U.S. AIR FORCE

USSF

AFRL

Next-Generation Materials: Government

Aerospace Composite Forum, Wichita, KS 2022

Hilmar Koerner, Research Lead, PMC M&P (RXCC)

Materials & Manufacturing Directorate (RX)

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Materials & Manufacturing Directorate

465 $M Total Resources (FY19, 2.2xCore)
400 ksqft, 9 Bldgs (55% Labs)

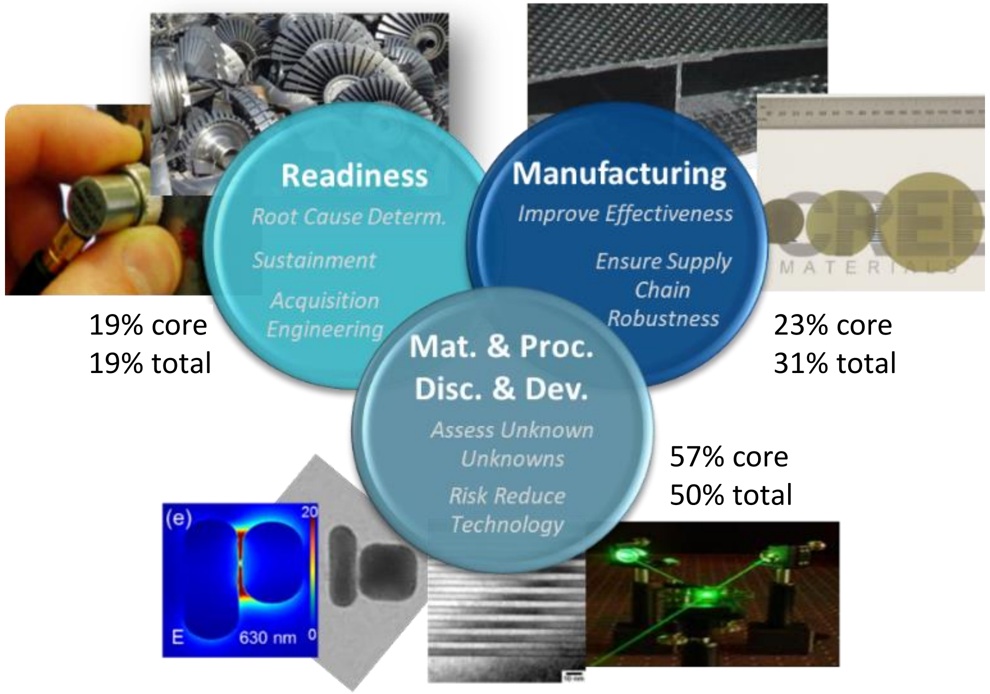
400 Gov. Staff (373 civ/27 mil, 50% PhD)
350 FTE On-site Staff, 50% PhD

Accelerating
Technologies, Industrial Base, & Capabilities

***Impose (Avoid) Tech Surprise** via Leading Cutting-Edge Foundational Research*

***Risk-Abate with Industry** to Insure Supply (materials, components, processes)*

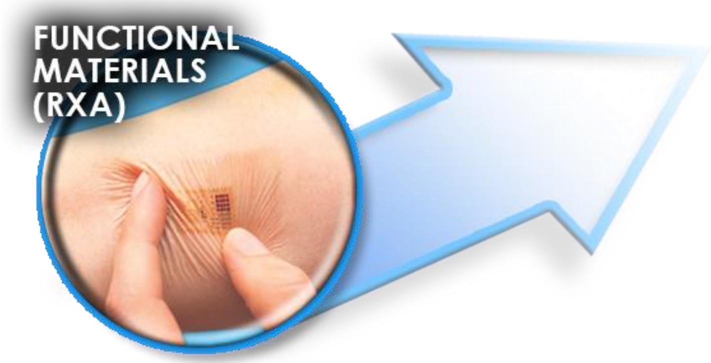
***Expert Advice** to DAF and OSD (operations, acquisition, policy, & planning)*



Cost-Imposing Technological Superiority Begins with Materials & Processes

Core Technical Competencies

- CERAMIC MATRIX COMPOSITES
- POLYMER MATRIX COMPOSITES
- METALS
- MATERIALS STATE AWARENESS



- MATERIALS FOR SURVIVABILITY AND PROTECTION
- MATERIALS FOR ISR AND ELECTRONIC WARFARE
- MATERIALS FOR MAN-MACHINE INTERFACE

Aerostructures

Agile Manufacturing

Airmen Performance Assessment

Energy Efficiency and Assurance

Hypersonics

Integrated Computational Materials Science and Engineering (ICMSE)

Intelligence, Surveillance, and Reconnaissance (ISR)

M&P Specification Standards

Mishap Prevention

Munitions

Nuclear Deterrence

Propulsion

Quick Reaction S&T Support

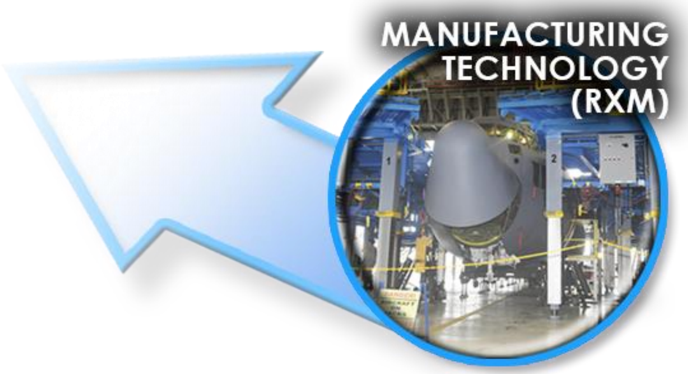
Space

Specialty Materials Affordability

Survivability

Sustainment

- SYSTEMS SUPPORT



- MANUFACTURING FOR ELECTRONICS AND SENSORS
- MANUFACTURING FOR PROPULSION AND STRUCTURES

Today's Strategic Environment

Global R&D

Human capital

Cyberspace

Electromagnetic spectrum

Space Access

Sophistication of adversaries

Tomorrow's Strategic Capabilities

Google: AF ST 2030 Strategy

Dominate Time, Space, and Complexity

- Global Persistent Awareness
- Resilient Information Sharing
- Rapid, Effective Decision-Making
- Complexity, Unpredictability, and Mass
- Speed and Reach of Disruption and Lethality

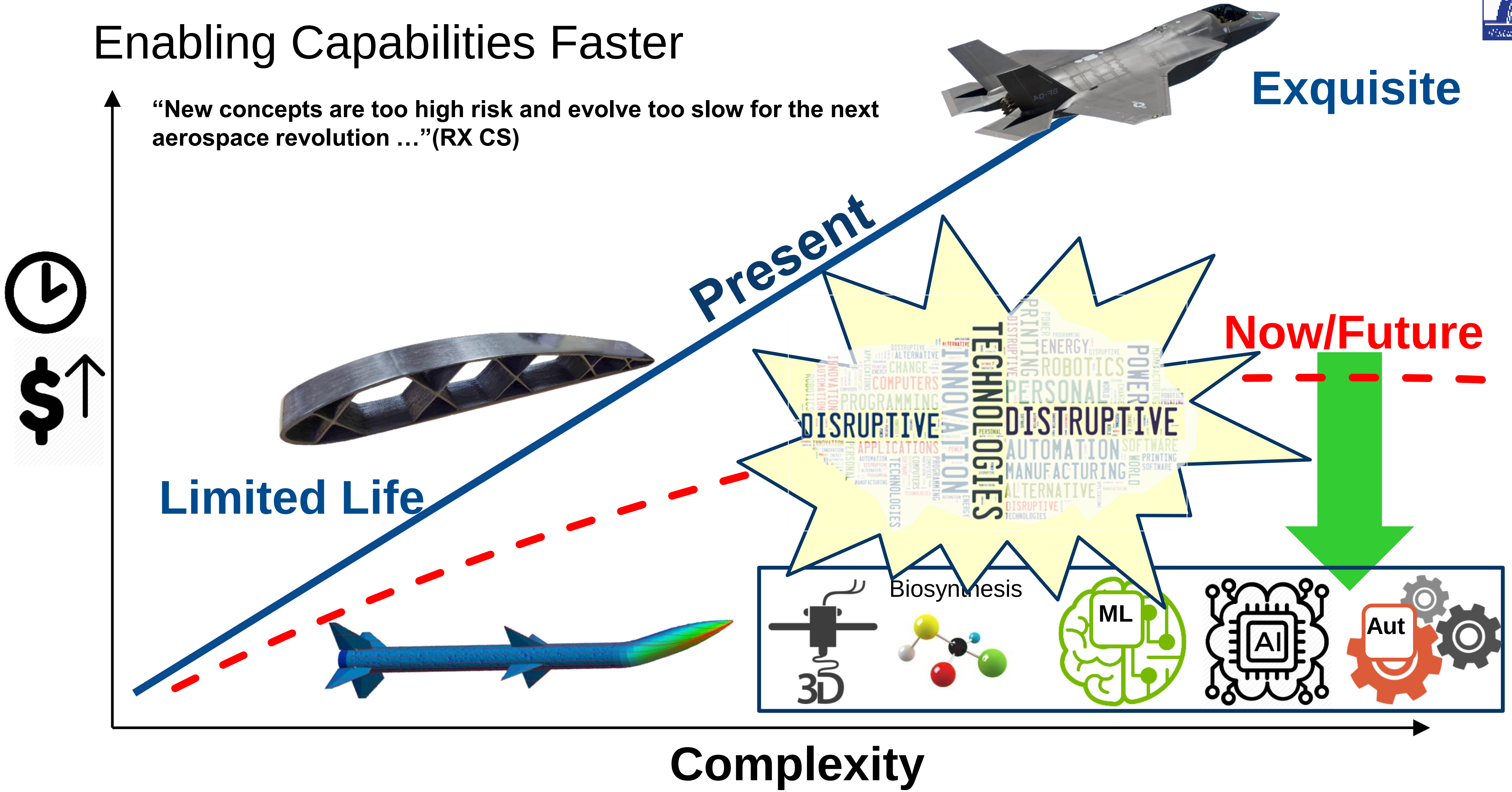
Deepen and Expand the Scientific and Technical Enterprise

- Engage and Support a Technical and Driven Workforce
- Drive Innovation Through Partnerships

providing deterrence options

Enabling Capabilities Faster

“New concepts are too high risk and evolve too slow for the next aerospace revolution …”(RX CS)



PMC Composite Summit/SAMPE 2019

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Polymer Matrix Composite Summit Motivation

- Polymer Matrix Composite Community Lacked Unified Vision for Next 10 Years
  - Last time the community was unified during Composites Affordability Initiative
- RX Composites Community Came to This Realization and Began Planned a Summit with Attendees From:
  - Original Equipment Manufacturers
  - Tier One Suppliers
  - Material Suppliers
  - Universities
  - Consultants
  - Government

THE AIR FORCE RESEAR

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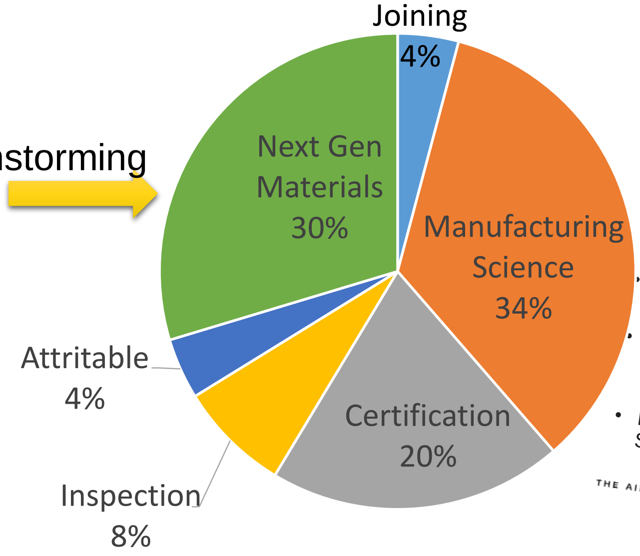
Results at a High-Level

- No surprises! Preaching to the Choir?
- The Air Force is already doing things in most of these areas
- Not DARPA hard or unifying enough for a POM initiative
- Questions
  - Where are thermoplastics?
    - Community seems to be talking and dipping toes in the water
    - Commercial industry adopting widely (Europe leading)

Brainstorming Input



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Next Gen Materials

TECHNICAL APPROACHES

- 3D Printing Fiber Placement w/ Engineered Thermoplastics for Secondary Structures
- Performance to Replace Metal Bulkheads w 3D Structural Composites
- Existing Next Gen Materials Applied to Existing Applications
- Existing Next Gen Materials Applied to New Complex 3D Applications
- Identify a High-Level next Generation Material Champion
- Develop Advanced Geometry / Complex 2D Composites w/ Current Materials
- Find New Architectures for 3D Loaded Structures

Difficulty

TECHNICAL APPROACHES

- Develop and Establish Factory Maturity Level (FML) process
- New Specs, Continuous Improvement Paths
- Next Gen/Next Gen Materials Applied to Complex 3D Applications
- Next Gen Materials Applied to Existing Applications
- Ensure Next, Next Gen Materials meet Next, Next Gen Threats (incl. multifunctional requirements)
- Molecular Composites (fiber/resin)
- Prototype, Build and Flight Demo with X% Performance Improvement
- MGI Approach for Next Gen Materials Discover (physics-based and data driven)
- Boron Nitride Fibers (structural, transparent, thermal control)
- Develop Step-Change Improved Fiber (next, next gen)

THE AIR FORCE RESEARCH LABORATORY

7

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Strategic Priorities Go Forward Plan

- **Strategic Priorities** clearly focus on **Low Cost, Agile Manufacturing Processes** and **Certification of Composites** technical areas

1. Technical Interchange Meetings may be held to further develop plans
2. Determine opportunities to strengthen these technical areas utilizing transformational technologies
3. Further develop these technical areas to position as part of a Vanguard program
   - OMC Processing-to-Performance Evaluation Research & Analysis
   - Modeling for Affordable Sustainable Composites
   - Non-traditional processes
   - Material families for multiple processes
   - High temperature thermoplastics
4. Meet with AFLCMC for input on future programs of record

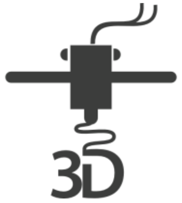
What are NextGen Materials for Composites?

