Additively Manufactured, Lightweight, Low-Cost Composite Vessels for Compressed Natural Gas Fuel Storage

Project ID: mat201

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Overview

Timeline:

- **Start:** July 2020
- **End:** August 2023
- 25% complete

Budget:

- Total project funding
- 1.38M / 3 Years
- 460K a Year / 1 Lab

Barriers:

- **Materials weight reduction for commercial automotive transportation**
- Carbon-Fiber-Composites (CFC's) offer weight savings up to 60% compared to steels with comparable strength/stiffness
- **Cost:** Broad use of CFC's hindered by the base cost of the fiber (feedstocks, processing)
- **Manufacturing**: Current methods and materials are costly & not well optimized for application the automotive industry

Partners:

- MSC Materials Sciences LLC.

Relevance

Additive Manufacturing Technology **for the fabrication of Lightweight Compressed Natural Gas (CNG) tanks at reduced cost**

Conventional filament-wound CNG storage tanks: lightweight, but costly to manufacture

- *New solutions are required for low cost, lightweight CNG storage for automotive transport applications.*
- *The predominant factor in limiting the spread of CNG driven freight and transport solutions for the alternative fuels' economy is the cost of the current generation of lightweight vessels employed for CNG onboard storage.*
- *This cost is a function of the base cost of the carbon fiber utilized in their production and the manufacturing cost associated the complex, multi-stage and labor-intensive process*
- *Emerging Additive Manufacturing (AM) technologies coupled with developments in resin phase nanomaterials offer enhanced performance and reduced cost potential for CNG fabrication*

We aim to demonstrate feasibility of cost reduction in Composite CNG tanks via a hybrid approach of; reduction in the overall volume of costly continuous filament fiber and use of cost-efficient Additive Manufacturing methods

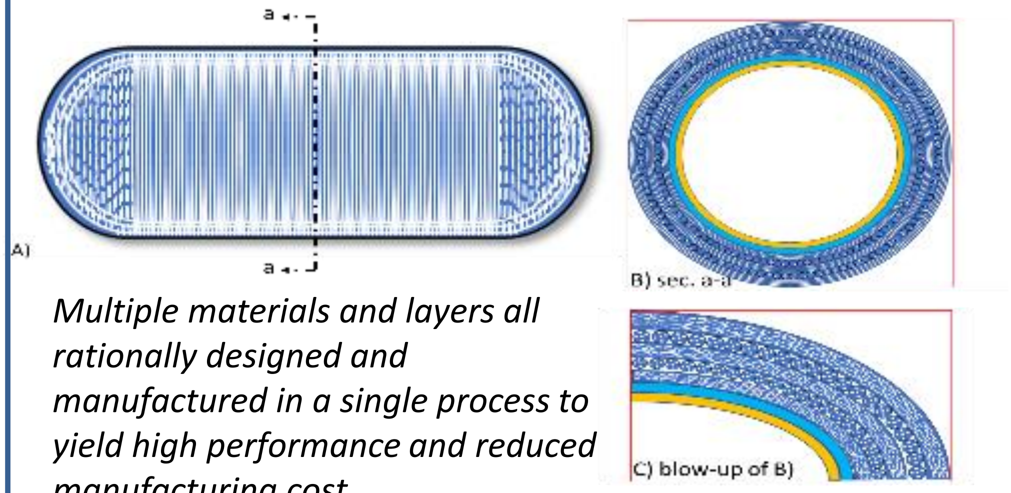
Relevance

Objectives:

We addresses three objectives that are critical to the additive manufacture of next-generation carbon fiber composites

- **Objective 1:** *Enhance resin properties via chemical and nanomaterial modifications*
- **Objective 2:** *Realize compositionally graded carbon fiber composites*
- **Objective 3:** *Additively manufacture and test contoured, hybrid carbon fiber vessels*

The AM Tank Concept:



Multiple materials and layers all rationally designed and manufactured in a single process to yield high performance and reduced manufacturing cost

Our Strategy:

Nano-materials enhancement of the resin-phase → Hybridization of continuous filament fiber into the AM DIW process → Rational design optimization of a multi-materials structure

Active FY20-21

We aim to demonstrate feasibility of cost reduction in Composite CNG tanks via a hybrid approach of; reduction in the overall volume of costly continuous filament fiber and use of cost-efficient Additive Manufacturing methods

Milestones

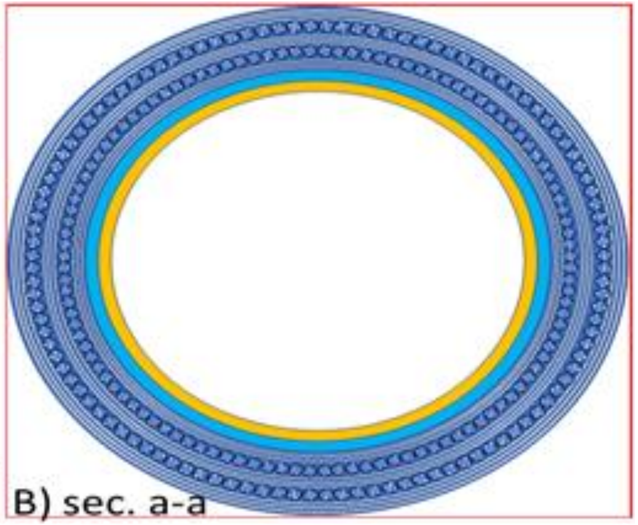
Date/Year	Description of milestone or Go/No-go decision	Status
July 2021	Optimize nanotube length and aspect ratio for dispersion in resin/ infuse the matrix material with high aspect-ratio, nanomaterial additives at low volume fractions (0.05-2 wt%), of ultra-long carbon nanotubes (CNTs) and optimize on the limits of loading as functions of length and aspect ratio in DIW-printed composites	On track/in-progress
Sept. 2021	**Go/No-Go Decision:** Demonstrate nanomodified thermoset resins with 10x improvements in yield strength and stiffness vs. baseline Epoxy winding resin & with gas barrier properties 70% of conventional EDPM polymer liner	On track/in-progress
Oct. 2021	Complete the design, build and testing of a hybrid continuous fiber/DIW feed system at MSC – demonstrating hardware and control functionality	On track/in-progress
Jan. 2022	Complete the integration of the hybrid feed system for DIW printing on LLNL's AM printing platform demonstrating basic operation and control	Inactive
April 2022	Demonstrate full-scale printing of parts with single, uniform material composition utilizing offline characterization to verify success	Inactive
July 2022	Compete validation of prototype of DIW feed system for hybrid continuous-short fiber AM by demonstrating manufacture of sub-scale with graded compositions	Inactive

