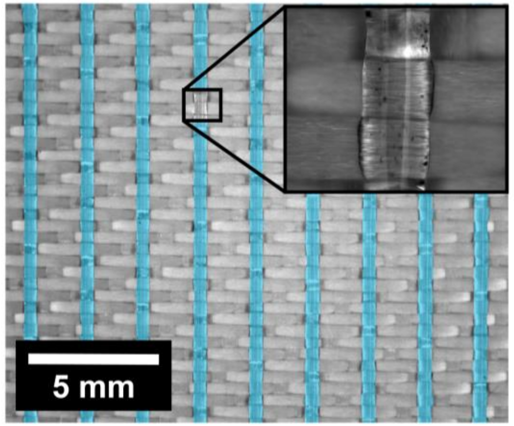
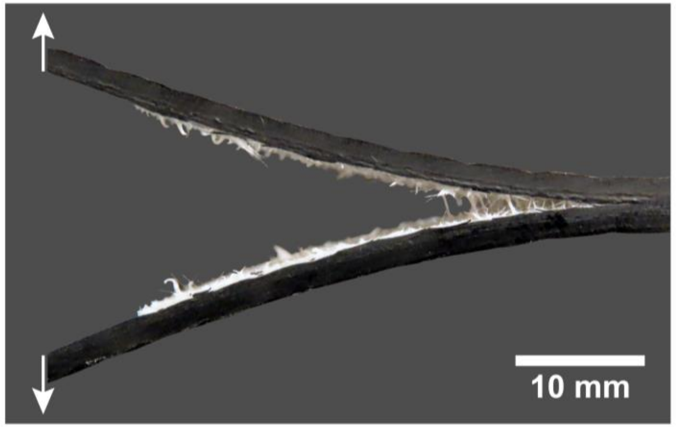
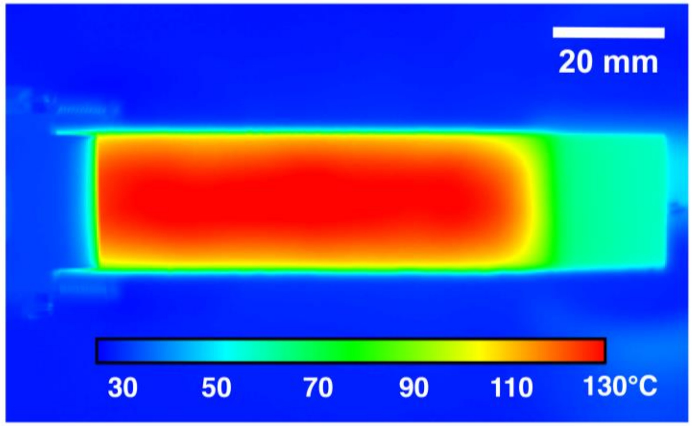
Prolonged Self-healing of Laminated Composites via *In Situ* Thermal Remending

Multifunctional Composites Group







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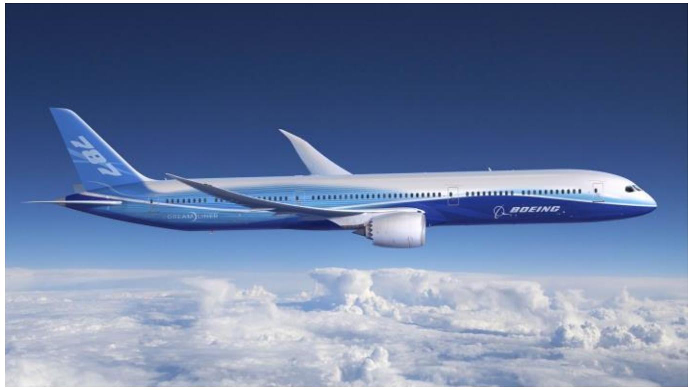
Outline

- Background/Motivation
- Constituent materials, System architecture, and Composite fabrication
- Mechanical Testing and Evaluation:
  - (I) in-plane tension
  - (II) mode-I fracture
- *In Situ* Self-Healing Results
- Investigation of Underlying Healing Mechanisms
- Summary/Conclusions

Motivation

- **Fiber-reinforced polymer (FRP) composites ubiquitous in modern engineered structures: (1) high specific strength/stiffness, (2) corrosion resistance, (3) geometric/constituent versatility**

Aerospace



Automotive

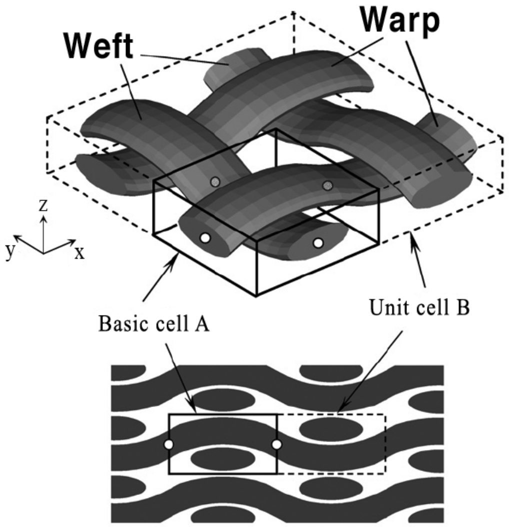
Naval

Energy

Civil

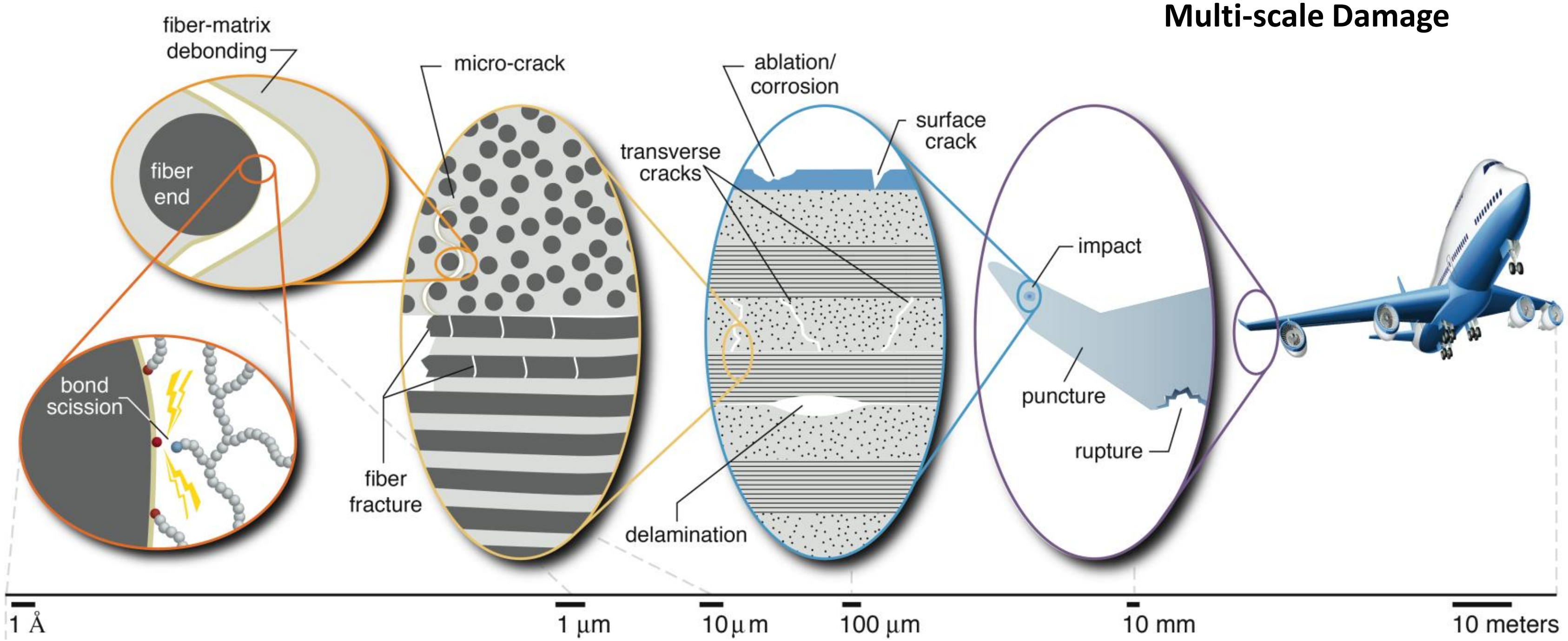
Woven FRP Composites

- **Hierarchical materials with structural advantage, but also inherent susceptibility to damage**

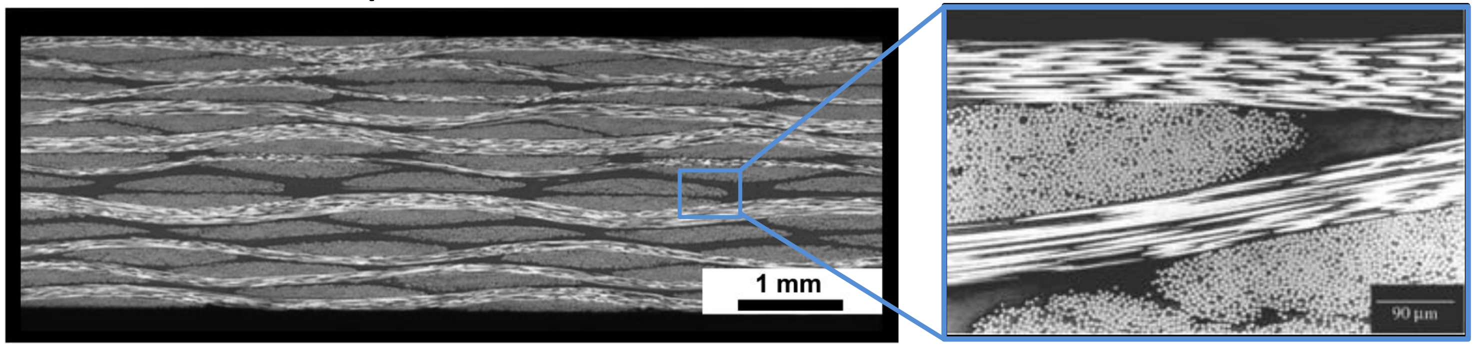


Compos. Struct. **79** (2007)

Multi-scale Damage

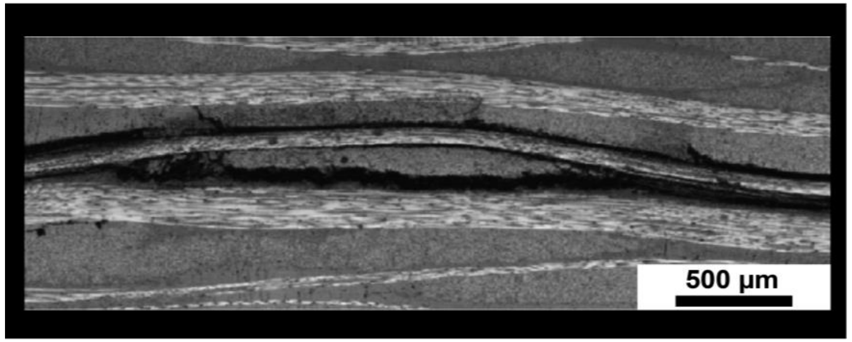


Laminated Woven Composite



ASM International (2010)

