Coal-Waste-Enhanced Filaments for Additive Manufacturing of High-Temperature Plastics and Ceramic Composites

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PROJECT OVERVIEW

Overview

- Funding
  - Federal = $998,840
  - Non-Federal = $259,949
  - Total Project = $1,258,789
- Period of Performance: 2/1/22 – 1/31/25
- Team Members
  - University of North Dakota Energy and Environmental Research Center (EERC)
  - Clemson University
  - Virginia Tech

Objectives

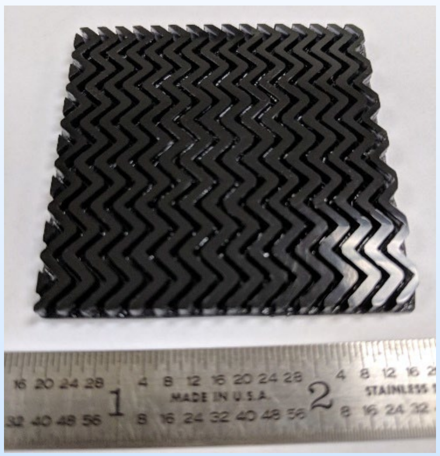
1. Leverage polymer technology to produce a coal-waste enhanced melt-processable resin system that can be extruded into a filament and show that it prevents leaching of undesirable elements.
2. Use coal waste materials as fillers to improve properties of an existing proprietary stable, inorganic, non-flammable resin.
3. Produce enough filament using each of the 2 coal wastes to manufacture test parts using a commercial 3D printer.
4. Produce 2 types of prototype parts through additive manufacturing: (1) composed of coal-waste enhanced high temperature resin and (2) a coal-waste filled ceramic composite part
5. Model the effect of the 2 different coal waste materials on the physical and mechanical properties of the resin
6. Perform a market analysis and techno-economic analysis. We will also describe how this technology will advance environmental justice by revitalizing hard-hit coal mining and energy generation communities.

TECHNOLOGY OVERVIEW

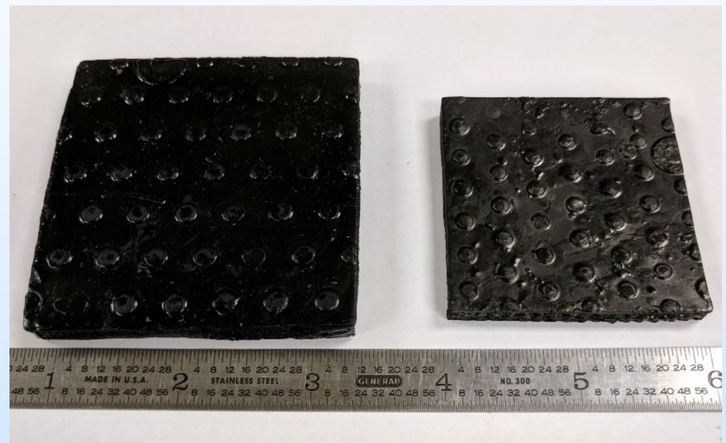
MODIFIED CERAMIC-FORMING POLYMERS

- Semplastics has spent the last four years working with coal and coal waste, and in this time, has developed processes to produce numerous building components out of mined carbon ore that have superior properties to competing products.
- Semplastics has developed and patented a family of inorganic polymers that can be 3D-printed into complex parts and converted into solid ceramic components.
- Semplastics will leverage its unique experience with both coal waste and 3D printing to develop 3D printer filaments using at least two of the most common coal waste materials – bituminous coal fines and fly ash
- Semplastics' technology utilizes most types of coal waste successfully without any pre-selection or pre-processing requirements other than a nominal particle-size reduction for wastes like bottom ash. ***This characteristic of Semplastics' solution will enable the use of much larger volumes of a more comprehensive range of coal wastes than any other coal-to-products technology.***

Technology Background cont.



(a)



(b) & (c)

Parts 3D printed by Semplastics in previous work. (a) part made from Semplastics' UV-curable resin with 3% coal fines; (b) cured (plastic) part; (c) fired (ceramic) part.