Approach – Materials development and structural design

- **To fulfill design requirements, we are developing a range of *printable* nanomaterial modified resins:**

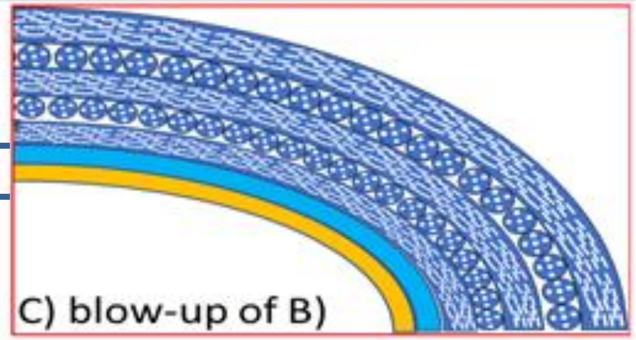
1. **An efficient Gas barrier resin epoxy-silicone filled with graphene**
2. **A Cyanate ester resin modified with carbon nanotubes with enhanced strength**
3. **A nano-silica/ nanofiber modified short CF filled Epoxy resin with enhanced strength**

All chemically unified & covalently interconnected



Structural layers – a hybrid of short and long fiber DIW carbon composite with a strength enhancing nanomaterial resin

Flexible gas barrier layers: epoxy-silicone 'rubberized resin', filled with high aspect ratio 2-D gas barrier nanofiller



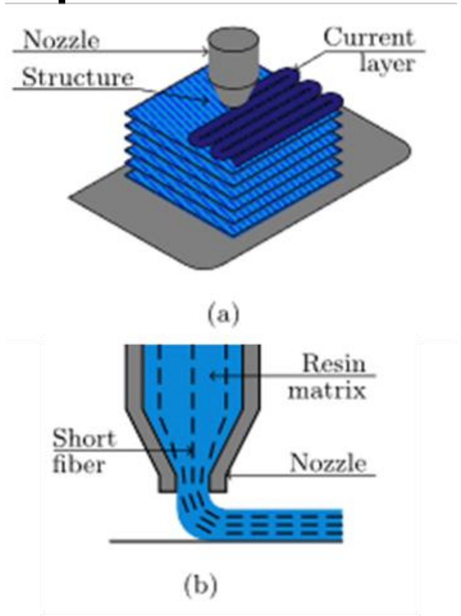
DIW = Direct Ink Write

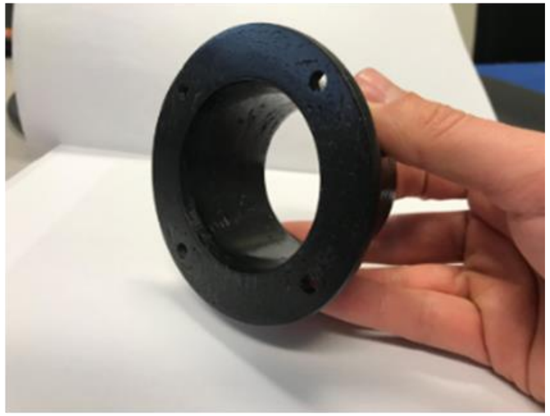
A Multi-materials approach will enable an efficient hybrid composite structure to be realized which incorporates continuous filament fiber where required most, and cost effective aligned short fiber, all within a unifying resin matrix enhanced with nano-modifiers

Approach – Manufacturing development

In order to implement our advanced hybrid tank design, we will:

1. **leverage existing Carbon fiber additive manufacturing platforms at LLNL :**



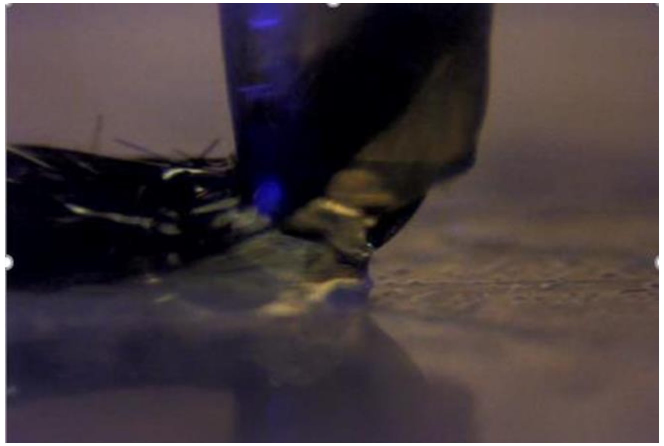


We will build on this versatile process as the manufacturing basis for our approach

