Lab-Scale Production of Particle Bonded Filaments with High-Loading Coal-Derived Carbon

FE0032147

Kelvin Fu

University of Delaware

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National Energy Technology Laboratory

Resource Sustainability Project Review Meeting

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Project Overview

– **Funding (DOE and Cost Share):**

DOE share: $1,000,000; cost share: $250,000

– **Overall Project Performance Dates:**

February 01, 2022-January 31, 2025

– **Project Participants:**

Prof. Kelvin Fu, Mechanical Engineering;

Prof. Feng Jiao, Chemical Engineering

University of Delaware

Project Overview

– Overall Project Objectives

The main goal of the project is to develop a lab-scale manufacturing process to fabricate filaments with high carbon content for FDM 3D printing use. Graphene particles derived from domestic US coal wastes will be used as feedstock for filament development.

(1) Develop a coal-enhanced filament production technology to fabricate filament containing high-loading of coal-derived graphene;

(2) Develop debinding and sintering post-processing to fabricate fully carbon structure;

(3) Develop a composite material based on fully carbon preform structure and evaluate composite as a potential alternative to carbon fiber composite;

(4) Perform a full techno-economic analysis to assess the coal-enhanced filament potential for the fast-growing and high-value additive manufacturing and composite market.

Technology Background

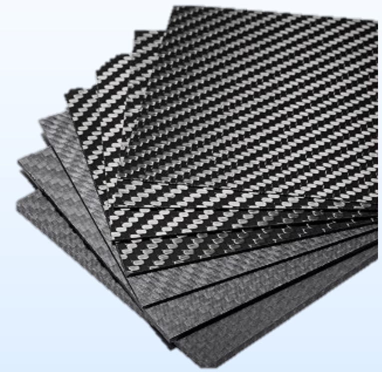
- Using particle-filled filaments to fabricate fully particle-sintered 3D parts based on FDM-extrusion printing and prost-processing (debinding and sintering) has received great interests in additive manufacturing.
- Particle-filled filament FDM 3D printing offers a simple, cost-efficient, safe production of fully particle-sintered parts, which has drawn many industrial players in this field.
- Metal-filled and ceramic-filled filaments have been commercially available on market.

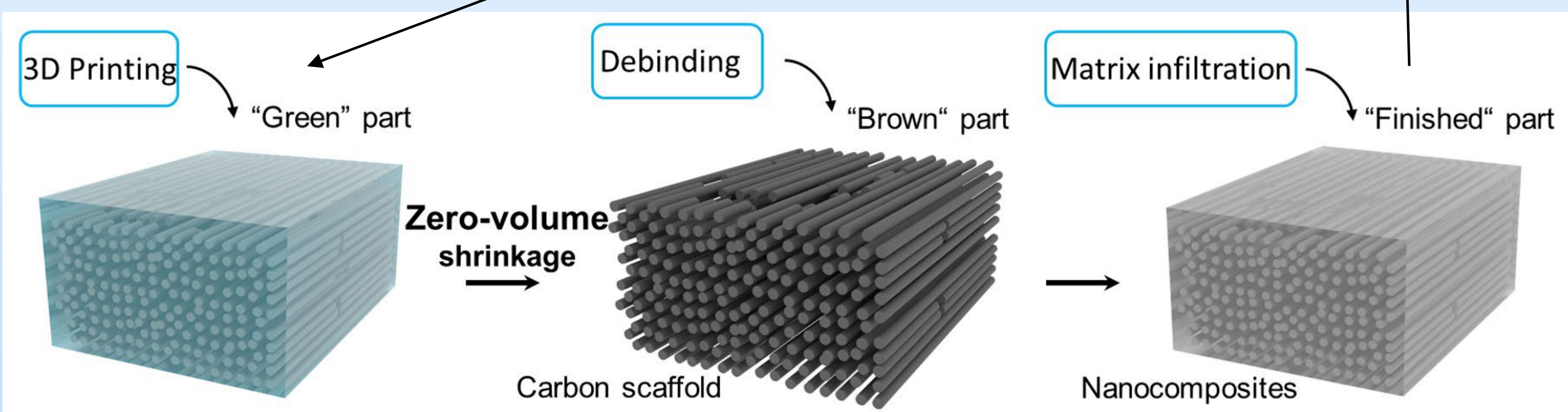
Motivation:

Carbon-filled filaments for making full-carbon part have not been developed.

