Luxinnovation Greater Region Plastics Workshop
Luxembourg
December 4th, 2018

Enhancing the Sustainability of Epoxy Resins and their Fiber Composites

Daniel F. Schmidt*

Associate Professor of Plastics Engineering
University of Massachusetts Lowell

*Lead Research & Technology Associate
Department of Materials Research and Technology
Luxembourg Institute of Science & Technology
(since September 1, 2017)

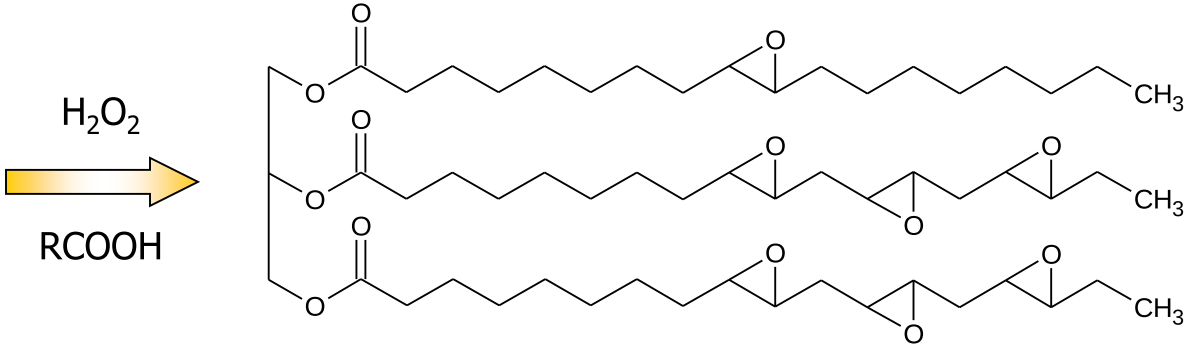
Introduction

- Epoxy resins find many uses
  - Adhesives and binders
  - Composites
  - Coatings
  - Encapsulants and potting compounds
- Nearly all epoxies are petroleum derived
- Health and safety can be a concern
  - Acute toxicity (hardeners especially)
  - Chronic toxicity (hardeners, bisphenols, etc.)
- Recycling and reuse are extremely challenging

→ Many opportunities to improve sustainability!

Selecting a Sustainable Epoxy Resin

http://dawnofthenewage.com/wp-content/uploads/2013/01/linseed-oil-and-flax-seeds.jpg



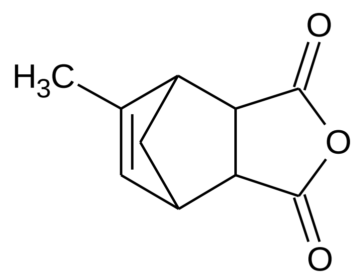
Epoxidized Linseed Oil (ELO)

- Clean, single-step synthesis
- Good availability (multiple large suppliers)
- Inexpensive (<€2/kg)
- Low viscosity (~1,000 cps)
- High functionality (f ~ 6, EEW ~ 170-180)
- Minimally toxic (FDA approved for food contact)
- Derived from a non-food crop
- Low reactivity (all secondary epoxies)

Forming a Network: Anhydride Cure

ELO

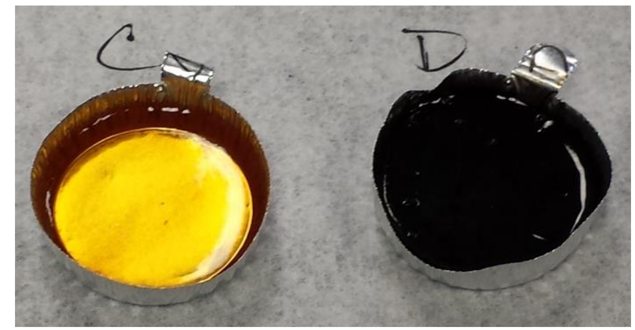
+



Ex.: Nadic Methyl Anhydride (NMA)

Various catalysts

160-200°C
2-24 hr.

