High Yield Microwave Plasma Conversion of Coal for Low-Cost 3D Printable Composites

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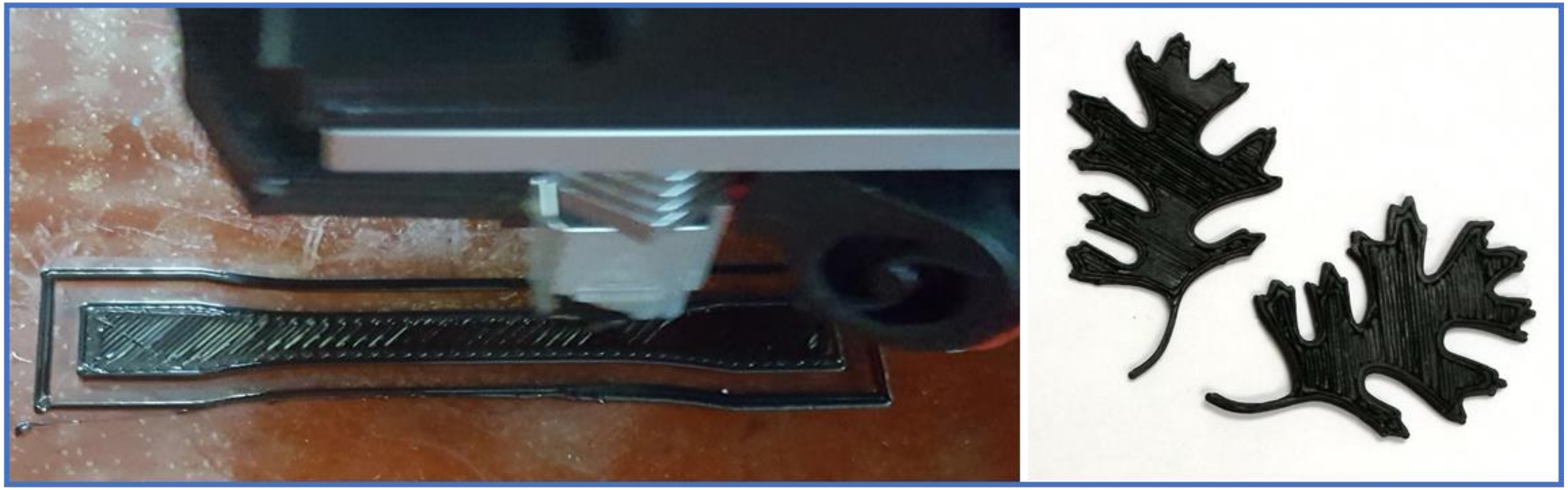


Project Description and Objectives

Objectives

Objective of this project is to advance and demonstrate rapid, efficient, high-yield conversion of representative domestic coals using a novel low-temperature microwave plasma coal conversion technology (Wave Liquefaction™) into solid, high-value products via a liquid intermediary with well-established as well as emerging pathways towards large commercial markets.

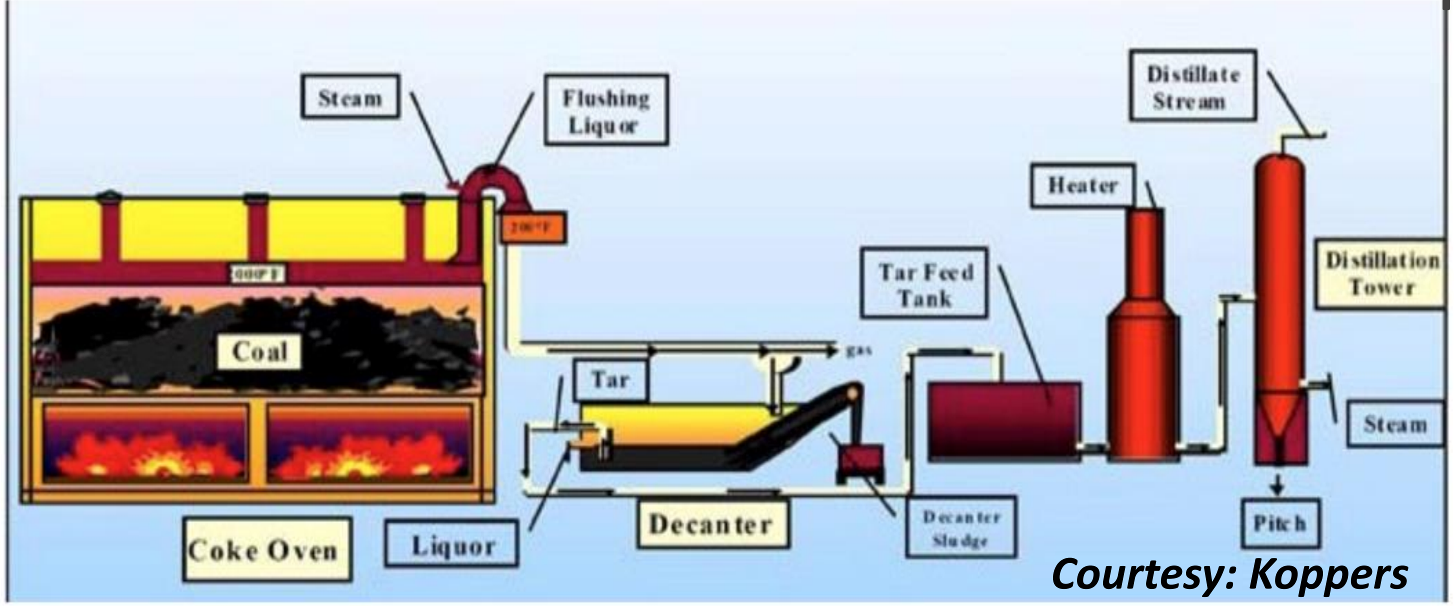
Proposed value-added products include injection-moldable resin that can be crosslinked by applying microwave or heat and composites that can be 3D printed.

These materials could contain 30-90% coal-derived matter and thus, could be carbonaceous in nature.

