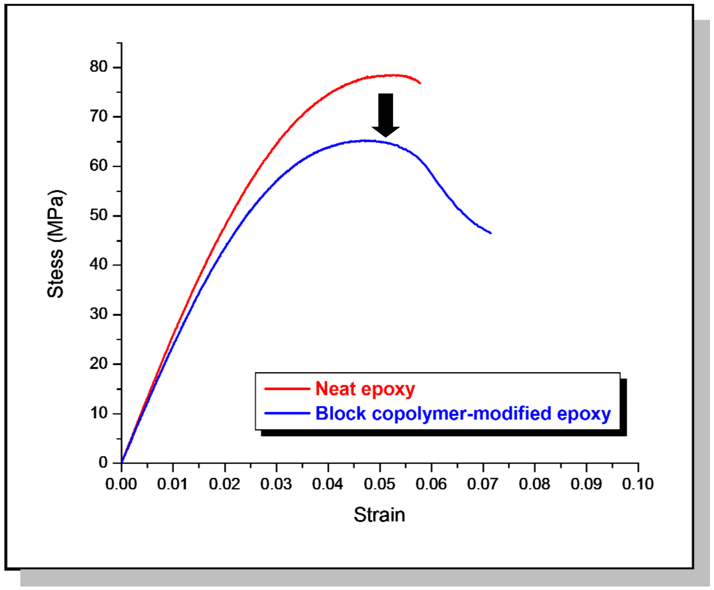


(d) crack propagates when the shear strain energy builds up to a critical value, with a damage zone surrounding the crack

Cavitation   Shear Banding

(The sizes of the crack, cavitation and shear banding zone are not drawn to scale.)