TECHNICAL APPROACH/PROJECT SCOPE

Project Scope

Budget Period 1 (Months 1-18)

- Develop filament materials by mixing melt-processable resin system with 2 types of coal waste
- Confirm reduction of leaching of undesirable elements
- Produce control material using commercial fillers
- Test material properties of experimental system against current for tensile strength and modulus, yield strain, impact and heat deflection temperature
- Build a performance model
- Begin techno-economic model

Budget Period 2 (Months 19-36)

- Produce filaments from best performing formulations for development of 3D printing parameters
- Demonstrate filament is compatible with current commercially available 3D printers
- Produce high-temperature resin-based components and ceramic components from each type of coal waste
- Perform leach testing on produced components
- Optimize mechanical / thermal performance model
- Update techno-economic model to consider tradeoffs

Milestones

Milestone	Milestone Title & Description	Planned Completion Date	Verification Method
M1	Required Materials Produced	12 Sep 2022	Materials property testing
M2	Fillers Mixed and Tested	23 Dec 2022	Correct flow behavior shown
M3	Improvements Demonstrated	22 Jun 2023	Mechanical property testing
M4	Initial Filament Produced	7 Dec 2023	Visual inspection
M5	Tested Filament Produced in Quantity	25 Apr-2024	Property testing
M6	Simple Components Produced	24 Oct 2024	Visual inspection
M7	Prototype Articles Produced	30 Jan 2025	Visual inspection

Process Development/Work Plan

- Produce 3 candidate resins designed for the dual cure process
- Demonstrate resin compatibility with fly ash and coal fines
- Determine range of loading for a filament
- Develop a Dual Cure process route to produce a solid filament that melts once in the printhead then cures after deposition without re-melting
- Produce enough filament to feed a 3D Printer and print demonstration parts

Success Criteria

- Production of filament that can be 3D Printed using a standard FDM printer

Risks and Mitigation Strategies

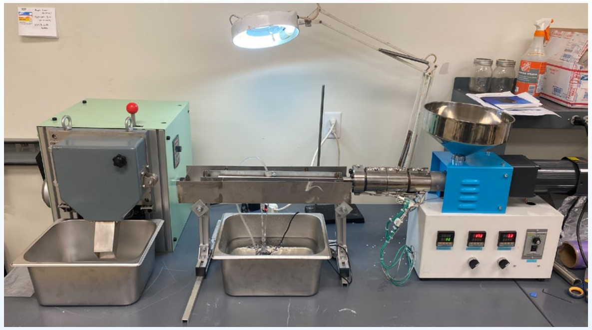
Primary risks

- Unable to produce filaments – minimal; proven on a small scale
- Unable to 3D print without distortion – will modify process

PROGRESS & ACCOMPLISHMENTS

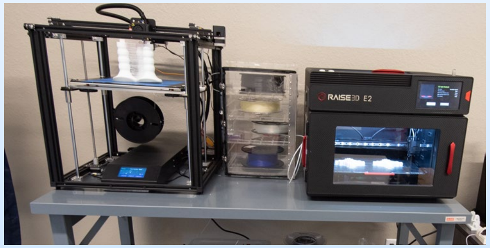
Facilities

- Facilities at a University of Central Florida Incubator
  - Equipment for Compounding plastic and coal waste
  - Equipment for Extruding composite material into a filament
  - Equipment for characterizing the resin formulation and some of the properties of the composite (TGA, FTIR, UTM)
- Facilities in Oviedo, FL
  - These labs are where the 3D Printers are located