Technology Background

Technology Path





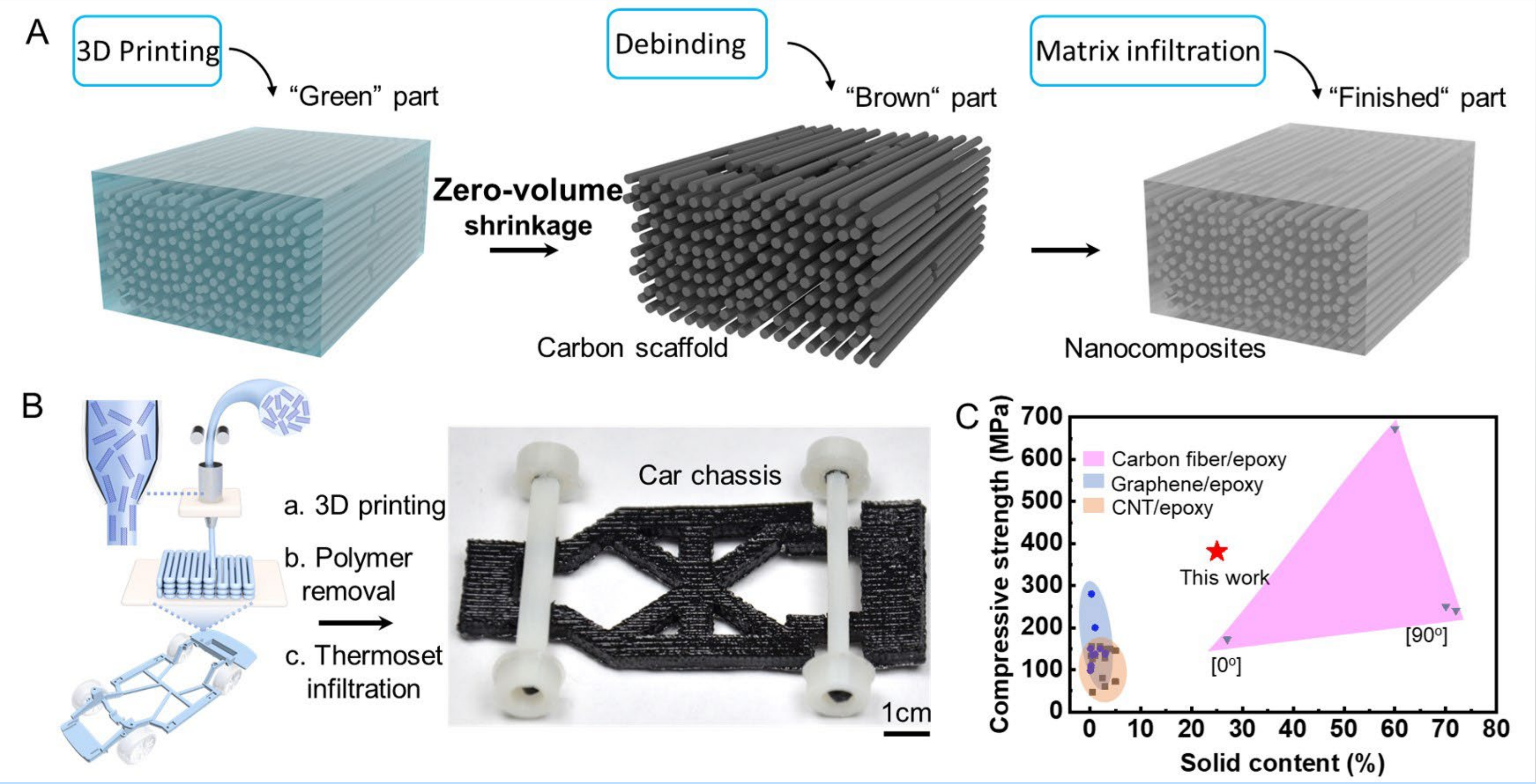
Technology Background

- Current carbon-filled filament, due to low carbon content (<10 wt.%), could not be used to fabricate full carbon parts for carbon composite applications.
- Carbon-filled filament with **high carbon particle loading** could be used to fabricate full carbon parts.
- Using carbon nanomaterials derived from abundant domestic US coals and their wastes provides abundant and low-cost feedstock resources for 3D printing, offering a great upgrading opportunity to develop high-value carbon-filled filament for new carbon economy.

If successful, coal-derived carbon nanomaterials, such as graphene, could be produced into macroscale carbon reinforcement with tunable alignment via extrusion 3D printing for structural and functional composite materials, such as mechanically strong composite, and battery electrodes.