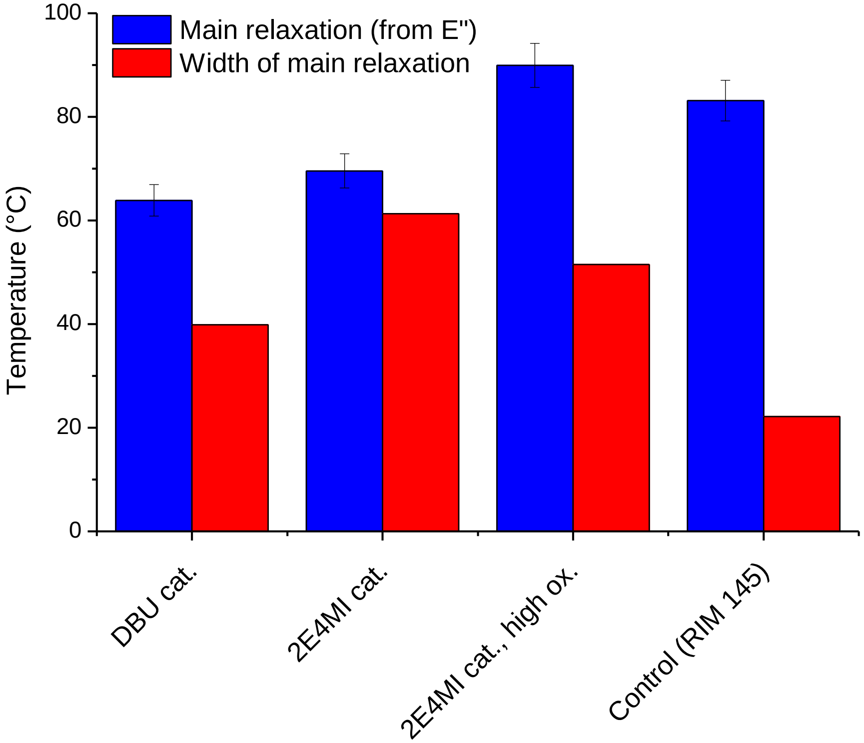


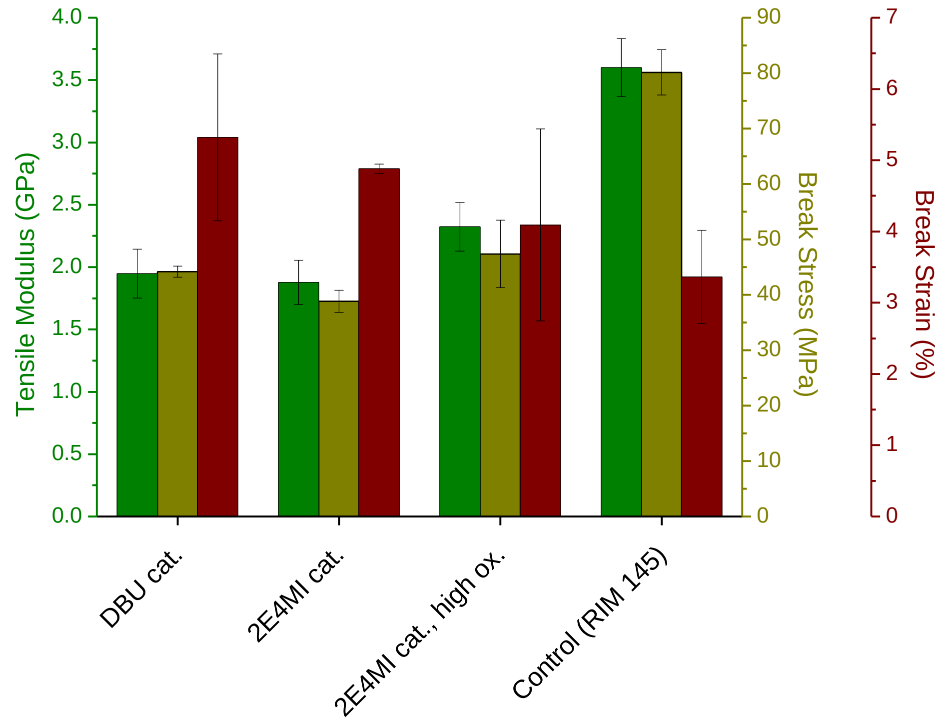
- Found workable with a range of liquid anhydrides
- Catalysis required for curing to proceed
- High curing temperatures necessary
- Homogeneous, void-free material produced
- Highest hardness, modulus values realized

→ For more, see: *Ind. Eng. Chem. Res.*, **2017**, 56 (10), pp 2658–2666
Ind. Eng. Chem. Res., **2017**, 56 (10), pp 2673–2679

Anhydride-cured ELO: DMA & Tensile Properties

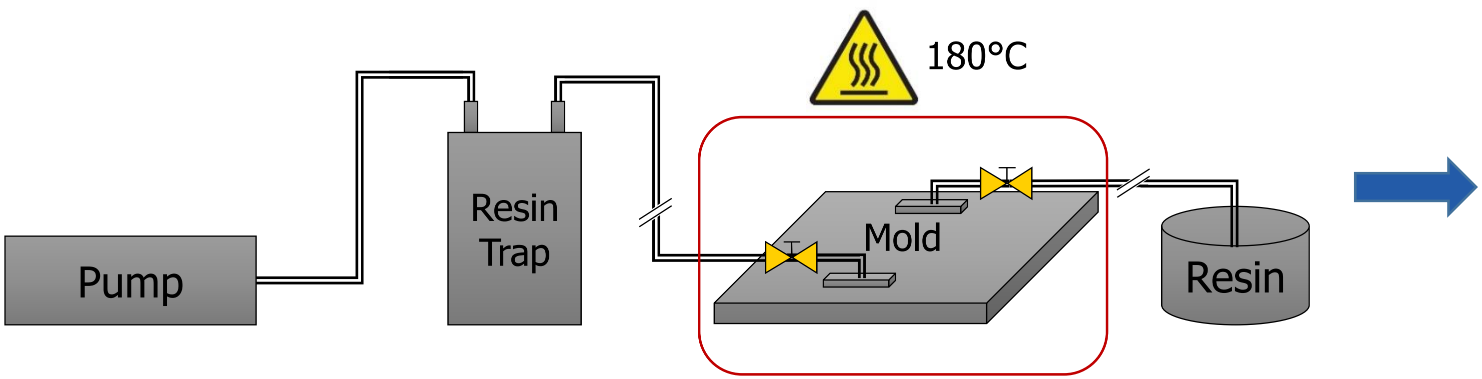
- Methyltetrahydrophthalic anhydride (MTHPA) identified as optimal hardener; two catalysts studied:
  - DBU = 1,8-Diazabicyclo(5.4.0)undec-7-ene – liquid, cures well but induces voiding during composite formation
  - 2E4MI = 2-Ethyl-4-methylimidazole – requires pre-heating, similar cure levels to DBU but no void formation
- Standard (9.6% oxirane oxygen) and high oxirane (10.4% oxirane oxygen) ELO used
- Control was Hexion RIM 145, a high performance anhydride-cured epoxy used in wind energy





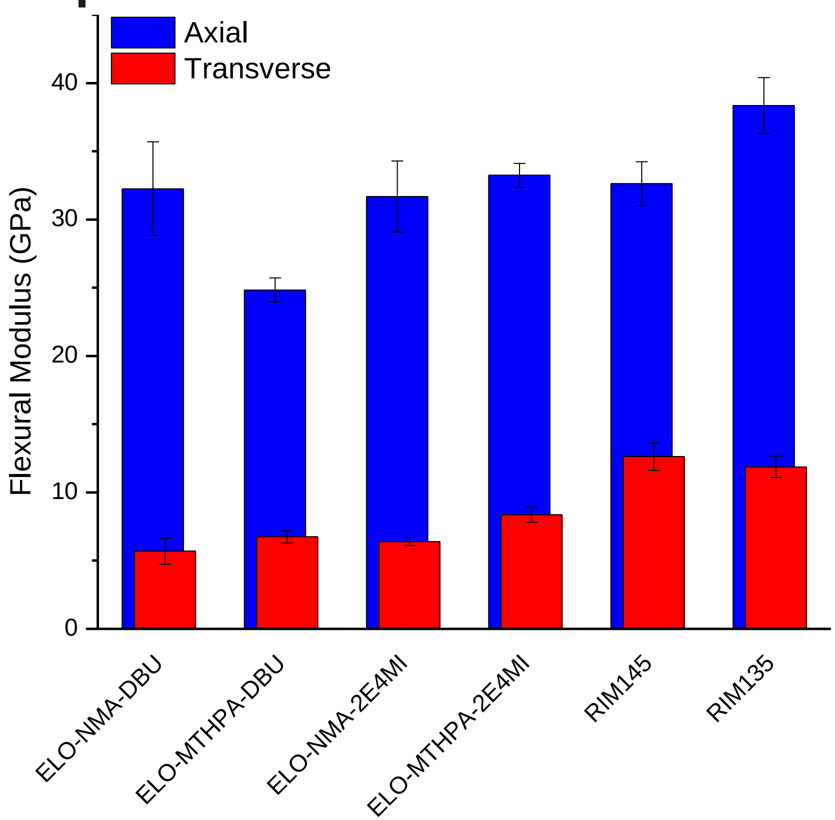
Anhydride-cured ELO: Composite Production

