DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Circular Economy of Composites enabled by *TUFF* Technology

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Plastics Deconstruction and Redesign

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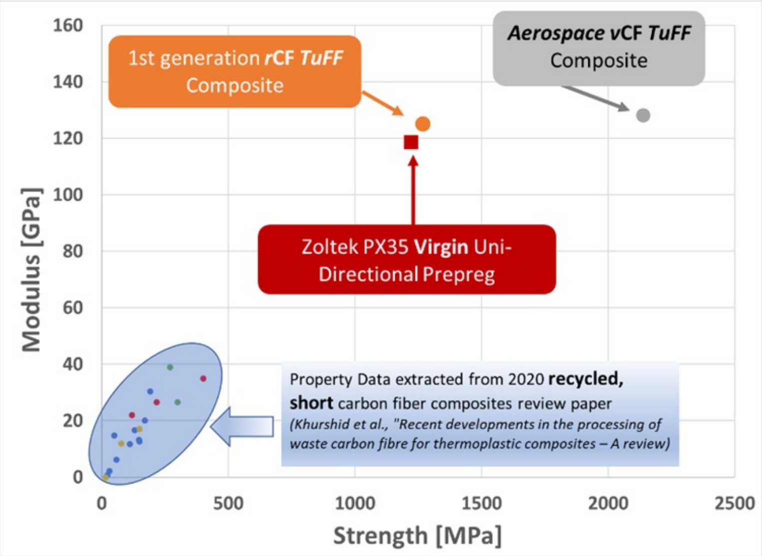
Technical Challenges for Composite Recycling

- Potential Waste streams
  - Waste precursors (Fiber, Prepreg)
  - End of Life composites
  - Fibers are discontinuous
- Methods
  - Solvolysis (Solvent based)
  - Pyrolysis (Thermal decomposition)
  - Typically destroys polymer



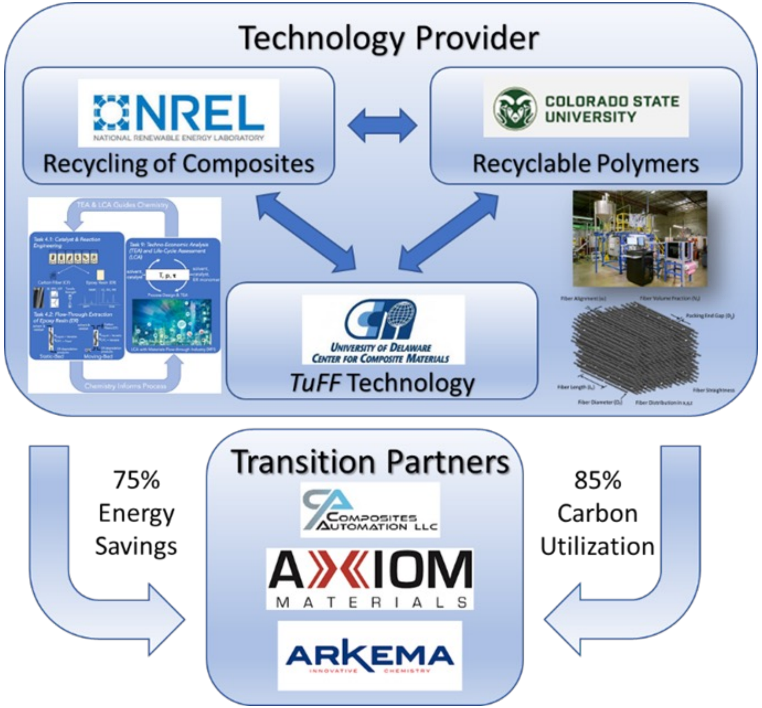
➢ Recycled Carbon Fiber Composites (CFC) typically have a low degree of fiber orientation and Fiber volume Fraction(FvF)

➢ This restricts their use to low value applications, i.e.. Down-Cycling

Main Program Objectives

- **Goal**
  - Demonstrate the viability of recycling Carbon Fiber Composites (CFC) through polymer/fiber separation via thermolysis and/or catalyst-controlled recovery of carbon fiber and monomer, followed by reuse of the fiber material in the *TuFF* process creating high-performance CFC with mechanical properties comparable to continuous CFC.
  - Demonstrate for the first time that a Green Economy for composites is possible with ***multiple*** recycling iterations, material recovery and near full property translation.
- **Benefits**
  - Reclamation of CFC precursors from multiple commercial waste streams
  - Reduce overall emission and green house gases
  - Recycled composite material lower cost as well meeting or exceeding targets of 70% energy savings and 85% carbon utilization from waste stream composites.

Technical Partners



- *Separate the CFC polymer and fiber content with catalyst and fiber recovery (NREL lead)*
- *Demonstrate a new class of recyclable by-design polymers (CSU lead)*
- *Process the recycled carbon fiber content into high-performance CFCs (UD-CCM lead)*

- *Transition partners*
  - *Axiom Materials: Pre-Preg manufacture*
  - *Composites Automation: Composite fabrication*
  - *Arkema: Resin production*
- *Monthly technical meetings are held with DoE and Partners to share information and address challenges*

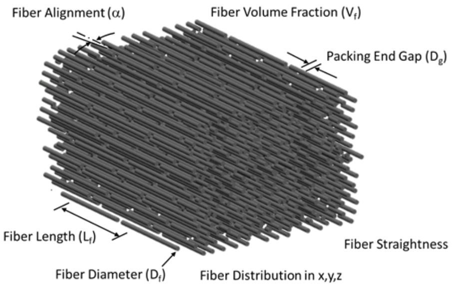
Enabling Technologies

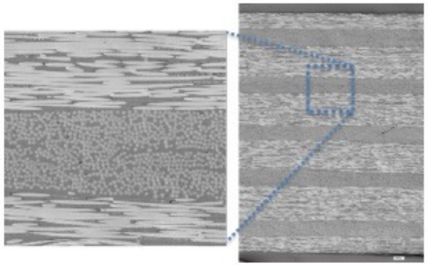
- **Tailored Universal Feedstock for Forming (TuFF) process for short fiber alignment (CA, UD-CCM)**
  - Enables fabrication of short fiber composites with properties equivalent to continuous fiber composites
  - Batch process can be used to functionalize recycled discontinuous fibers for resin compatibilization
- **Catalytic depolymerization of epoxy systems (NREL)**
  - Enables reclamation of CF and monomer from composite waste streams and end of life parts
- **Recyclable Resins (CSU, Arkema)**
  - Elium Resin (Arkema)
    - Commercially available, enables reclamation of fiber and monomer source
  - Resin chemistries utilizing bio-derived monomer sources (CSU)
    - Reduction of embodied energy , optimization of de-polymerization temperature

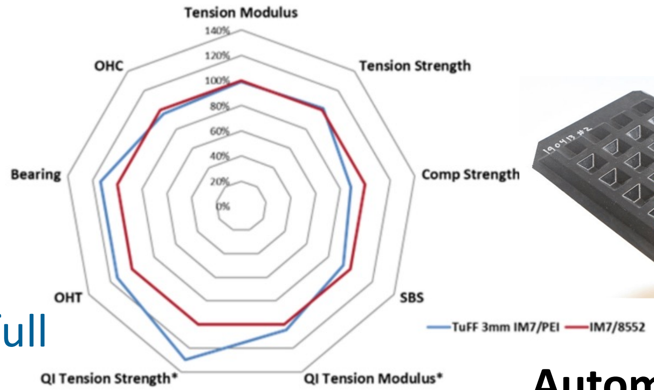
What is *TuFF*?