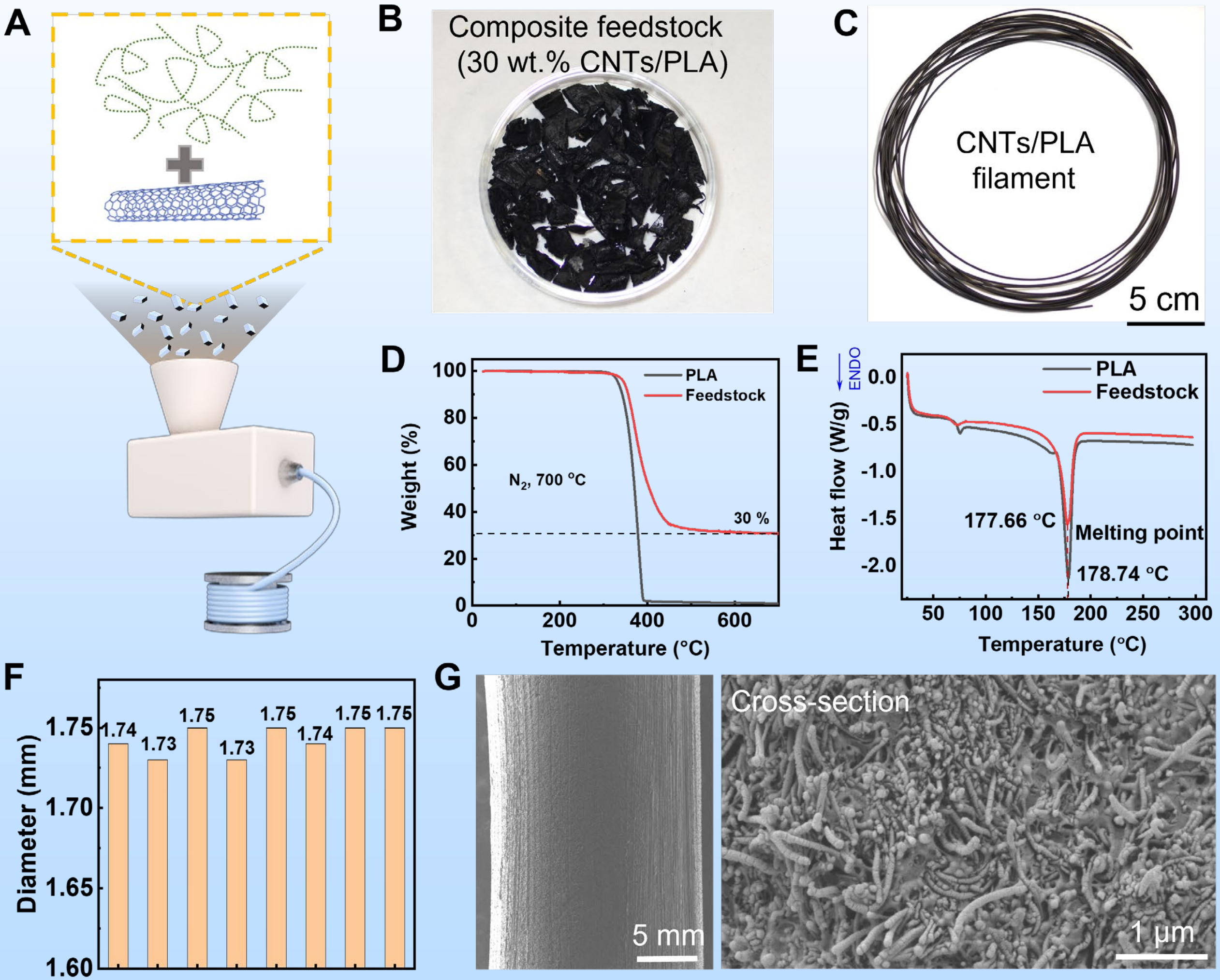
Technology Background

Previous Technology Development



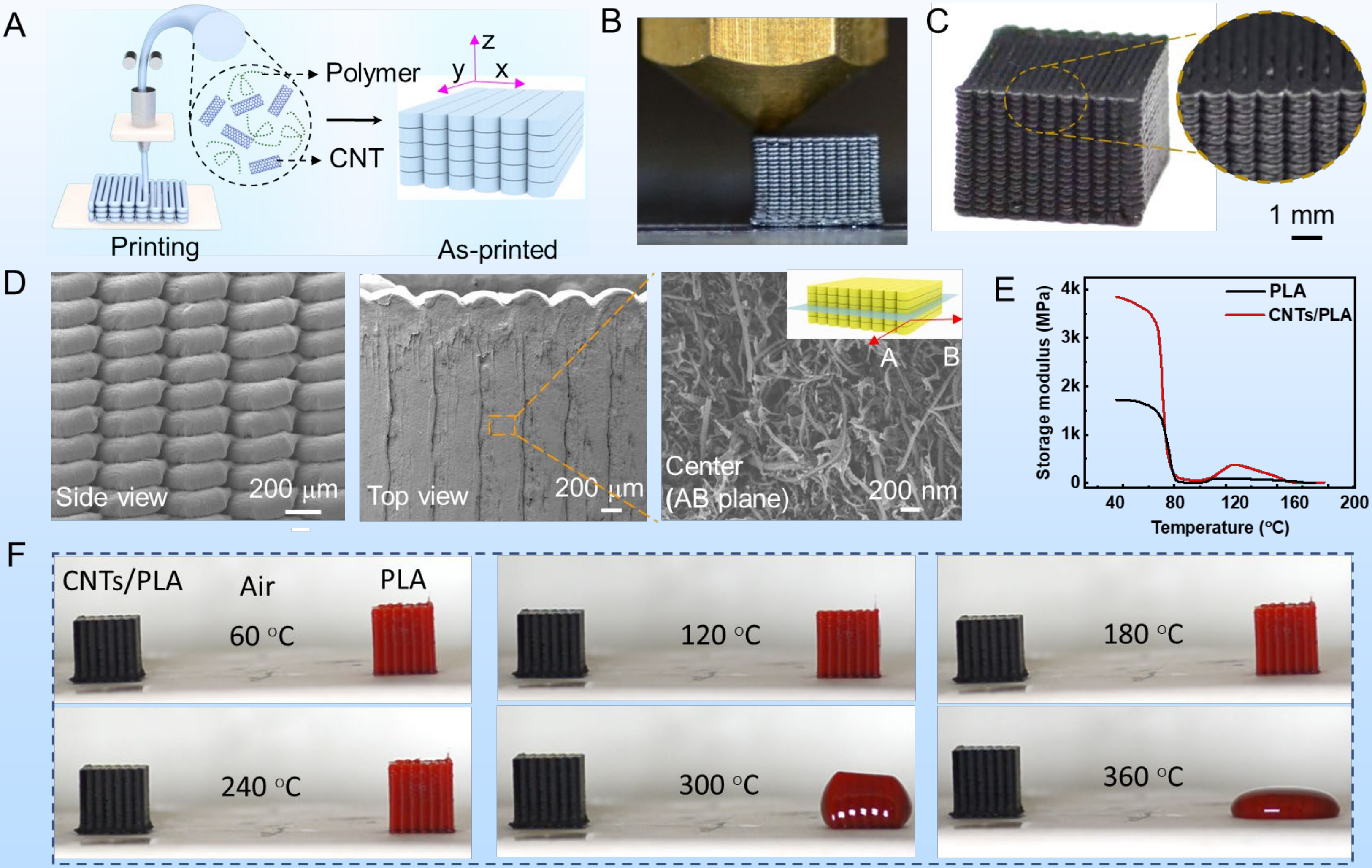
Technology Background

Previous Technology Development



Technology Background

Previous Technology Development

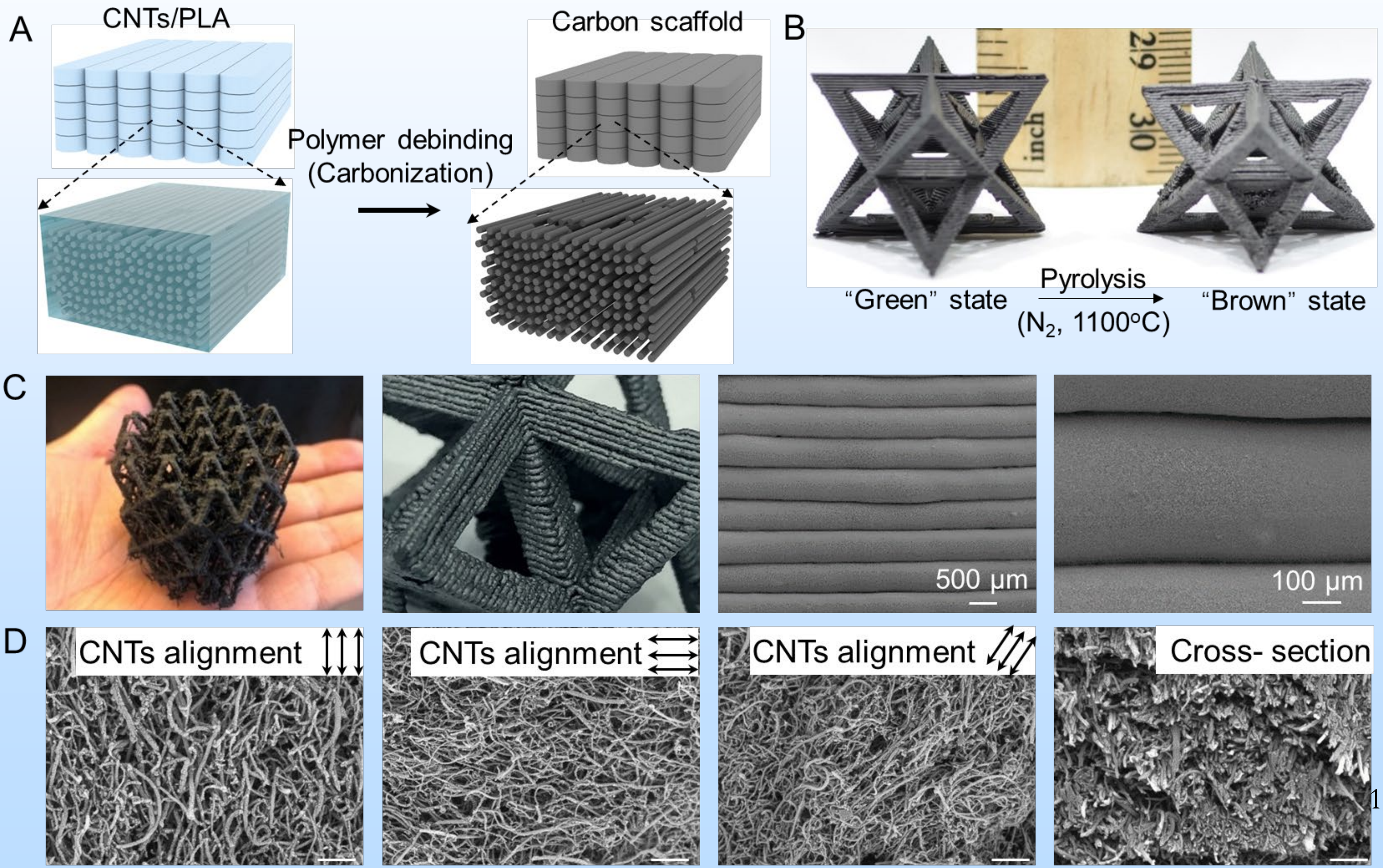


Technology Background

Previous Technology Development

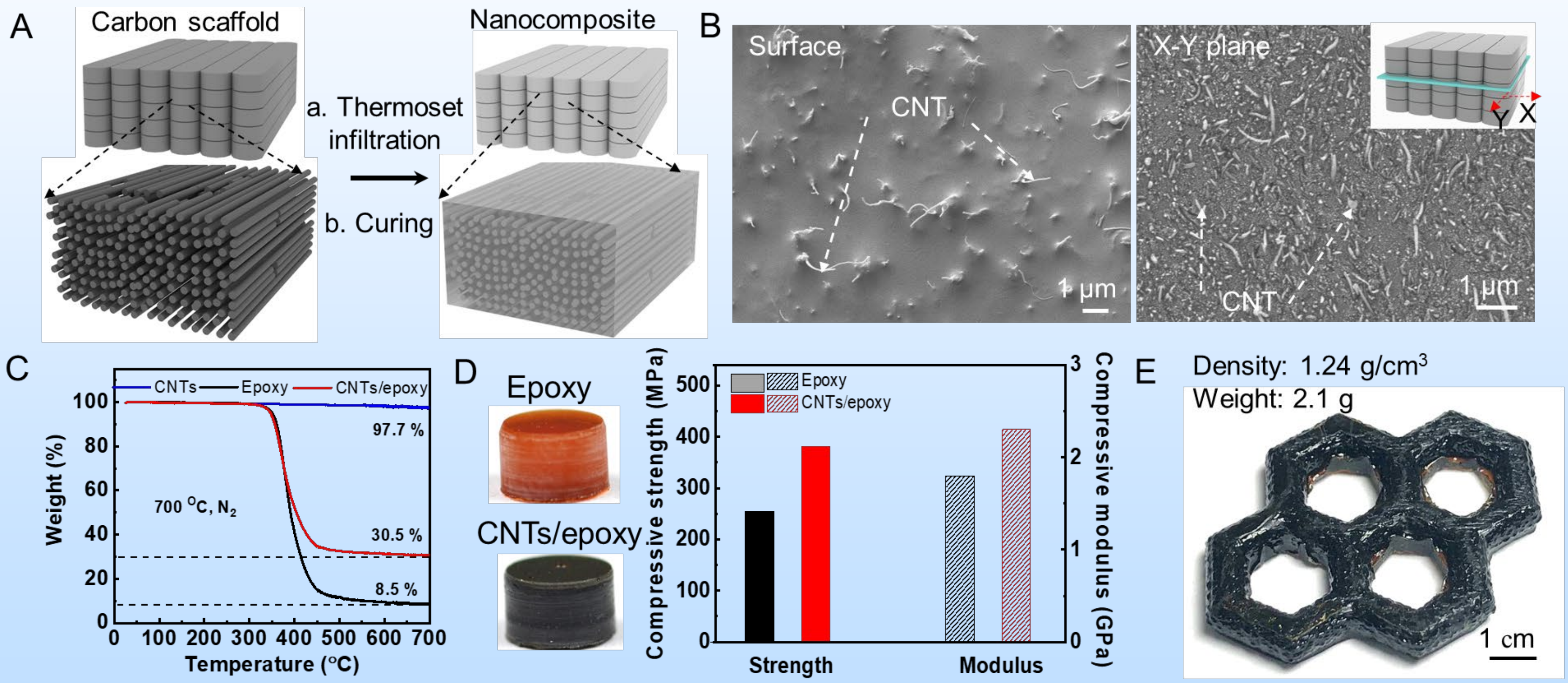
Technology Background

Previous Technology Development



Technology Background

Previous Technology Development



Technical Approach/Project Scope

a. Experimental design or project steps and work plan

Particle Bonded Filament Technology

Coal-derived carbon treatment and polymer crafting

Phase I

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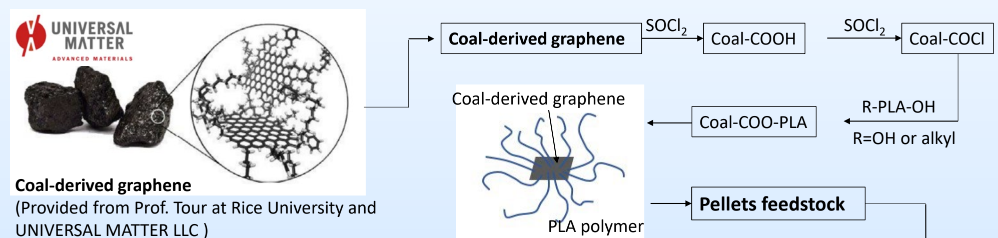
Filament production (target loading 50 wt. %)

Phase I

↓