Interlaminar Delamination

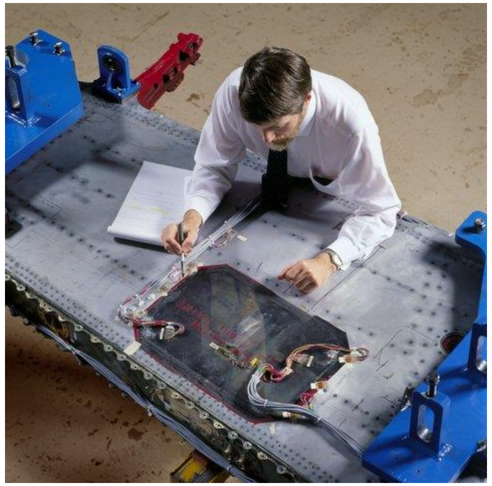


Polymer **53** (2012)

Self-healing Background

- **Delamination detection is difficult and manual repairs are costly – self-healing offers a bioinspired solution**

Repairs costly/time consuming



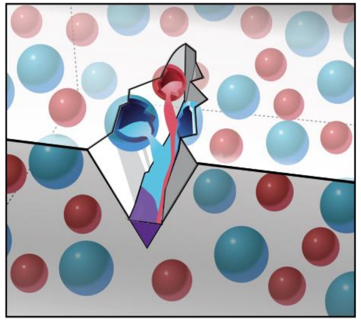
www.dsto.defence.gov.au

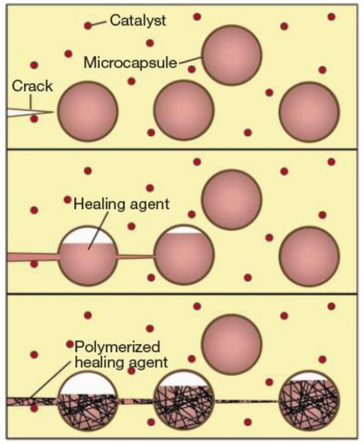
Possible catastrophic failure

USAF Hilltop Times

Self-healing Strategies

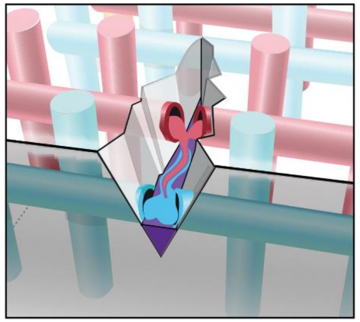
Capsule-based

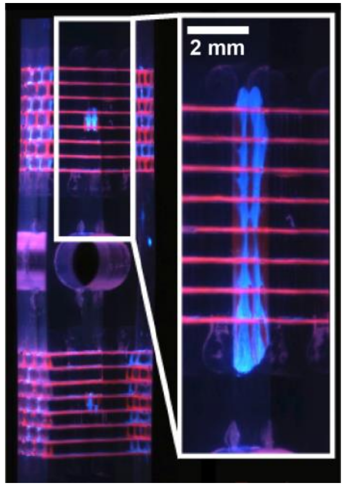




Nature **409** (2001)

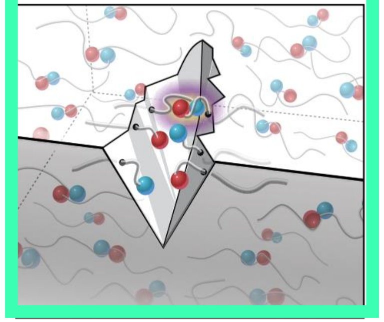
Vascular



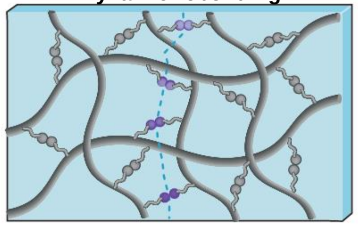


Adv. Mater. **22** (2010)

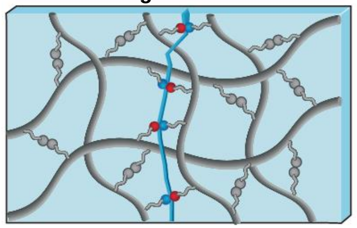
Intrinsic



Dynamic rebonding



Damage restoration



Nature **540** (2016)

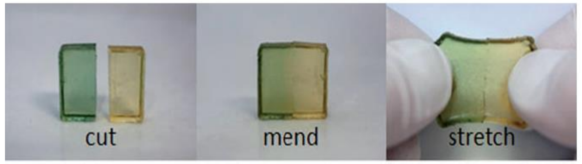
Limitations:

- Single-heal
- Small-scale repair
- Mixing difficult
- Blockages

Advantages:

- Multiple-heals
- No external agent

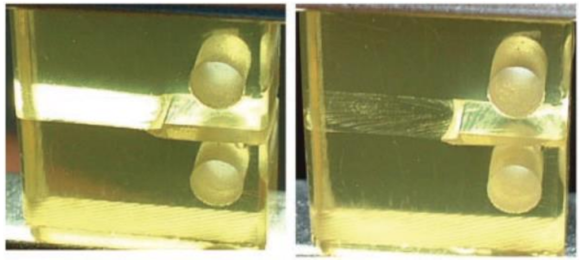
Soft Materials



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

- **Interface contact**
- **Room-temperature repair**

Structural Materials



Science **295** (2002)

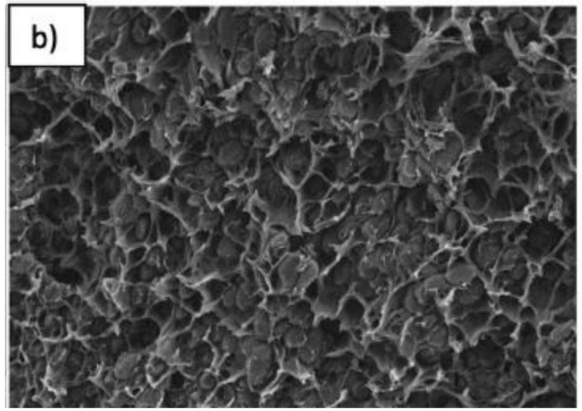
- **Elevated temperature repair**

Thermal Remending

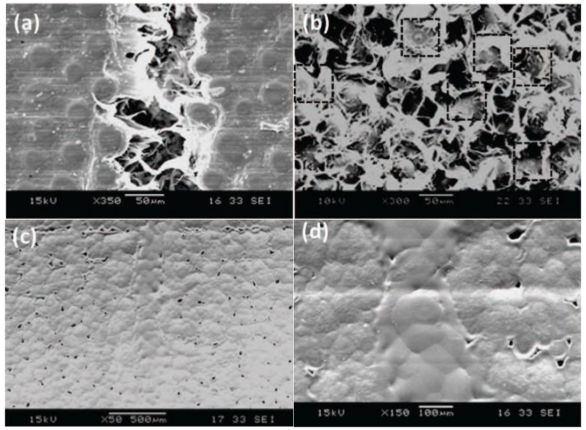
- **Inclusion of thermoplastic phase + heat provides capacity for structural composite repair**
- **Poly(ethylene-*co*-methacrylic acid) – EMAA – is a commodity polymer with proven self-healing ability**

Self-healing achieved *ex situ* and/or above glass-transition temperature (T_g)

Thermoplastic-modified Matrices

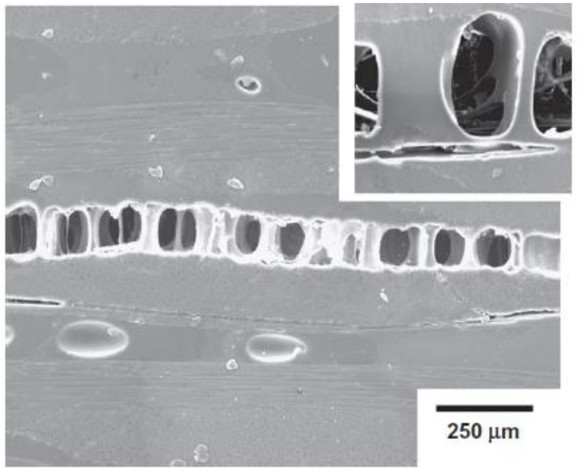


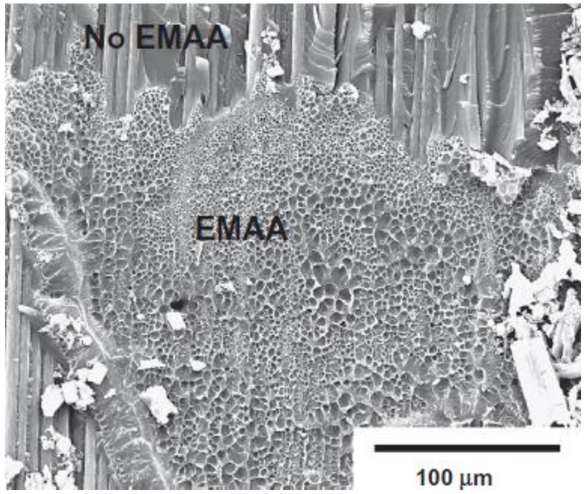
Polymer **92** (2016)



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

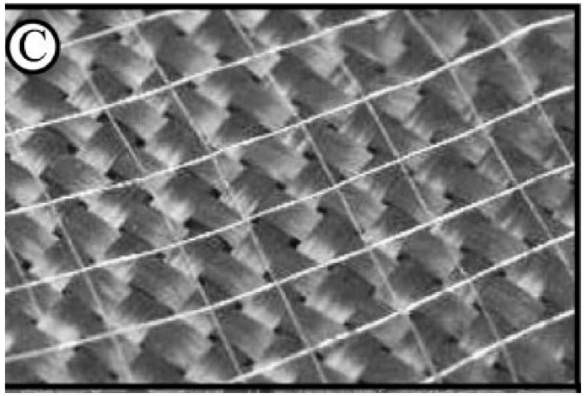
Particles and Interwoven Fibers



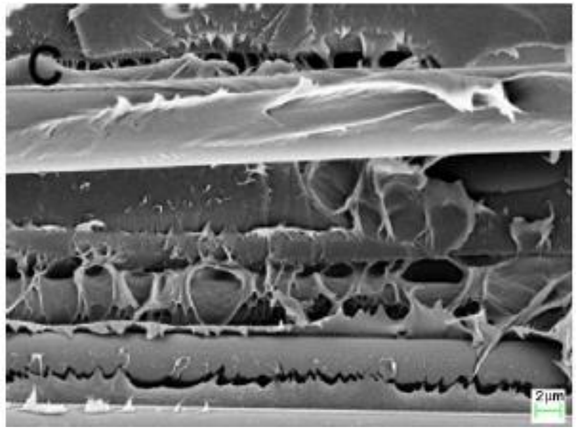


Compos. Part A **43** (2012)