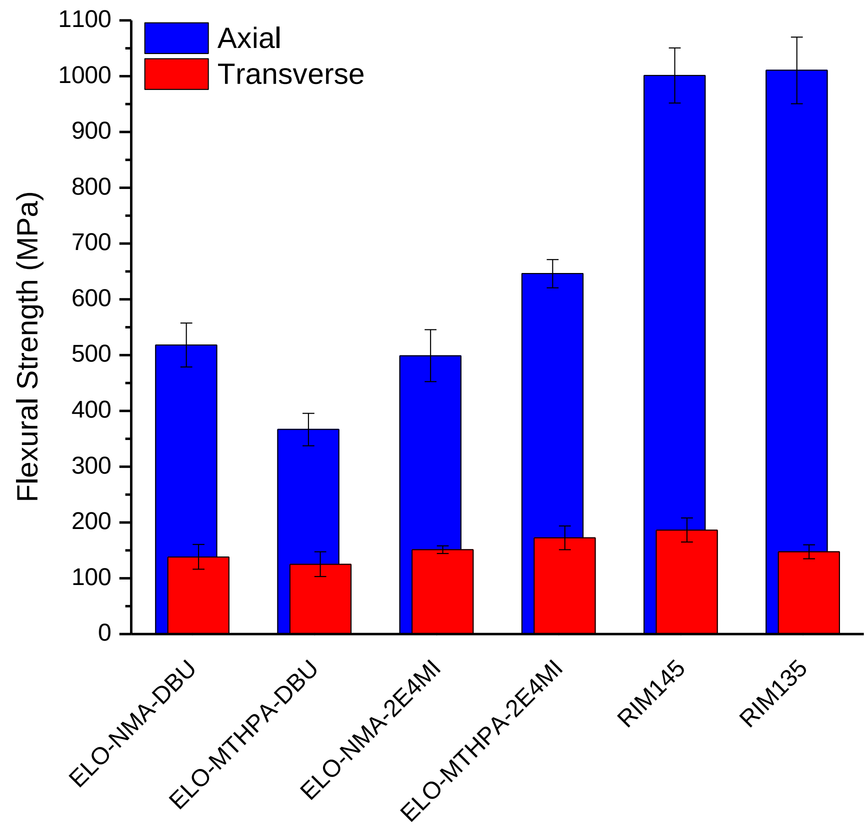
- **V**acuum **A**ssisted **R**esin **T**ransfer **M**olding (VARTM) gives test coupons



- Bioepoxies are ELO cured with MTHPA or NMA, catalyzed with DBU or 2E4MI
- Conventional controls are Hexion RIM 135 (amine-cured) and RIM 145 (anhydride-cured), both used in wind energy
- Unidirectional (UD) stitched E-glass (Saertex 955) provides reinforcement
- Constituent component analysis:
  - Fiber fraction = 52-57 vol%
  - Resin fraction = 42-46 vol%
  - Void fraction = 0.7-1.4 vol% (5.5 vol% for ELO-MTHPA-DBU)

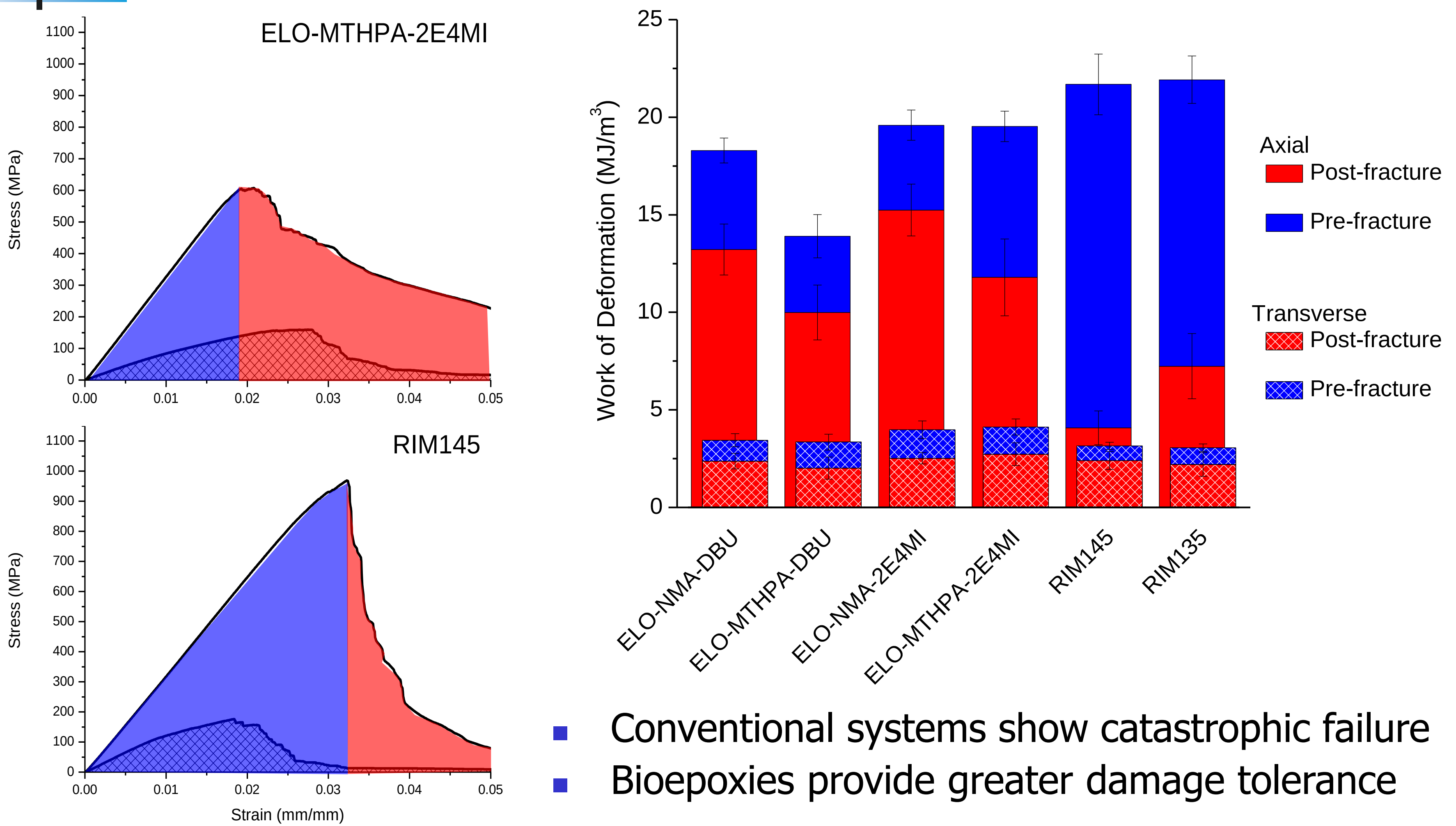
UD E-glass Composites: Flexural Properties