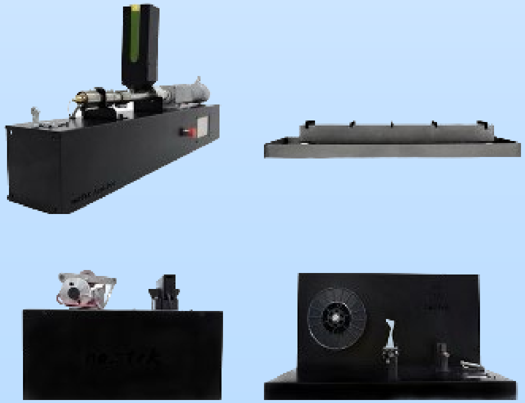


Compounding Line Setup

100L Resin Reactor



3D Printers



Filament Extrusion and Winding

Current Progress

- Obtained equipment
  - High Temperature 3D Printer
  - Extrusion, Pulling and Winding System
- Tested equipment to ensure it's working properly
- Obtained samples of both the coal fines and lignite fly ash that will be used for the research
- Demonstrated the encapsulation process for coating coal fly ash particles with a high-temperature-stable inorganic resin
- Demonstrated ability to coat fly ash with 1st generation melt-processable resin and produce crude extrusions

Current Progress cont.

- Produced samples of different fly ash and resin ratios to begin determining the effect of filler content on the melt temperature of the baseline B182 resin using lignite fly ash
- Began evaluating the melt-flow temperature of each formulation
- Designed a 2nd formulation that demonstrated a higher melting point which would resulted in a decrease to the room temperature tackiness.
- Produced a filament containing -45 micron fly ash at a 67% filler loading using a small hand extruder

Initial Leach Testing

Table 1. RCRA Elements Results

Element	LP Minerals Coal Extract
Arsenic	0.018 mg/L
Barium	0.070 mg/L
Cadmium	0.022 mg/L
Chromium	0.095 mg/L
Lead	<0.010 mg/L
Mercury	<0.2 µg/g
Selenium	0.047 mg/L
Silver	<10 µg/L

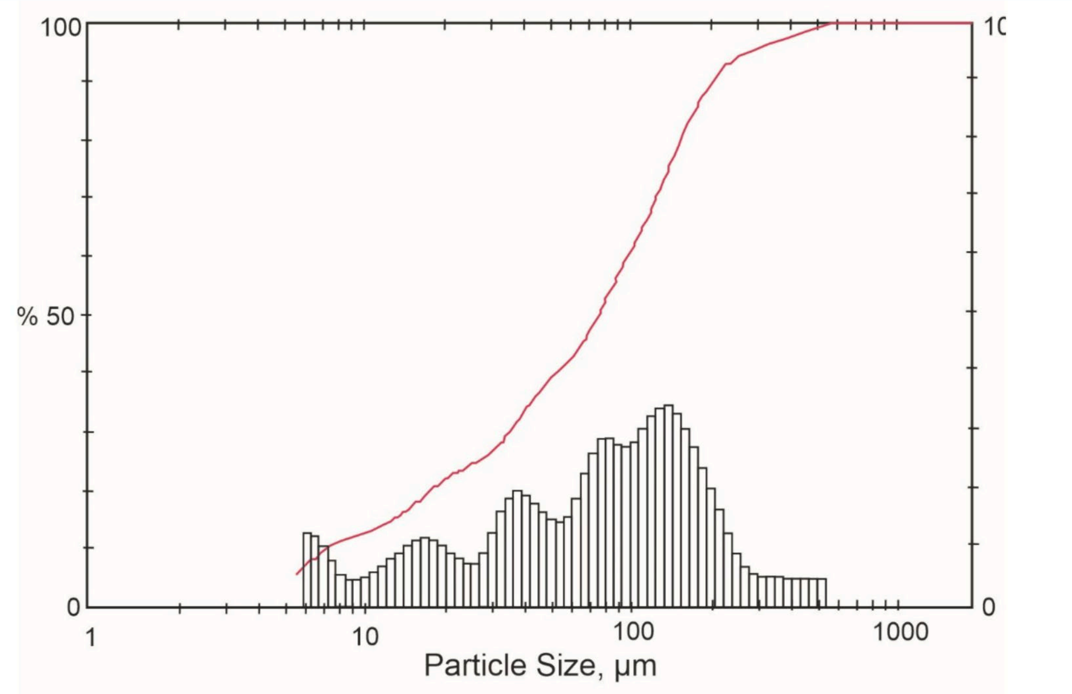
Table 2. EPA Regulatory Limits for RCRA Metals from TCLP Extracts, mg/L