Interlayer Integration



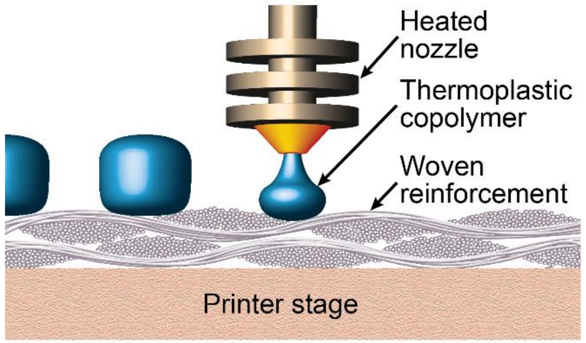
Macromol. Mater. Eng. **295** (2010)



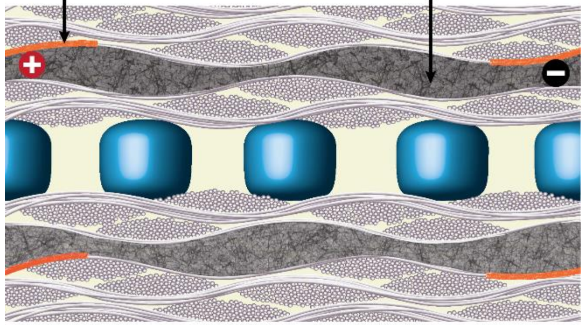
Compos. Part A **43** (2012)

New Approach: *In Situ* Thermal Remending

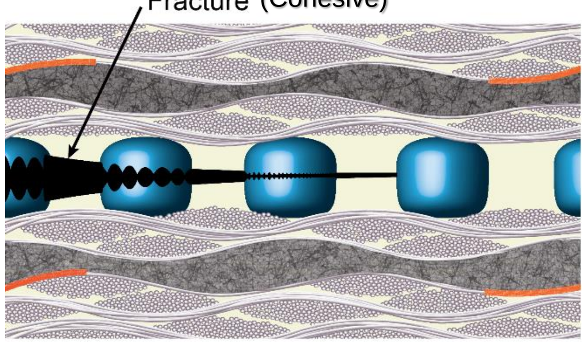
- **Self-healing below laminate glass-transition temperature (T_g) via *in situ* heating**



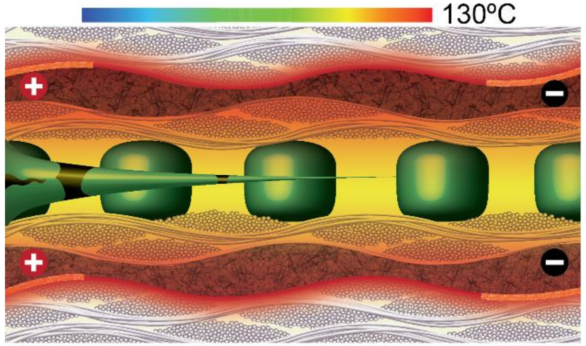
3D-printing onto preform substrate



Pristine multifunctional composite laminate

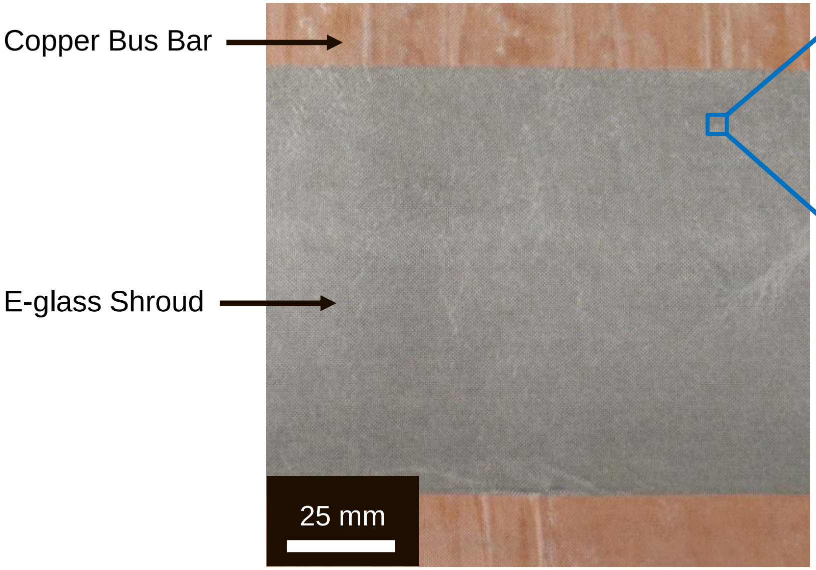


Internal delamination damage

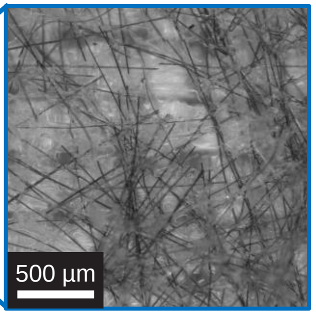


Self-healing via *in situ* thermal remending

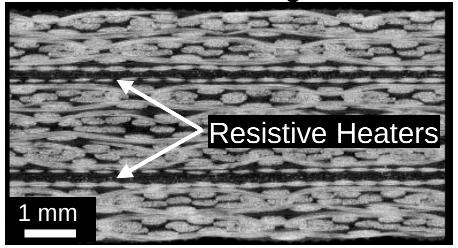
Textile Resistive Heaters



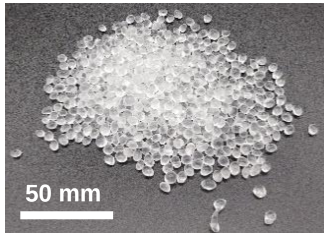
Conductive Carbon Whiskers



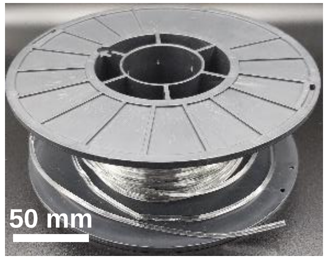
Laminate Integration



Virgin EMAA Pellets

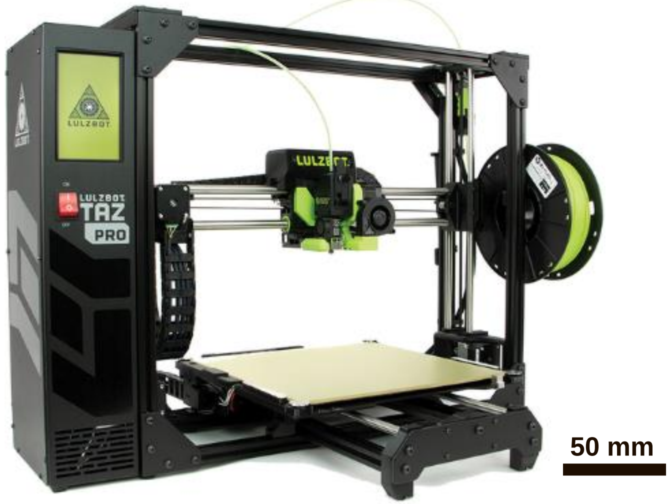


In-house Filament



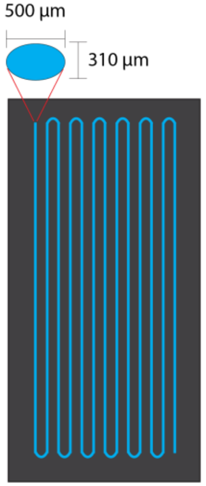
3D Printing EMAA

Fused Deposition Modeling (FDM)

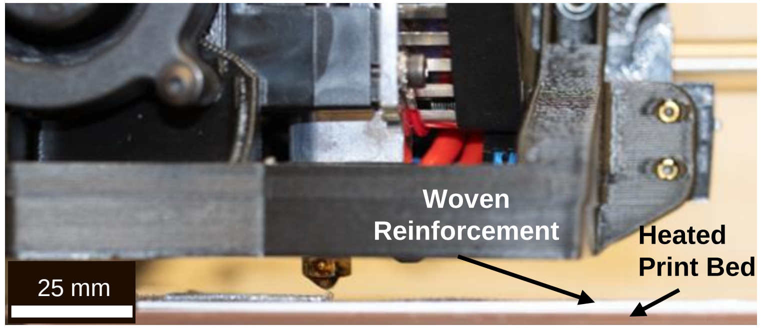


Preform Patterning and Laminate Fabrication

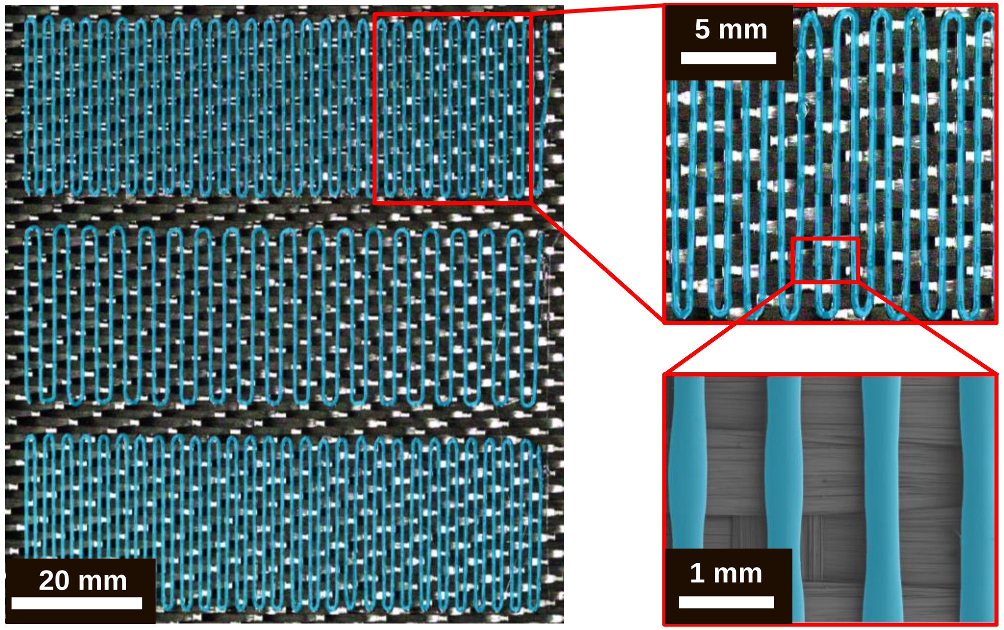
- **FDM to micro-pattern EMAA in serpentine geometry directly onto woven reinforcement = scalability**



