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

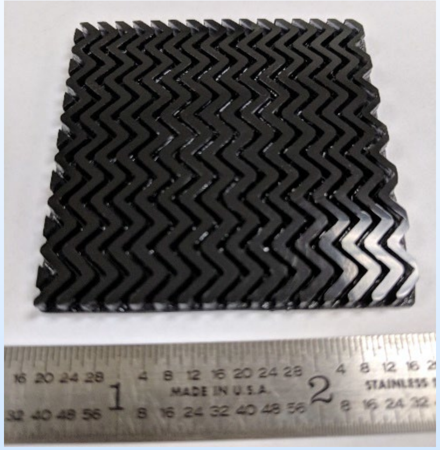
1. Leverage polymer technology to produce a coal-waste enhanced melt-processable resin system that can be extruded into a filament and show that it prevents leaching of undesirable elements.
2. Use coal waste materials as fillers to improve properties of an existing proprietary stable, inorganic, non-flammable 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

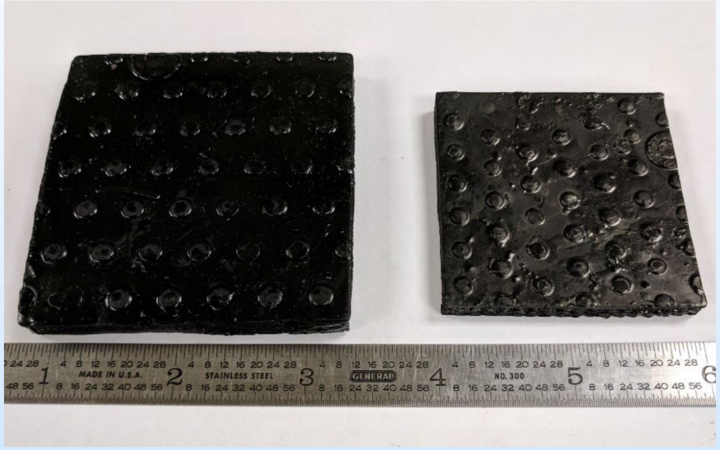
MODIFIED CERAMIC-FORMING POLYMERS

- 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	Completion Date	Verification Method
M1	Required Materials Produced	12 Sep 2022	8 Sep 2022	Materials property testing
M2	Fillers Mixed and Tested	23 Dec 2022	22 Dec 2022	Correct flow behavior shown
M3	Improvements Demonstrated	22 Jun 2023	29 Jun 2023	Mechanical property testing
M4	Initial Filament Produced	7 Dec 2023	1 Oct 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