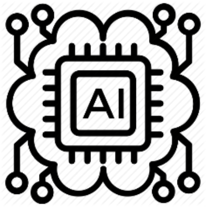
Next Generation implies

- Imagination, innovation, novelty and revolutionary
- Leaves past behind, e.g. old processes
- Rooted in the past but with greater quality and efficiency

Adapt material form factor to new disruptive processes and functions

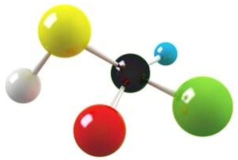
- High performance polymers into filament, powders rods etc
- Epoxy into inks
- Teach materials new tricks (self-sensing, resilience, self-healing)
- Hollow carbon fibers for light weighting
- Materials for extreme, "new" environments, e.g. space, underwater arteries, extraterrestrial





Accelerate invention

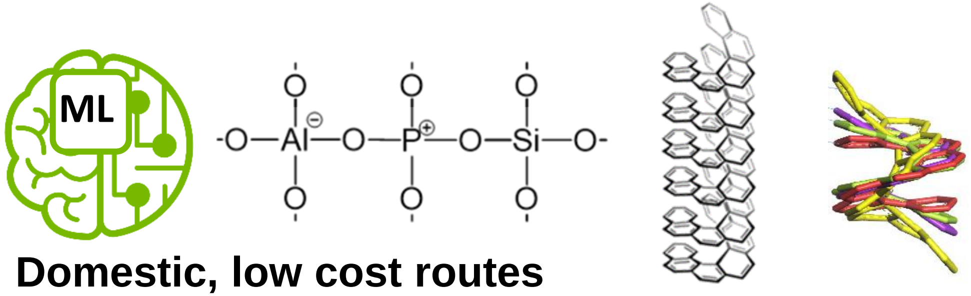
- Materials discovery
- Machine learning, artificial intelligence
- Synthetic biology



PMC M&P addresses the design and synthesis of specialty polymers, real-time sensors, processing science, and predictive modeling

Materials Discovery

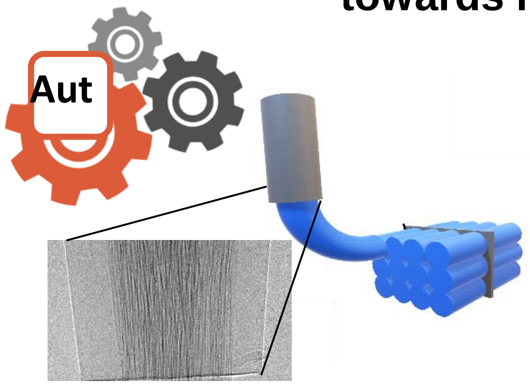
- Synthesis 600ºF - 1000ºF resins
- Resin discovery via ML/AI
- Geopolymers
- SynBio



Domestic, low cost routes towards high performance, resins

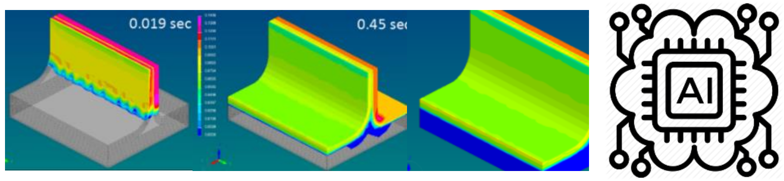
Agile Processing

- Additive Manufacturing and Infusion
- Real-time measurements
- Process modeling & Integrated sensing



alignment, velocity

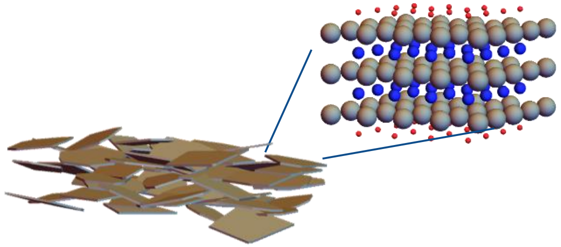
Agile, low cost processes



Process automation and part unitization

Multifunctional

- Boron rich epoxies (Nuclear)
- MXenes (CDEW)



Resilient structures

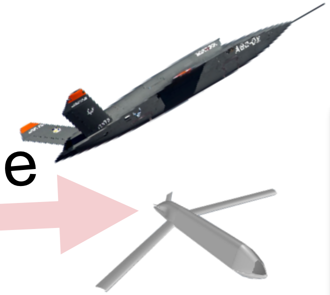
PMC M&P focus areas

Exquisite

Demand for Increased Performance
(range/speed/maneuverability)
- Higher temperature materials
- Lighter weight structures
- Complex geometries / bonding

- **OPPERA** (Process Modeling for unitized structures)
- **PSYCHE** (CDEW, resilient PMCs)
- High temp PMCs for small engines

THE UNIVERSITY OF SOUTHERN MISSISSIPPI · GE · NSF · RENEGADE MATERIALS CORPORATION UNBRIDLED INNOVATION



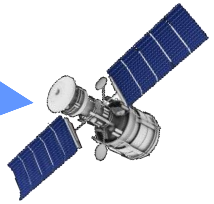
Attritable

Demand for **Affordability**
- Low cost material options
- Design for Limited life
- Speed / Ability to surge

- **PICARD SDCP, MASS** (AM of PMCs, thermoplastic PMCs)
- SymBio

OAK RIDGE National Laboratory · DARPA · BOEING · Continuous Composites

Space

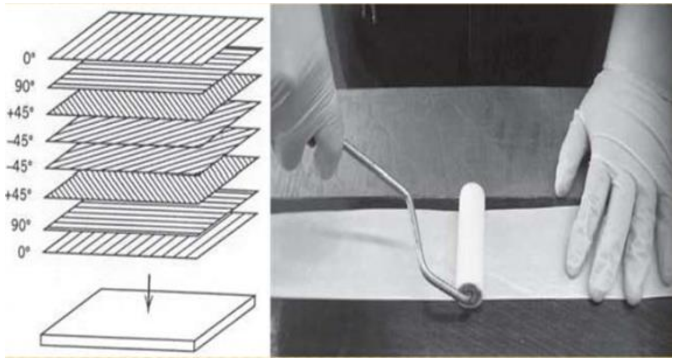


Composites in Space
- Affordability
- Temperature Resiliency
- Radiation Effects

- AM for space structures
- Hardening of materials for space
- **Rocket Cargo Vanguard** (geopolymers)

NORTHROP GRUMMAN

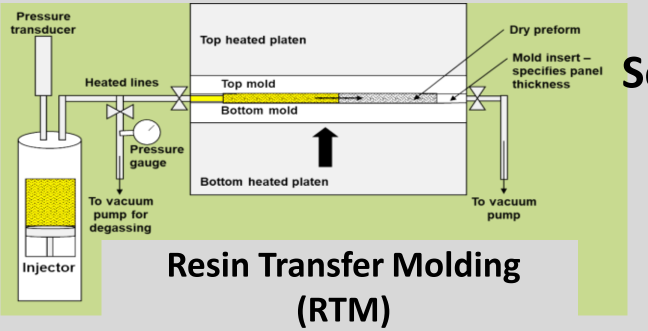
From Traditional to Agile Manufacturing



Hand Lay-Up of PMC's

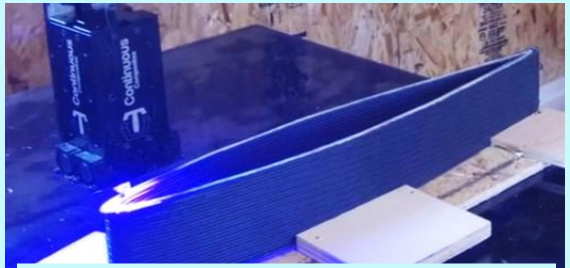
Autoclave Processing

⇓Time, ⇓Cost



Resin Transfer Molding (RTM)

Solvent-Free/Imidized Resin
Unitized Components
Tolerances
⇓Cycle Time
3D Preforms

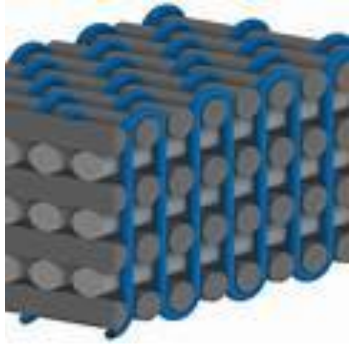


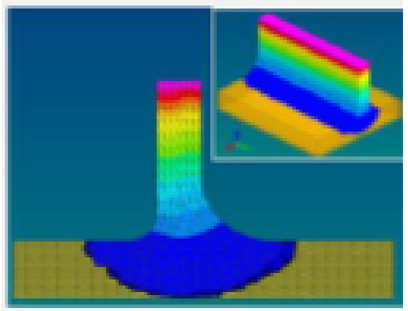
3D Printed Composites

Rapid Prototyping
Complexity

Characterization and Modeling of Resin Infusion Processes – Voids, Permeability and Filling

AFRL working with OEM through CRADA to study 3D architectures and RTM processing of high temperature PMC





Key challenges :

- Interlaminar capability at vane-band joint (3D architecture)
- Processing complex airfoils with minimal defects (Part filling, porosity …)
- Fiber architecture and HT resin with improved processibility

Univ of Delaware
(Dr. Suresh Advani : 3 years)

Process Modeling and building block approach to eliminate voids in complex geometries fabricated using the RTM process

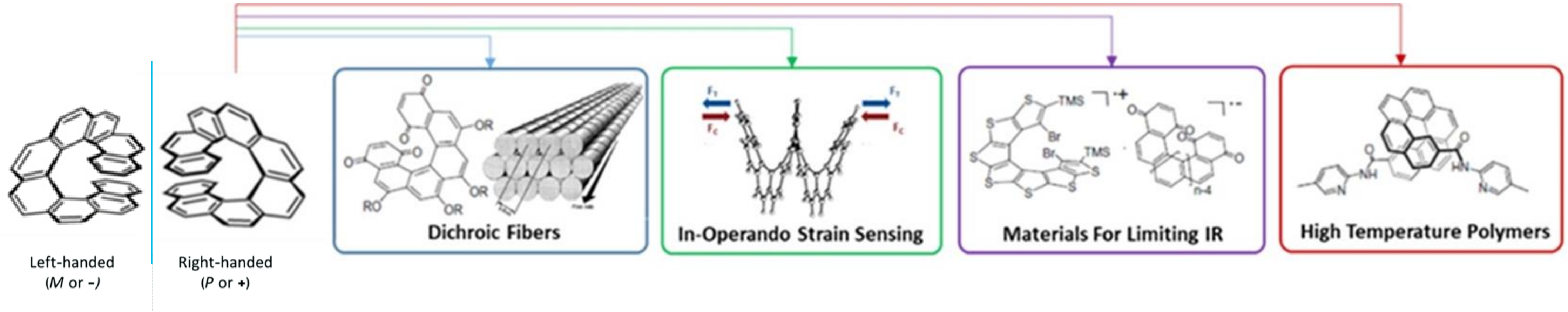
- Develop permeability measurement in 3 directions in 2D and 3D preforms
- RTM process modeling studies to investigate effects of process parameters, resin properties and preform architectures; Dual scale flow modeling
- Experimental validation of flow models at tow and preform level

BYU
(Dr. Andy George : 2 years)

Void formation and mortality during liquid composite molding using high temperature resins

- Experimental characterization of formation and transport of voids in HT-PMC
- Development of fast acting models to represent formation and transport of voids in resin during processing of HT-PMC
- Optimization of LCM process to minimize voids during processing

Materials Discovery: Helically Chiral Molecules and Polymers



Hypothesis

- Thermally Robust monomers for high temperature applications.
- Large Dichroism along the helical axis, has implications for sensing.

Synthetic Hurdles

- Syntheses tend to be lengthy and low yielding.
- Enantioselective synthesis is key for some applications.