Crack Tip Blunting

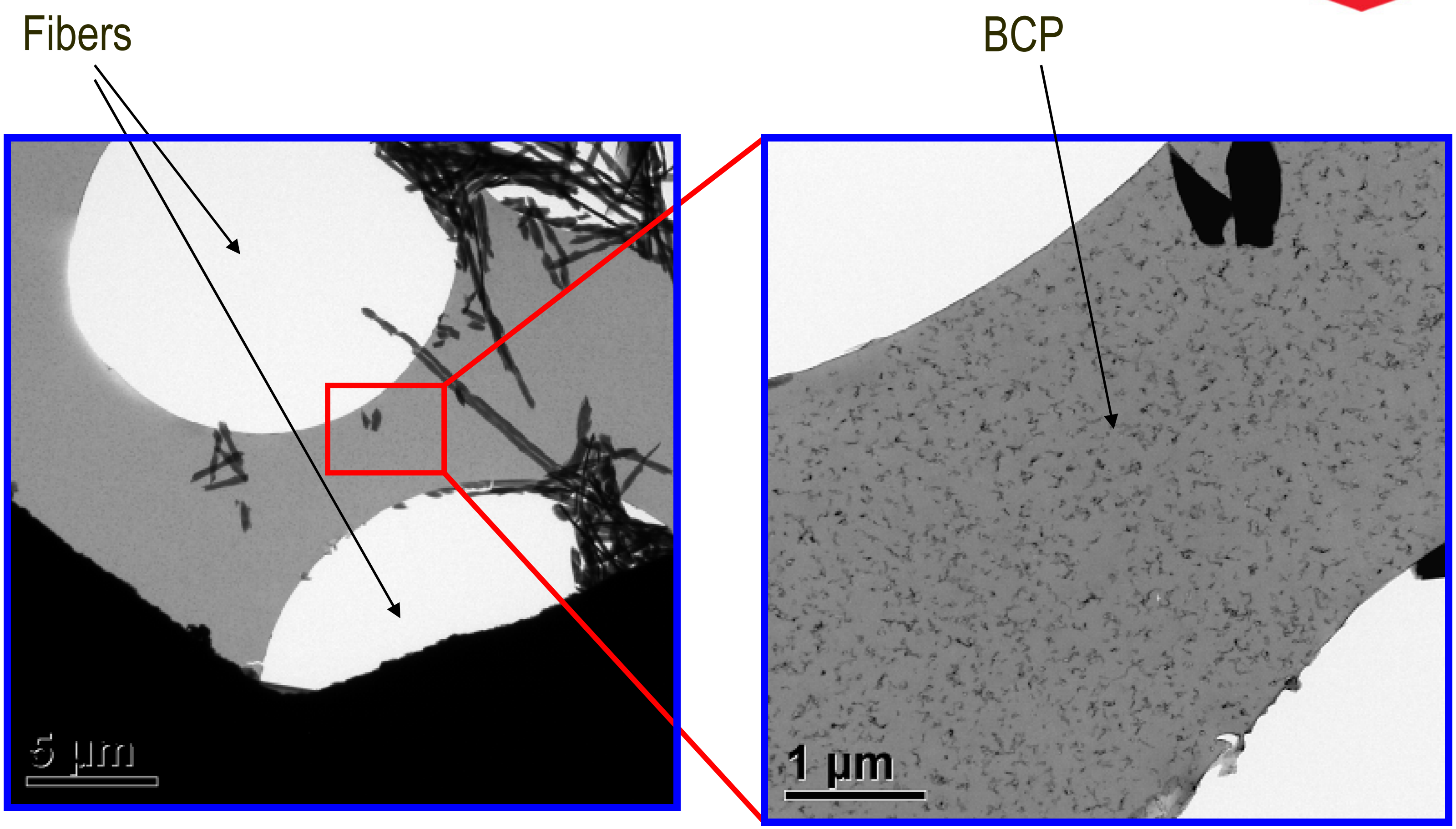


- A reduction of yield stress implies that the plastic deformation ahead of the crack tip is easier
- Localized plastic deformation at the crack tip favors the crack tip being severely blunted