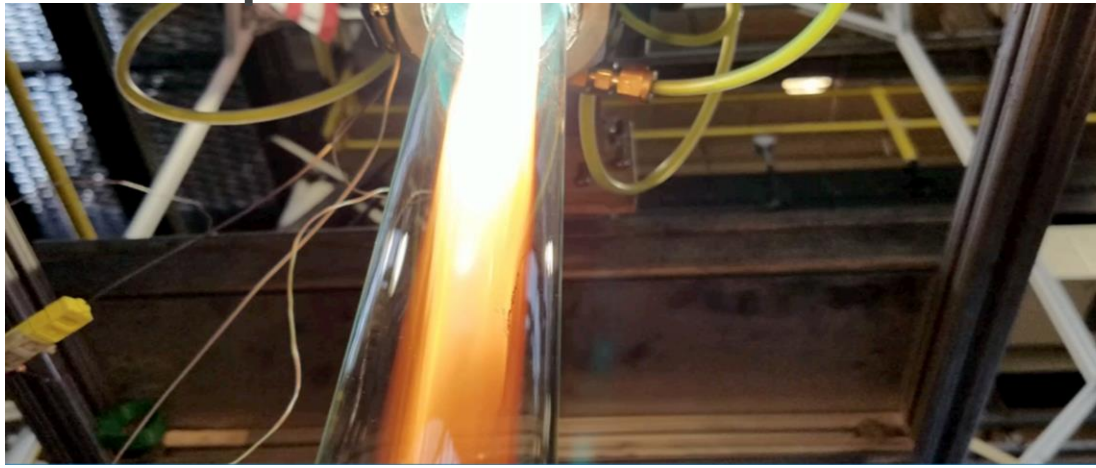
H Quest's approach: Wave Liquefaction™

Ionized gas as energy transfer media

Coke Oven Process | Wave Liquefaction™



Courtesy: Koppers



Low coal tar yield: 120 lbs per ton of coal (5 - 15%)

Limited feedstock: Metallurgical coal only

Poor product quality: High sulfur, QIs

Grave environmental and health impact

Rapid, high-throughput **flash pyrolysis** of coal particles entrained in a gas stream.

Process Characteristics

- High coal tar yield (> 50 wt%)
- Coal-agnostic
- Zero QI, low sulfur
- No process CO_2 emissions

Utilization of Coal Components

Polymer modification

Wave Liquefaction™

Tars condensed with polymers (Plasticizer, rheology modifier, rigid functional segments)

Utilization of pyrolysis residues in polymer matrices as filler

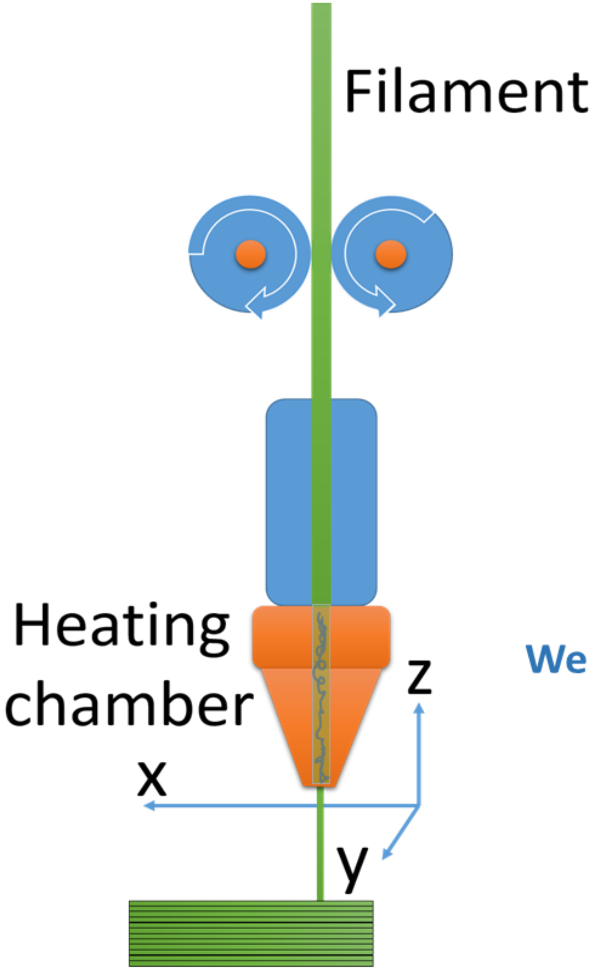
The research challenges we address here include
(a) increased utilization of coal
(b) with increased product value
(c) without or with decreased emissions of CO2

Market Opportunity for Coal-Derivates

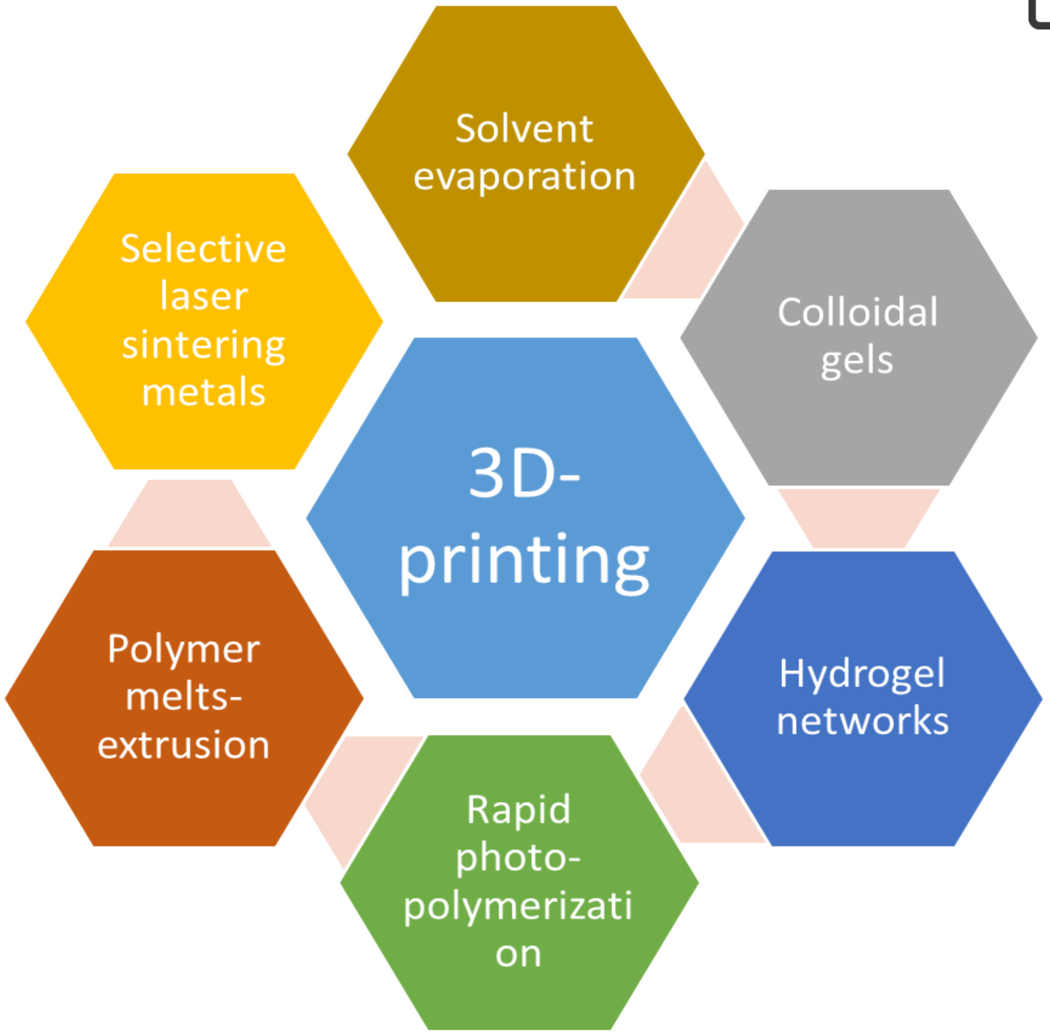
Modification of thermoplastics

Extrusion and characterization facilities that are utilized to synthesize and analyze the products.

