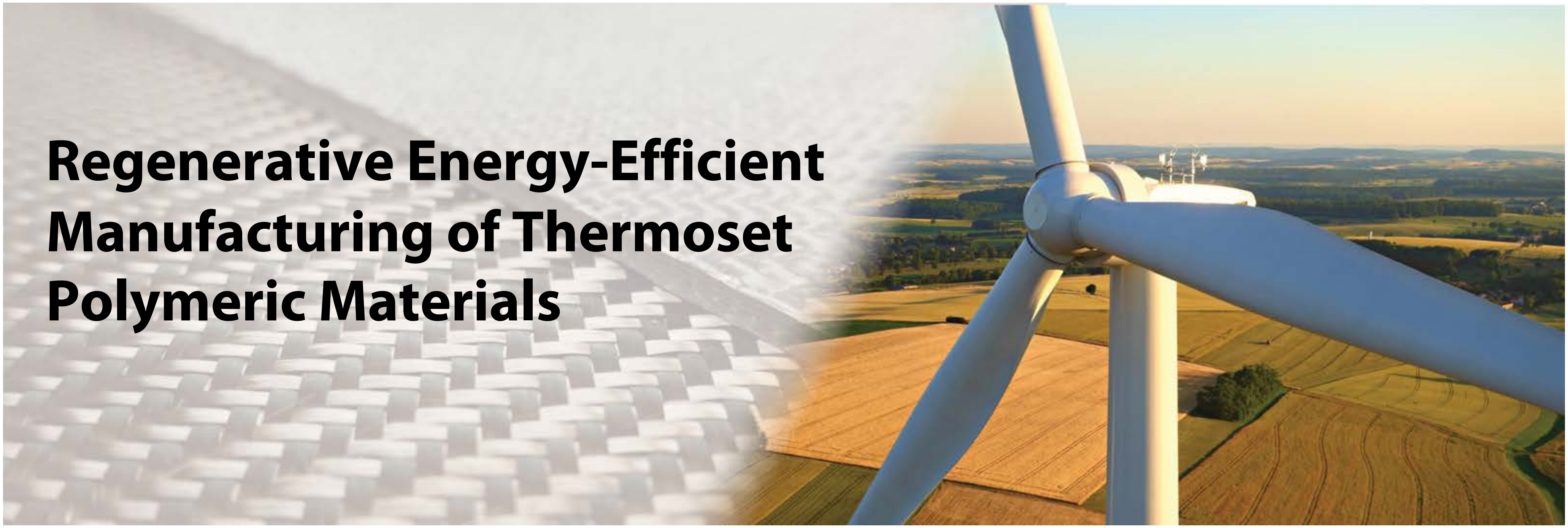
Regenerative Energy-Efficient Manufacturing of Thermoset Polymeric Materials



Nancy Sottos

Materials Science and Engineering
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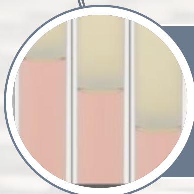
ILLINOIS

Outline

Background and motivation



Rapid curing by frontal polymerization

Energy efficient manufacturing of composites

Deconstruction and regenerative strategies

Motivation: Thermoset Polymer and Composite Linear Lifecycle

Energy Intensive Manufacturing → **Thermoset Polymer Composite Structures**

- **Long cure times (hours)**
- **Energy intensive (Gigajoules)**
- **Energy scales with part size**

Stiffness ~ 10^2 GPa
Strength ~ 10^2 MPa
Service life ~ 30 years

Motivation: Thermoset Polymer and Composite Linear Lifecycle

Energy Intensive Manufacturing → **Thermoset Polymer Composite Structures** → **Landfill (no end–of–life strategy)**

- Long cure times (hours)
- Energy intensive (Gigajoules)
- Energy scales with part size

- Stiffness ~ 10^2 GPa
- Strength ~ 10^2 MPa
- Service life ~ 30 years

REMAT

Complex materials problems require collaboration

Philippe Geubelle
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Jeff Moore
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Jeff Baur
AE, UIUC

Randy Ewoldt
ME, UIUC

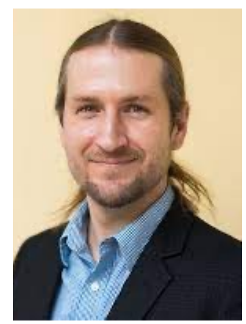
Sam Tawfick
ME, UIUC

UIUC Beckman Institute

EFRC for Regenerative Energy Efficient Manufacturing of Thermoset Polymeric Materials

Leah Appelhans
Sandia

Adam Cook
Sandia

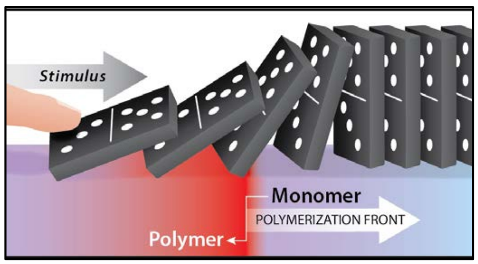


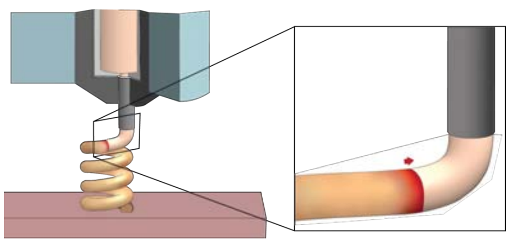
Jeremiah Johnson
Chemistry, MIT

Sam Leguizamon
Sandia

Vision: Circularize the Lifecycle of Thermoset Polymers

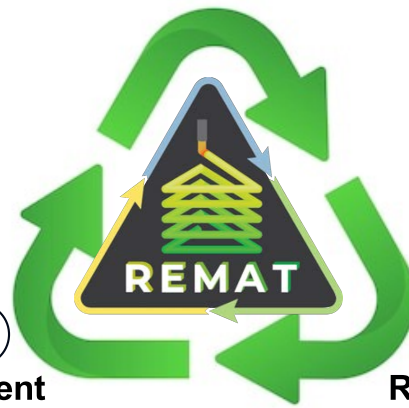
Manufacturing platform based on frontal polymerization





