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Co-Extrusion of Polymers Filled with Particulates and a Eutectic Alloy

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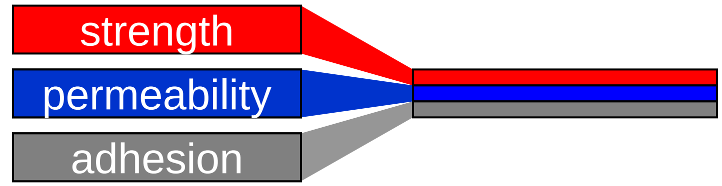
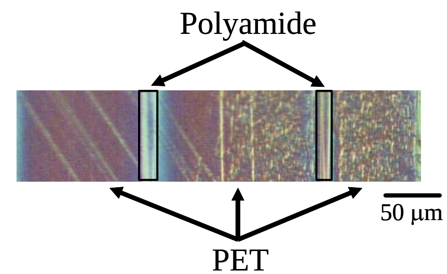
Multilayered Materials

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



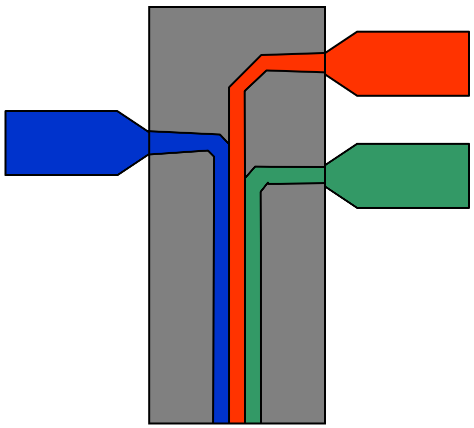
Emerging Technologies

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

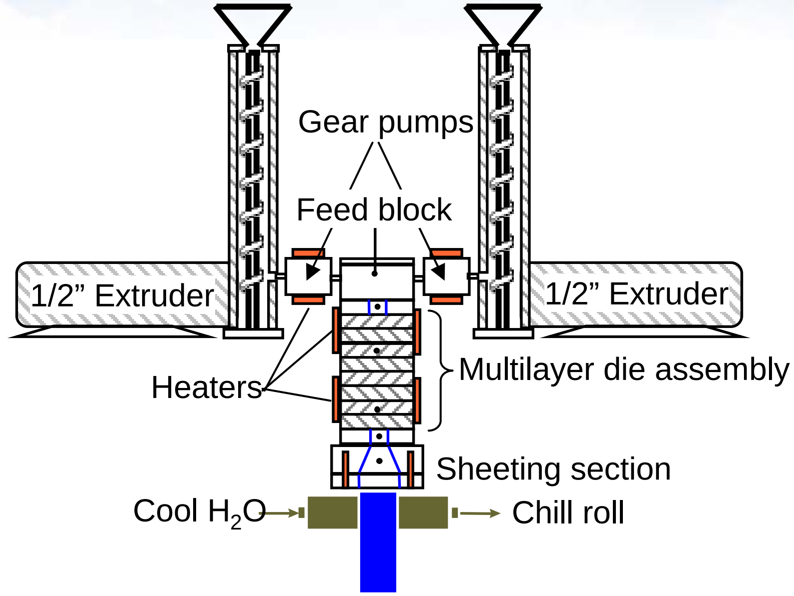
Cargotech Airliner®
maintains temperature during extended transport

Multilayer Coextrusion Processing

Multiple Extruders



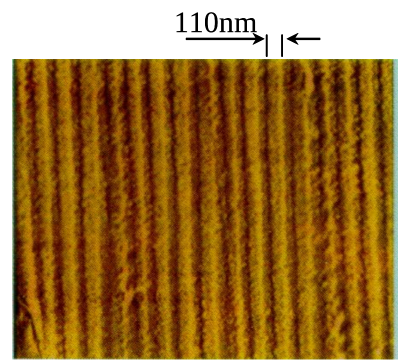
Multiplication Die



- **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**

3M

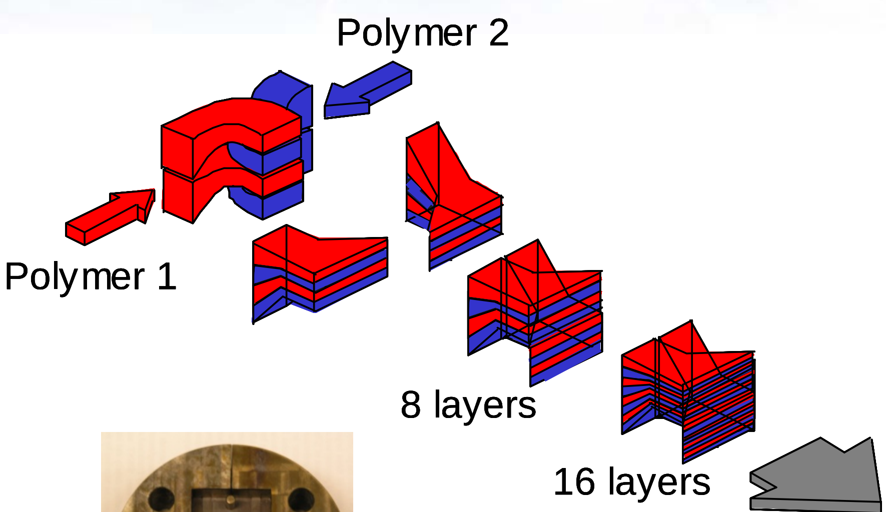
$$\delta_{PS} = 23.8 \pm 4.0\ (\mu m)$$
$$\delta_{PP} = 22.9 \pm 5.1\ (\mu m)$$

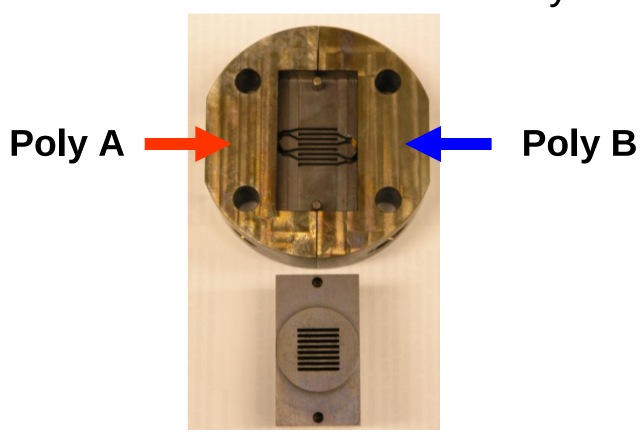


PC/PMMA multilayer, Dow Chem.