3D-Printing Technologies: Materials and Printability

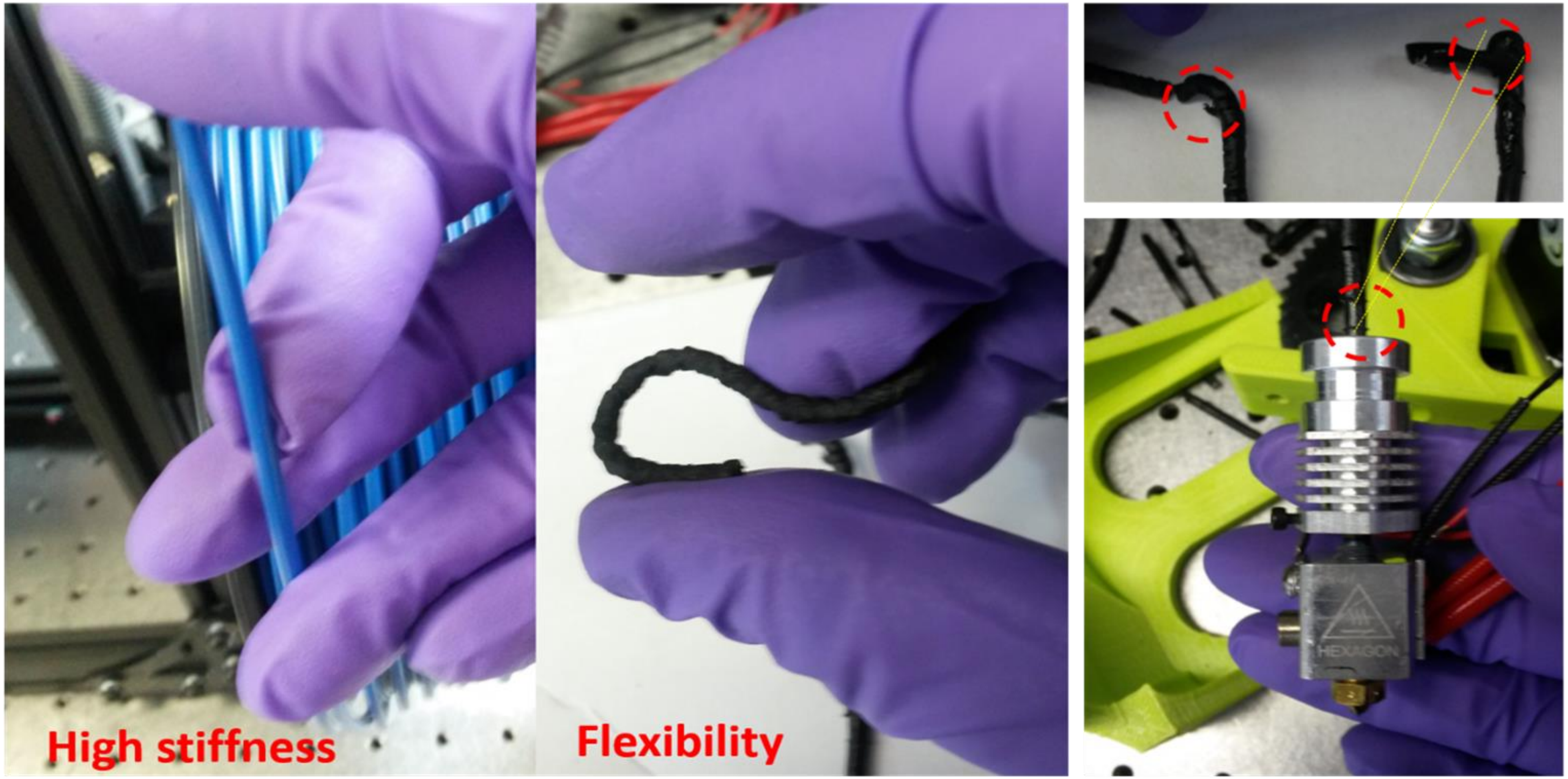


We are here!



Rheological properties of the material controls printability along with many other factors.

Printability requires high enough stiffness of the material with controllable viscosity



Status at beginning of project

Can we use any of the coal components to make polymer derivatives, specifically 3D printable materials?

3D printing of ceramics and polymers have been studied extensively. Ceramics are printed using either polymeric precursors of ceramic or binder jet printing.