Contaminates examining and treatment

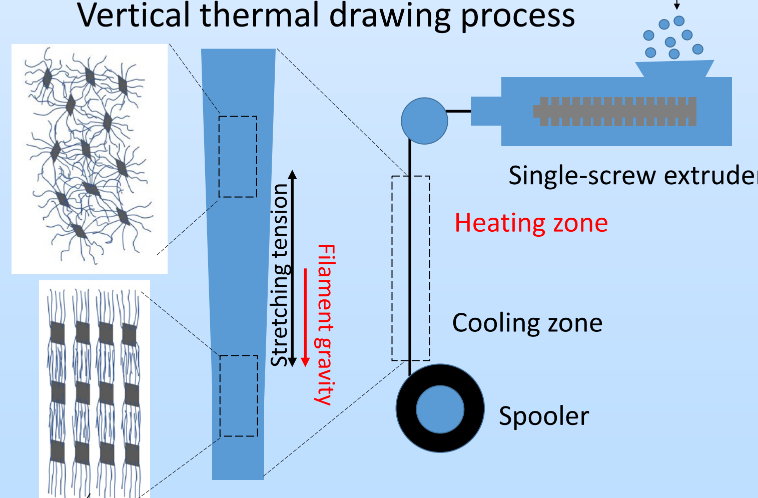
Polymer grafted coal-derived graphene hybrid



Coal-derived graphene
(Provided from Prof. Tour at Rice University and UNIVERSAL MATTER LLC)

Vertical thermal drawing process

- Polymer chains flow and orient along with shear flow-induced coal-derived graphene alignment in heating zone
- Aligned and densely packed polymer chain and coal-derived graphene can be freezed in cooling zone.



Technical Approach/Project Scope

FDM 3D printing, debinding and sintering to fabricate fully carbon preform

Phase II

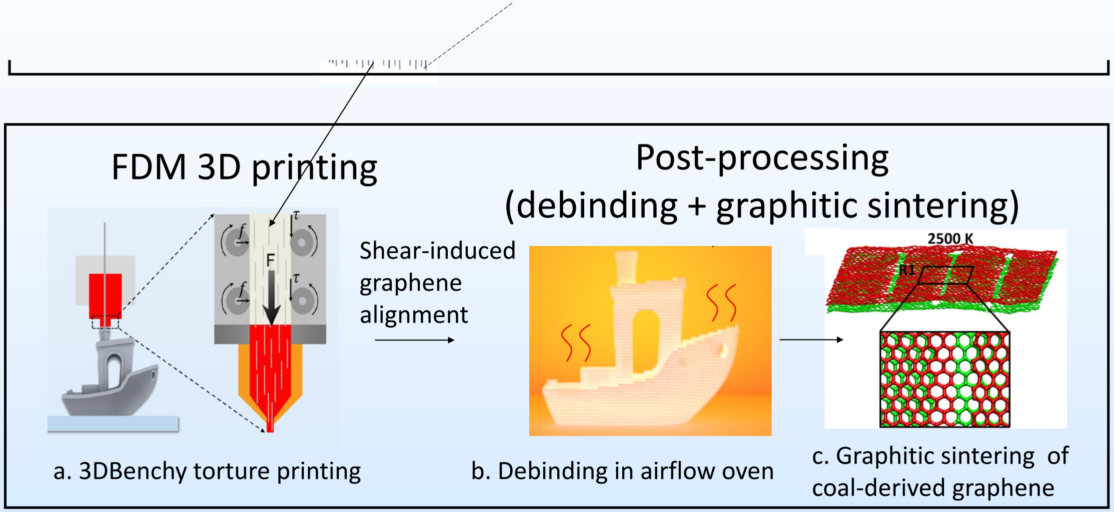
↓

Coal-derived graphene preform reinforced polymer composite

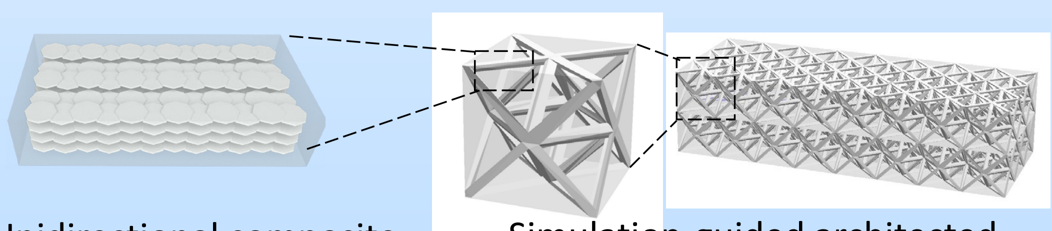
Phase II

↓

Techno-economic assessment



Coal-derived graphene preform for multiscale reinforced composite with high strength and toughness