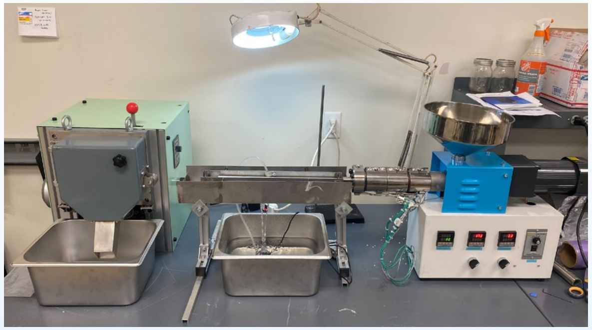
Primary risks

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

PROGRESS & ACCOMPLISHMENTS

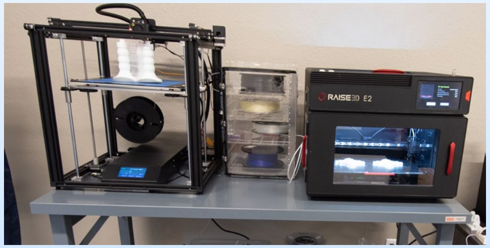
Facilities

- 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

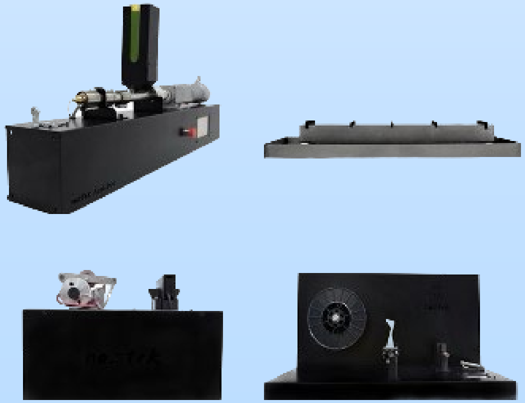


Compounding Line Setup

100L Resin Reactor



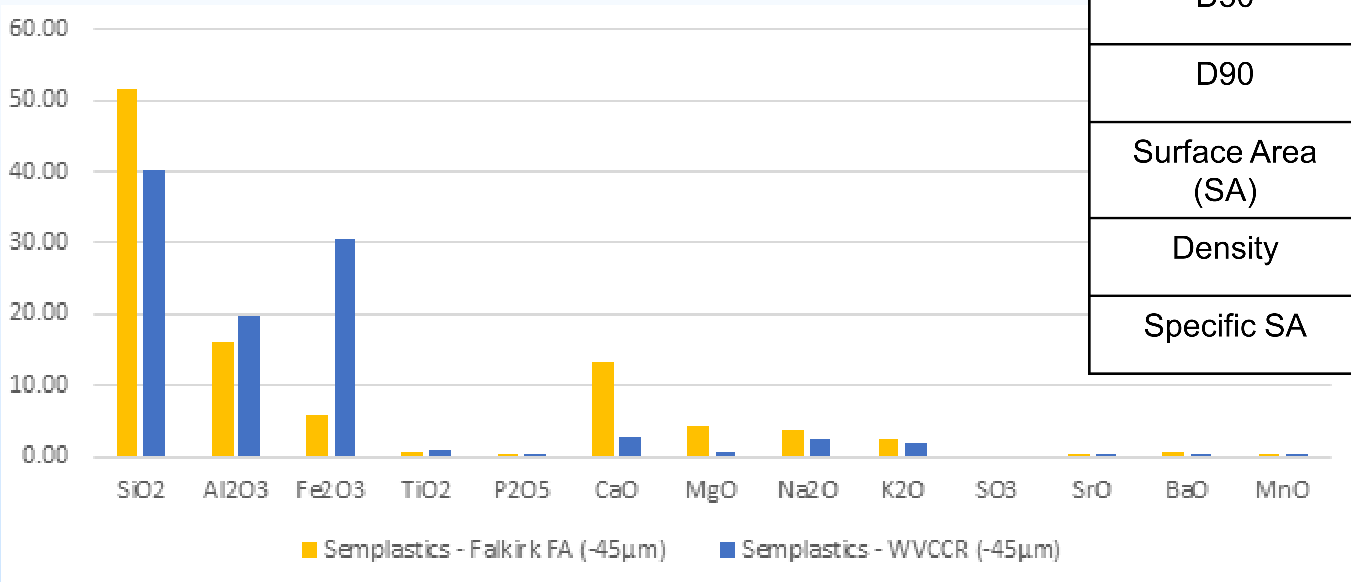
3D Printers



Filament Extrusion and Winding

Task 2.0 – Coal Waste Encapsulation and Leach Testing

Compositional Analysis of Fly Ashes



	Lignite FA	Bit. FA
D50	5.9µ	15.8µ
D90	15.8µ	33.6µ
Surface Area (SA)	0.966 m^2/cc	0.506 m^2/cc
Density	2.564 g/cc	2.688 g/cc
Specific SA	0.377 m^2/cc	0.188 m^2/cc

The Falkirk FA (lignite fly ash or “NDFA”) is quite different from the WVCCR (bituminous fly ash) in composition. The lignite fly ash has much more silica, much less iron, and more metal oxides than the bituminous fly ash, which has a great deal of iron and more alumina. The variations in composition and particle size explain why the materials behave differently in the resins.