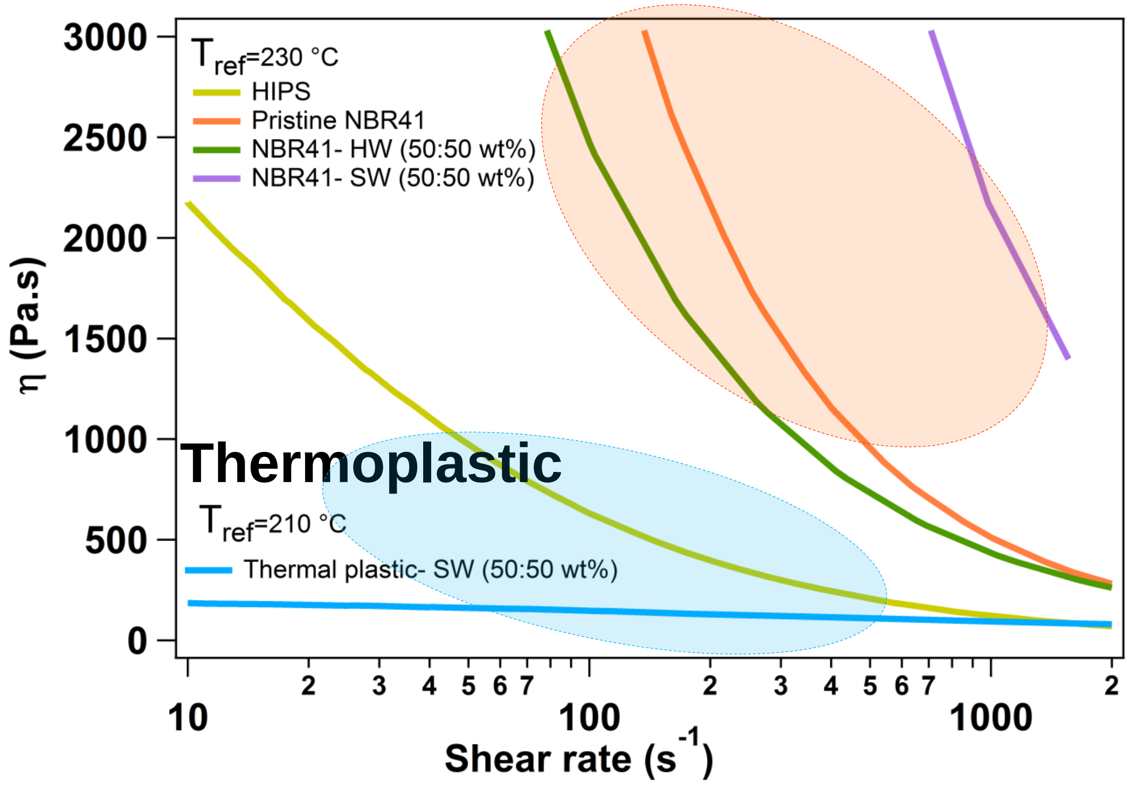
Received H Quest's material pelletized and powder carbon products.

Our goal is to find efficient utilization methods of rigid and soft coal products aimed towards new 3D printable products. Can these additives help processing difficult-to-process polymers? High loading is expected to give brittle products.

Prior Work

Biomass components to 3D printing

Better flow control in thermoplastic polymers



Good printability

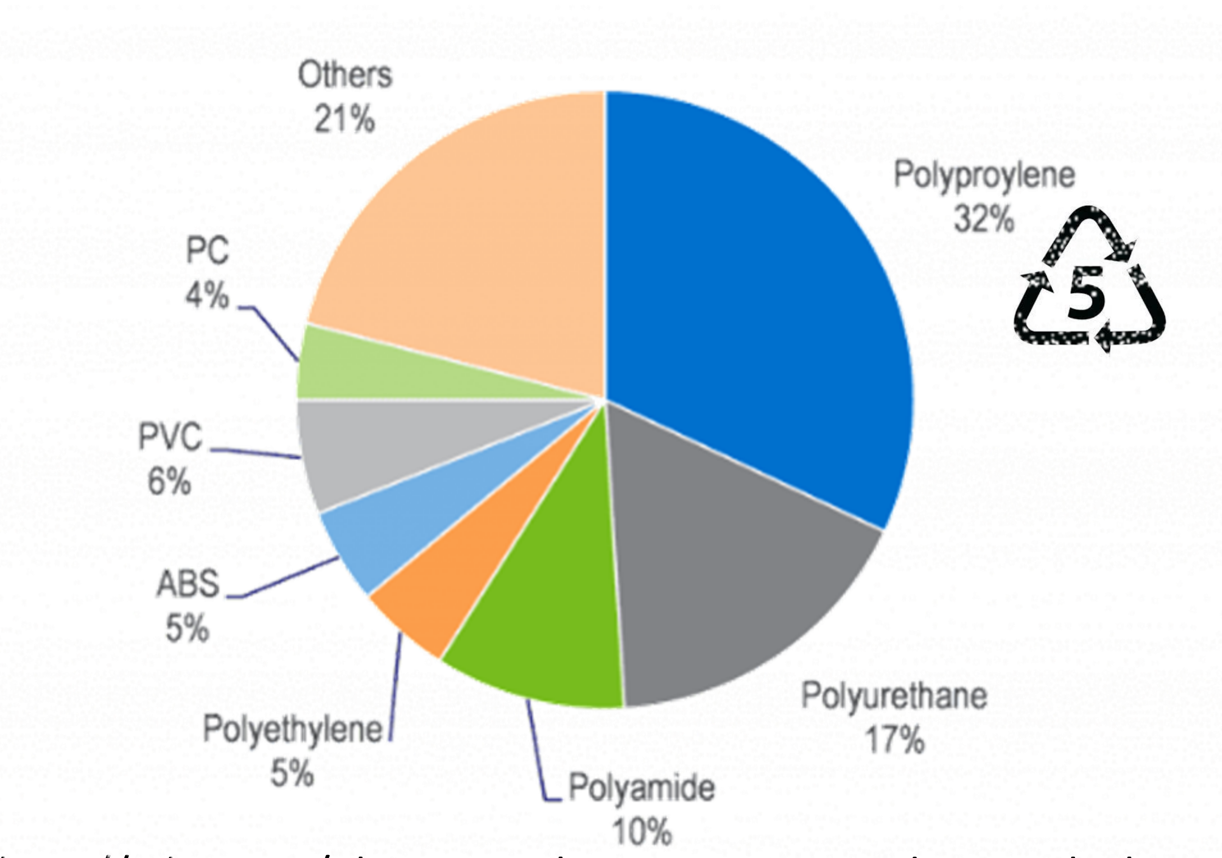
Prior Work: 3D Printing of Lignin Derivatives

We delivered a composition that yields 50-60 MPa tensile strength and processability at 40 wt.% lignin loading in a thermoplastic without compromising matrix properties significantly.

What polymer matrix shall we target?

Polyolefins are the lowest hanging fruit as it has the largest share of the commodity plastics.

North America Plastics Consumption in Automotive Sector, 2017

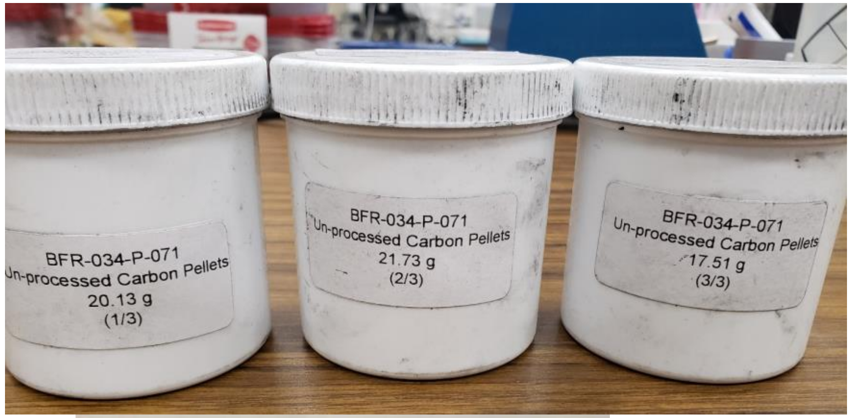


http://adapt.mx/plastics-in-the-automotive-industry-which-materials-will-be-the-winners-and-losers/

Polypropylene (PP) shares the largest volume (32%), among all plastics, in automotive usage. Its 3D printing is difficult due to complex crystallization kinetics and instabilities caused by it. Often it exhibits poor dimensional stability in printed material. In contrast, acrylonitrile-butadiene-styrene (ABS) and polylactic acid (PLA) have higher stiffness and T_g than the PP.

