Development of Novel Feedstocks: Final Review

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Project Background

- In-space additive manufacturing has the potential to reduce the costs and improve the safety of space operations
- It currently costs roughly $10,000 per kilogram of supplies put into orbit
- Additionally, massive depots of speciality duplicate parts must be maintained on Earth in case of emergency on the ISS
- As of 2016, 3D printers have become compact and sophisticated enough to be installed in the ISS
- Since then, much effort has gone into improving the capabilities of the ISS's Additive Manufacturing Facility (AMF) with better printers, better tooling and stronger materials to help close the performance gap between printed parts and standard aerospace metals

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Project Need

- **2016:** UConn team produces a modified 3D printer to perform in microgravity environments
- **2017:** UConn team produces a system with optimized extrusion parameters for continuous production of recycled ABS filament
- **2018:** UConn team is tasked with the research and development of novel feedstocks compatible with fused deposition modeling (FDM) printers, special interest is in:
    - A robust dissolution and doping procedure for ULTEM-based feedstocks
    - Feedstocks with practical electrical properties
    - Feasibility of in-situ resource utilization in the form of regolith dopant and feedstock recycling

Project Goal

Expand NASA's FDM toolbox with specialized feedstocks

- Development of higher strength filament feedstocks compatible with the standard FDM process
- Bring added functionality (i.e. dielectric properties, piezoelectric properties) to the filaments currently used by NASA
- Incorporate simulants of planetary in-situ materials (such as regolith), and/or materials that would otherwise represent nuisance/discarded materials on space missions.
- Develop a consistent and effective doping process for PEI feedstock
- Post-processing or heat treatment techniques:
  - Must be adaptable to the microgravity environment of ISS
  - Must preserve the characteristic dimensions of the part to the greatest extent possible.

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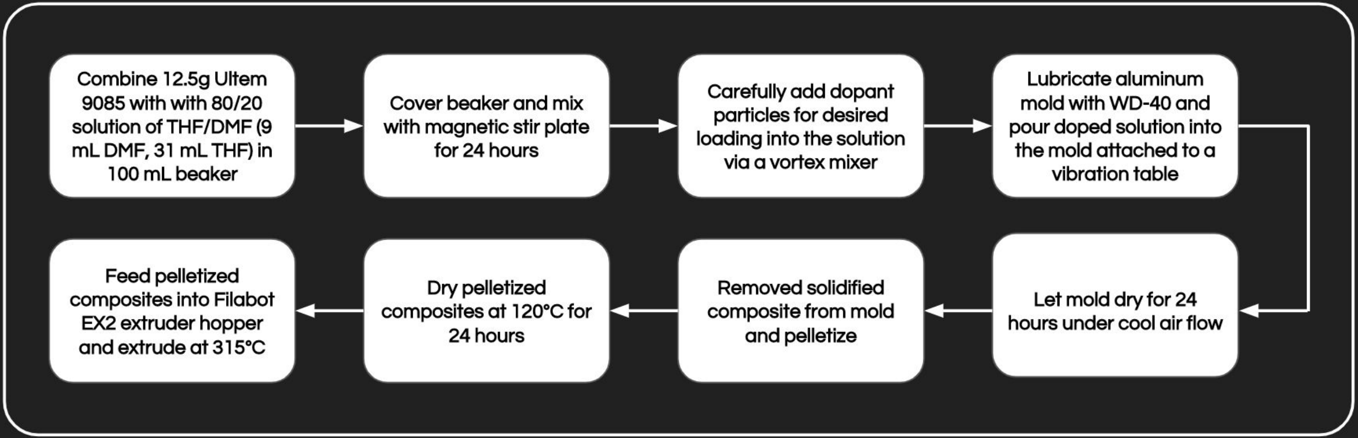
Dopant Materials

Composite Type	Dopant	Wt. Percent Produced
Strength #1	Carbon nanofibers	1, 2, 4
Strength #2	Silicon carbide whiskers	5
Conductive #1	Graphene	1, 2, 4
Conductive #2	Nickel	10, 25, 50
Dielectric #1	Barium titanate	5, 10, 15
Dielectric #2	Lunar regolith	10, 25, 50

Procedure for Fabrication of Composite Filament



Notes:

- 3.4:1 THF-to-DMF ratio for optimal particle suspension
- Particles should be over 200 mesh (under 74 microns) to allow for adequate suspension within solutionized Ultem
- All mixing and casting should be performed in the fume hood due to toxicity of the solvent
- 15 grams of pelletized polymer produces roughly 10 feet of feedstock

Characterization Process

Pelletized matrix material

→

Chemical Dissolution

Mix solvent (e.g. DMF), matrix and dopant for 12-24 hours, vortex mixed

→

Sample Preparation

Sets of four wafers will be injected in custom Al molds for vibe casting and allowed to air dry for 48 hours

