Coal Enhanced PEEK Filament Production for Additive Manufacturing in Industrial Services

DE-FE0032146

Dr. Lakshmi Vendra, Baker Hughes

Dr. Patrick Johnson, University of Wyoming

U.S. Department of Energy

National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
April 2-4, 2024

Project Overview

- Project Duration: 24 months
- Start Date: July 12, 2022
- Kick-off meeting: September 8, 2022

$1,118,348	$829,573	$288,775
Total Project Cost	Federal Commitment	Cost Share

Project Objectives

Project Status

Task/ Subtask	Milestone Title & Description	Completion Date	Verification Method
1.0	**Kick-off meeting**	**Sep 8, 2022**	**Project kick-off meeting**
2.3	**Successful integration of coal in PEEK filament**	**Sep 2023**	**Being able to extrude filament with coal and inspecting for desired volume fraction**
2.4	**Coal Enhanced Filament Performance Data**	**March 2024**	**Coal-derived material property data**
2.5	Successful printing of test coupons using modified PEEK	June 2024	Print test coupons to desired shape and size using commercial 3D printer and coal-enhanced PEEK filament. Verified for dimensional accuracy.

Project Objectives

- **Performance Period 1**: 12 months
  - Development of coal-enhanced PEEK filament
  - Integration of coal-enhanced PEEK filament with commercially available 3D printer
- **Performance Period 2**: 12 months
  - Print and test a product to quantify properties of coal-enhanced PEEK filament
  - Compare & Contrast performance to quantify benefits