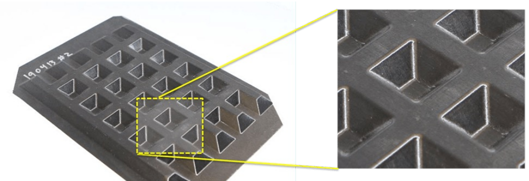
TuFF is a feedstock with near ideal aligned short fiber microstructure in tape, sheet and blank formats:

- Low cost short fiber (fiber and resin agnostic,
  hybrids) with filament level alignment control: > 95% (±5º)
- Aerospace quality and performance
- Automotive-like forming at high throughputs (~100k/yr)
- Enables recycling of composites with full property translation





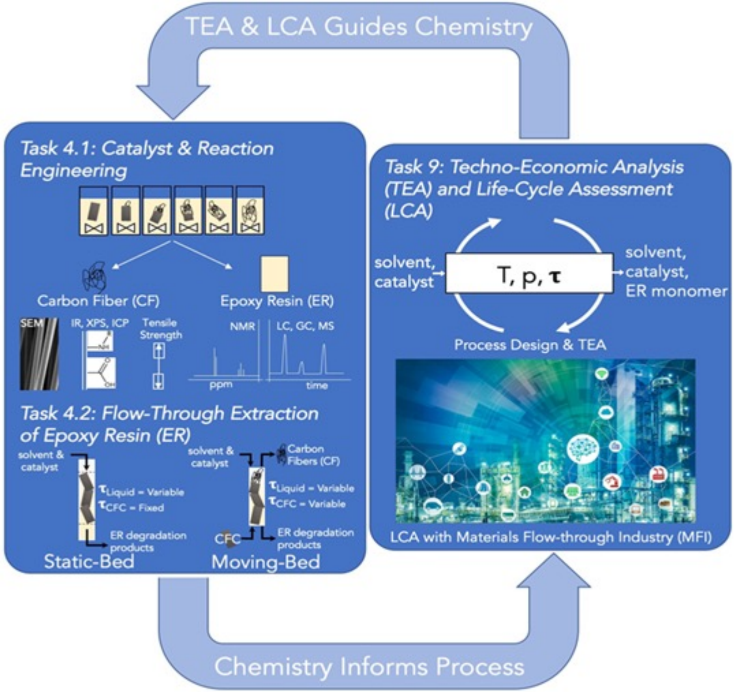




54% Fiber Volume Fraction maintained in CFRP

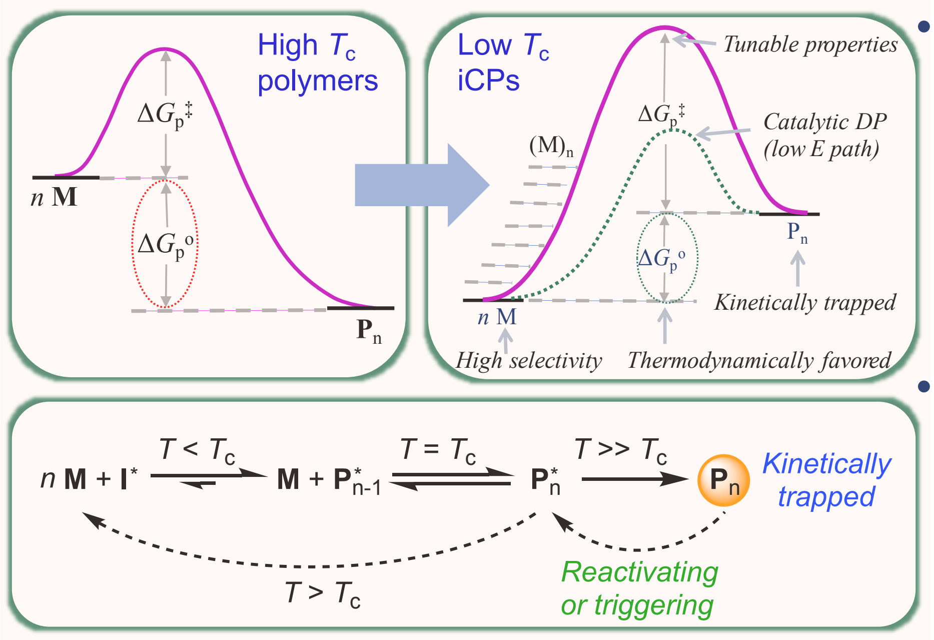
Automotive Rate Forming

Recycling of Epoxy-based CFC (NREL)



- **Use of catalyst to break down epoxy-based matrices**
  - Lewis Acid based Catalysis
  - Oxidation Catalysts
  - Base Salt Catalysis
- **Addresses Prepreg Waste and End of life Composite Recycling**
- **TEA and LCA tools will be used to drive the recycling of Epoxy-based CFC effort**

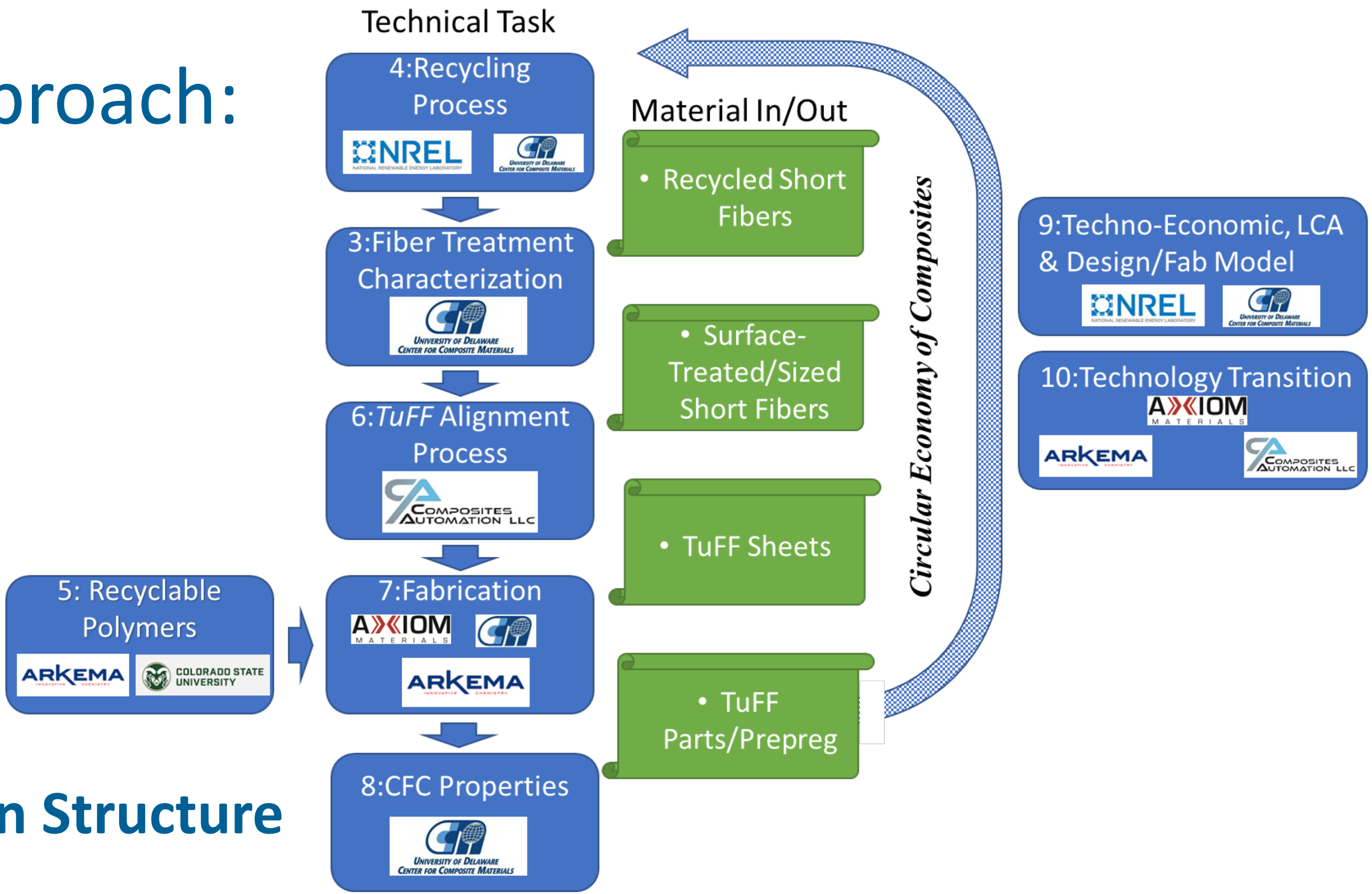
Recyclable-by-design (RBD) circular polymers



