AICHE Meeting 2007

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Multilayer Coextrusion of Polymer Nanocomposites

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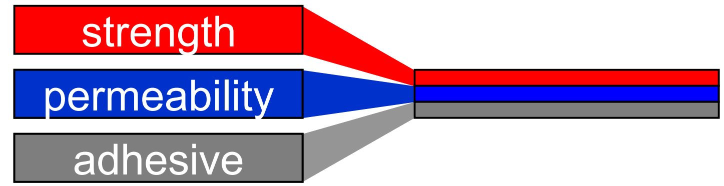
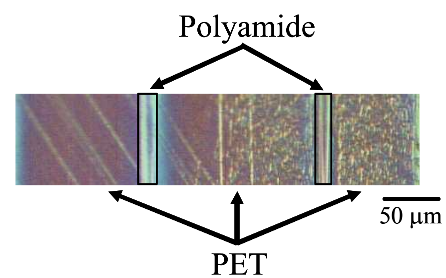
Multilayered Materials

Multilayered coextrusion combines multiple polymers in a layered structure to produce properties not found in a single polymer



Current Applications

- Packaging (bottles, bags, etc.)
- Protection coatings
- Barrier properties



Emerging Technologies

- Energy storage devices
- Display devices
- Sensors
- Optical devices
- Barrier materials
- Membranes
- Microcomposites
- Armor applications
- Responsive clothing

Cargotech Airliner®
maintains temperature during extended transport

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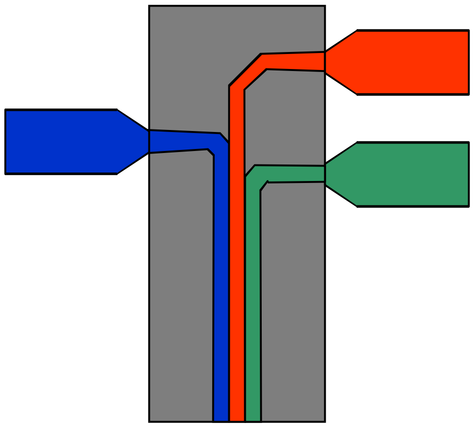
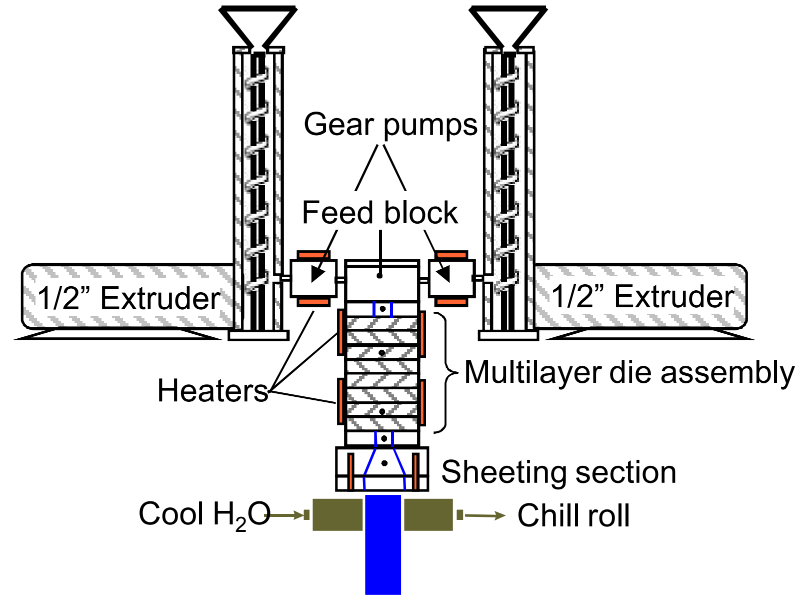
Multilayer Coextrusion Processing

