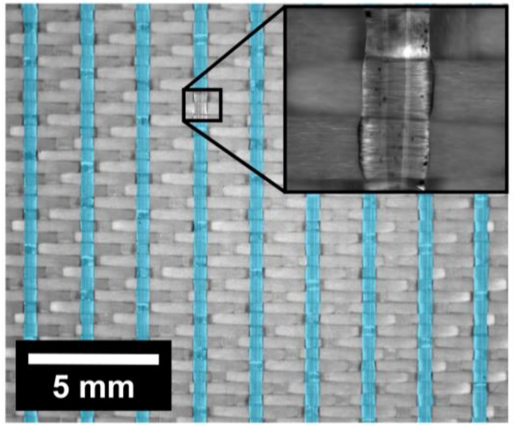
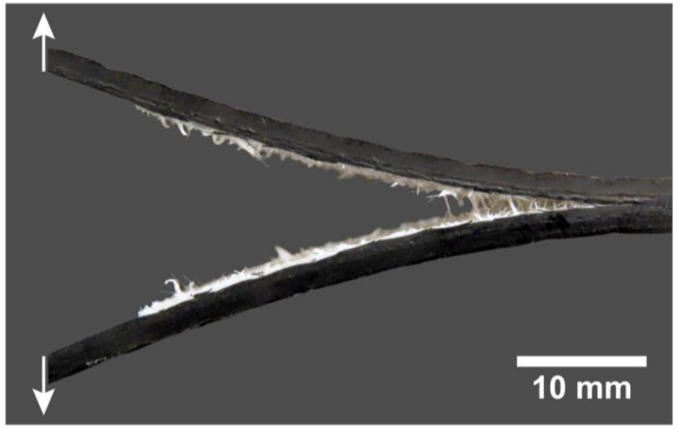
Synchronal Toughening and in situ Self-healing of Laminated Fiber-reinforced Composites via Copolymer Interlayers





Jack Turicek[1], A. Snyder[1], Prof. Patrick[1,2]

[1] Department of Mechanical and Aerospace Engineering

[2] Department of Civil, Construction, and Environmental Engineering

North Carolina State University (NCSU)

Outline

- Motivation / Background
- 3D-printing and Composite Fabrication
- Investigation of Toughened / Self-healing Composites
  - In-plane Tensile Comparison
  - Thermo-mechanical Property Evaluation
  - Interlaminar Fracture Toughening
  - *In Situ* Self-healing via Thermal Remending
- Summary / Conclusions

Motivation

Aerospace

Automotive

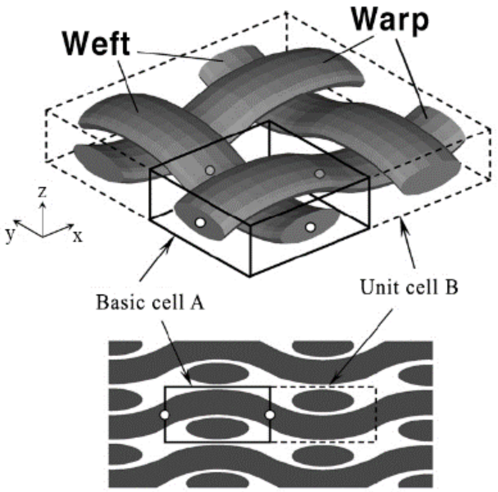
Civil

Naval

Energy

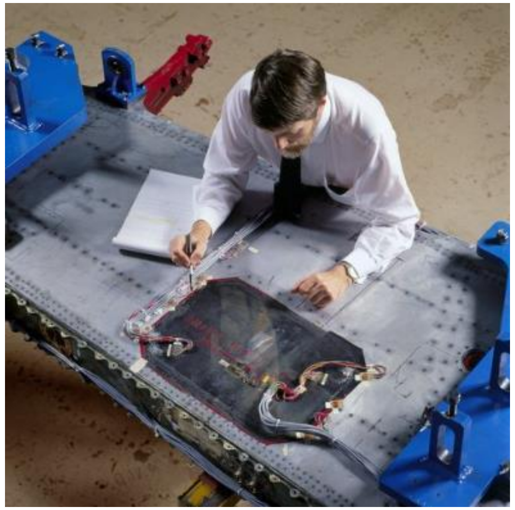
Motivation/Background

Composite architecture



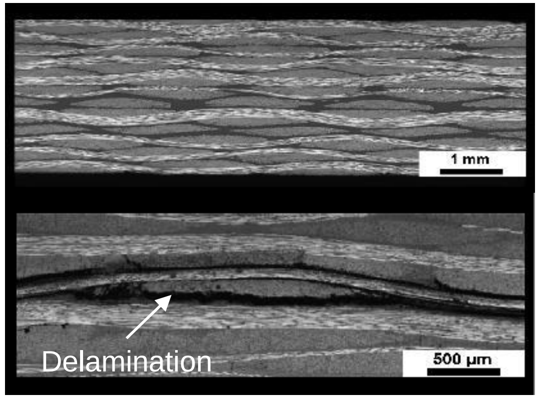
Compos. Struct. **79** (2007)

Difficult to inspect/repair



www.dsto.defence.gov.au

Fracture damage

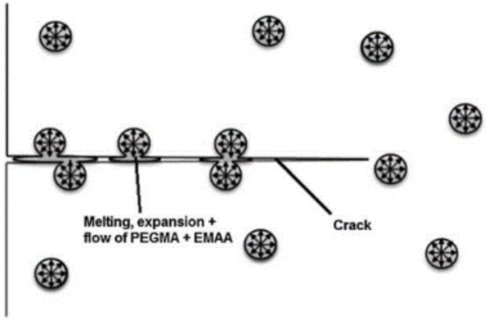


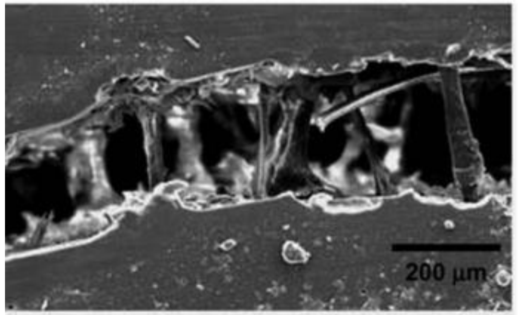
ASM International (2010) *Polymer* **53** (2012)

Catastrophic failure

USAF Hilltop Times

Proactive Toughening to Prevent Delamination

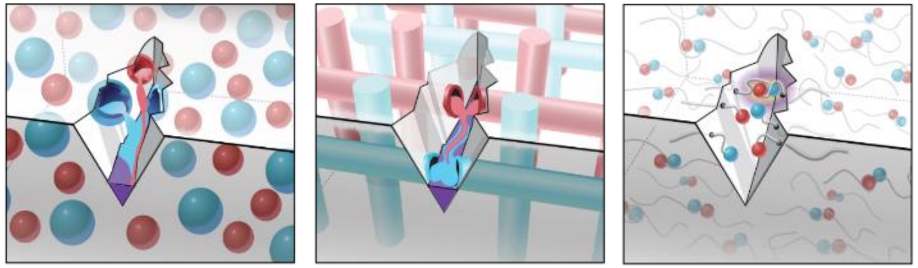




Polym. Chem. **4** (2013)

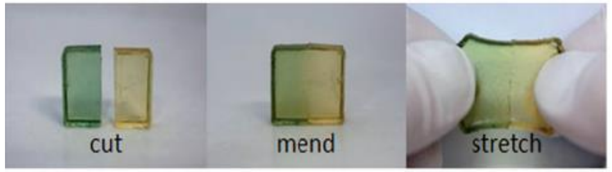
Reactive Self-healing to Address Delamination

Capsule Vascular Intrinsic



Annu. Rev. Mater. Res. **40** (2010)