- Resin dominates transverse properties
- Axial modulus is fiber-dominated, while strength is more sensitive to interface
- Excessive voiding compromises properties of ELO-MTHPA-DBU in particular

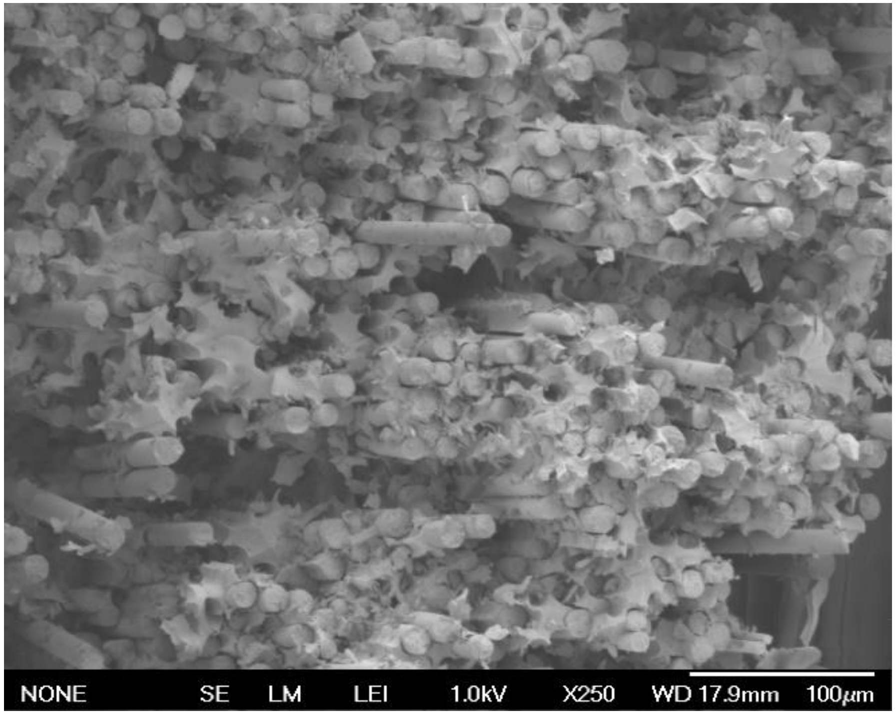
UD E-glass Composites: Flexural Properties



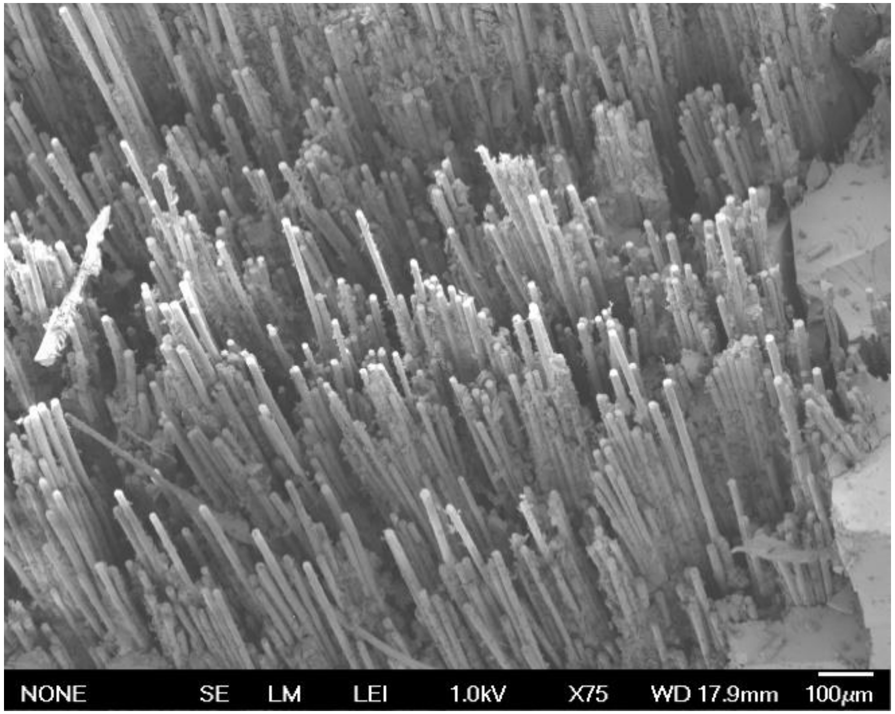
- Conventional systems show catastrophic failure
- Bioepoxies provide greater damage tolerance

UD E-glass Composites: Post-fracture Analysis

RIM145



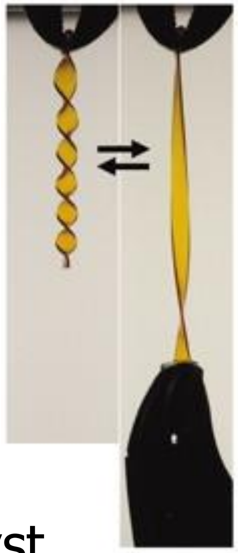
ELO-MTHPA-2E4MI



- Conventional control shows strong matrix adhesion, fiber breakage
- Bioepoxy shows much more debonding, implying a weaker interface