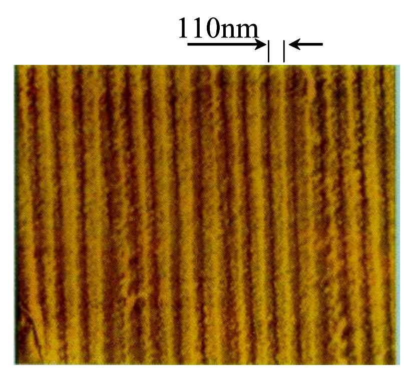
Multiple Extruders



Multiplication Die



$\delta_{PS} = 23.8 \pm 4.0\ (\mu m)$
$\delta_{PP} = 22.9 \pm 5.1\ (\mu m)$

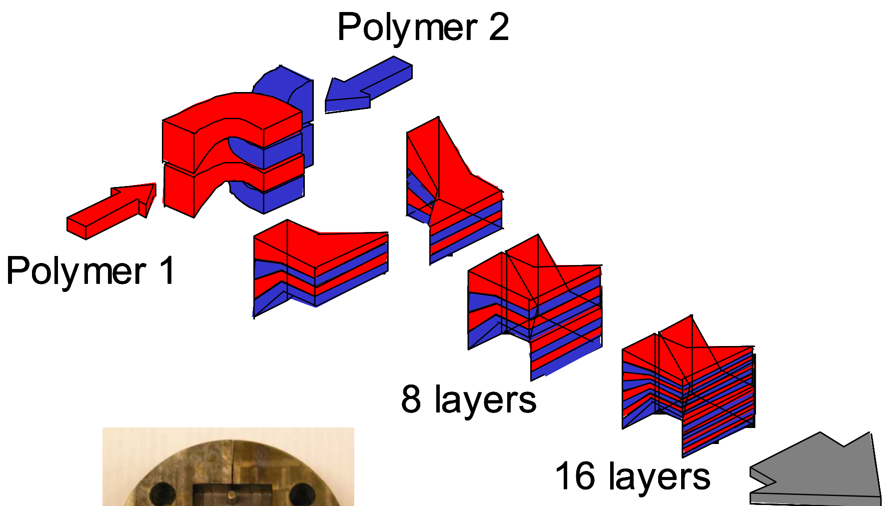


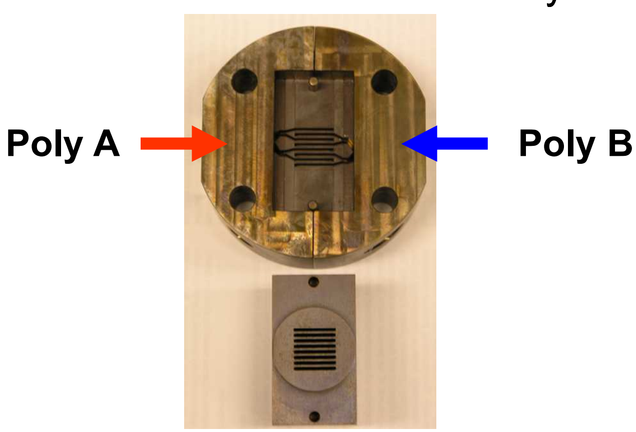
PC/PMMA multilayer, Dow Chem.

- Multilayer die assembly increases the number of layers within the same cross-section
  - Decreases layer thickness
- Gear pumps provide precise flow rate control
- Sheeting die creates ~ 1 mm tape