Highly dichroic, non-planar, oxidatively robust fused aromatic rings.

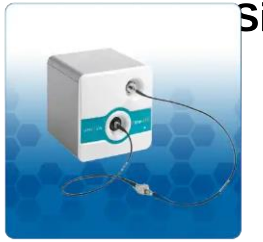
Materials Discovery: Molecule Maker

Reagents, Solvent, Waste

Workup and Silica Columns

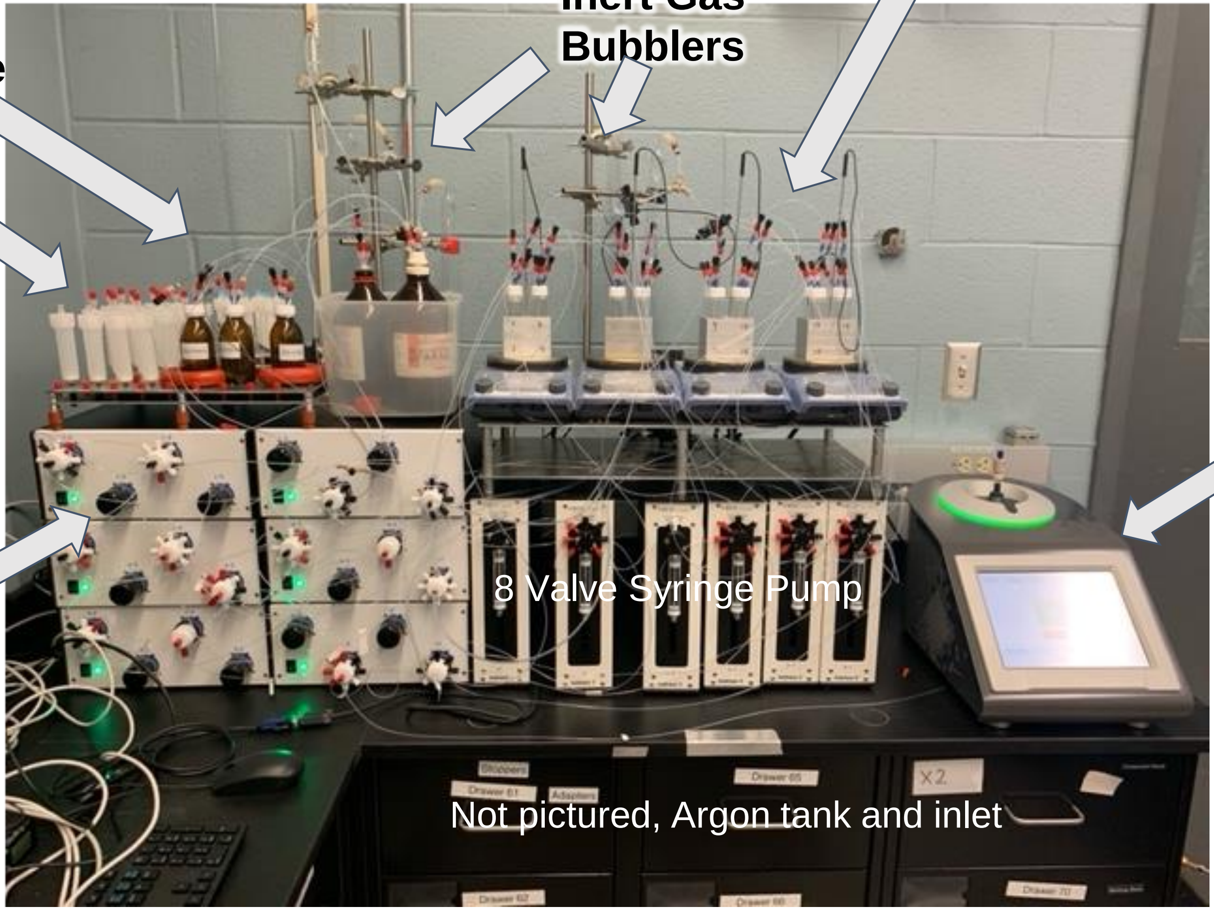
Inert Gas Bubblers

Hot Plate/Stirrer 16 vials x 20 mL



Uv-vis Spectrometer

Fluorescence Detector

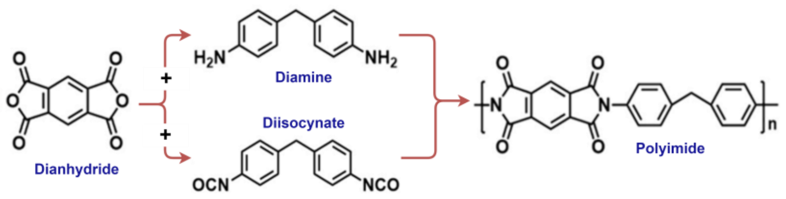


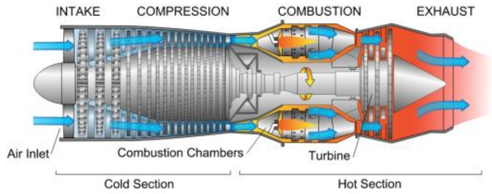
4/8 Teflon Valve Array (192 valves)

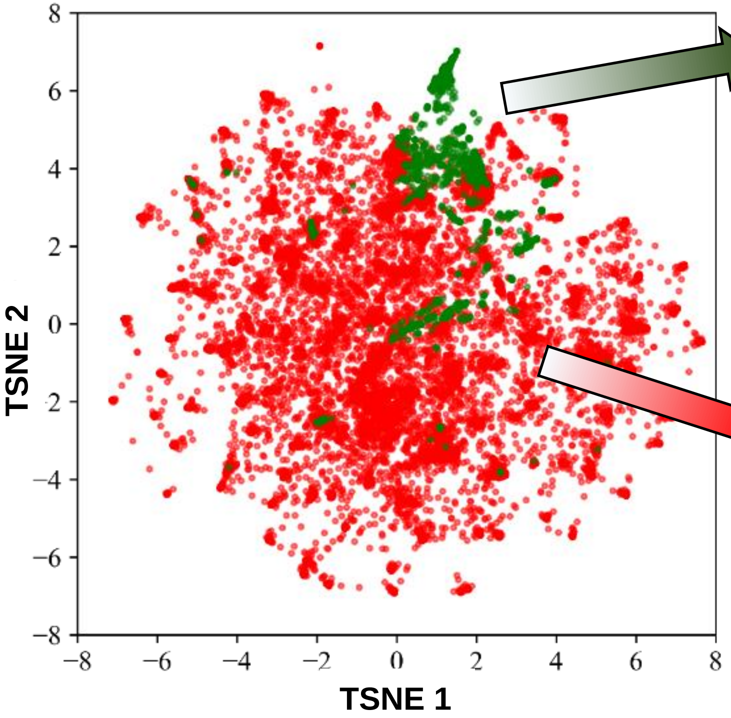
60 MHz(1.4T) ^{1}H and ^{19}F NMR 1D and 2D Capability

First Molecule Maker with Closed Loop (Autonomous) NMR Analytical Tool: Direct Structural Evidence of Reaction Outcome(s)

Materials Discovery: ML/AI for High Temp Resins



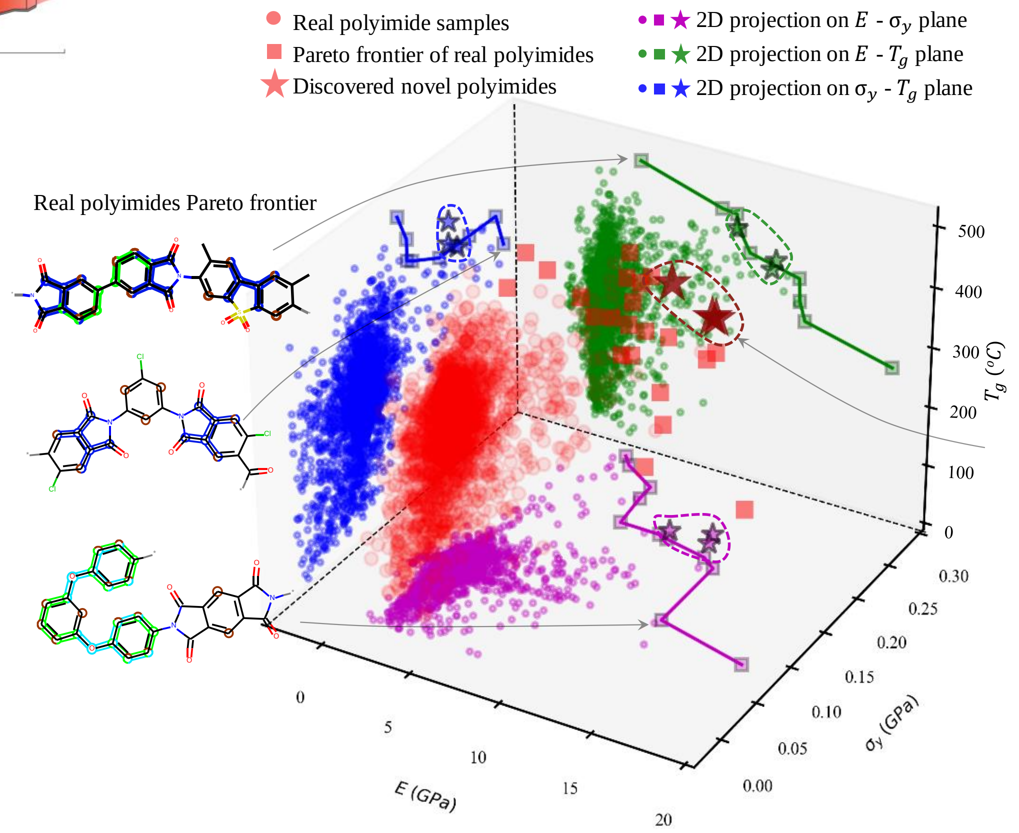


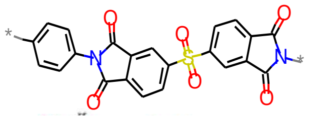


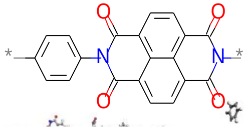
2233 real experimentally synthesized **polyimides**

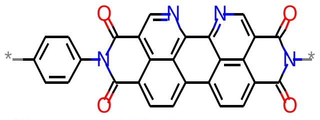
8 million hypothetical **polyimides** (poly-condensation by dianhydride and diamine/diisocyanate from PubChem)

Multi-objective Optimization (T_g, E, σ_y, η, T_d) for Polyimides Discovery



#1 

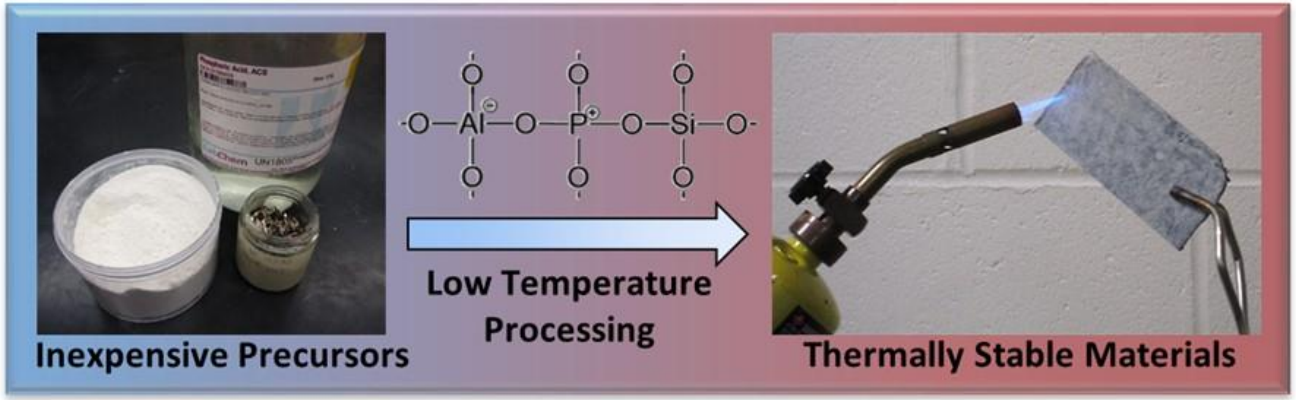
2 

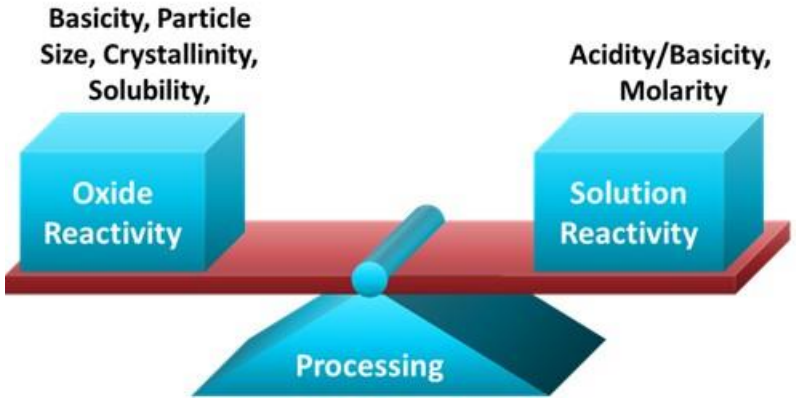
3 

Current Focus: Incorporation of viscosity and thermal degradation temperature.