Scope: ***Successfully print product using coal-enhanced PEEK filament***

Project Team

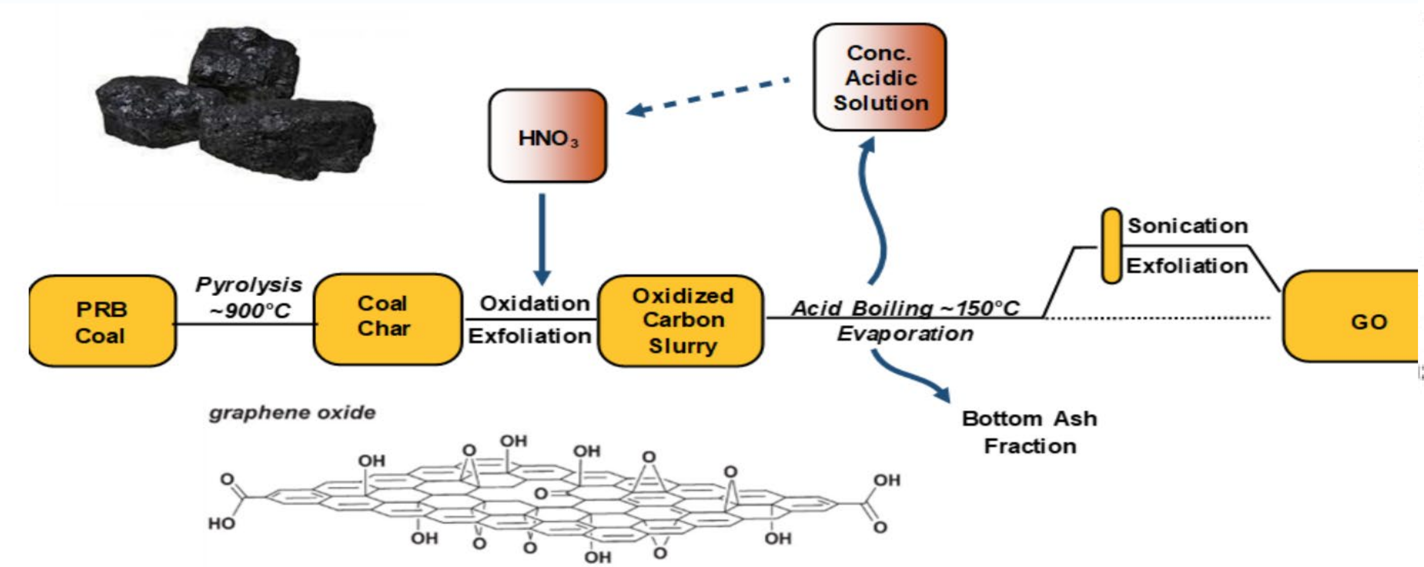
Baker Hughes Team

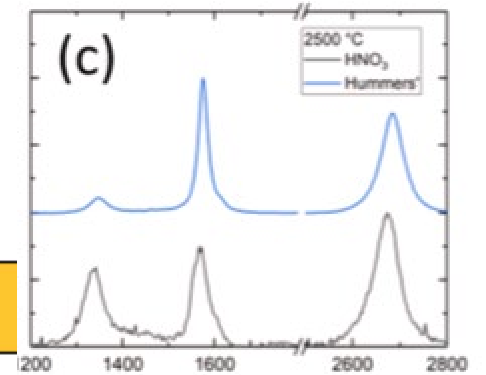
- Dr. Lakshmi Vendra (PI)
- Brian Wieneke
- Dr. Wei Chen
- Chad Yates
- David Leach
- Kathleen Hanson
- Ryan Antle
- Monte Lively Jr.

University of Wyoming Team

- Dr. Patrick Johnson
- Anthony Richard
- Hud Wahab
- Jacob Heil
- Maxwell Rathweg
- Jacob Wozny
- Caleb Johannesmeyer
- Abigail Gruner

Technology Background





Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

ELSEVIER

Evolution of structural and electrical properties in coal-derived graphene oxide nanomaterials during high-temperature annealing

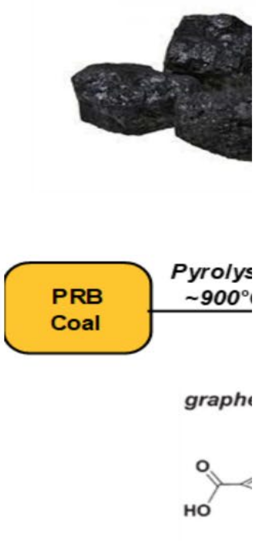
Ana Paula Martins Leandro, Michael A. Seas, Kaitlyn Vap, Alexander Scott Tyrrell, Vivek Jain, Hud Wahab*, Patrick A. Johnson*

Department of Chemical Engineering, University of Wyoming, 1000 E University Avenue, 82071 Laramie, WY, United States of America

Table 3
Comparison of powder electrical conductivity with literature.

Material	Annealed temperature [°C]	Conductivity [10^3 S m^{-1}]	Ref.
Ordered mesoporous carbon	1500	2.82	[39]
Graphite	–	2.12	[38]
Graphene		0.26	
Graphite	–	2.50	[66]
Reduced GO		2.42	
Reduced GO	–	1.50	[67]
Anthracite	950	1.00	[34]
Flake graphite	–	10.6	[42]
Natural graphite		19.7	
Graphene microflower	2000	4.5	[60]
	3000	21.2	
Catalytic-microwave exfoliated graphite oxide	–	53.1	[63]
Graphite	2500	8.98	This work
HNO_3 rGO nanocrystals	2000	2.38 (2.63)	
(Hummers' rGO nanocrystals)	2500	4.81 (4.34)	

Technology Background



US 20210214231A1

(19) **United States**

(12) **Patent Application Publication**

JOHNSON et al.

(10) **Pub. No.: US 2021/0214231 A1**

(43) **Pub. Date: Jul. 15, 2021**

(54) **METHODS FOR PRODUCTION OF GRAPHENE OXIDE**

(71) Applicant: **UNIVERSITY OF WYOMING**, Laramie, WY (US)

(72) Inventors: **Patrick JOHNSON**, Laramie, WY (US); **Ana Paula MARTINS LEANDRO**, Laramie, WY (US)

(73) Assignee: **UNIVERSITY OF WYOMING**, Laramie, WY (US)

(21) Appl. No.: **17/149,242**

(22) Filed: **Jan. 14, 2021**

Related U.S. Application Data

(60) Provisional application No. 62/961,550, filed on Jan. 15, 2020.

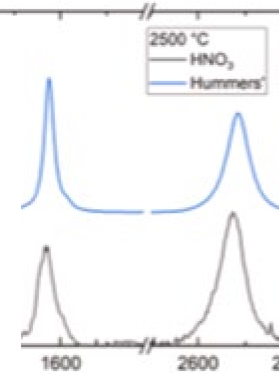
Publication Classification

(51) **Int. Cl.**
C01B 32/198 (2006.01)

(52) **U.S. Cl.**
CPC *C01B 32/198* (2017.08)

(57) **ABSTRACT**

Methods for producing graphene oxide products are disclosed. In one embodiment, a method of producing a graphene oxide product includes contacting a carbon-containing feedstock with an oxidizing composition comprising aqueous nitric acid, wherein the concentration of nitric acid is 50 to 63 wt %, to from a reactant slurry, in response to the contacting step, oxidizing the carbon-containing feedstock of the reactant slurry to form a graphite oxide slurry; and processing the graphite oxide slurry into a graphene oxide product.



ty with literature.