LLNL's Carbon fiber additive manufacturing (CFAM) DIW process is capable of fabricating complex structures with the strength of Aluminum at ½ the density

2. **Work with our industrial partner, design and implement hybrid long-fiber deposition hardware:**

LLNL demonstrated a breadboard system in 2015 for 3D printing continuous filament CFC's



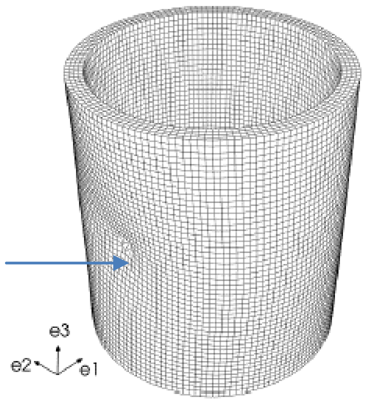
Though our partnership with MSC we are taking this technology past TRL-2 and implementing a prototype technology for hybridizing long-filament deposition with DIW

Marrying short fiber DIW with long fiber deposition technology in a unified chemical and deposition process will be a game-changing advance for CFAM that will enable a new generation of hybrid composites to be manufactured

Approach – Design optimization and testing

Our approach relies on rational design and structural computational optimization to yield the optimal benefit from the degrees of freedom offered by materials and manufacturing hardware developments

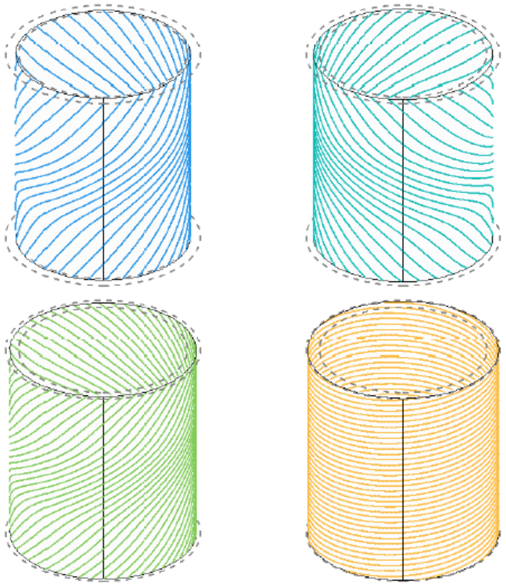
Model in-silico parametrized with load factors



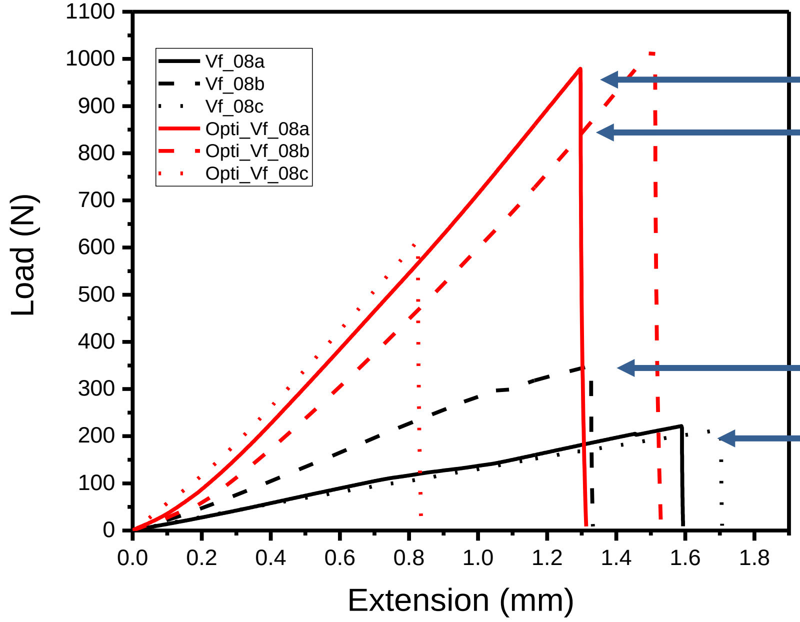
e.g. Point stress applied to mesh

OPTIMIZE

RUN TOOLPATH FUCNTION



G-codes that produce a part optimized to resist deformation



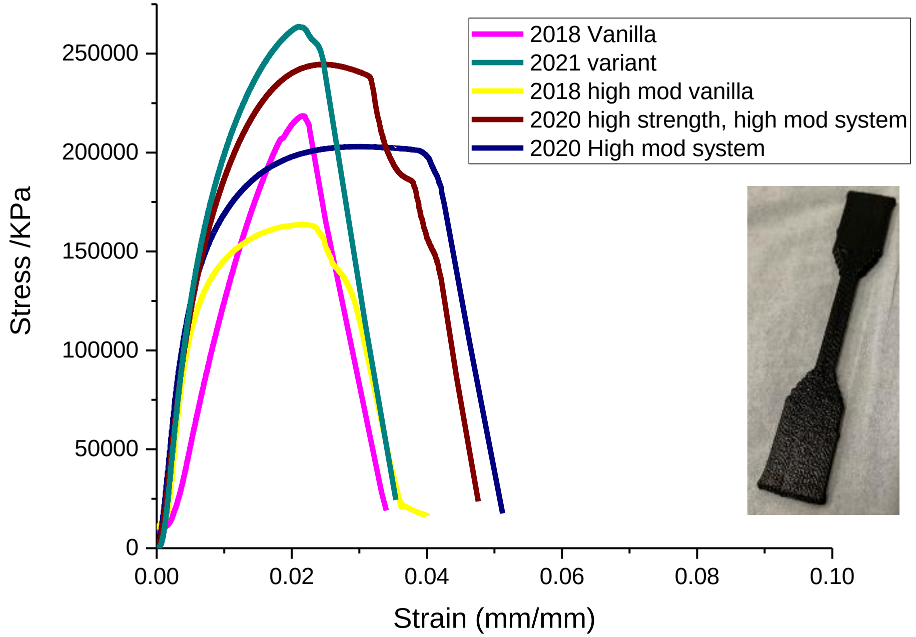
Optimized AM build paths at equivalent volume fraction