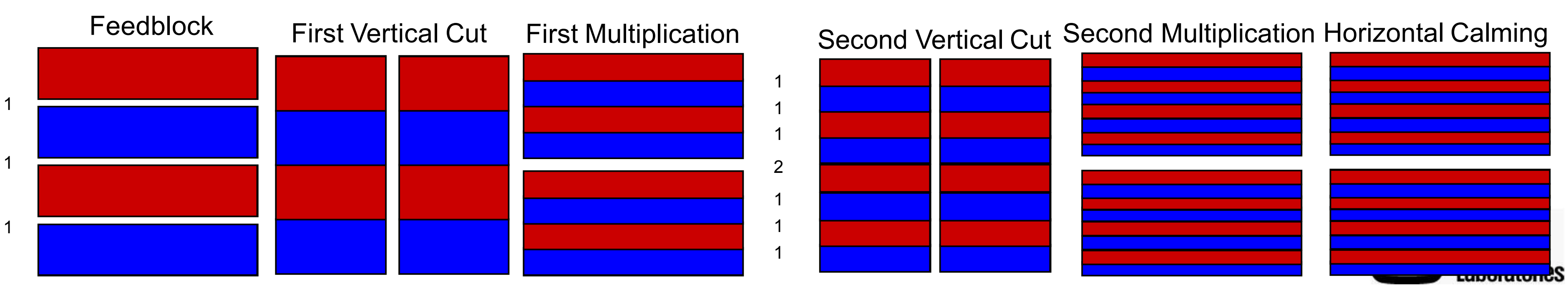
Multiplication Scheme

Multiplication Scheme

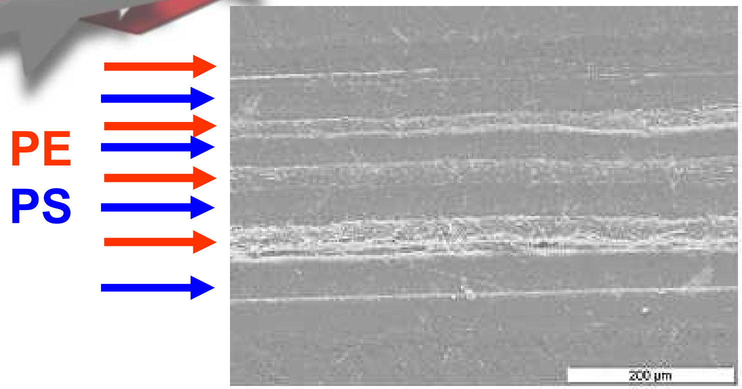


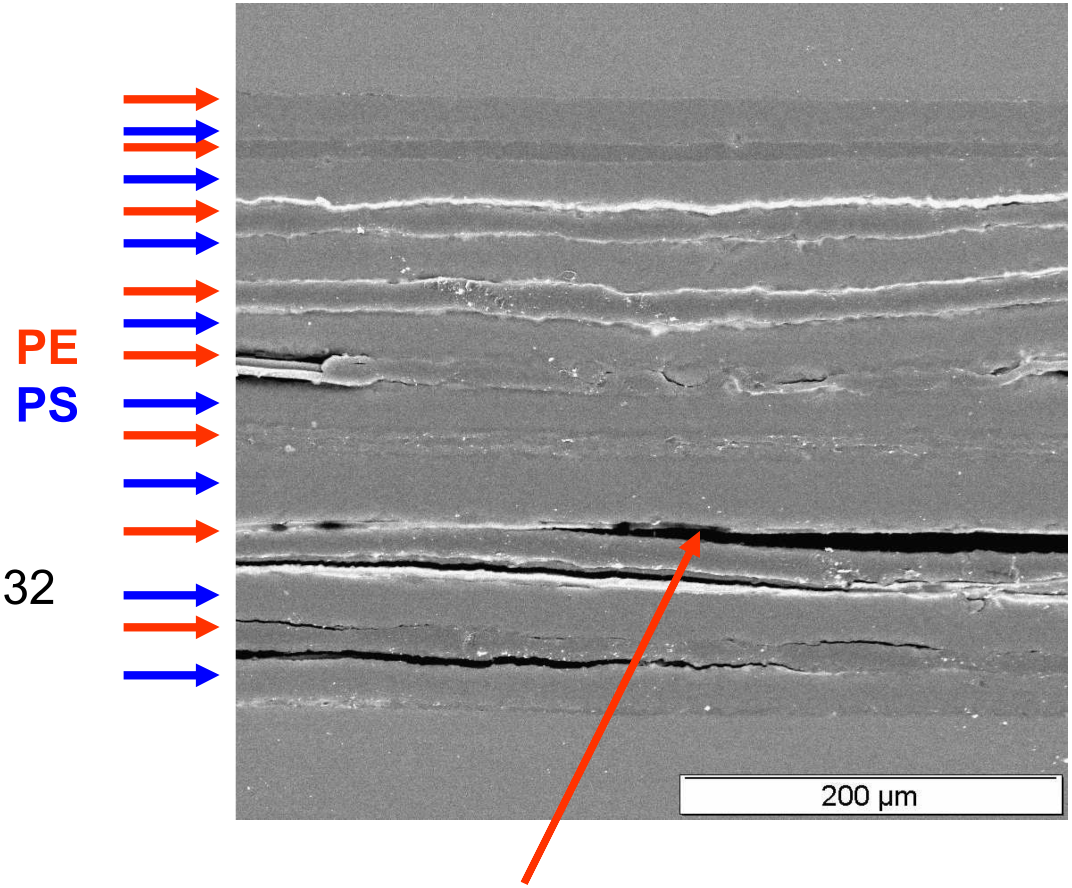


- Feedblock produces initial layered structure
- Each multiplication element doubles the number of layers
- Stacking "n" multiplication dies results in 2^{n+3} layers
- Layer stability is largely dependent on uniform laminar flow
- Thin layers (submicron) can easily break-up due to instabilities



Initial Layered Structures





- Successfully extruded 8, 16, and 32 layered structures
- End thickness ~ 0.35 mm
- 10 micron layers with reasonable uniformity
- Next step: produce layered structures of filled polymers

Delamination from potting in epoxy and polishing for SEM not due to poor extrusion

Incorporating Fillers

- Coextrusion of composites can increase the versatility and applicability of the technique
- Incorporation of fillers can enhance material properties
  - Mechanical properties
  - Permeability
  - Thermal stability
  - Flame retardancy
  - Chemical resistance
  - Electrical conductivity

www.faa.gov

www.dtaps.com, DTAPS®, Geomet

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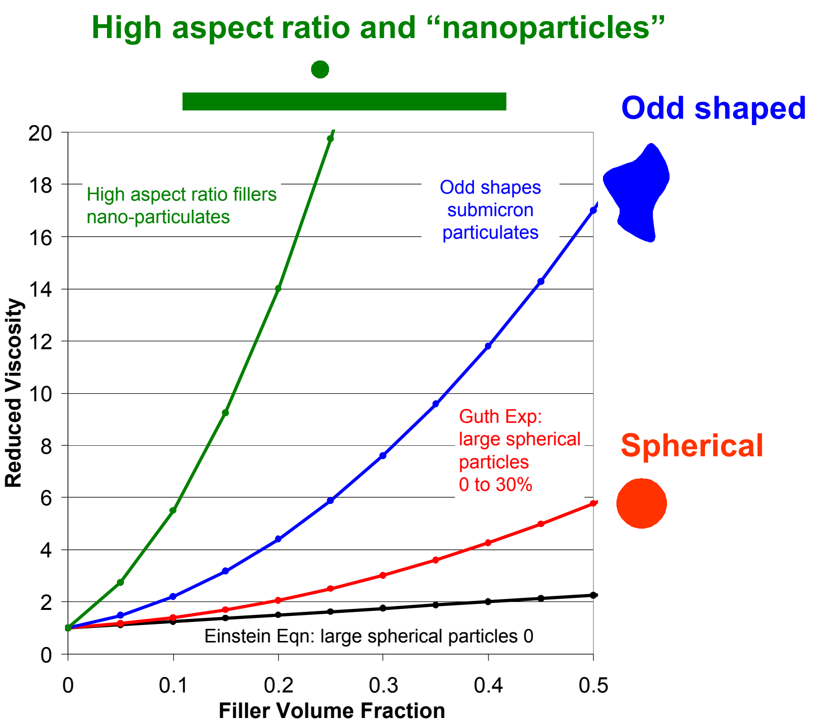
Processing Issues of Filled Systems