	C]	Conductivity [10^3 S m^{-1}]	Ref.
		2.82	[39]
		2.12	[38]
		0.26	
		2.50	[66]
		2.42	
		1.50	[67]
		1.00	[34]
		10.6	[42]
Natural graphite		19.7	
Graphene microflower	2000	4.5	[60]
	3000	21.2	
Catalytic-microwave exfoliated graphite oxide	–	53.1	[63]
Graphite	2500	8.98	This work
HNO_3 rGO nanocrystals	2000	2.38 (2.63)	
(Hummers' rGO nanocrystals)	2500	4.81 (4.34)	

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Evolution of structural and electrical properties in coal-derived graphene oxide nanomaterials during high-temperature annealing

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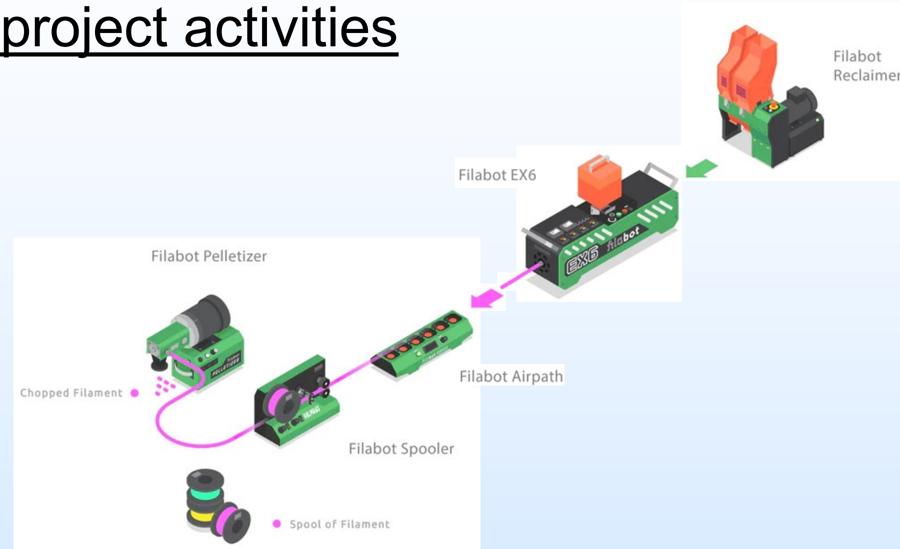
Department of Chemical Engineering, University of Wyoming, 1000 E University Avenue, 82071 Laramie, WY, United States of America

University of Wyoming - Major project activities

Equipment in place

- Extruder system
- Injection molding system



Extruder system parameters: Initial parameters determined with virgin PEEK

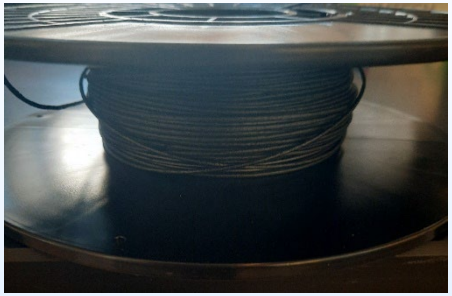
- Temperature profile in extruder
- Extruder screw speed
- Airpath speed
- Spooler speed

Injection molding system parameters: Initial parameters determined with virgin PEEK

- Heater and mold temperatures
- Injection stage times
- Injection stage pressures

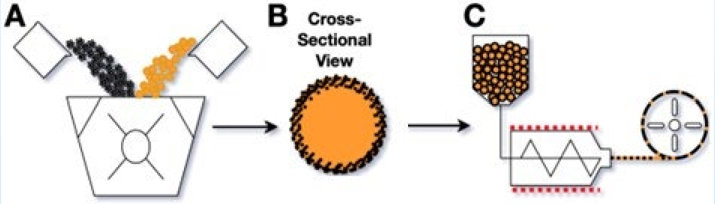
Subtask 2.4 Successful printing of test coupons using modified PEEK	To improve material testing accuracy, this has been altered to use injection molded coupons. Initial injection molding parameters have been determined using PEEK with no filler.