Task 2.0 – Coal Waste Encapsulation and Leach Testing

Leach Testing Results

Element	B203+NDFA	B219+NDFA	B203+WVCCR	B219+ABCoal	EPA Limit
Arsenic	0.012 mg/L	0.010 mg/L	0.022 mg/L	<0.010 mg/L	5 mg/L
Barium	0.722 mg/L	1.04 mg/L	0.033 mg/L	0.027 mg/L	100 mg/L
Cadmium	<0.005 mg/L	<0.005 mg/L	<0.005 mg/L	<0.005 mg/L	1 mg/L
Chromium	0.013 mg/L	0.031 mg/L	0.006 mg/L	<0.005 mg/L	5 mg/L
Lead	<0.010 mg/L	<0.010 mg/L	<0.010 mg/L	<0.010 mg/L	5 mg/L
Mercury	<0.2 µg/L	<0.2 µg/L	<0.2 µg/L	<0.2 µg/L	0.2 mg/L
Selenium	<0.010 mg/L	<0.010 mg/L	<0.010 mg/L	<0.010 mg/L	1 mg/L
Silver	<10 µg/L	<10 µg/L	<10 µg/L	<10 µg/L	5 mg/L

The leach testing showed very low levels of unwanted impurities of the leaching that was observed when the coal waste was embedded in the resin matrix.

Task 3.0 – Demonstration of Improvements from Use of Coal Waste Fillers

- Demonstrated improved properties of two melt processable resins by the addition of North Dakota fly ash
- For resin B235, 71% by mass fly ash increased the strength by 80%
- The addition of the filler made the material much less brittle.
- Resin B236 was an attempt to decrease the brittleness of the base resin by reducing the cross-link density.
- B236 resin exhibited a 38% increase in flexural strength vs. B235 and similar modulus.

Test results for resins B235 and B236.
All samples were cured at 250°C for 4 hours.

Sample Group	Max Stress (psi)	Max Stress (Mpa)	Modulus (ksi)
B235 (control) Group A	3584	24.72	303
B235 (control) Group B	2769	19.10	284
B235 (control) Group C	2610	18.00	NM
B235 (control) Group D	2566	17.70	256
B235 (control) Group E	3277	22.60	299
B235 (control) Average:	*2961*	*20.42*	*286*
B235 + -45 NDFA Group A	5311	36.63	107
B235 + -45 NDFA Group B	5394	37.20	112
B235 + -45 NDFA Average:	*5353*	*36.91*	*110*
Change from B235 (control):	*+80.7%*	*+80.7%*	*-61.5%*
B236 (control) Group A	3572	24.63	284
B236 (control) Group B	3769	25.99	304
B236 (control) Group C	3305	22.79	272
B236 (control) Group D	5247	36.19	288
B236 (control) Group E	4565	31.48	289
B236 (control) Average:	*4092*	*28.22*	*287*
Change from B235 (control):	*+38.2%*	*+38.2%*	*+0.0%*

Task 3.0 – Demonstration of Improvements from Use of Coal Waste Fillers

- B183,addition of 71% fly ash improved the strength by 13%
- Increased the modulus by 280%
- Evaluating the adhesion to the particles using scanning electron microscopy (SEM) at Clemson.
- Note that the effectiveness of the catalysts varies
- Cat D has the same effect as 0.25% Cat 5 + 1% Cat D
- Cat 5 is the “B-staging” catalyst, while Cat D is the curing catalyst.

Test results for resin B183.
All samples were cured at 310°C for 4 hours.