- Under this condition, the strain energy release rate is greater resulting in a higher K_I value

Kinloch, A. J.; Williams, J. G. *J. Mater. Sci.* **1980**, 15, 987.

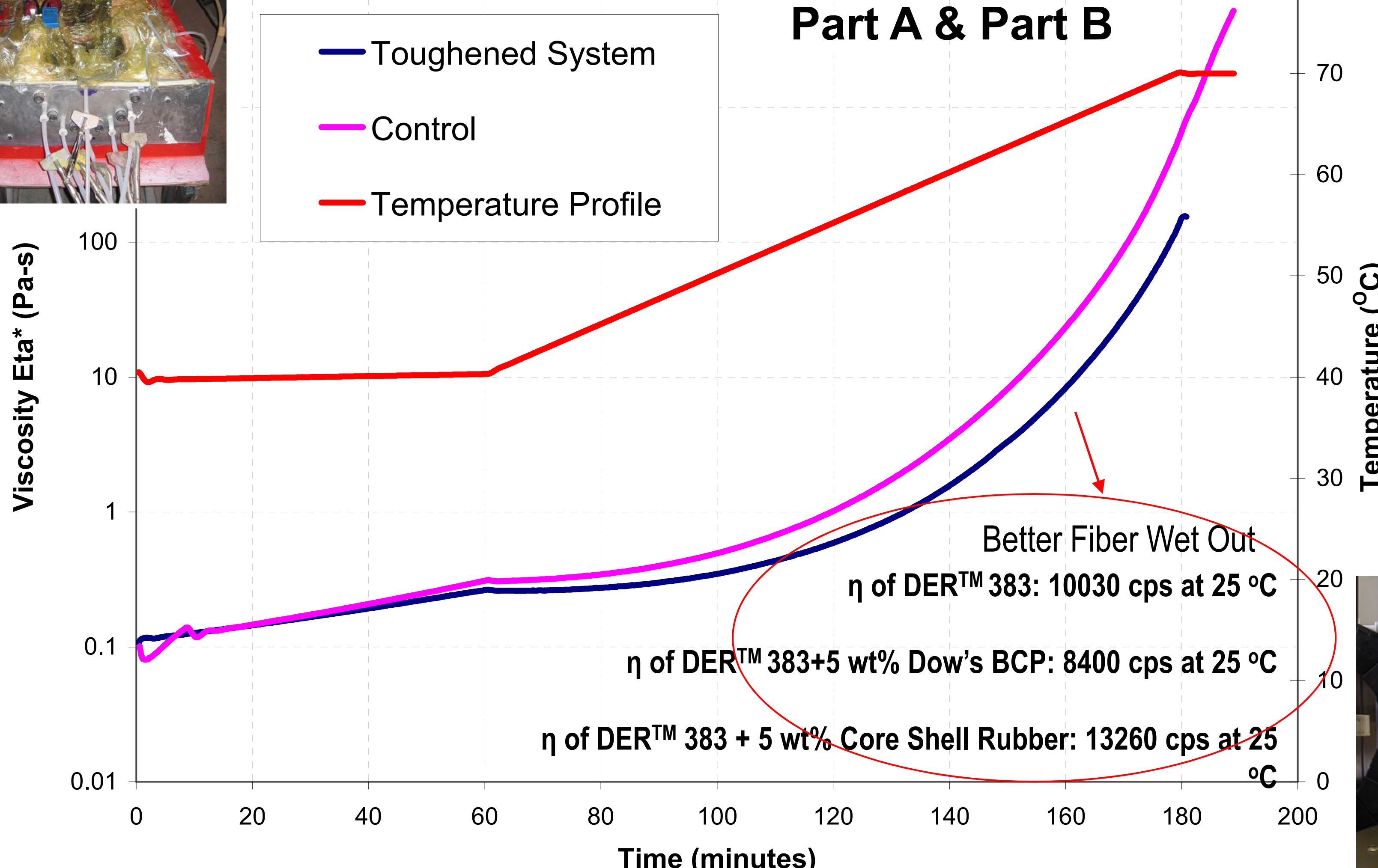
Composite Processing Attributes of the BCP