University of Wyoming - Major project activities



Materials preparation achieved

- Coal char (grinding, sieving, drying)
- Graphene oxide (synthesized from coal char)
- PEEK polymer (from Solvay, drying)



Blending of polymer/filler

A. Addition of coal char and polymer to extruder
B. Peak particles are coated with filler material
C. Blended at high temperature and shear rate through extruder

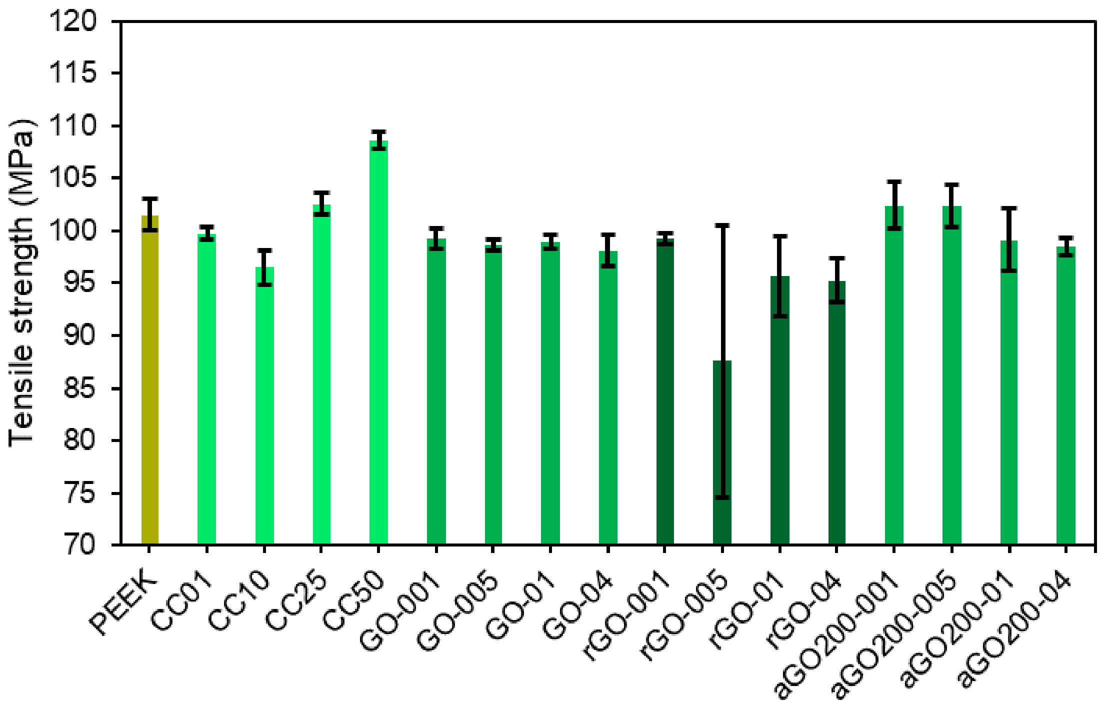
- Blends up to 50 wt% coal char have been produced
- Production of mechanical testing coupons via injection molding
- Graphene oxide and reduced graphene oxide filler tested

University of Wyoming - Major project activities

Characterization of materials

Material characterizations		
Modified polymer		Coal-derived filler
Tensile Strength Tensile Modulus Tensile Elongation, Break Flexural Strength Flexural Modulus Hardness Izod Impact (notched) Thermal Conductivity	Coefficient of Linear Thermal Expansion Deflection Temperature at 0.45 MPa Glass Transition Temperature Dielectric Strength (Short Term) Surface Resistance Water Absorption Density Crystallinity	Density Surface Area Particle Size Thermal Conductivity Molecular Weight Degradation Temperature

Tensile testing comparison of fillers



- GO was annealed at 200C prior to blending
- Tensile strength improved for aGO200 over PEEK
- Also tested aGO400
- Results still being analyzed

Filament production

Filament production for testing at Baker Hughes continues

Spools of 0.5% GO/PEEK and 0.5% rGO/PEEK have been made and shipped

Ongoing activities

- Analysis of aGO200 and aGO400 mechanical testing results
- Perform DSC on annealed GO/PEEK samples

Future activities

- Testing of printed samples from Baker Hughes
- Examine drying method for PEEK before blending
- Complete remaining characterizations