Sample Group	Max Stress (psi)	Max Stress (Mpa)	Modulus (ksi)
B183 + 2% Cat D (control) Group A	6772	46.70	287
B183 + 2% Cat D (control) Group B	5997	41.36	284
B183 + 2% Cat D (control) Group C	6478	44.68	312
B183 + 2% Cat D (control) Group D	5652	38.98	287
B183 + 2% Cat D (control) Group E	6359	43.86	307
B183 + 2% Cat D (control) Group F	7565	52.17	327
B183 + 2% Cat D (control) Group G	6842	47.19	279
B183 + 2% Cat D (control) Group H	7889	54.41	315
B183 + 2% Cat D (control) Group I	7393	50.99	327
B183 + 2% Cat D (control) Group J	6792	46.84	325
Average:	*6774*	*46.72*	*305*
B183 + 0.25% Cat 5+ 1% Cat D + -45 NDFA	6453	44.50	1104
B183 + 0.25% Cat 5 + 1% Cat D + -45 NDFA	7678	52.95	1186
B183 + 0.25% Cat 5 + 1% Cat D + -45 NDFA	8063	55.61	1122
B183 + 0.25% Cat 5 + 1% Cat D + -45 NDFA	8513	58.71	1232
Average:	*7677*	*52.94*	*1161*
Change from B183 (control):	*+13.3%*	*+13.3%*	*+281*

Task 4.0 – Determination of Best Extrusion Parameters for Filaments

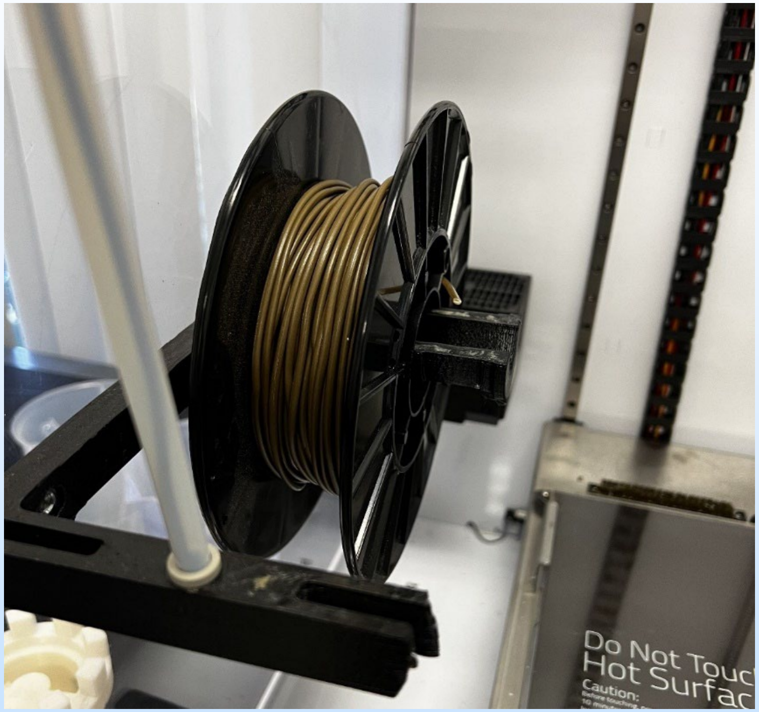
- Evaluated the extrusion behavior of North Dakota fly ash (less than 45 microns) with resin mixes using different catalysts. The catalysts evaluated were:
  - A platinum-based catalyst as a low-temperature catalyst at 0.5% and 1%
  - Cat 5, which is a peroxide initiator, as a low-temperature catalyst at 0.1 to 0.5%
  - Cat D, which is a peroxide initiator, as a high-temperature catalyst at 1% to 2%

- 0.3-0.5% Cat 5 with 1% Cat D provided consistent B-staging behavior for B235
- Extrusion produced a smooth, non-tacky filament
- Bituminous fly ash not as compatible with the B235 resin
- Tended to separate out
- Evaluating bituminous fly ash with B183 and B236

Filament (1.5mm dia.) produced using B235 and lignite fly ash.