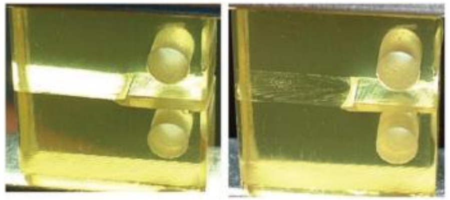
Soft Materials



Agnew. Chem. **51** (2012)

- Interfacial contact enables room-temperature repair

Structural Materials



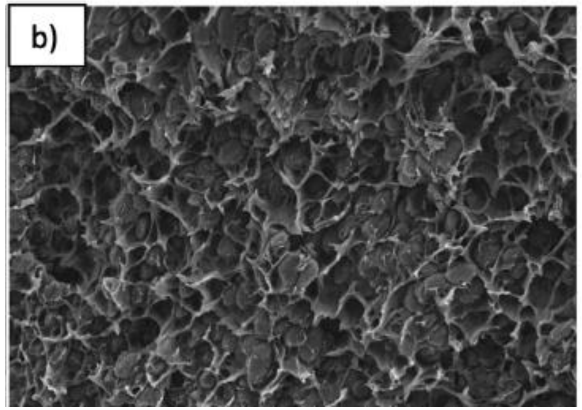
Science **295** (2002)

- Requires external energy for repair (e.g., elevated temperature)

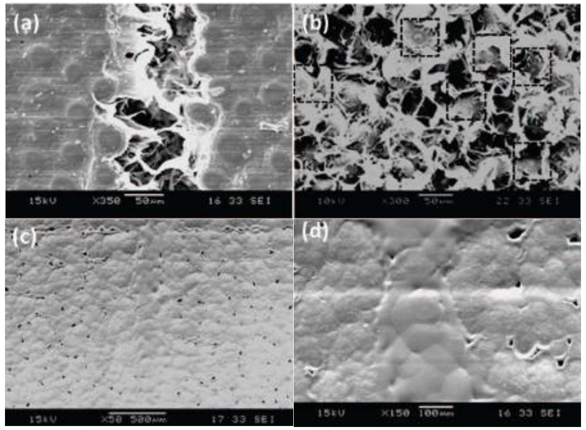
Thermal Remending

- **Thermal remending** is a hybrid (extrinsic-intrinsic) technique with **thermoplastic inclusions** embedded in **structural material**
- After damage, application of **heat** enables the **bond reformation** of thermoplastic to provide healing of the larger structural host
- Poly(ethylene-*co*-methacrylic acid) – **EMAA** – is a commodity polymer with proven **thermal remending** ability

Modified Matrices

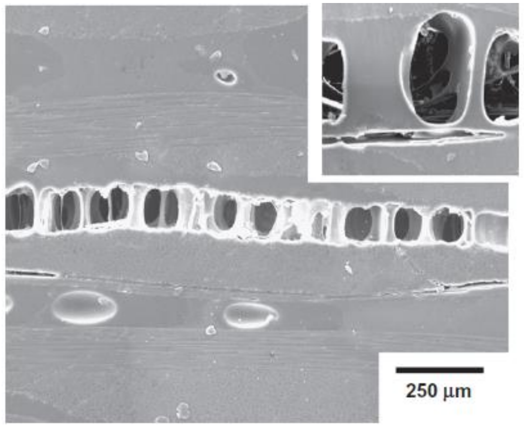


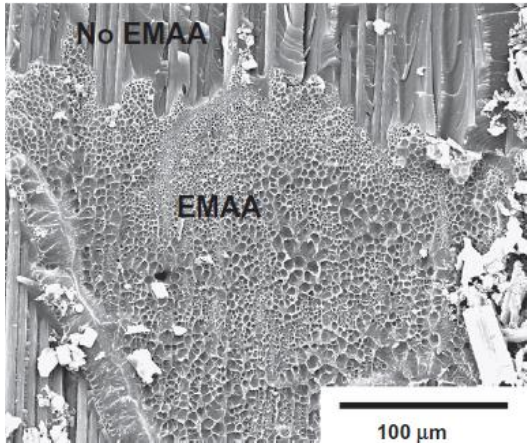
Polymer **92** (2016)



ACS Appl. Mater. Inter. **1** (2009)

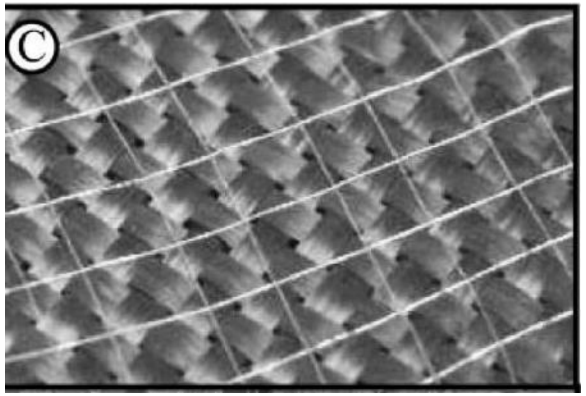
Particles and Woven Fibers



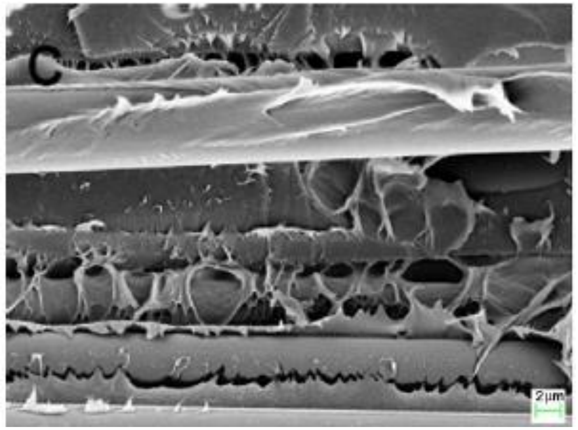


Compos. Part A **43** (2012)

Interlayers



Macromol. Mater. Eng. **295** (2010)



Compos. Part A ***43*** (2012)