Programmed Deconstruction

2



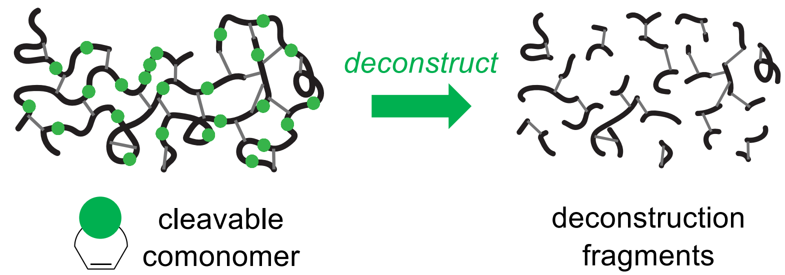
1

Efficient Manufacture

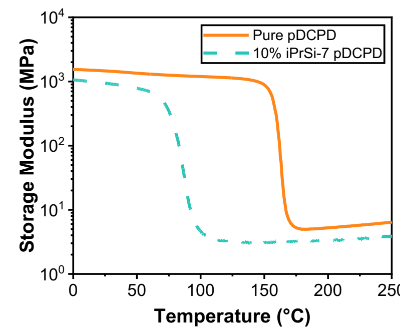
3

Regeneration & Upcycling

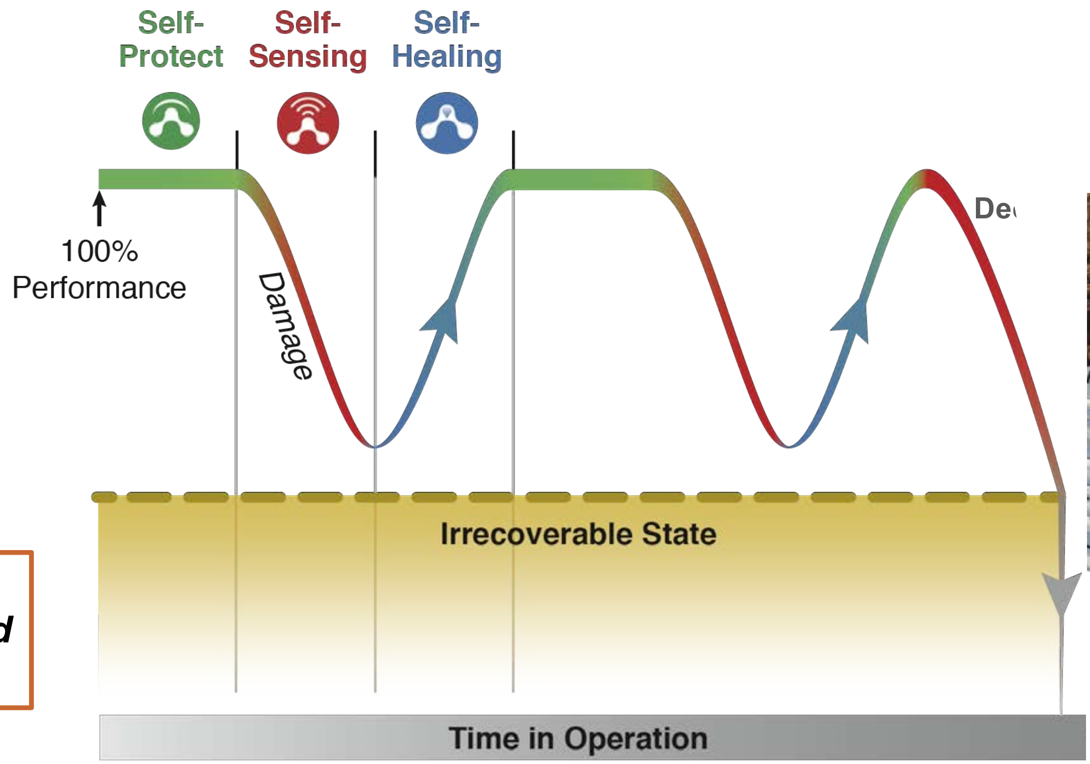
Deconstructable Thermoset Networks

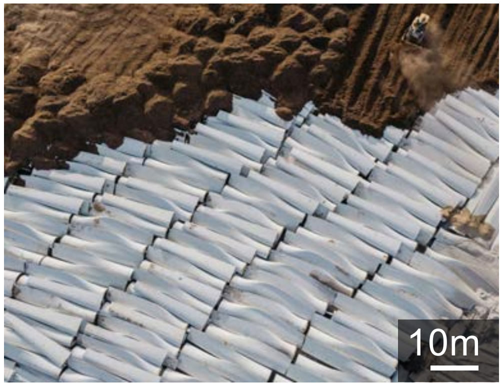


Maintain Properties



Autonomous Strategies for Life Cycle Extension





Bloomberg (2020)

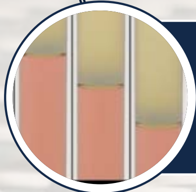
Sustainability starts in material design and manufacturing.

Sustainability **Durability** **Sustainability**

Adapted from Patrick, J. *et al., Nature* (2018)

Outline

Background and motivation

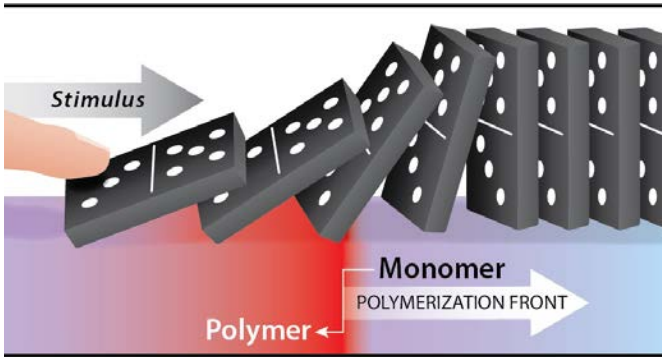


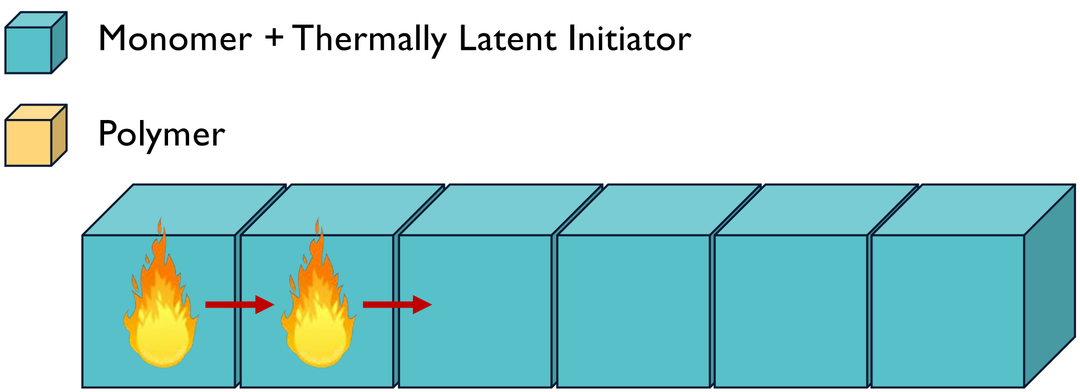
Rapid curing by frontal polymerization

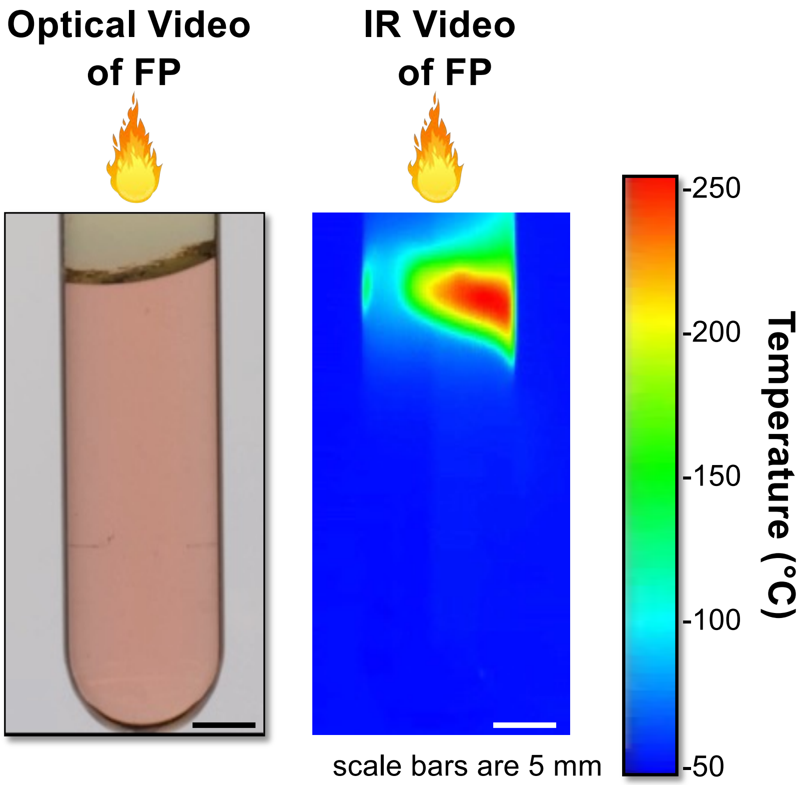
Energy efficient manufacturing of composites

Deconstruction and regenerative strategies

Frontal Ring Opening Metathesis Polymerization (FROMP)





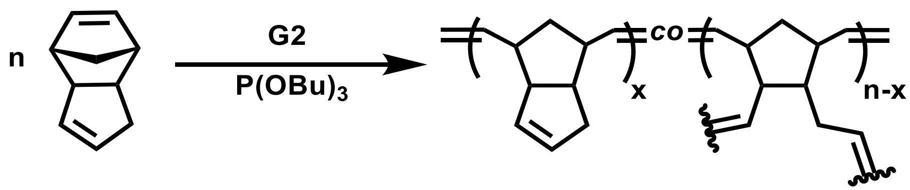


Robertson *et al. Nature* (2018)

Frontal Ring-Opening Metathesis Polymerization (FROMP) of Dicyclopentadiene

Mechanical Properties

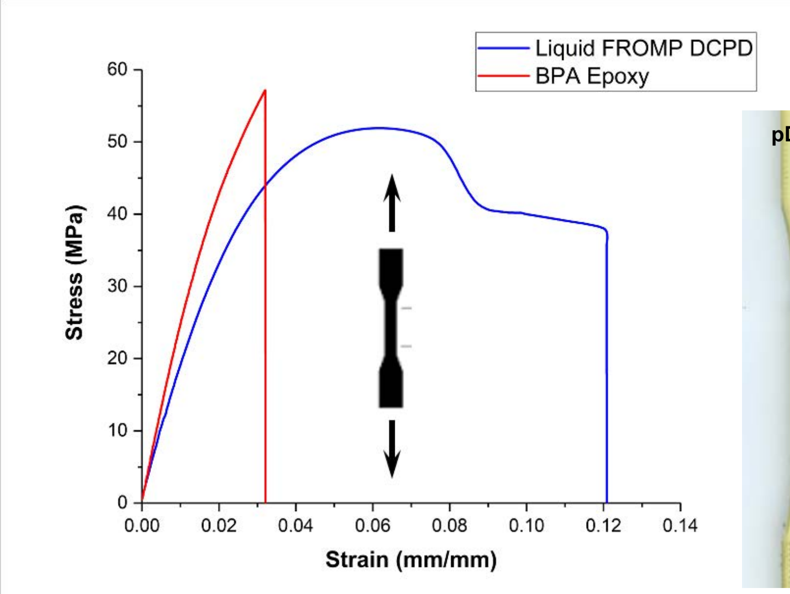
Frontal Ring-Opening Metathesis Polymerization (FROMP)



dicyclopentadiene (DCPD) polydicyclopentadiene (pDCPD)

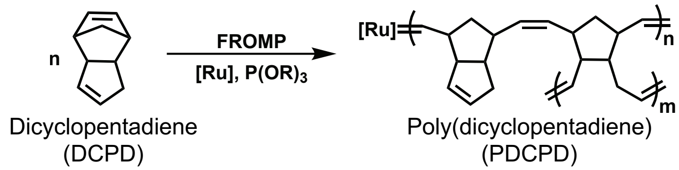
- *Endo*-DCPD
- 5-ethylidene norbornene (ENB)
- Grubbs' catalyst (GC2)
- Tributyl phosphite (TBP) inhibitor