FDM Process



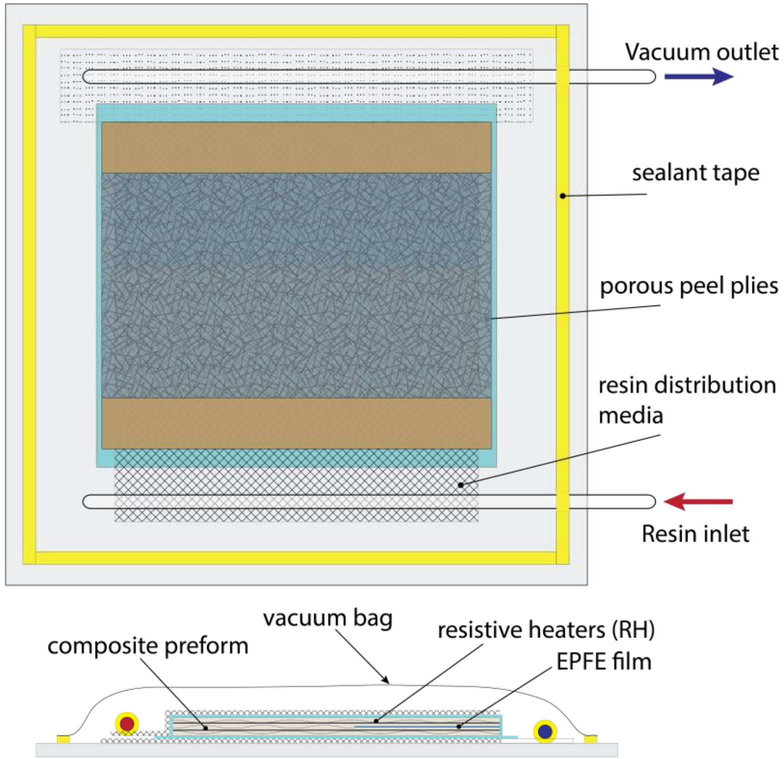
Print head registration with textile substrate



EMAA patterned carbon-fiber

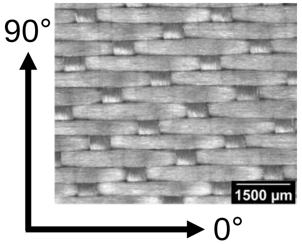
SEM of print + weave

Vacuum Assisted Epoxy Matrix Infusion



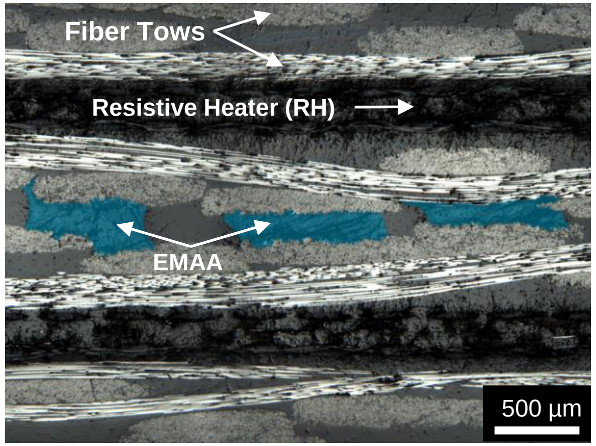
GFRP layup (16 plies):
$[0/90]_2$/**RH**/0/90/0/**EMAA**
/90/0/90/**RH**/$[0/90]_2$

CFRP layup (8 plies):
0/90/**RH**/0/**EMAA**/90/**RH**/0/90

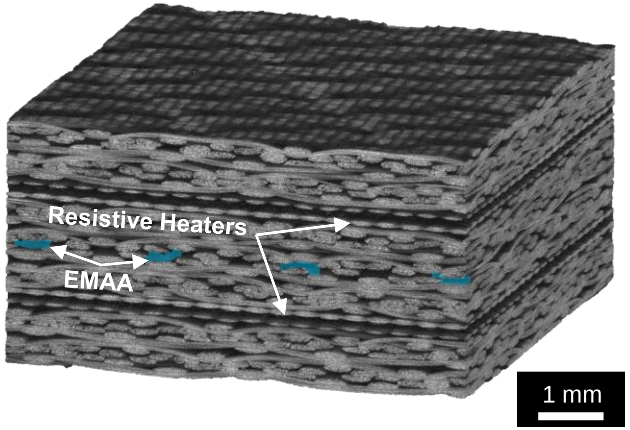


Post-cure: 2h @ 121°C + 2h @ 150°C

Laminated Composite Cross-Section



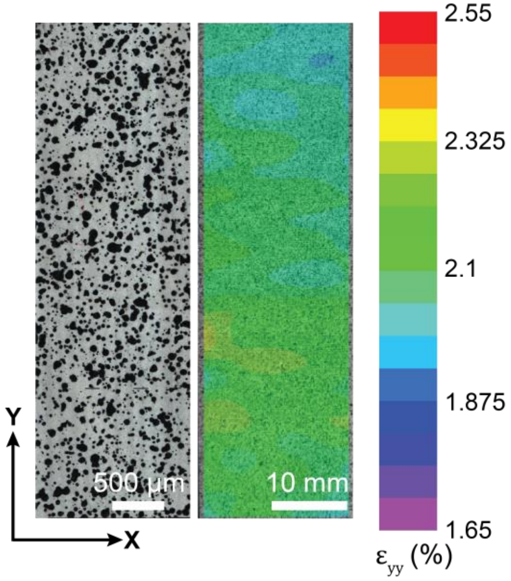
X-ray Computed Tomography Reconstruction

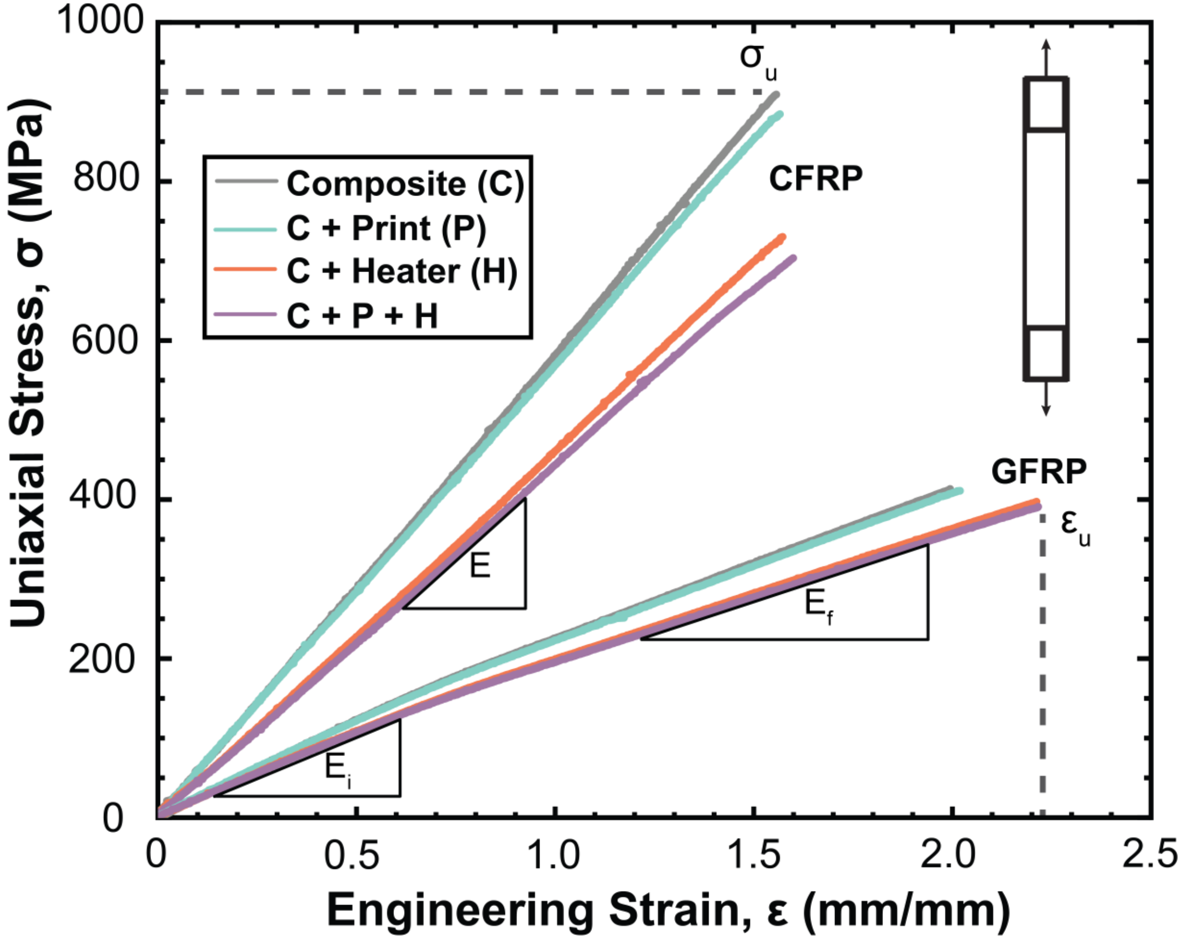


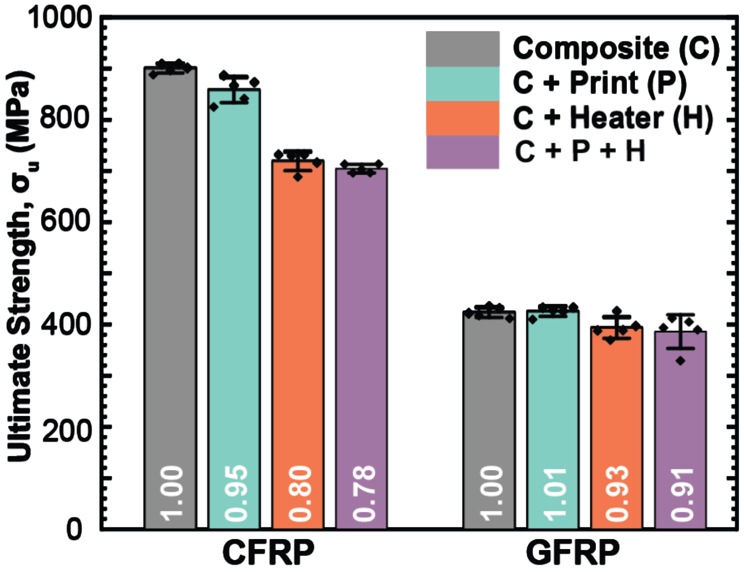
Structural Integrity: In-Plane Tension

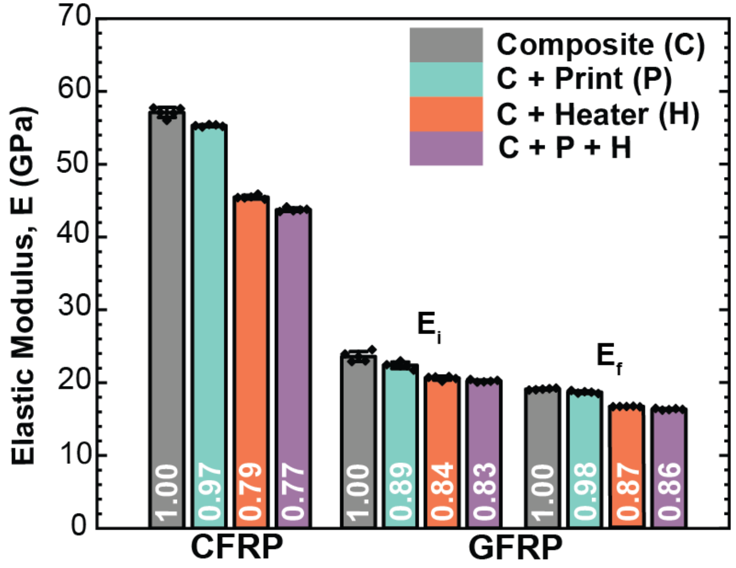
- **Investigate effect of composite modification(s) on in-plane tensile performance†**