→

Level One Characterization

- DSC & MFI
- SEM & VLM
- FTIR
- Hardness Testing
- Electrical Testing

→

Filament Preparation

Favorable composite batches will be scaled to the large filament mold

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Level Two Characterization

- SEM & VLM
- Tensile Testing
- Electrical Testing
- Print Testing

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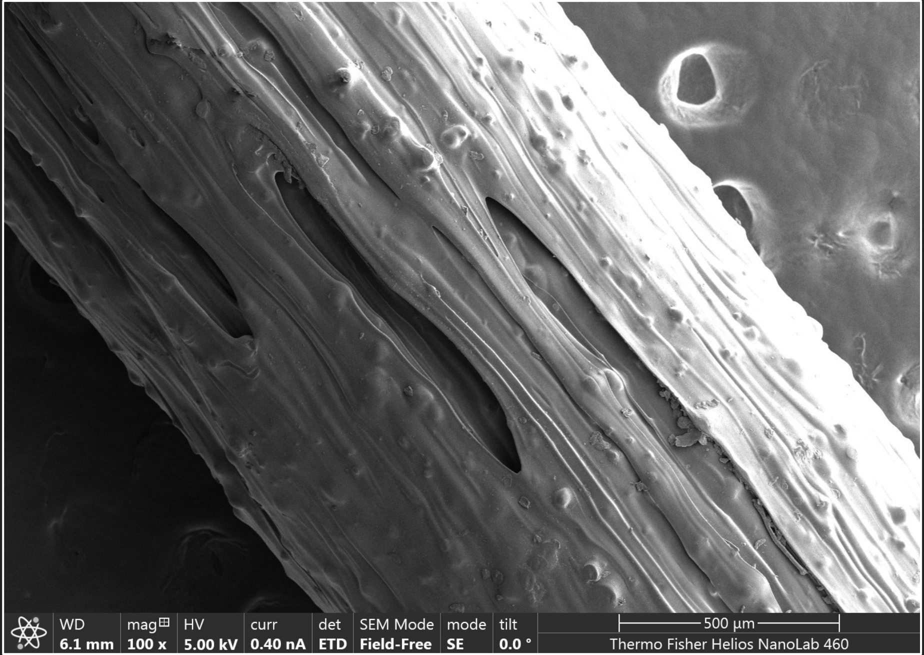
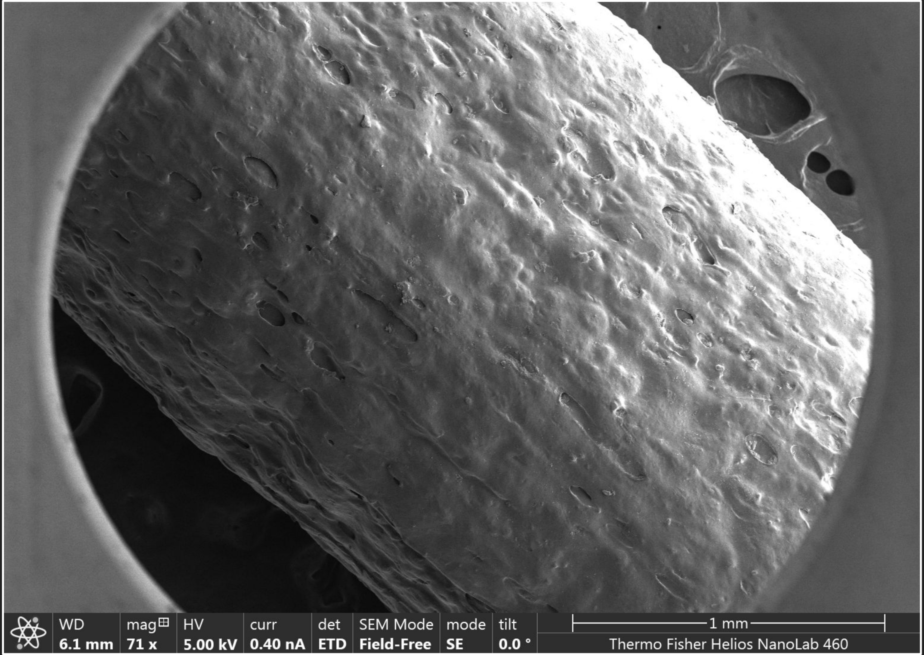
SEM Analysis





SEM Images of Ni (left) and CNF (right) filaments

- Both surfaces have significant roughness
- Ni filament showing significant craters on surface compared to CNF filament
  - Larger particle size compared to nanofiber diameter