Filtration During Liquid Molding Processes



Nano-sized domains exist between fibers →No filtration effect

Effect of BCP on Formulation Rheo-kinetics



TM – Trademark of the Dow Chemical Company

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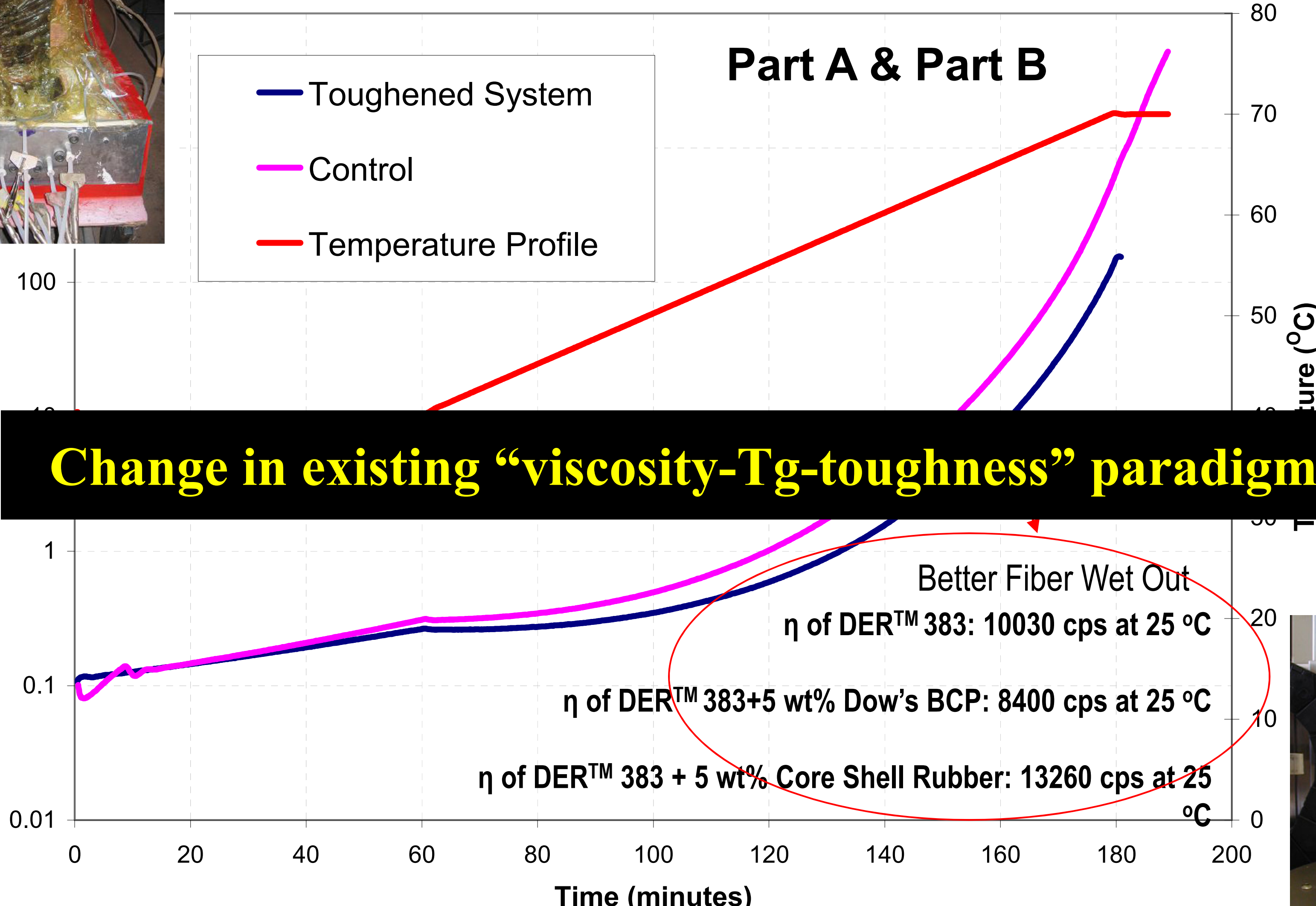
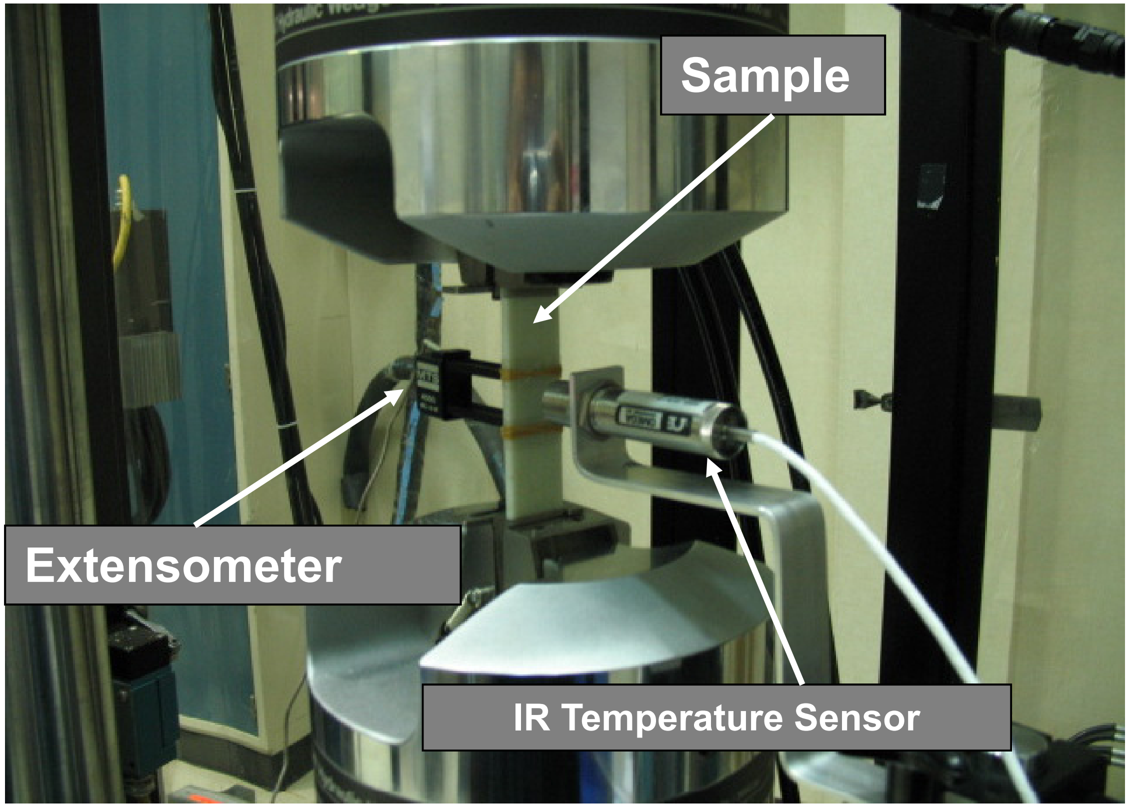