Adding Reworkability

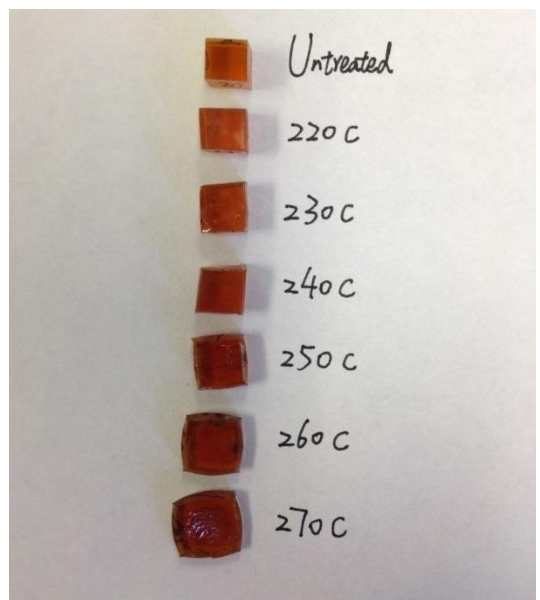
- Montarnal et al achieve reworkability in epoxies via transesterification – *Science* 334 965 (**2011**)
  - DGEBA / dicarboxylic acid / tricarboxylic acid
    - Modulus = 4 MPa
    - Failure stress = 9 MPa
    - Failure strain = 180%
  - DGEBA / glutaric anhydride
    - Modulus = 1.8 GPa
    - Failure stress = 55 MPa
    - T_g ~ 80°C
  - Zinc acetylacetonate used as transesterification catalyst
  - Implication is that excess hydroxyls are needed

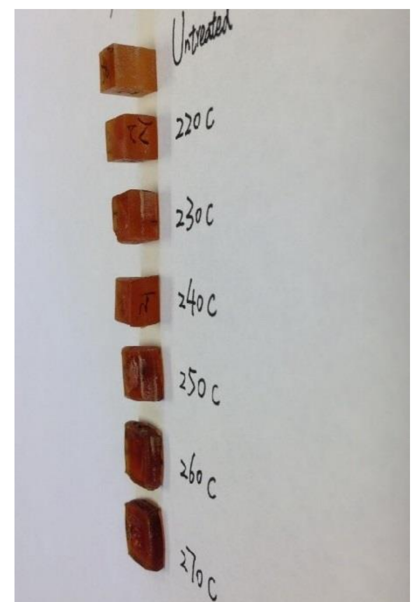


- We successfully apply this approach to systems <u>without</u> significant quantities of excess hydroxyls

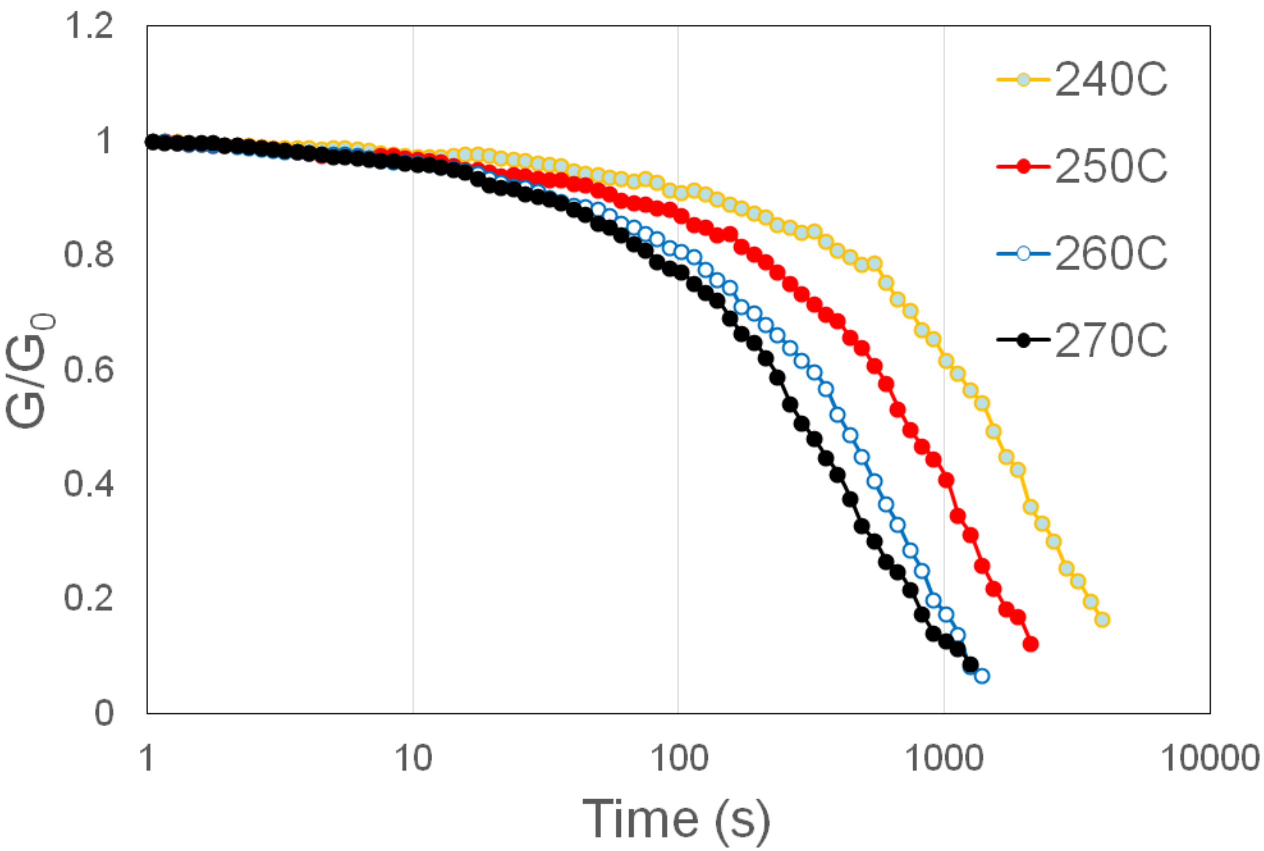
Assessing Reworkability: Catalyst Screening

- Static load applied to RIM 145 specimens for 4 hours
  - In the absence of catalysts, <4% strain is observed
  - In the presence of catalysts, can see up to ~70% strain
  - No significant changes in hardness after testing