Build paths possible with conventional composite manufacture

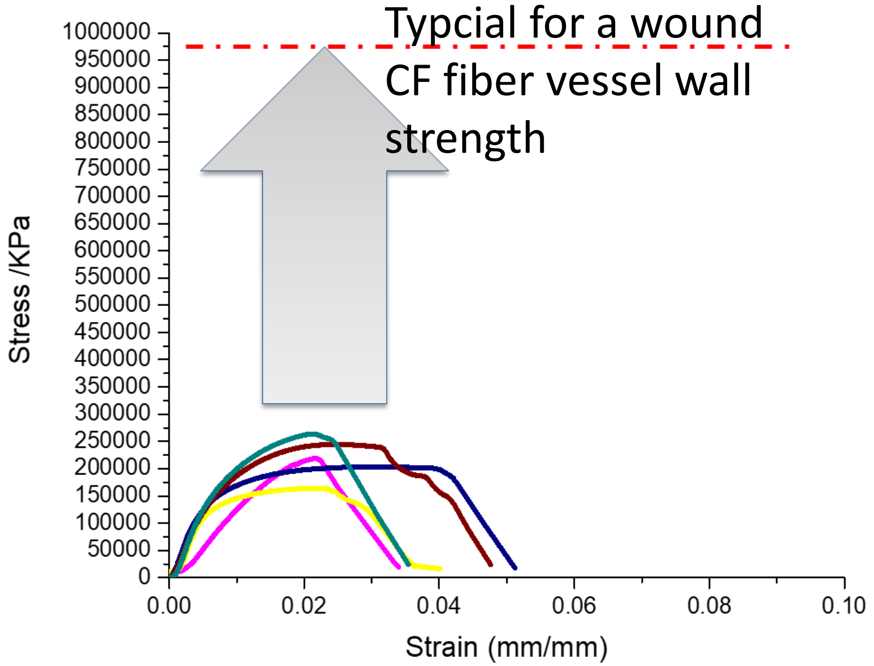
Optimization yields significant improvements in real materials tests – we more efficiently use the composites components

With our new manufacturing degrees of freedom in hand, we approach the microstructural design of AM CNG tanks on a rational basis, with the goal of attaining the maximal performance from our composite for application at the minimum mass and loading of continuous CF