<u>Important Notes</u>

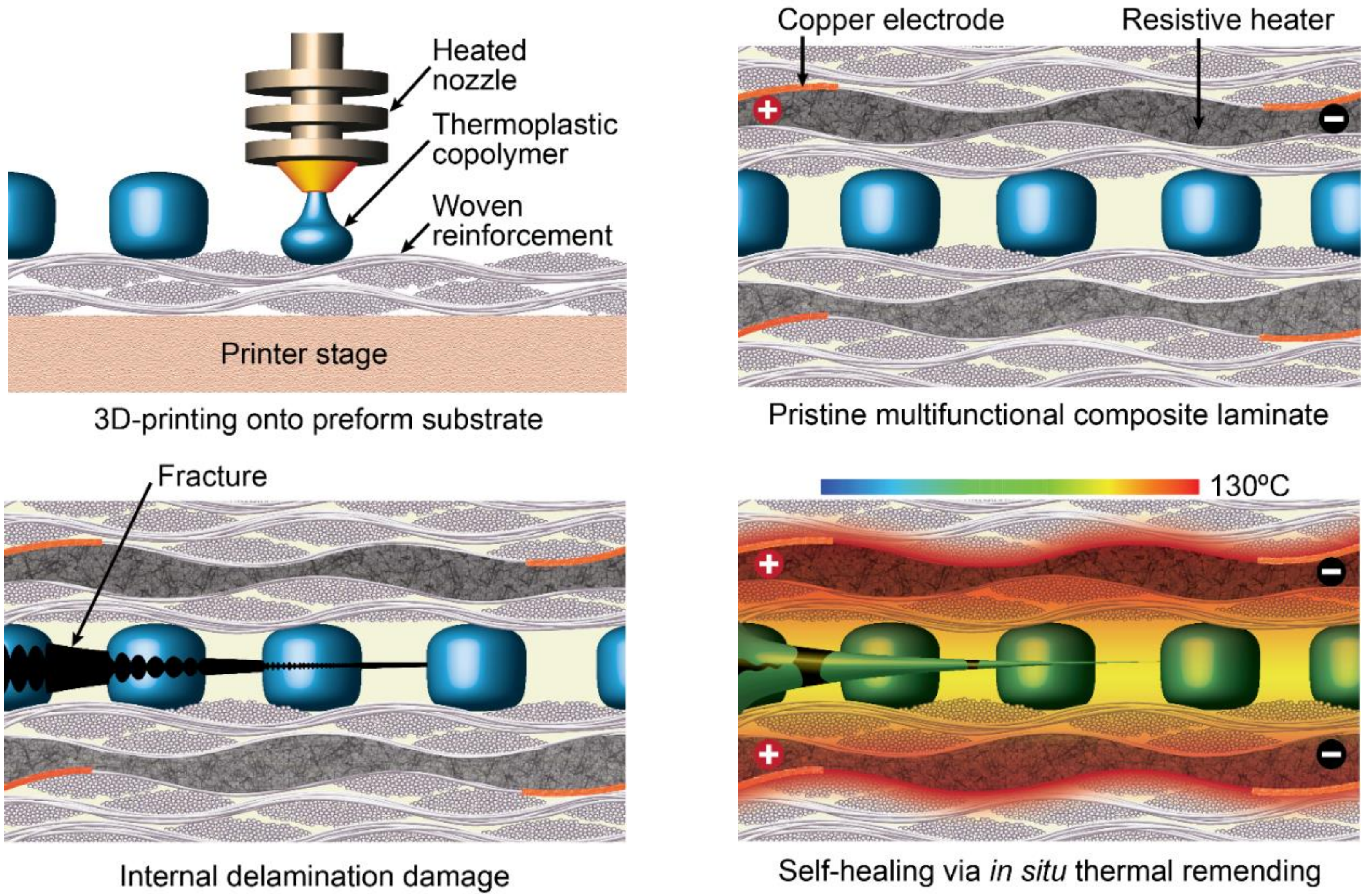
1. Healing achieved ***ex situ*** - (in an oven)

2. Healing requires heating **above the glass-transition** temperature (T_g) - (softening)

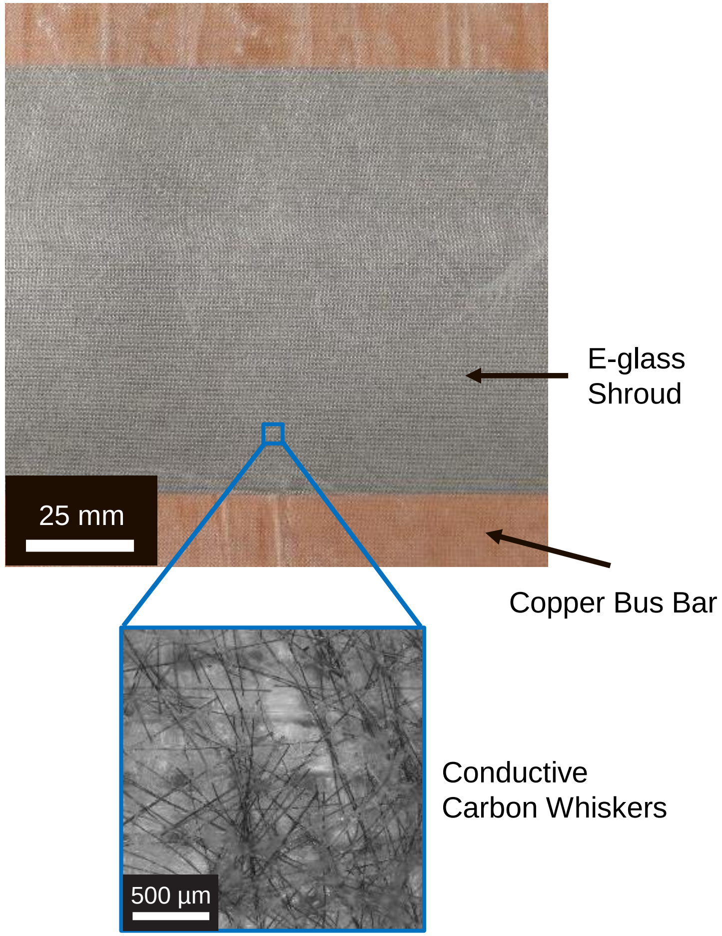
Toughening
+
Self-healing

State-of-the-Art Thermal Remending Technique

- Recently our lab has developed a thermal remending platform for ***in situ* self-healing** below the **glass-transition temperature (T_g)**



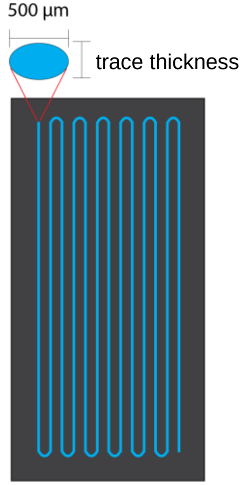
Textile Resistive Heaters



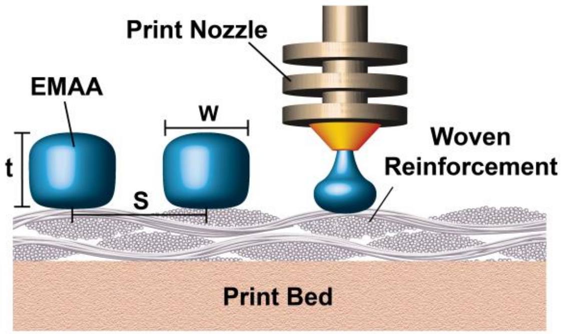
Snyder et al. Prolonged in situ self-healing in structural composites via thermo-reversible entanglement, *Nature Communications*: **13** 6511 (2022).

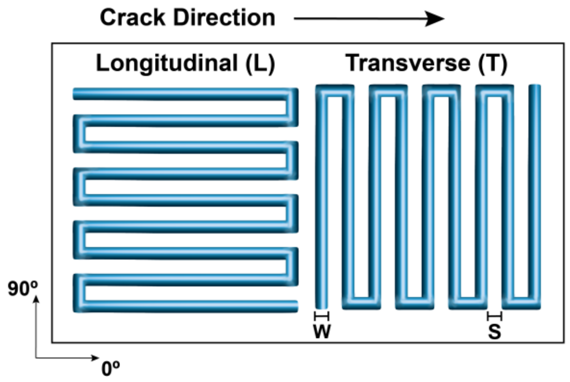
3D-Printing and Composite Fabrication

- Investigate effect of EMAA pattern **thickness, areal coverage**, and **orientation** on toughening and healing performance
- Fused deposition modeling (FDM) to precisely print EMAA patterns directly onto woven substrate