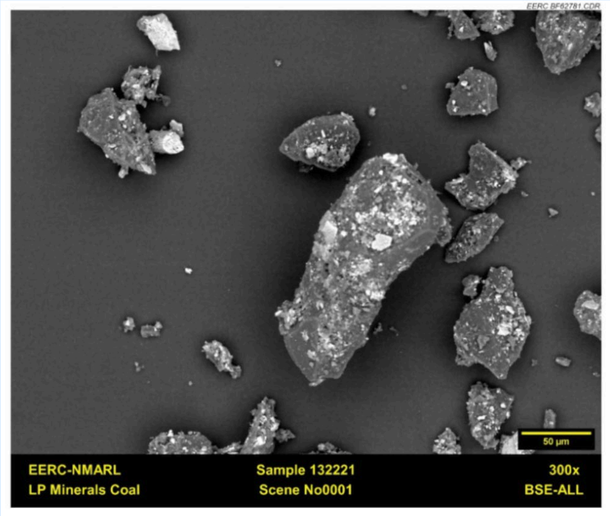
Arsenic	5
Barium	100
Cadmium	1
Chromium	5
Lead	5
Mercury	0.2
Selenium	1
Silver	5

The leach testing showed very low levels of unwanted impurities of the raw coal (well below the EPA allowable limits). Additional testing of the coated coal and the coated coal embedded in plastic will also be tested.

Characterization

The coal fines were analyzed after removal of most of the moisture and found to contain 45.60% fixed carbon, 31.94% volatiles and 20.92% ash along with 1.54% residual moisture.





Particle size analysis using a Malvern particle size analyzer indicated a multimodal size distribution with a median particle size of 75 micrometers, ranging from 7 micrometers to 300 micrometers. The material will have to be sieved to provide the <45 micron material needed for filament development.

Initial Trials

3 mm Filament of B215 Resin and 67% Fly Ash

3 Layers of Stacked Filaments
after 250°C Cure

Summary and Next Steps

Key Findings

- Have developed and confirmed formulations of inorganic melt processable resin that utilize a dual cure mechanism
- Can produce extrudable filaments with greater the 60% mass loading of fly ash/CCR
- Can produce extrudable material with greater than 55% carbon ore fines
- Can produce filled resin that can be extruded, stacked in layers, then re-heated sufficiently to bond layers together with minimal distortion

Next Steps

- Optimize the filler to resin ratio for each carbon ore waste type
- Produce filaments of each carbon waste in resin
- Develop 3D printing parameters for each filament type
- Produce 3D printed parts as demonstration
- Determine microstructure and properties of the 3D printed materials

Key Takeaways

- Unlike many other coal-to-products technologies, this solution does not require high levels of pre-selection or pre-processing outside of size reduction and therefore will enable the use of much larger volumes of a more comprehensive range of coal waste than most any other technology
- Through this project we will demonstrate filament material for 3D Printing utilizing 30-60% by mass of coal waste.
- We anticipate this coating technology could also be applicable for loading coal waste as filler in most commercial organic resins which would dramatically increase the amount of coal waste used each year into billions of pounder per year.