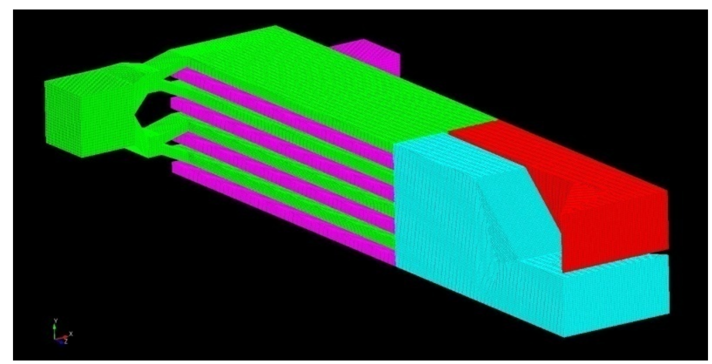
Multiplication Scheme

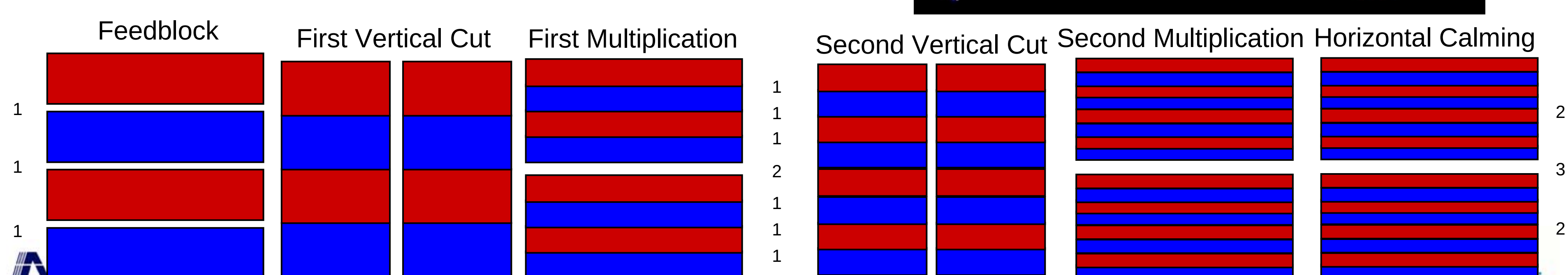
Multiplication Scheme





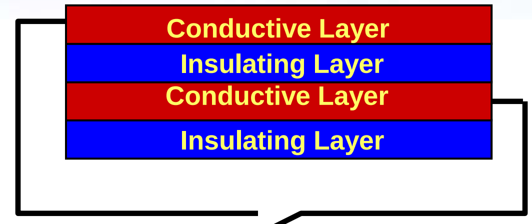
- Feedblock produces initial layered structure
- Each multiplication element doubles the number of layers
- Stacking "n" multiplication dies results in 2^{n+3} layers
- Layer stability is largely dependent on uniform laminar flow
- Thin layers (submicron) can easily break-up due to instabilities



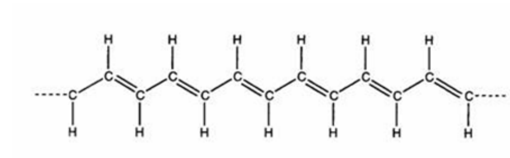


Goal: Process Filled Polymers to Create Multifunctional Layers

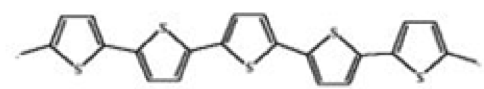
- **Coextrusion of composites can increase the versatility and applicability of the technique**
- **Incorporation of fillers can enhance material properties**
  - **Thermal stability**
  - **Flame retardancy**
  - **Chemical resistance**
  - **Permeability**
  - **Mechanical properties**
  - **Electrical conductivity**
- **Targeted Application: Capacitors**
- **Technical Challenge: Extrudable conductive polymer**
  - **Inherently conductive polymers difficult to process**
    - **Rigid polymer backbone results in high viscosity**
    - **Degradation before melting**
  - **Addition of conductive fillers**
    - **Ideally would be at percolation threshold to form a conductive path**
    - **Dramatic impact on viscosity!**
    - **Likelihood that layers mismatched in density and viscosity**



Capacitor consisting of alternating layers of conducting and insulating material

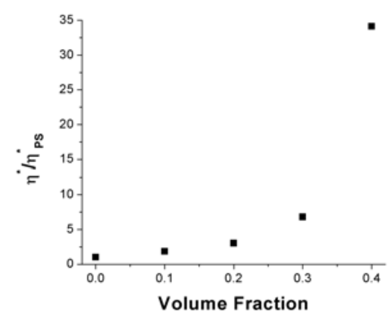


polyacetylene



polythiophene

Inherently conductive polymers are not extrudable



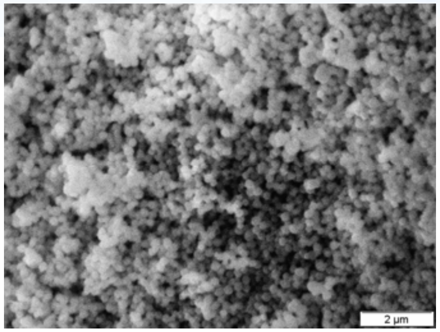
Exponential increase in viscosity above 30% (uniform spherical particles)

Conductive Filled Polymer System

- Stategies to minimize viscosity
  - Multi-modal size distribution
  - Surfactants, processing aids
  - Add a low melting point eutectic

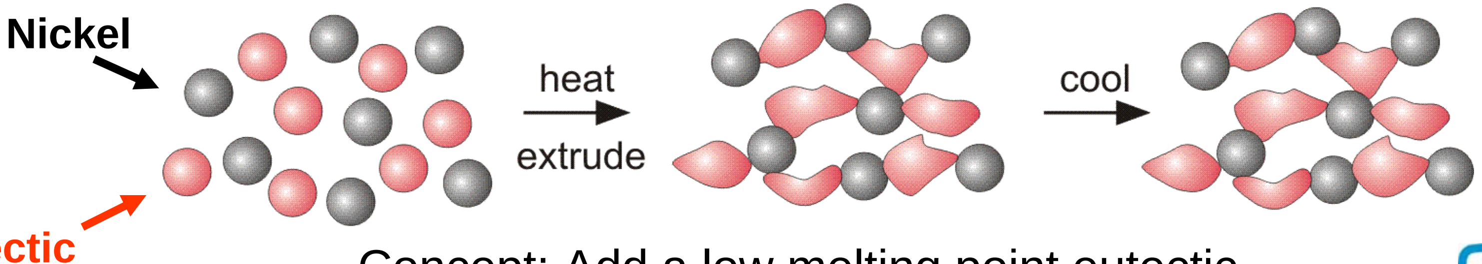
Proof-of-principle test with this formulation:

- Nickel particles
  - Conductive
  - Relatively stable to oxidation
  - Commercially available in several sizes with small size distributions
- Polystyrene matrix (currently)
  - Inexpensive and available in large quantities
- Eutectic
  - 58% Bi / 42% Sn (Cerrotru)
  - T_M = 138 °C
  - Net expansion after cooling of .05 % (.0005 in./in.)
  - Good mechanical and electrical contacts with Nickel
  - Similar density to Nickel