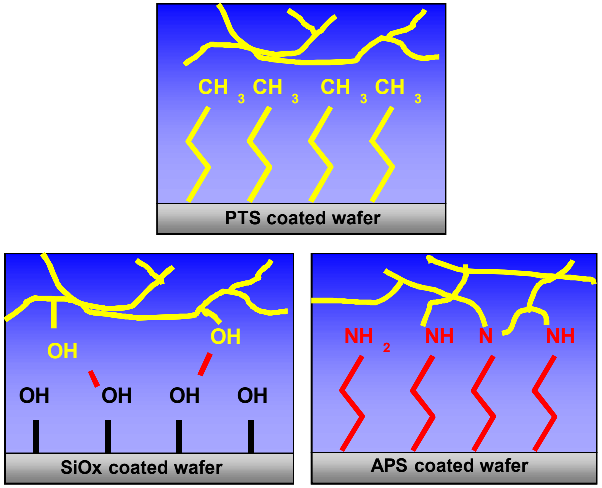
- Sub-micron layers require sub-micron fillers
- Several processing issues associated with sub-micron fillers
  - As with many fillers, property enhancement can require high loadings
  - Difficult to disperse (aggregate at high loadings)
  - Can have a dramatic impact on viscosity even at low loadings
    - Viscosity mismatch between materials in coextrusion leads to layer instability
  - Limited commercial availability in large quantities with small size and shape distributions



Focus of Mitigation Strategies

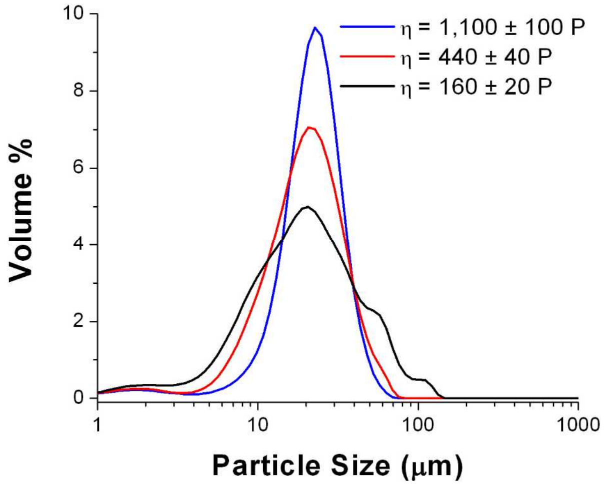
1) Filler surface chemistry

- Control interparticle and particle – polymer interactions by altering the surface chemistry



2) Particle size, shape, and size distribution

- we have observed a decrease in the composite viscosity by broadening the particle size distribution at a set loading of micron sized fillers



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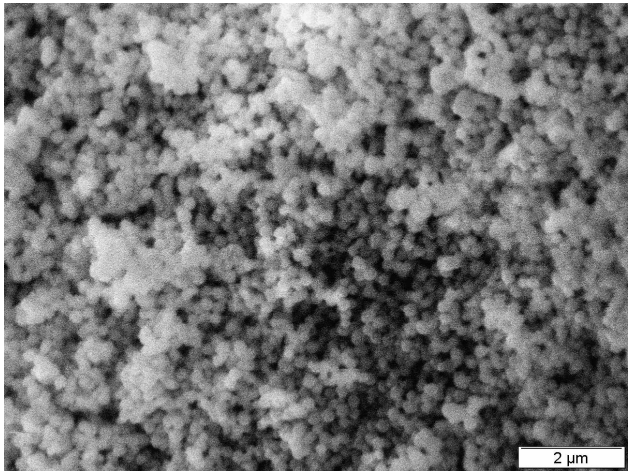
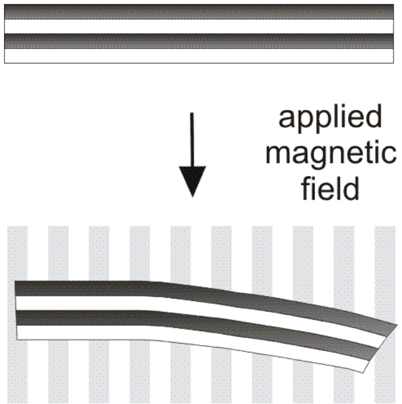
Filled Polymer System

- Nickel nanoparticles
  - Relatively stable to oxidation
  - Conductive
  - Magnetic
  - Commercially available in several sizes with small size distributions
- Polystyrene matrix (currently)
  - Available in large quantities
  - Inexpensive
  - Extrudable
- Elastomers (future)
  - Magnetic field to produce mechanical motion