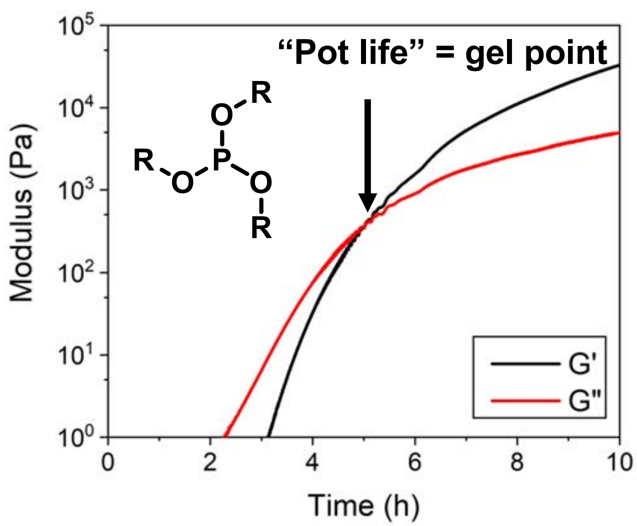
Robertson, et al., *ACS Macro Letters*, 6, 609-612 (2017)
Robertson, et al., *Nature, 557, 223 (*2018)

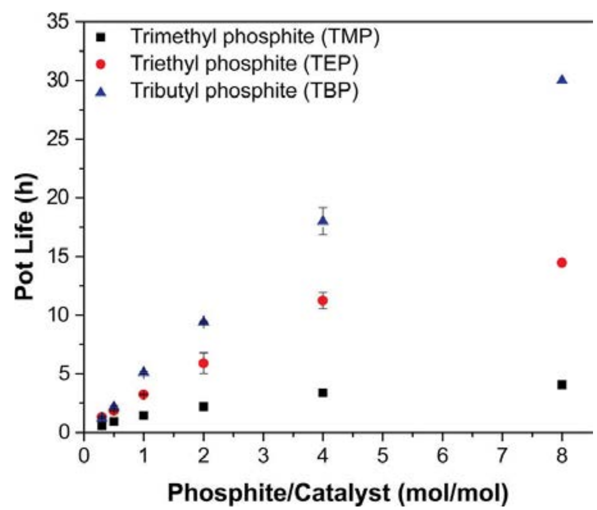


T_g	165°C
E	2.0 GPa
K_{Ic}	3.0 MPa m $^{1/2}$
σ_y	55 MPa

Alkyl Phosphites as FROMP Inhibitors







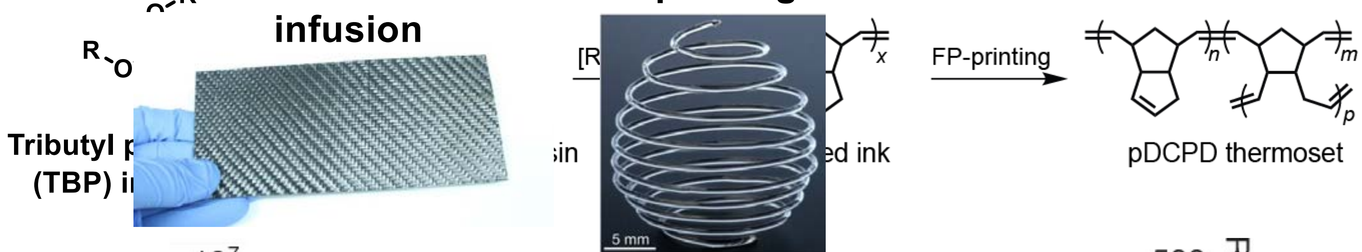
Pot life extended to over 30 h while still allowing FROMP

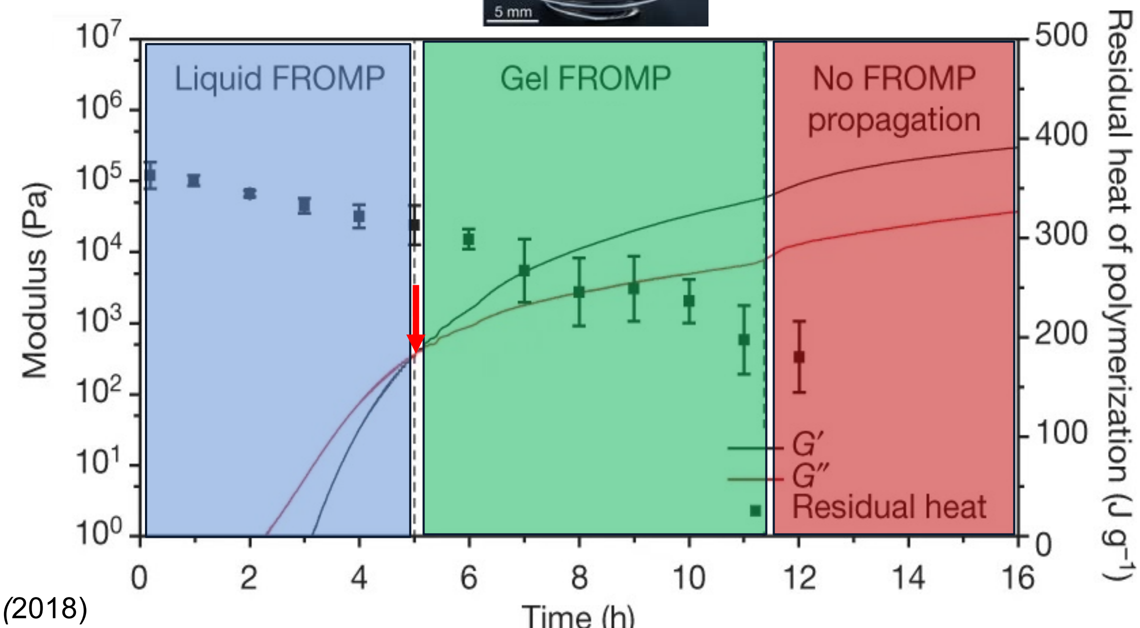
Robertson, et al. *ACS Macro Letters,* 6 (2017)

Control of DCPD Rheology

Resin infusion

3D printing

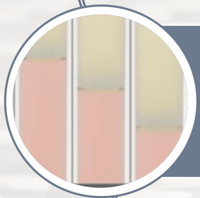




Robertson, et al., *Nature, 557 (*2018)
Aw, et al., Adv. Mater. Technol. 2200230 (2022)

Outline

Background and motivation



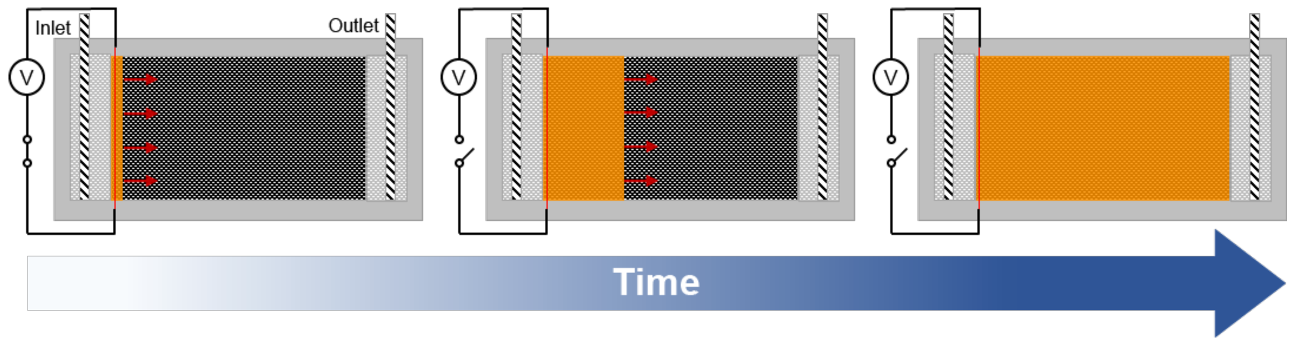
Rapid curing by frontal polymerization

Energy efficient manufacturing of composites

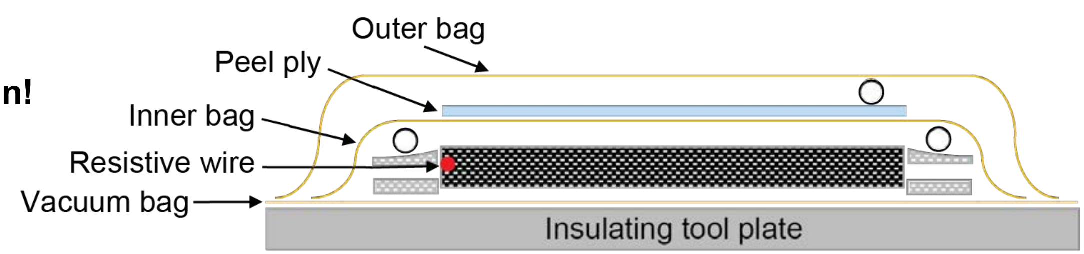
Deconstruction and regenerative strategies

Frontal Curing of Composites

- Vacuum Assisted Resin Transfer Molding (VARTM)
- Infusion of liquid DCPD resin into Toray T300 2x2 Twill carbon fabric
- Frontal polymerization triggered by heater along laminate edge

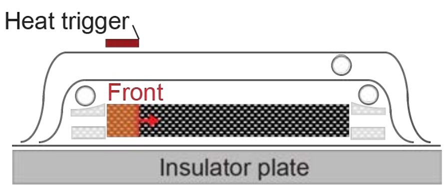


A 10 cm × 20 cm panel cures in 2 min!