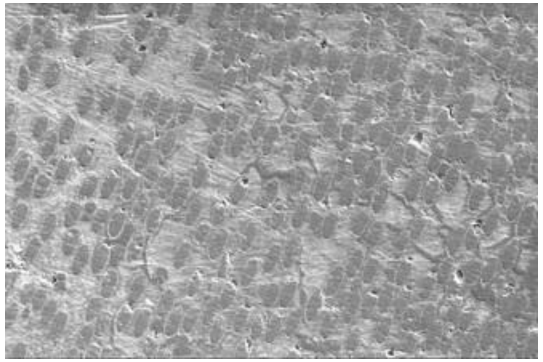
UCONN IBM

Geopolymers: Silico-Alumino-Phosphates and Alkaline-Aluminosilicate and Their Composites



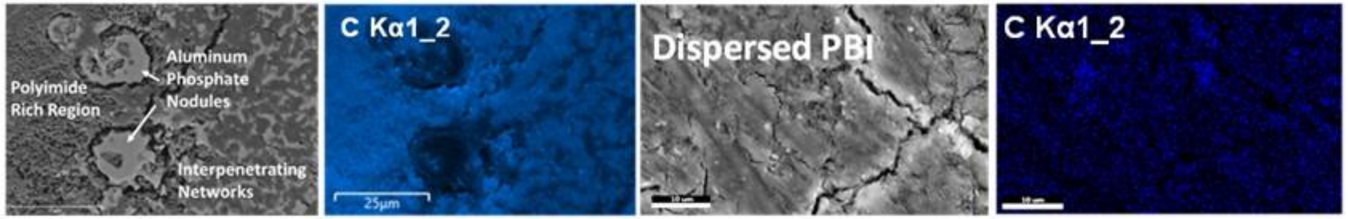


Oxide + reactive solution
High Shear Mixing
Dissolution, Condensation Polymerization, Dehydration
Molding, Low Temp Cure
Amorphous Solid
Heat Treatment
Glass Ceramic



Multi-Functional Composites

Alkaline Geopolymer Composites Tested at Elevated Temperature

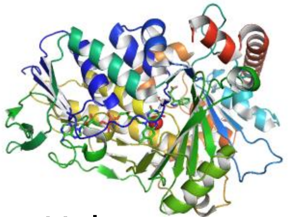


Polymer-Geopolymer Hybrids with PI and PBI

Davide Simone

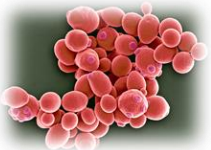
Biosynthesis of Monomers and Sensors for High Temperature Composites

Objectives:
- Alternative routes to aerospace relevant monomers.
- Elimination of precious metal catalysts lowers cost and eliminates a thermo-oxidative liability in the cured resin.
- Halogenation does not rely on corrosive bromine or iodine.
- Harness the selectivity that biology so elegantly achieves.

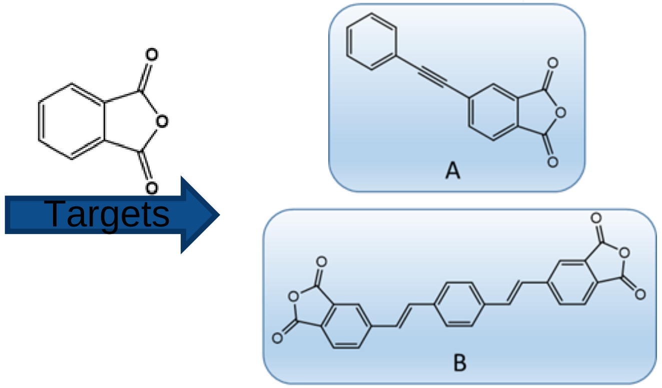


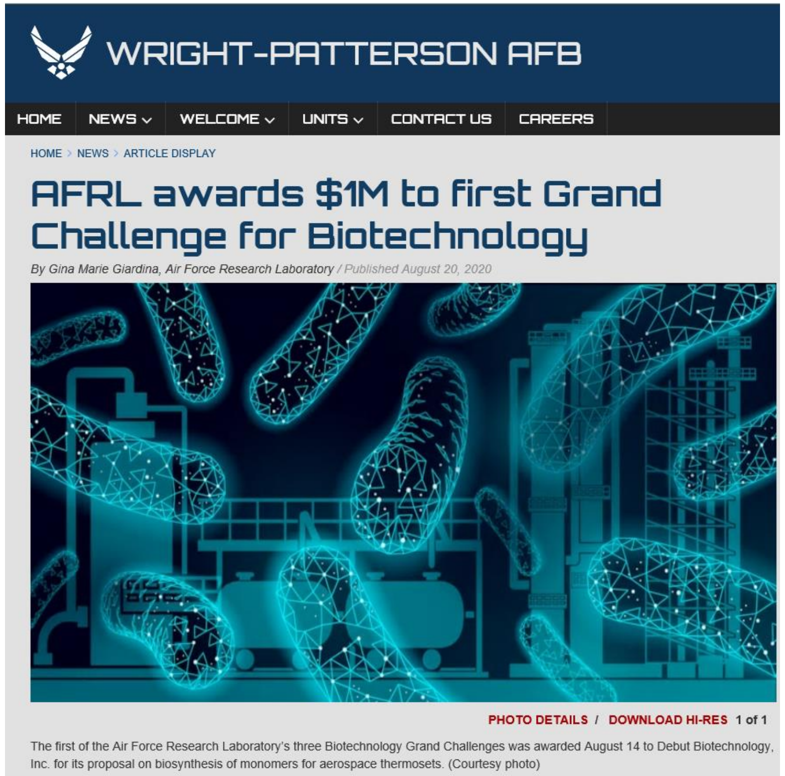
Halogenases

Metallo-enzymes



Modified Yeasts

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AFRL awards $1M to first Grand Challenge for Biotechnology

By Gina Marie Giardina, Air Force Research Laboratory / Published August 20, 2020

PHOTO DETAILS / DOWNLOAD HI-RES 1 of 1

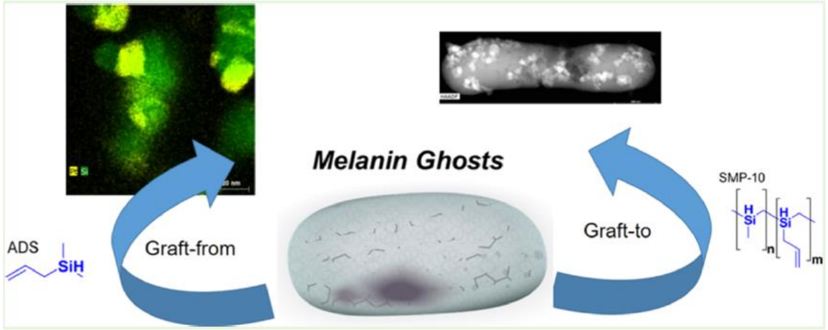
The first of the Air Force Research Laboratory's three Biotechnology Grand Challenges was awarded August 14 to Debut Biotechnology, Inc. for its proposal on biosynthesis of monomers for aerospace thermosets. (Courtesy photo)

Biosynthesis of Structural Ceramic Precursors

Preceramic polymer synthesis of novel precursors for new chemistries, ceramic morphologies, and enhanced processing efficiencies

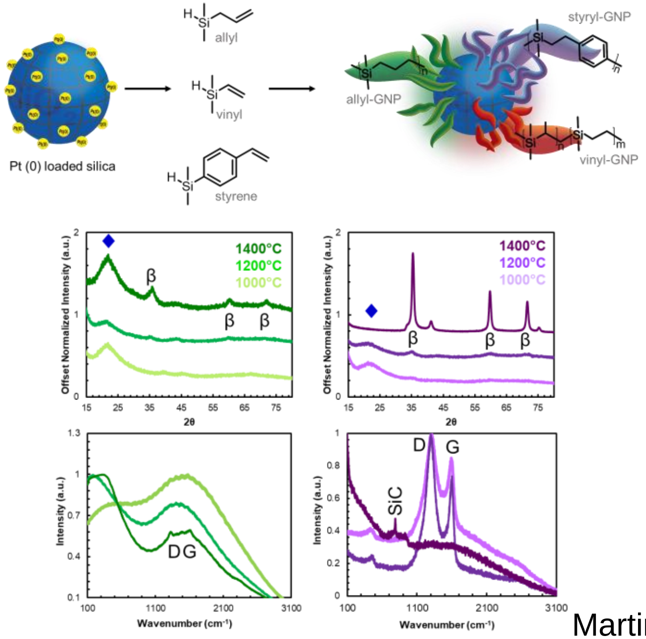
- First biosynthetic approach to SiC, a potential low-cost precursor
- Hybrid polymers with inorganic particle cores synthesized for enhanced processing – patent filed
- Developed click chemistry approach to polymers for refractory carbides – patent to be filed

Synthetic Biology Route to SiC



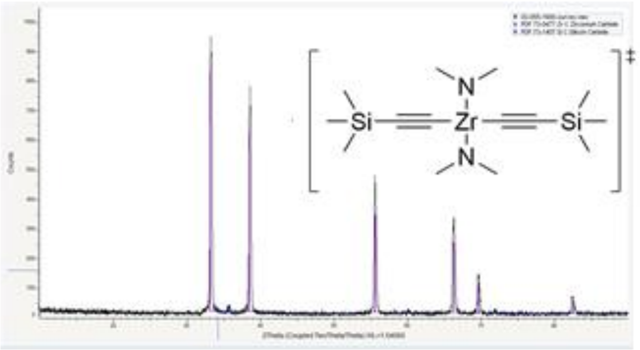
Parvulescu et al., ACS Biomater.Sci.Eng., 2021

Hybrid Polymer-Inorganic Precursor

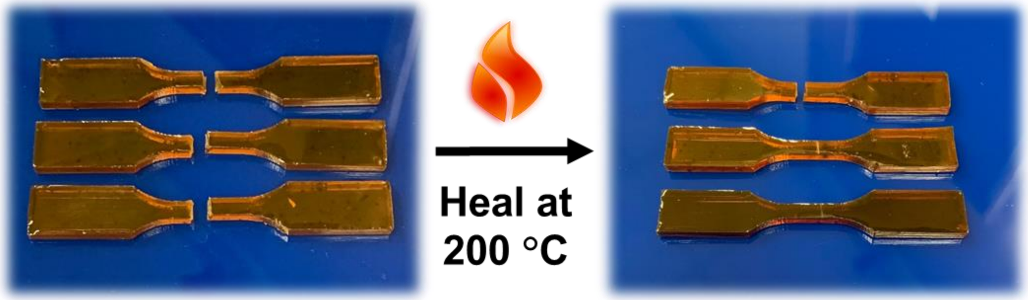


Martin et al., Chem.Mater., 2020

Precursors for Refractory Carbides

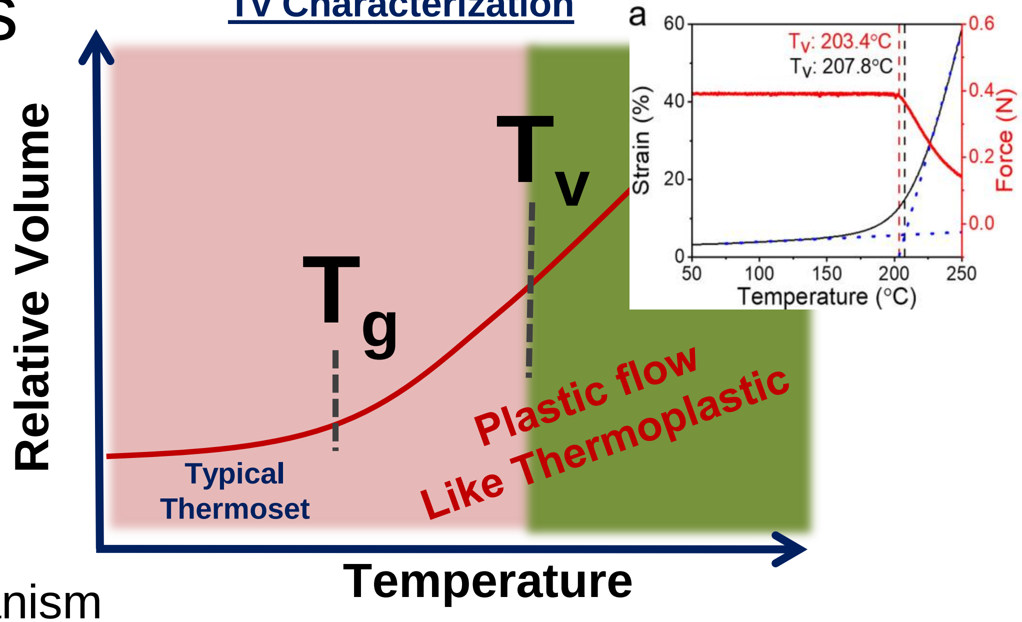


Self-Healing Composites: Vitrimers



30 min
1 hr
2 hr

Tv Characterization

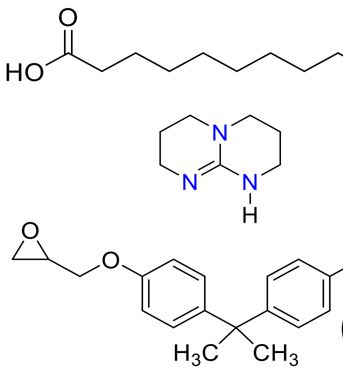


Advantages

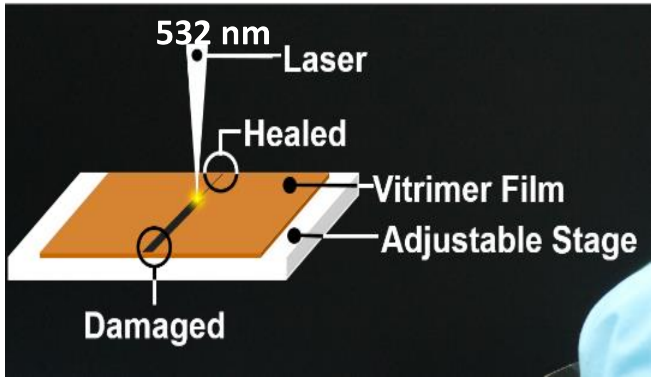
- Reprocess/Remold
- Self-healing
- Mechanical properties