Nickel Sub-micron Particles





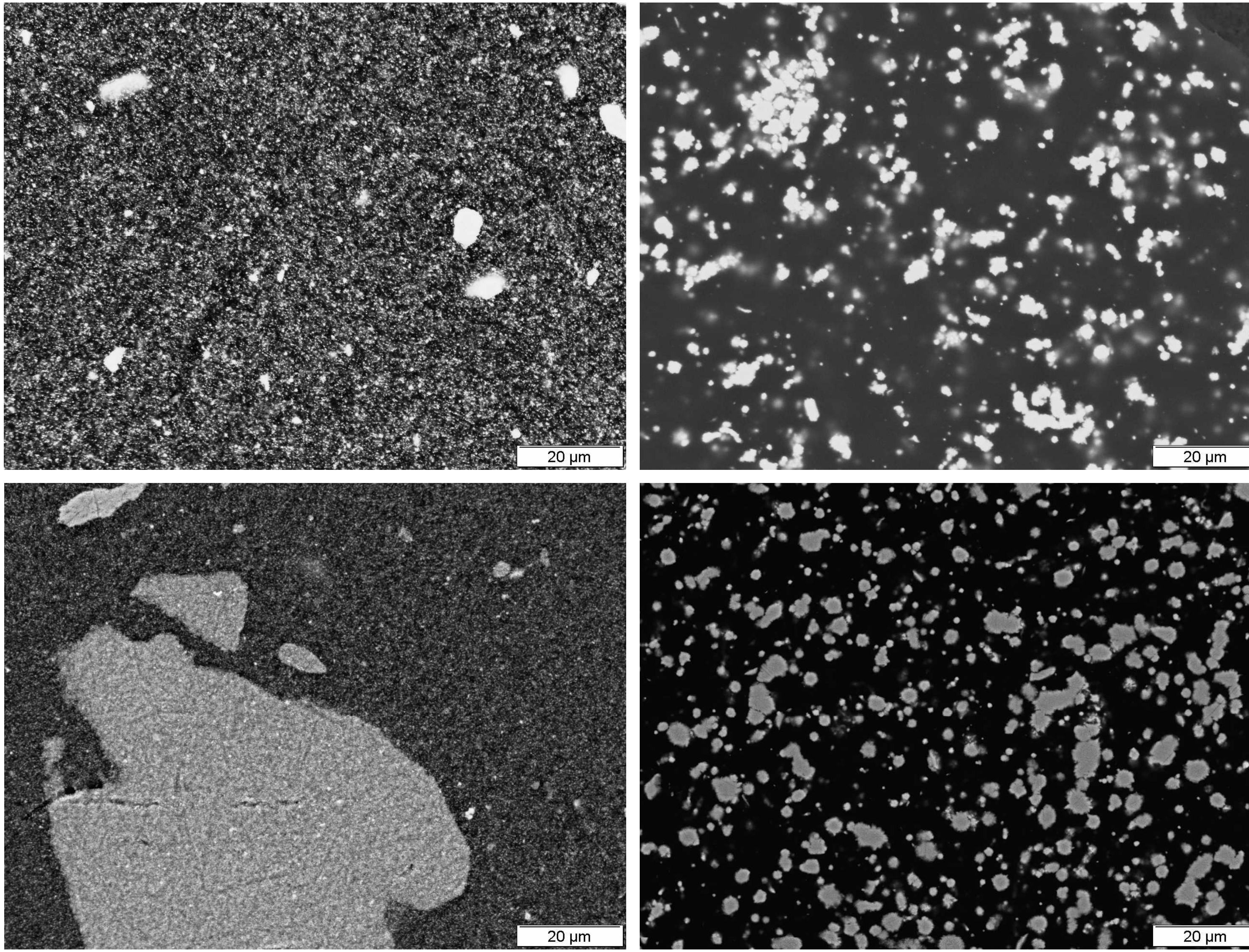
magnetic field to produce mechanical motion

SEM Images

200 nm | *3-5 μm*

10 vol %

20 vol %



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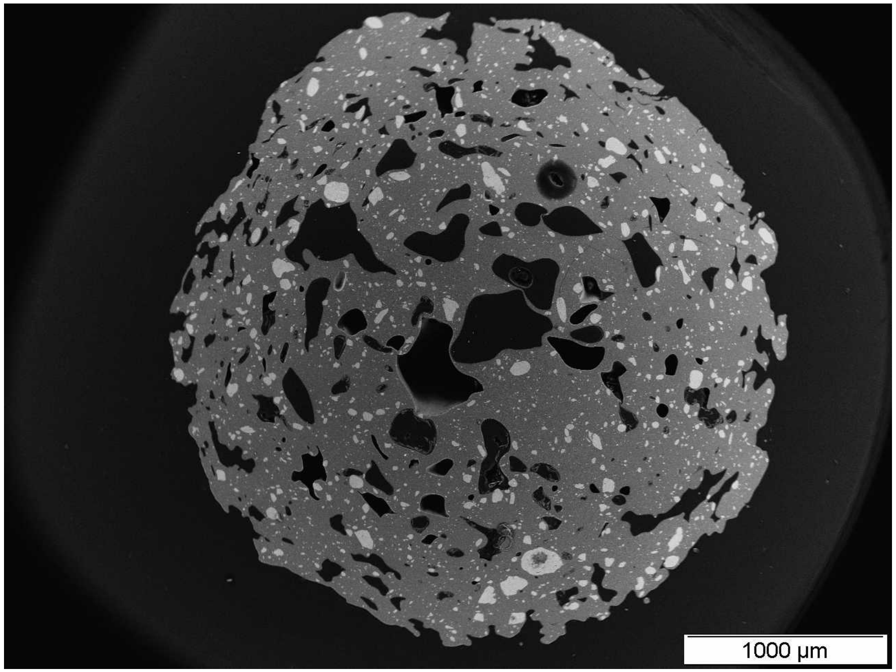
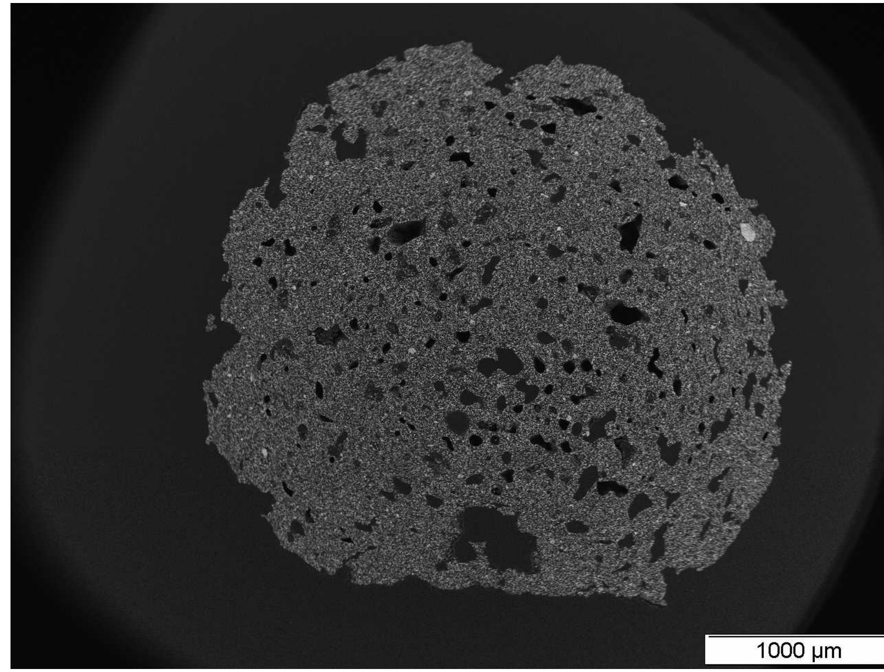
Cross-section SEM Images