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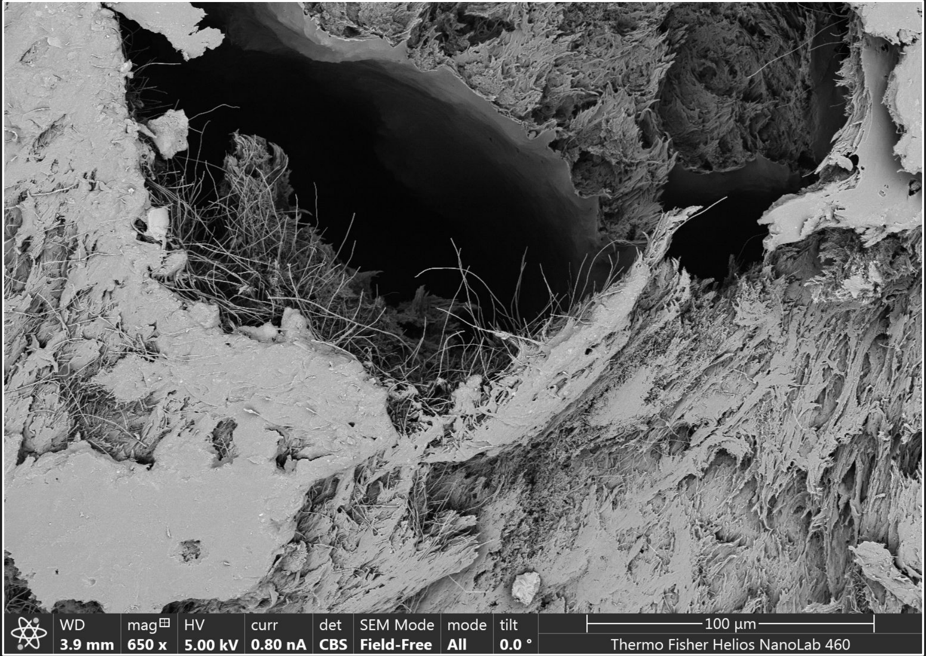
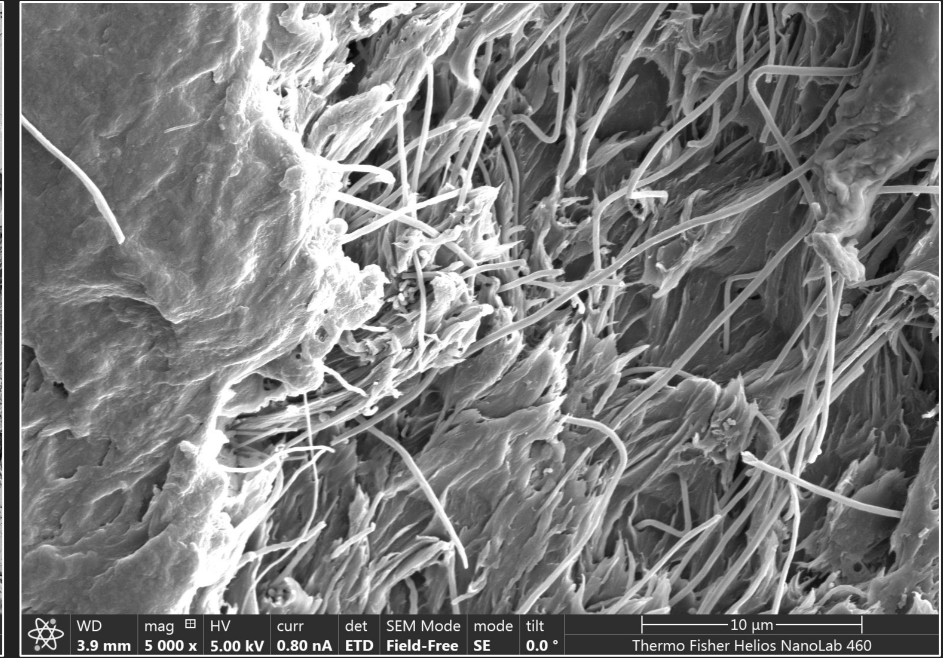
SEM Analysis





SEM Images of CNF wafers (650x on left; 5000x on right)

- Expected random orientation of nanofibers within matrix
- Nanofibers protruding from one side of a pore but not the other (in right image)

