High Strength, Encapsulated, Commercially Useful Components and Particles Made from Coal Combustion Residuals

DOE Office of Fossil Energy

Award No. DE-FE0031932

Project Period of Performance:
10/1/2020 – 9/30/2023

Program Objectives

1. Demonstrate ability to encapsulate CCR particles with a tailorable coating to reduce leaching of toxic elements by at least 80% over uncoated particles
2. Utilize the encapsulated CCR as a large volume filler/reinforcement to produce 9”-diameter support column prototypes with compressive strength and flexural strength 5-10X that of current concrete
3. Develop and demonstrate CCR encapsulated in a tailored, reactive resin coating as a filler for polypropylene that will increase the modulus and strength by 30-50% while reducing toughness and elongation by only 20-30% compared to traditional fillers
4. Develop initial predictive models for the behavior of CCR that reasonably predicts the effects of CCR and encapsulant composition and microstructure on mechanical properties in columns and polypropylene components

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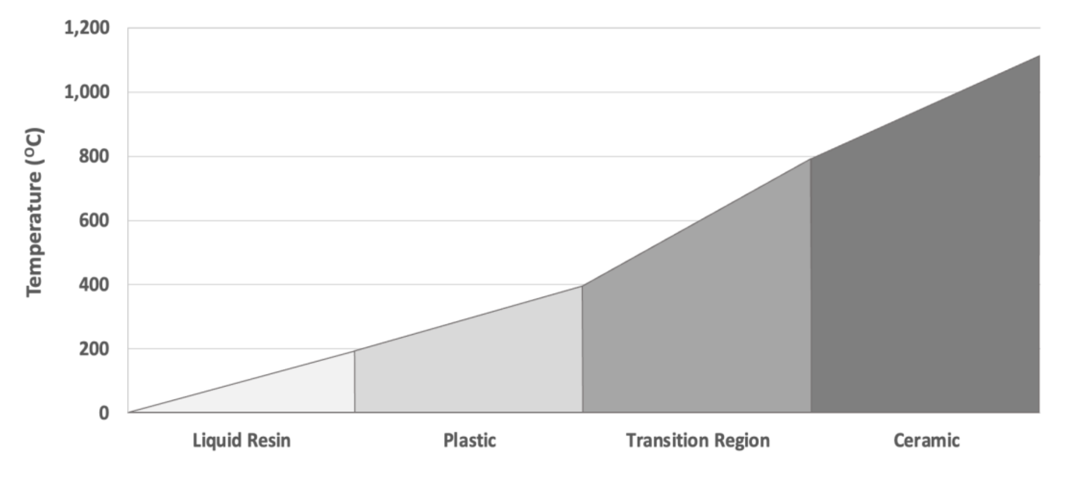
High Level Technology Overview

- Our Polymer Derived Ceramic resins can be tuned at the Atomic Level to contain varying amounts of silicon, oxygen and carbon
- Easily manufactured compared to typical ceramics
- Resin acts as binder between particles - no pressure sintering needed
- Resin fully coats and encapsulates the particle – ***prevent leaching of toxic elements from CCR*** (As, Se, Hg)
- Low-cost and Scalable



Typical Polymer Derived Ceramic Processing Cycle

High Level Technology Overview – cont.

- Utilized a dilute solution of the resin mixed with the CCR particles The resin binds to, coats, and **encapsulates** CCR particles
- Coating thickness can be controlled by the amount of resin in the solution and mixing speeds in the process
- For Columns:
  - Press the coated CCR into a cylindrical mold
  - Cure in air to 150-180°C for 2 hours
  - Pyrolyze in inert gas to 1000°C to convert polymer to a ceramic
- Cure in air to 150-200°C to harden the resin to solid plastic
- Pyrolyze in inert gas to 1000°C to convert the polymer to ceramic

High Level Technology Overview – cont.

- For Coated Filler in Plastics:
  - Cure the coated CCR in inert gas to 130-150°C for 1 hour
  - Mix the coated CCR with polypropylene or other resin
  - Feed the mixture through a compounding extruder heated to 180°C three times (or until the CCR is uniformly distributed)
  - Run the mixed CCR filled plastic through an extruder/chopper system to produce “pellets”
  - Use the pellets to produce components by extrusion, compression molding, or injection molding

Project Milestones

Milestone Num.	Task / Sub-task	Milestone Title / Description	Planned Completion Date	Actual Completion Date	Verification Method
M1	2.3	Encapsulated CCR samples produced with desired properties	16 Mar 2021	30 Mar 2021	Testing by team members
M2	3.3	Polypropylene samples with encapsulated CCR filler produced	1 Sep 2021	24 Aug 2021	In-house testing
M3	3.4	Initial phase CCR composite modeling completed	28 Sep 2021	30 Sep 2021	Report from Clemson
M4	3.5	Large composite components produced	15 Feb 2022	28 Feb 2022	In-house testing
M5	4.1	Ceramic component testing complete	7 Jun 2022	27 Jul 2022	Material results reports from team members
M6	4.2	Plastic matrix samples and large components testing complete	1 Aug 2023	n/a	Material results reports from team members
M7	4.2	Clemson model development complete	1 Aug 2023	n/a	Model documentation / report from Clemson

Partners

Clemson University

- Materials characterization
- Specimen testing
- Microstructural Analysis
- Prototype Processing
- Leading effort in process modeling

Energy and Environmental Research Center (EERC)

- Leachate testing experience and processes
- CCR Assay Capabilities
- Securing lignite-based CCR in North Dakota for testing
- Particle size analysis

Partners

The Center for Applied Research and Technology (CART)

- Prototype development support
- Product design
- Project lead in scaling up ceramic columns to 9 inches in Diameter

Mosser Resource Consulting LLC

- Provides project managements and coordination with coal combustion power plants in the Appalachian region