Change in existing "viscosity-Tg-toughness" paradigm

TM – Trademark of the Dow Chemical Company

Performance in Fiber Reinforced Composites

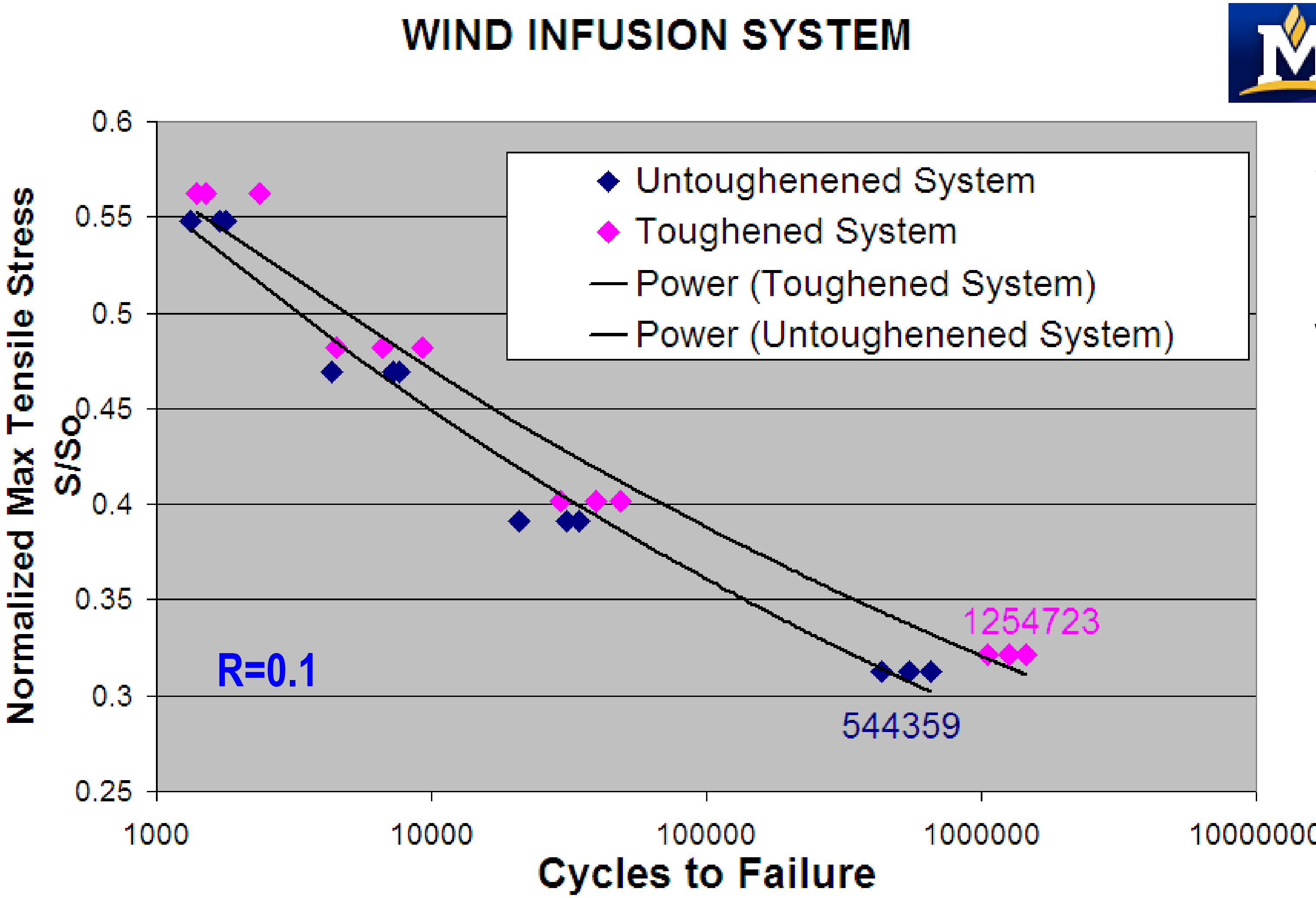
Test setup



Monitor/Data

- Load
- Strain
- Temperature
- Cycles to failure

Fatigue Results @ Composite Level



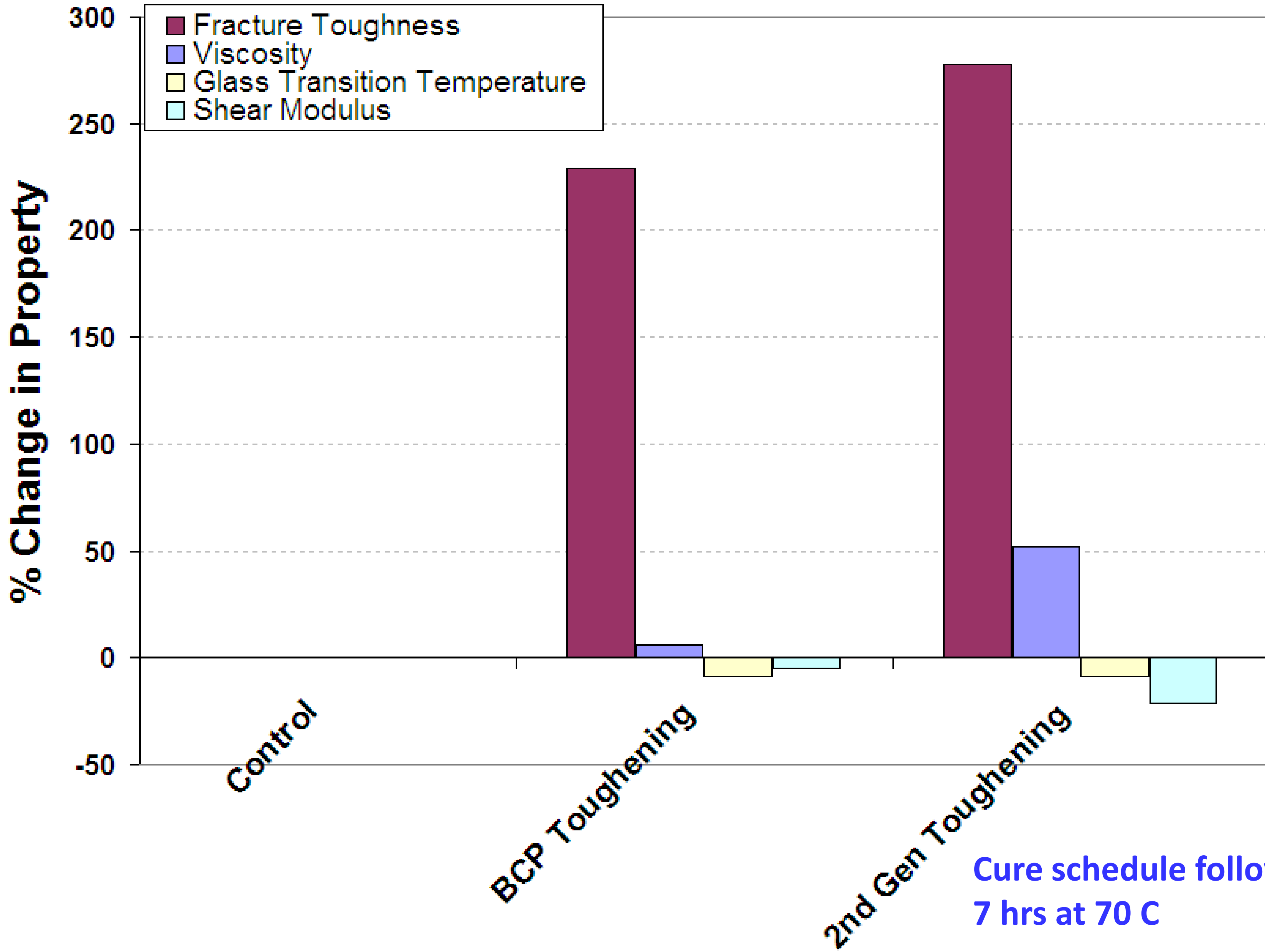