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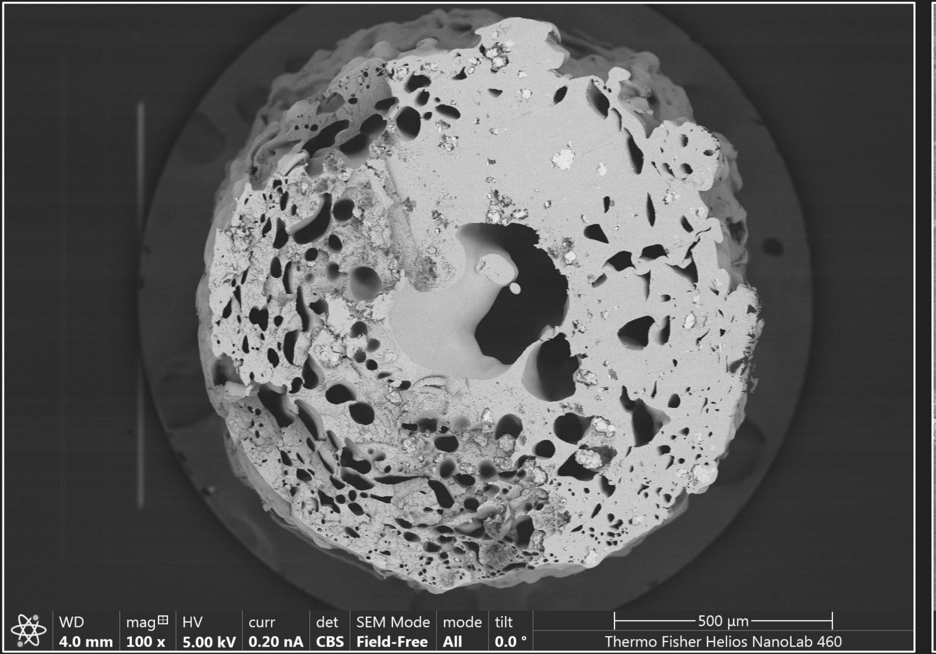
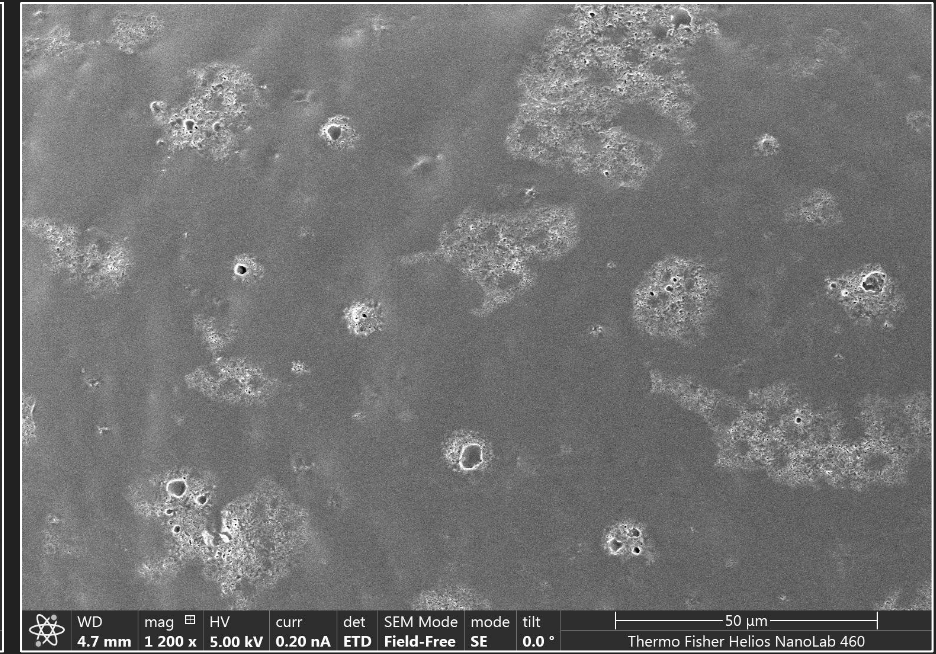
SEM Analysis





SEM Images of Ni filament and wafer (100x filament on left; 1200x wafer on right)

- Significant porosity within extruded filament (left), as well as on surface of cast wafer (right)
- Particle distribution of Ni powder seen (left)