200 nm



3-5 µm



- Dark spots attributed to air voids
  - likely result of viscosity increase
- 3-5 µm sample exhibits modest conductivity (10^{-4} S/cm)

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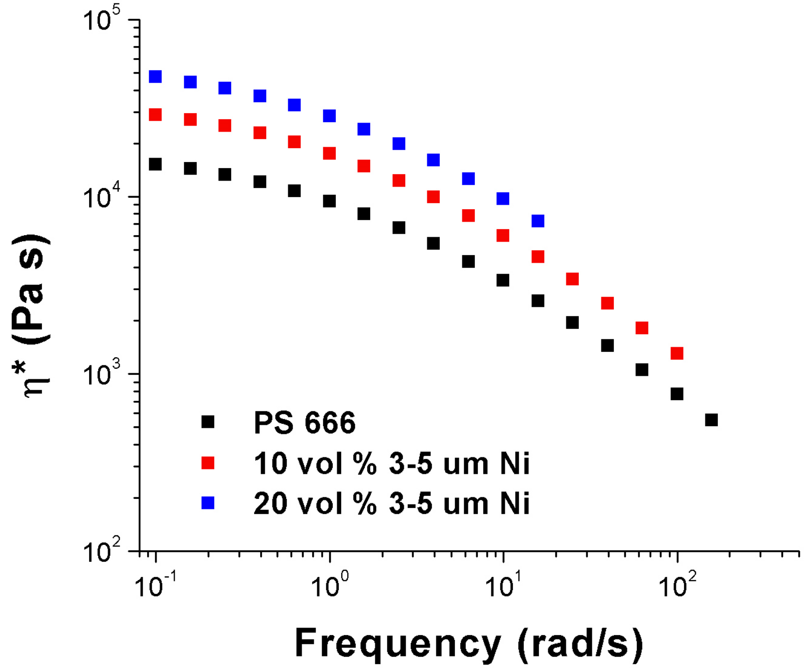
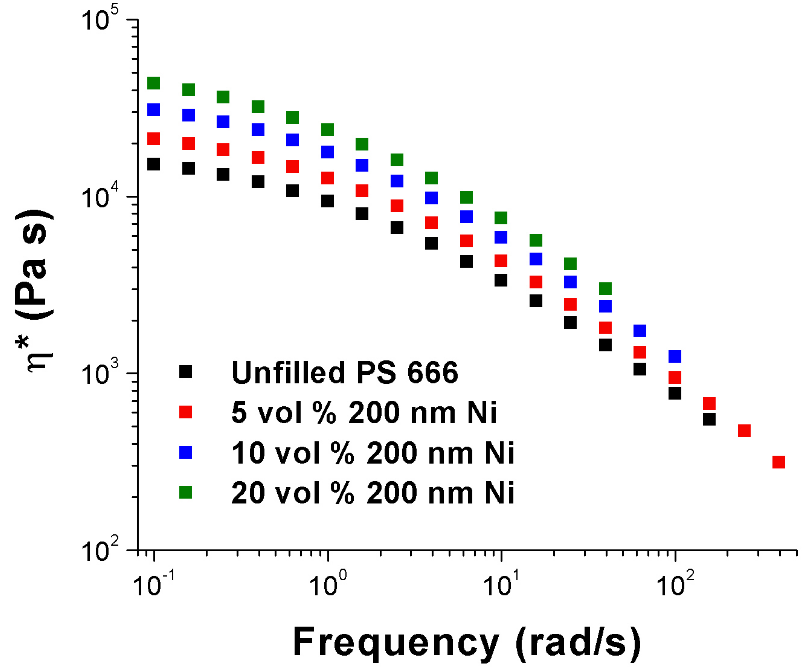
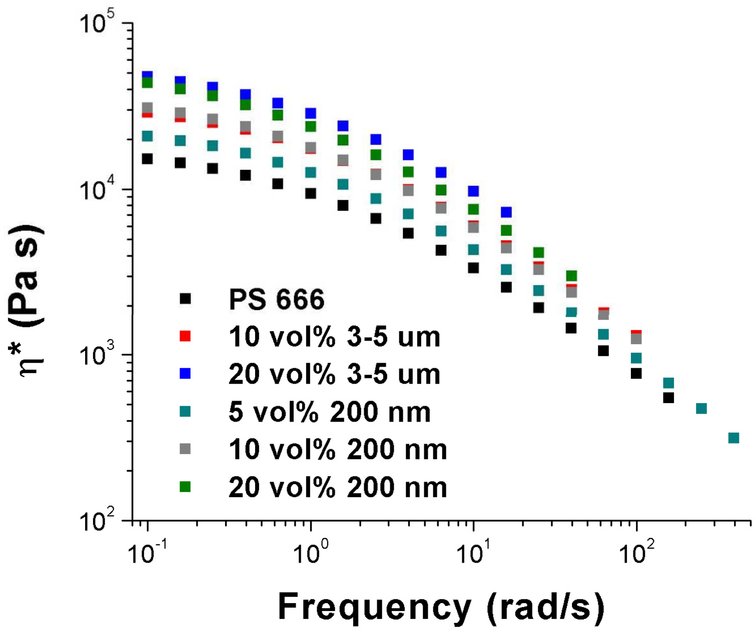
Viscosity Effects