Technical Approach/Project Scope

b. Project schedule

Task/ Subtask	Milestone Title & Description	Planned Completion Date	Verification method
Task 2.2	Milestone A – Complete the development and evaluation of PLA grafted coal-derived graphene hybrid	06/30/2022	Documented performance data
Task 2.4	Milestone B – Complete the development and evaluation of feedstock pellets	09/30/2022	Documented performance data
Task 3.2	Milestone C – Complete of the trial production of medium-loading (20wt. %) filament to meet criteria: filament with 1.75 ± 0.05 mm diameter, continuous 25 g filament	12/3/2022	Documented performance data
Task 3.3	Milestone D – Complete the fabrication and evaluation of high-loading (50 wt. %) filament to meet criteria: coal-derived graphene loading up to 50 wt. % in filament, alignment of coal-derived graphene up to 50% in filament, filament with 1.75 ± 0.05 mm diameter, 100g filament	6/31/2023	Documented performance data and filament deliverables
Task 4.2	Milestone E – Complete the printing performance evaluation on commercial desktop and industrial 3D printers	12/31/2023	Documented performance data and photo images of printed parts
Task 5.1	Milestone F – Complete the development of coal-derived graphene carbon structure to meet criteria: volume change less than 10 wt. %, coal-derived graphene over 95 wt. % in carbon framework after carbonization.	06/30/2024	Documented performance
Task 5.2	Milestone G – Complete the development of coal-derived carbon preform and composite development to meet criteria: composite density 1.55 g/cm^3, flexural strength/modulus 600 MPa/45 GPa, tensile strength/modulus 700 MPa/50 GPa, Compression strength/modulus 400 MPa/50 GPa, and interlaminar shear strength 45 MPa	12/31/2024	Documented performance and composite coupon deliverables
Task 6.0	Milestone I – Complete the Techno-Economic Analysis	12/31/2024	Documented analysis results

Technical Approach/Project Scope

c. Project success criteria

Decision	Date	Success Criteria
Go/no-go Decision Point #1	06/30/2023	coal-derived graphene loading up to 50 wt. % in filament, alignment of coal-derived graphene up to 50% in filament, filament with 1.75 ± 0.05 mm diameter, 100 g filament.
Go/no-go Decision Point #2	12/31/2024	Filament can be printed on commercial desktop and industrial FDM 3D printers; 3D printed samples: 3DBenchy model torture-test sample with volume shrinkage less than 5%, no delamination or warpage; Graphitized coal-derived graphene framework: volume change less than 10 wt. %, coal-derived graphene over 95 wt. % in carbon framework; Graphitized coal-derived graphene reinforced thermoset composite coupons: density 1.55 g/cm^3, flexural strength/modulus 600 MPa/45 GPa, tensile strength/modulus 700 MPa/50 GPa, Compression strength/modulus 400 MPa/50 GPa, and interlaminar shear strength 45 MPa; Total filament weight: 1kg.

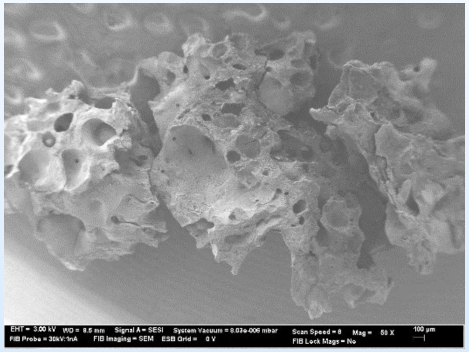
Technical Approach/Project Scope

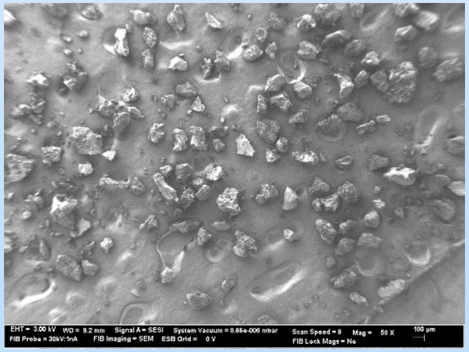
d. Risks and Mitigation

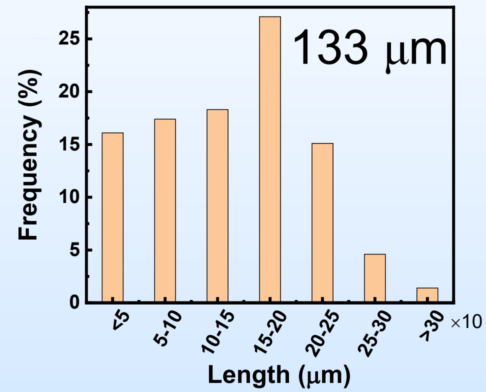
Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
	(Low, Med, High)			
Technical/Scope Risks:				
Single screw pellet extruder can cause a decreased coal-derived graphene particle dimension (particle size, thickness) due to the shear extrusion process	Med	Low	Low	The mitigation plan will be to balance the solids, temperature, and extrusion speed in the extrusion operation.
Fabricated filament diameter may have a large variation.	Med	Med	Med	The mitigation plan will be to extend the filament formation length (the distance from pellet extruder to filament winding machine) while optimizing the two-stage zone temperature. If a much larger filament is inevitable, sanding will be used to reduce diameter to 1.75 mm.
Filament cannot be automatically extruded into hot end in FDM 3D printer due to lack of sufficient gear torque to overcome high viscosity of molten filament.	High	Med	Med	The mitigation plan will be (a) to slightly decrease coal additive loading to reduce viscosity, and (b) to increase gear torque by replacing with a high stepping torque motor

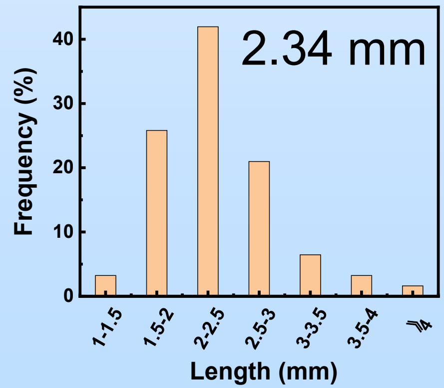
Progress and Current Status of Project

Coal-derived graphene (Universal Matters)