Unmodified Filament or Resin*1	PEEK				
Coal Derived Additive*2	Coal derived char (plain, GO, rGO)				
Coal Additive Source*3	Powder River Basin coal (subbituminous)				
Injection molded coupon performance					
	Units	Unmodified	PEEK + coal char	PEEK + GO	PEEK + rGO
Cost	\$/kg	~100-200	<100	TBD	TBD
Additive Loading	Wt. %	0	1-40	0.1-4	0.1-4
Tensile Strength	MPa	101.5	96.5-108.6	98.1-99.2	87.6-99.3
Tensile Modulus	MPa	5190	5164-8049	4785-5099	4571-5000
Tensile Elongation, Break	%	109	3.6-39.9	29.2-90.5	16.3-64.4
Flexural Strength	MPa	141	152-179	156-163	152-165
Flexural Modulus	MPa	3787	3336-5545	2890-3429	3770-3906
Hardness*5	M, R, Shore D	84.5[19]	TBD	TBD	TBD
Izod Impact (notched)	J/m^2	8000[19]	TBD	TBD	TBD
Coefficient of Linear Thermal Expansion	10^{-6} m/(m °C)	45[19]	TBD	TBD	TBD
Deflection Temperature at 0.45MPa	°C	152[19]	TBD	TBD	TBD
Glass Transition Temperature	°C	136.6	140.7-143.8	138.9-142.3	141.7-143.2
Thermal Conductivity	W/mK	0.32[19]	TBD	TBD	TBD
Dielectric Strength (Short Term)	MV/m	23[19]	TBD	TBD	TBD
Surface Resistance	Ohm/sq	NA	>20 MOhm	>20 MOhm	>20 MOhm
Water Absorption*6	Wt. %	0.45[19]	0.18-0.33	0.02-0.1	0.02-0.45
Density	g/cm^3	1.30	1.27-1.37	1.20-1.27	TBD
Crystallinity	%	33.3	26.2-34-8	32.4-35.9	32.9-42.0

Technical/Economic Challenges

Perceived Risk	Risk Rating			Mitigation/Response Strategy
	Probability	Impact	Overall	
Financial Risks:				
Raw material supply risk	Low	High	High	Well-established relationships with raw material suppliers. Look for alternative suppliers as applicable
Cost/Schedule Risks				
Cost estimates could be affected by delays in project schedule	Low	Medium	High	Regular report-outs to ensure the project is on schedule and doesn't impact cost estimates
Technical/Scope Risks				
Coal derived material is not compatible with PEEK	Medium	Medium	High	Robust test matrix for blending parameters. Go/No go decision
Modified PEEK filaments cannot be extruded	Medium	Medium	High	Leverage Univ. of Wyoming extrusion expertise. Go/No go decision
Modified part performance is not improved	Low	Medium	High	Explore economic impacts, consider other end use applications
Health, Safety, & Environmental Risks:				
Competency of operators working on 3D printers and handling coal-enhanced PEEK material	Low	High	High	AM process and procedures handling 3D printers and polymer materials following HSE guidelines and standards are well established at Baker Hughes.

Project Status

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Plans for future testing/development/ commercialization

After the project:

- Partnering with raw material suppliers to commercialize enhanced PEEK filament fabrication
- Collaborating with OEMs to address scalability challenges
- Wyoming state investing in demonstration plant for coal char and pilot plant for graphene oxide material generated from coal wastes – improves future availability, utilization and applications of the material

Outreach and Workforce Development Efforts or Achievements

- Workforce Development
  - 2 post-doctorate students at University of Wyoming
  - 2 undergraduate students currently working on the project
  - 2 previous undergraduates (graduated)
  - 1 graduate student (MS)

Summary Slide

- Successfully developed PEEK filament enhanced with coal additives – coal char, graphene oxide & reduced graphene oxide
- Filament extrusion process and optimal volume fractions of additives established
- Printing trials ongoing for using coal-enhanced PEEK filament on commercial 3D printer

Next Steps:

- Print and test a product to quantify properties of coal-enhanced PEEK filament
- Compare performance & quantify benefits

Appendix

Organization Chart

FE

Principal Investigator

Dr. Lakshmi Vendra (HOU)

Additive Manufacturing Team

Brian Wieneke, Dr. Wei Chen, Chad Yates, Monte Lively Jr.