Broadbelt, Beckham, Chen, *et al.* *Chem* **2021**

- Three key challenges in the design of circular polymers —*Energy Input, Selectivity, and Recyclability/Performance tradeoffs* — can be effectively addressed by kinetically trapped, low ceiling temperature (T_c) RBD polymers
- Kinetically trapped polymers can be designed to exhibit not only closed-loop lifecycles but also thermal and mechanical properties rivaling or even exceeding commodity plastics.

Program Approach:



Work Breakdown Structure

Program Schedule

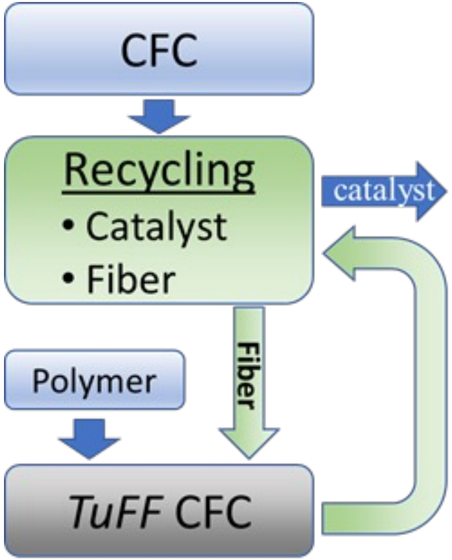
Budget Period	*BP1*	*BP2+6 month NCE*							*BP3*						Lead Performer	Support Performer
Task	**Year 01**				**Year 02**				**Year 03**				**Year 4**			
	Q1	**Q2**	**Q3**	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**	**Q1**	**Q2**	**Q3**	**Q4**	**Q1**	**Q2**		
1. Verification			1					2						3	UD	All
2. Material and Recycling Process Survey				1											UD	NREL
3. Fiber Material Charaterization and Surface Treatment															UD	All
Baseline Virgin Materials			1			1										
Surface Treatment of Recycled Fiber Stock									1			2				
Recycled Materials																
4. Recycling of Epoxy-based CFC															NREL	UD
Catalyst and Reaction Engineering						1			2							
Process Engineering for Batch Reactor Development										1				2		
5. Recyclable-by-design acrylic polymers															CSU	Arkema
Chemically recyclable vinyl ester acrylic plastics						1		2								
Renewable circular vinyl lactone acrylic bioplastics												1		2		
6. TuFF Processing of Recycled Fiber Materials															CA	UD
Effect of Length Distribution on CFC Properties						1										
Effect of Fiber-Resin Adhesion on CFC Properties							1									
Dispersion Challenges of Recycled Fiber Feedstock						1										
TuFF Dry Sheet Fabrication						1										
7. Prepreg and Part Fabrication															UD	Axiom Arkema
Prepreg Fab								1								
Coupon Fab																
8. Mechanical Property Evaluation						1				2					UD	CA
9. Model Development (Techno-Economic, LCA and Process/Part Design)						1								2	NREL	All
10. Technology Transition											1			2	TBD	All

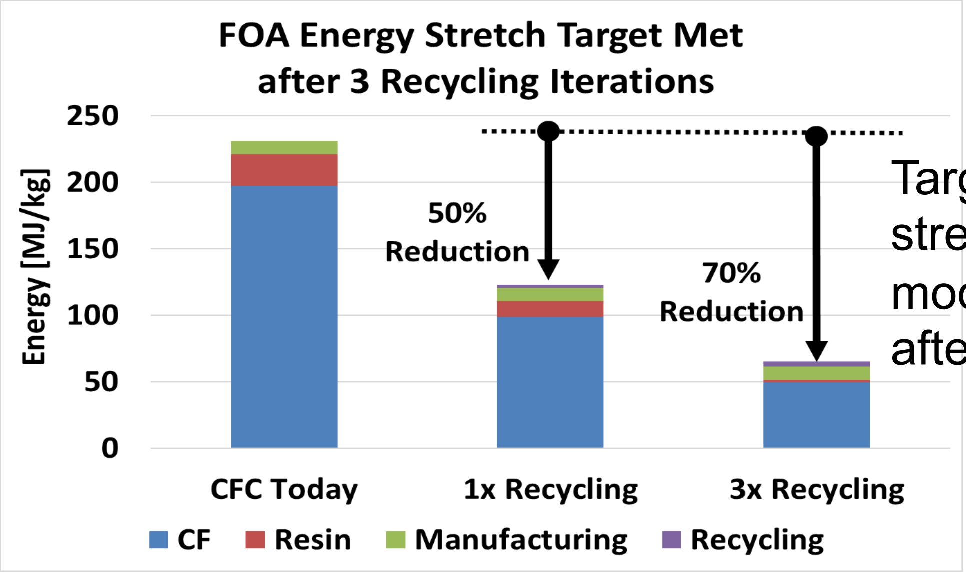
Go/No-Go Milestone

- Program duration: 07/01/2021-06/30/2024
- Total Award ~$2.55 M over 3 years
  - $751,656 in cost share
- Official start delayed due to delay in:
  - Notification of receipt of award, time required to get sub-awards finalized, time needed to complete verification- *Granted 6 month NCE for BP2 Dec, 2022*
  - SOPO revision in review to accommodate delay

UNIVERSITY OF DELAWARE CENTER FOR COMPOSITE MATERIALS

Motivation for Go/No Go Milestones





Target ~>90% strength and modulus retention after each iteration

Our CFC recycling approach allows multiple iterations with fiber and catalyst recovery (left), 50% energy saving after first recycling and ~70% after 3 recycling steps