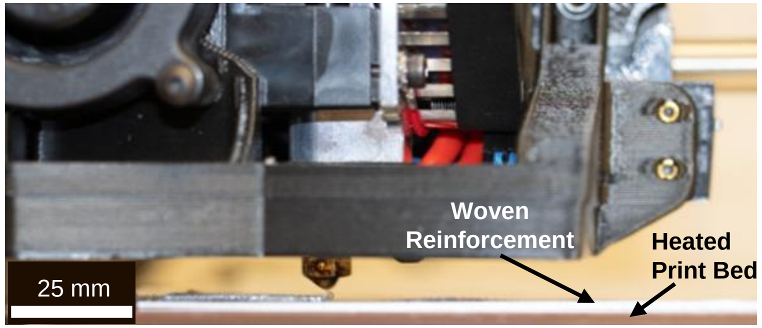
Printing Parameters



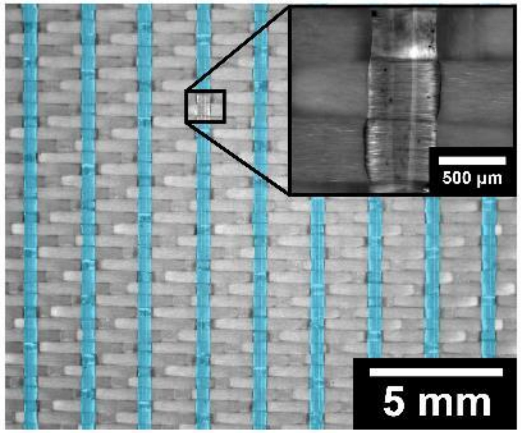


t – pattern thickness **S** – pattern spacing **W** – trace width

Printing directly on woven fabric

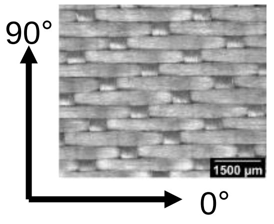


Completed prints with high precision



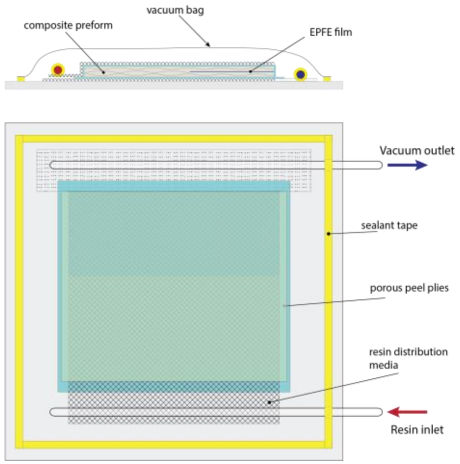
VARTM Process and Composite Fabrication

EMAA Toughened GFRP layup
$[90/0]_4$/**EMAA**/$[90/0]_4$

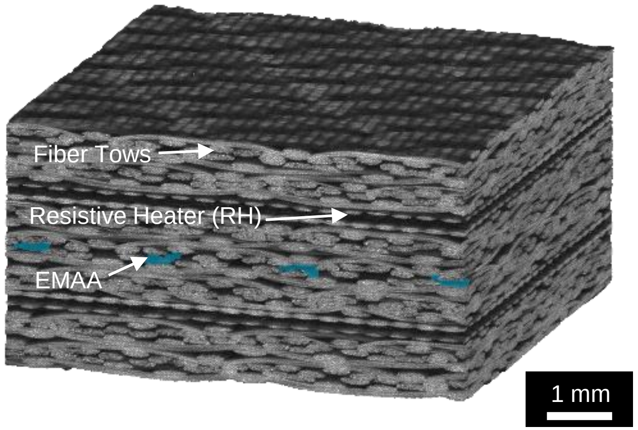


Self-healing GFRP layup
$[0/90]_2$/**H**/0/90/0/**EMAA**/90/0/90/**H**/$[0/90]_2$

GFRP – Glass Fiber Reinforced Polymer



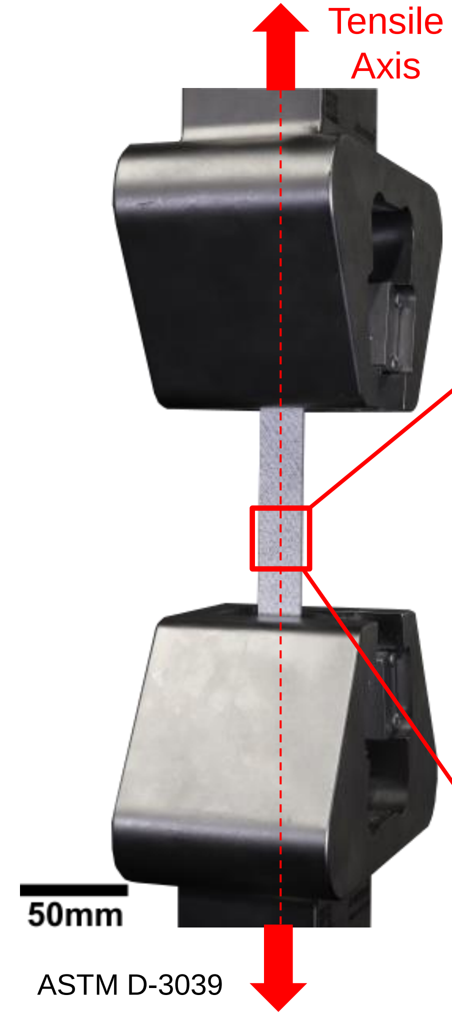
Laminated Composite Full Thickness CT Scan



Curing conditions: 24h @ RT + 2h @ 121°C + 2h @ 150°C

In-plane Tensile Performance

- EMAA inclusions have **minimal impact** on **in-plane tensile** performance

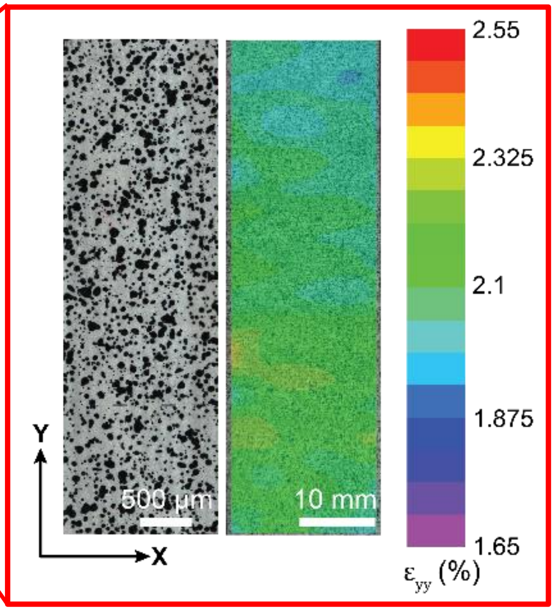


ASTM D-3039

Plain GFRP layup: $[90/0]_8$

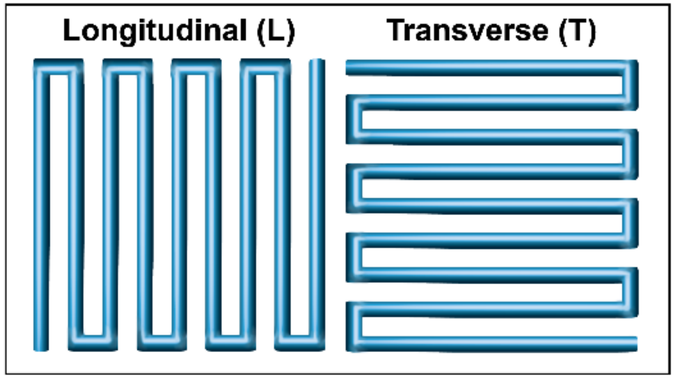
EMAA Toughened GFRP layup: $[90/0]_4$/**EMAA**/$[90/0]_4$

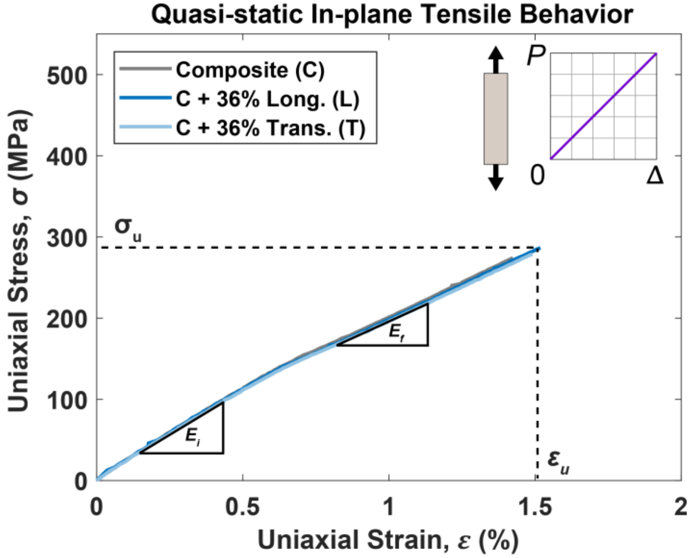
Digital Image Correlation (DIC)