Digital Image Correlation (DIC)









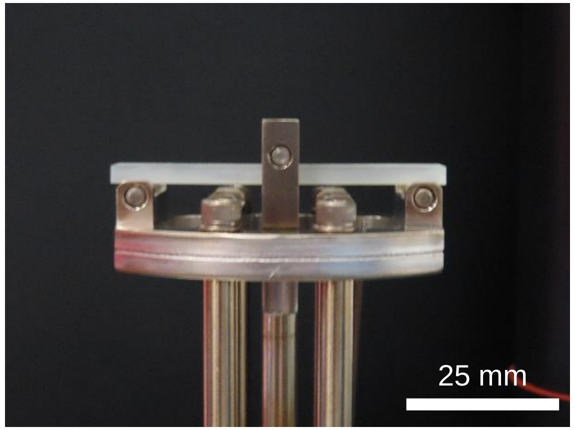
† ASTM D-3039

n = 3

Thermo-mechanical Characterization

- **Dynamic mechanical analysis (DMA) to determine thermal remending below T_g and retain in-service structural performance**

DMA Fixture & Specimen



3-pt Flexure (1Hz, 5°C/min)†

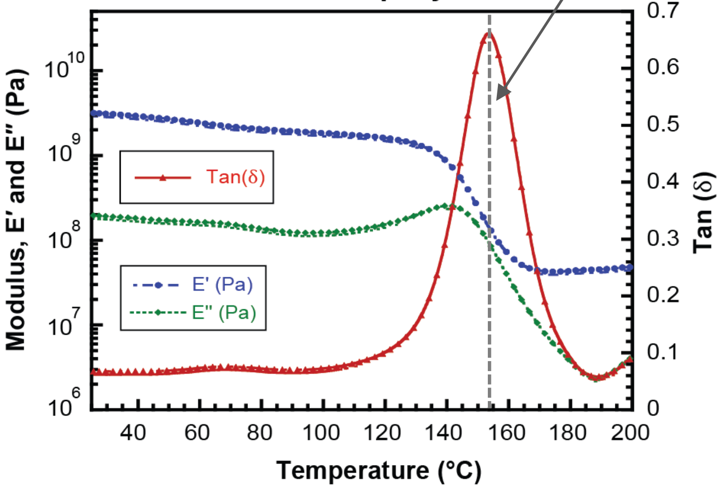
$$E^* = E' + iE'' \qquad \tan(\delta) = \frac{E''}{E'}$$

Fiber-Composite Constituents:

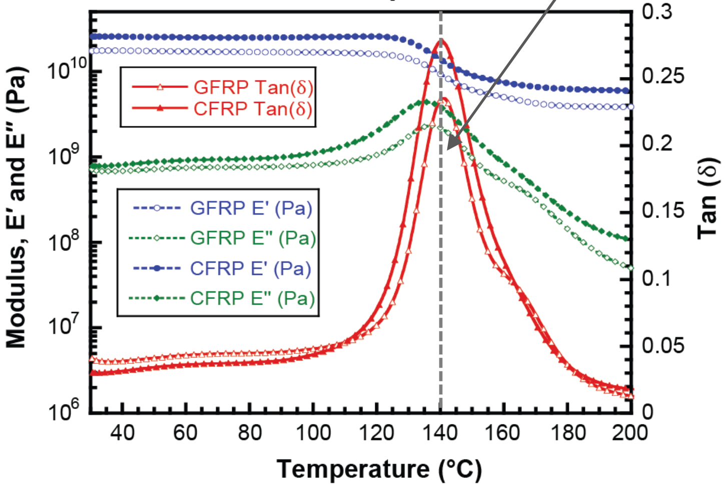
Matrix: DGEBA epoxy system

Reinforcement: Glass (GFRP) and Carbon Fiber (CFRP); $V_f = 0.51$‡

Neat Epoxy



Fiber Composites

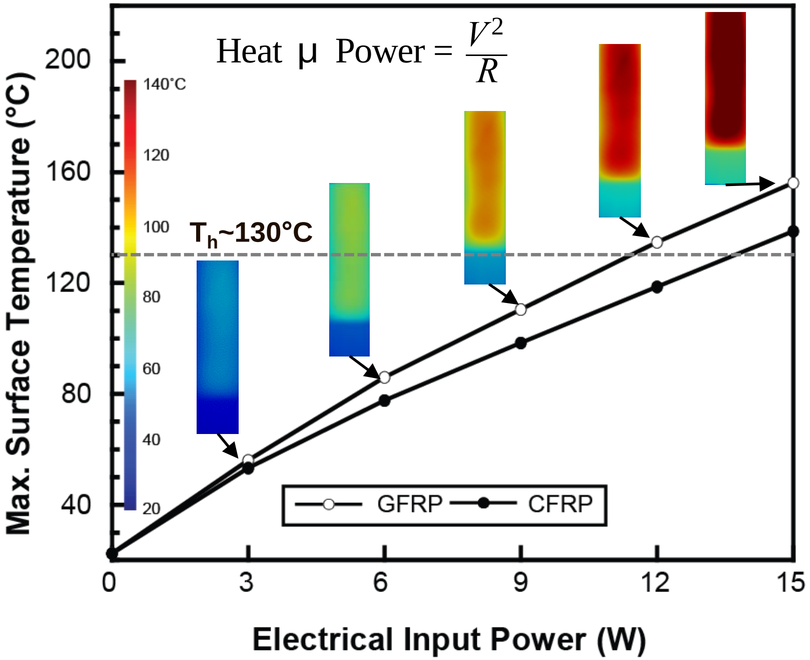


Elastic (storage) Modulus Comparison

	E' 23°C, GPa	E' T_g, GPa	E' 130°C, GPa
Epoxy	2.9	0.1 (3%)	1.3 (45%)
GFRP	16.7	8.7 (52%)	14.2 (85%)
CFRP	25.7	13.5 (53%)	22.5 (88%)