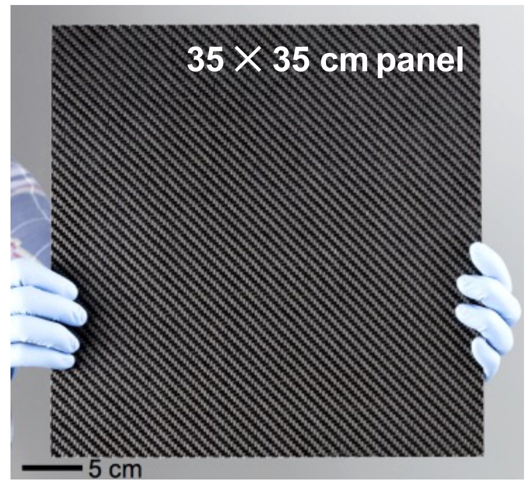


Edge Triggered Frontal Cure of Composite Laminate

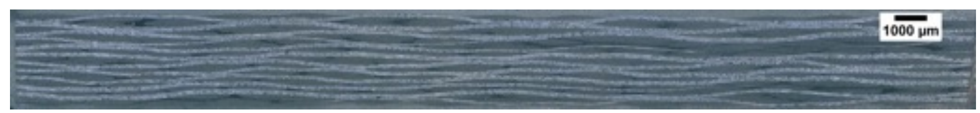
One front (in plane)



A 10 cm × 20 cm panel cures in 2 min!



Corrugated part

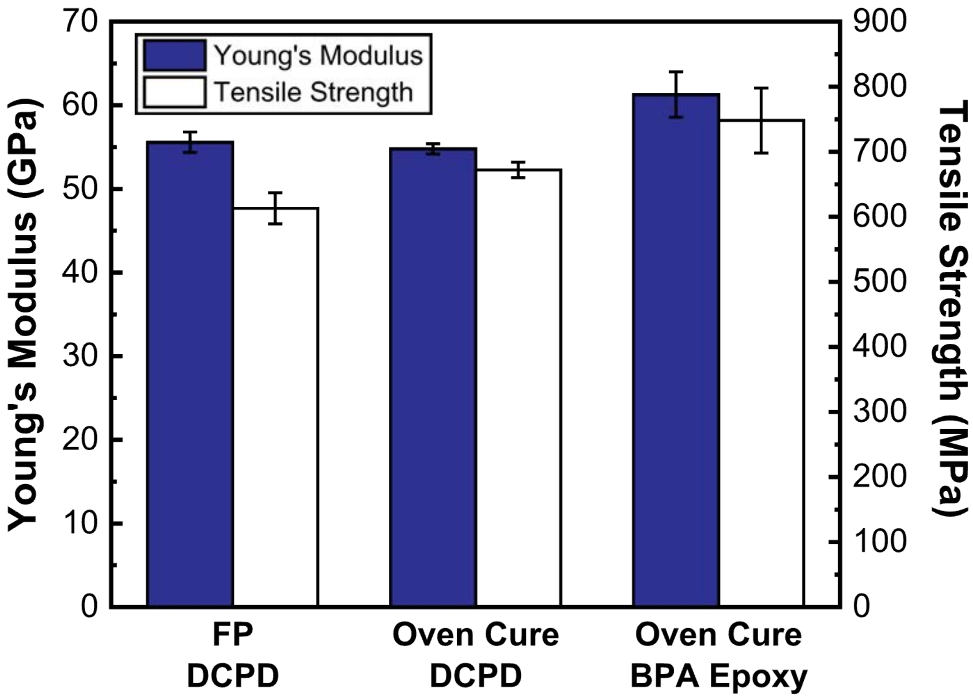


V_f ~ 51% , V_{void} < 1%, Tg~134°C

Robertson, et al., *Nature*, **557**, 223 (2018)

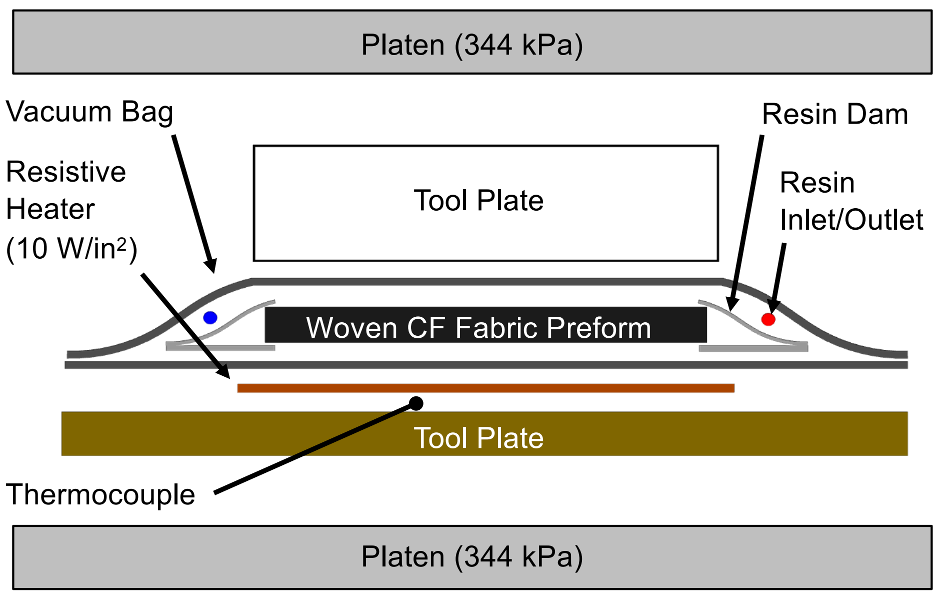
Composite Properties

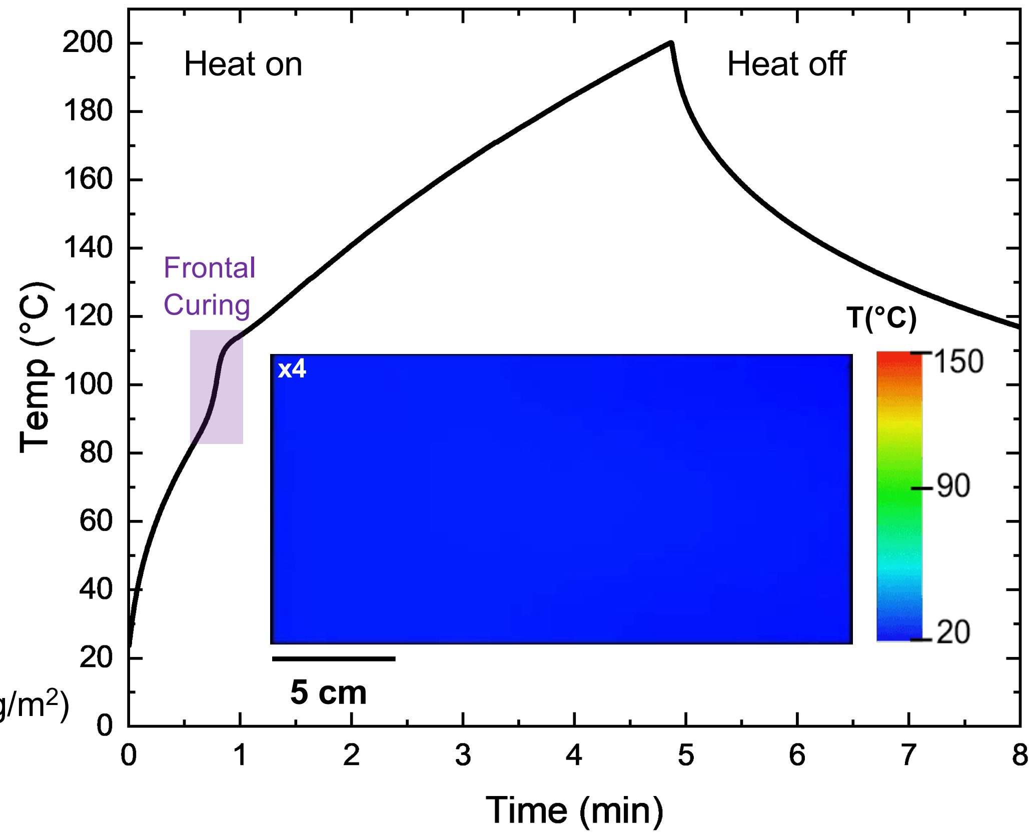
Epoxy (left), FP DCPD (right)