Go/NoGo

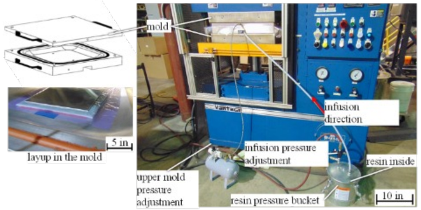
- BP2 Go/NoGo
  1. Demonstration of Single Step Recycling with 95% Property retention-CCM
  2. Provide recovered fiber material for TuFF sheet production (~500gr) in support of Task 7 and 8- NREL
     - Moved to BP3 due to delay in contracting for NREL
  3. Exploratory synthesis of PMEA and PMVL to achieve the polymer with adequate molecular weights and evaluation of its chemical recyclability to achieve recovery of the monomer with >80 % yield and purity for repolymerization. 10 gram quantities of resin to be provided for evaluation of fiber/resin interface properties in Task 3 –CSU
- BP3 Final- Demonstration of 3 Recycling Step Iterations with 90% Property Retention

Progress and Outcomes

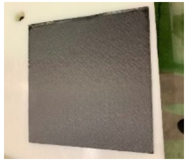
BP2 Go/No Go 1(UD-CCM): On Schedule at 13 months

- Demonstration of Single Step Recycling with 95% Property retention-CCM
  - To date for Elium resin/T700 composite we have shown for one iteration for 27% FvF 100% translation of modulus, 60% translation of tensile strength (compared to starting TuFF part with virgin material)
  - ~50% FvF Elium/T700 TuFF composites have been fabricated and under evaluation
  - Composite fabrication with NREL epoxy recycled fibers delayed until BP3 due to delay in NREL program start

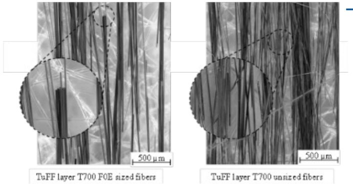
Recycled TuFF Process

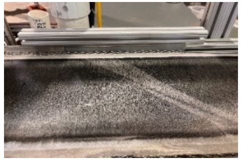


VARTM/High Pressure Bladder Mold

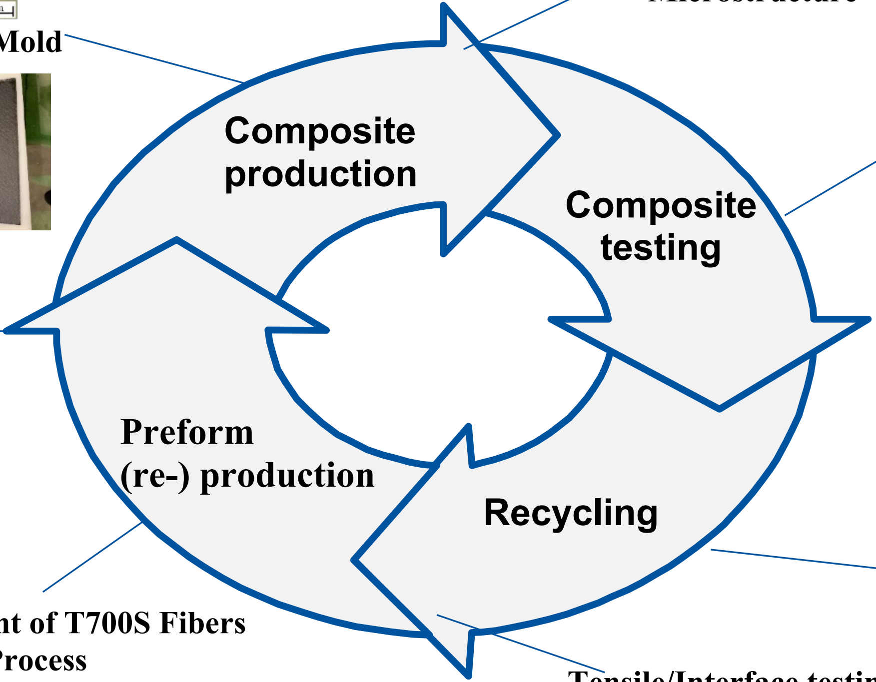


Compaction testing,
Alignment Quality

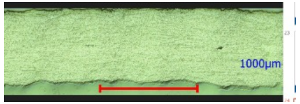




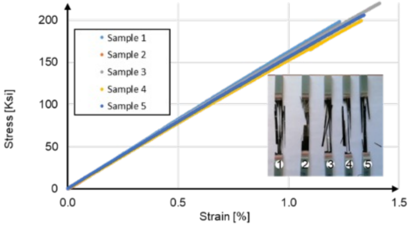
(Re-) Alignment of T700S Fibers
within TuFF-Process