Assessing Reworkability: Stress Relaxation

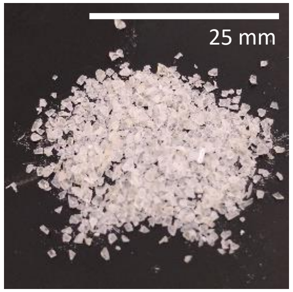


- Characteristic relaxation time (τ^*) defined according to Brutman et al. (*ACS Macro Lett.*, 2014, 3, 607)
  - $G/G_0 = 1/e \rightarrow \tau^*$
- Values of τ^* follow Arrhenius relation in RIM 145 control
  - E_a ~ 95-170 kJ/mol
  - τ^* ~ 80-500 s @ 270°C
  - Correlation between ln τ^* and strain under static load

Using Reworkability: *Mechanical Recycling*

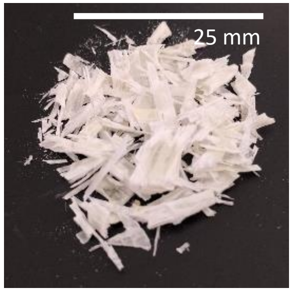
- Mechanical grinding

Regrind 5 mm



Regrind 2 mm

Regrind 0.2 mm



Regrind Composite

- Reprocessing via compression molding


Pristine cast resin

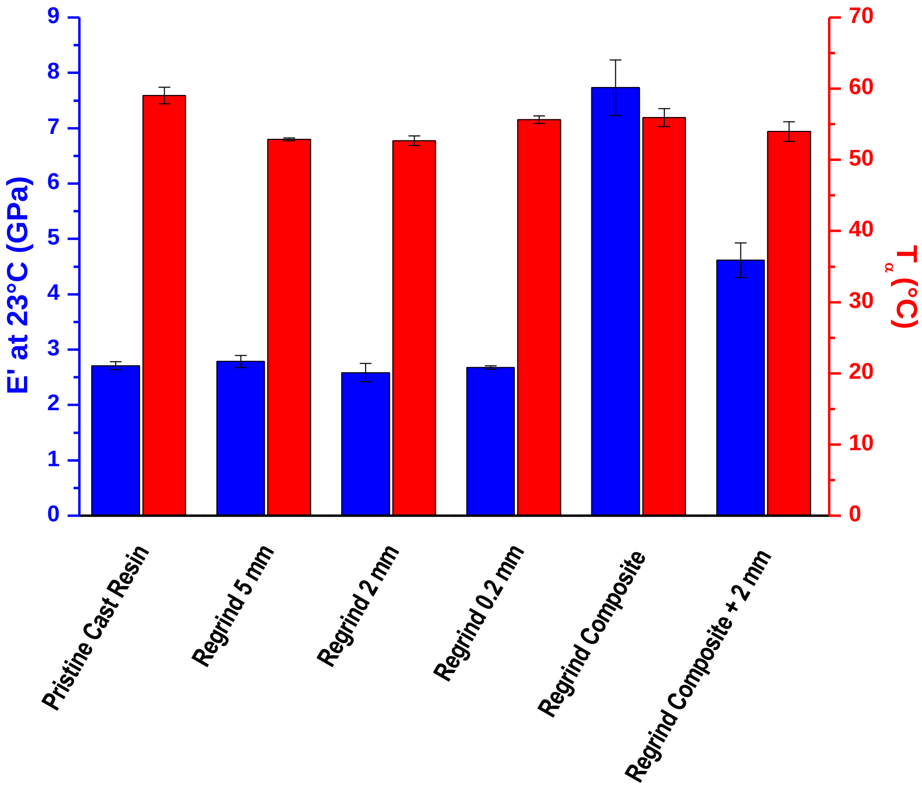

Regrind 5 mm

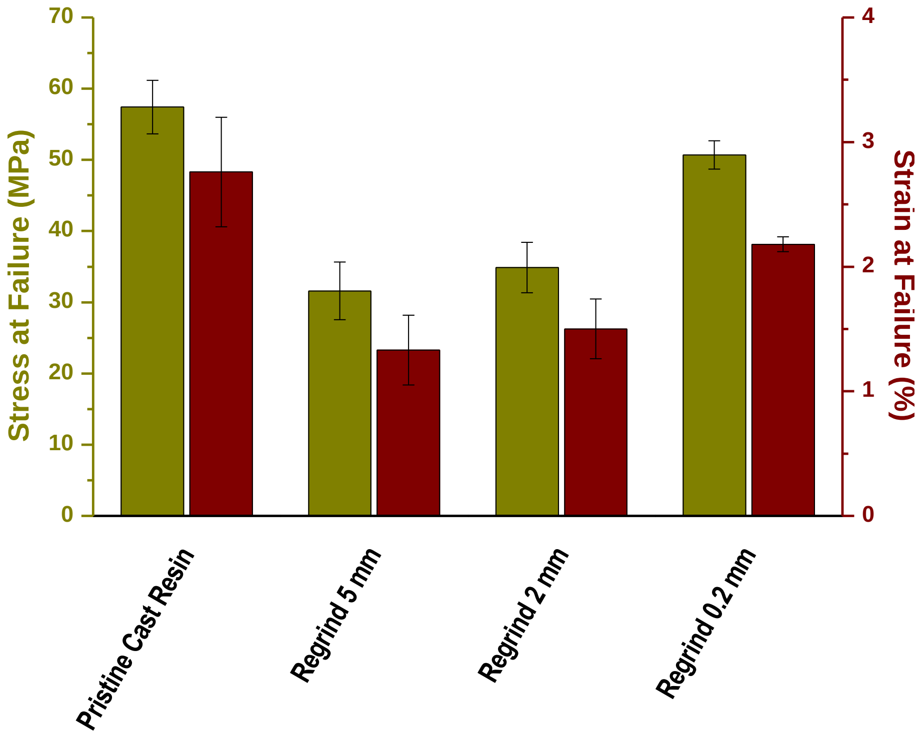

Regrind 2 mm


Regrind 0.2 mm


Regrind Composite

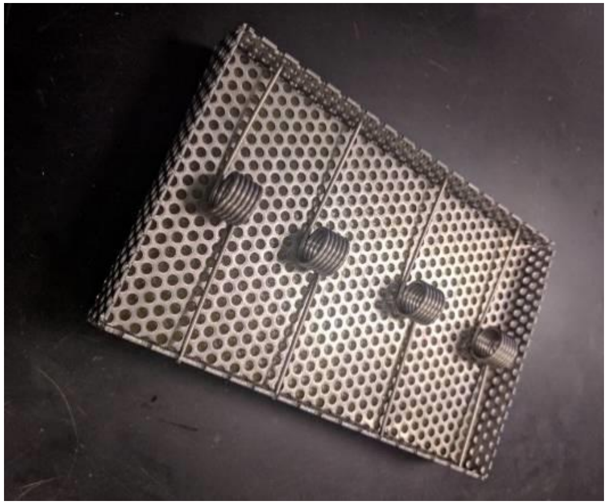
Using Reworkability:
Mechanical Recycling