- Increase Tg
- Improve fiber/matrix interface

Through-Thickness Frontal Curing



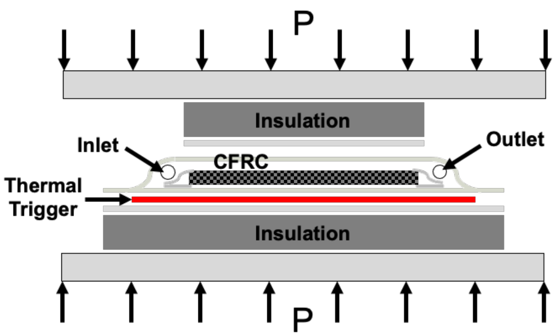


Reinforcement: 6 plies T300 2x2 twill weave fabric (3k tow; 204g/m^2)

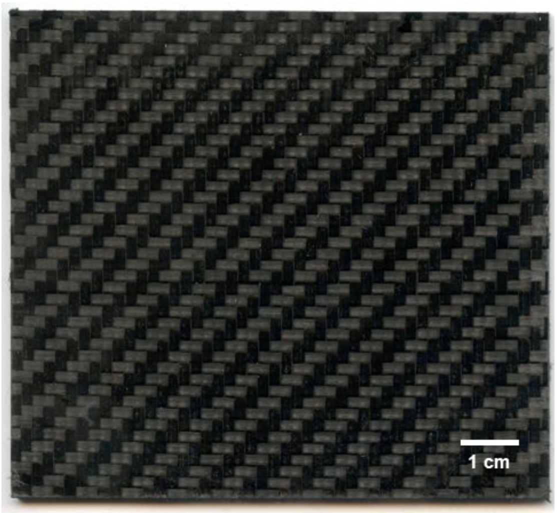
Cure Cycle: Resistive heater until thermocouple reaches 200 °C

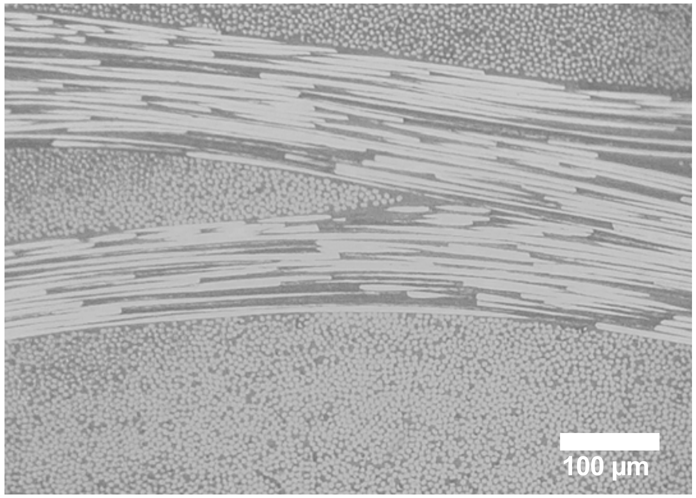
Vyas et al., *Composites: Part A*, **180**, 108084 (2024)

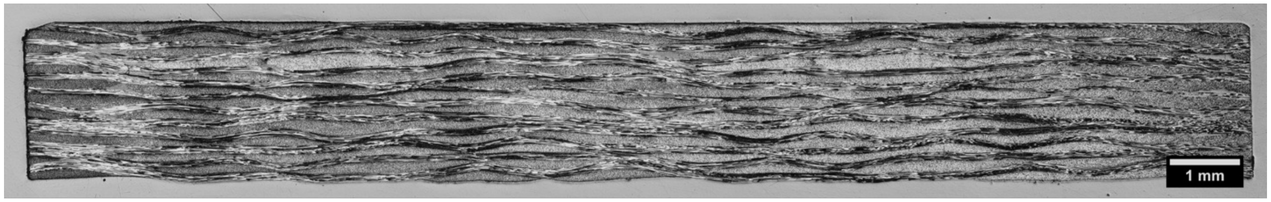
Through Thickness Frontal Curing



Trigger: *15 sec*
Cure Time: *30 sec*
V_f = 65%
V_{void} = 0.1%
T_g = 156°C



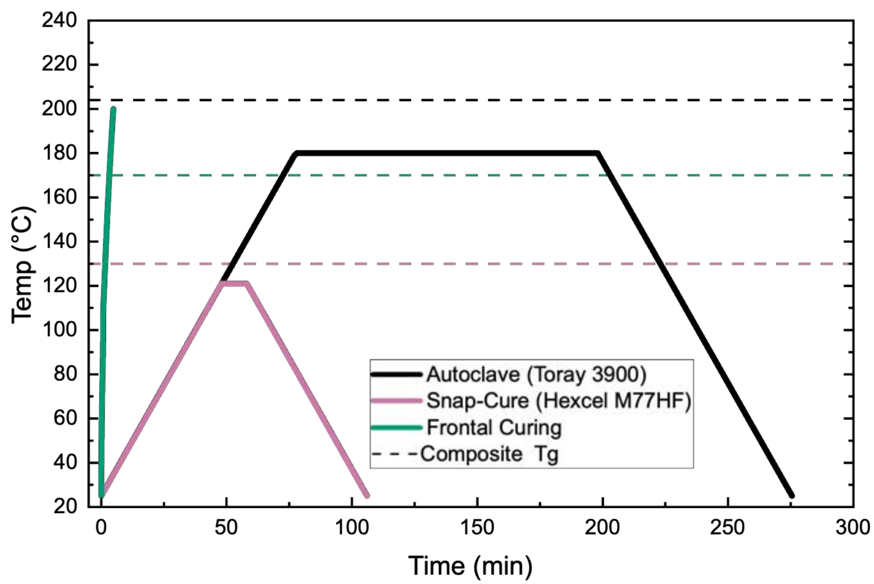




Vyas et al., *Composites: Part A*, **180**, 108084 (2024)

Frontal curing reduces manufacturing energy and time

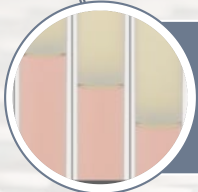
Comparison of processing temperature and time



- Up to 10 orders of magnitude reduction in energy consumed
- Up to 2 orders of magnitude reduction in time to cure

Outline

- Background and motivation

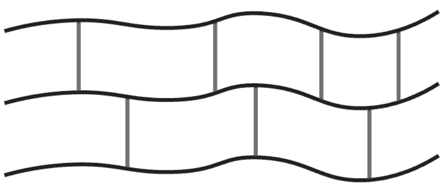


- Rapid curing by frontal polymerization

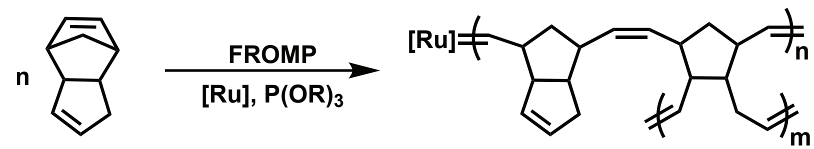
- Energy efficient manufacturing of composites
- **Deconstruction and regenerative strategies**

Deconstruction Strategies for pDCPD Thermoset

Crosslinked network
(not deconstructable)



pDCPD is permanent network / no recycle

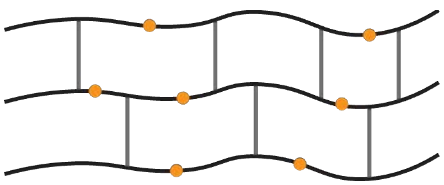


Dicyclopentadiene
(DCPD)

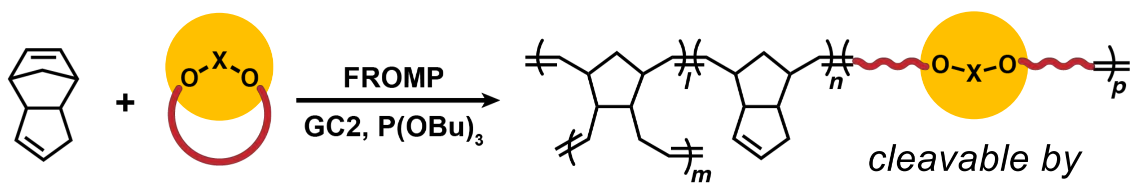
Poly(dicyclopentadiene)
(PDCPD)