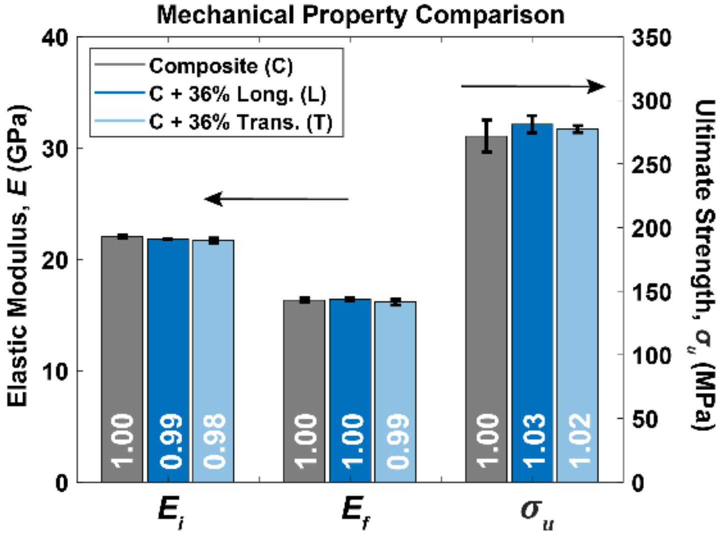


Note

- EMAA at maximum 36% areal coverage





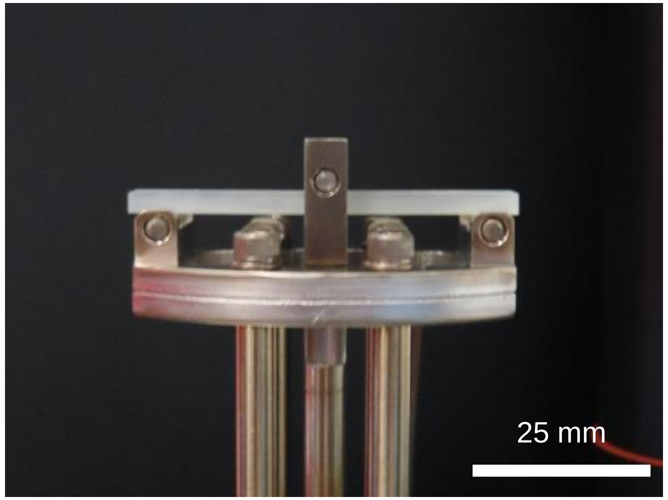


- Bilinear stress vs. strain response is nearly **indistinguishable** between EMAA toughened and plain composites
  - Initial modulus, final modulus, and ultimate tensile strength exhibit **<5% difference**

Thermomechanical Characterization

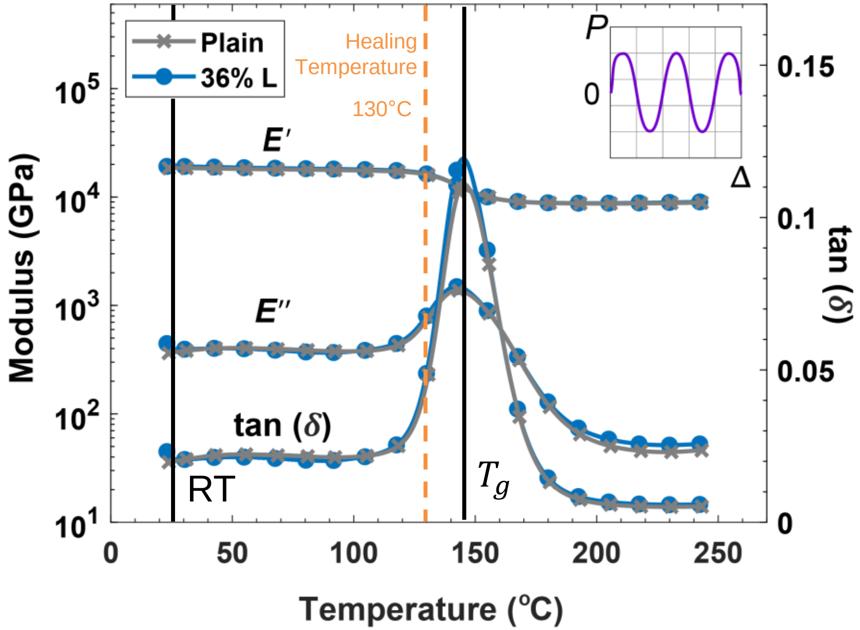
- EMAA inclusions have **minimal impact** on **thermomechanical performance**

DMA Fixture & Specimen

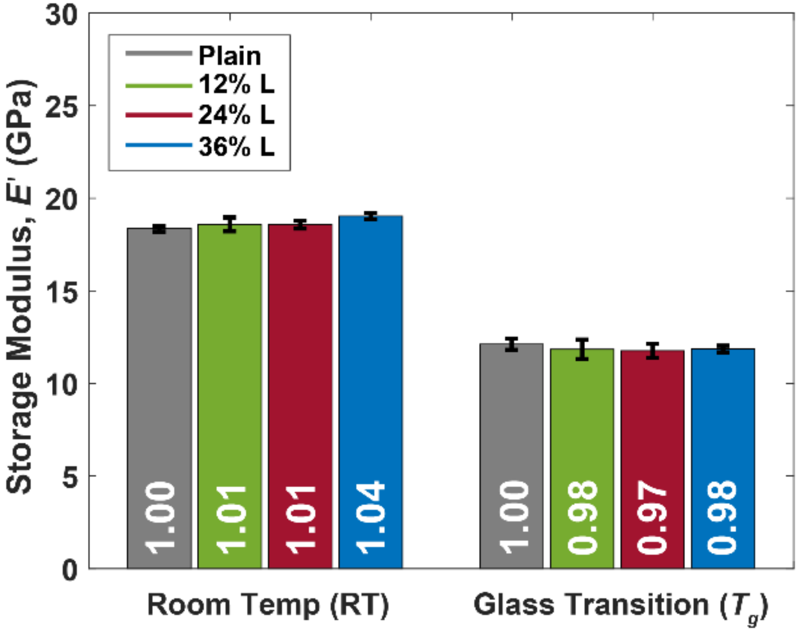


3-pt Flexure (1Hz, 5°C/min)

Dynamic Thermo-mechanical Flexural Behavior



Elastic (Storage) Modulus Comparison



$$E^* = E' + iE'' \qquad \tan(\delta) = \frac{E''}{E'}$$

ASTM D-7028, E-1640

- Evolution of E’, E’’, and $\tan(\delta)$ are nearly **indistinguishable** between EMAA toughened and plain composites
- Elastic storage modulus exhibit **<5% difference** at room temperature and the glass transition temperature

Because thermal remending (130°C) occurs below the T_g of the composite matrix:

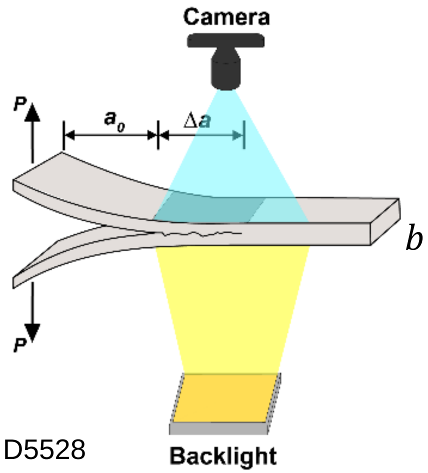
- Maintain **structural integrity** during healing
- EMAA inclusions **do not meaningfully affect** thermomechanical performance within operating temperature range