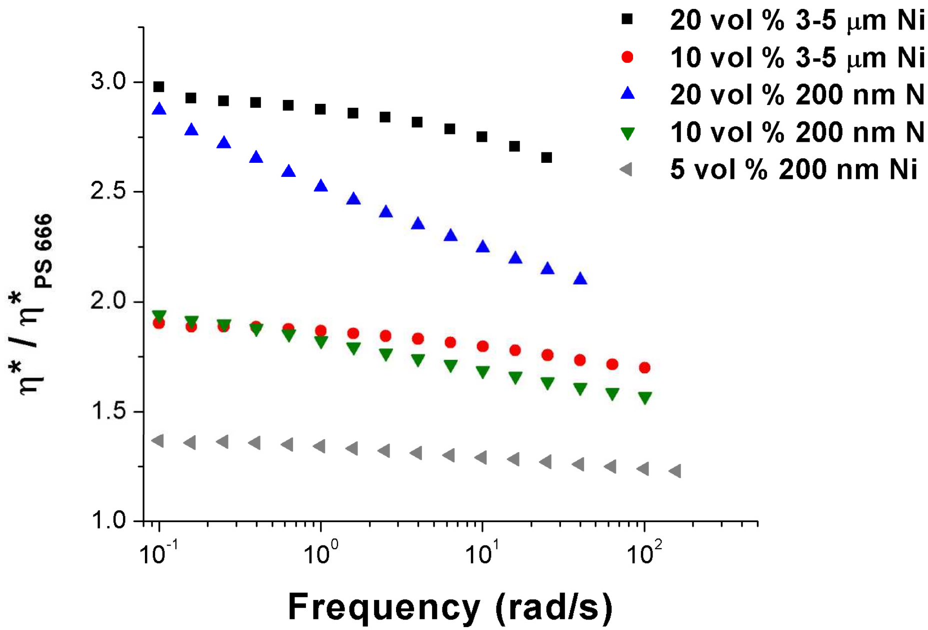




- Viscosity increases with loading
- Similar increase with loading regardless of particle size

Viscosity Comparison





- Low frequency data is similar with loading
- Enhanced shear thinning at higher frequencies
  - Break up of agglomerates

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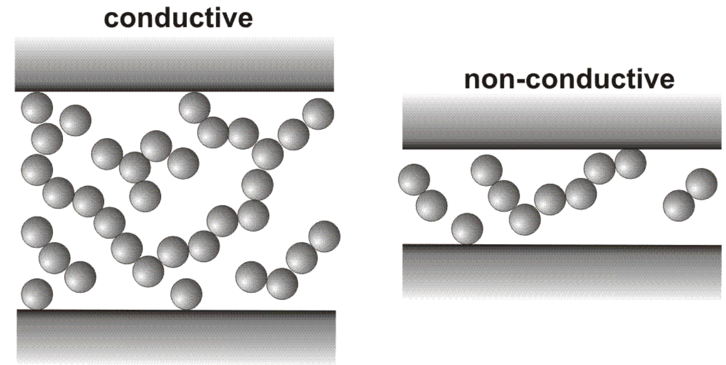
Impact of Filler on Processability

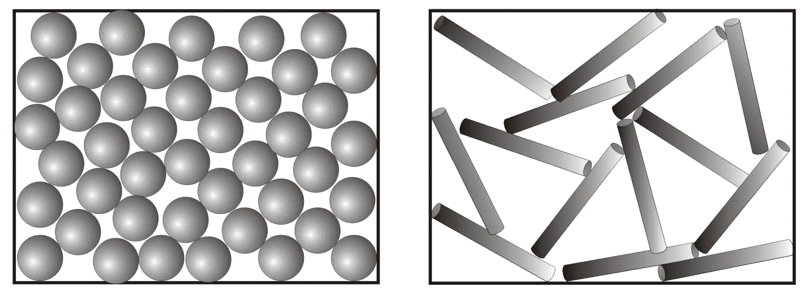
Impact of filler on the viscosity and layer stability

- Percolation behavior vs. layer thickness
  - Particle size/ layer thickness ratio can change percolation threshold