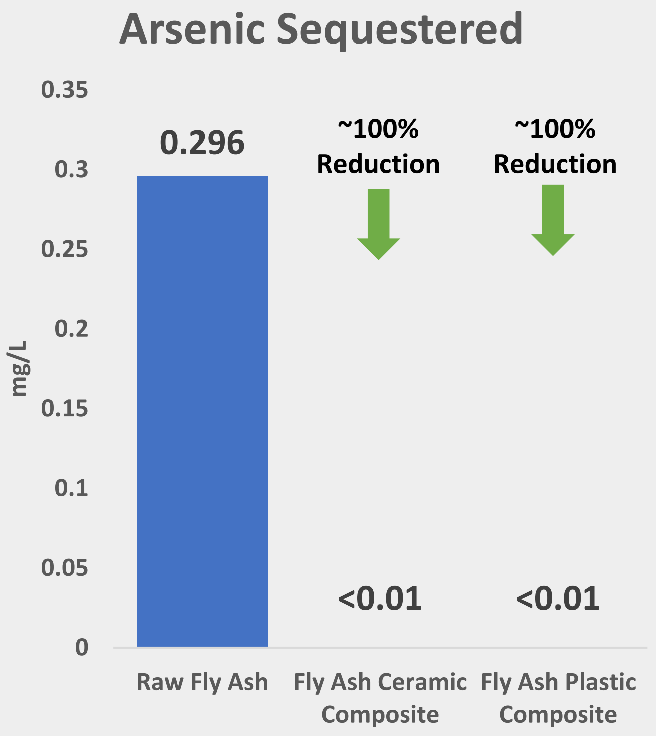
CCR Tested

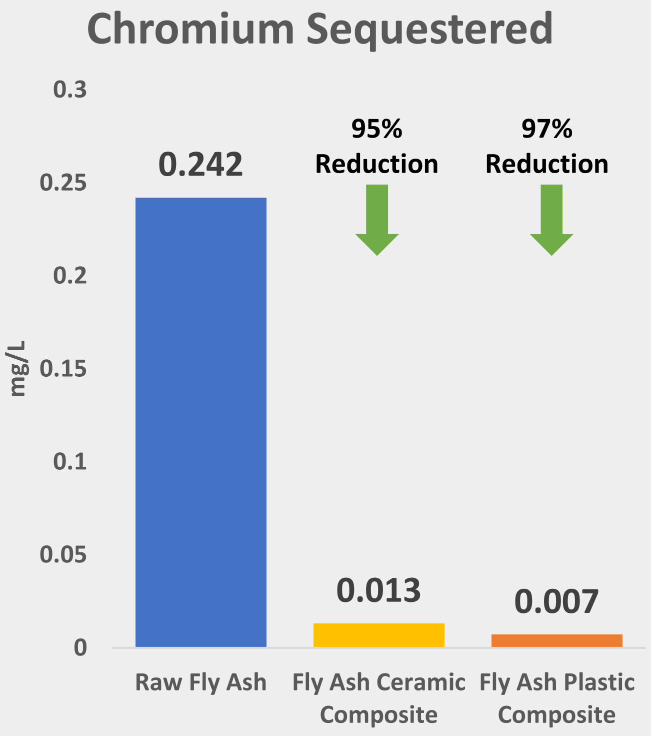
Ash ID	Source
FM-MM-fly ash	Mosser Resource Consulting
Bottom Ash 3-14-14 N001	Mosser Resource Consulting
Fly Ash 3-14-14 N002	Mosser Resource Consulting
BR-MM-Fly Ash	Mosser Resource Consulting
ME-MM-Fly Ash	Mosser Resource Consulting
ME-MM-Bottom Ash	Mosser Resource Consulting
124851 Middle Wyoming PRB Sub-Bituminous	EERC
124562 ND Lignite fly ash	EERC
124586 ND Lignite Fly Ash	EERC
Scrub Grass Fly Ash	Mosser Resource Consulting
FM Gypsum Scrubber Material	Mosser Resource Consulting
FM Fly Ash	Mosser Resource Consulting
FM Bottom Ash	Mosser Resource Consulting
American Bituminous ash	Mosser Resource Consulting
Pittsburgh Pond Fines	Mosser Resource Consulting
NA 219 Floor Northern Appalachia LK PA	Mosser Resource Consulting
#4 JLHR Pit Floor B Coal	Mosser Resource Consulting
Fly Ash from Anthracite Coal	Mosser Resource Consulting
MEA Fly Ash	Mosser Resource Consulting
FM Fly Ash Pit Coal	Mosser Resource Consulting
BRC LK Underclay	Mosser Resource Consulting
Wyoming PRB fly ash	Southern Company
Sherer Ash (26 samples)	Southern Company / Josh Dickey
Falkirk Lignite Fly Ash	EERC

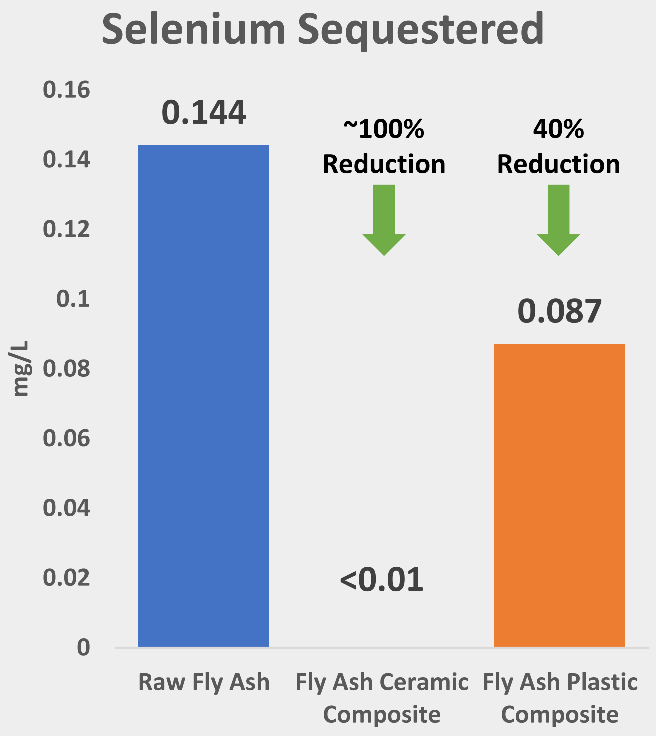
- Obtained CCR samples from 24 different sources. Samples consisted of various types of CCR
- Selected a ND Lignite Ash as the primary candidate in the encapsulation and leachate work due to the relatively high levels of toxic metals and compounds.

Initial encapsulation trials using a “dry mixing” method. This method was primarily used for initial screening.

Leaching Results

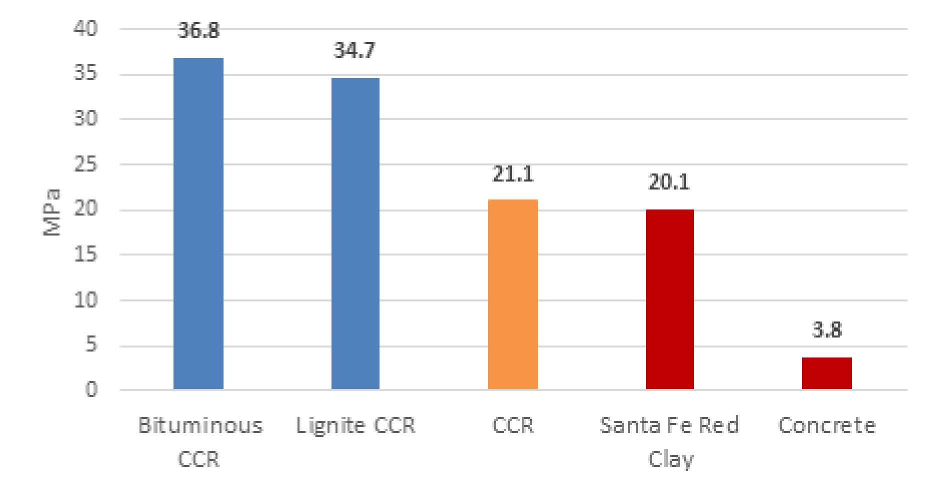




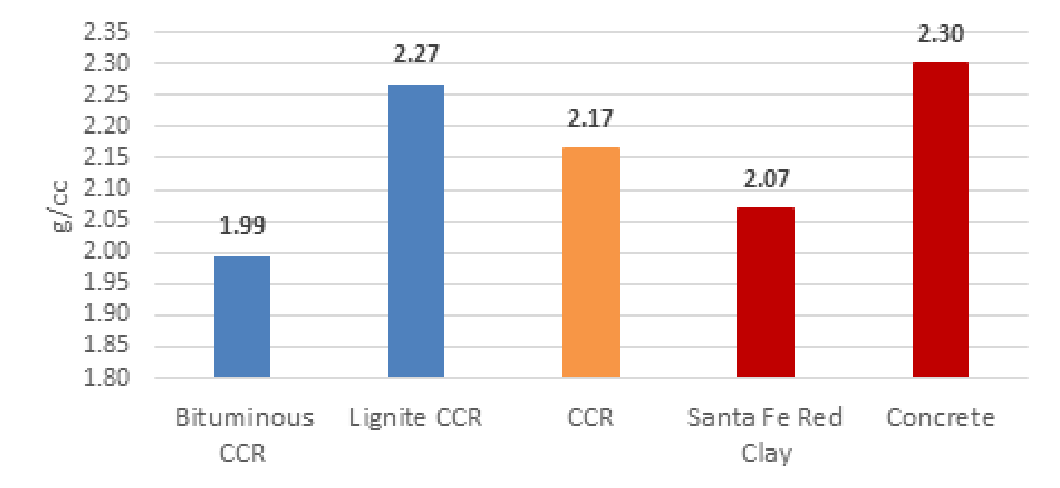


*All Materials are well below the allowable limits set by the EPA

CCR Material Strengths



Flexural strength testing results for CCR-based materials vs. clay tile and concrete.



Average bulk densities of CCR-based materials vs. clay tile and concrete.