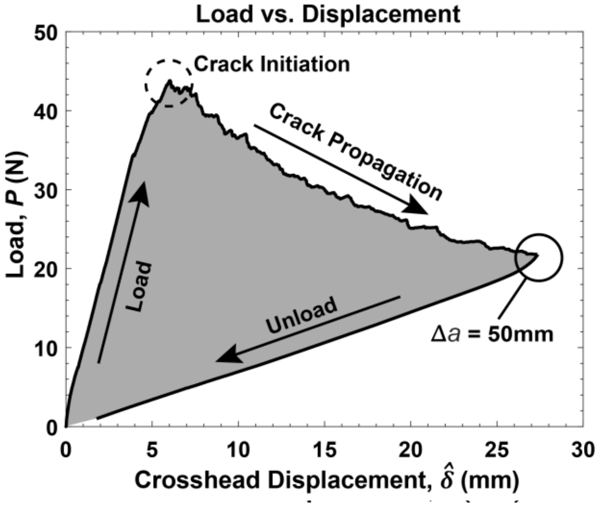
Fracture Testing and *In Situ* Thermal Remending

- **Mode-I fracture** testing is used to characterize **toughening** and **self-healing** performance

Fracture Testing to Evaluate Interlaminar Toughness

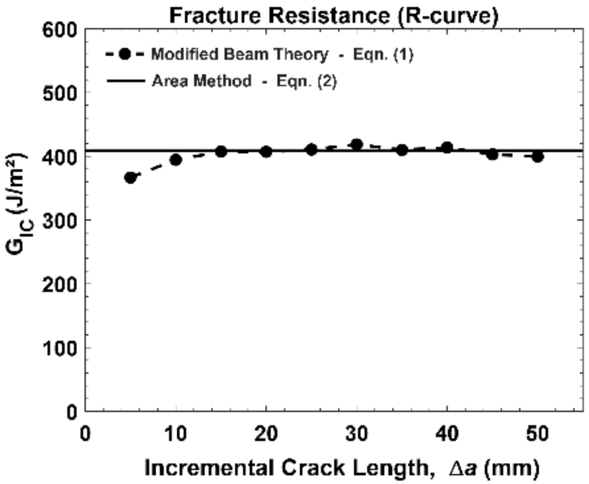
Double Cantilever Beam (DCB)





ASTM D5528

Critical Strain Energy Release Rate



Modified Beam Theory **(Eq. 1)**

$$G_{\mathrm{IC}} = \frac{3P\hat{\delta}}{2b(a + |\Delta|)}$$

a = total crack length ($a_0 + \Delta a$)

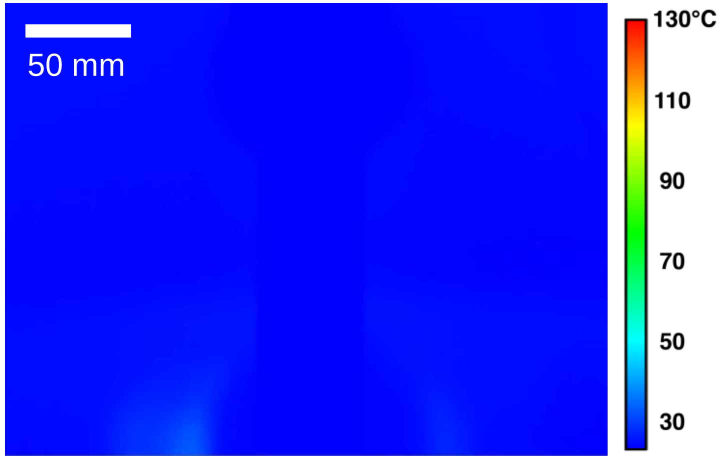
$|\Delta|$ = fixed end correction factor*

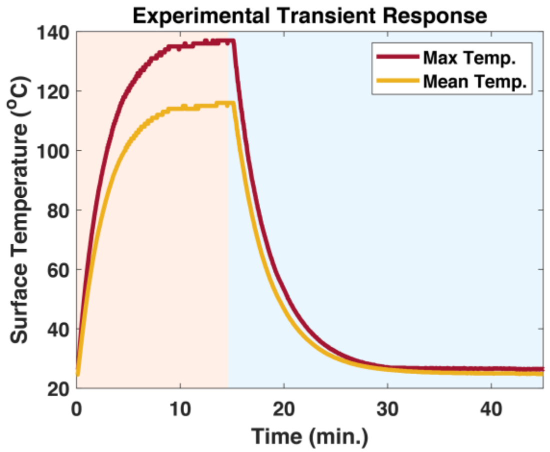
Area Method** **(Eq. 2)**

$$G_{\mathrm{IC}} = \frac{1}{b}\frac{\Delta U}{\Delta a} \qquad \Delta U = \int_0^{\hat{\delta}} P\, d\hat{\delta}\Big|_{\Delta a}$$

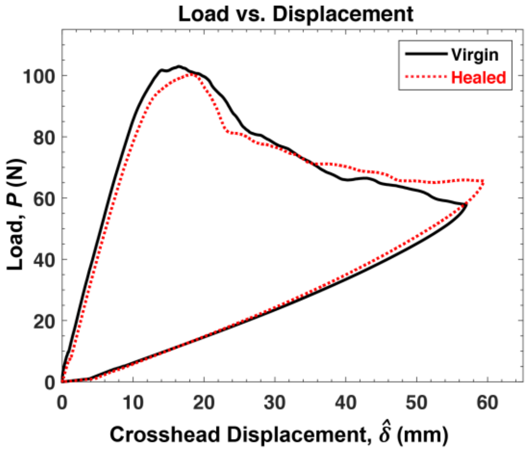
Thermal Remending to Evaluate Self-healing Performance

***In Situ* Heating**





Healing Cycle: (heat) 15 min. @ 130°C (cool) 30 min. until RT



Healing Efficiency** **(Eq. 3)**

$$\hat{\eta} = \frac{G_{\mathrm{IC}}^{\mathrm{healed}}}{G_{\mathrm{IC}}^{\mathrm{virgin}}} \times 100\%$$