Technical Accomplishments – Short Fiber Resin Development



Short fiber-printed composites have advanced considerably since project start

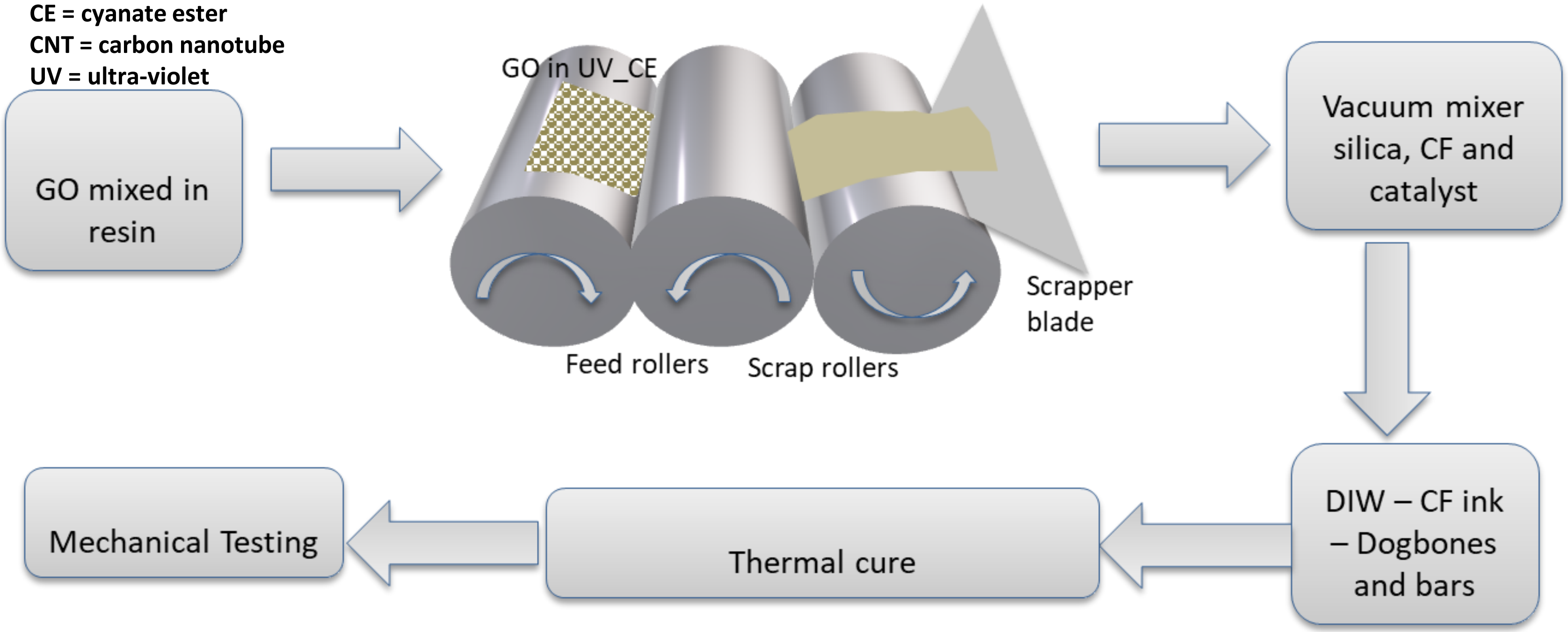


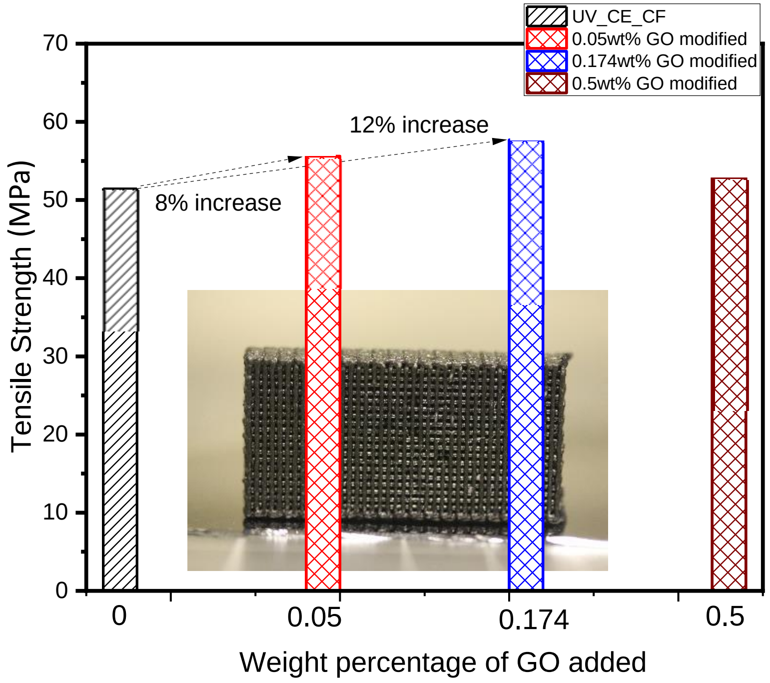
We have a considerable gap to address in terms of properties

Short Fiber DIW materials are not intended to carry the sole mechanical burden of vessel wall, but for every improvement we make, our design gets more freedom to reduce continuous CF content

Technical Accomplishments – GO Nanofillers

GO = graphene oxide
CE = cyanate ester
CNT = carbon nanotube
UV = ultra-violet



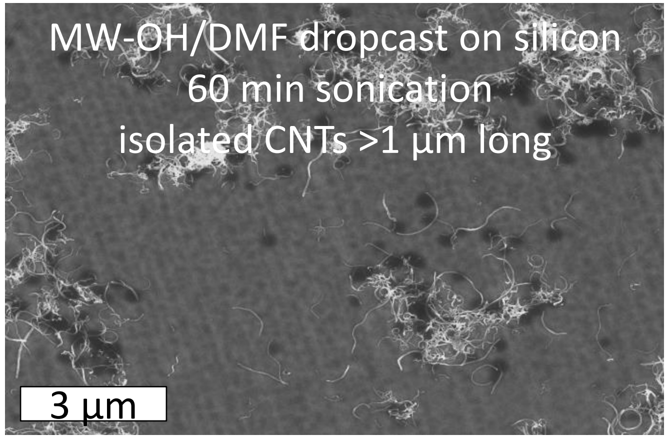


The nano-effect: 8% increase in strength with just 0.05wt% addition of GO. Tensile properties decreases with higher loading of GO (0.5wt%).

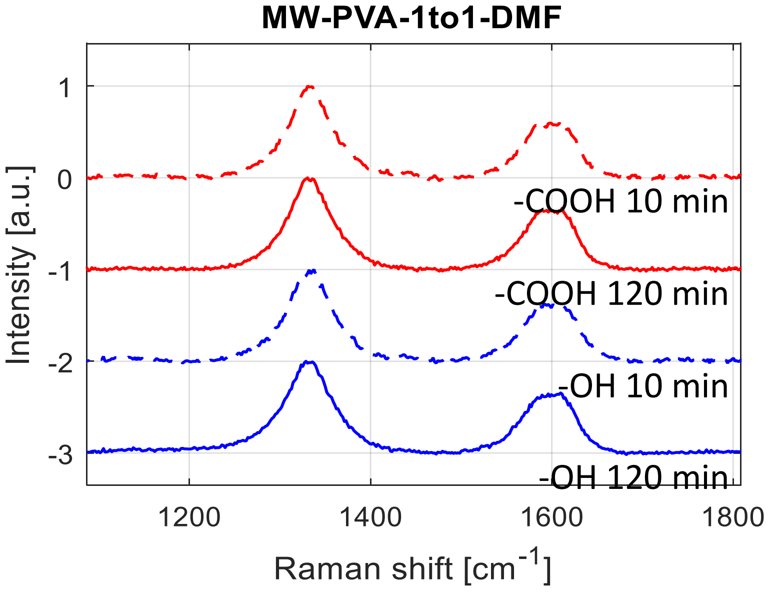
Roll-mill methods are scalable, and we are successfully dispersing GO and CNT's in advanced cyanate ester resins with this approach

We are developing the processes for scalable means of incorporating high-aspect ratio nanofillers into our resins, to enhance thermal and mechanical properties

Technical accomplishments - Development and characterization of MWNT 'Inks' for DIW printing