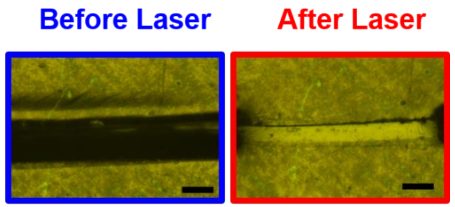
Challenges

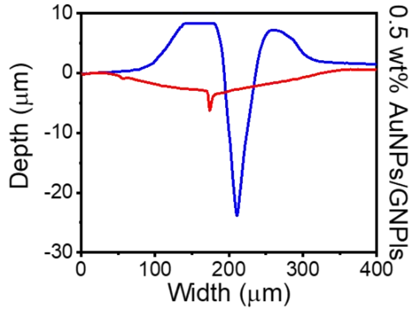
- Slow Response Time
- Lack of Understanding on Mechanism
- Only Heat Sensitive
- Understand and Control of Creep



(DGEBA)





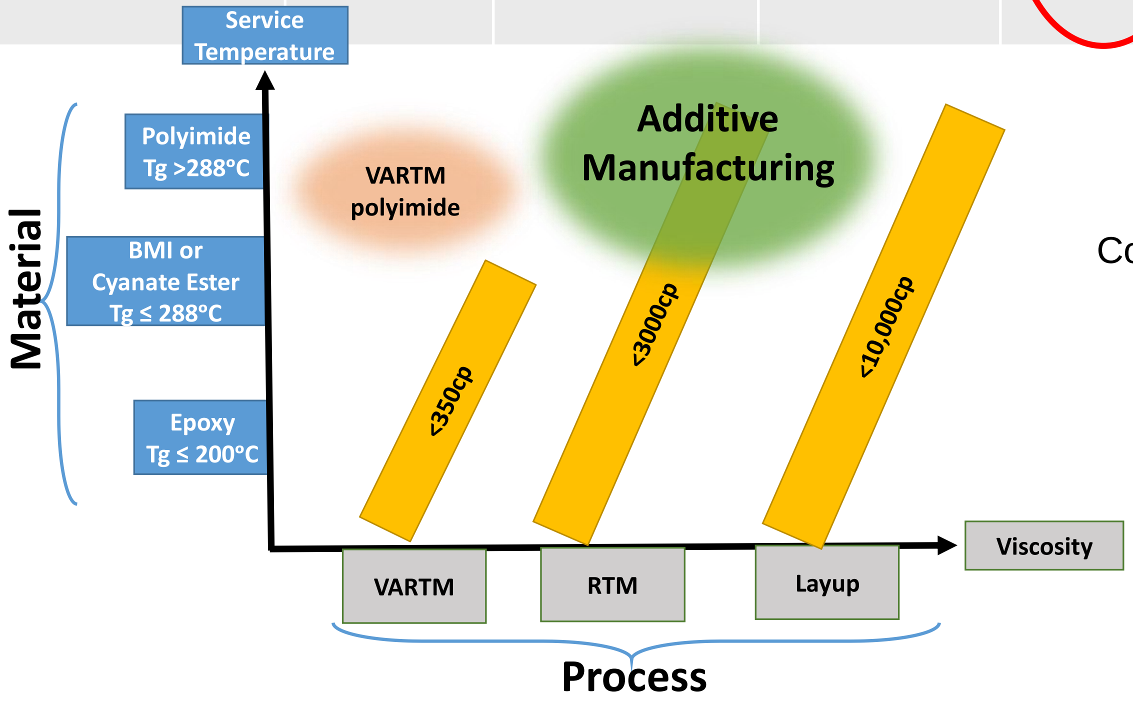


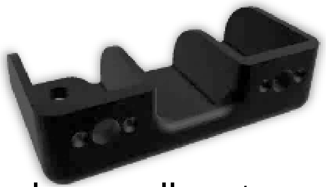
AuNP/graphene filled vitrimer is efficient for photo-thermal healing.
Instantaneous

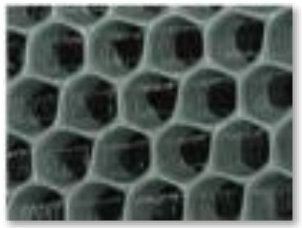
Hubbard et al., *ACS Appl. Poly. Mater.* 2022, 4, 4254–4263

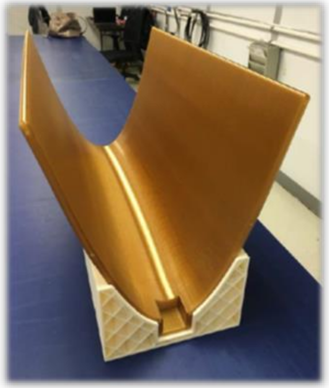
Additive Manufacturing of PMCs

Parameter/ Weight (0-1)	Source/ Origin	Least Acceptable Target	Best Projected Target	Expected		Current			Planned or How Demo'd
				Values	Basis	Values (2015 TP)	Values (2019)	Basis	
Complex Structures Weight=1	**Tech Pull OEMs Tech Push AF**	**>250C 140 MPa tensile strength 10GPa tensile modulus**	**>320C 700 MPa strength 70GPa modulus**	**300C, 175MPa strength; 17.5GPa modulus**	**DSC, DMA, tensile tests**	**300C ~110MPa strength; ~10GPa modulus**	**330C ~170MPa strength; ~12GPa modulus**	**DSC, DMA, tensile tests**	**Bracket, fixture, avionics bay, wing**




Complex small parts

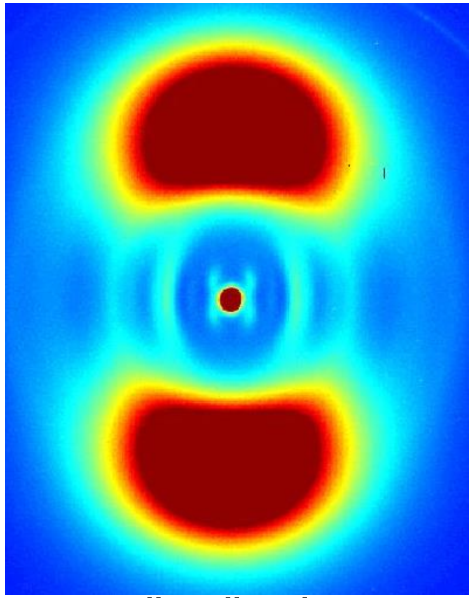

Thin-walled core


Composite tooling

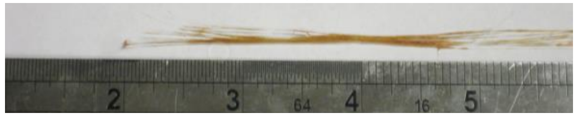
AM of High Temperature Polyimides

- Short-range, fluid-like positional correlations
- Four-spot pattern cybotactic clustering in nematic phase:
    - Short-range smectic C-like ordering (tilted layering) in the nematic phase
    - Characteristic of bent-cored LC molecules

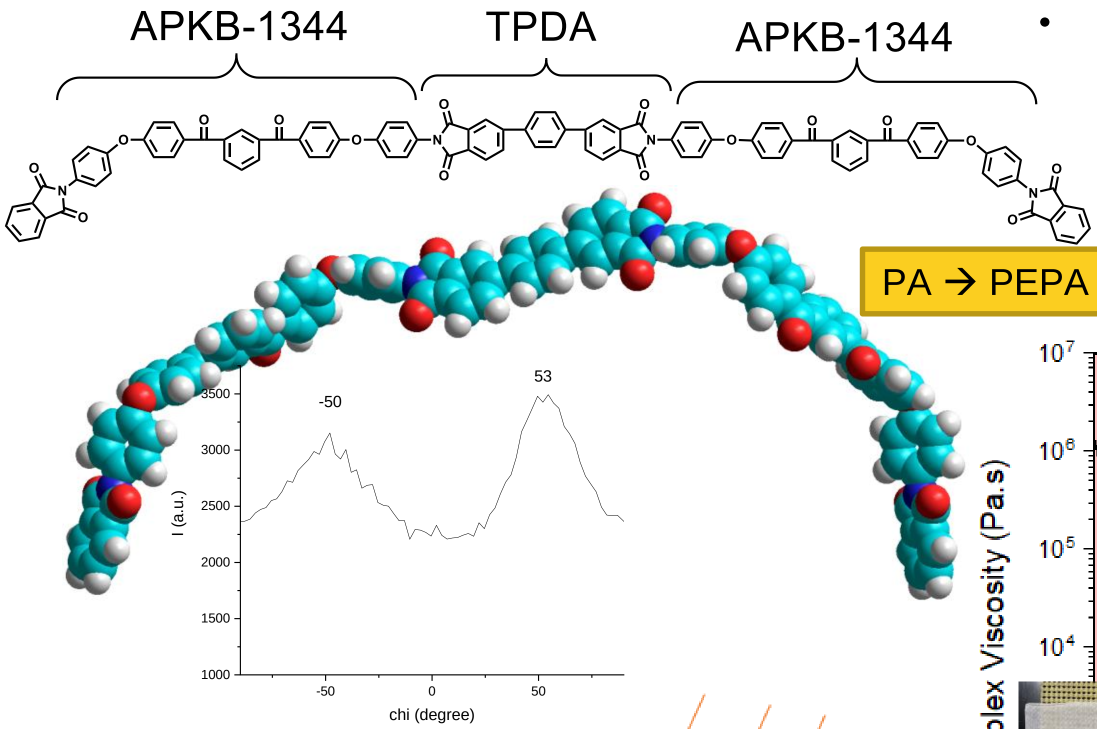
XRD



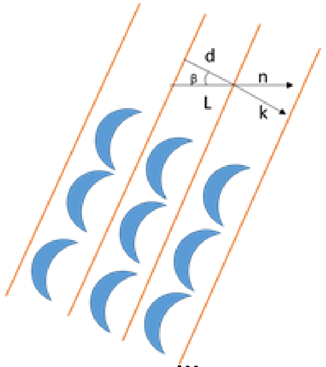
Fiber direction



pulled from Isotropic phase (~340°C) and quenched to RT. WXAS at RT.