- Can we slow down the crystallization kinetics of polypropylene by incorporating coal derivatives?
- Can we make a better printed product?
- Can we make functional polymer after incorporating additives (e.g., EMI shielding, a TPE grade without copolymerization)?

Melt Compounding



Homogenized Powder (3,10, 30 wt%)

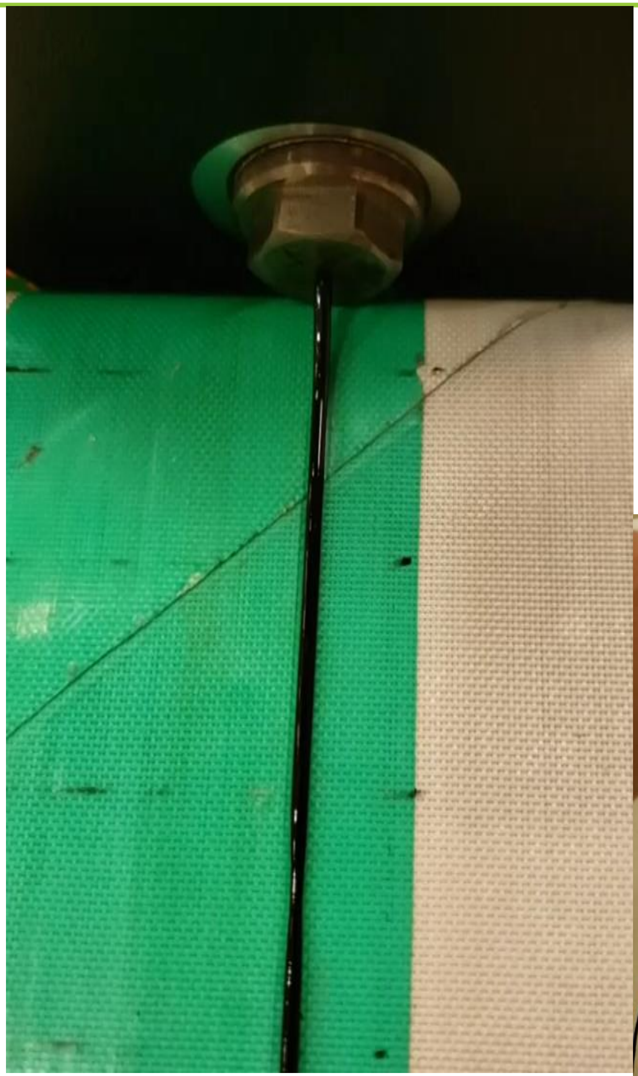
Commercial i-PP

*PP selected as candidate resin to optimize interfacial compatibility

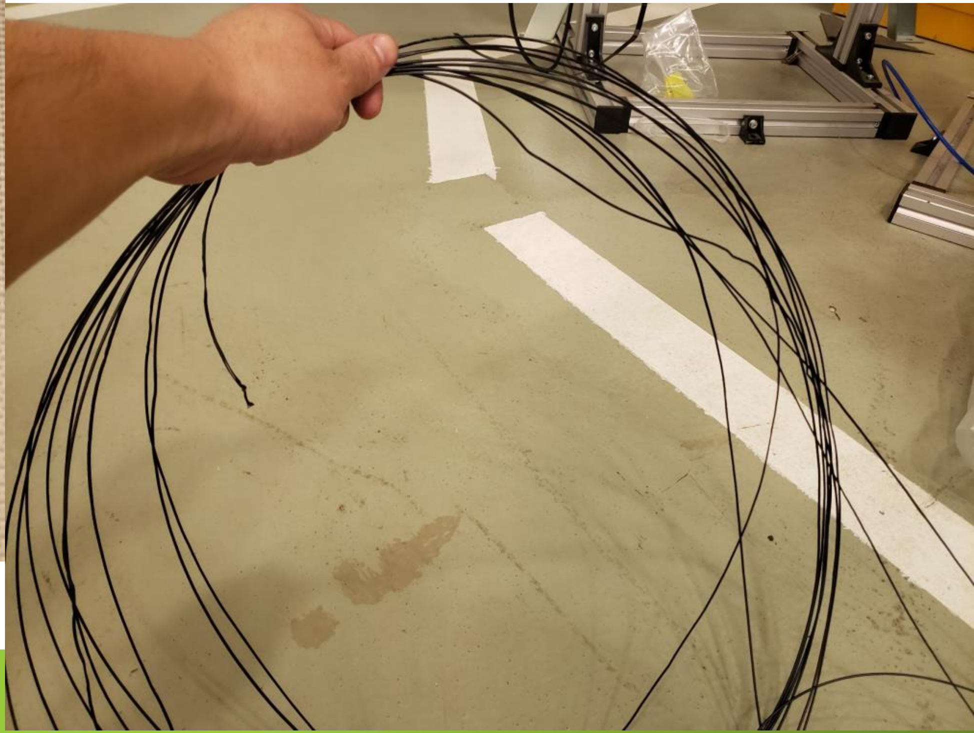
Melt Compounding
30 min, 180 °C @ 100 RPM