Nickel Sub-micron Particles

Bi/Sn Eutectic

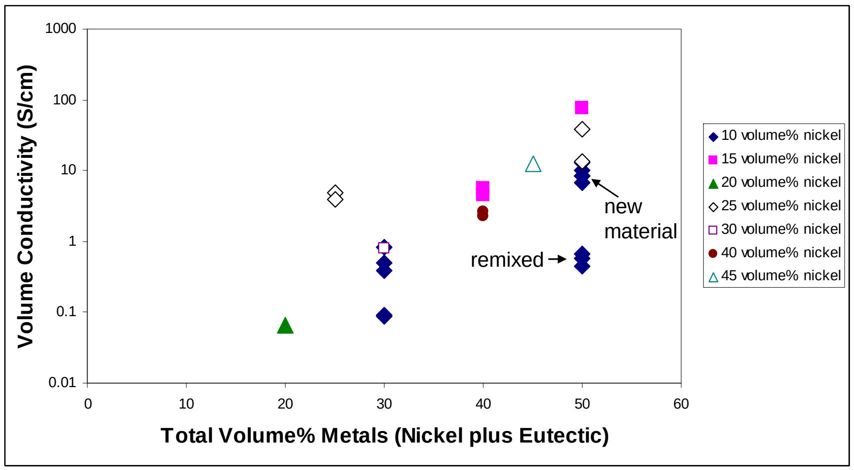


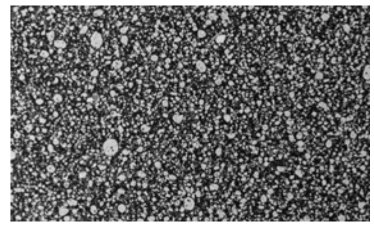
Concept: Add a low melting point eutectic

Electrical Properties of Our Materials

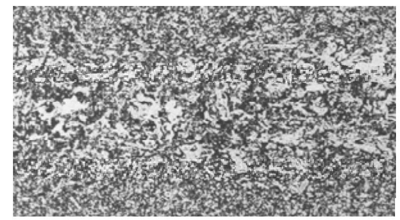
Conductive Material

- In general conductivity dependent on volume% of total metal
- Conductivity very dependent on microstructure/ degree of mixing
- Addition of eutectic does not dramatically affect conductivity





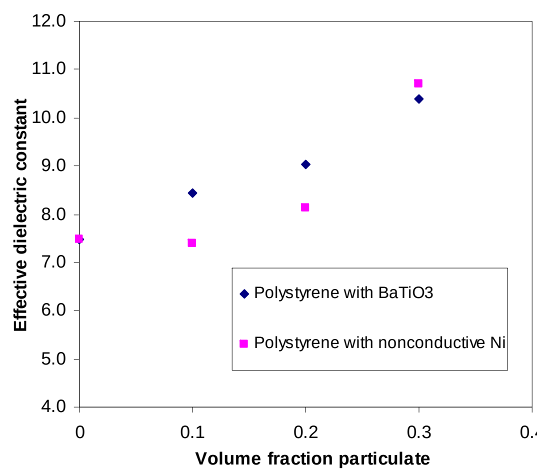
Poor conductivity



Good conductivity

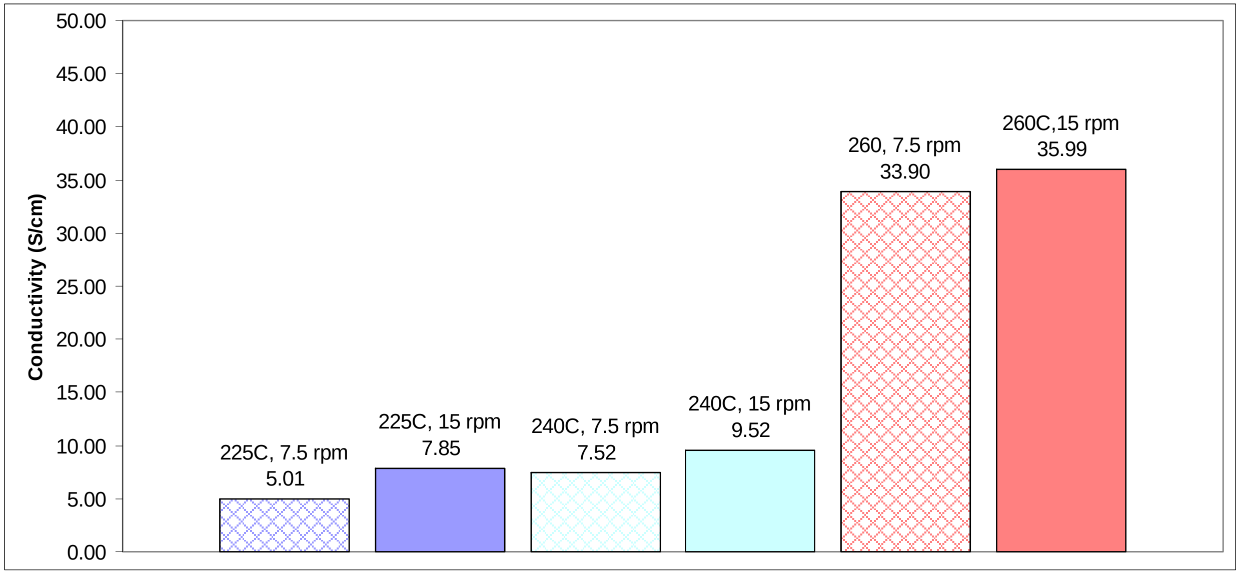
Dielectric Material

- Use a filled polymer to minimize density mismatch
- BaTiO^3 chosen because of good dielectric properties

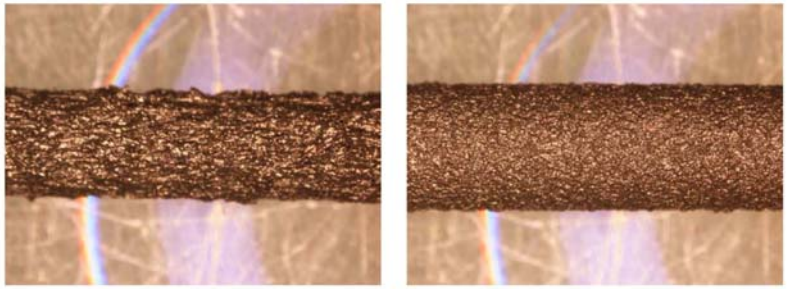


Twin-Screw Extrusion of Conductive Material

- Conductivity improved at higher temperatures
- Conductivity slightly improved at faster rates
- BUT quality of extrudate decreases