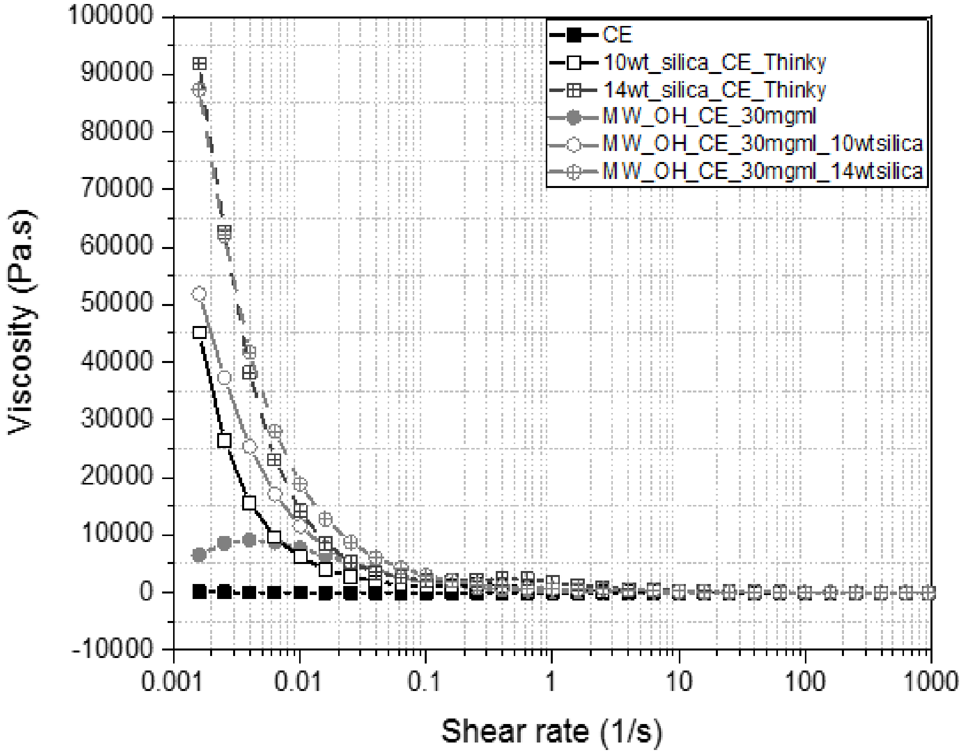


MWNT = multi-walled nanotube
PVA = poly(vinylalcohol)
DMF = dimethylformamide



Structure not damaged by dispersion process

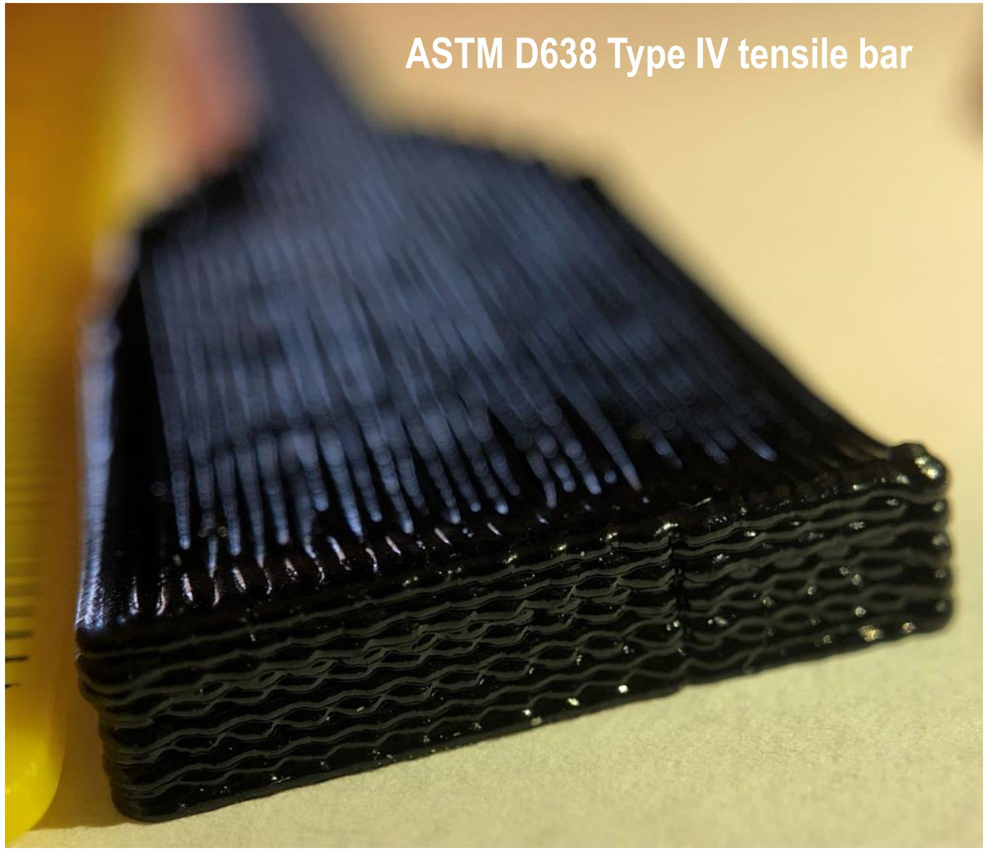
Industrial grade MW-OH equivalents (95%) @ $3,850/10kg at current initial CNT loadings that is to +$0.02/g-ink versus +$0.52/g-ink