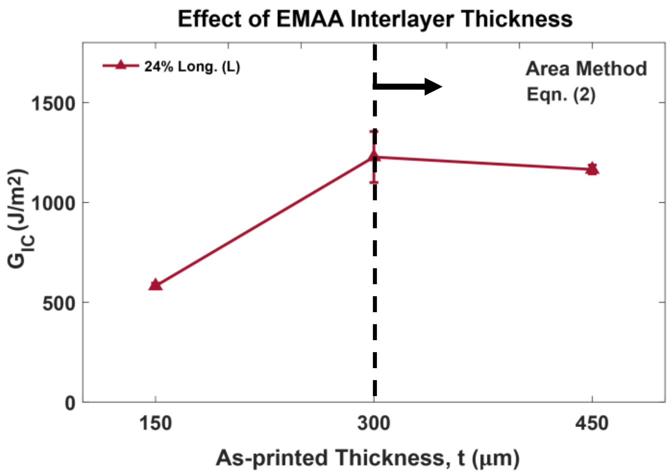
G_{IC} calculated with area method

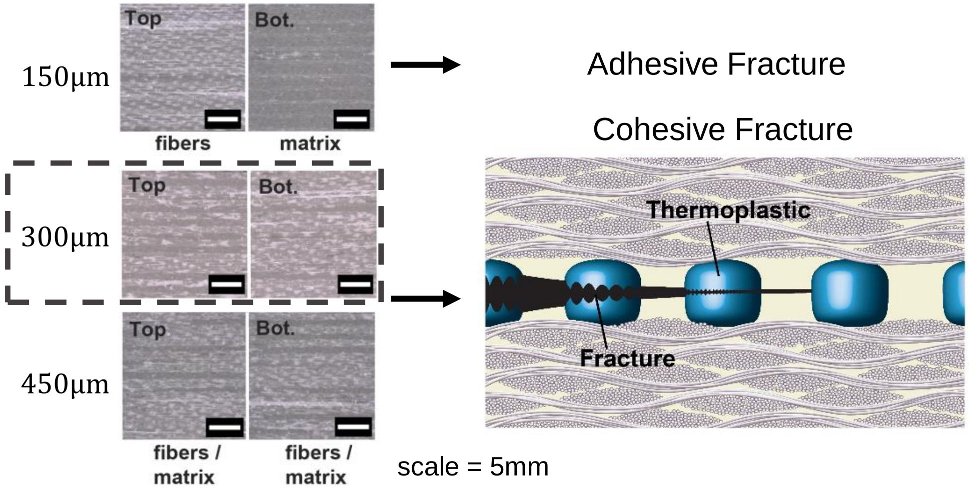
Journal of Materials Science Letters **8** (1989). ** *Advanced Materials* **26** (2014).

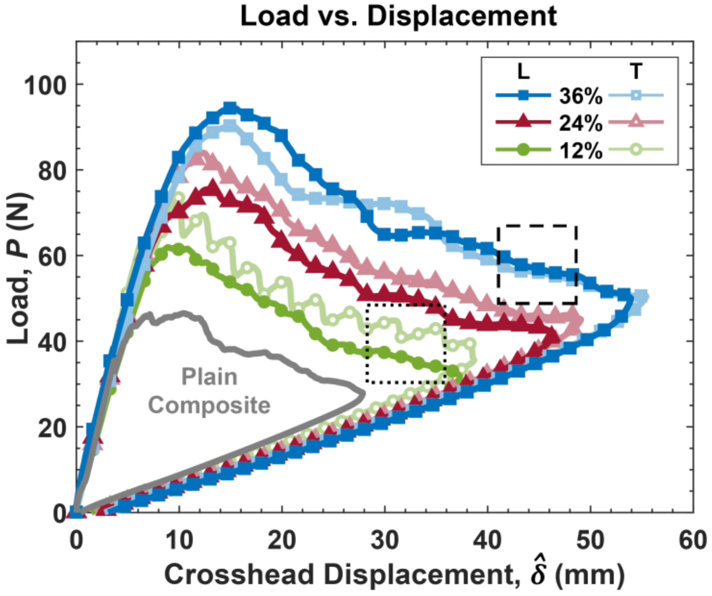
Interlaminar Toughening Performance

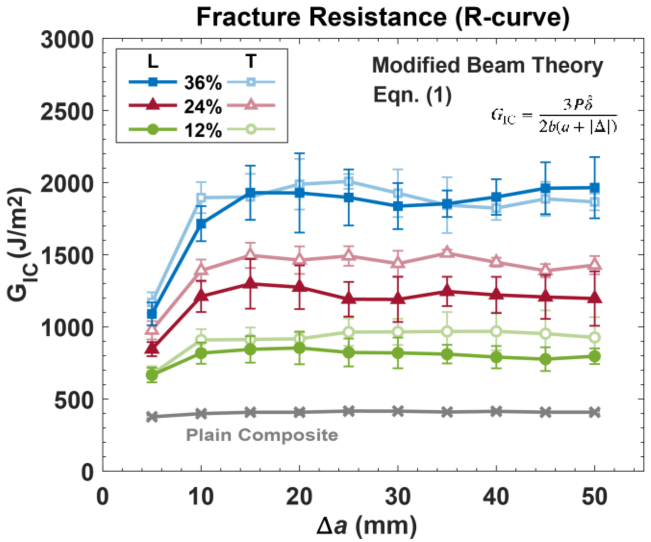
EMAA Toughened GFRP layup
$[90/0]_4$/EMAA/$[90/0]_4$

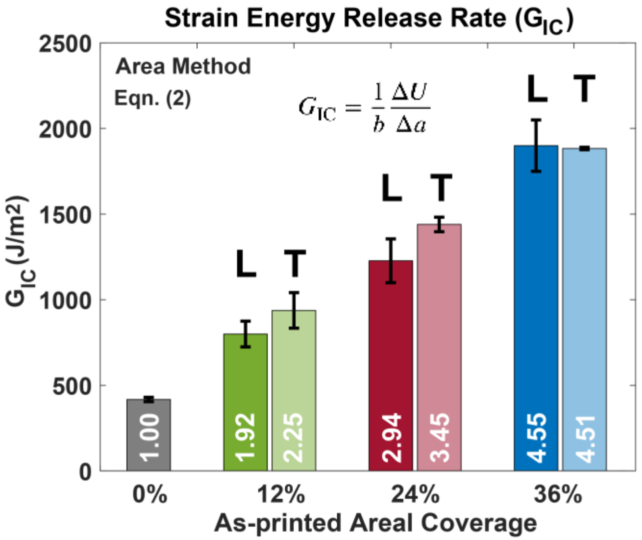
- **Areal coverage** and **thickness** dominates **global** toughening while **orientation** controls **local** crack propagation behavior

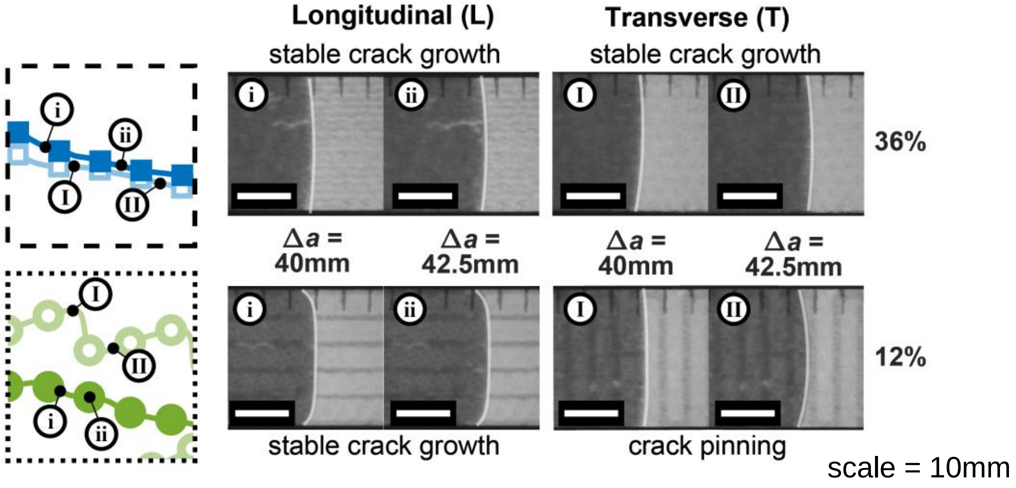










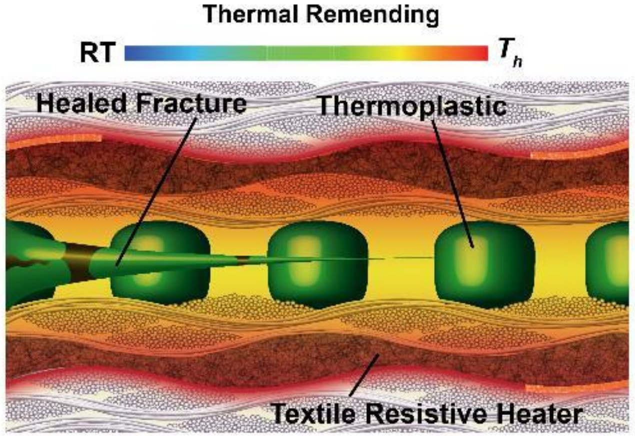


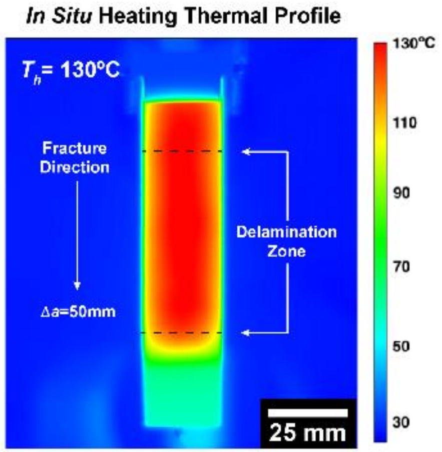
- Up to **450%** increase in interlaminar fracture resistance!
- L vs. T less pronounced at higher areal coverages