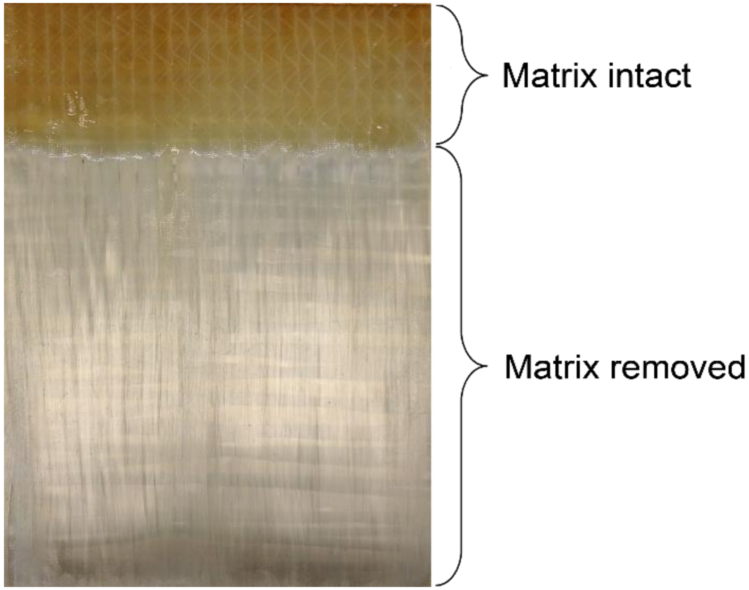




- Modulus and T_α are mostly retained regardless of particle size (similar results in bioepoxy systems)
- Stress and strain at failure are highest with finest particle size

Using Reworkability: Chemical Recycling



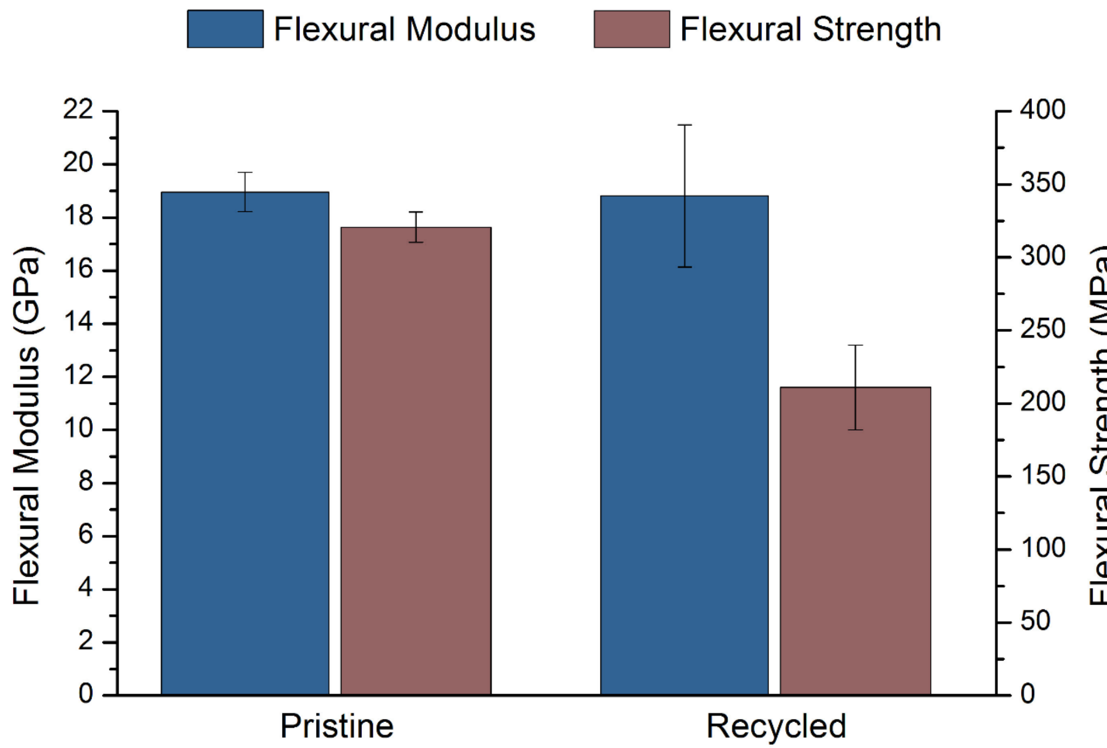


- Composite: RIM145 / E-glass
- Solvent: 1-Dodecanol
- Catalyst: *n*-butyltin tris(2-ethylhexanoate)
- Heated for 12 hours
- Cleaned in solvent, then water