Represents Ceramic Material

Represents Green/Plastic Material

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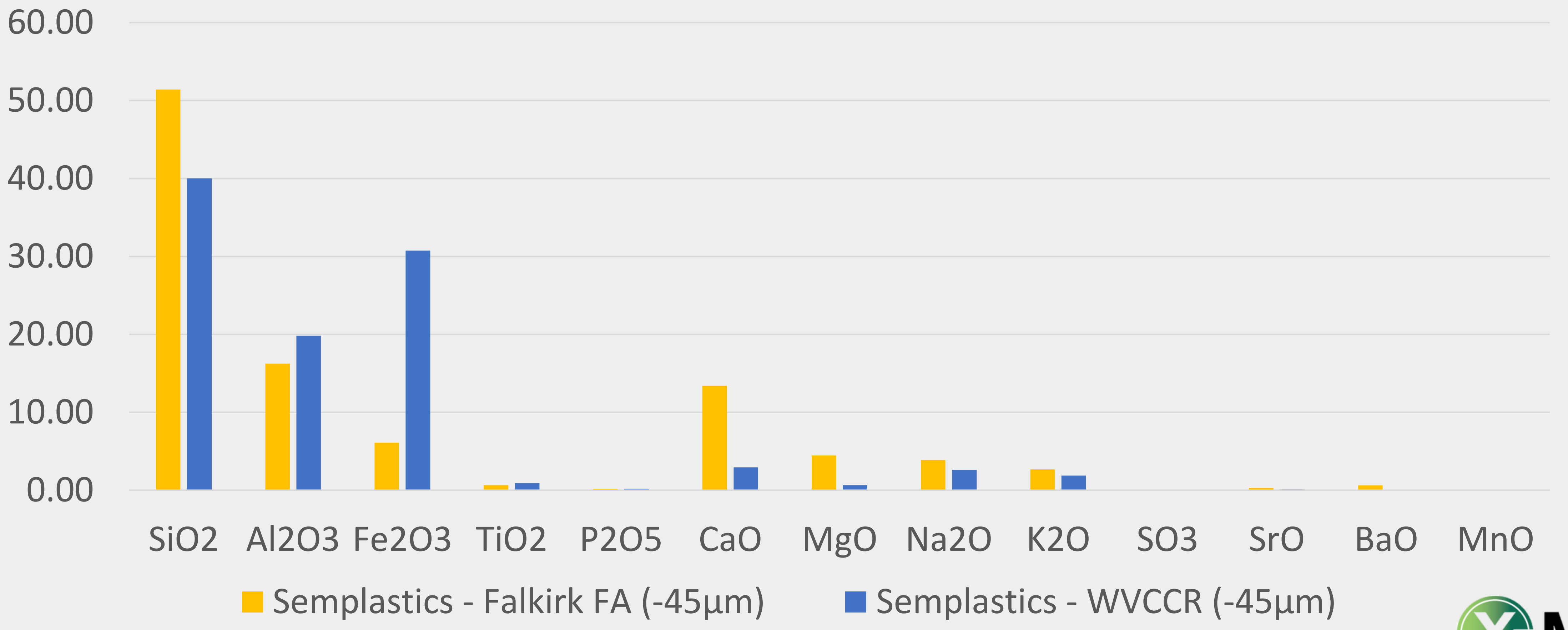
Composition of Fly Ashes



Composition of Fly Ashes – cont.

- Lignite fly ash showed higher silica and light metal oxide concentrations, while the bituminous fly ash had higher alumina and much higher iron content with lower light metal oxide content
- The densities and particle sizes differed – the bituminous fly ash was two to three times the size of the lignite fly ash
- **Lignite fly ash:** Density = 2.564 g/cc Particle size: D50 = 5.90 microns, D90 = 15.79 microns
- **Bituminous fly ash:** Density = 2.688 g/cc Particle size: D50 = 15.76 microns, D90 = 33.62 microns

Commercial Opportunities

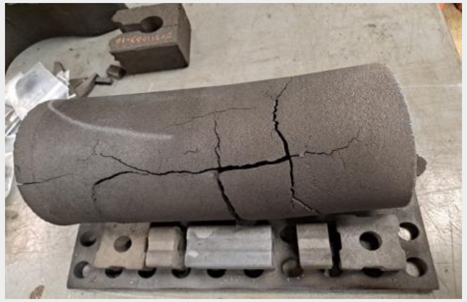
- In 2020, almost 70 Million short tons of Coal Combustion Products (CCP) were produced
- Of what was produced, only about 41 Million tons were beneficially used
- The global polyolefin (polypropylene, polyethylene, etc.) market is expected to exceed 207 Million Tons by 2026.
  - With a 40% filler loading this could result in utilization of 8.3 Million Tons of of CCP at 10% adoption
- Utilizing the CCP encapsulated by our resin not only would result in a lower-cost, higher strength polypropylene but it would also provide a significant, value-added avenue for the beneficial use of Coal Combustion Residuals.
- CCR coated with Semplastics' resins would be competitive with current plastic fillers such as calcium carbonate, talc, and mica - $0.08-$0.16 per pound of Semplastics coated particles vs. $0.20-$0.40/lb for commercial fillers
- Coated CCR ceramic aggregate expected to provide significantly enhanced properties for concrete vs. current CCR additions to concrete

Accomplishments – Columns

- After optimizing a formulation through a statistical screening process, we made the first 4”-diameter prototype
- Then we transferred the process to CART, our scale-up partner in WV, and found that at 6” in diameter cracks formed due to shrinking during pyrolysis
- Explored doing a hollow column design which allows for more even heating of the material

1st Solid Ceramic Column – About 3.5” X 7”

Cured Fly CCR Column – About 6” X 12”



Showed extensive shrinkage cracking after pyrolysis

Accomplishments – Columns – cont.

- The change in design to hollow columns resulted in full-ceramic, full-size prototypes
  - We hypothesize this shape allowed for more even heating and cooling of the parts
- 5 intermediate-sized columns were fabricated
- 5 full-size columns were fabricated

Testing Results for CCR Columns

Average Compressive Strength	6450 psi
Average Flexural Strength	1510 psi
Average Density	1.84 g/cc
Average Open Porosity	21.24%

(Back) – Full Size, 9” X 18” Ceramic Columns
(Front) – Intermediate Size, 6” X 12” Ceramic Columns

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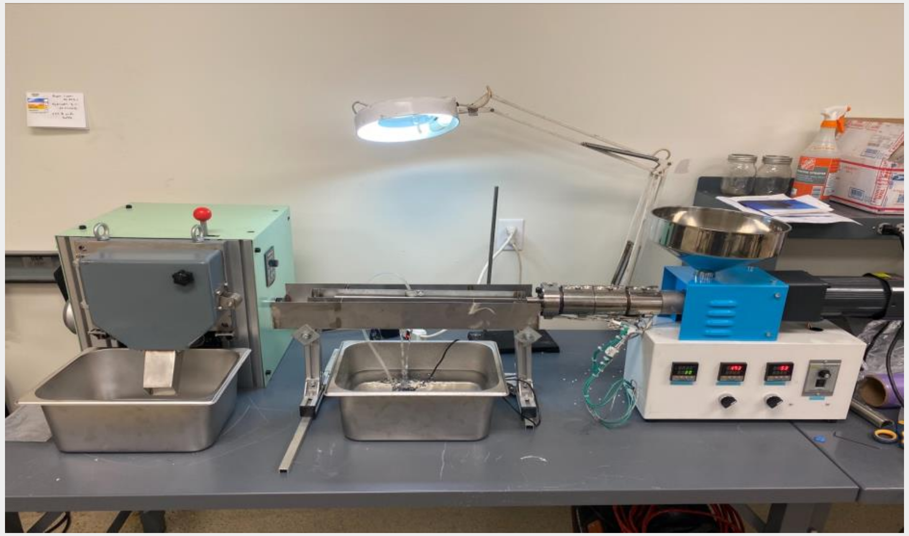
Accomplishments – Plastic Filler

Encapsulation

- Developed process to coat/encapsulate CCR particles with a thin layer of polymer for minimal agglomeration
- Coating is 2.5% to 5% of the mass of the material ~ \$.08 – \$0.16/lb of coated particles
- Used vacuum casting to produce initial flexure test specimens and to determine the effect of varied filler percentages in the polypropylene
- Have demonstrated that the cured resin coating encapsulates the CCR and significantly decreases leaching of undesirable elements

Accomplishments – Plastic Filler – cont.

Demonstrated that standard screw extruder mixing (compounding) of coated CCR and polypropylene powder/pellets is feasible

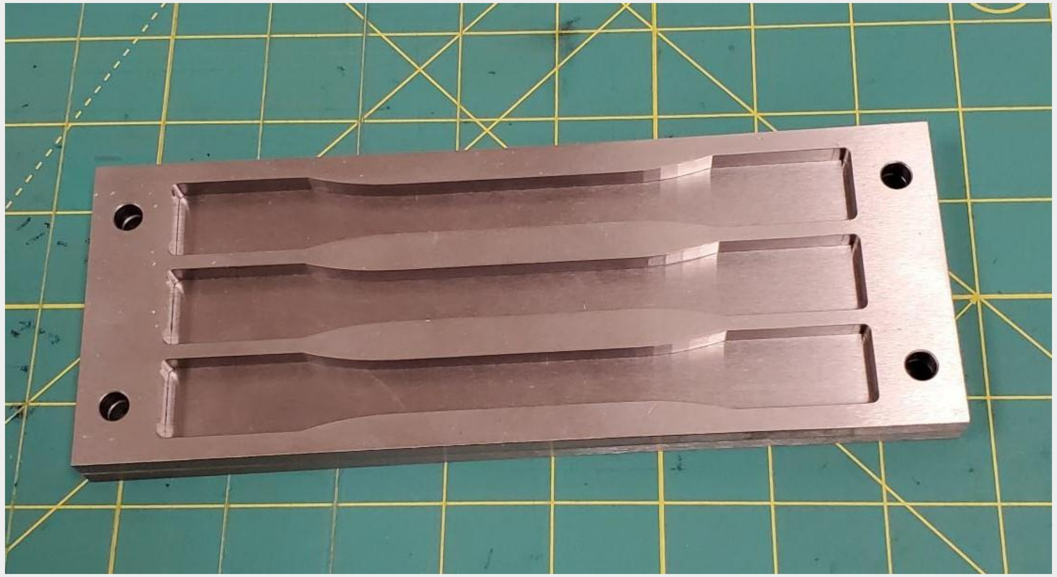


Assembled Compounding line for CCR/polypropylene

50% CCR/50% Polypropylene Pellets

Tensile Test Specimen Fabrication

WV CCR filled polypropylene (left) and ND fly ash filled polypropylene (right) tensile samples