Similar results have been duplicated within Dow

Fabric Architecture: ±45°: Resin Sensitive

- Resin toughness translates into improved fatigue lifetimes especially at low- stress levels

2^{nd} Generation Toughening

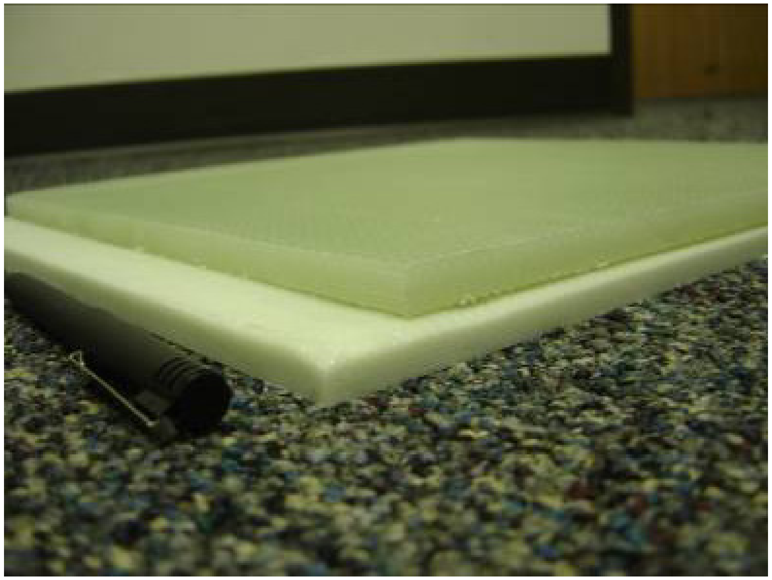
Effect of 2nd Gen Toughening on Properties – Clear Castings