Filament Production

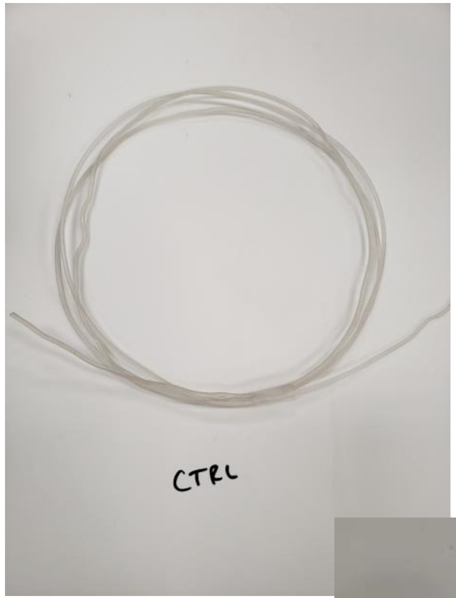
iPP control

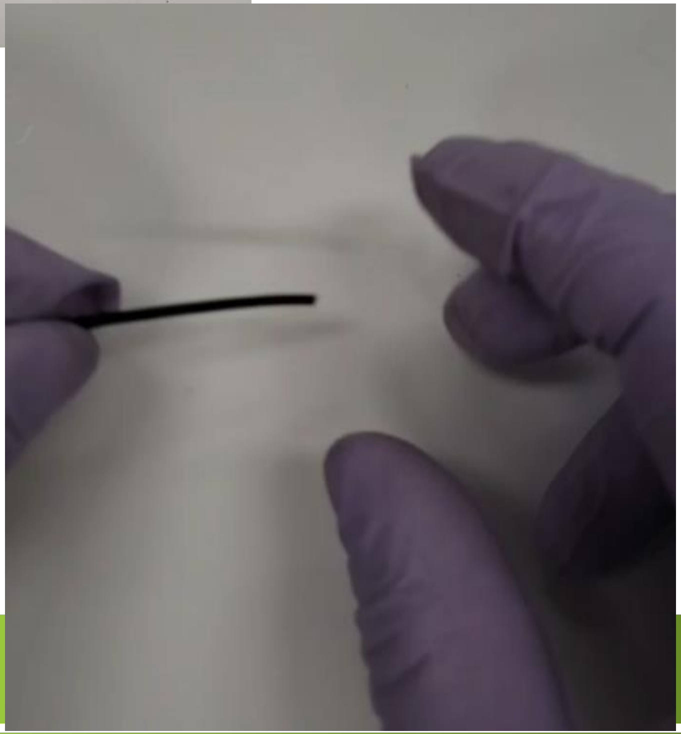


iPP-10 wt% CP blend



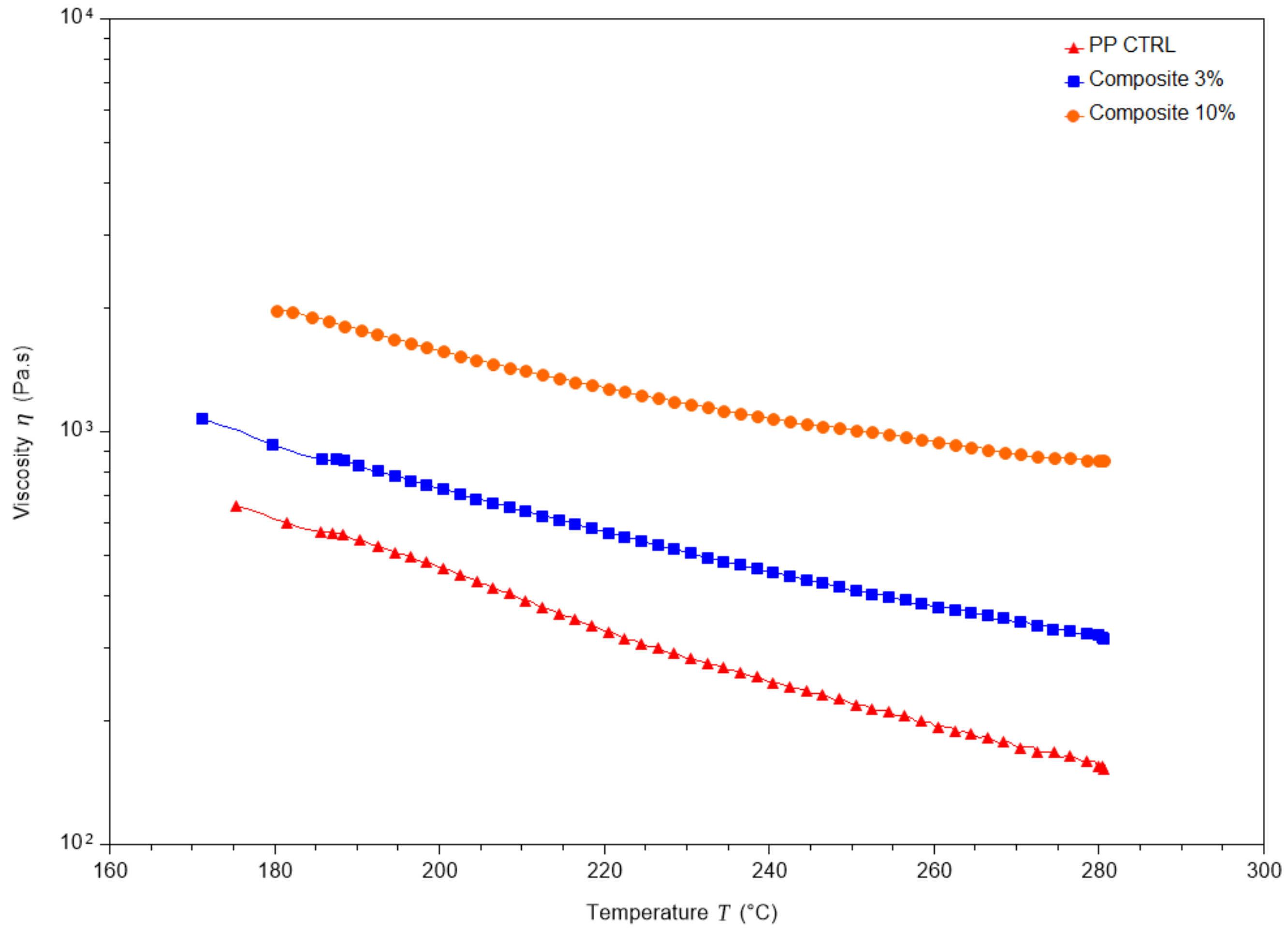
Filament Formulations





Rheological Properties

Viscosity vs Temperature response

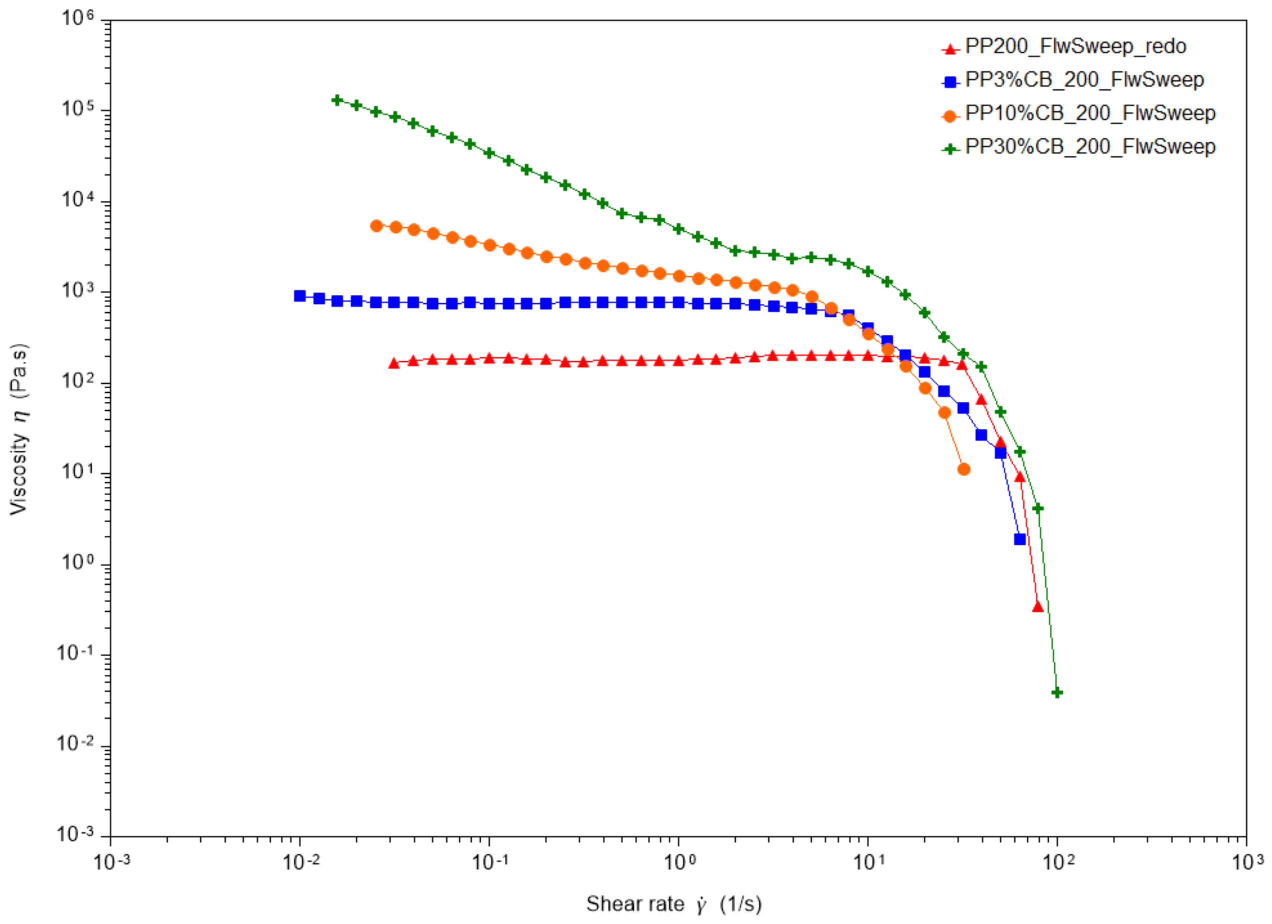


As expected, Viscosity drops with an increase in temperature.