Steel Injection Mold for Production of Tensile Testing Samples

Testing of Injection Molded Samples

Testing Completed by Clemson

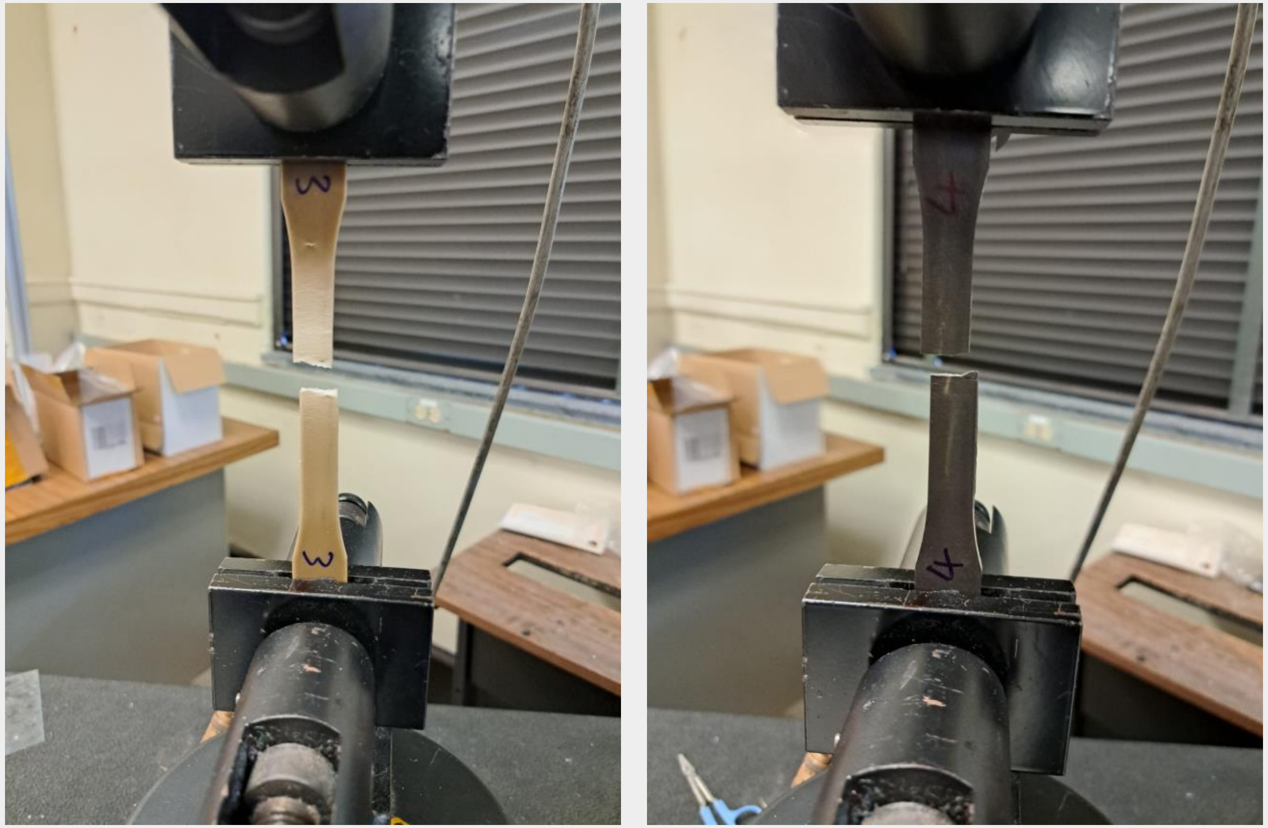
- Standard: **ASTM D638**
- UTM: **Instron 5582**
- An **extensometer** was attached to the specimen to record the displacement
- Load cell used: **10 KN**
- Pre-load: **5 N**
- Loading rate:
- No. of Tests:

  Minimum of 8 for each sample

  Total no. of tests performed: 78

Tensile Testing Setup

Testing of Injection Molded Samples – cont.



Representative images of the tensile specimens after testing
ND Fly Ash Filled Polypropylene (left) WV CCR Filled Polypropylene (right)

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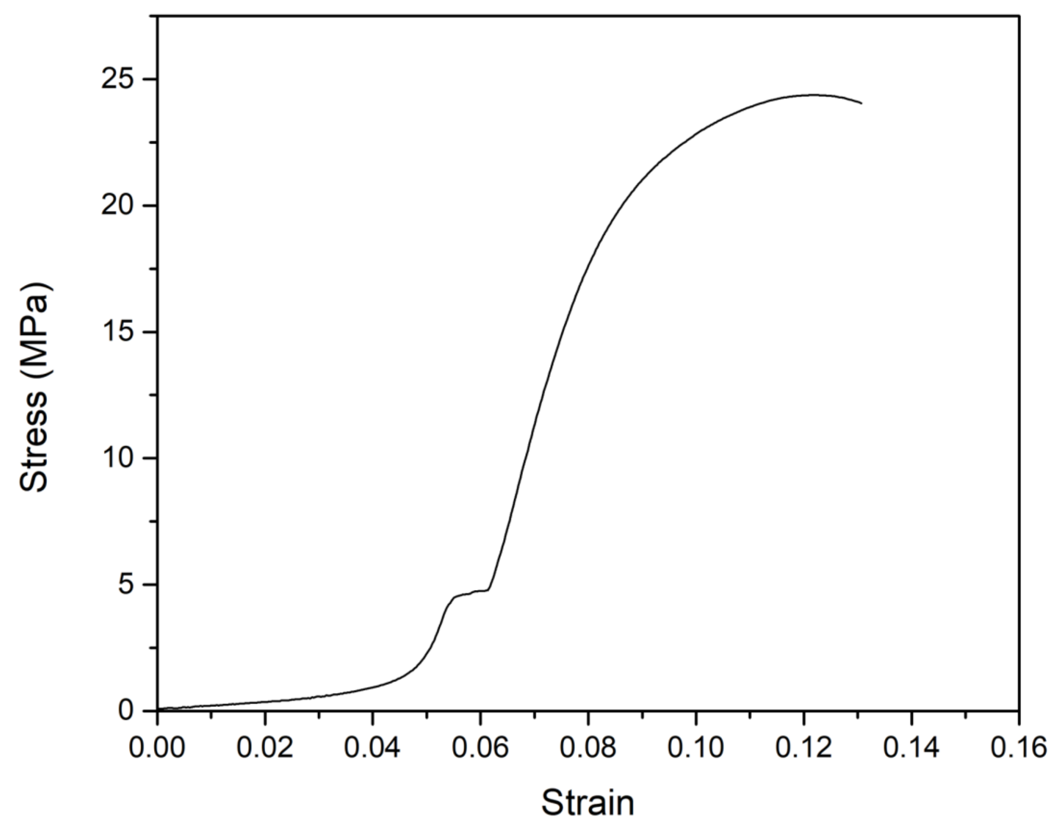
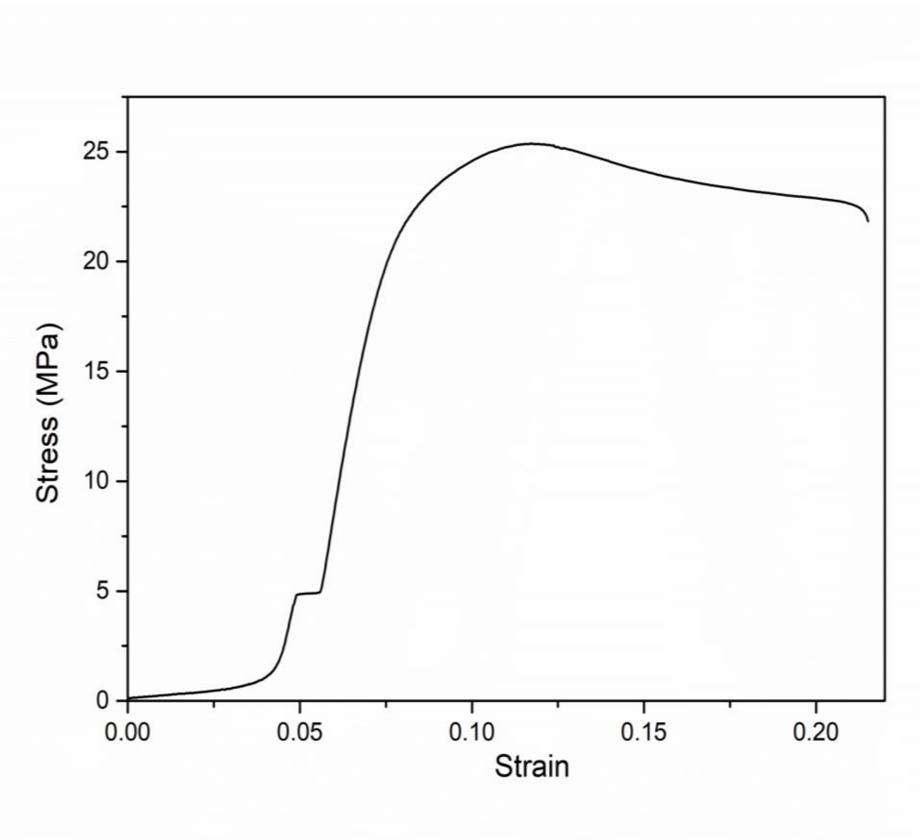
Testing of Injection Molded Samples – cont.