Task 4.0 – Determination of Best Extrusion Parameters for Filaments

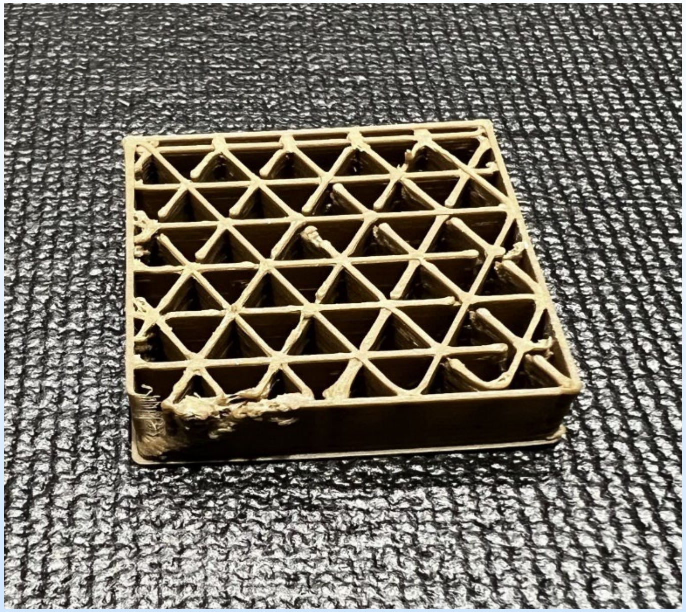
- Semplastics extruded filament made from polypropylene filled with lignite fly ash.
- The filament contains lignite fly ash coated with B207 coating resin that was compounded in our compounder at a 50% mass level
- The pellets were then run through the filament extruder to produce the spool of printer filament.
- It is expected that this coating could also aid in incorporating the various fly ashes into our high temperature resins.



Coated fly ash as 50% mass filler in polypropylene 3D filament in the 3D printer

Task 5.0 – Prototype Test Article Production

The lignite fly ash filament shown in the previous slide was used to 3D-print a small test part using the initial printing parameters that we have established.



A small part made from 50% coated fly ash in polypropylene.

Summary and Next Steps

Outreach and Workforce Development

- Hosted Students from NeoCity Academy for a tour of our labs and introduction to our technology
- Several members of the technical team attended and presented a poster at the NSF ENGINE Workshop: “Catalyzing Additive Manufacturing” at the University of Central Florida

Key Findings

- B-staging temperature range 140-180°C for 1-2 hrs
- Filament extrusion temperature 110-140°C
- Post bake (after printing part) 105-110°C for 12 hrs + 140°C for 4 hours + 250-310°C for 4 hours
- Maximum use temperature (resin dependent) 250-350°C

Next Steps

- Optimize filament extrusion parameters for high temperature resin and fly ash composites
- Extrude enough filament to use in 3D Printer
- Optimize 3D Printing Parameter and post-printing processing as needed
- Produce Test Specimens other Prototype Parts
- Develop model showcasing the impacts of adding fly ash in the materials
- Produce Techno-Economic Analysis and Workforce Implications

Acknowledgments

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  - Professor – Dr. Rajendra Kumar Bordia
  - Professor – Dr. Fei Peng
  - Lab Manager – Lee Williams
- Virginia Tech
  - Professor - Dr. Aaron Noble
- Lignite Energy Council
  - Mike Holmes

APPENDIX

Organization Chart

Semplastics (Prime)

PI leading a team of Engineers & Techs

Primary Technology & Prototype Development
Project Management

Clemson (SubK)

Characterization of composites
Modeling effects of coal waste of mechanical properties

VA Tech (SubK)

Techno-Economic Analysis
Environmental and Social Analysis
Economic Revitalization and Job Creation Assessment

EERC (SubK)

Characterization and Analysis including Leach Testing, SEM, ICP-MS

Gantt Chart

		Year 1				Year 2				Year 3			
Task	**Description**	**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	Resin / Fillers Mixed and Tested				■								
3.0	Demonstration of Improvements from Coal Waste				■	■	■						
M3	Improvements Demonstrated						■						
4.0	Determination of Best Extrusion Parameters						■	■	■	■			
M4	Initial Filament Produced								■				
M5	Tested Filaments 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				■	■	■	■	■	■	■	■	■