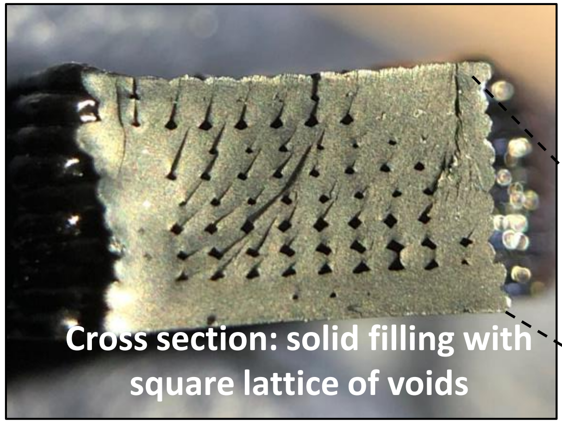


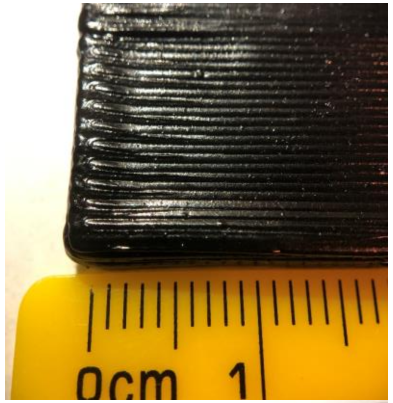
Mixing 1:1 with cyanate ester resin + silica particles → favorable viscosity characteristics for printing

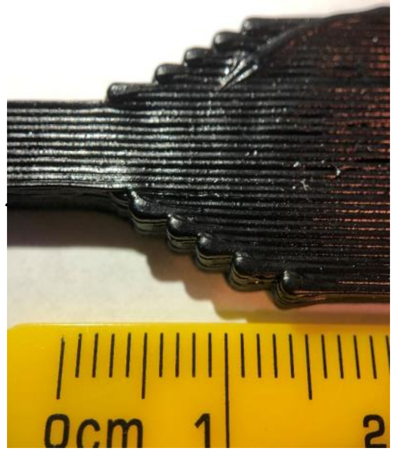
We have been able to disperse a range of concentraiotions of low cost MWNT's into DIW compatible cyanate ester based resins

Technical accomplishments - Development and characterization of MWNT ‘Inks’ for DIW printing





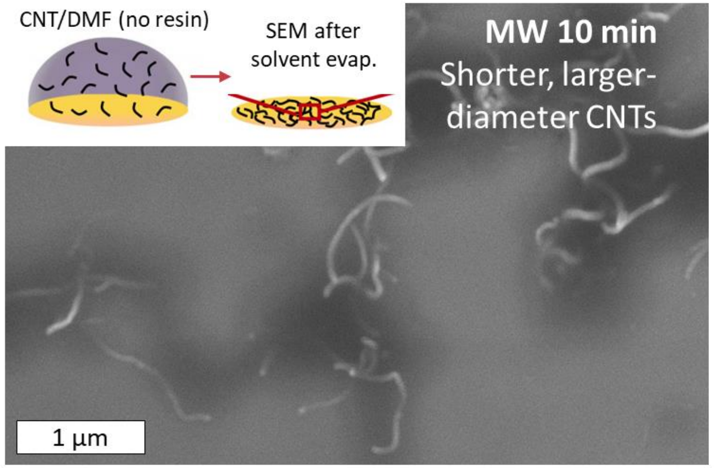


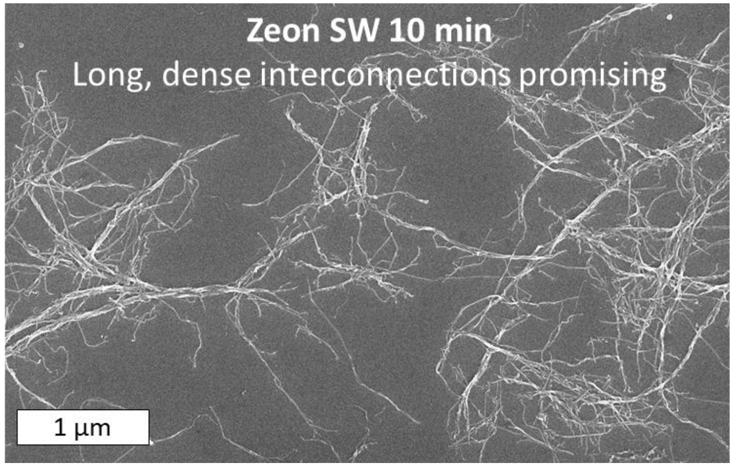


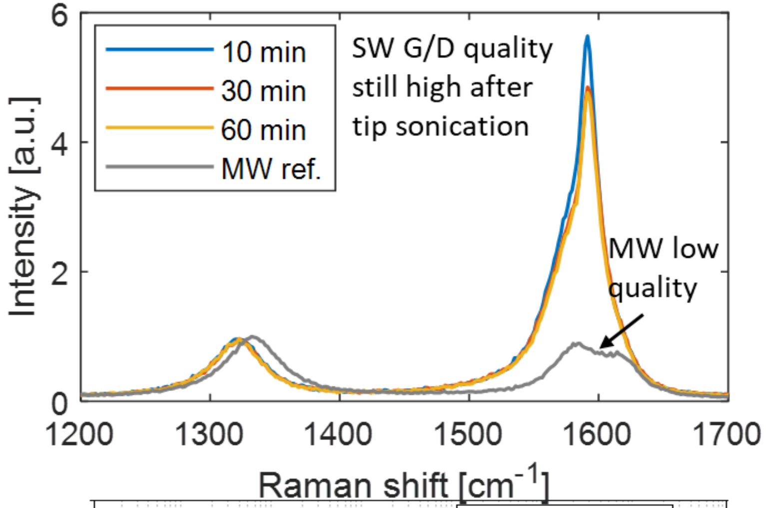
MW-OH ink enabled structures have been successfully 3D-printed for future mechanical characterization