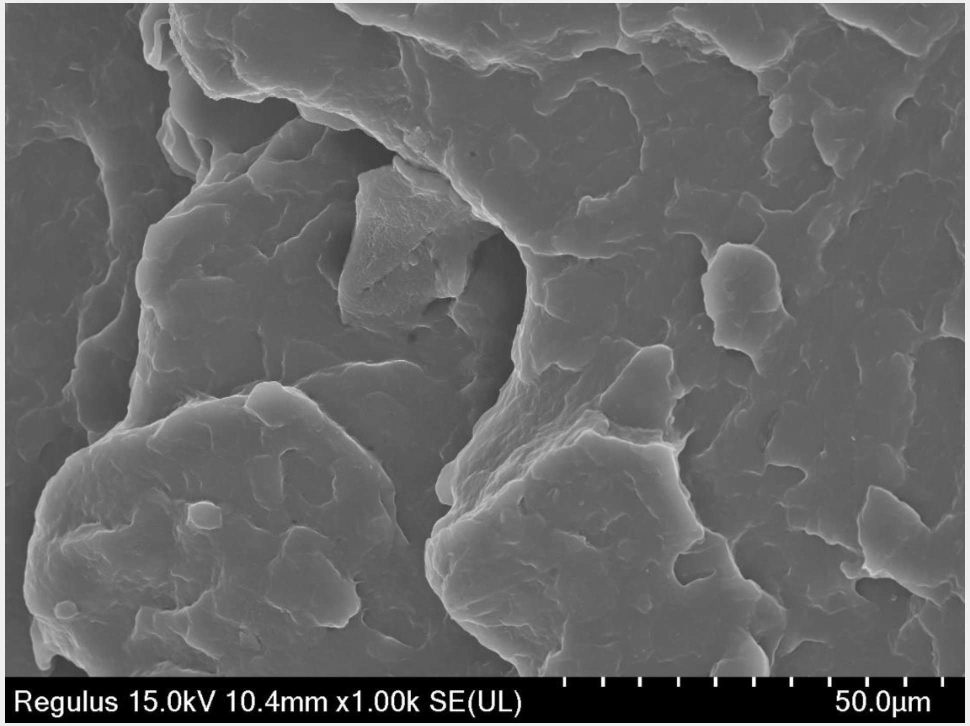


- Slightly delayed fracture was observed in few CCR/Fly Ash filled specimens

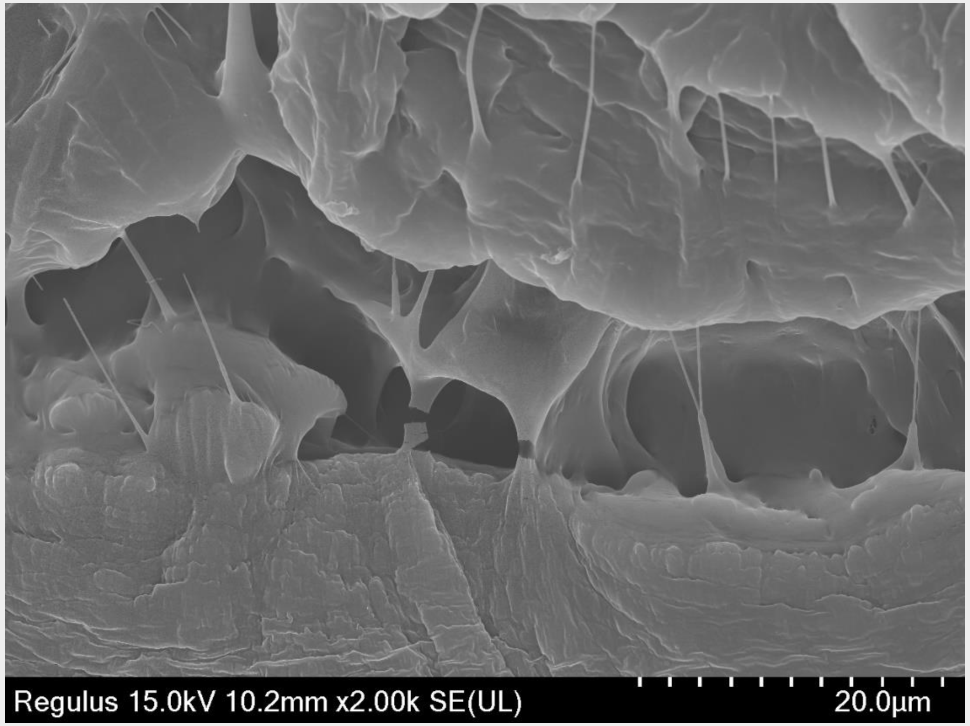
Mechanical Properties of Coated Fly Ash in Polypropylene Injection Molded Tensile Bars

Filler	Coating	Calc. Coating Mass%	Mass % Filler in PP	Volume % Filler in PP	Average Tensile Strength (Mpa)	Average Tensile Strength (psi)	Average Modulus (GPA)	Average Modulus (kpsi)	Strain at Fracture	% Strength of Unfilled PP
NA	NA	NA	0	0	35.19	5104	1.49	216	1.392	100%
NDFA	VTES	3.0	28	12.0	29.24	4241	1.82	264	0.277	83.1%
NDFA	VTES	3.0	33	14.7	29.46	4273	2.18	316	0.188	83.7%
NDFA	B207	1.5	40	19.0	28.52	4136	2.22	322	0.149	81.0%
NDFA	B207	1.5	50	26.0	25.69	3726	2.64	383	0.111	73.0%
WVCCR	B207	1.5	40	18.2	26.65	3865	2.27	329	0.152	75.7%
WVCCR	B207	1.5	50	25.1	24.92	3614	2.83	410	0.128	70.8%
WVCCR	VTES	3.0	40	18.2	25.9	3756	2.38	345	0.236	73.6%
WVCCR	VTES	3.0	50	25.1	24.83	3601	2.72	395	0.147	70.6%
WVCCR	None	NA	40	18.2	19.457	2822	NM	NA	0.08	55.3%