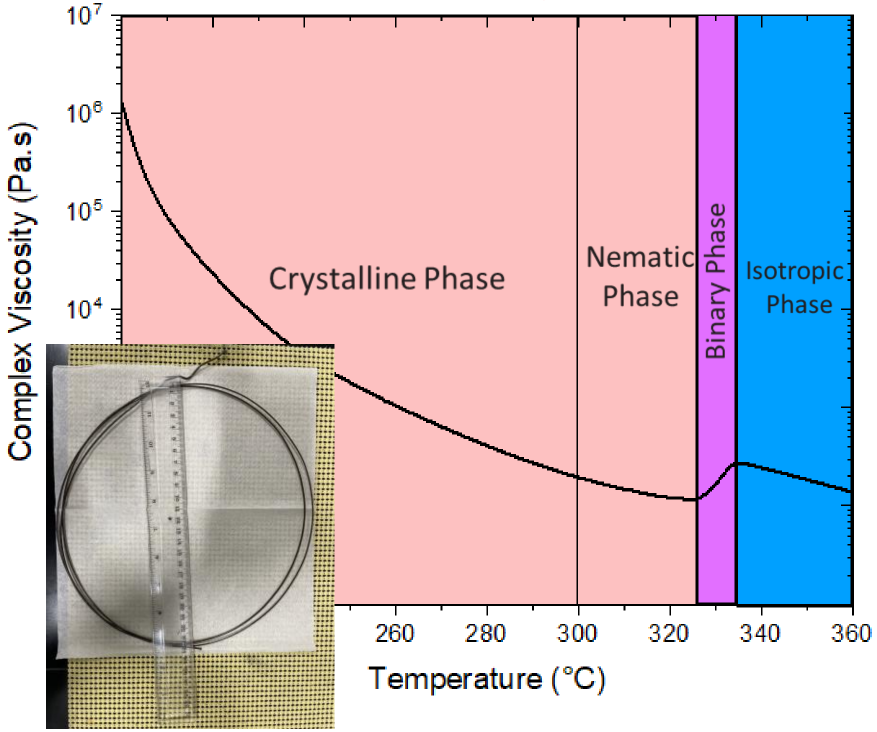


PA → PEPA



Banana-like

Rheology



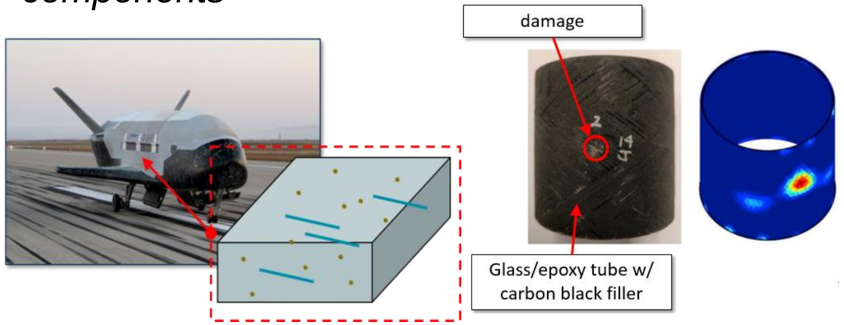
Loon-Seng Tan, Zhenning Yu (RXAS)
Bingqian Zheng, Hilmar Koerner
5 Patents

Roneisha Haney

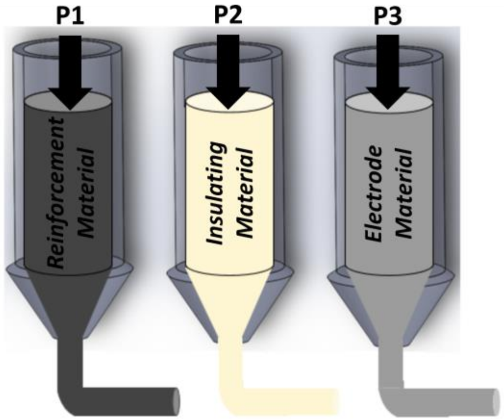
Additive Manufacturing of PMCs

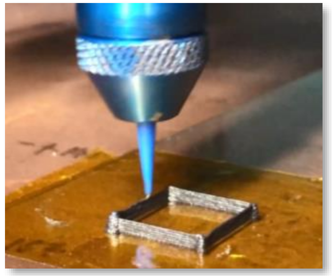
Additive manufacturing of composite parts with self-sensing functionality

-Utilization of structural health monitoring techniques to reveal damage in of additively manufactured components



Damage mapping of a CFRP Thomas et al., 2019

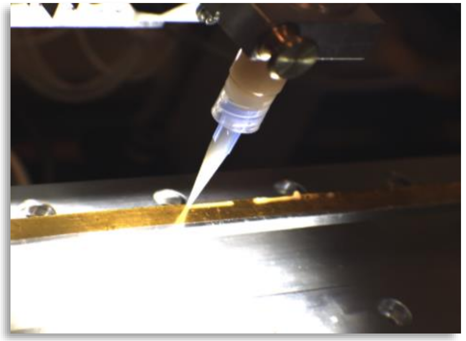




Direct ink write of a conductive PMC
Haney et al., 2020

Structure-function-processing relationships in thermosetting resin composites

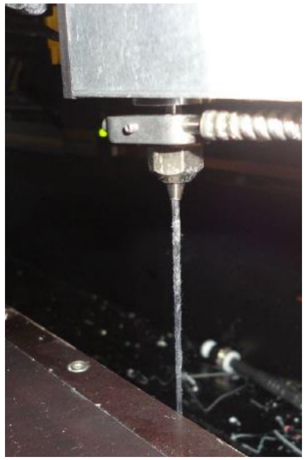
-X-ray photon correlation spectroscopy (XPCS) as a tool to develop design rules for novel, particulate-filled thermosetting resins



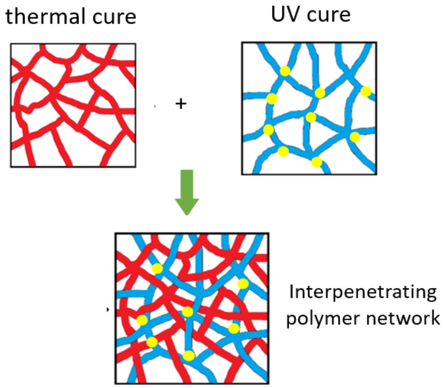
Use of XPCS to monitor the structure and dynamics of a highly filled cellulose nanocrystal thermoset composite during processing

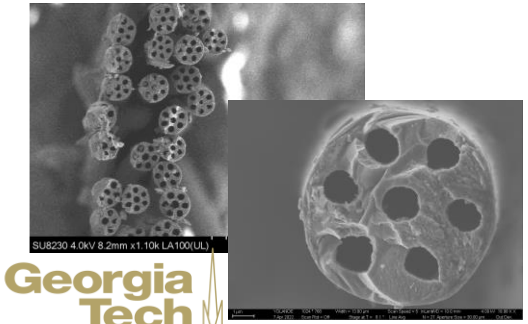
3D Printing of high performance, continuous fiber PMCs

-Development of novel resin blends to produce continuous fiber reinforced, high performance composite structures



Continuous fiber 3D-printing



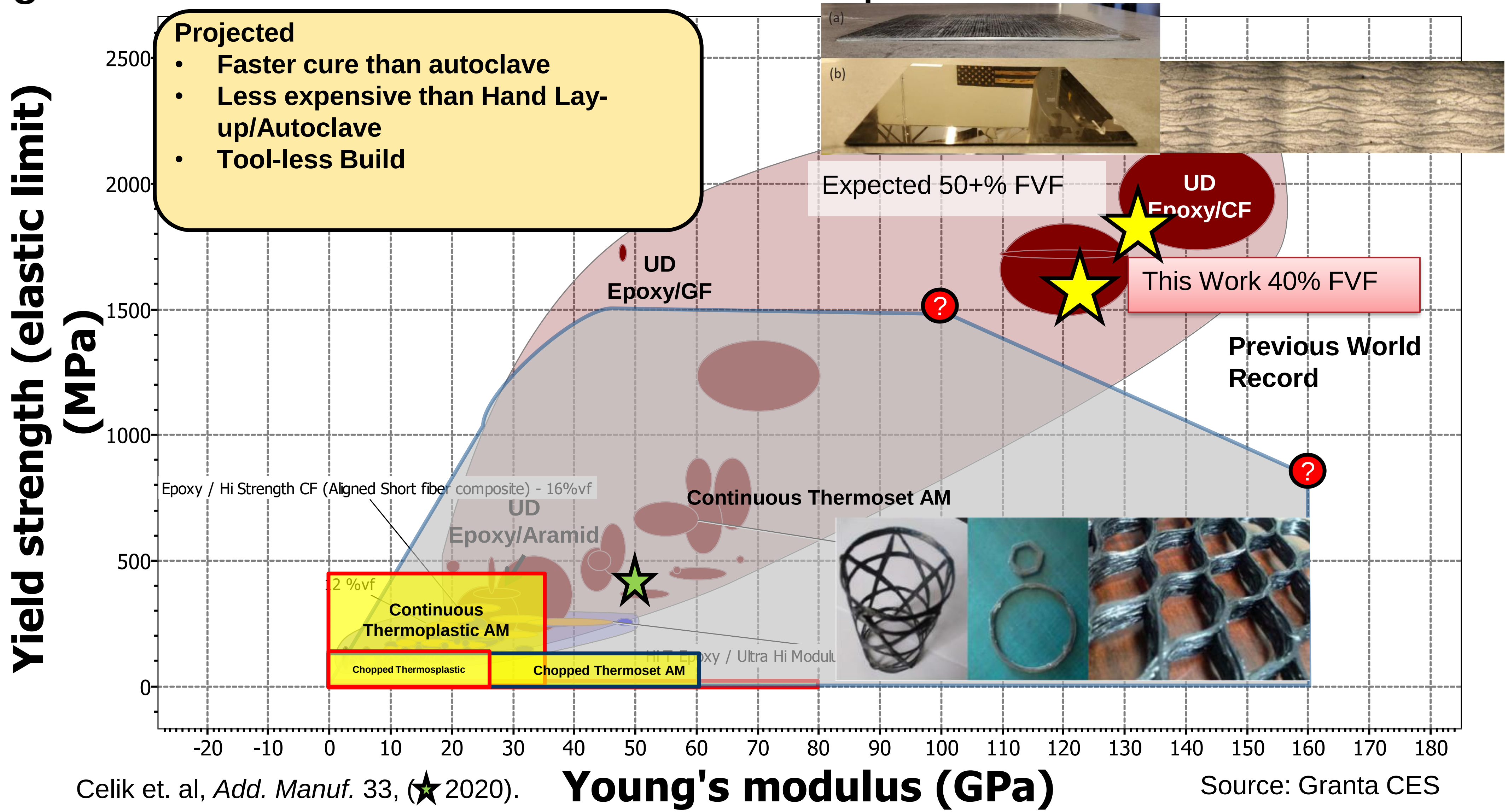


Georgia Tech

Dennis Butcher

Continuous Composites

Large Scale AM of Continuous CF Composites



Celik et. al, *Add. Manuf.* 33, (★ 2020). Source: Granta CES

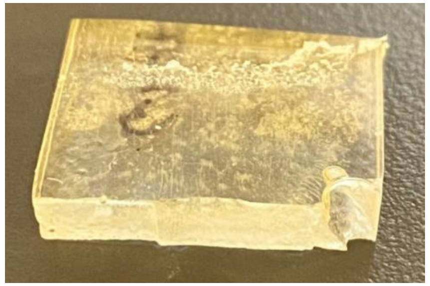
Low Cost AM Resins: Photoinitiated Snap-curing Acrylate

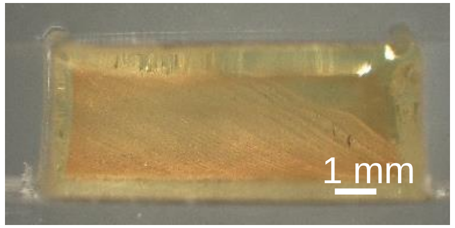
SARTOMER ARKEMA GROUP

Matrix Properties

Test	Strength (MPa)	Elongation @ Break (%)	Modulus of Elasticity (GPa)	Toughness (J)
Tension	36.6 ± 4.0	1.13 ± 0.10	3.71 ± 0.49	0.07 ± 0.03
Flexure	53 ± 3	1.81 ± 0.13	3.01 ± 0.29	0.13 ± 0.02

Test	Mode	G' @ 25°C (MPa)	G" peak temp (°C)	Tan δ peak (°C)
DMA	cantilever	2500	155	237



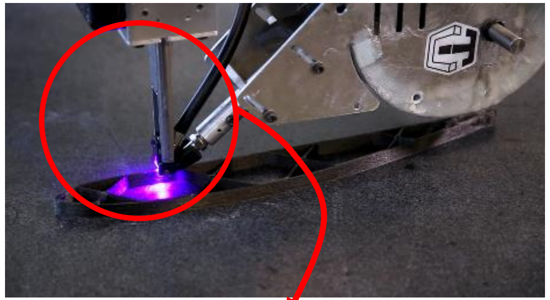


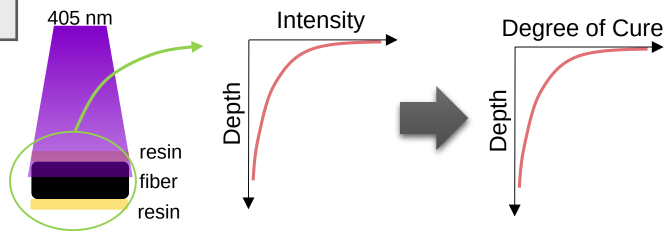
Moisture Uptake	
2 hr	0.02%
24 hr	0.30%
7 day	0.93%