Acknowledgments

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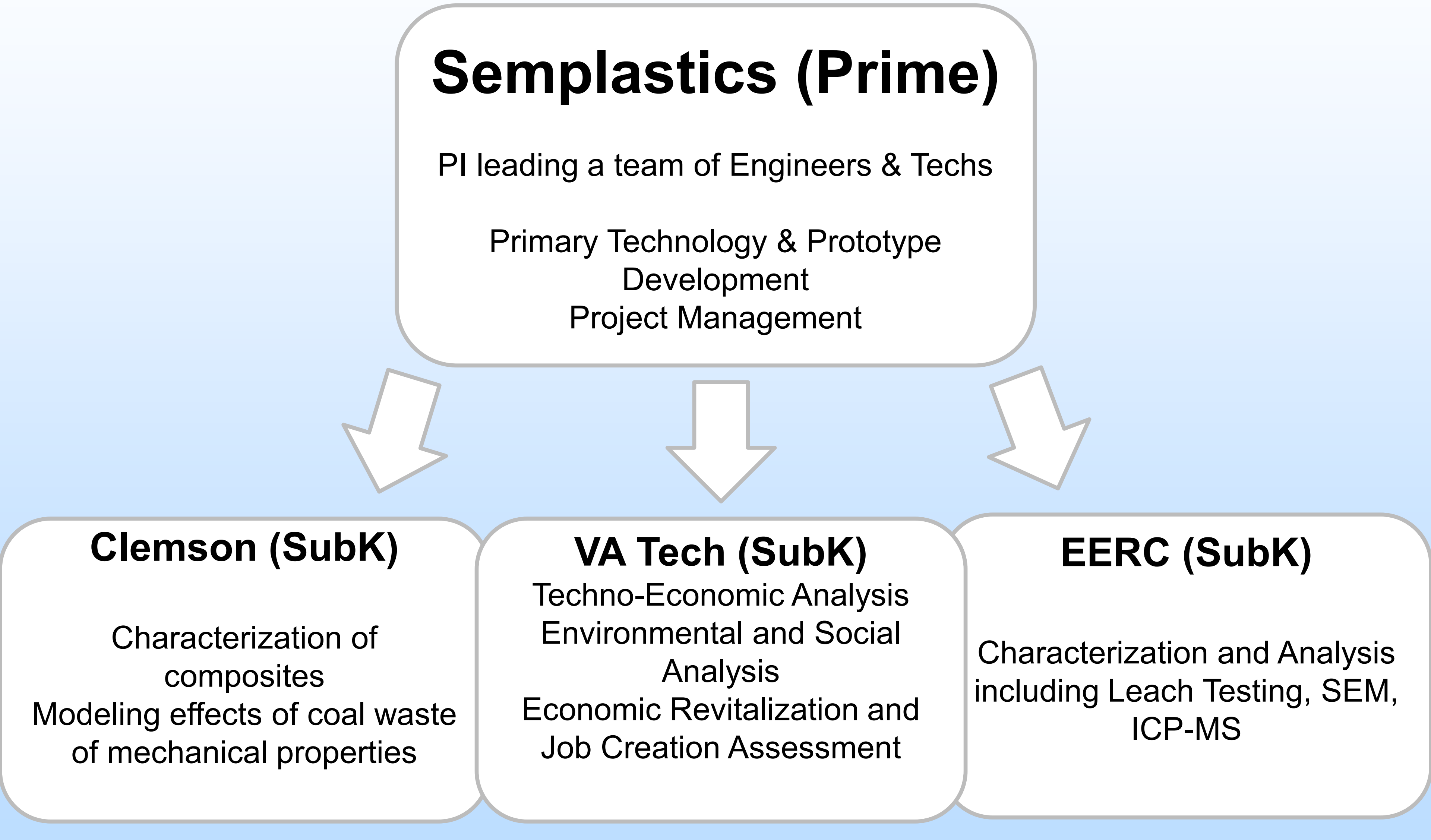
- Clemson
  - Professor – Dr. Rajendra Kumar Bordia
  - Professor – Dr. Fei Peng
  - Lab Manager – Lee Williams
- Virginia Tech
  - Professor - Dr. Aaron Noble

APPENDIX

Organization Chart



Gantt Chart

Task	Description	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.0	Project Management & Planning												
2.0	Coal Waste Encapsulation and Leach Testing												
M1	Required Materials Produced												
M2	Resins / Fillers Mixed and Tested												
3.0	Demonstration of Improvements from Use of Coal Waste Fillers												
M3	Improvements Demonstrated												
4.0	Determination of Best Extrusion Parameters for Filaments												
M4	Initial Filament Produced												
M5	Tested Filament Produced in Quantity												
5.0	Prototype Test Article Production												
M6	Simple Components Produced												
M7	Prototype Articles Produced												
6.0	Physical & Mechanical Performance Modeling												
7.0	Market and Techno-Economic Analysis												