Panel QC(C-scan,
Microstructure



Mechanical Properties

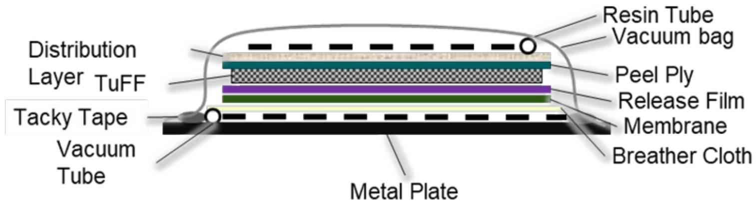


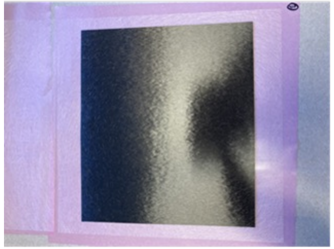
Pyrolysis
Thermalysis
Solvolysis

Tensile/Interface testing,
Dispersion Evaluation

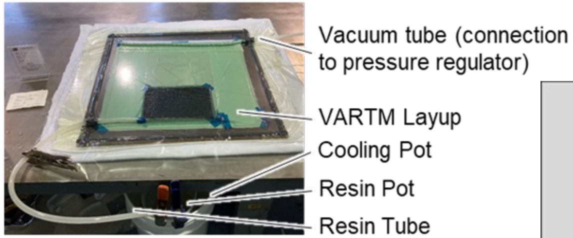
BP2 Go/No Go Milestones: UD-CCM

VARTM Processing Of TuFF/Elium Composite

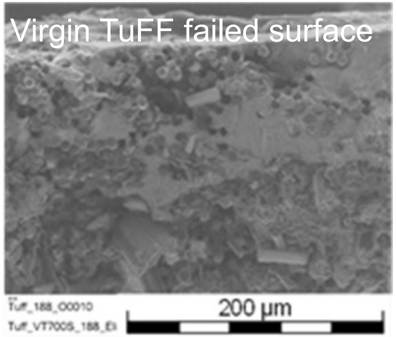


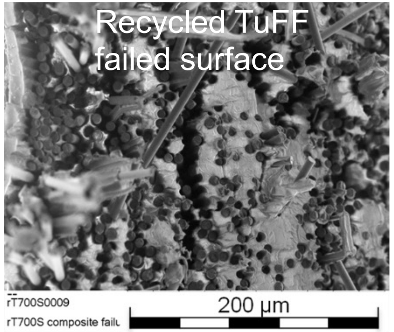


24 layer Dry TuFF Preform

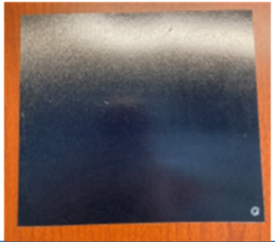


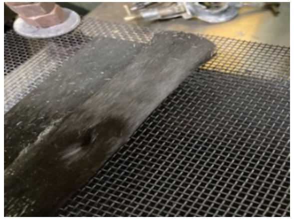
Experimental VARTM Setup

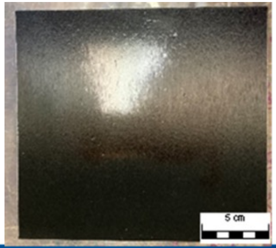




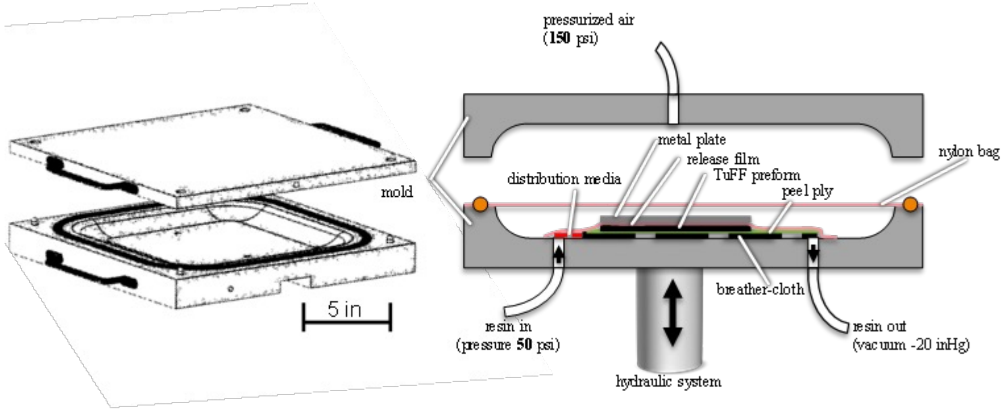
	FVF [%]	ø Tensile Strength [MPa]	ø Modulus of elasticity [GPa]	ø Strain to failure [%]
Virgin T700S Composite	27	814 ± 51	61 ± 3	1.34 ± 0.06
Recycled T700S Composite	24	484 ± 12	61 ± 1	0.93 ± 0.05

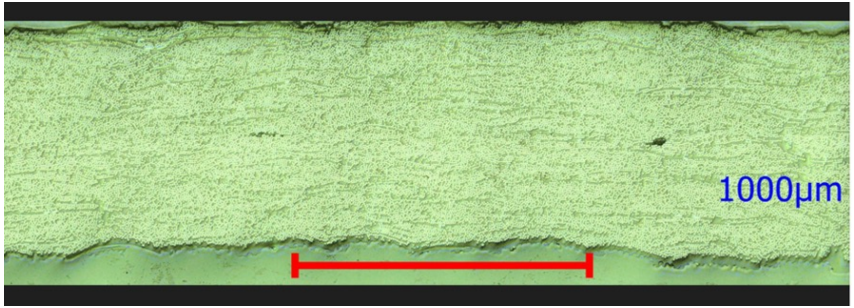






High Pressure Bladder Molding





- ➢ Enables infusion of TuFF preforms while maintaining 100 PSI transverse consolidation pressures
- ➢ Applicable to Epoxy, Elium/acrylic resins

- ➢ Elium/T700 FOE Composite cross section
  - Arkema recommended Sizing
  - 1 mm thick panel with ~55% FvF
  - Initial testing and recycling studies are ongoing

Summary: TuFF Composite Recycling Accomplishments to Date

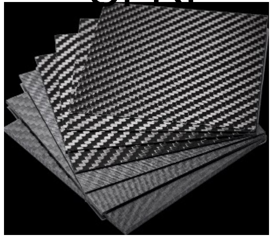
- Establishment of Baseline Epoxy/T700 composite properties
- Initial demonstration of single iteration recycling for VARTM processed Elium/T700 part
  - Identified Depolymerization time and temperature(400°C in N2, 6Hrs)
  - Demonstrated Dispersibility of recycled fiber(required High temperature cleaning step (400°C in air, 20 minutes)
- Measurement of Baseline interfacial shear strength for Elium thermoplastic and T700 with Elium compatible FOE sizing
- Successful fabrication of high fiber volume fraction (~50%) Elium T700 TuFF panels
- First successful fabrication of Epoxy/TuFF prepreg materials using commercial equipment (Axiom)

BP2 Go/No 2 (NREL): On Schedule with adjusted SOPO

- Provide recovered fiber material for TuFF sheet production (~500gr) in support of Task 7 and 8.
    - Estimated minimum required amount of fiber needed to carry out 3 recycling iterations with mechanical testing
    - Original Go/No Go moved to BP3 due to delay in contracts being signed/approved
    - Critical milestone to identify optimal catalyst for epoxy deconstruction has been completed

Goals of Recycling of Epoxy-based CFC (NREL)

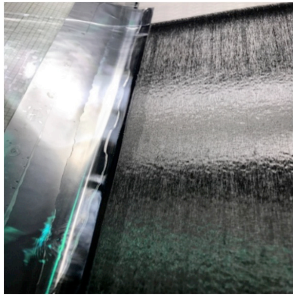
CFRP



Thermal deconstruction

Unaligned fiber tow

Short fiber alignment with Tuff

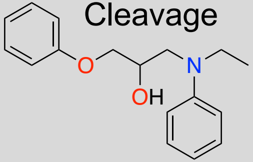


University of Delaware

Incorporate novel polymers

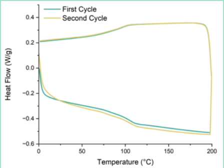
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

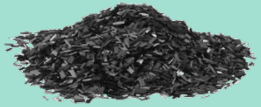
Model Compounds: C-N and C-O Cleavage



Model Thermoplastics

Thermosets and Composites

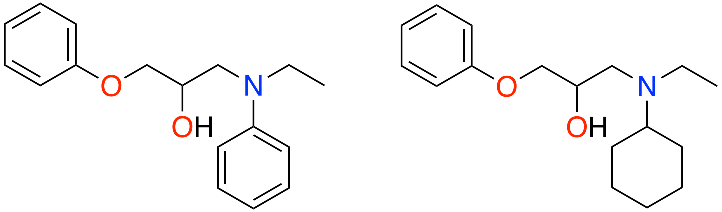




Modified Recycling of Epoxy-based CFC (NREL)

Model compounds:

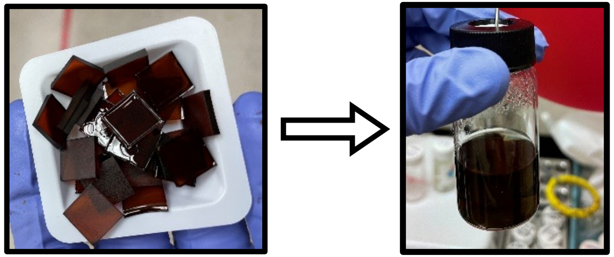
(reflect aromatic and aliphatic amines in real polymers)



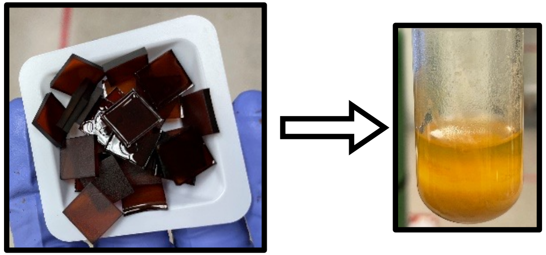
Analytical tools used here: NMR, GC-FID/MS