*Percentages (%) represent retained E' vs. value at RT = 23°C

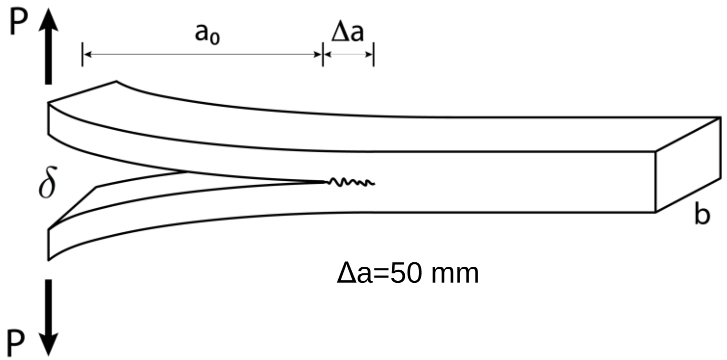
Resistive Heater Calibration

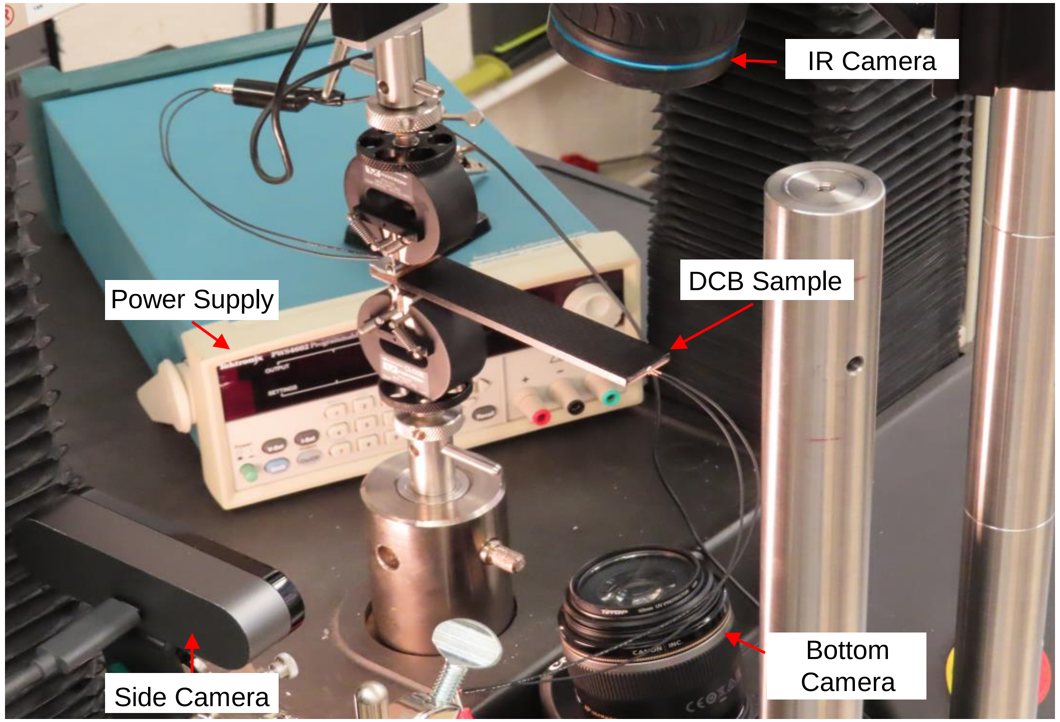


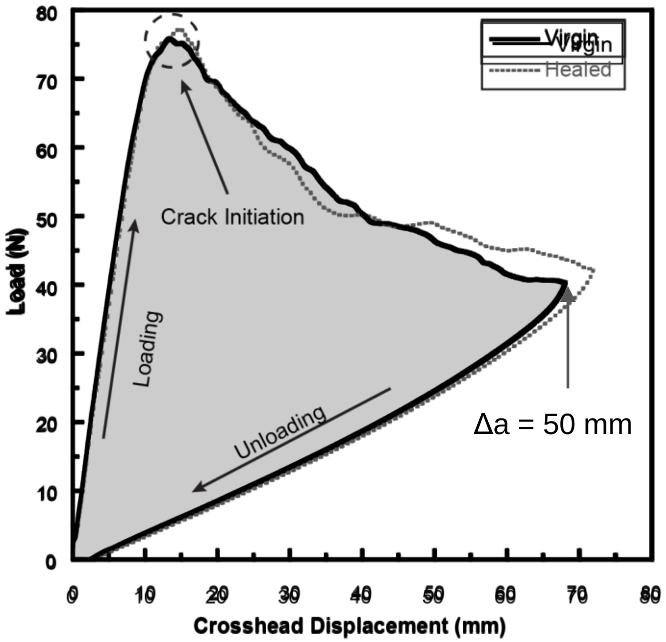
† ASTM E-1640
‡ ASTM D-2584

Mechanical Evaluation: Mode I Fracture

- **Double Cantilever Beam* (DCB) for self-healing assays**





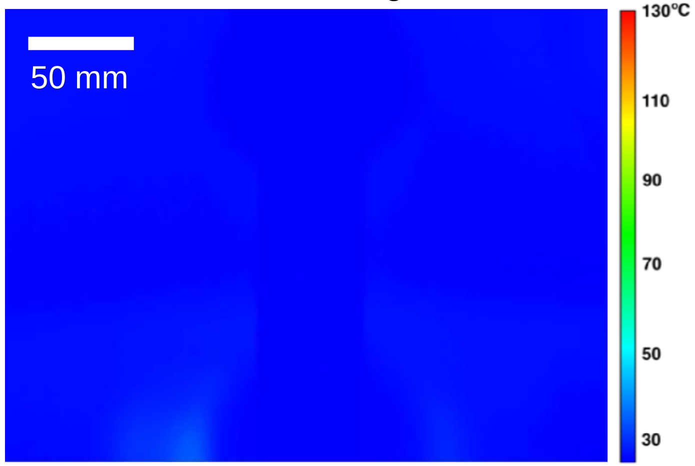


$$^{\dagger}G_{\mathrm{I}} = \frac{1}{b}\frac{\Delta U}{\Delta a}$$

$$\Delta U = \int_0^{\hat{\delta}} P d\hat{\delta}\Big|_{\Delta a}$$

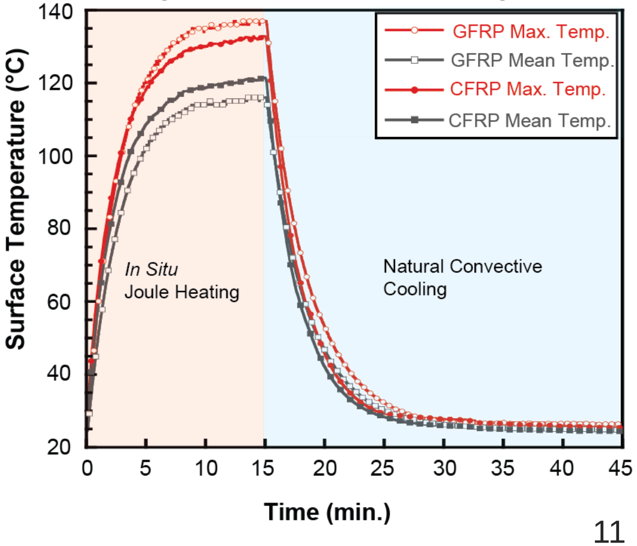
$$^{\ddagger}\hat{\eta} := \frac{G_{\mathrm{IC}}^{\mathrm{healed}}}{G_{\mathrm{IC}}^{\mathrm{virgin}}} \times 100$$

***In Situ* Heating**



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

Experimental Transient Response

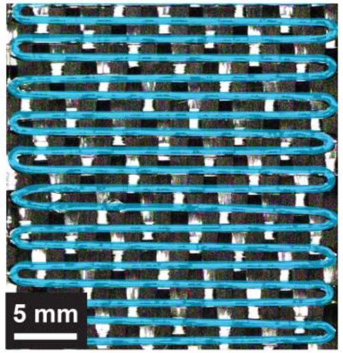


*ASTM D-5528 †*J. Mater. Sci. Lett.* **8** (1989) ‡*Adv. Mater.* **26** (2014)

Virgin Fracture and *In Situ* Self-Healing Behavior

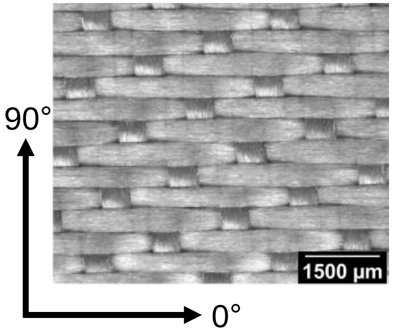
- **Virgin fracture resistance & healing efficiency scale w/ EMAA areal coverage**