J. Johnson
MIT

Before cleaving

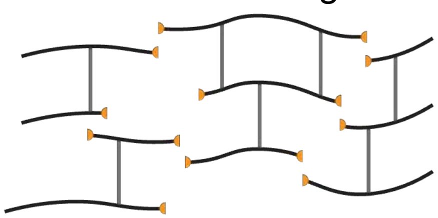


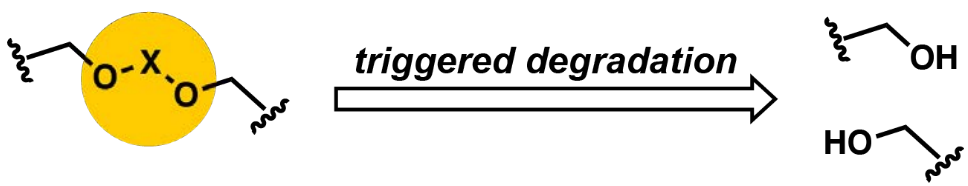
cleavable group



cleavable by hydrolysis

After cleaving

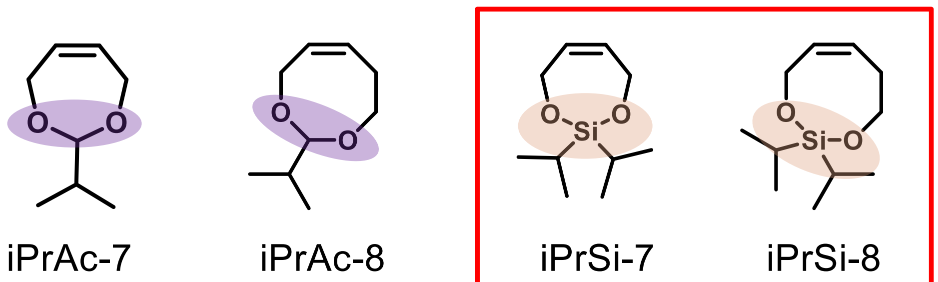




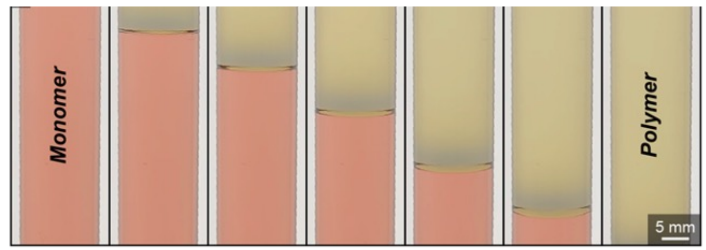
Deconstructed oligomeric fragments

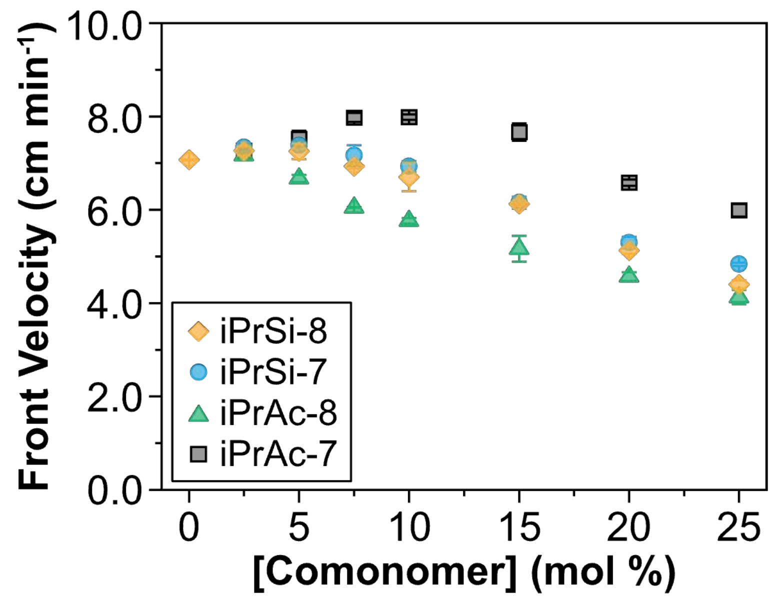
Frontal Polymerization with Cleavable Comonomers

Investigated four different cleavable comonomers



- iPrAc-7 exhibits the fastest fronts at higher comonomer loadings, and iPrAc-8 the slowest
- The iPrSi-8 comonomers have similar front speeds

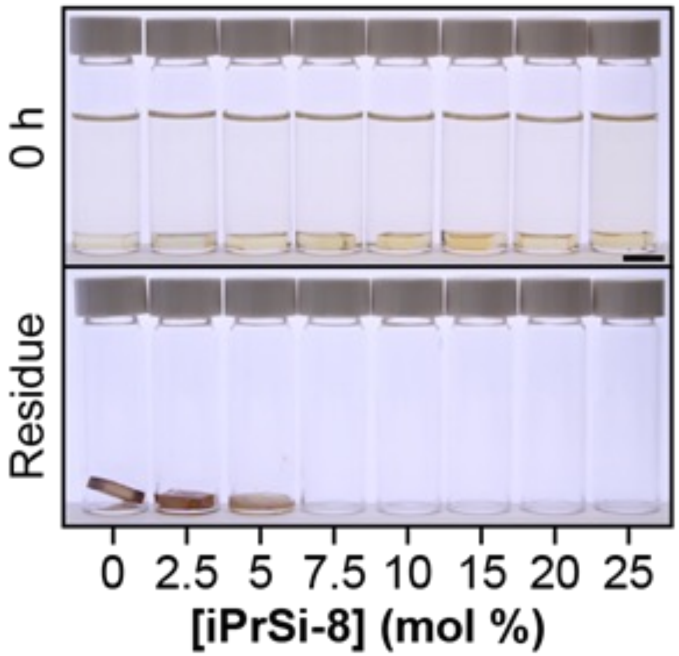




Lloyd, et al, *ACS Appl. Eng. Mater.* 2023, 1, 477–485

Screening Degradability of Comonomers

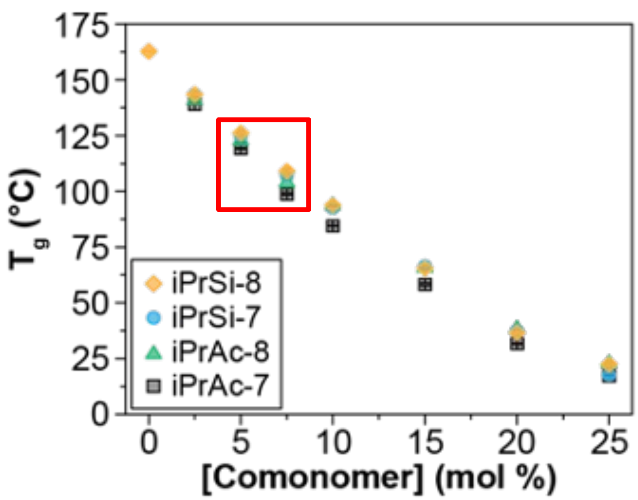
Deconstruction of copolymers:
Soak in 1.0M TBAF in THF or
1.0M HCl in CPME solution



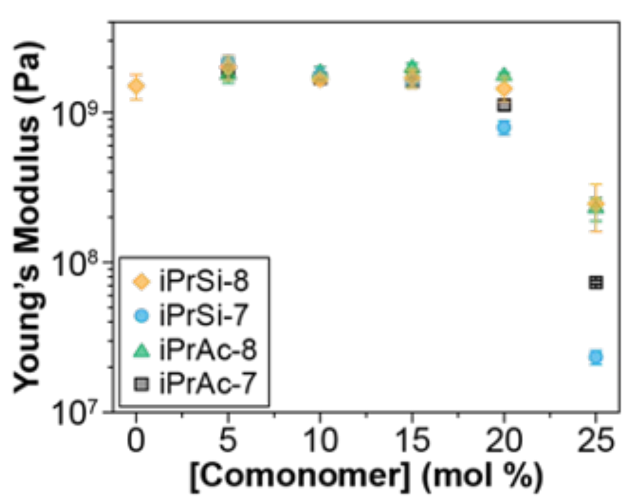
Lloyd, et al, *ACS Appl. Eng. Mater.* 2023, 1, 477–485

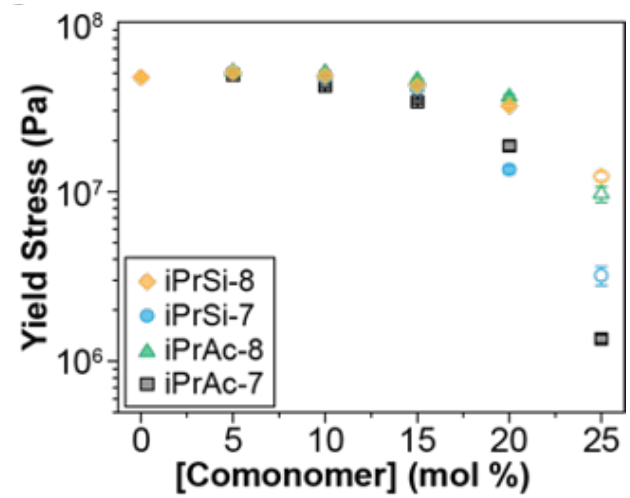
Effect of Cleavable Comonomer on pDCPD Polymer Properties

Significant reduction in T_g



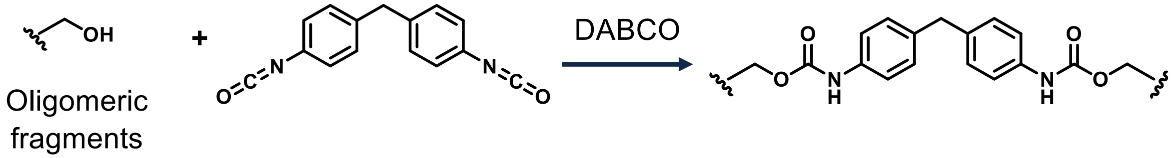
No effect on elastic modulus and yield at low concentrations