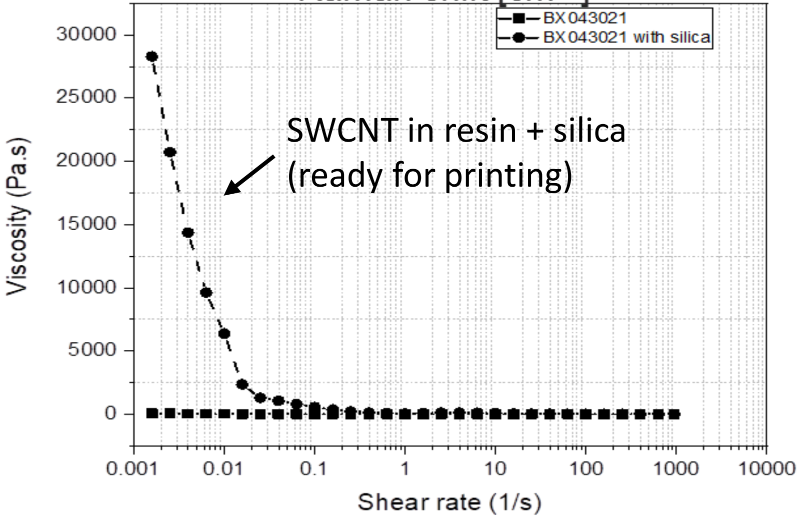
Directly 3D-printing test-specimens using our Direct Ink Write platform allows ‘printability’ and representative structure to be assessed in addition to mechanical properties

Technical accomplishments - Development and characterization of SWNT ‘Inks’ for DIW printing









Commercially available long single wall (SW) nanotubes show promise as more efficient reinforcers than MWNT’s

Initial characterization data suggests that a commercially available ultra-long single waled nanotube material may be a highly efficient modifier

Response to Previous year’s reviewer comments

New start project in Q4 FY21, no previous year’s reviewer comments available

Collaborators

- **MSC Materials Sciences LLC (sub):** joint design, hardware build for hybrid deposition system. collaborator on tank design and testing. *Considered central partner in project objectives in hardware development*

- **The University of Texas High-Resolution X-ray Computed Tomography Facility** (Dr J. Maisano): Academic service center responsible for non-destructive analyses of test materials and sub-scale printed articles. *Versatile academic partner willing and able to team on designing and optimizing x-ray based NDE of low Z-composites.*

- ***University of Illinois** (Prof. John Lambros):* Academic collaborator in quantitative mechanical testing of AM composites.

Remaining Barriers and Challenges

Hardware:

- **There is risk to be bought-down on the continuous filament deposition approach** (test data and test article fabrication are required to validate this approach before we can be assured that the process is viable at scale

Materials Development:

- **There remains uncertainty as to the ultimate potential of the nanomaterials approach resin modification approach**. We need further test data to perform both the materials performance and cost benefit analyses.

Tank Design & optimization:

- **The design and testing and validation of a complex, hybrid tank article will be an order of magnitude more complex task than attempted before for a CFAM composite.** We have confidence based on experience, but there may be a range of unforeseen hurdles

Cost-benefit:

- **We are not yet able to fully assess the cost-benefit of the approach.** How much can we reduce the continuous fiber loading? Do the increased costs of high-performance resins pay for themselves in properties?

Proposed Future Work in FY21 and FY22

Hybrid Print head hardware

- **Complete our print head:** *We will be aiming to complete the hardware build of the continuous filament head and begin testing at MSC to verify system functionality per design*
- *Integrate the hybrid print head onto LLNL's current 3D printing platform and validate hardware functionality*

Resin Nano-modification

- **Baseline a new 'production ready' structural resin:** *We will be aiming to complete the primary development of a strength and stiffness enhanced structural resin and demonstrate through testing and characterization that 1-D nanofiller reinforced printed parts are x10 improvements in yield strength and increased stiffness*
- *Validate the gas barrier performance of the inner layer resins*

Next-Generation hybrid printing

- **Demonstrate the hybrid concept through printing and characterization:** *We will demonstrate full functionality of the long fiber system by printing uniform long fiber cylinders with mechanical optical and X-Ray CT characterization of structure*
- *Perform an initial demonstration of the full hybrid capabilities by printing a graded test articles combining sho firber DIW and long fiber zones in the composite*

Summary

Accomplishments:

- Successfully formulated, printed and tested initial nano-modified AM feedstocks
- Progressed design for continuous filament 'printhead'
- Successfully printed short fiber parts of ~6000cm3 in CFAM

Technical highlights:

- We have demonstrated significant mechanical improvements in resins with ultra-low loadings of graphene oxide nanofillers
- We have 3D printed and tested graphene & nanotube modified short carbon fiber cyanate ester resins (a first for the field)
- We have early data supporting the ability to disperse fibular networks of ultra-long nanotubes in our resin matrixes using a scalable process

Impact towards VTO Objectives:

This project has the potential to enable a transformative means of realizing the extant benefits of CFCs for lightweight, high performance CNG storage at significantly reduced cost. If successful, and a feasible means of manufacturing Type-5 format tanks is demonstrated , then commercial natural gas fueled transportation could significantly benefit. **Less CF, less manufacturing burden:** *Our 3-pronged approach levering additive manufacturing, design optimization and nanomaterial modification aims to yield a high performance CNG tank that is cheaper to manufacture from less expensive feedstocks*

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