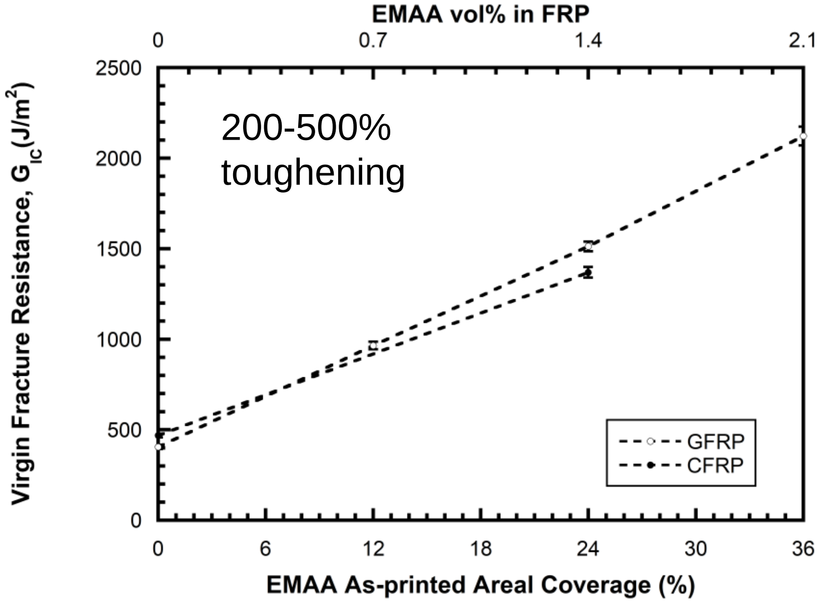
3D Printed Pattern

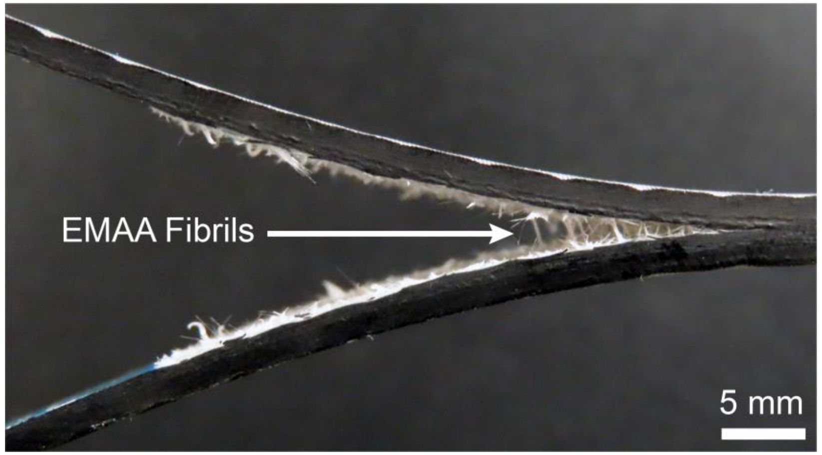


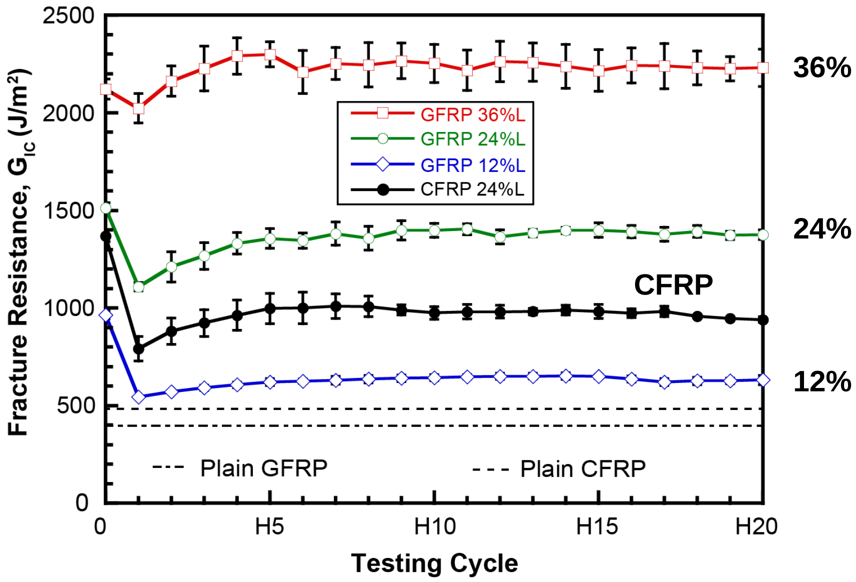
Fracture direction

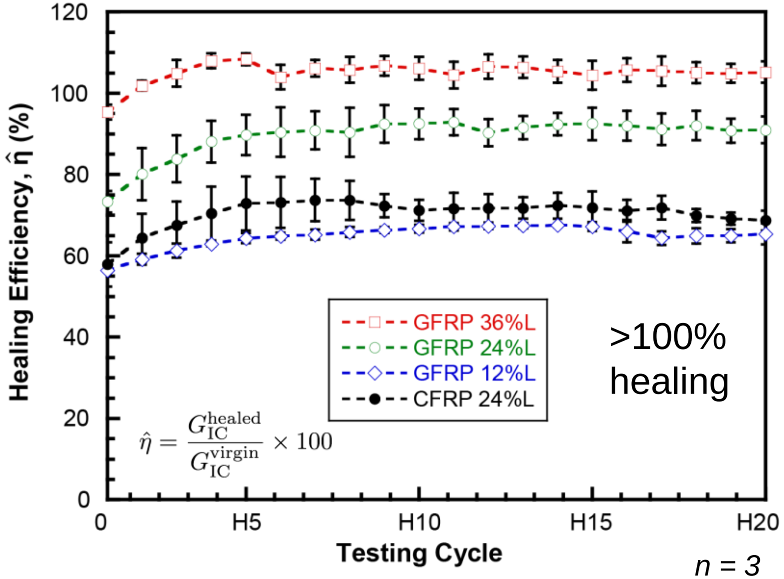
8H Satin Weave







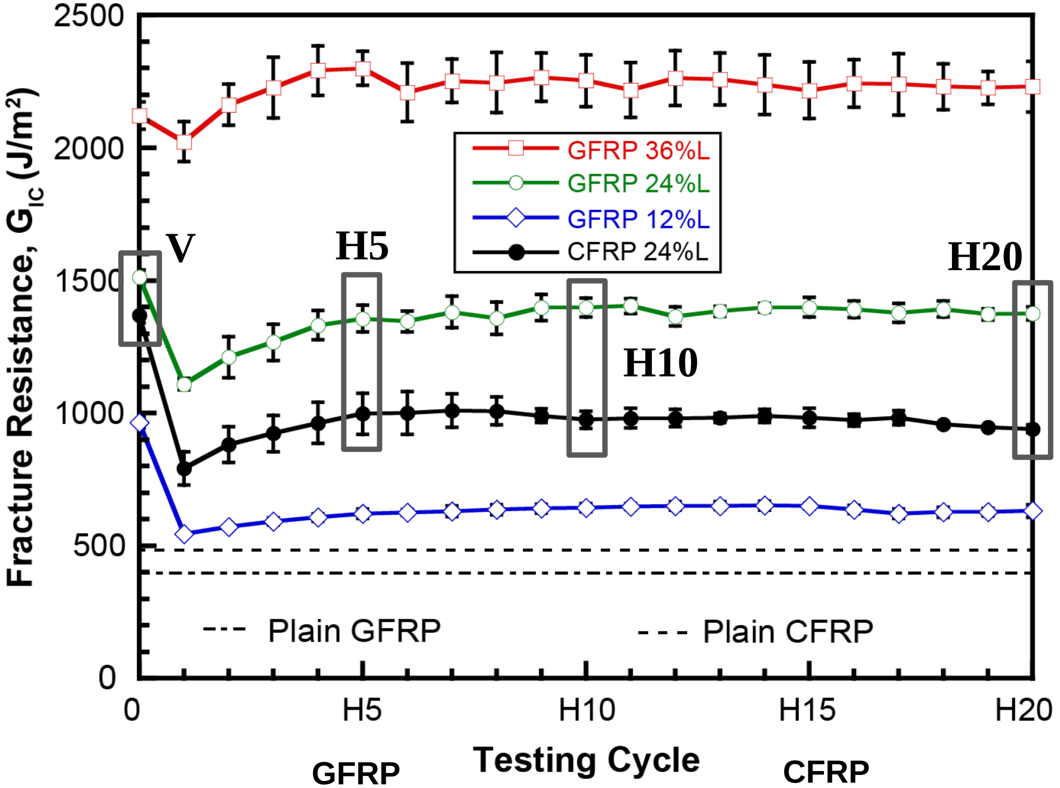




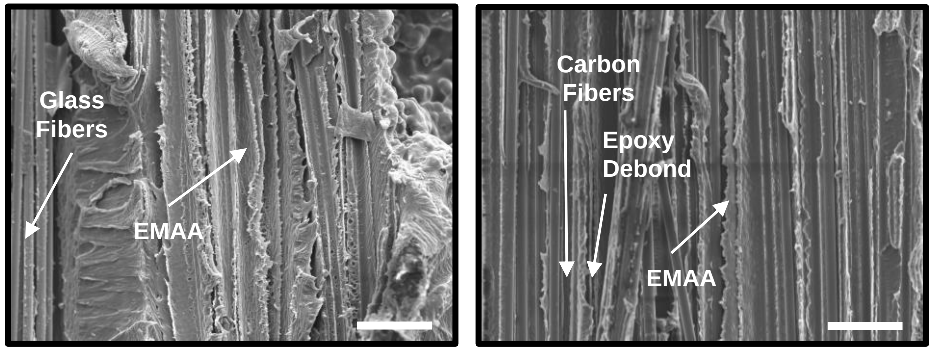
n = 3

Topological Investigation of Healing Performance

- **Fiber-reinforcement type influences self-healing behavior**

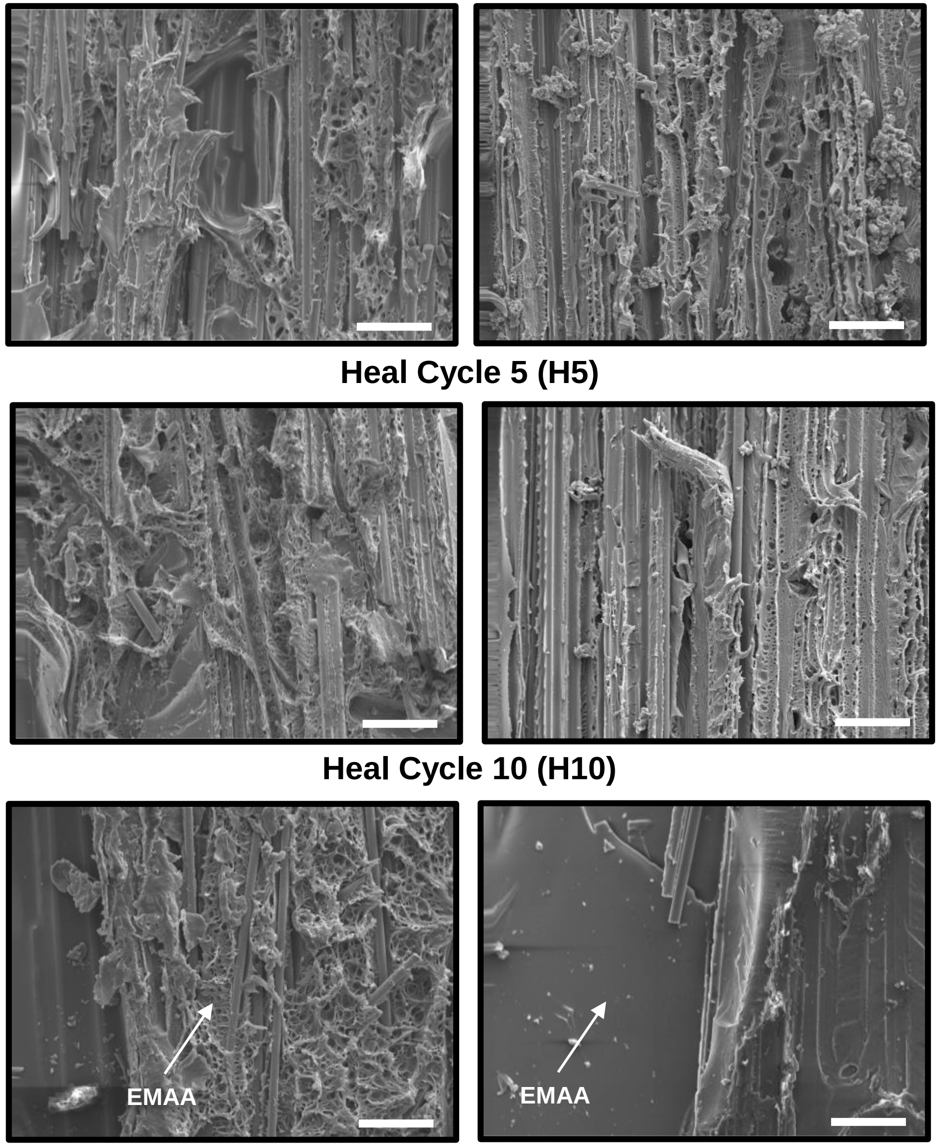


GFRP **CFRP**



Virgin Cycle (V) *scale bars = 50 µm

GFRP **CFRP**

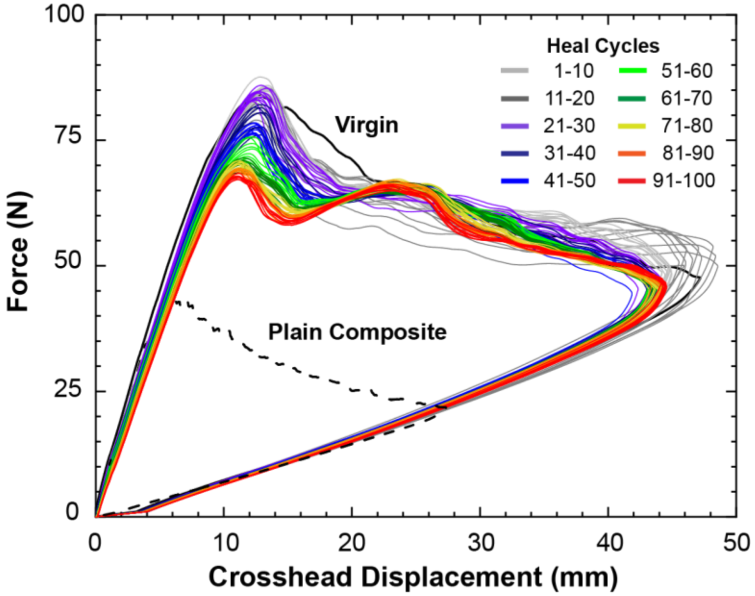


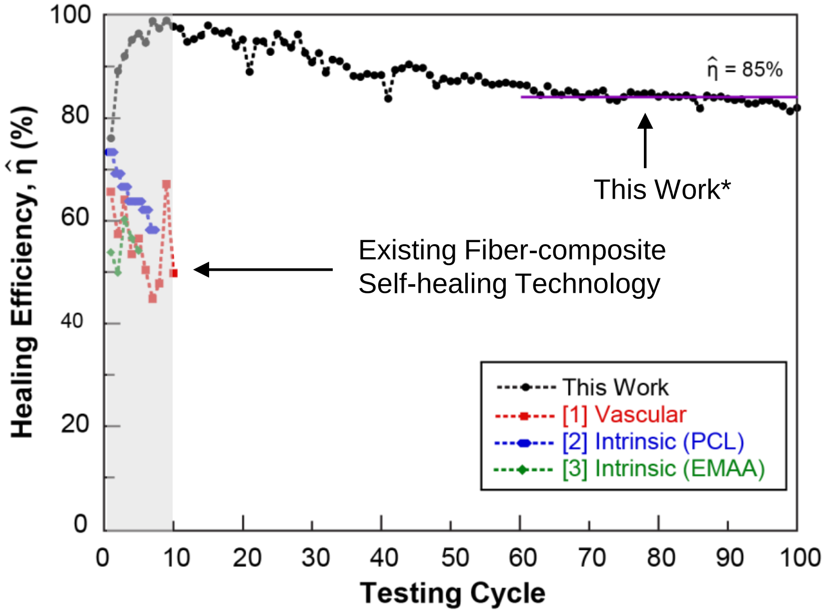
Heal Cycle 20 (H20)