Using Reworkability: Chemical Recycling

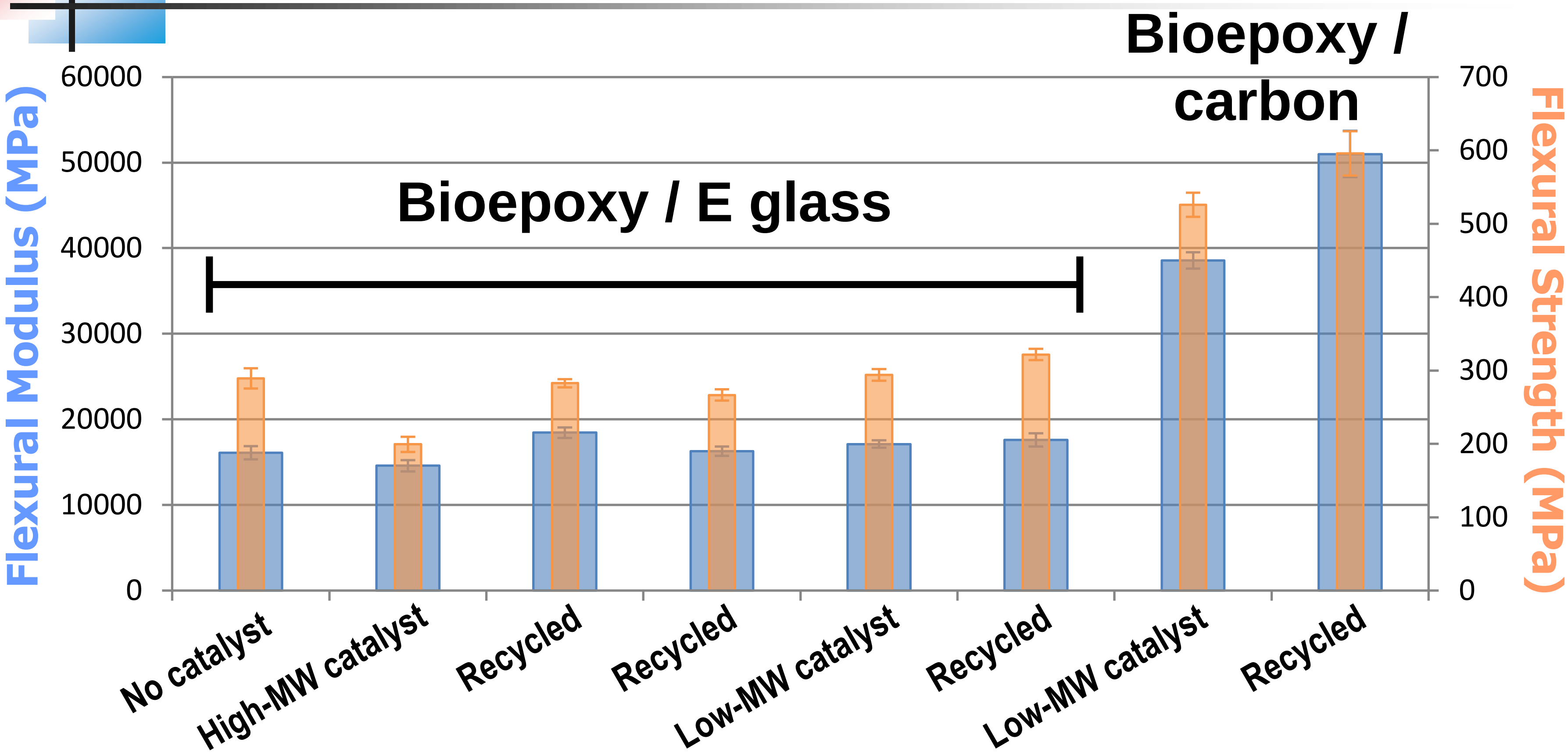
Reclaimed E-glass fibers

Reclaimed E-glass composite



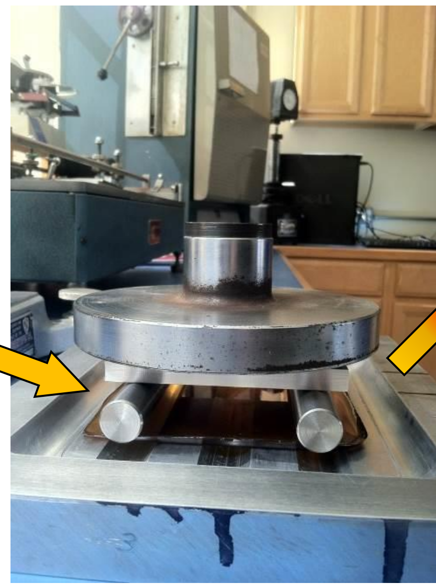
- Stiffness entirely retained
- Strength reduced, likely due to changes in fiber sizing

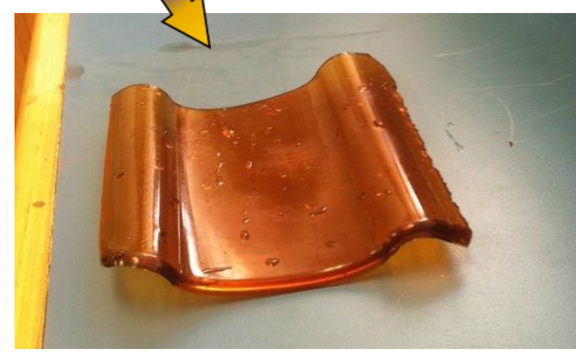
Using Reworkability: Chemical Recycling



- Can <u>improve</u> properties with reclaimed fibers in bioepoxies(!)
- Rate of chemical recycling is much faster as well

Using Reworkability: Reuse via thermoforming





- Flat sheet of RIM 145 epoxy resin prepared in the presence of transesterification catalyst
- Sample placed in tooling, heated to rework temperature, pressure applied
- Sample cooled in water to yield rigid, permanently deformed epoxy part!

Summary & Conclusions

- Anhydride-cured structural thermosets successfully produced based solely on epoxidized linseed oil (ELO)
- Bioepoxy composites provide good mechanical properties
  - Results are competitive with highly optimized controls
  - Bioepoxy composites are more damage tolerant than controls
  - Interfacial debonding, lower axial strength imply weak interface
  - Performance may be improved via optimization of fiber sizing
- Transesterification catalysts enable recycling and reuse
  - Mechanical recycling demonstrated, particle size effect noted
  - Chemical recycling demonstrated, reclaimed fibers give high performance composites, especially effective with bioepoxies
  - Thermoforming demonstrated, promises reuse of existing parts

THANK YOU FOR YOUR ATTENTION!

Acknowledgements

Collaborators and Group Members

- **Assoc. Prof. Emmanuelle Reynaud (UML Mechanical Engineering)**
- **Chris Kuncho (PhD), Wenhao Liu (PhD), Johannes Möller (PhD), Julia Kammleiter (MS), Julia Stehle (MS), Dr. Akshay Kokil**

Financial Support

- **National Science Foundation** (Award #1230884)
- **Massachusetts Toxics Use Reduction Institute**

Materials and Analytical Support

- **ACS Technical Products** (Epoxidized linseed oil)
- **Huntsman Advanced Materials** (MTHPA)
- **Hexion** (RIM 135 & 145)

General Support

- **W. Liu, Dr. A. Kokil & the Reynaud-Schmidt Research Group**
- **P. Casey, Dr. E. Ada & the UML Core Research Facilities**
- **D. Rondeau, M. Shone, Dr. X. Chen, Prof. S. Johnston, UML Plastics Engineering and the UML Composites Lab**

FOR MORE INFORMATION:

ACS Symp. Ser., **2018**, vol. 1310, ch. 18, pp 281-295