260°C @ 7.5 rpm



225°C (2nd run) @ 7.5 rpm

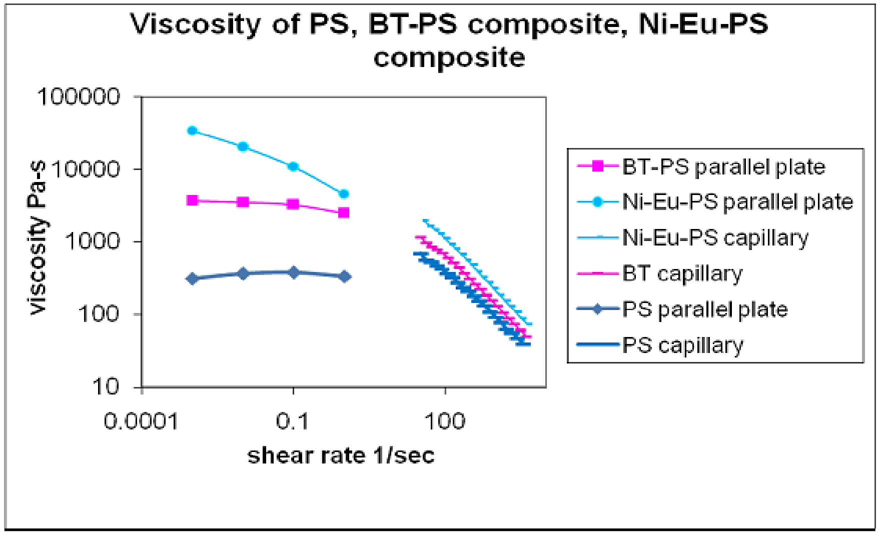
Rheology of Our Materials

- **Short time horizon dictated that we use what material we either had on hand or could make quickly**
- **Density mismatch unavoidable**
- **Rheology measurements showed that viscosity mismatch severe**

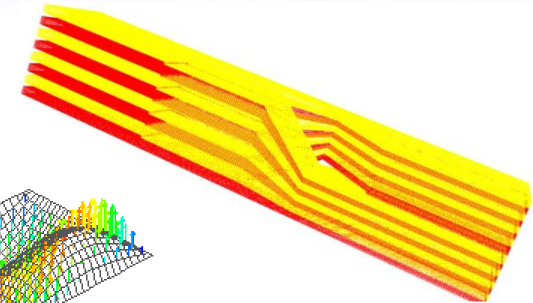
Formulations for first "proof-of-principle" testing:

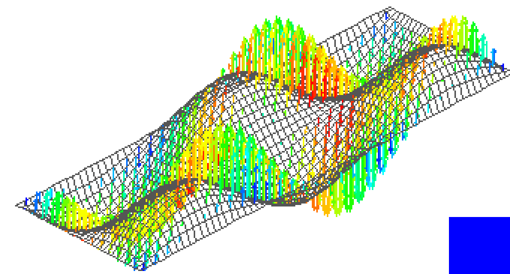
12 vol% Ni, 28 vol% Eutectic, 60 vol% polystyrene

25 vol% BaTiO3, 75% polystyrene

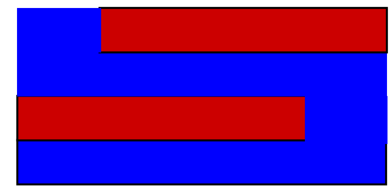


Development of Modeling to Help Design Materials and Process

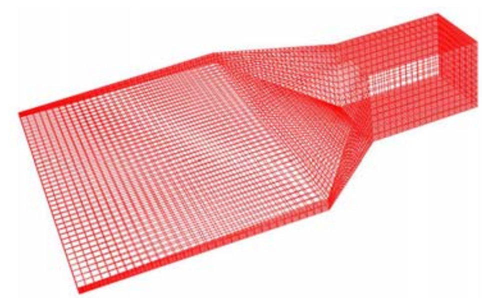




- How do we produce stable films (ribbing, barring, rivulets, encapsulation, etc.)?
    - What viscosity ratios will be stable?
    - What density ratios will be stable?
        - Linear stability analysis
        - 3D modeling
- Effects of rheology?
- Operating window?



- Can we directly create an offset die that produces an encapsulated red phase?
- Can we design better splitters and sheeting sections?



Methods developed for coating flows used for coextrusion: Coating consortium at Sandia (CRMPC) driver for computational analysis tools for manufacturing processes

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Free Surface Flow: Level Set Method

Given fluid velocity field, u(x,y,z), evolution on a fixed mesh is according to:

$$\frac{\partial \phi}{\partial t} + u \cdot \nabla \phi = 0 \qquad\qquad \vec{n} = \nabla \phi, \kappa = \nabla \cdot \nabla \phi$$

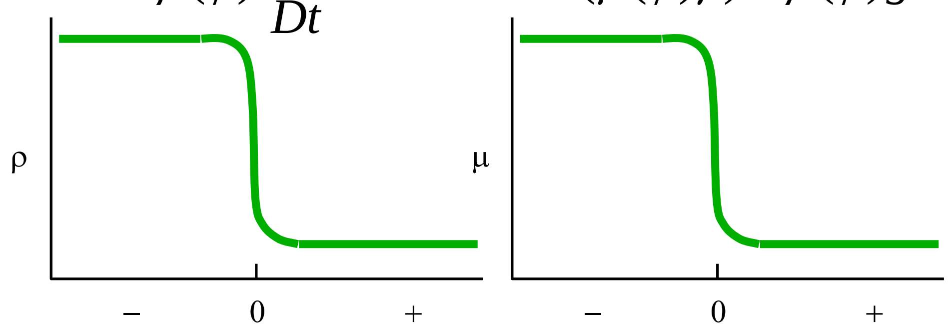
Purely hyperbolic equation … fluid particles on $\phi(x,y,z) = 0$ should stay on this contour indefinitely

$$\rho(\phi) = \rho_{-}(1 - H_{\alpha}(\phi)) + \rho_{+} H_{\alpha}(\phi)$$
$$\mu(\phi) = \mu_{-}(1 - H_{\alpha}(\phi)) + \mu_{+} H_{\alpha}(\phi)$$

- Does not preserve $\phi(x,y,z)$ as a distance function
- Introduces renormalization step.