Cure schedule followed:
7 hrs at 70 C

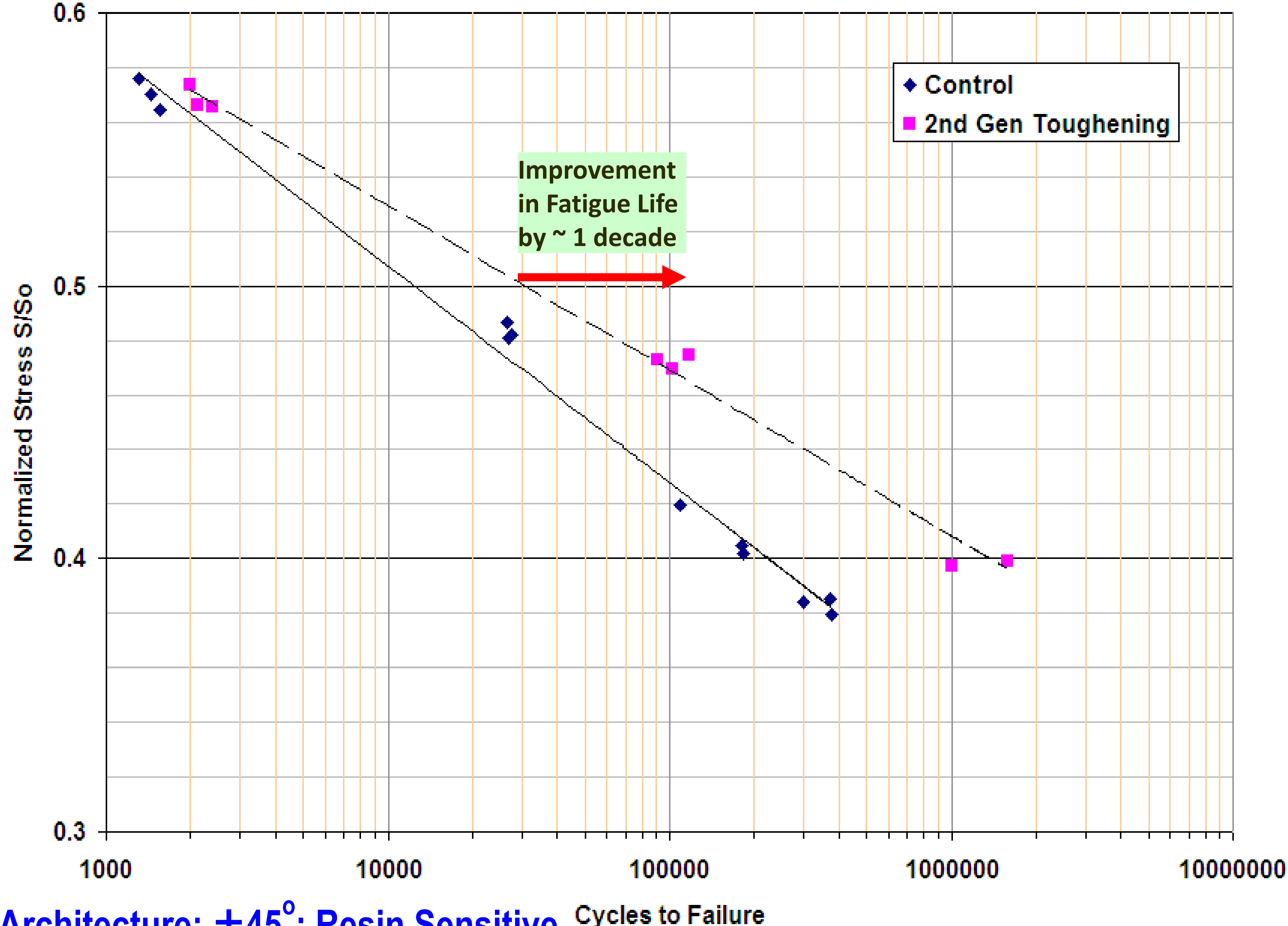
Moving from Clear Castings to Composites

- VARTM Composites made using typical epoxy infusion formulation – 7 hour, 70 C cure
- No major issues observed such as filtration etc.



Fatigue Life Improvement @ Composite Level

IP Captured



Fabric Architecture: ±45°: Resin Sensitive

Summary and Conclusions

- Block copolymer technology offers an opportunity to change the viscosity-Tg-toughness balance in epoxy resin infusion systems
- Block copolymer toughening approach has advantages in wind turbine blade composite processing
  - Low viscosity
  - No filtration
- Block copolymer toughening has a positive influence on composite fatigue
- Over 1 decade improvement in composite fatigue life obtained through Dow's 2nd generation toughening