Fracture Toughness

K_Q (MPa √m)	0.39 ± 0.01

Cure modeling

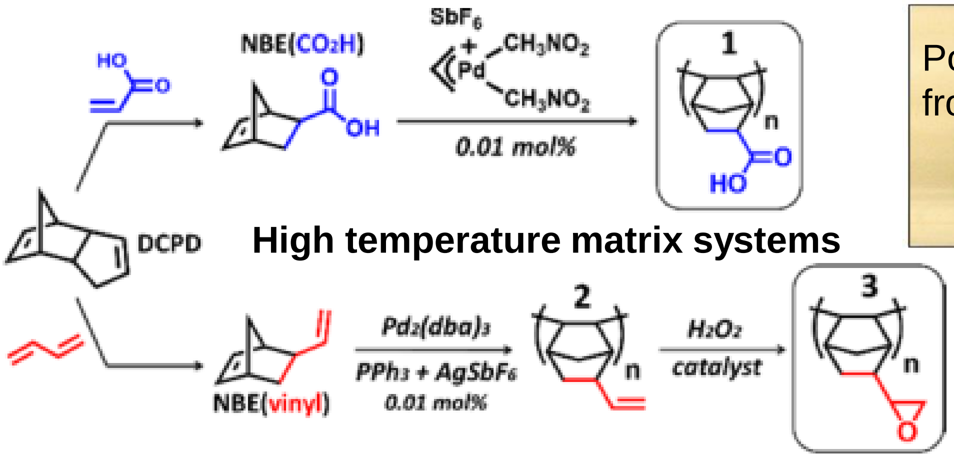


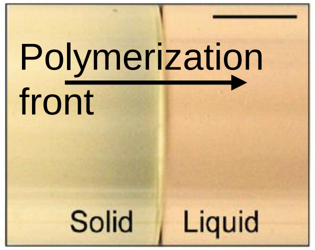


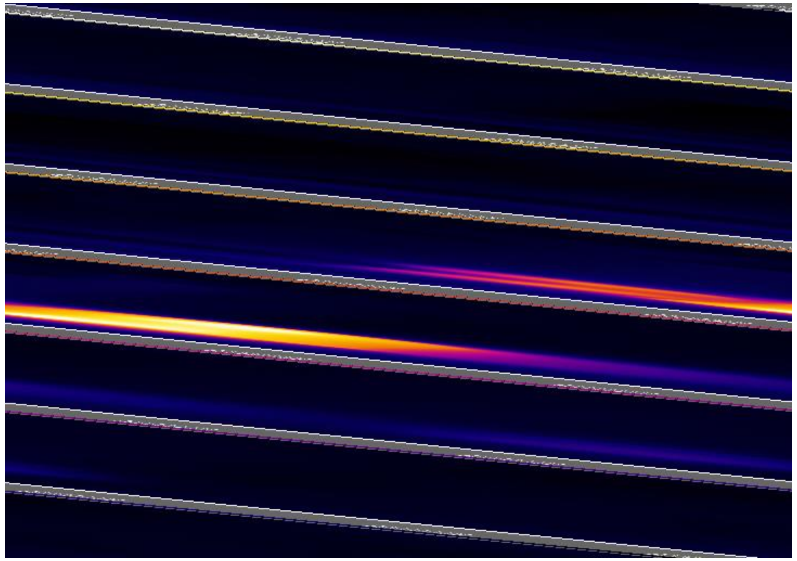
- Light attenuation by carbon fiber
- Degree of cure as f(UV dosage)
- Extent of cure through fiber tow

Novel resins systems – Frontal polymerization

- Requires no post-cure → faster & cheaper manufacturing
- Current resins are low temperature
- *Objectives*: investigate chemistries for higher Tg, additives to control front and increase toughness

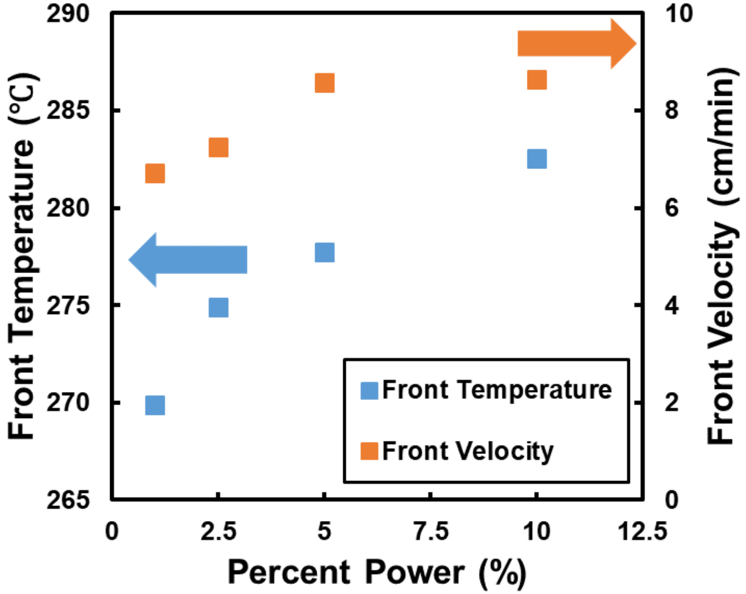






1% Power – Hyrel 405 nm Pen

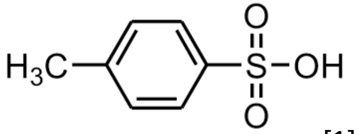
EPON 826 with iodonium containing photoacid generator (0.5 mol%) and thermal initiator (TPED, 1 mol%). Full conversion with Tg of 136°C.



C/C Composites via AM

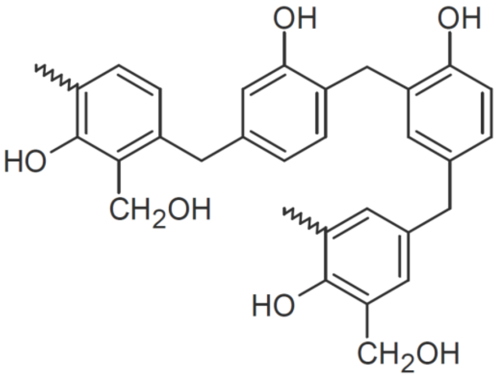
Resole Phenolic Resin and Catalyst


[1]



[1]

Resole



[1]

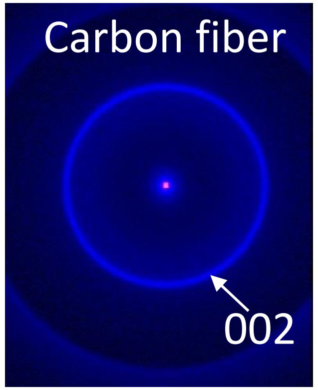
Filler/Rheology Modifier

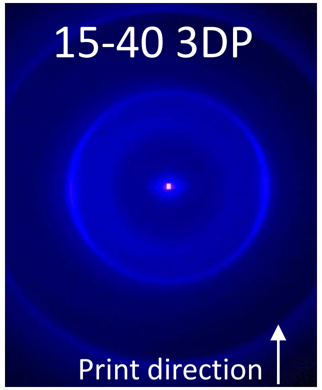

[1]

Carbon black: LD50 0.765 μm

High shear mixing under vacuum

Reinforcement






[2]

DIALEAD^{TM} Milled Pitch carbon fiber: 10μm diameter x 50μm

Composition

Carbon black:

15 wt% (~8vol%)

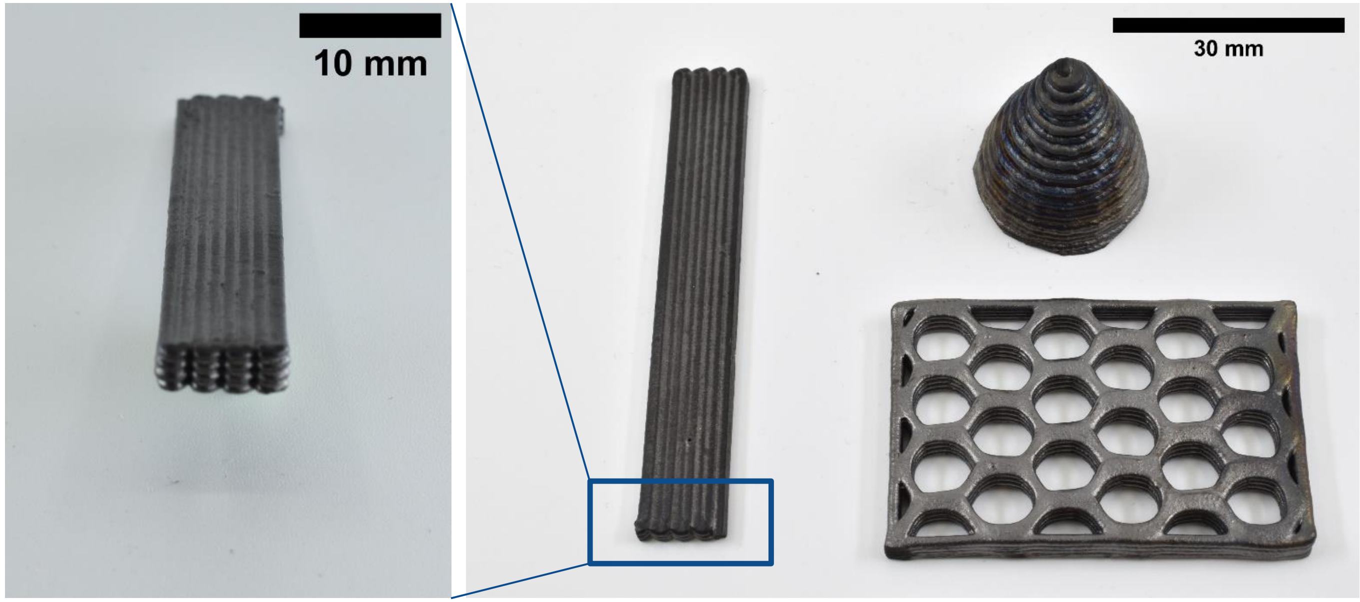
Carbon fiber:

20-40 wt% (10-20 vol%)

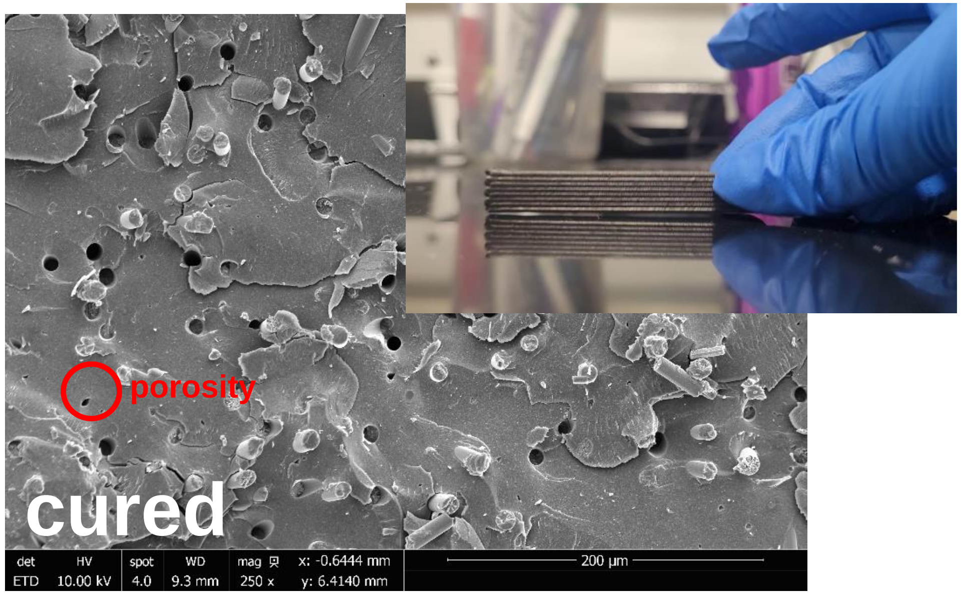
[1] Google images.

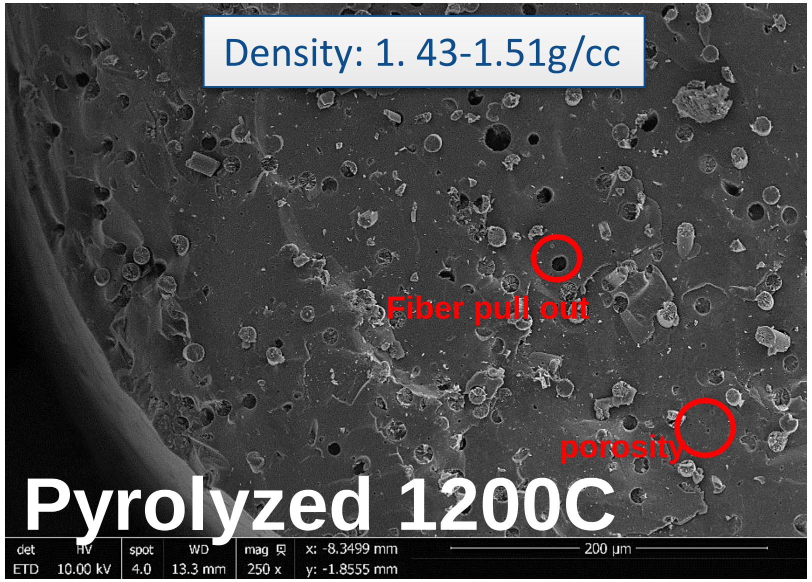
[2] https://www.cf-composites.toray/products/carbon_fiber/milled.html