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Continuous Improvement

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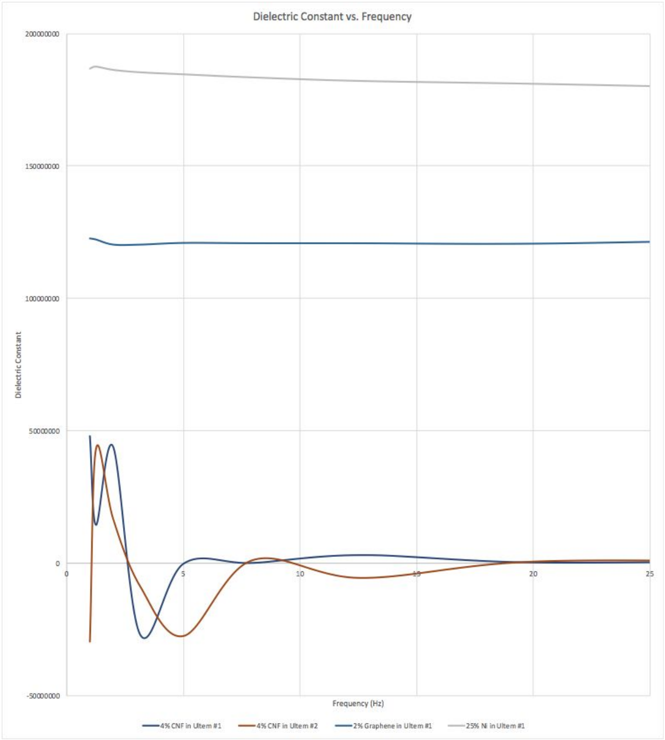
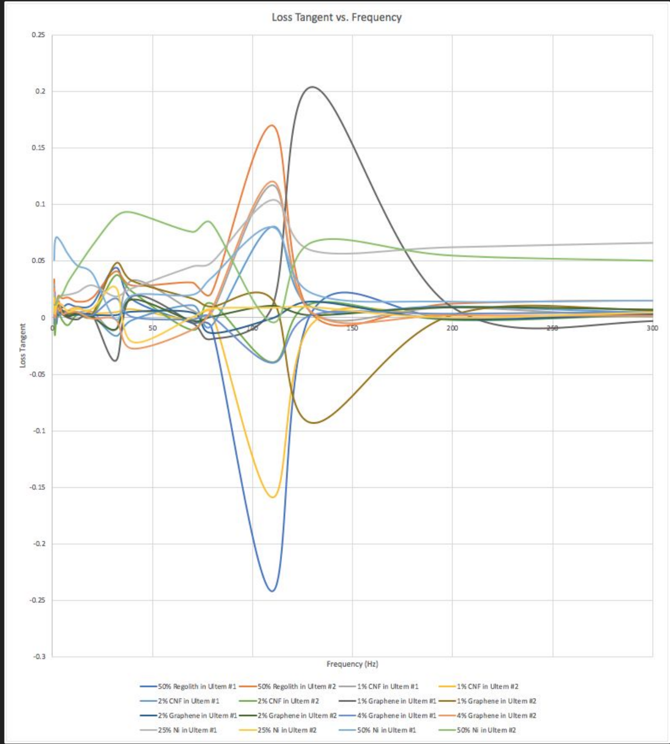
Dielectric Data - Low Frequencies

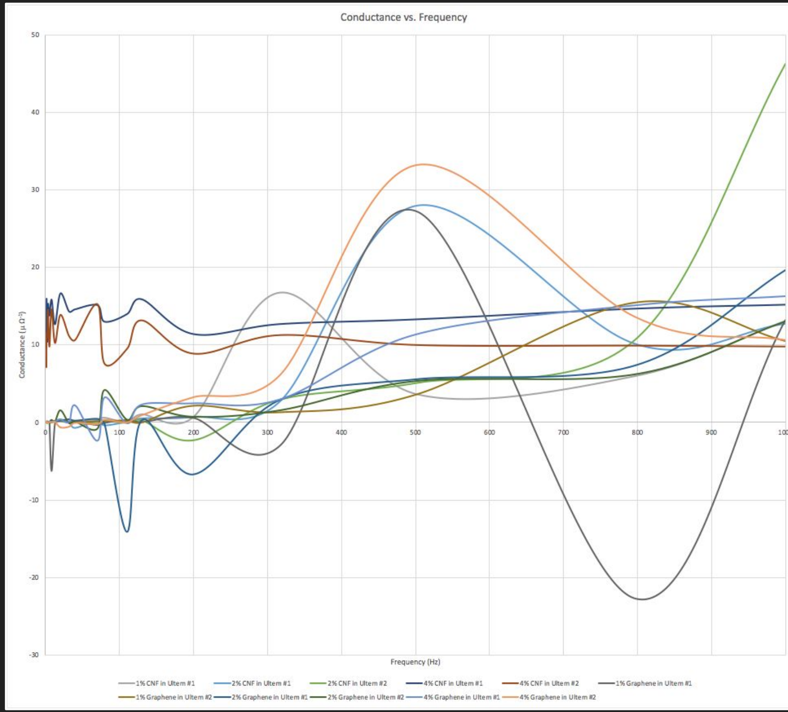




Carbon nanofiber samples show minimal dielectric response

Conductivity Data

- Carbon nanofibers showed greatest conductance among conductive samples
  - Range of conductance for nickel composite: 0.04-0.2 $M\Omega^{-1}$
  - Range of conductance for CNF composite: 0.25-10 $M\Omega^{-1}$
  - Graphene showed sensitivity to conductive tests
- Inconsistent conductivity measurements
  - Likely due to porosity within wafer samples