Takeaway: Bases or reductants preferred instead of oxidants or acids for epoxy resin deconstruction

Oxidation: Polyaniline Generation



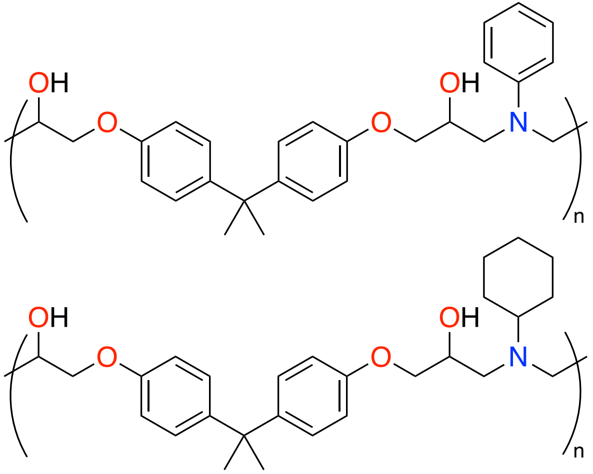
Basic Conditions: Significant Monomer Yields



DiPucchio, *et al.*, *In preparation.* 2023

NREL Recycling Accomplishments with Model Polymers

Sample model polymers:



Up to 56% yield of bisphenol A

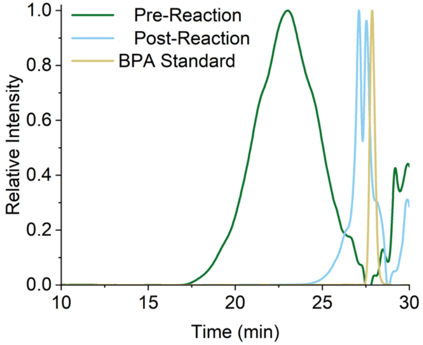
Up to 60% yield of bisphenol A

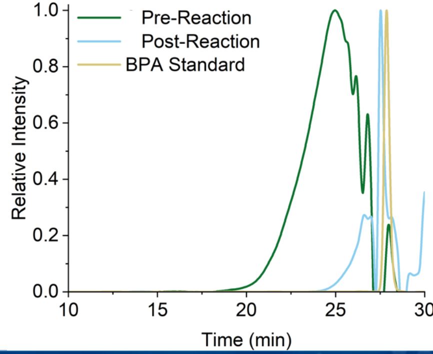
Analytical tools used here: TGA, DSC, GPC, GC-FID, NMR

Takeaway: Model compound work translates to BPA recovery from thermoplastic epoxy resins

DiPucchio, *et al.*, *In preparation.* 2023

GPC Data Before/ After Deconstruction





Takeaway: Polymers are successfully depolymerized, and not simply dissolved during reactions

Summary: NREL Recycling Accomplishments To Date

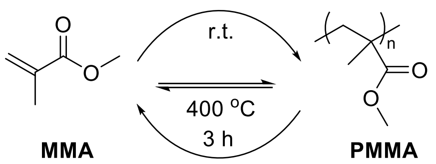
- Synthesis and characterization of model small molecule compounds, thermoplastics, and epoxy thermosets for assessment of deconstruction reactivity
- Development of a GC-FID-based analytical method to assess yields from deconstruction products
- Screened oxidants, Lewis acids, homogeneous/heterogeneous reductants, and bases to compare C-O and C-N cleavage abilities as well as product stabilities
  - Redeveloped proposed deconstruction conditions with model compounds as a result of these findings (up to 88% yield from C-O cleavage products and 47% from C-N cleavage products)
  - Applied basic conditions developed to a selection of thermoplastics and then an example thermoset (up to 65% yield of bisphenol A)
  - Assessed reaction progress via a combination of small molecule and polymer analytical techniques

BP2 Go/No Go 3 (CSU): On Schedule at 13 months

- Exploratory synthesis of PMEA to achieve the polymer with adequate molecular weights and evaluation of its chemical recyclability to achieve recovery of the monomer with >80 % yield and purity for repolymerization. 10 gram quantities of resin to be provided for evaluation of fiber/resin interface properties in Task 3.
    - Evaluated 4 acrylic monomers(including MEA) and down selected to MVL
    - 10 grams of PMVL and 30 grams of MVL monomer to UD-CCM for evaluation
    - Highly exploratory chemistry, 10 grams was set as minimum needed for initial characterization.

Polymerization and depolymerization studies of PMEA and PMVL

Polymerization



MMA PMMA

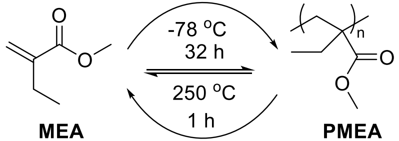
53 % (Yield)

Depolymerization

- Petroleum based
- Poor recyclability
- Char or by-product formation during recycling

T_g = 110 °C
T_d = 300 °C
T_{max} = 330-370 °C
T_C = 296 °C (bulk)

Polymerization
Sec-BuLi



MEA PMEA

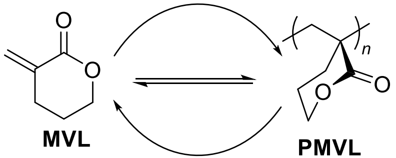
95 % (Yield)

Depolymerization

✓Biobased
✓Recyclable near quantitatively under mild conditions
- Poor polymerizability
- Low T_g

T_g = 65 °C
T_d = 321 °C
T_{max} = 353 °C
T_C = 82 °C (bulk)

Polymerization



MVL PMVL

99 % (Yield)

Depolymerization

✓Biobased
✓Recyclable quantitatively under mild conditions
✓Excellent polymerizability
✓Good thermal properties

T_g = 184 °C
T_d = 307 °C
T_{max} = 349 °C
T_C = 159 °C (bulk)

Summary: Recycle-by-Design Accomplishments to Date

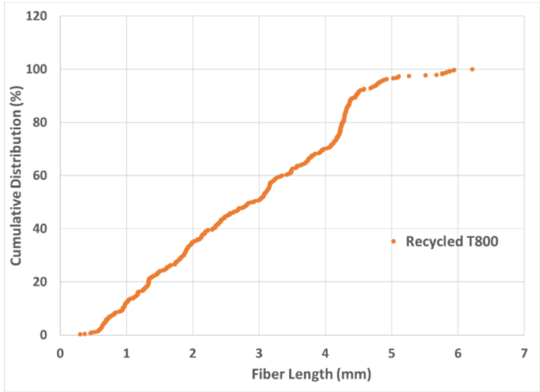
- MEA and MVL monomers have been evaluated as candidates for recyclable resins. MEA was a key candidate at first but suffered from low polymerizability at room temperature and exhibited low Tg. MVL was selected to address the polymerizability. Upon further study, PMVL showed enhanced thermal properties and recyclability (~99% monomer recovery for 1 gram samples).
- Adjusted the initially reported small scale synthetic pathway for MVL based on initial TEA to bring sustainability and economic feasibility to the forefront of the large-scale (>100 g) synthesis.
- Shipped 10 g of PMVL to University of Delaware for initial studies and will soon send 30 g of MVL monomer for further studies.
- Techno-Economic Analysis (TEA) of the large-scale synthesis, polymerization, and recycling is in progress via collaborators at NREL.