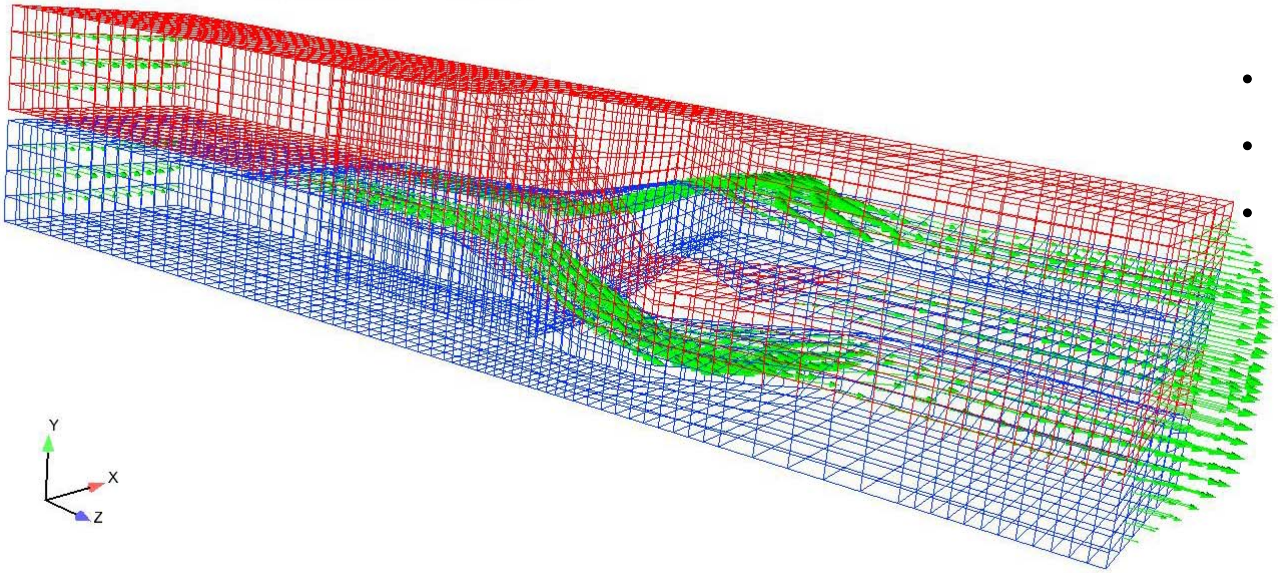
Fluid velocity evolves as one-phase fluid with properties that depend on ϕ

$$\rho(\varphi)\frac{Du}{Dt} = -\nabla P + \nabla \cdot (\mu(\varphi)\dot{\gamma}) + \rho(\varphi) g + I.T., \quad \nabla \cdot u = -\frac{D\rho(\varphi)}{Dt}$$



$$\underline{T}_{\sigma} = \sigma \delta_{\alpha}(F)\left(\underline{I} - \vec{n}\vec{n}\right)$$

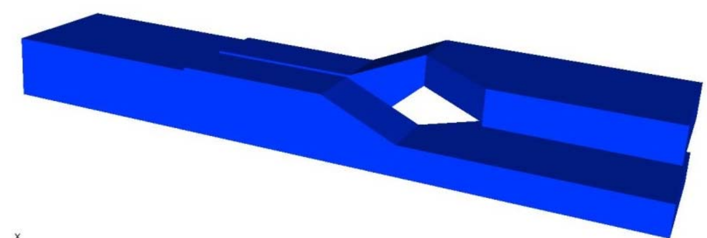
3D Mesh of Two-Layer Coextrusion Multiplication Region to Four-Layer Structure



- 9276 8-Node hexahedral elements
- 12040 Nodes
- 84280 total degrees of freedom

- Flow splitters and duct wall all have no slip boundary conditions
- Free surface exists between red and blue fluid in the downstream region, where surface tension and kinematic condition are applied
- Inflow boundaries have constant applied pressure
- Boundary conditions must be applied to momentum equations and mesh equations
- Sixteen different side sets in the mesh

Fluid 1: Top fluid



Fluid 2: Bottom fluid

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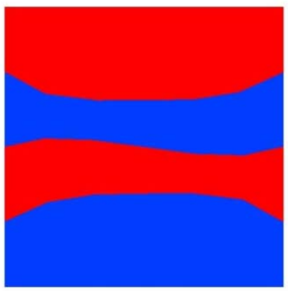
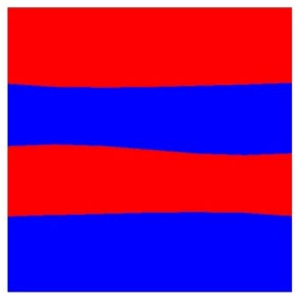
Validation Experiments Help Define Boundary Conditions

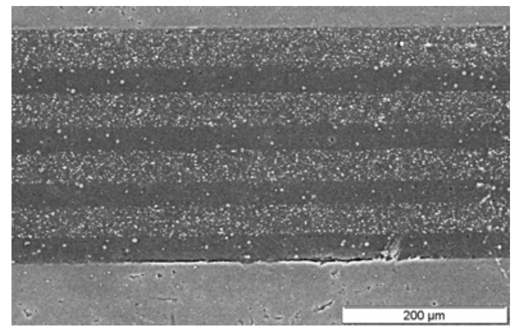
Steady-state solution (ALE) with no slip at walls



Level set simulation

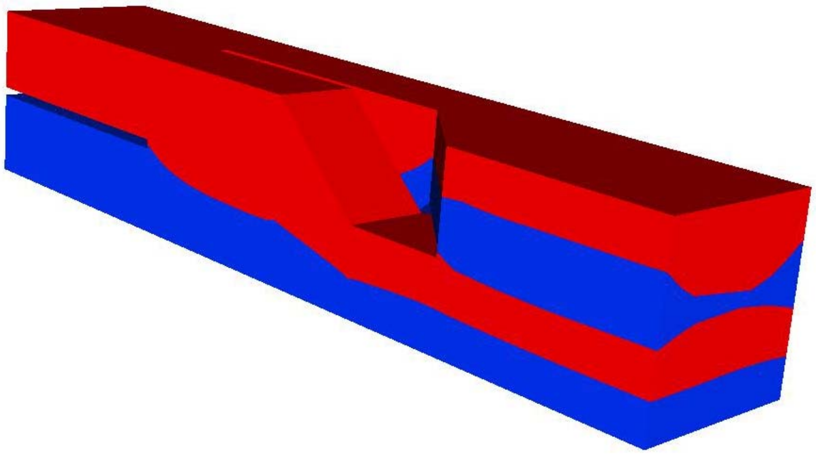


Does it slip or stick? Transient level set simulations naturally incorporate slip, which looks more like the experiment below.