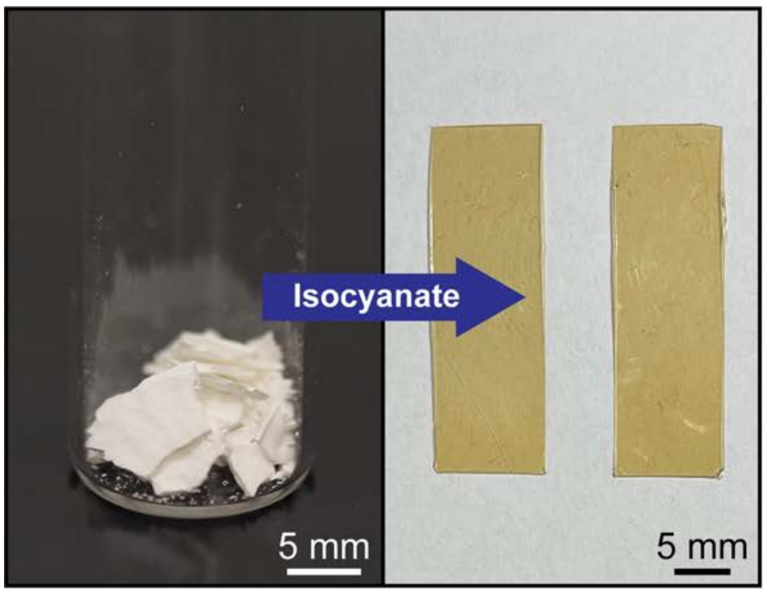


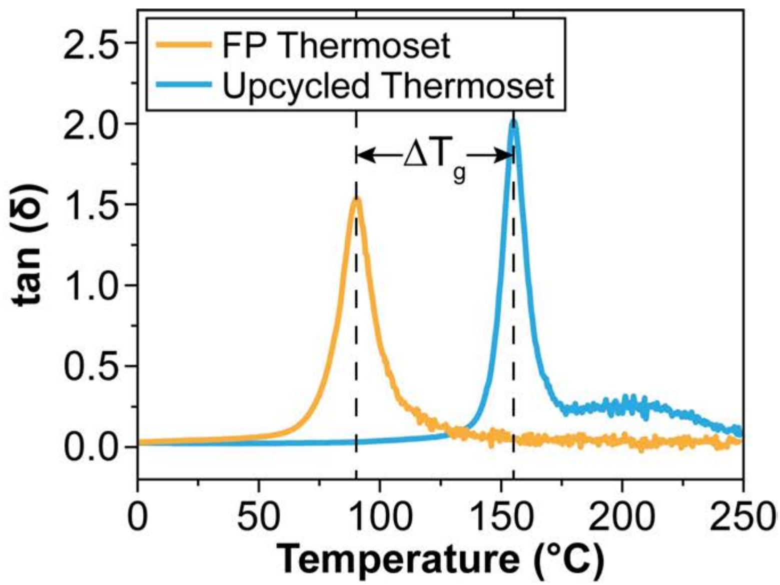


Lloyd, et al, *ACS Appl. Eng. Mater.* 2023, 1, 477–485

Upcycling of Degradation Fragments





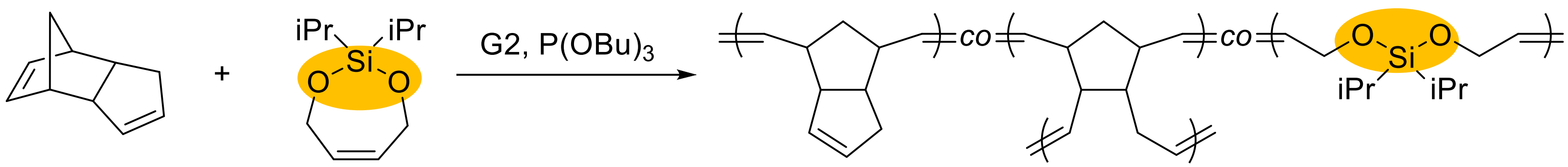


- The T_g of the upcycled product is 60 °C higher than the original iPrSi-7 10 mol% network!

Lloyd, et al, *ACS Appl. Eng. Mater.* 2023, 1, 477–485

Fiber Reinforced Composite with Cleavable Comonomer

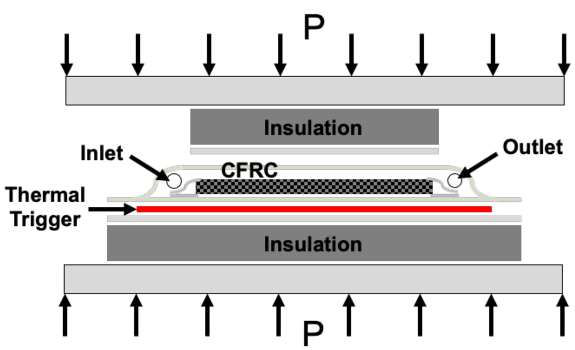
Deconstructable Resin System

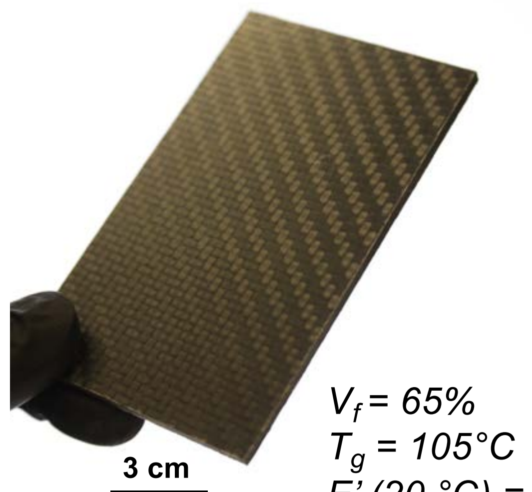


DCPD iPrSi-7

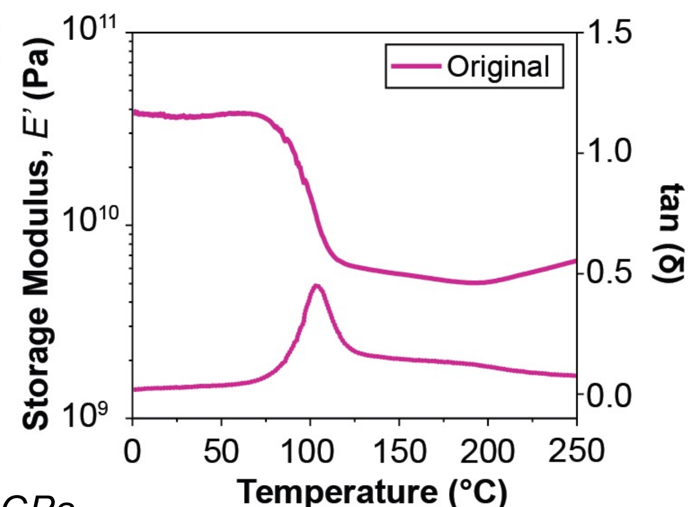
Composite with 10 mol% iPrSi-7 comonomer

Through Thickness Frontal Curing



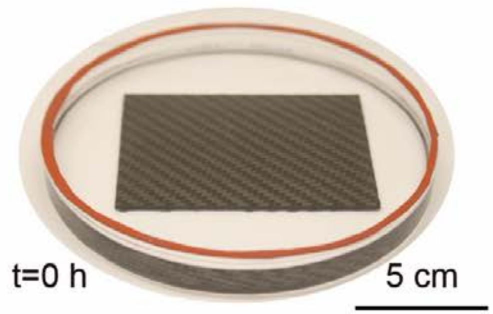


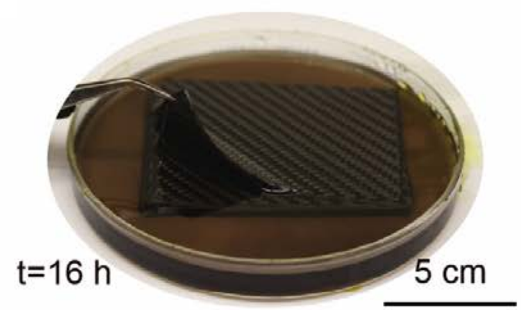
V_f = 65%
T_g = 105°C
E' (20 °C) = 37 GPa