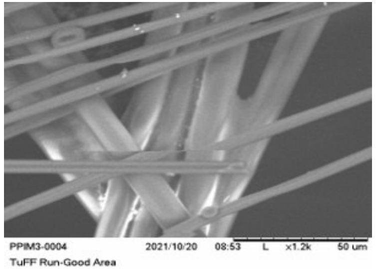
Program Impact

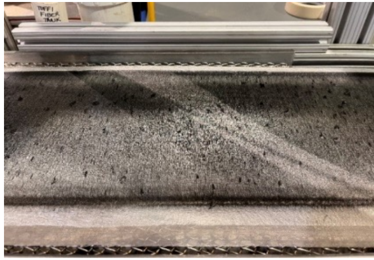
- Demonstrate that recycled Carbon fibers can be used in applications requiring similar performance to virgin continuous carbon fiber composites
    - Targeting Automotive and Electronics industries to replace virgin CF with rCF
    - Reclamation of CFC and Resin precursors from multiple commercial waste streams
- Recycled composite material will lower cost as well meeting or exceeding targets of 70% energy savings and 85% carbon utilization from waste stream composites.
- With Industry partners Composite Automation, Arkema, and Axiom, demonstrate that the TUFF material form can be processed into a prepreg using standard industrial processes, providing a pathway to future commercialization.
- Increase the overall amount of carbon fiber available to meet the increasing demand in carbon fiber composites due to drive to reduce weight in the vehicle and energy industries

Final Thoughts: Technical Challenges

- Incoming feedstock quality
  - Fiber Aspect ratio/length distribution
  - Longer fibers precipitate flocking, Short fibers pass through collection belt, limit property translation
- Fiber dispersion: Fibers must be able to be dispersed in an aqueous bath in order to be used in the TuFF process.
  - Fiber surfaces must be clean of residuals.
  - Requires improvement in resin reclamation efficiency and/or low-cost surface prep/cleaning
- Efforts to develop cleaning and sorting procedures for incoming fiber are ongoing and will be a focus in BP3







Quad Chart Overview

Timeline
- *7/1/2021*
- *12/31/2024*

	FY22 Costed	Total Award
DOE Funding	*$458,980*	*$1,799,983*
Project Cost Share *	$133,775	$751,656

TRL at Project Start: 1
TRL at Project End: 3

*Only fill out if applicable.

Project Goal
Demonstrate the viability of recycling Carbon Fiber Composites (CFC) through polymer/fiber separation via thermolysis and/or catalyst-controlled recovery of carbon fiber and monomer, followed by reuse of the fiber material in the *TuFF* process creating high-performance CFC with mechanical properties comparable to continuous CFC.

End of Project Milestone
Demonstration of 3 Recycling Step Iterations with 90% Tensile Property Retention

Funding Mechanism
- Joint FY20 Bioenergy and Advanced Manufacturing DE-FOA-0002245 / 000001
- Topic area 3: BOTTLE Consortium Collaborations to Tackle Challenges in Plastic Waste

.

Project Partners*
- NREL
- Colorado State University
- Composites Automation
- Arkema
- Axiom

University of Delaware Statement on Diversity and Inclusion

The University of Delaware does not discriminate against any person on the basis of race, color, national origin, sex, gender identity or expression, sexual orientation, genetic information, marital status, disability, religion, age, veteran status or any other characteristic protected by applicable law in its employment, educational programs and activities, admissions policies, and scholarship and loan programs as required by Title IX of the Educational Amendments of 1972, the Americans with Disabilities Act of 1990, Section 504 of the Rehabilitation Act of 1973, Title VII of the Civil Rights Act of 1964, and other applicable statutes and University policies. The University of Delaware also prohibits unlawful harassment including sexual harassment and sexual violence.

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  - Eugene Chen
- **Arkema**
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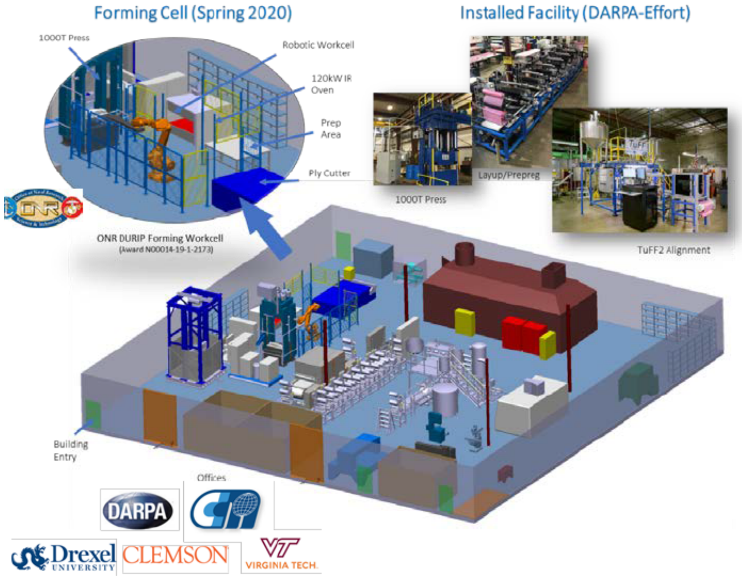
  - Evan Martz
  - Mark Aubart

Department of Energy and the Bottle Consortium

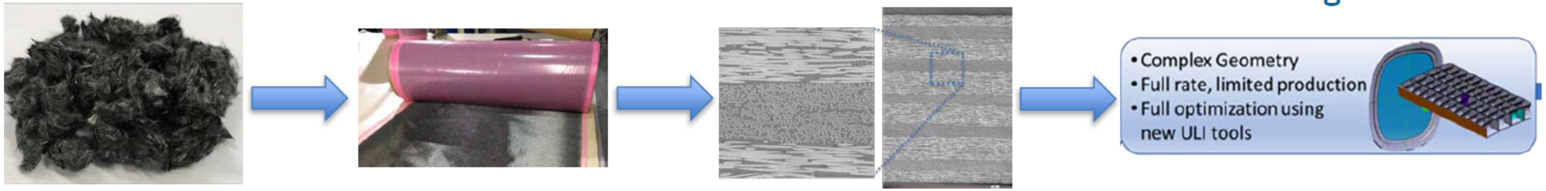
Back Up Slides

TuFF Integrated Pilot Manufacturing Facility



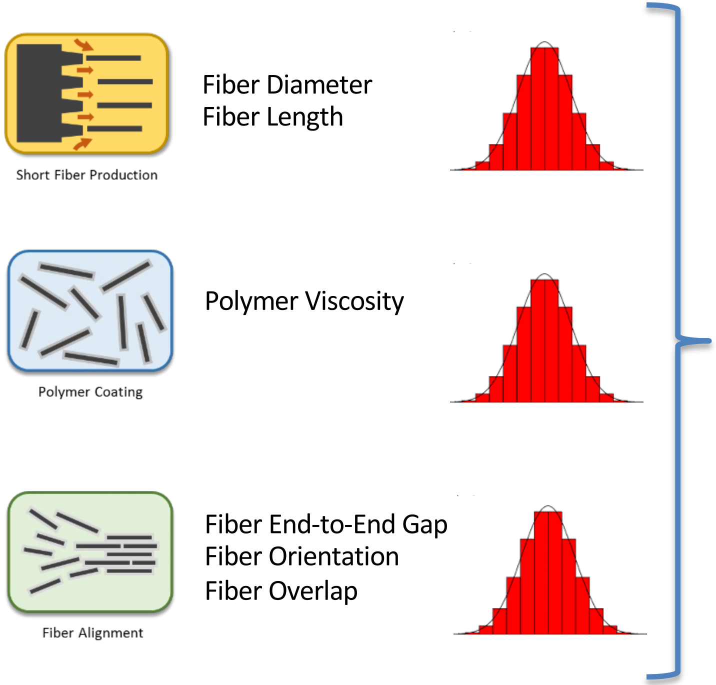
UD-CCM's 9000 Sqft *TuFF* Integrated Manufacturing Facility (Funded by DARPA)