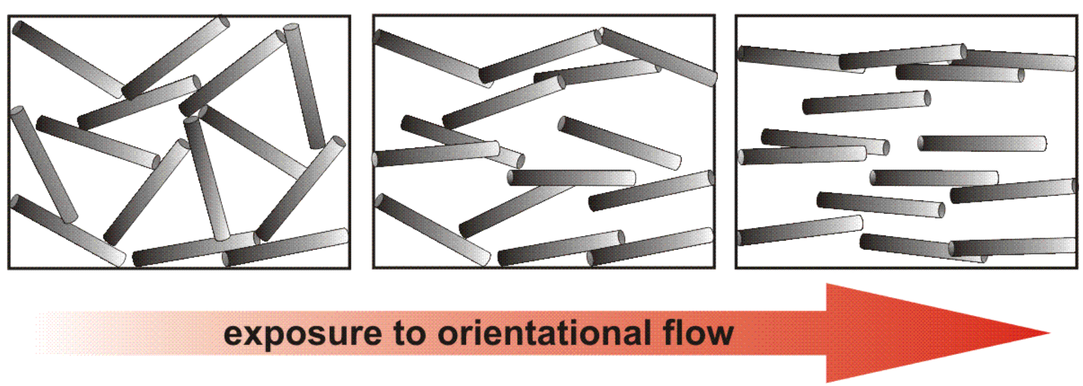


percolation vs. layer thickness

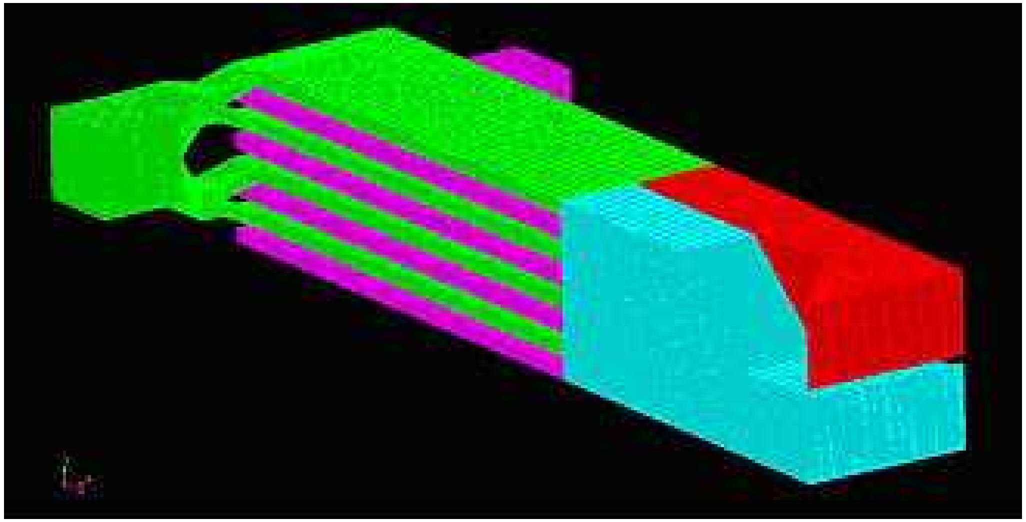
- Particle size, shape, and size distribution on viscosity
  – Viscosity mismatch between layers leads to instability



sphere vs. cylinder percolation



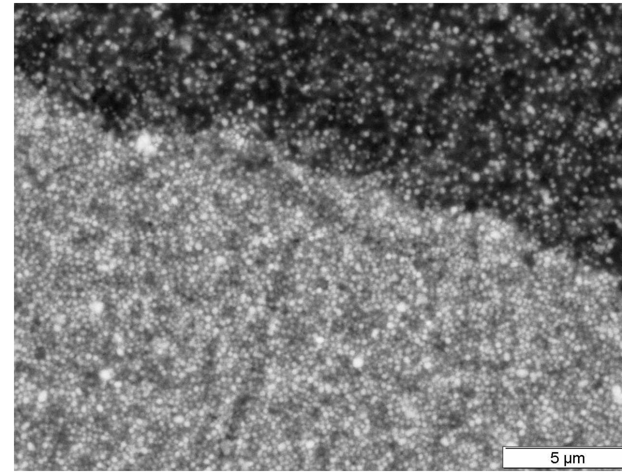
Modeling the Flow Field



- Model the flow field to aid in identifying potential sources of layer instability
  - Instrumental design
  - Instabilities increase as the layer thickness decreases
  - Adhesion issues
  - Determining the allowable window of viscosity mismatch
  - How do the particles influence the flow field?

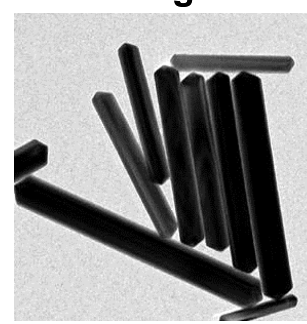
Current Work / Summary

- Enhance the dispersion of the nanoscale Nickel particles
  - Elongational mixing
- Determine processability window for coextruded nanocomposites
  - How big of a viscosity mismatch can be tolerated?
  - How do the nanoparticles influence the flow field?
- Elongated vs. spherical fillers
  - Elongated fillers can enhance the properties at lower loadings than spherical fillers but typically have a larger influence on the viscosity
- Produce layered structures with layer thicknesses < 10 µm composed of nanocomposites



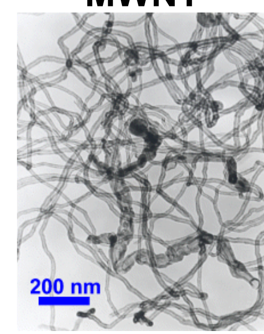
200 nm Ni in polystyrene

Ag



Seashell Technologies
Diameter = 75 nm
a.r. ranges from 10 - 1000

MWNT



NanoAmor
Diameter = 20 - 30 nm
Aspect Ratio = 15 - 100

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