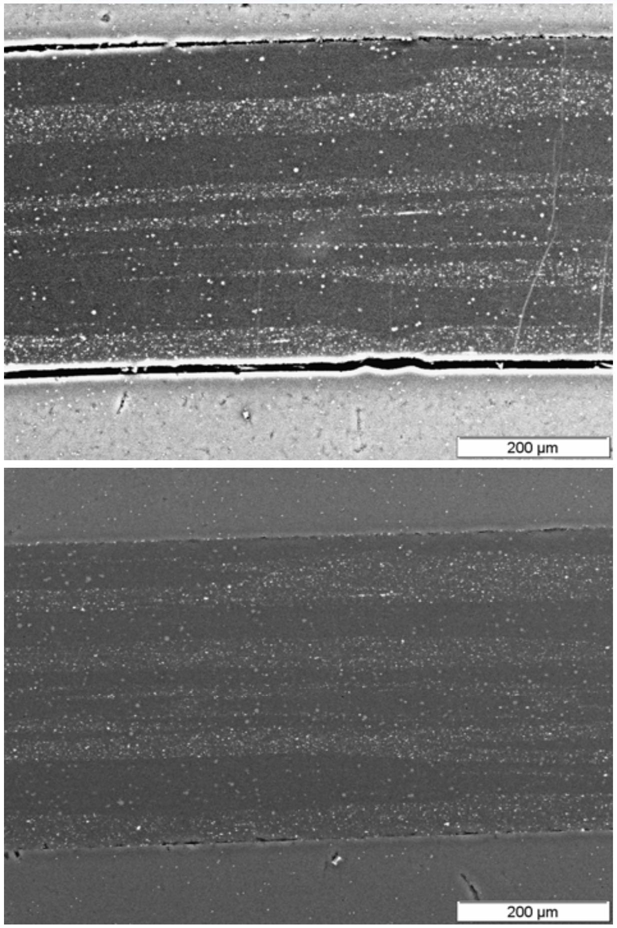


Lightly filled (3 vol%) layers of polystyrene with carbon black and titanium dioxide co-extruded for validation

Validation Experiments with Materials Flowing at Two Rates



Pressure mismatch creates thinner layers of the slower flowing material (blue). Ratio of red to blue pressure =1.76.



SEMs of coextruded material shows similar distortion of layers at a ratio of flowrate = 1.5 (above). Here light is equivalent to blue in the model. At higher ratio (1.75) layers lose integrity and mixing begins.

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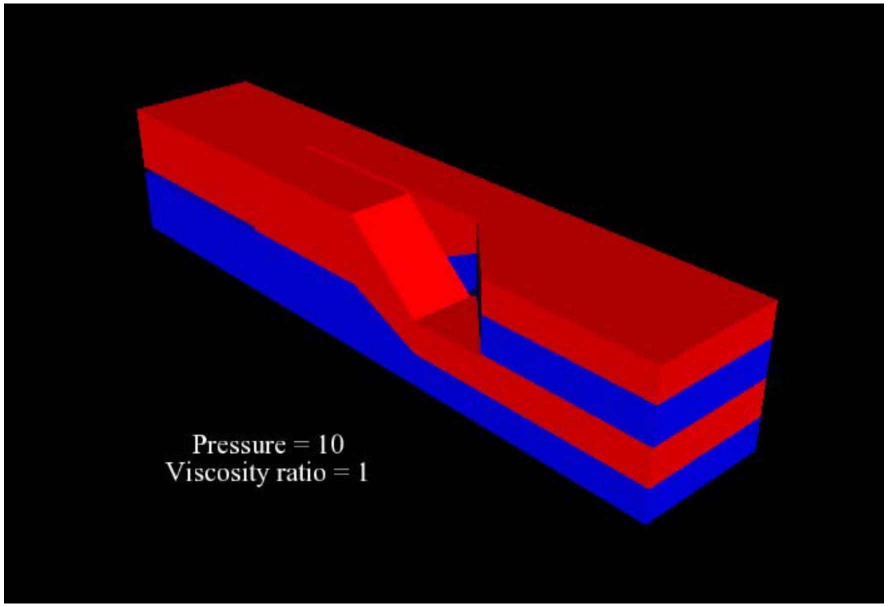
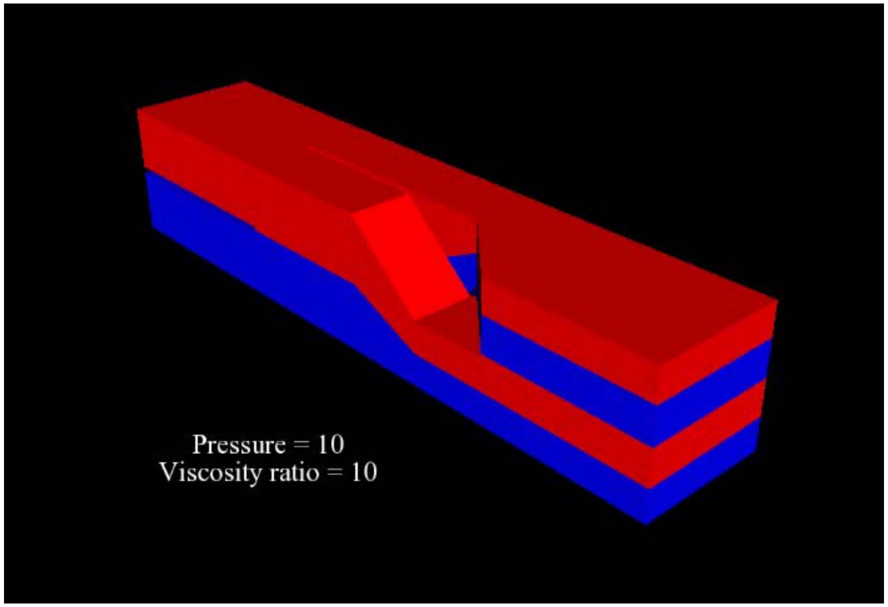
What Viscosity Ratios Can The Process Tolerate?





- Time-dependent simulations of two-layer coextrusion using level-set interface tracking
- Blue fluid squeezes out red fluid, thinning the bottom red layer
- At high viscosity ratios, the more viscous (blue) fluid layers merge in part of the channel, destroying the integrity of the lamellae

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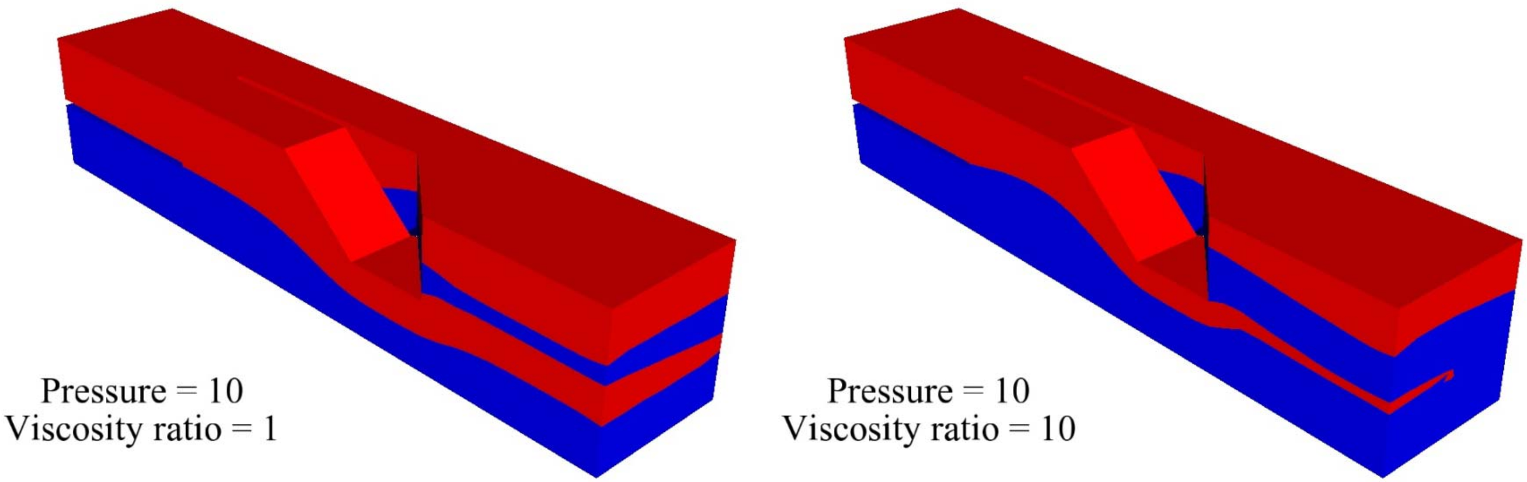