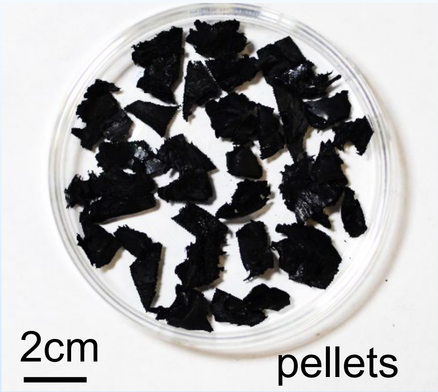






Progress and Current Status of Project

Filament preparation



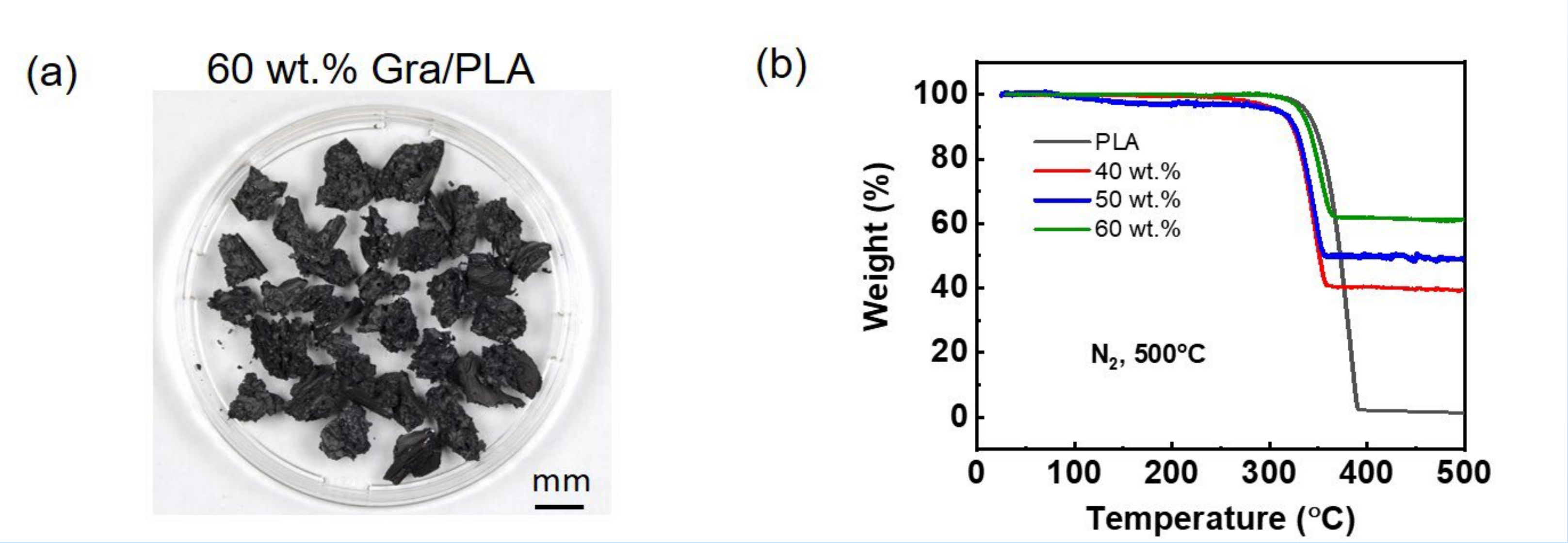
20 wt.% grinded graphene/PLA pellet

- PLA/graphene/dichloromethane
- Drying and grinding

Filament with a diameter of 1.75 mm (extruded at 150^{o}C)

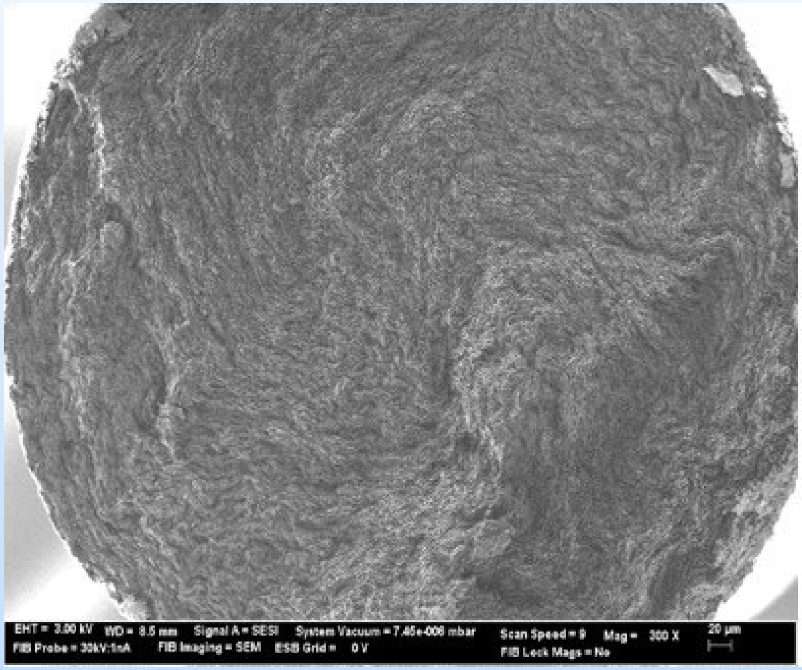
Progress and Current Status of Project

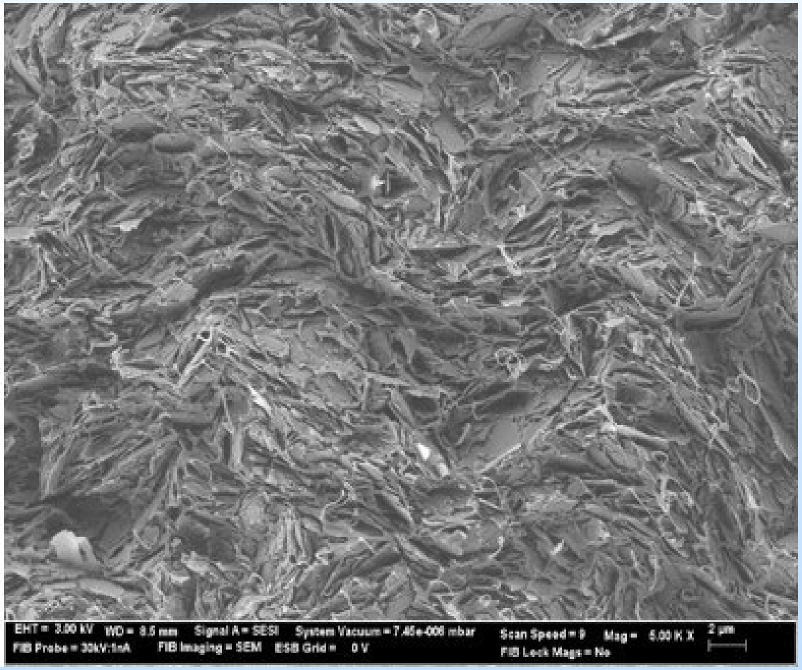
Graphene flakes (Cheaptubes.com)