Micrographs of Tensile Bar Fracture Surfaces



Unfilled polypropylene showing lower deformation fracture



Unfilled polypropylene showing ligament type, higher deformation fracture

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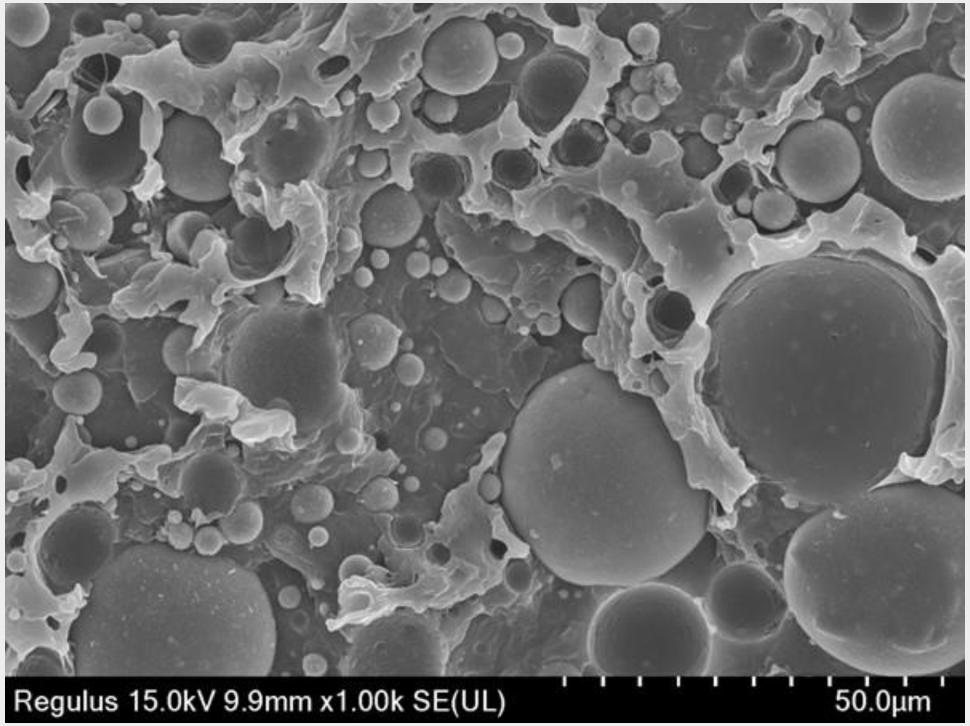
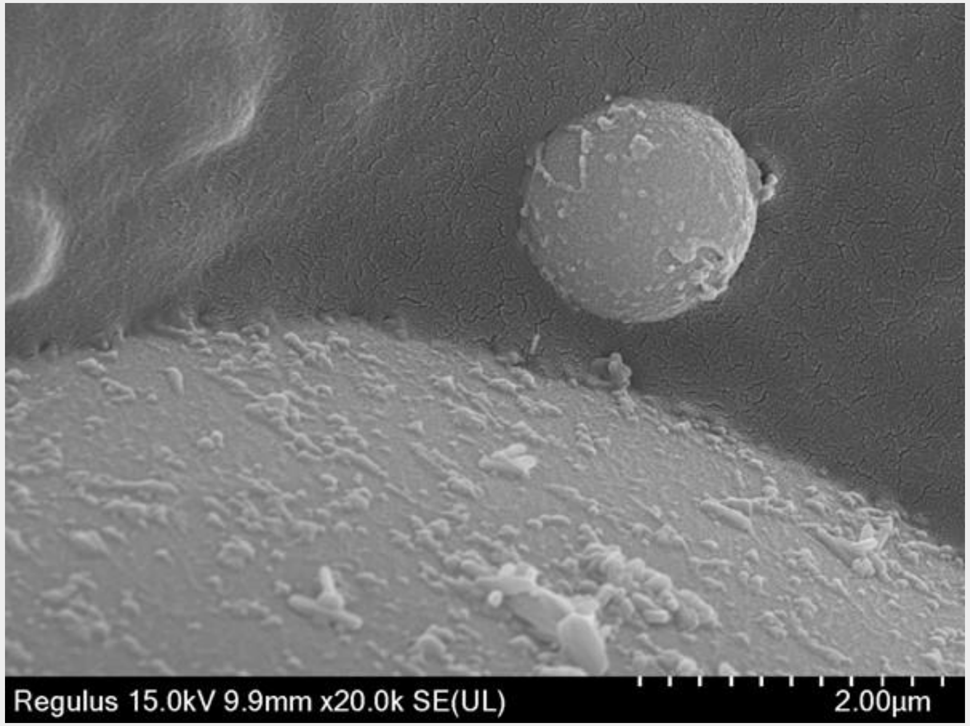
Micrographs of Tensile Bar Fracture Surfaces – cont.

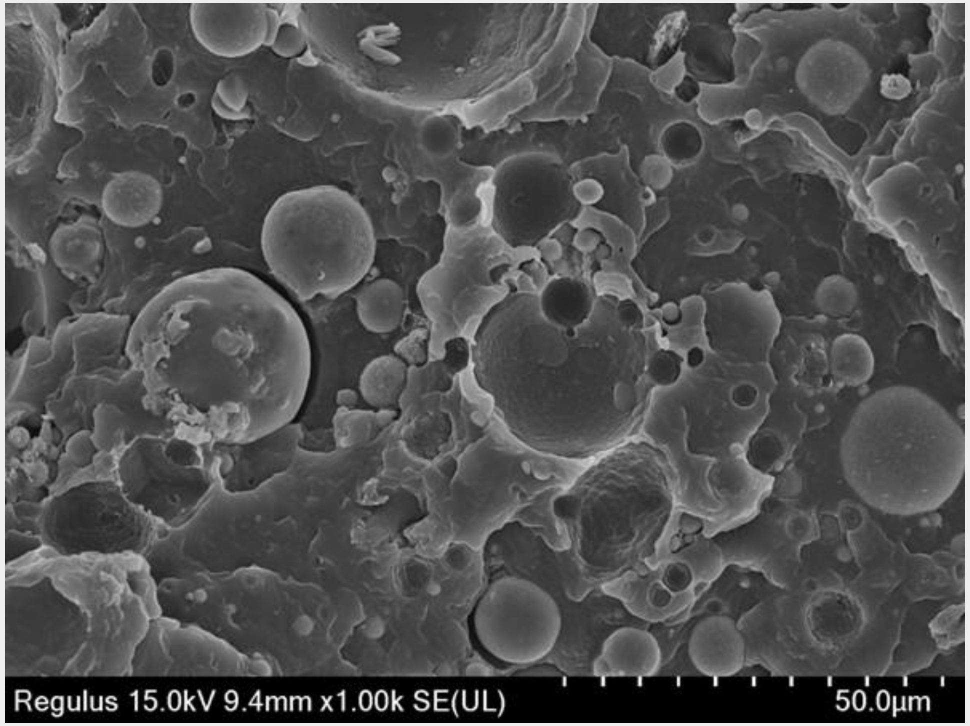


40% B207 Coated NDFA in Polypropylene at lower magnification showing good bonding

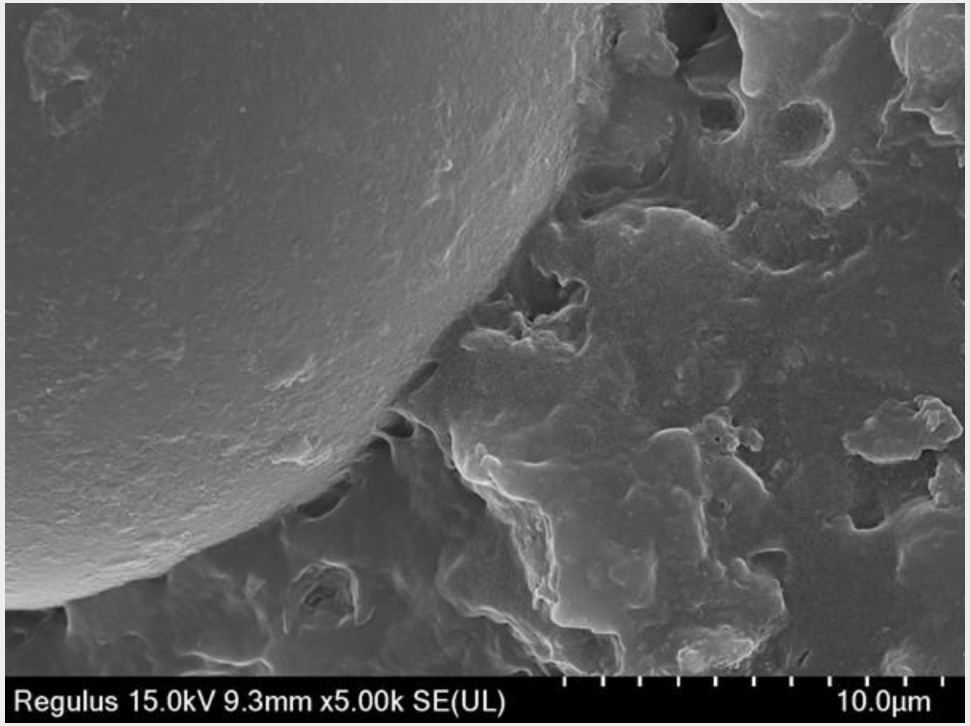


40% B207 Coated NDFA in Polypropylene at higher magnification showing very good bonding

Micrographs of Tensile Bar Fracture Surfaces – cont.