Incorporation of 10 wt.% tar-modified carbon increased viscosity by order of magnitude.

Rheological Properties

Shear flow (Steady)

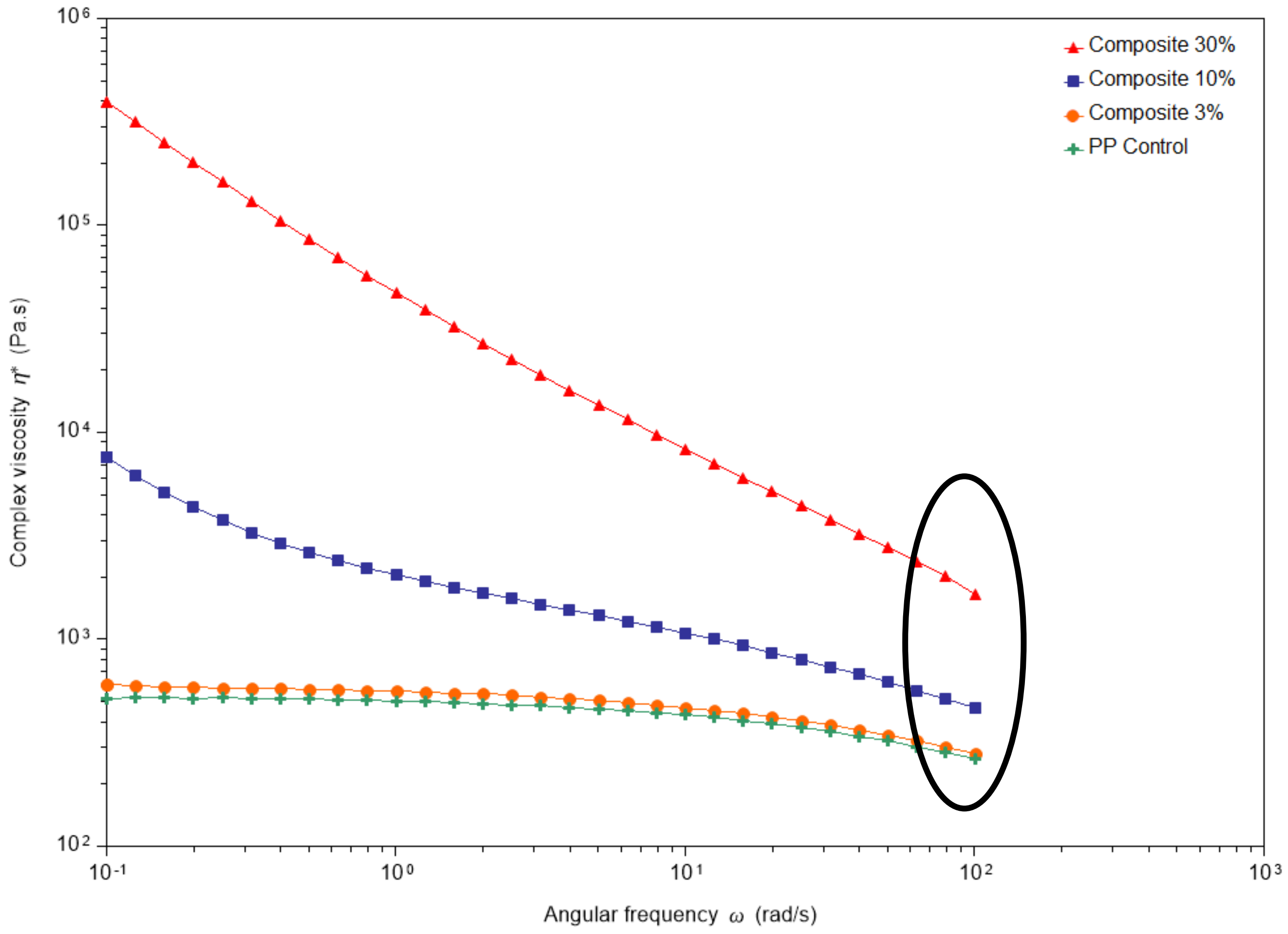


Shear thinning behavior is visible with 30 wt.% carbon loading. At the melt condition, the iPP matrix has low zero-shear viscosity and filler loading increases the zero-shear viscosity.