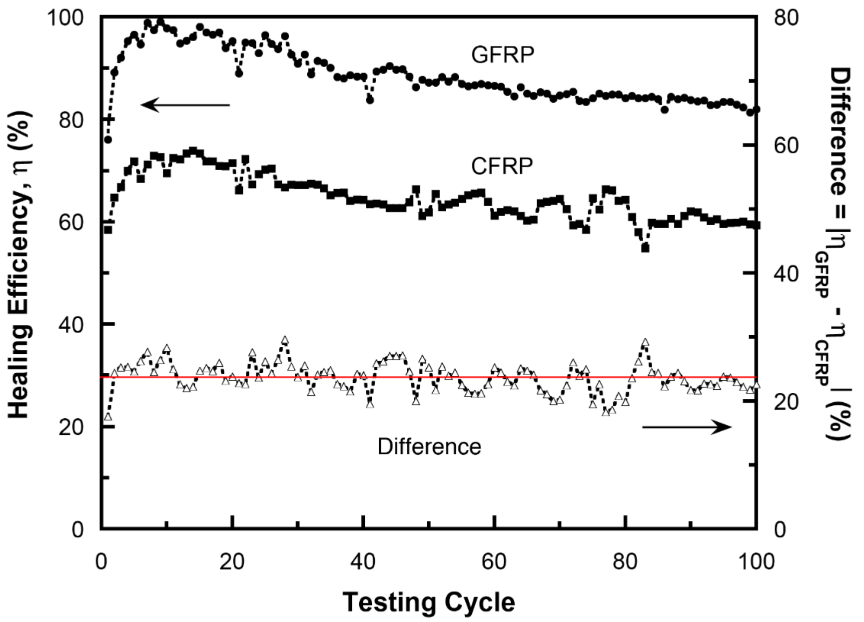
Capacity for Sustained Self-healing

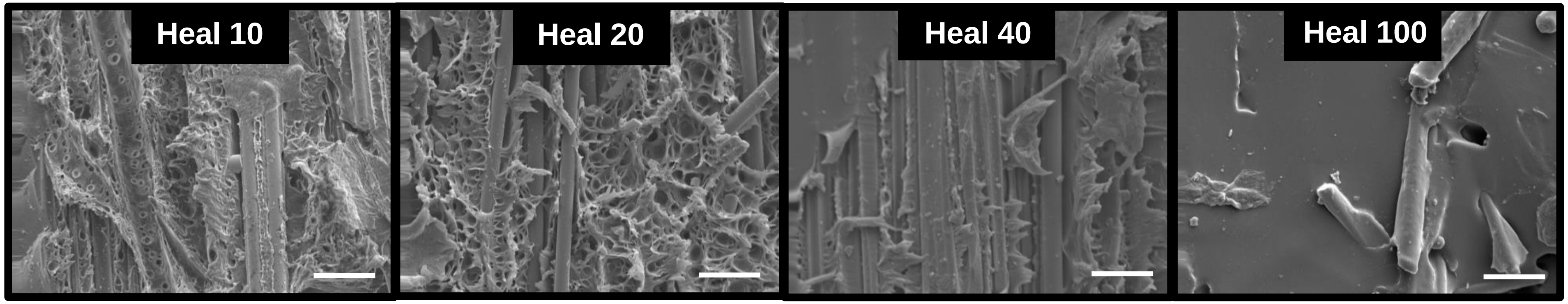
- **100 heal cycles achieved in GFRP (and CFRP) w/o significant degradation in recovery**

*Nat. Comm. **13** (2022)*









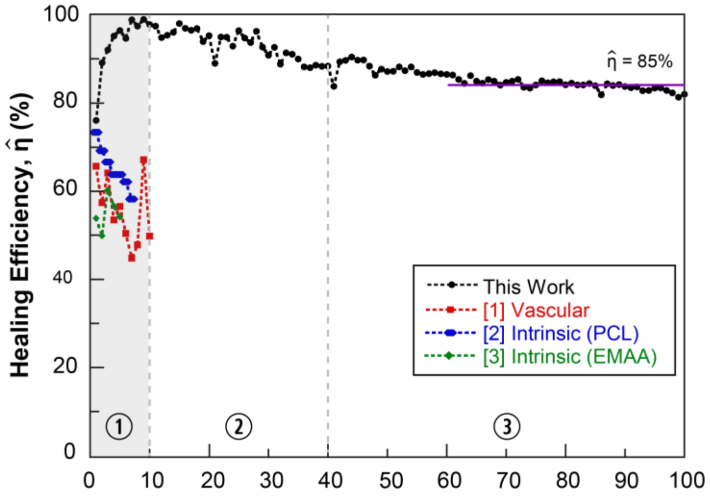
*scale bars = 25 µm

Eventual collapse of microporous network by heal cycle 40

[1] *Compos. Sci. Tech.* **151** (2017) [2] *Mater. Today Comm.* **8** (2020) [3] *Macromol. Mater. Eng.* **295** (2010)

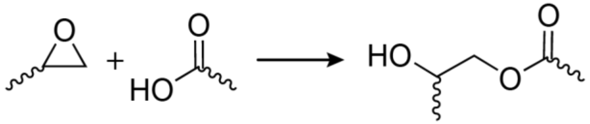
FTIR Spectroscopy Reveals Chemical Mechanisms

- **ATR-FTIR spectroscopy of EMAA supports propensity for perpetual healing**

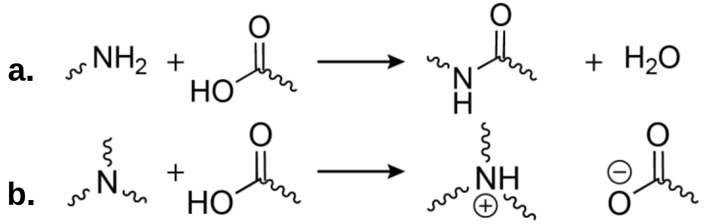


Key Chemical Reactions†

TYPE I - Oxirane/Carboxylic Acid

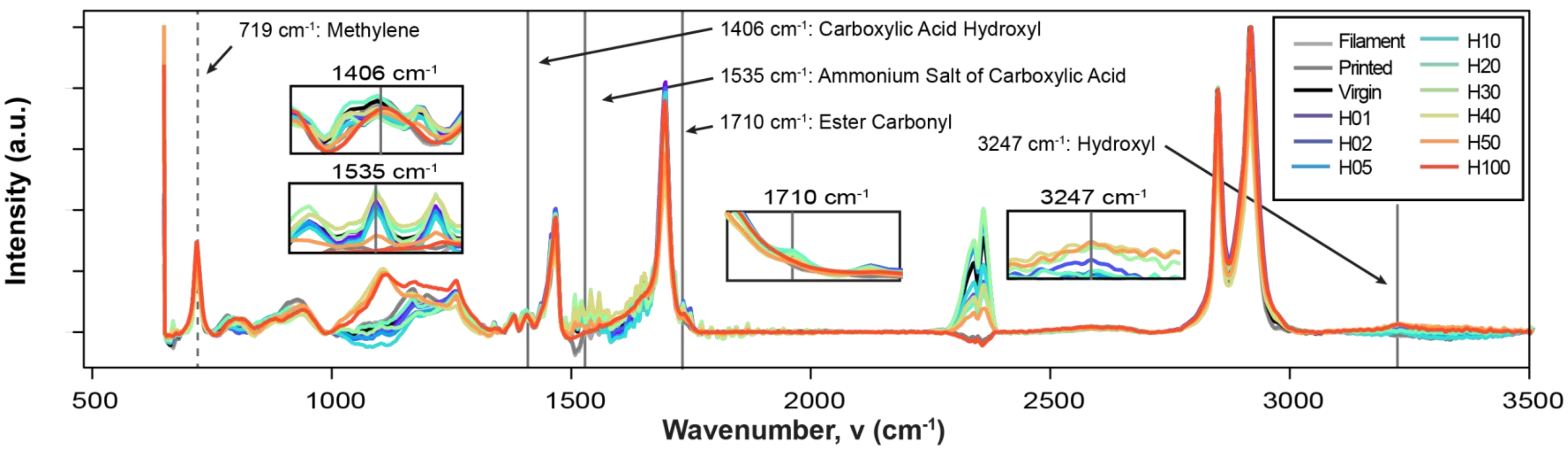


TYPE II – Amine/Carboxylic Acid

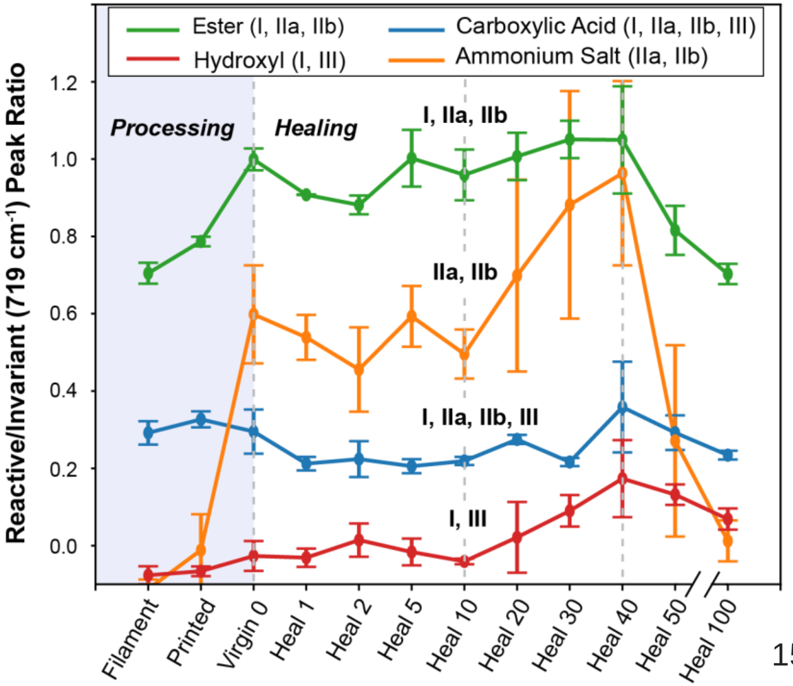


†*Vib. Spectrosc.* **52** (2010)

FTIR Spectroscopy of EMAA



FTIR Spectral Evolution of EMAA



Invariant: 719 cm^{-1} *Methylene rocking*

Reactive: 1406 cm^{-1} *Carboxylic Acid Hydroxyl stretch*, 1535 cm^{-1} *Carboxylic Acid Ammonium Salt stretch*, 1710 cm^{-1} *Ester Carbonyl stretch*, 3247 cm^{-1} *Hydroxyl stretch*

w/ Prof. C. Diesendruck (Technion)

Summary/Conclusions

- Achieved ***in situ self-healing*** via thermal remending in fiber-composites below the ***glass-transition temperature*** (T_g).

- ***3D printed EMAA*** patterns have ***negligible impact*** on in-plane ***structural integrity*** and ***increase mode-I fracture resistance*** (G_{IC}). Textile ***resistive heaters*** have ***minor impact*** on GFRP properties.

- ***Increasing*** EMAA areal ***coverage increases*** virgin ***fracture resistance*** and ***healing efficiency*** (> *100%*).

- ***Superior*** healing performance in ***GFRP*** vs. CFRP due to physical properties of ***fabric architecture*** and ***surface chemistry*** that promotes ***EMAA microporous network*** and ***crack tortuosity.***

- ***Rapid*** sub-hour (45 min.) and ***extended*** *in situ* heal cycles (100+) demonstrates propensity for ***practical*** and ***perpetual*** in-service repair.

Snyder *et. al*, Prolonged In situ Self-healing in Structural Composites via Thermo-reversible Entanglement, *Nat. Comm*. **13** (2022).

U.S. Patent No. 16/944,675 (Issued March 2023)

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Prof. Patrick **Zach** **Sandeep** **Jack**

Academic Collaborators:

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