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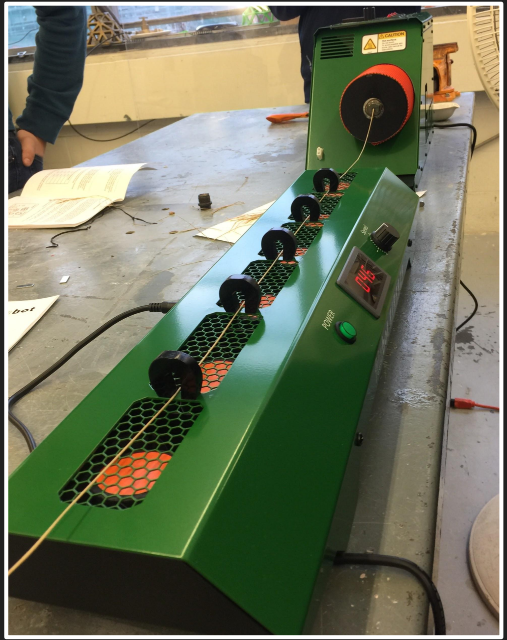
Filament Production (Filabot EX2 Extruder)

Operational concerns

- Humidity fluctuations in the extrusion environment
- Imprecise analog control settings
- Unreliable temperature readings



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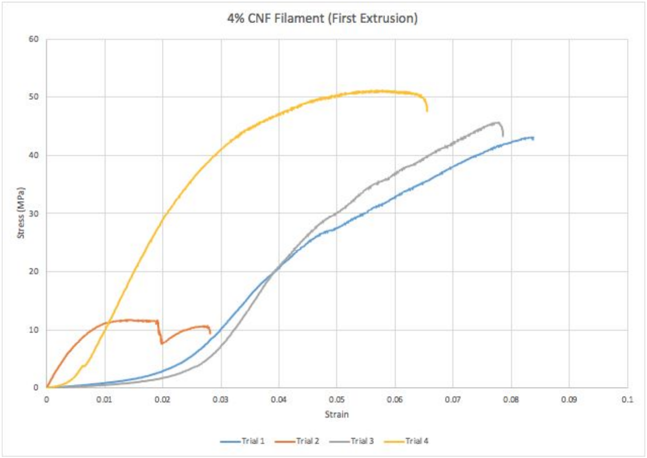
Nickel Feedstock

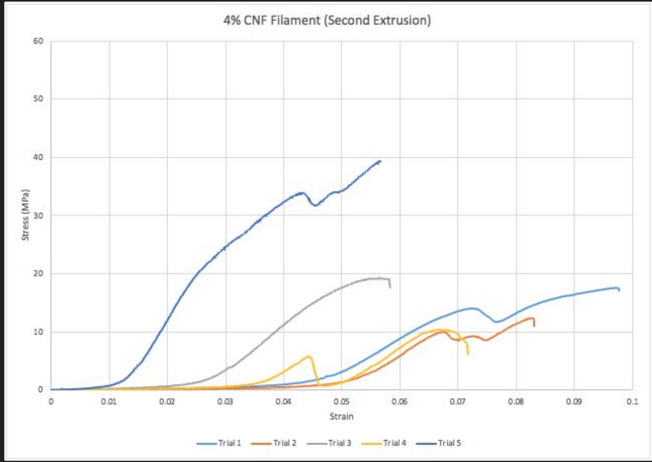
- Ultem with 50 wt% nickel powder
- First attempt at composite extrusion
- Significant porosity throughout filament
- Inconsistent diameter
- Likely poor mechanical properties
    - Tensile testing not completed
- Intended as a conductive feedstock

Carbon Nanofiber Feedstock (4% by wt.)

- Decrease in strength versus plain solutionized Ultem, higher strength than Ni or BTO feedstocks
- Reduced filament quality post-recycling (unlike Ni)



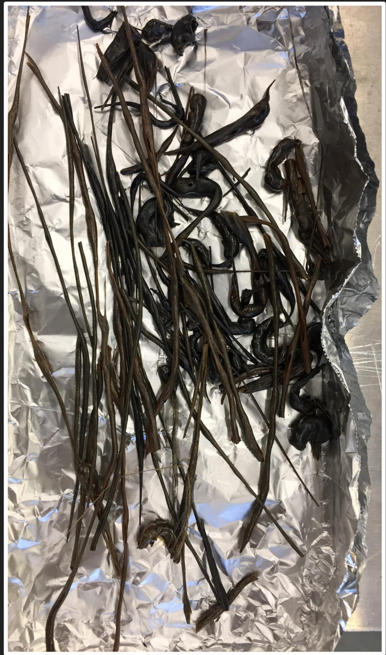
Average UTS: 38 MPa



Average UTS: 20 MPa

BTO Feedstock

- Ultem with 20 wt% BTO
- Initial extrusion attempt failed
  - Material burned at temperatures previously used for extrusion (315°C)
- Second extrusion successful
  - Increased drying time
  - Lowered extrusion temperature
  - Decreased loading to 8% BTO
- Lower filament quality compared to CNF
  - Inconsistent diameter
  - Brittle with significant porosity