Viscosity at a high shear rate is very low, suggesting the feasibility of extrusion-based printability.

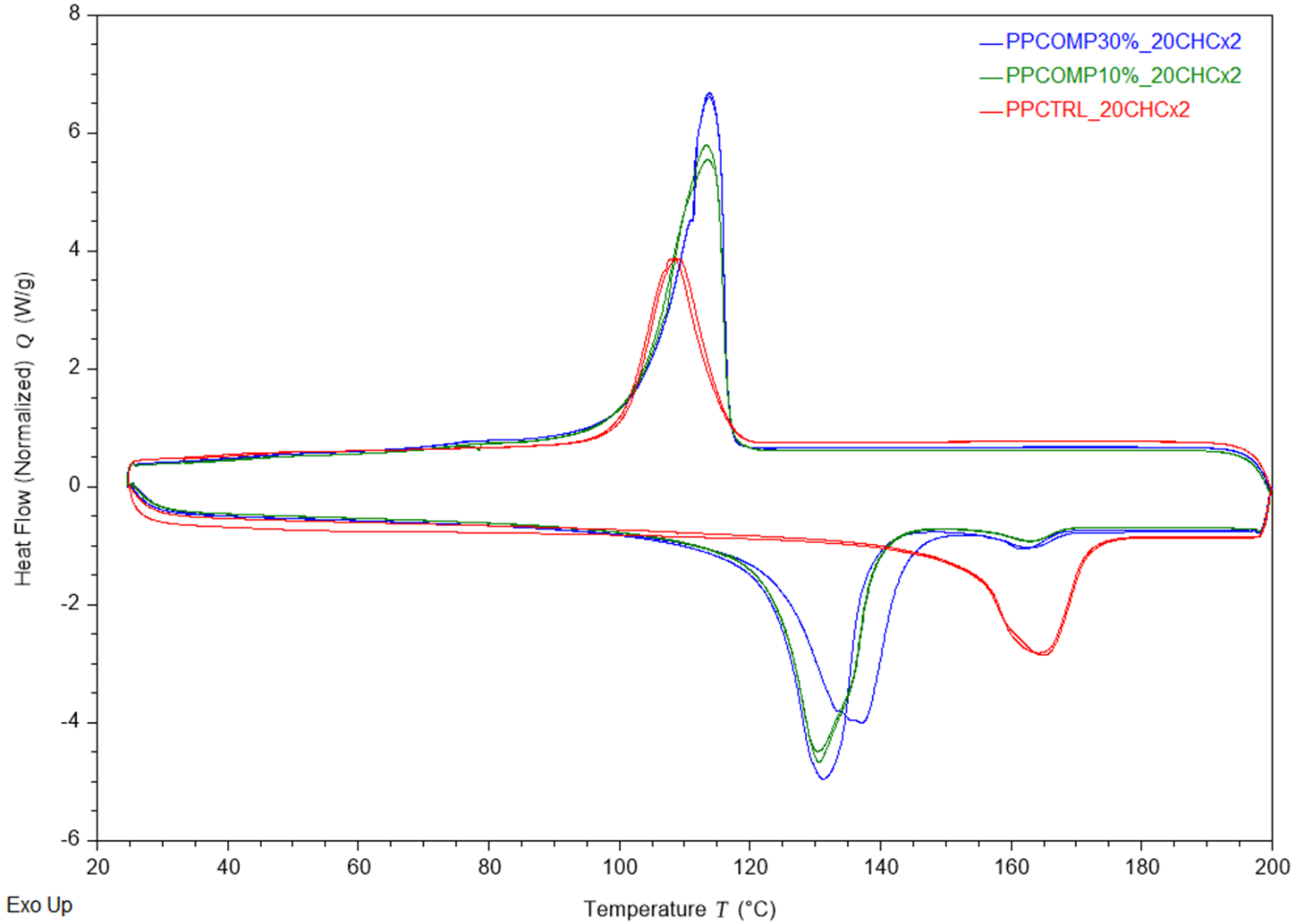
Rheological Properties

Oscillatory shear response



Shear thinning behavior and < 2000 Pa· s @ 100 1/s of 30 wt.% filler loading suggest good printability.

Tar-bound carbon influences PP crystallization behavior



Carbon or tar accelerates crystallization as demonstrated by rapid crystallization of melt. However, the crystals are imperfect as it melts at very low temperature. This would help interlayer diffusion during 3D printing.

Preparing Project for Next Steps

Market Benefits/Assessment

- Usually polymer processing industries tend to avoid incorporation of heterogeneous mix filler in the formulation. We aim to demonstrate beneficial effects caused by the additives.
- 20-30 wt% incorporation of coal-derivatives, without causing processing and performance issues, is a possibility.

Technology-to-Market Path

- Demonstration of the performance of printed material is needed.
- Development of compositional IP and licensing of the IP.
- Identify unlike tars from coking oven, tars from Wave Liquefaction will have higher aromaticity and could offer better functionality in polymer compositions.
- Currently working with H Quest Vanguard.

Future Work

- We will be receiving a new tar and residue composition from H Quest Vanguard.
- Conduct printing of materials and testing. We got significantly delayed, caused by COVID-19.
- Validate the role of coal-derivatives in polymer product processing.
- Development of new IP is a possibility.

Concluding Remarks

- Developed a strategy to use coal-derived hydrocarbon as a functional additive for polyolefin compositions.
    - Polypropylene matrix exhibits excellent processability with 30 wt.% tar-bound carbon produced by H Quest Vanguard.
    - The approach addresses the utilization of clean coal derivatives.
- Several compositions will be studied based on PP matrices.
    - Printability will be demonstrated.
    - New compositions will be developed that will demonstrate additional functionalities in the iPP matrix.
    - The compositions may find good usage in automotive applications.
    - Once printability is demonstrated, we will work on finding feasibility of the injection molding in the compositions.

Acknowledgement

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