- Fibers to Parts under One Roof will be used for ULI tasks
- Training for HBCU faculty and student internships
- Technology Demonstrations with the UAM Industry Supply Chain for Material, Process and Product Development at Rate
- Equipment funded by DARPA, ONR DURIP and UD-CCM industrial gifts



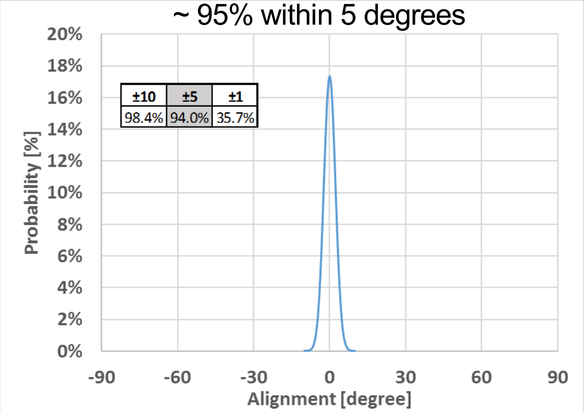
From Short Fibers to Parts under One Roof

Controlled *TuFF* Microstructure (Fiber Level) Necessary to Maximize Performance



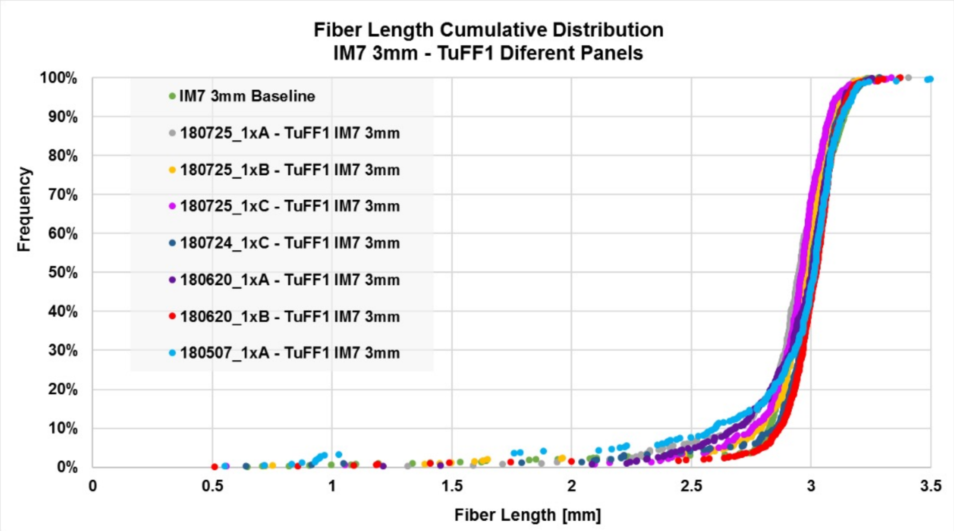
- What parameters can we actually control?
  - Fiber Length and Diameter
  - Incoming Fiber Type
  - ***Fiber Alignment***
  - Ply Areal Weight
  - Polymer Type
  - Fiber Volume Fraction
- Process stochastic parameters
  - Fiber end-to-end gap
  - Fiber overlap

TuFF Microstructure : Alignment Quality, Fiber Length and FVF Metrics Met for 3mm

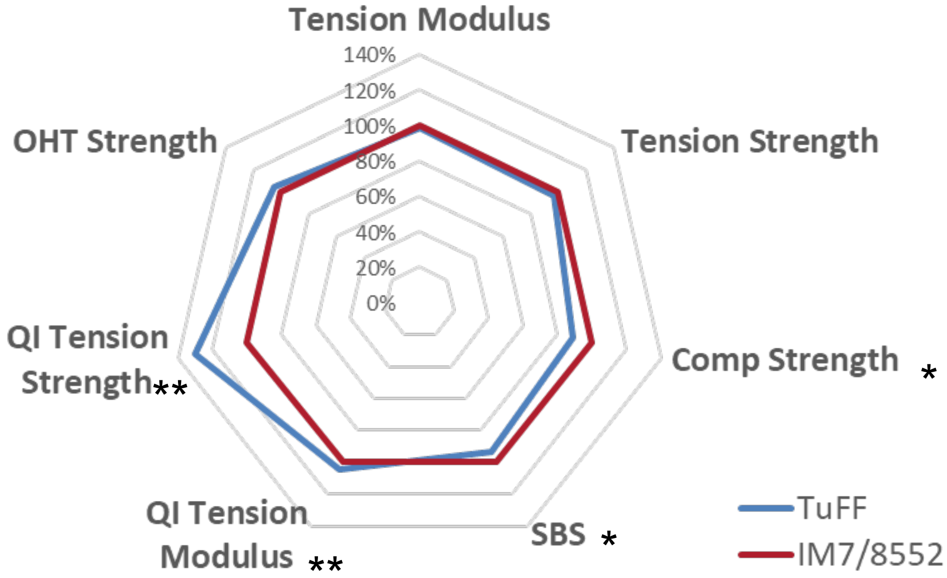


±10	±5	±1
98.4%	94.0%	35.7%

57-63% FVF Demonstrated



TuFF IM7/PEI Composite Properties in-line with Continuous IM7/8552 (NIAR Database)



*** Compression Strength and SBS are resin dominated (PEI vs 8552 Epoxy)**
****QI comparison is thin-ply (60 gsm FAW) to thick-ply (192 gsm FAW)**
OHT Strength is from TuFF1, Rest are TuFF2; Normalized values

QI-Quasi Isotropic
OHT-Open Hole Tension

Energy of Raw Material Manufacture

Table1 Energy intensity of steel and CF

	Steel (MJ/kg)	CF (MJ/kg)	
		In 1999	In 2004
Raw material production	-	42	39
Processing and assembly	-	436	247
Total	33	478	286

Table2 Energy intensity of matrix resins

	Energy intensity (MJ/kg)
Epoxy	76.0
Unsaturated polyester	62.8
Phenol	32.9
Flexible polyurethane	67.3
High-density polyethylene	20.3
Polypropylene	24.4

Suzuki, T; Takahashi, J; “Prediction of Energy Intensity of Carbon Fiber Reinforced Plastics for Massed Produced Passenger Cars”; The Ninth Japan International SAMPE Symposium; 2005

Publications, Patents, Presentations, Awards, and Commercialization

- NREL: 1 publication in preparation and 1 patent application filed for catalytic depolymerization approach.
- CSU: 1 publication in preparation
- Discussions with major phone manufacturer, and automotive OEMS to evaluate Recycled TuFF materials for their applications are ongoing