Relevant Dow Publications

1. Jia (Daniel) Liu, Hung-Jue Sue, Zach Thompson, Frank S. Bates, Marv Dettloff, George C. Jacob, Nikhil Verghese, Ha Pham, *"Nano-Cavitation in Self-Assembled Amphiphilic Block Copolymer-Modified Epoxy"*, Presented at the **2008 Materials Research Society (MRS) Meeting**, March 2008, San Francisco, CA, USA.
2. Marv Dettloff, George C. Jacob, Ha Pham, *"Amphiphilic block copolymer toughening technology for epoxy thermosets"*, Presented at the **2008 SCI (Society of Chemical Industry) Conference on Advances in the Epoxy Chemistry**, August 2008, Limerick, Republic of Ireland.
3. Jia (Daniel) Liu, Hung-Jue Sue, Zach Thompson, Frank S. Bates, Marv Dettloff, George C. Jacob, Nikhil Verghese, Ha Pham, *"Nano-Cavitation in Self-Assembled Amphiphilic Block Copolymer-Modified Epoxy"*, **Macromolecules,** Vol. 41, (2008) p. 7616-7624.
4. Jia (Daniel) Liu, Hung-Jue Sue, Zach Thompson, Frank S. Bates, Marv Dettloff, George C. Jacob, Nikhil Verghese, Ha Pham, "*Nano-Sized Micellar Structures of Self-assembled Amphiphilic Block Copolymers and their Toughening Effects in Epoxy Matrices"*, Presented at the **236th American Chemical Society (ACS) National Meeting**, August 2008, Philadelphia, PA, USA and published in the Conference Proceedings.
5. Rajesh Turakhia, George C. Jacob, Marv Dettloff, Ha Pham, *"Novel Epoxy Toughening for Coatings and Composites Applications"*, Presented at the **2008 TRFA Annual Meeting,** September 2008, Chicago, IL, USA and published in the Conference Proceedings.
6. J. Liu, H.-J. Sue, Z.J. Thompson, F.S. Bates, M. Dettloff, G. Jacob, N. Verghese, H. Pham, *"Strain Rate Effect on Toughening of Nano-Sized PEP-PEO Block Copolymer Modified Epoxy"*, **Acta Materialia**, Vol 57, No. 9, (2009) p. 2691-2701.
7. Jia (Daniel) Liu, Hung-Jue Sue, Zach Thompson, Frank S. Bates, Marv Dettloff, George C. Jacob, Nikhil Verghese, Ha Pham, *"Effect of Crosslink Density on Fracture Behavior of Model Epoxies Containing Block Copolymer Nanoparticles"*, Submitted to **Polymer** (2009).
8. Jia (Daniel) Liu, Hung-Jue Sue, Zach Thompson, Frank S. Bates, Marv Dettloff, George C. Jacob, Nikhil Verghese, Ha Pham, *"Toughening of Epoxy Using PEP-PEO Block Copolymer Nanoparticles"*, Accepted to be Presented at the **2009 ANTEC Conference**, June 2009, Chicago, IL, USA and published in the Conference Proceedings.
9. George C. Jacob, Marv L. Dettloff, Ha Q. Pham, Nikhil E. Verghese, Rajesh H. Turakhia, Carol O'Connell, Gary Hunter, Theophanous Theophanis, Jack Lesko, *"Epoxy Thermoset Toughened with Amphiphilic Blcok Copolymers"*, Accepted to be Presented at the **2009 ANTEC Conference**, June 2009, Chicago, IL, USA and published in the Conference Proceedings.
10. Nikhil E. Verghese, George Jacob, Marv Dettloff, Ha Q. Pham, Jia Liu, Hung-Jue Sue, Zachary J. Thompson, Frank S. Bates, *"Toughening of Epoxy Thermosets using Nano-Scaled, Self-Assembled Amphiphilic Block Copolymer: A Look into the Toughening Mechanisms"*, Presented at the **14th International Conference on Deformation, Yield and Fracture**, April 2009, Rolduc, Kerkrade, The Netherlands and published in the Conference Proceedings.
11. Bernd Hoevel, George Jacob, Gary Hunter, Marv Dettloff, Ha Pham, *"Advanced Epoxy Technology for Wind Turbine Blade"*, Presented at the **2009 JEC Composite Show**, Wind Energy Forum, March 2009, Paris, France.
12. Bernd Hoevel, Marv Detloff, George Jacob, Gary Hunter, Ha Pham, *"Advanced Epoxy Technology for Wind Turbine Blade"*, Submitted to **Renewable Energy** (2009).
13. George C. Jacob, Bernd Hoevel, Ha Q. Pham, Marv. L. Dettloff, Nikhil E. Verghese, Rajesh H. Turakhia, Gary Hunter, John F. Mandell, Daniel Samborsky, *"Technical Advances in Epoxy Technology for Wind Turbine Blade Composite Fabrication"*, Accepted to be Presented at the **2009 SAMPE Conference**, October 2009, Wichita, KA, USA and published in the Conference Proceedings.

Thank you!

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