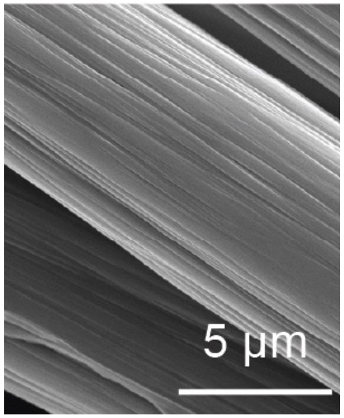
Deconstruction of Composite Laminate

Immersion in 1M HCL in CPME for 16 hours

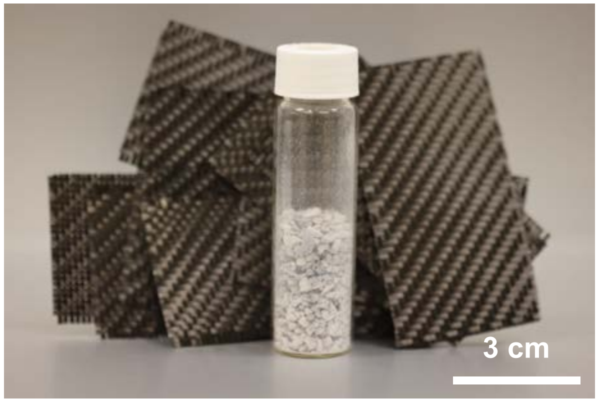




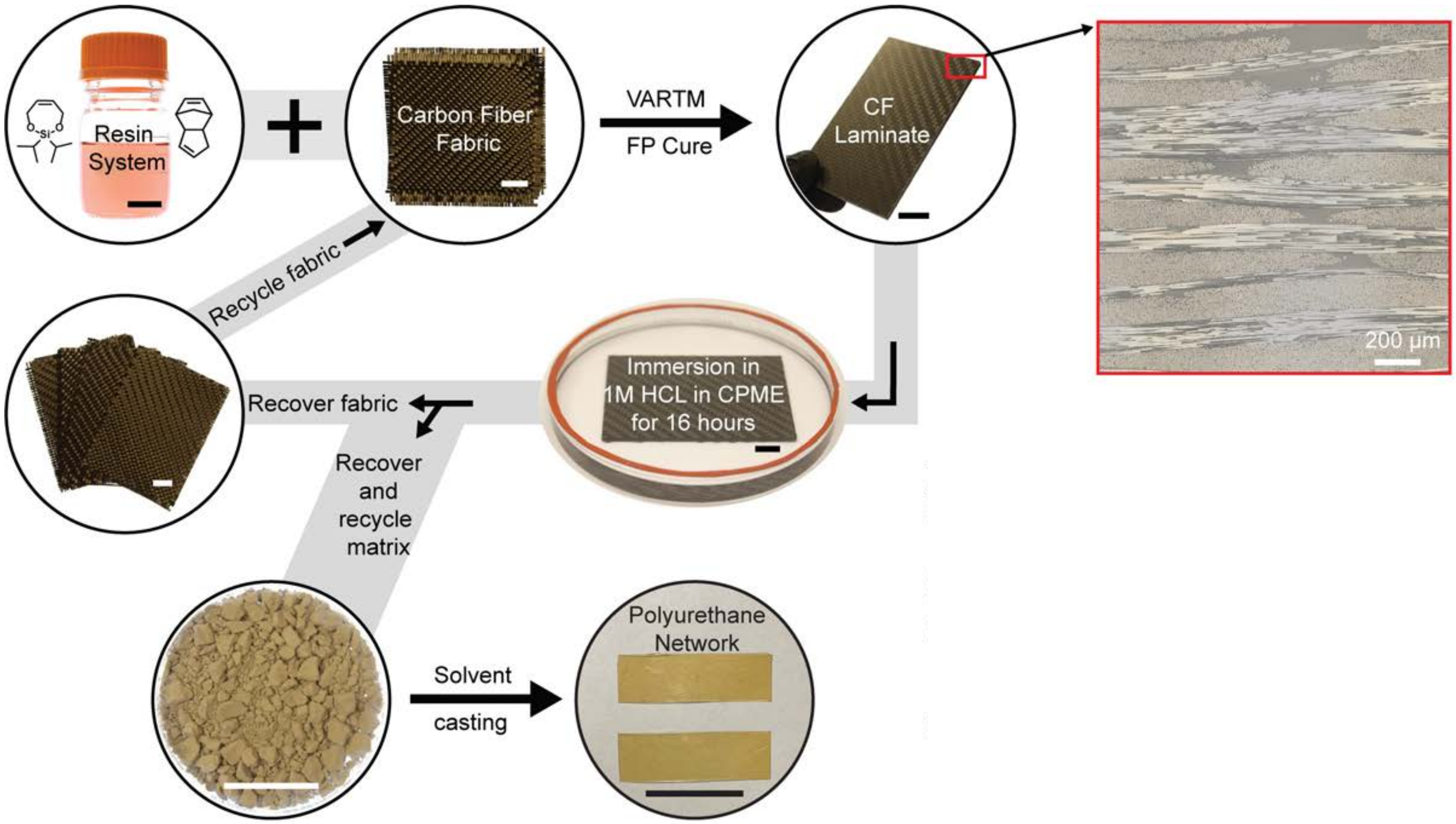
SEM of upcycled fibers



Recovered carbon fabric and matrix oligomeric fragments



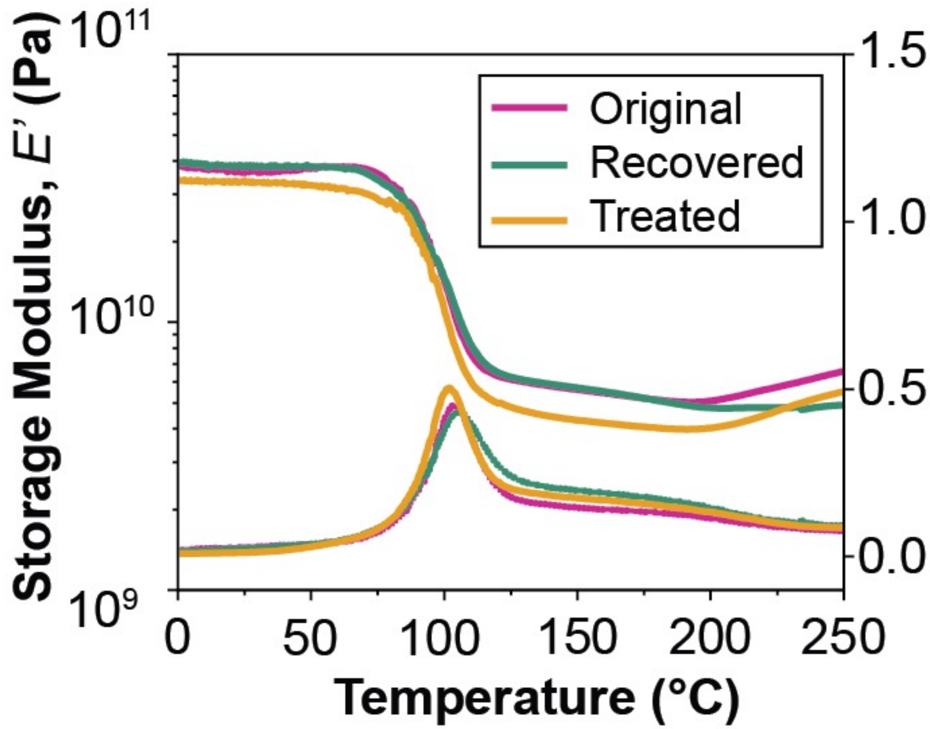
Regenerative Composite Manufacturing Cycle



Scale bars: 2 cm

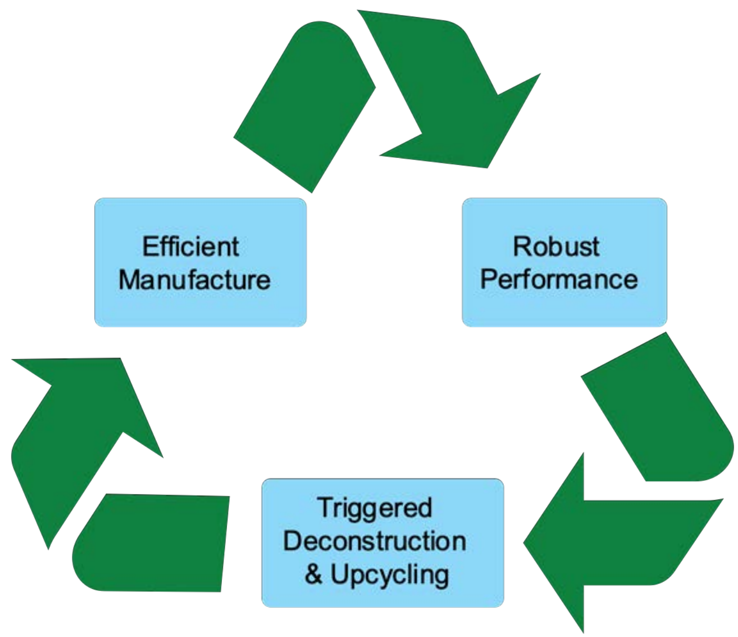
Composite Properties After Upcycle

- **Original:** **Generation 1 composite with pristine carbon fabric + DCPD + 10 mol% iPrSi-7**
- **Recovered:** **Generation 2 composite with recovered carbon fabric + DCPD + 10 mol% iPrSi-7**
- **Treated:** **Generation 1 composite with pristine carbon fabric + DCPD + 10 mol% iPrSi-7 soaked in HCl for 24hrs**



Summary

- **Frontal polymerization enables rapid, energy efficient processing of thermoset polymers and composites**
- **Successfully cured high Tg carbon-fiber reinforced composite in less than 30 sec and achieved properties comparable to autoclaved cured carbon/ epoxy composites.**
- **Incorporation of cleavable comonomers enable deconstruction and upcycling of thermoset pDCPD and composites.**
- **Successfully recovered fibers and reprocessed into new composites.**



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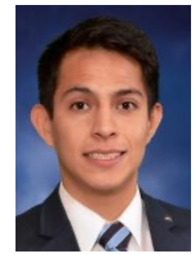
Edgar Mejia


Polette Centellas


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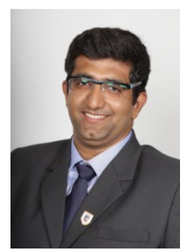
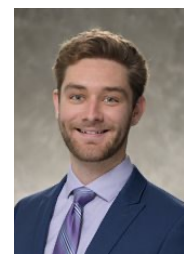

Sagar Vyas


Mostafa Yourdkhni


Tyler Price