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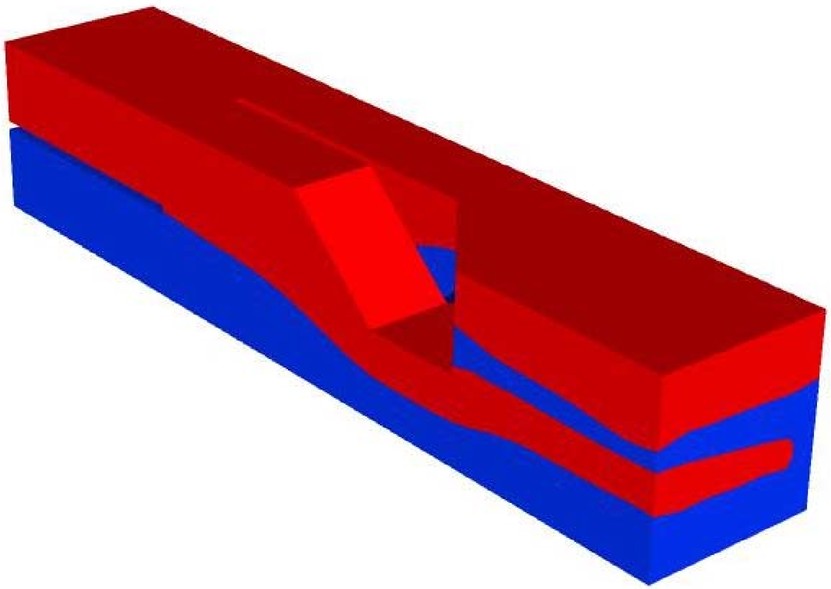
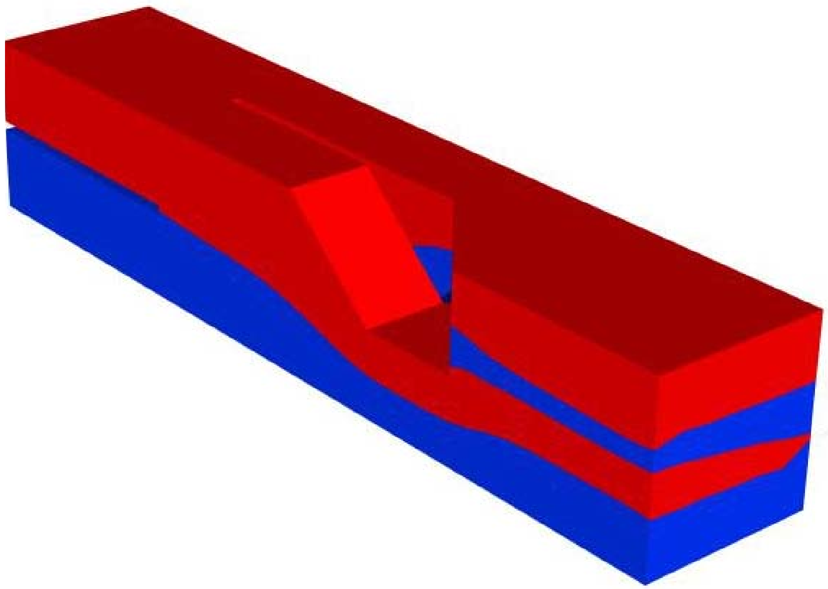
Experimental Conditions

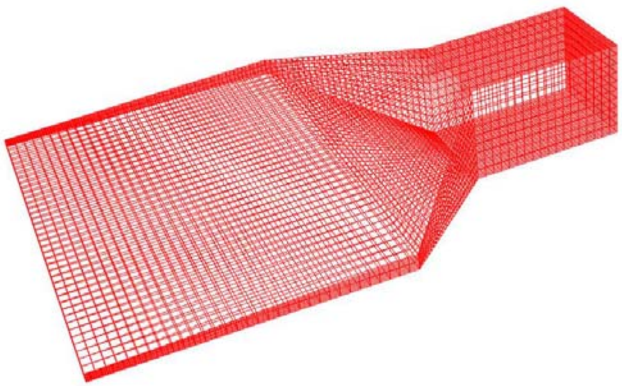
Model predicts that layers will lose integrity if screw speeds of the two materials are equal