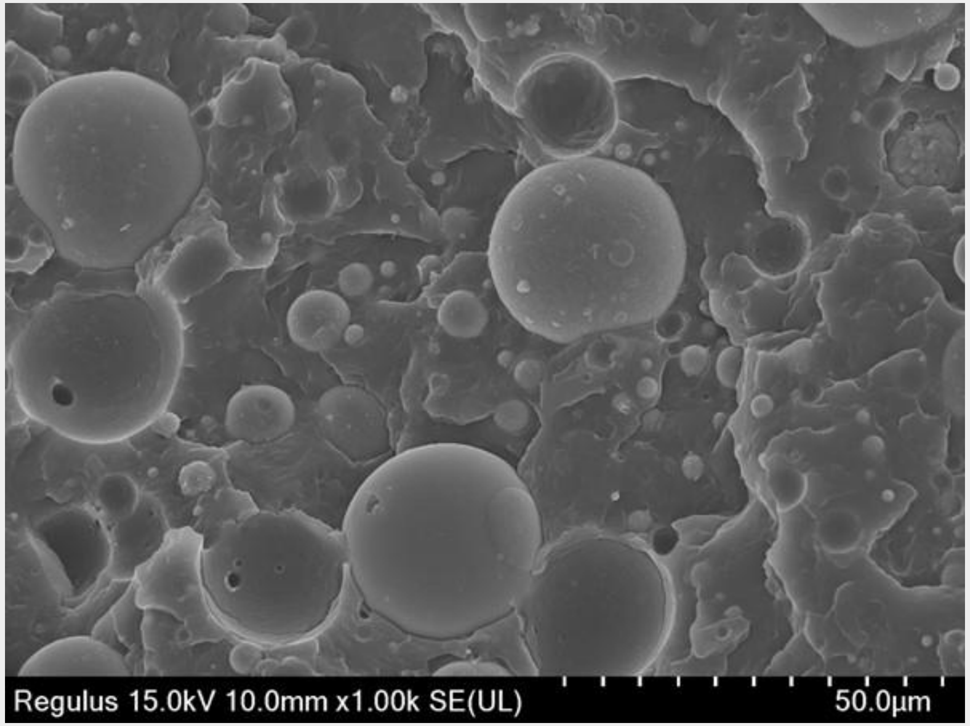


40% B207 Coated WVCCR in Polypropylene at lower magnification showing good bonding

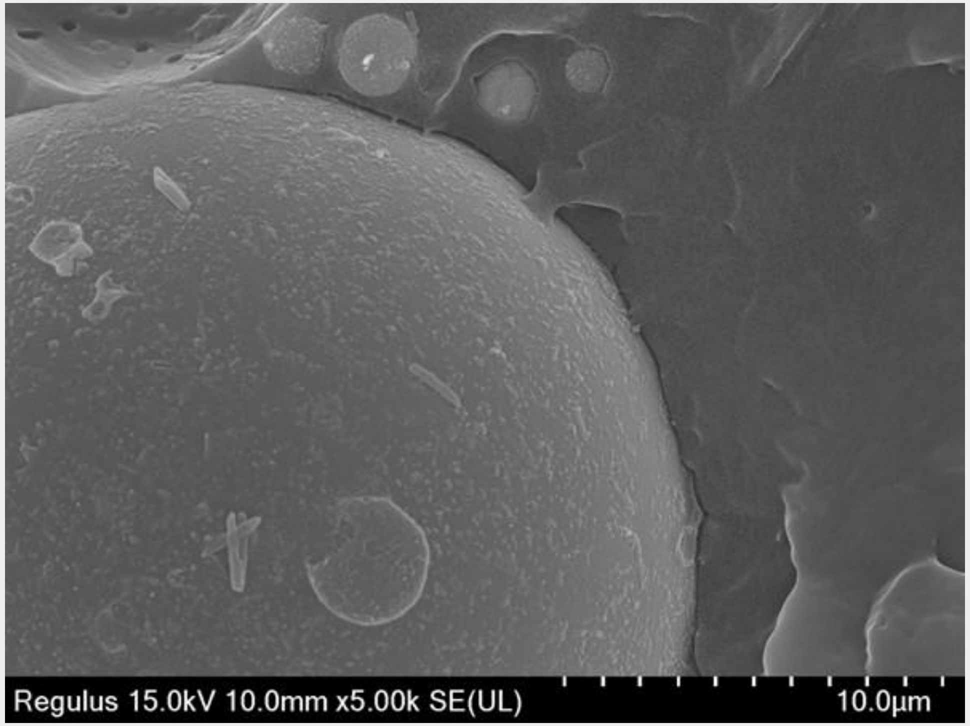


50% B207 Coated WVCCR in Polypropylene at higher magnification showing good bonding

Micrographs of Tensile Bar Fracture Surfaces – cont.

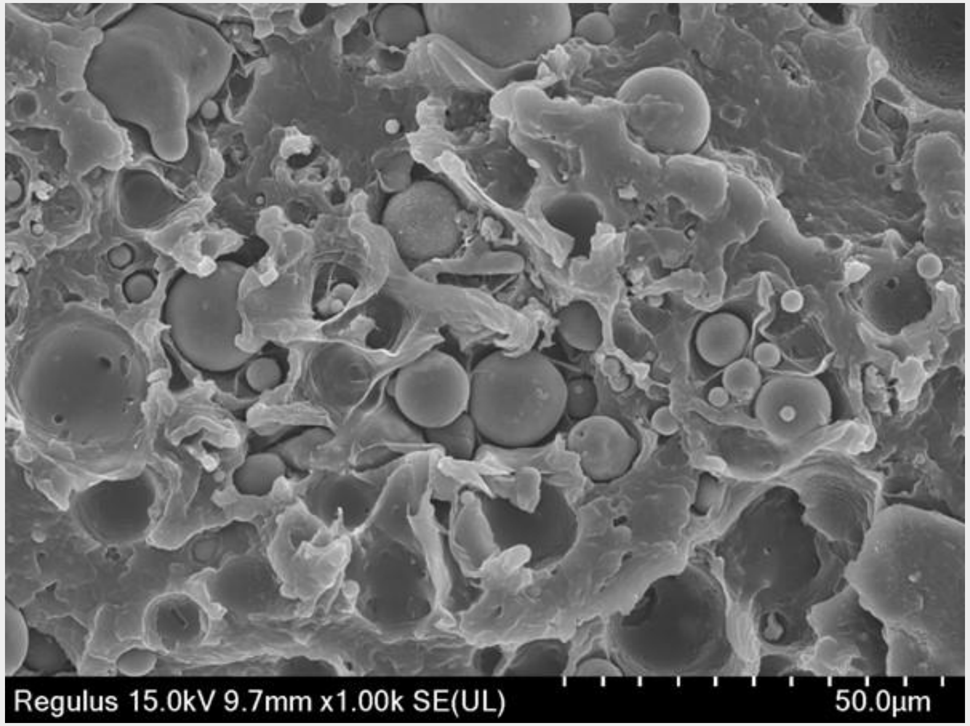


33% VTES coated NDFA in Polypropylene at lower magnification showing slightly poorer bonding

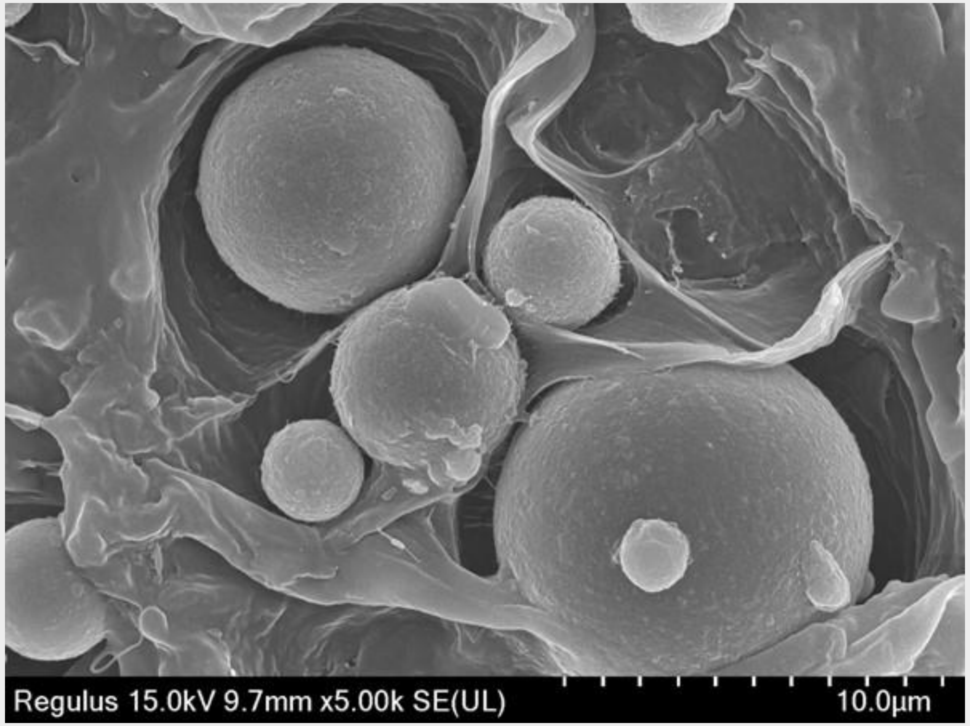


33% VTES coated NDFA at higher magnification showing slightly poorer bonding around filler particle

Micrographs of Tensile Bar Fracture Surfaces – cont.