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Conclusion

- A solutionization process for OTS Ultem 9085 for the integration of dopant fibers and particulates has been described
- This process was refined for consistent hybrid gel batches incorporating a wide range of dopant materials, varying in size, geometry and properties
- Composite wafers and filament feedstocks were successfully produced from these gels and tested for electrical and mechanical properties
- The solutionization process for Ultem composite formation shows potential with minimal UTS reduction in some cases, however, far more consistency in processed sample properties must be seen for real-world application

Future Work

→ Benefits of scale (surface area ratio, consistency, equipment, etc.)

→ Surfactant/plasticizer coatings for dopant particles[3]

→ Regolith tumbling (reduce particle edge wear on processing equipment)

→ Experimentation with ULTEM/PVDF matrix blend

→ Electrospinning potential of hybrid Ultem gels

→ Look forward to additional data from collaborators (Dr. Cheng)

→ Electrical testing and print testing of composite feedstocks (Ni, CNF, BTO)

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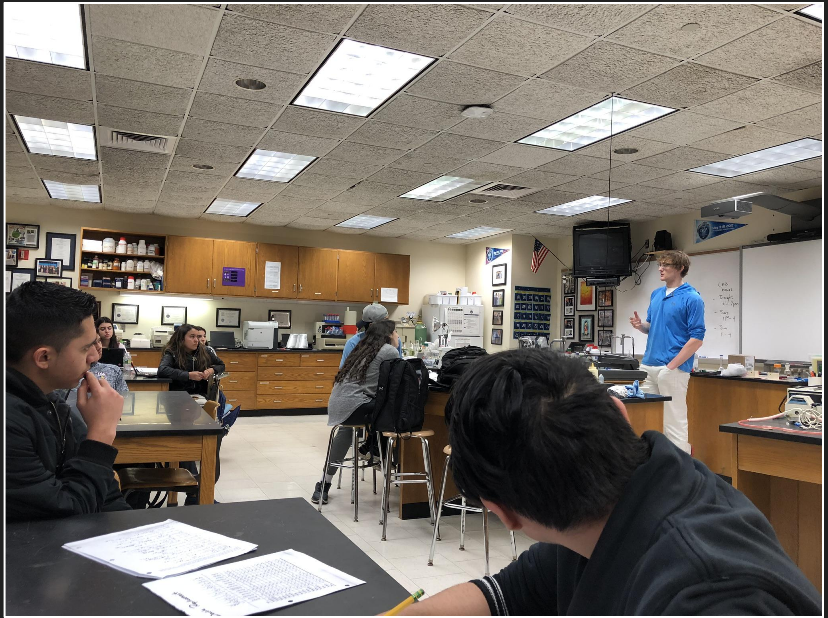
Community Outreach

Engineering Ambassadors' 4th Annual STEM Night

- **Location:** Connecticut Science Center in Hartford, CT
- Between 200-300 students from historically underrepresented schools across Connecticut were in attendance
- Opportunity to interact with students and show them what we are doing with our exciting NASA project
- Goals
  - Teach students about our project and the basic engineering principles behind it
  - Inspire students to show them that they could get involved in engineering and make a significant impact in the world in doing so

Community Outreach - CT Science Center

Community Outreach - GHS and UConn Maker Faire



ESL Chemistry Class

UConn Maker Faire

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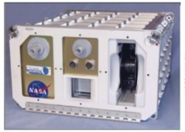
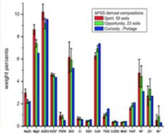
Development of Novel Feedstocks for In-Space Additive Manufacturing

Jon Gager, Spencer Matonis, Zach Putney, Ryan Wrobel
University of Connecticut, Department of Material Science and Engineering

Background

- As of 2016, 3D printers have become compact and sophisticated enough to be installed in the ISS
- Since then, much effort has gone into improving the capabilities of the ISS's Additive Manufacturing Facility (AMF) with better printers, better tooling and stronger materials to help close the performance gap between printed parts and standard aerospace metals





Figures 1-2: Tethers Unlimited Additive Manufacturing System; launched to ISS in 2018 (left). Composition of Martian regolith via rover sampling (right).

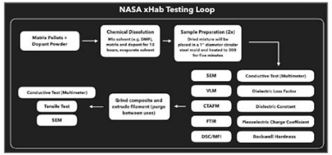
Objectives & Approach

Research and development novel feedstocks for in-space additive manufacturing with an emphasis on in-situ resource utilization. Formulate a robust dissolutionization process for the doping of ULTEM, PC and other thermoplastic matrices.