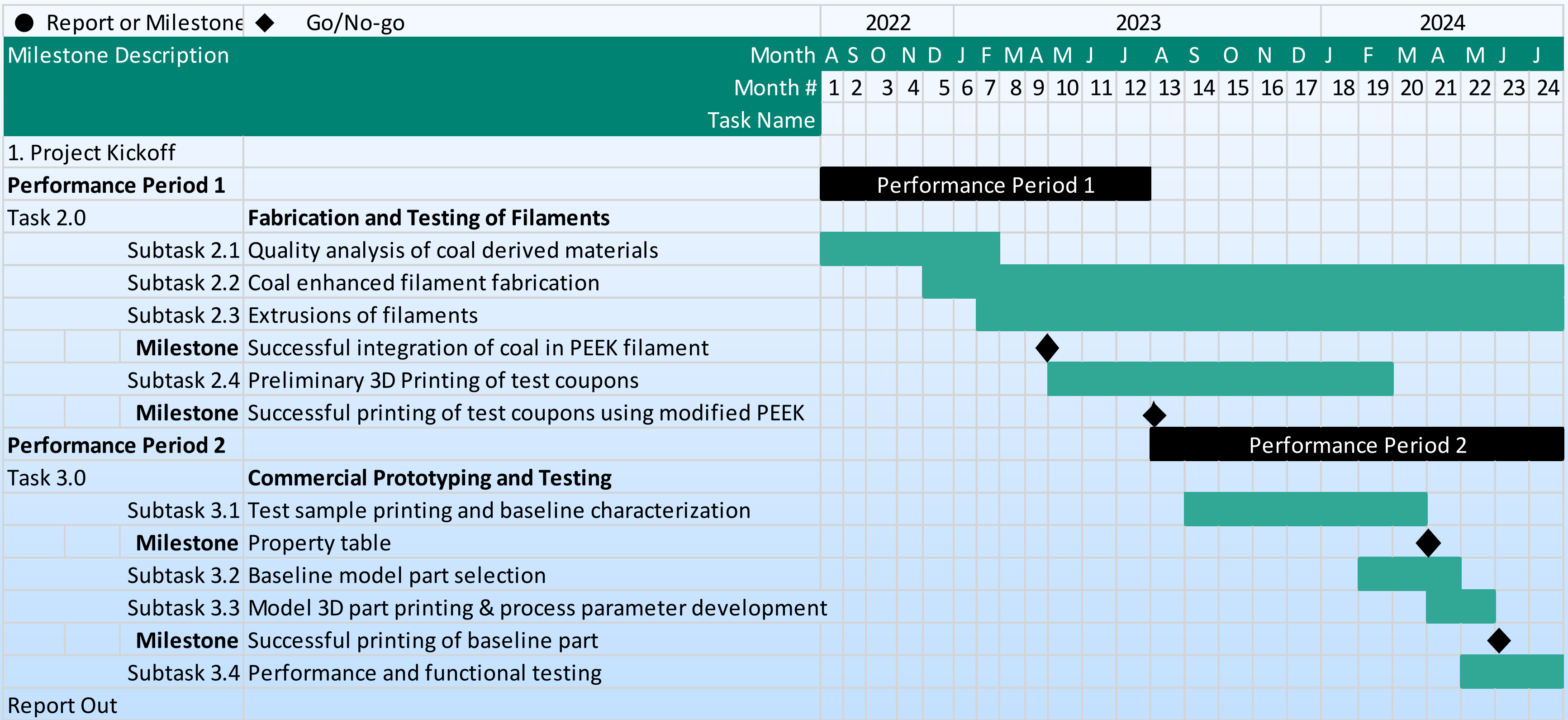
Project Management Support Team

Ryan Antle (OKC), , Kathleen Hanson, David Leach (HOU)

University of Wyoming Team

Dr. Patrick Johnson, Maxwell Rathweg, Jacob Wozny, Anthony Richard

Gantt Chart


Report or Milestone
Go/No-go
2022
2023
2024
Milestone Description
Month A S O N D J F M A M J J A S O N D J F M A M J J
Month # 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Task Name
1. Project Kickoff
Performance Period 1
Performance Period 1
Task 2.0 Fabrication and Testing of Filaments
Subtask 2.1 Quality analysis of coal derived materials
Subtask 2.2 Coal enhanced filament fabrication
Subtask 2.3 Extrusions of filaments
Milestone Successful integration of coal in PEEK filament
Subtask 2.4 Preliminary 3D Printing of test coupons
Milestone Successful printing of test coupons using modified PEEK
Performance Period 2
Performance Period 2
Task 3.0 Commercial Prototyping and Testing
Subtask 3.1 Test sample printing and baseline characterization
Milestone Property table
Subtask 3.2 Baseline model part selection
Subtask 3.3 Model 3D part printing & process parameter development
Milestone Successful printing of baseline part
Subtask 3.4 Performance and functional testing
Report Out