40% VTES coated WVCCR in Polypropylene at lower magnification showing poor bonding to particles



40% VTES coated WVCCR in Polypropylene at higher magnification showing very little bonding to the particles

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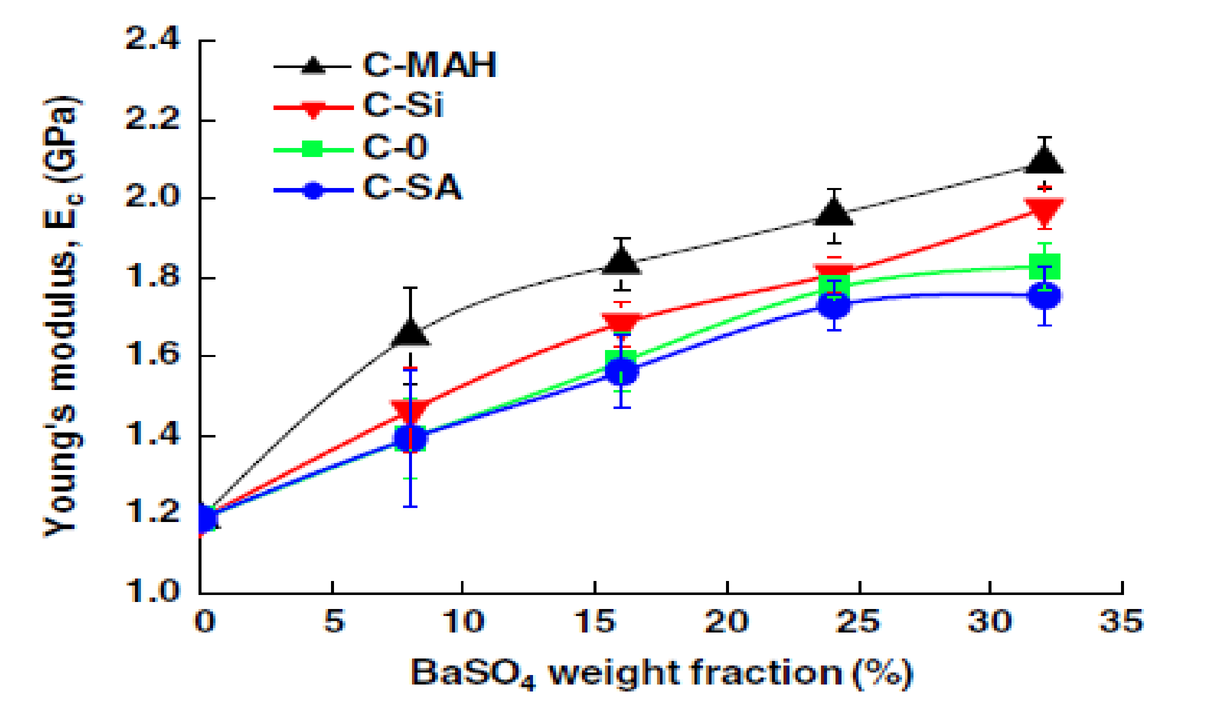
Modeling of Filled Plastics

Polypropylene/barium sulfate composites



The effect of filler content on the modulus of polypropylene

The Young's modulus of the PP/$BaSO_4$ composites. M-0: virgin PP + $BaSO_4$ without pretreatment; M-SA: virgin PP + $BaSO_4$ pretreated with 1 wt% stearic acid; M-SI: virgin PP + $BaSO_4$ pretreated with 1 wt% silane AMPTES; M-MAH: PP-g-MAH + $BaSO_4$ without pretreatment. The resultant composites were designated hereafter as C-0 for PP/M-0, CSA for PP/M-SA, C-SI for PP/M-SI and C-MAH for PP/M-MAH, respectively.

Wang K, Wu J, Ye L, Zeng H. Mechanical properties and toughening mechanisms of polypropylene/barium sulfate composites. Composite Part A 2003;34:1199–205

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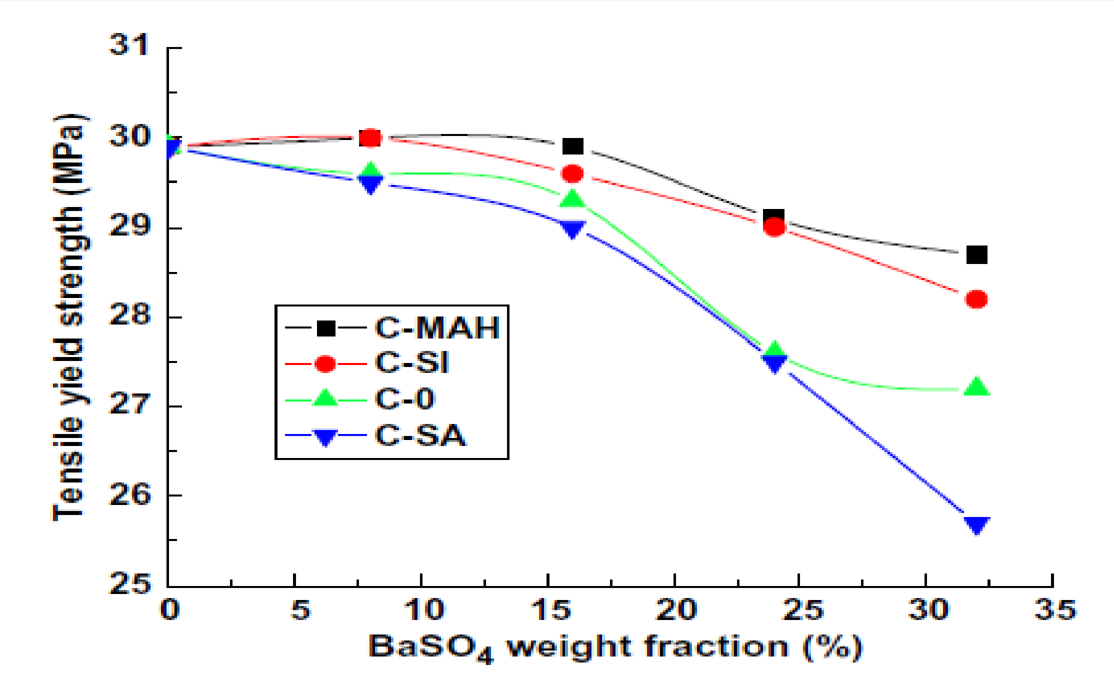
Modeling of Filled Plastics

Polypropylene-$BaSO_4$ composites



The yield stress of the neat PP and the PP/$BaSO_4$ composites

interfacial modification. C-MAH
(PP/M-MAH) and C-SI (PP/M-SI), with interfaces
modified
with PP-g-MAH and silane, have higher yield
strength
than that without modification (C-0) or modified
with stearic acid (C-SA), showing pronounced
reinforcements

Wang K, Wu J, Ye L, Zeng H. Mechanical properties and toughening mechanisms of polypropylene/barium sulfate composites. Composite Part A 2003;34:1199–205

Summary

- Full-size columns were successfully fabricated
- Promising versions of the plastic filler have been produced
  - North Dakota and West Virginia fly ash have been investigated
  - Tensile testing and microscopy show the efficacy of our formulations
- Modeling of material properties is ongoing
- All project milestones have been met except the final two, which will be completed by Semplastics and Clemson within the next 5 months

Acknowledgments

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  - Joe Stoffa
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  - Mark Render
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  - Dr. Fei Peng
  - Dr. Sanat Maiti
  - Dr. Ummen Sabu
  - Lee Williams
- Mike Mosser

Thank You for Your Time

Questions / Discussion