In situ Self-healing via Thermal Remending

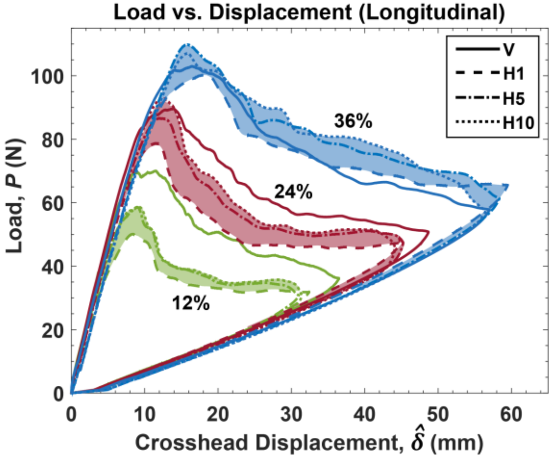
Self-healing GFRP layup
$[0/90]_2$/H/0/90/0/EMAA/90/0/90/H/$[0/90]_2$

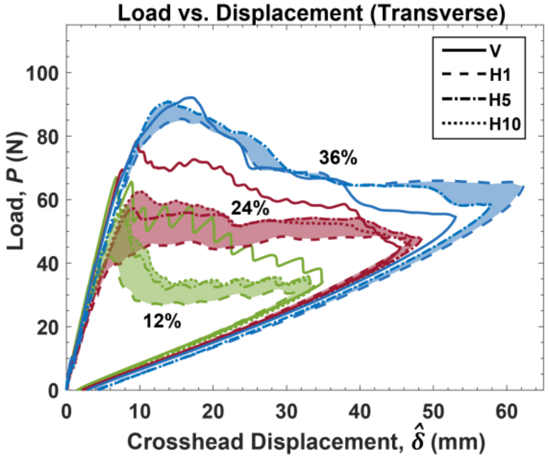
- Up to **100% healing efficiency** is achieved for **10 heal cycles** where EMAA pattern **areal coverage** dominates healing response

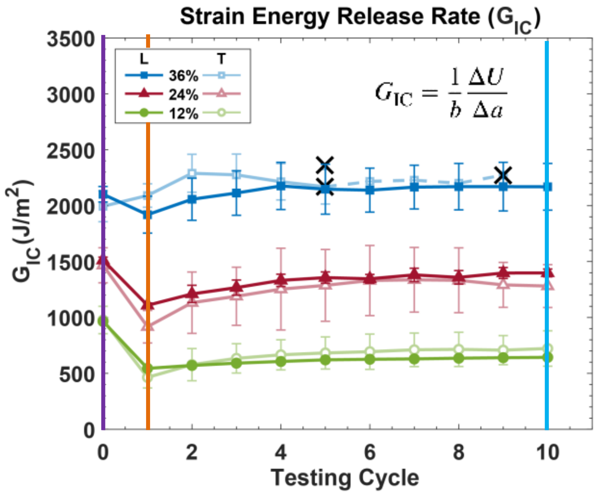


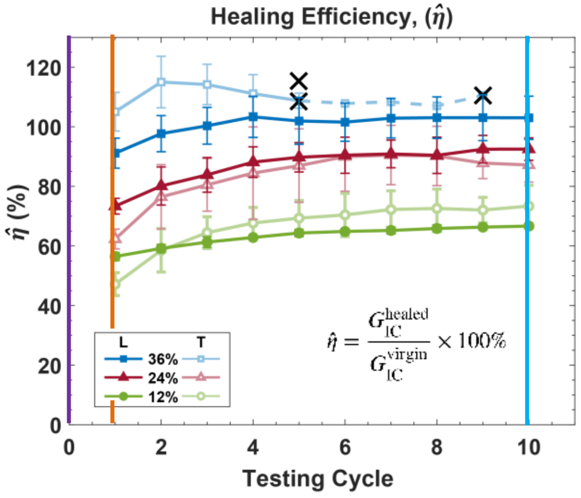


Healing Cycle: (heat) 15 min. @ 130°C (cool) 30 min. until RT

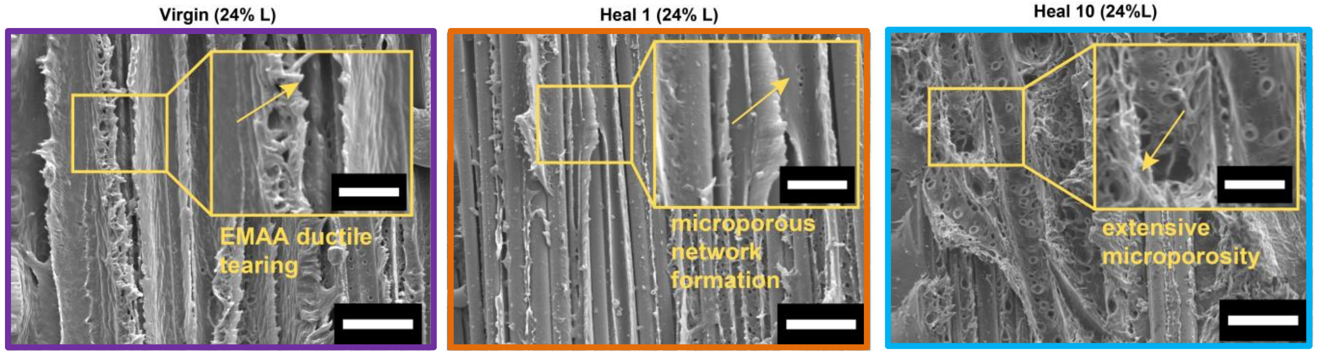








Scanning Electron Microscope Images



main scale = 25μm, inset scale = 10μm

- Cohesive fracture shows signs of **ductile tearing**
- **Micro-porous networks** form after Heal 1
- **Micro-porous networks** are fully developed by Heal 10

Summary / Future Work

- Designed a proactive **toughening** and reactive **healing** strategy to mitigate **delamination**.
- Achieved up to a **450% increase** in mode-I fracture resistance via incorporation of **3D-printed EMAA interlayers**.
- Minimal (**< 5%)** effect of interlayer modifications on **in-plane tensile** and **thermomechanical** performance compared to plain composite laminates.
- Demonstrated repeated complete (**100%) restoration** of fracture resistance for **10 consecutive heal cycles** without degradation in healing performance.
- Discovered EMAA **areal coverage** and **thickness** dominates the **global** fracture and self-repair response while interlayer pattern **orientation** controls **local** crack propagation behavior.

Turicek et al. *Composites Science and Technology* (2023) https://doi.org/10.1016/j.compscitech.2023.110073

Acknowledgements

Funding Source: **U.S. Army Corps of Engineers - Strategic Environmental Research and Defense Program (SERDP)**

US Army Corps of Engineers®

SERDP
DOD ▪ EPA ▪ DOE

Multifunctional Composites Group
Innovating Materials & Structures

Prof. Patrick

Alex

NC STATE UNIVERSITY

Academic Collaborators:

Prof. Nakshatrala