Progress and Current Status of Project

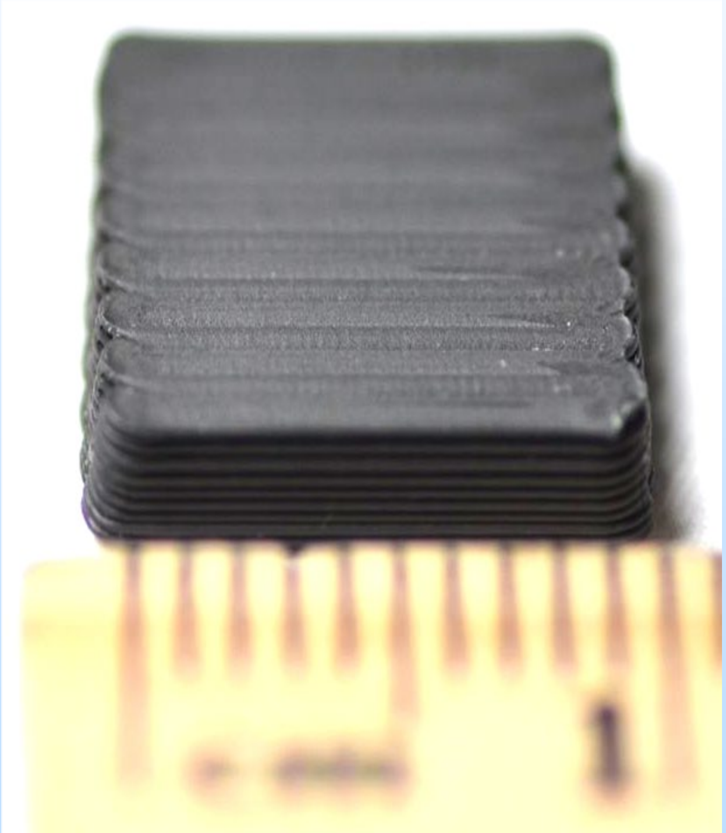
Filament with 60wt.%

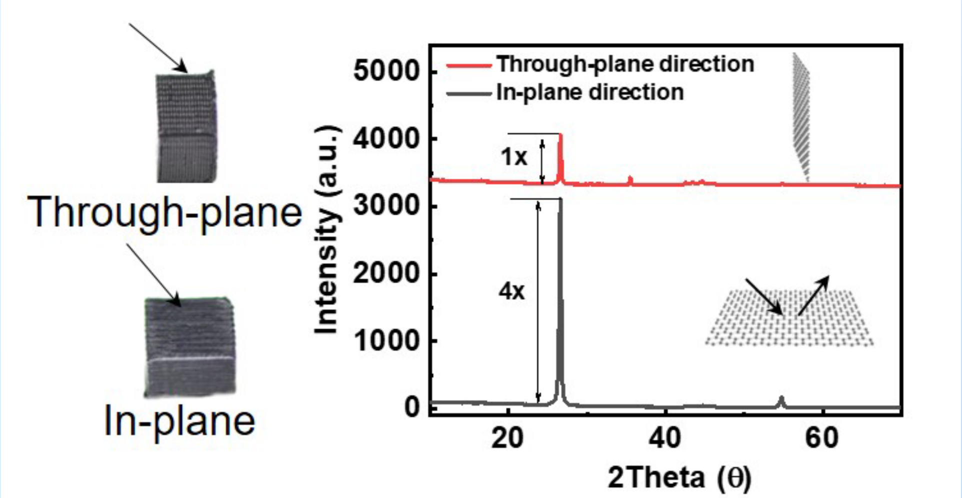




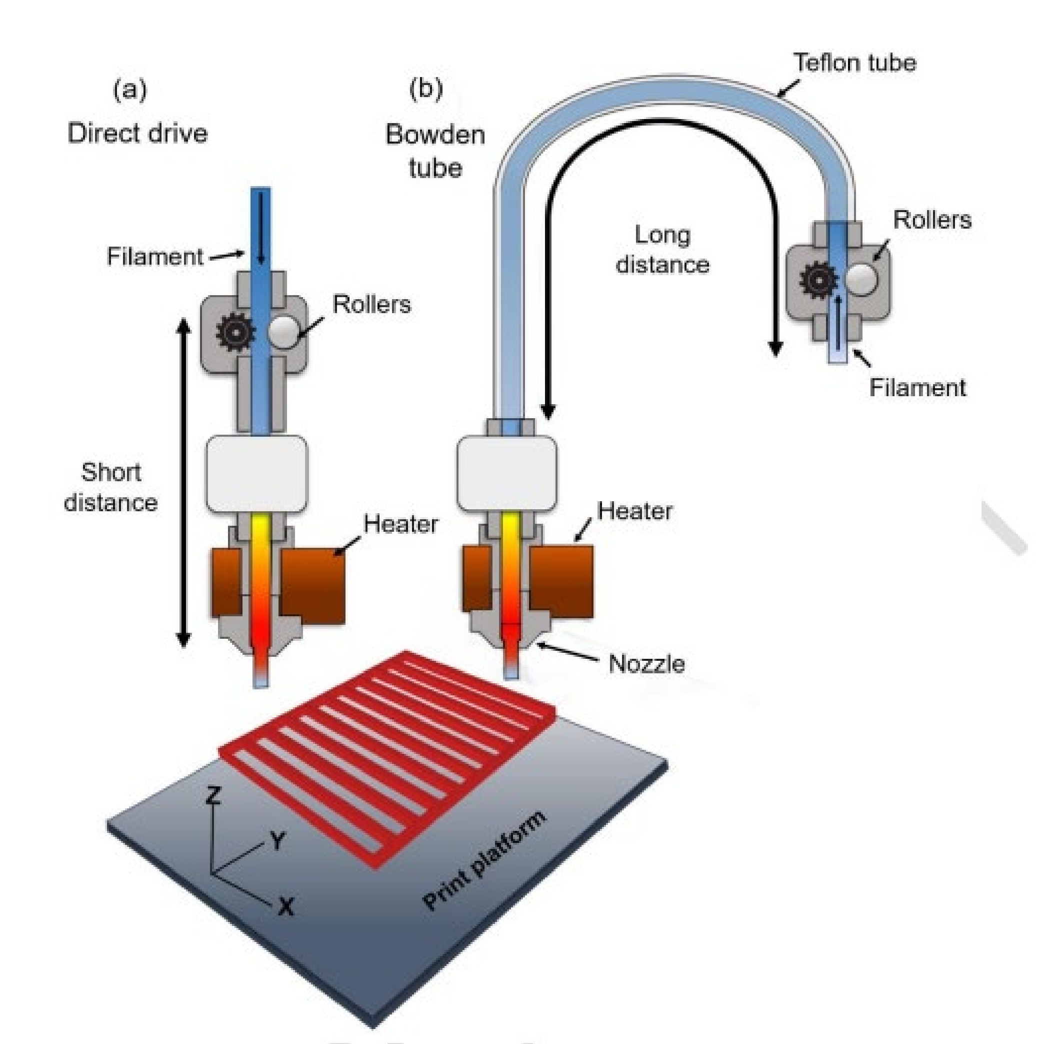
Progress and Current Status of Project

Printer: Qidi 3D X-Plus; Filament: 50 wt.% Graphene-filled filament





Progress and Current Status of Project



Qidi 3D (Direct drive): Good

Ender 3 (Bowden drive)： Bad

Progress and Current Status of Project

Status: Complete

Task/ Subtask	Milestone Title & Description	Planned Completion Date	Verification method
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Task 2.4	Milestone B – Complete the development and evaluation of feedstock pellets	09/30/2022	Documented performance data

Plans for future testing/development/ commercialization

Future testing:

- Electrical and thermal characterizations of filaments;
- Thermo-mechanical characterizations of 3D printed parts