Establish robust evaluation cycle for a wide range of dopant materials:

- Carbon fiber
- Graphene
- SiC whiskers
- Non-FM Simulant*
- FM Simulant*
- Copper
- Nickel

* FM: Ferromagnetic



Testing

Dissolution
- Dissolved polymers in various chemical solutions before doping
- Chemical solutions include tetrahydrofuran (THF)/N-N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP)
- Dissolution allows for even distribution of particles in plastics used

Tensile Testing
- Performed to see how well any composite materials perform when pulled (in tension)
- Data gathered produces stress/strain curves (stress: force per area; strain: system's response to a particular stress)

DSC
- Performed to gain information regarding the thermal properties of created composites
- Can be used in conjunction with melt flow indexing to find an optimum extrusion temperature

FTIR
- Performed to observe chemical changes in composite materials versus initial materials
- Can be used to identify if solutionizing polymers effects the structural integrity of the polymer chains

OM
- Uses visible light to show images of small samples at high magnification
- Can be used to show particle dispersion within dissolved and solidified composites

Extrusion
- Takes pelletized composite material and turns it into long strands of filament that can be used for 3D printing
- Parameters that need to be controlled during extrusion include the extrusion temperature, extrusion rate, fan speed (to cool hot composite material), spooling rate
- Each parameter must be optimized for each individual composite that is created (various additives can change the properties of the composite as a whole)

Figure 3: Image shows the extruder and fan track. Material is extruded a specified temperature and rate at the top of the screen. It then passes over the fans to help it cool and solidify by the time it reaches the spool (not pictured)

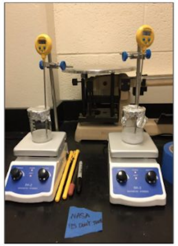


Figure 4: Image shows the dissolution setup. Left: PVDF dissolving in acetone
Right: PC dissolving in acetone

Acknowledgments

We would like to thank the NASA eXploration Systems and Academic (X-Hab) Challenge for the making this possible through its funding. We would also like to thank the Institute of Materials Science (IMS) for access to their facilities, and advisement provided by Dr. Volkan Ortalan, Dr. Anson Ma, Dr. Yang Cao and Dr. George Rossetti.

Discussion

- The retention of the solute mixture is much greater than expected in composites - making it necessary for an additional heat treatment step before extrusion
- Drying composites out after mixing will help prevent porosity, minimize inclusion of moisture, and increase strength
- Uneven dopant distribution has been a challenge - using a centrifugal mixer will likely help to overcome this
- High quality custom molds have been made to test mechanical and electrical properties of composites

Figures 5-6: Stainless steel wafer and dog bone molds for formation of dissolutionized test samples (left). Carbon fiber reinforced ULTEM samples made using rudimentary molds (right).

Future Work

Electrical Testing
- Dielectric constant, conductivity, voltage breakdown, piezoelectric properties of composite wafers

Composite Extrusion
- Optimize extruder parameters for composite materials
- Ensure additives do not damage extruder
- Tensile testing on composite filaments vs dogbones

SEM analysis
- SEM on cross-sections to determine porosity changes
- Fracture surfaces

Viscosity manipulation
- Melt-flow indexer can determine extrusion viscosity
- Fine-tuning of solutionized solvent/solute ratio can increase viscosity to better suspend dopant particles

By the numbers...

- $18,000 dollars spent
- Over 100 individual experiments completed
- 500' of ULTEM used
- 60 wafers produced
- Over 100' of composite filament extruded
- Outreach to hundreds of students
- 1 Department article

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Points of Contact

Contact	Purpose
Dr. Alexandru Asandei (UConn faculty)	Expert in polymer chemistry
Conor Townsend	Preliminary electrical testing
Dr. Anson Ma (UConn faculty)	Information regarding polymers
Dr. Yang Cao (UConn faculty)	Dielectric/piezoelectric characterization
Dr. George Rossetti (UConn faculty)	Dielectric/piezoelectric characterization
Dr. Montgomery Shaw (UConn faculty)	Use of pelletizer
R&D Technologies (3D printing company)	Use of high-temperature 3D printers

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References

[1] https://www.nasa.gov/centers/marshall/news/background/facts/astp.html

[2] Gebisa, A.W., Lemu, H.G. [2018] Investigating Effects of Fused-Deposition Modeling (FDM) Processing Parameters on Flexural Properties of ULTEM 9085 using Designed Experiment, Materials 11:500. DOI: 10.3390/ma11040500

[3] Wu, Yingwei, Dmitry Isakov, and Patrick Grant. "Fabrication of composite filaments with high dielectric permittivity for fused deposition 3D printing." Materials 10.10 (2017): 1218.

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