C/C Composites via AM



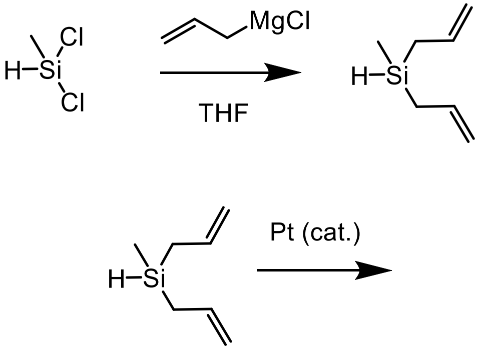
Composition	Shrinkage in height (%)	Shrinkage in width (%)	Shrinkage in length (%)	Conversion Furnace 1200° (%)
15-0-30	-	-	-	-
15-0-35	9.38 ± 0.51	9.74 ± 0.37	2.90 ± 0.20	81.22 ± 0.3
15-0-40	10.56 ± 1.87	8.68 ± 2.1	2.33 ± 0.43	82.65 ± 0.88

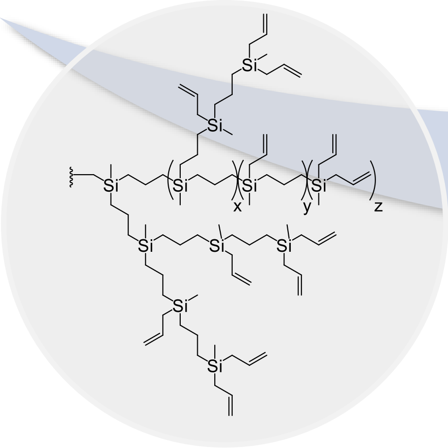




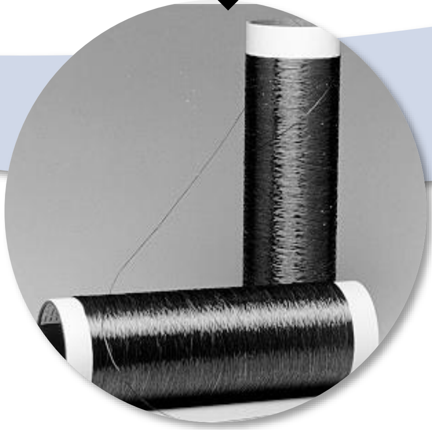
Preceramic Polymers from Organics to High-Temperature Ceramics

Polymer Synthesis

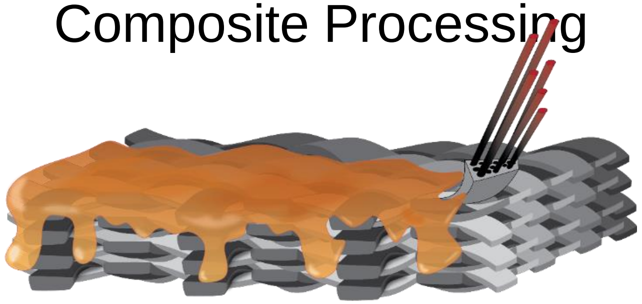




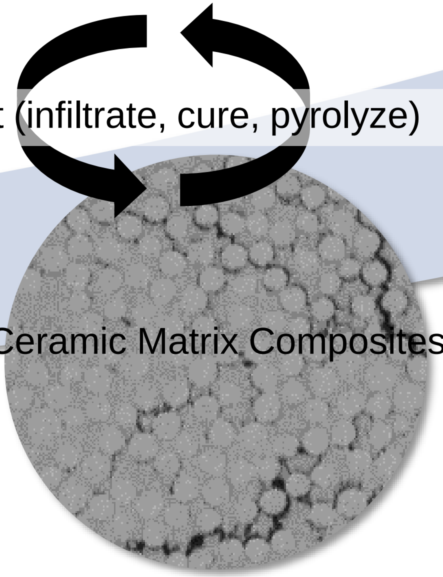
SiC Fiber Spinning



Composite Processing

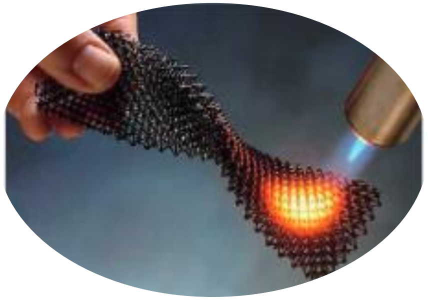


Infiltration/Pyrolysis



Application

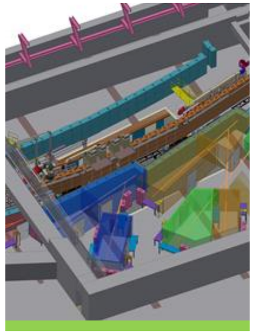
Emerging: Ceramic AM



Real-time Measurement Tools

Hilmar Koerner

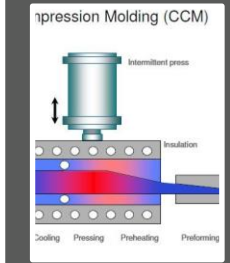
- Robust and routine measurement tools that enable faster qual/cert, automation, standardization and processing



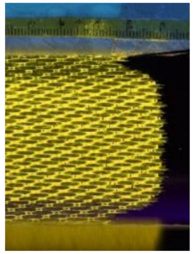
CHESS
CORNELL HIGH ENERGY SYNCHROTRON SOURCE

Material Solutions Network - **FMB**

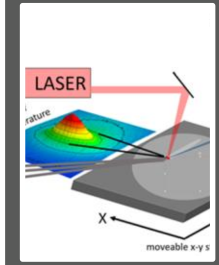
- Real-time composite processing, rapid, automated phase diagram mapping, phase contrast imaging, SAXS/WAXS micro-beam imaging, AI-driven materials discovery



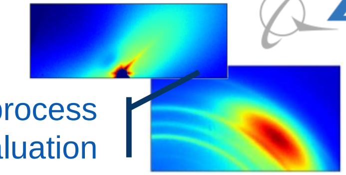
Direct DoD



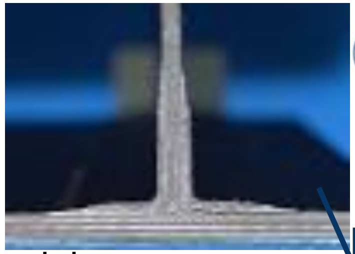
Long-term DoD



Other OEM/academic

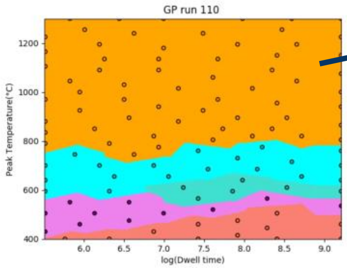


Real-time process evaluation



π-joint

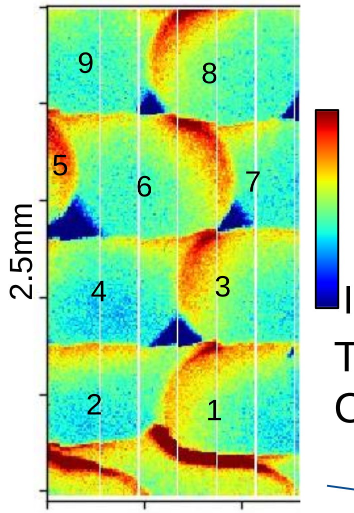
Residual stress and defect mapping during processing and performance



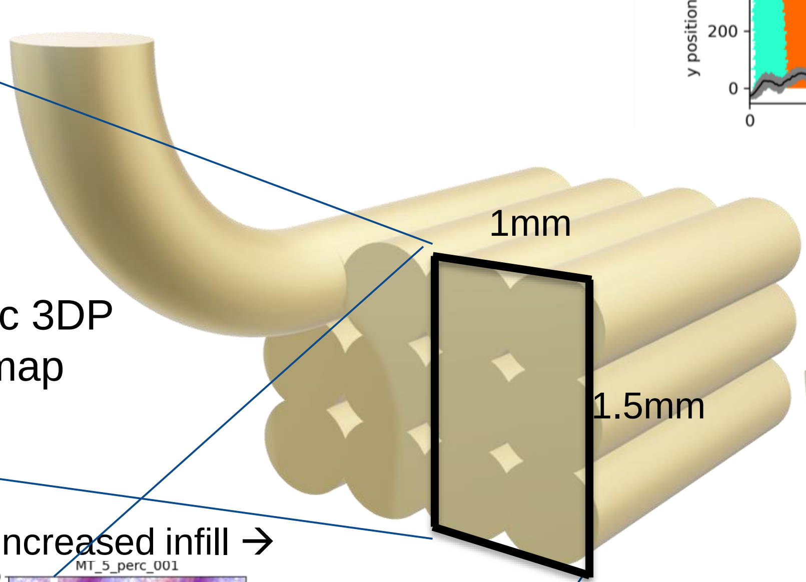
'active learning' system based on XRD data of oxide thin films.

Operando Measurements

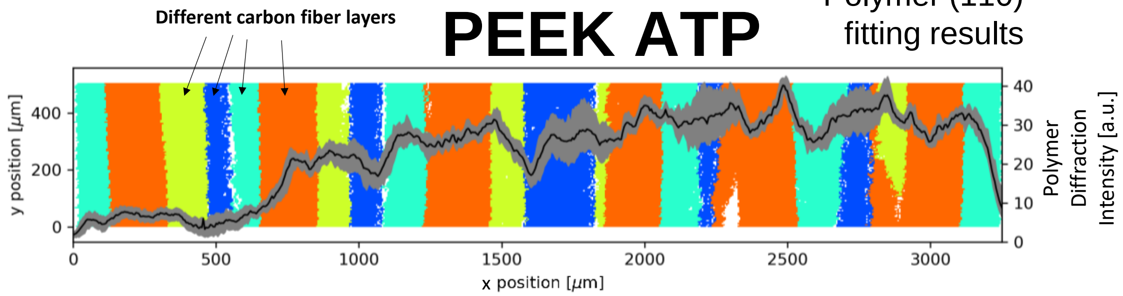
PEEK FFF



Thermoplastic 3DP
Crystallinity map



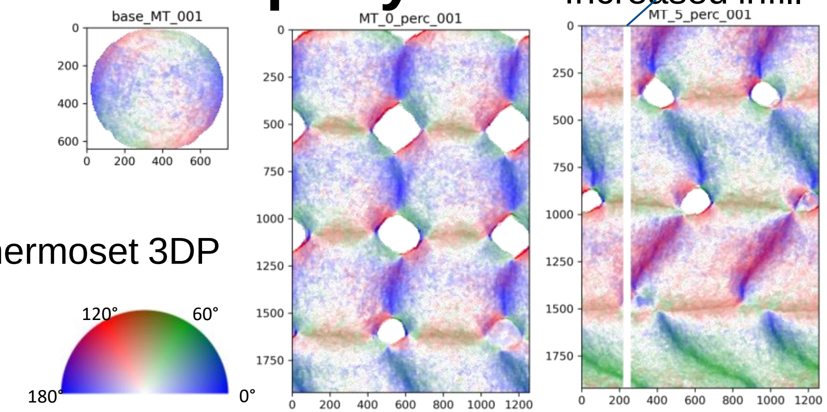
PEEK ATP



All automated fly-scanning
Ex-situ and Operando
A few hours → 2d property maps
Couple to modeling and performance

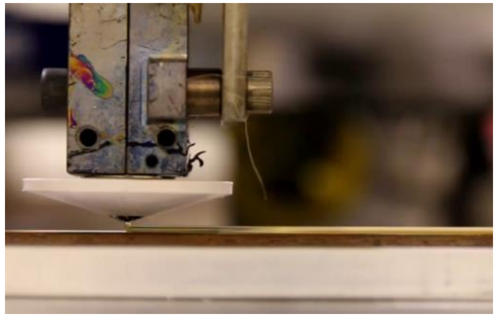
Epoxy DIW

Increased infill →



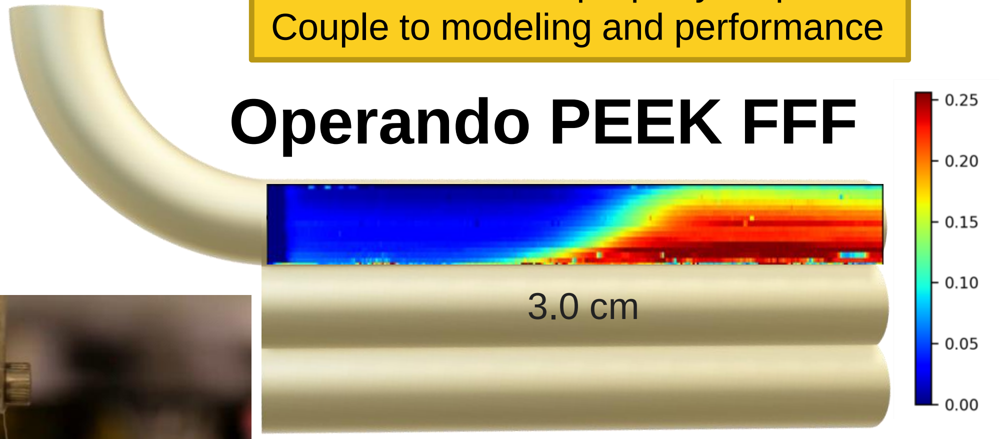
Thermoset 3DP

Colormap of nanoparticle orientation



Stratasys Fortus printhead

Operando PEEK FFF



Real-time flyscanning
Crystallinity index

BOEING

Enabling Capabilities Faster