Scale-up potential

- CarbonForm Inc. (filament, 3D printer, and post-treatment process)

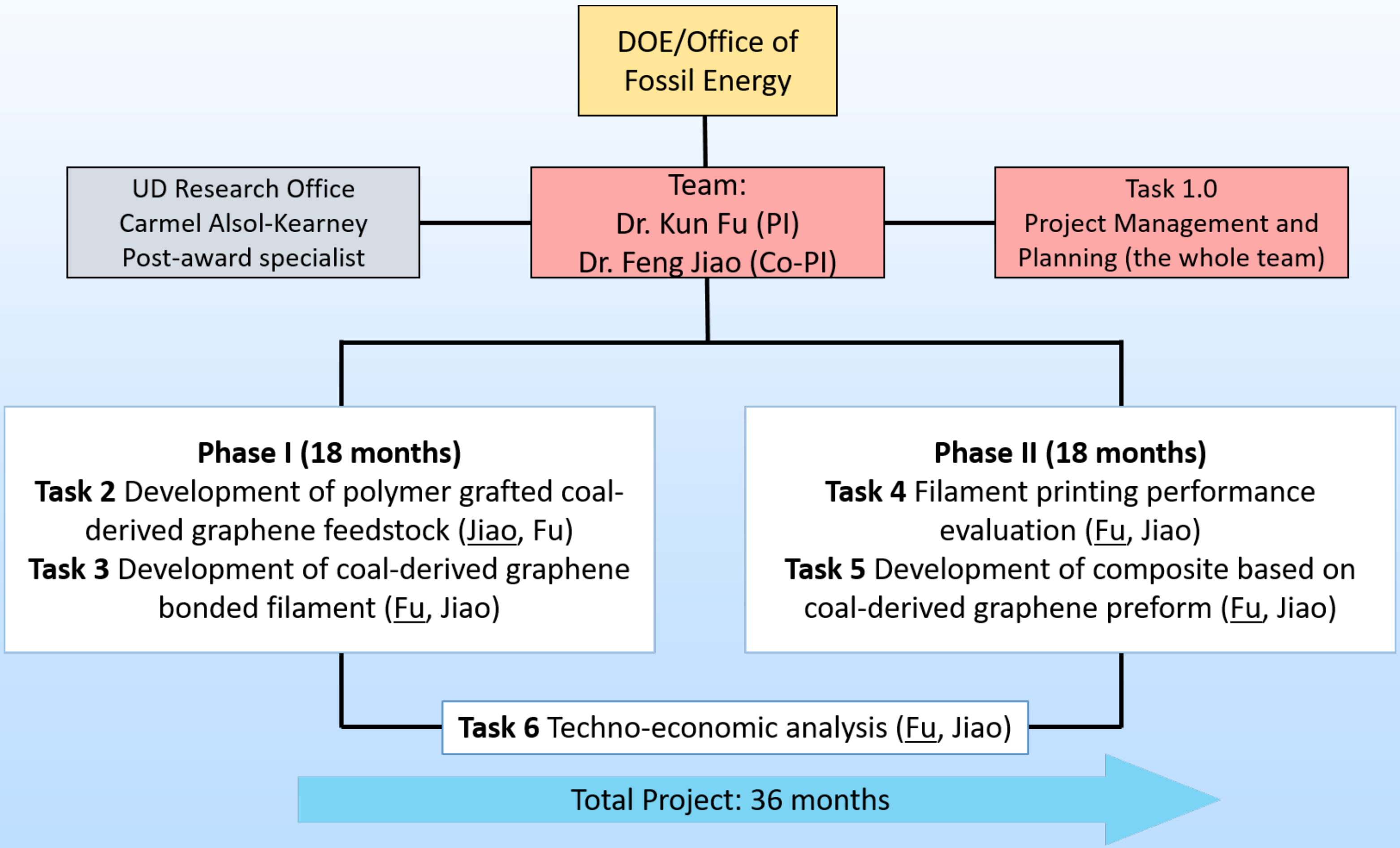
Summary Slide

- Highly loaded carbon-filled (up to 60 wt.%) filament can be achieved
- Vertical filament extrusion is better than horizontal filament extrusion to make filaments
- Direct drive 3D printer is better than Bowden drive 3D printer to print high loading filament
- Highly loaded graphene can be aligned through shear extrusion at FDM nozzle

Appendix

- These slides will not be discussed during the presentation but are mandatory.

Organization Chart



Gantt Chart

Complete

Complete

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Task 6.0	Milestone I – Complete the Techno-Economic Analysis	12/31/2024	Documented analysis results

Task Name	Assigned Resources	Year 1 Q1	Year 1 Q2	Year 1 Q3	Year 1 Q4	Year 2 Q1	Year 2 Q2	Year 2 Q3	Year 2 Q4	Year 3 Q1	Year 3 Q2	Year 3 Q3	Year 3 Q4
Task 1.0 - Project Management and Planning	**Fu**	■	■	■	■	■	■	■	■	■	■	■	■
Task 2.0 – Development of polymer grafted coal-derived graphene feedstock	**Jiao, Fu**	■	■	■									
Subtask 2.1 Examining contaminates in coal-derived graphene	Jiao	■											
Subtask 2.2 Synthesis of polymer grafted coal-derived graphene	Jiao		■										
Milestone A – Complete the development and evaluation of PLA grafted coal-derived graphene	Jiao		◆										
Subtask 2.3 Evaluation of polymer grafted coal-derived graphene	Jiao			■									
Subtask 2.4 Fabrication of feedstock pellets	Fu			■									
Milestone B - Complete the development and evaluation of feedstock pellets	Jiao, Fu			◆									
Task 3.0 – Development of coal-derived graphene bonded filaments	**Fu, Jiao**				■	■	■						
Subtask 3.1 Optimization of manufacturing parameters	Fu, Jiao				■								
Subtask 3.2 Fabrication of medium-loading filament	Fu, Jiao				■								
Milestone C - Complete of the trial production of medium-loading (20 wt. %) filament	Fu, Jiao				◆								
Subtask 3.3 Fabrication and evaluation of high-loading filament	Fu, Jiao					■	■						
Milestone D - Complete the fabrication and evaluation of high-loading (50 wt. %) filament	Fu, Jiao						◆						
Decision Point 1	Team						●						
Task 4.0 – Filament printing performance evaluation	**Fu, Jiao**							■	■				
Subtask 4.1 Filament printing performance on commercial FDM 3D printers	Fu, Jiao							■					
Subtask 4.2 Evaluation of printed panels	Fu, Jiao								■				
Milestone E - Complete the printing compatibility evaluation of filaments on commercial desktop and industrial 3D printers (0.5 kg filament)	Fu, Jiao								◆				
Task 5.0 Development of composite based on coal-derived graphene preform	Fu, Jiao									■	■	■	■
Subtask 5.1 Fabrication of coal-derived graphene carbon preform	Fu									■	■		
Milestone F - Complete the development of coal-derived graphene preform	Fu										◆		
Subtask 5.2 Fabrication and evaluation of composite based on coal-derived graphene preform	Fu											■	■
Milestone G - Complete the development of graphitic coal-derived graphene reinforced composite coupons	Fu, Jiao												◆
Task 6.0 Techno-economic analysis	Fu, Jiao						■						■
Decision Point 2	Fu, Jiao												●