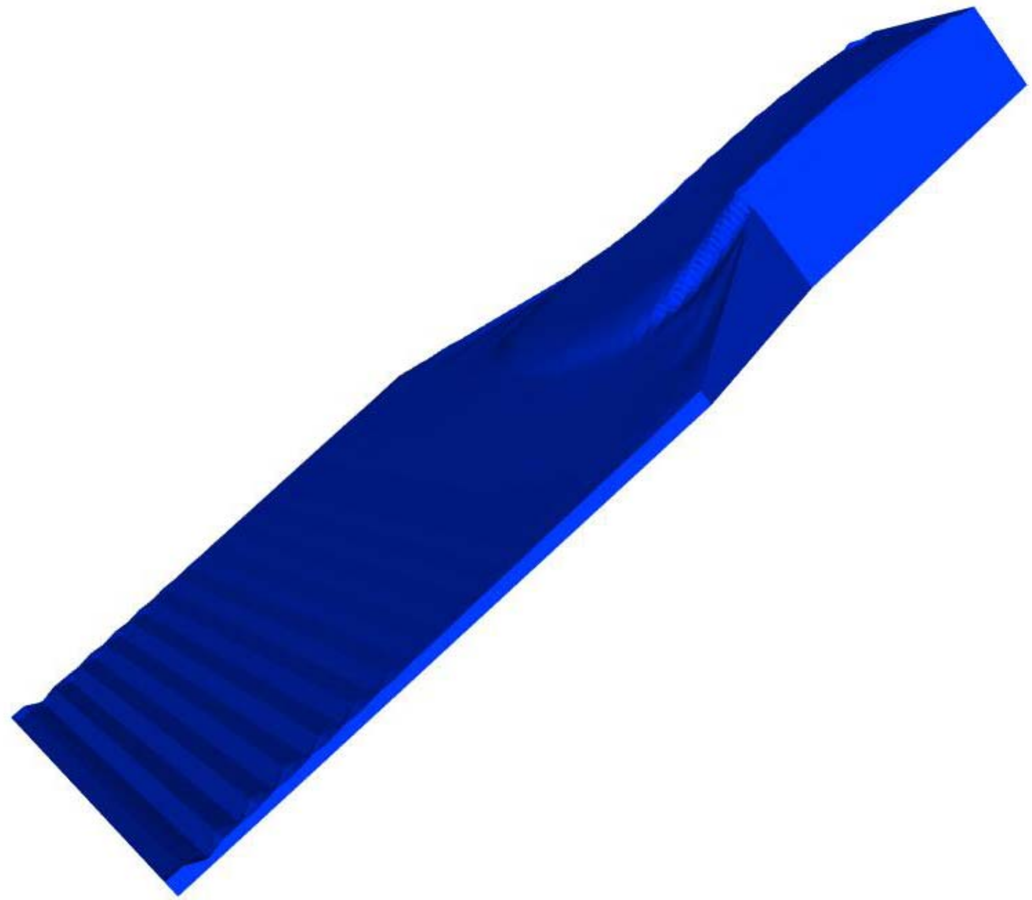


Density red 4.09 g/cc viscosity red 25,000 Poise
Density blue 2.06 g/cc viscosity blue 15,000 Poise

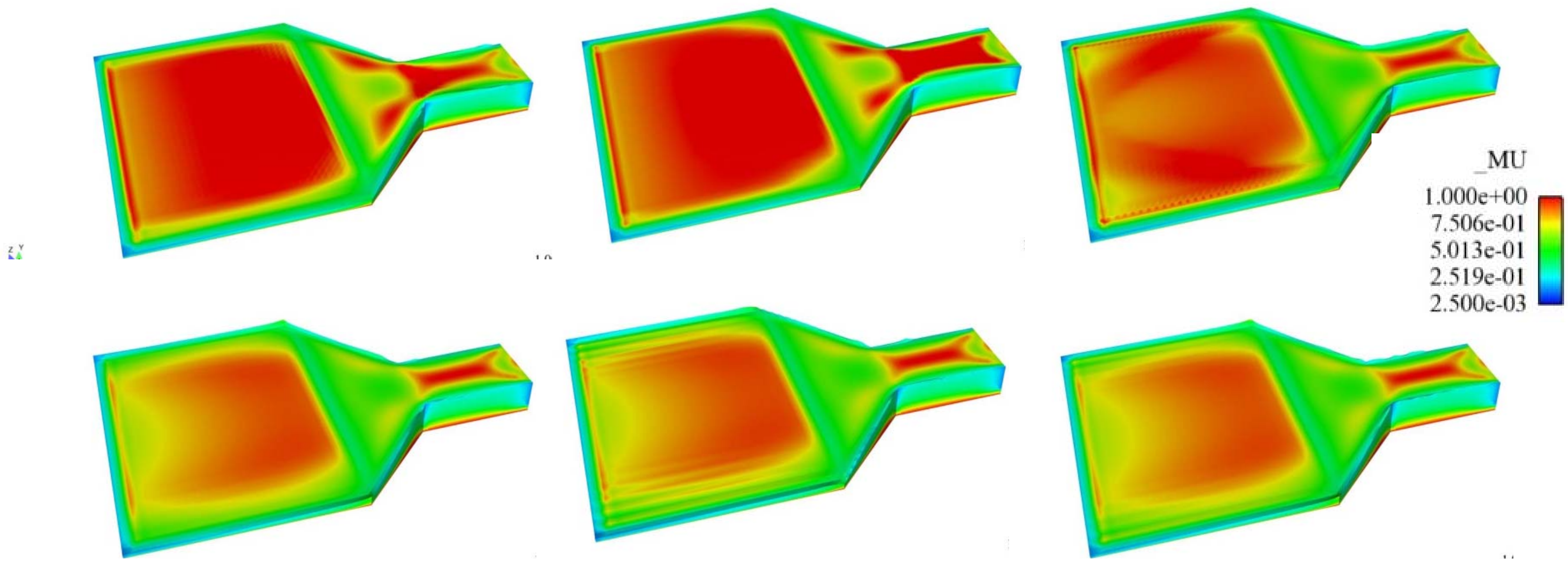
Model Predicts Instabilities in Sheeting Section



Bottom fluid free surface for Newtonian properties: Top fluid has 10 time the viscosity of the bottom fluid and twice the density



Model Takes Into Account Shear Thinning Nature of the Materials

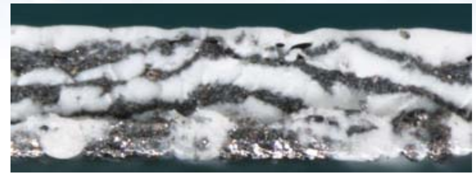


Viscosity of the lower fluid with time

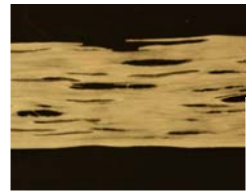
0.5s,1.0s,2.0s, 5s,7s,10s

Proof-of-Principle Experiment

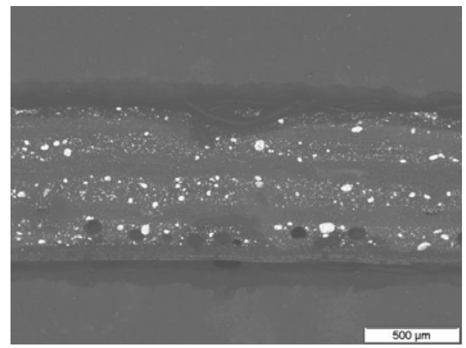
- Model correctly predicted that layers would not remain stable
- Cavitation was the biggest problem resulting in bubbles stretching and ribbon tearing during sheeting
- Better results at slow flow rates and with the flow rate of each material proportional to its viscosity
- Capacitance measured in pico-Farads, but it worked



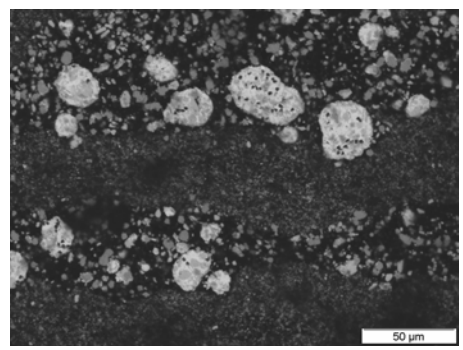
X-section
Equal flow rates



Bird’s eye view
High flow rate



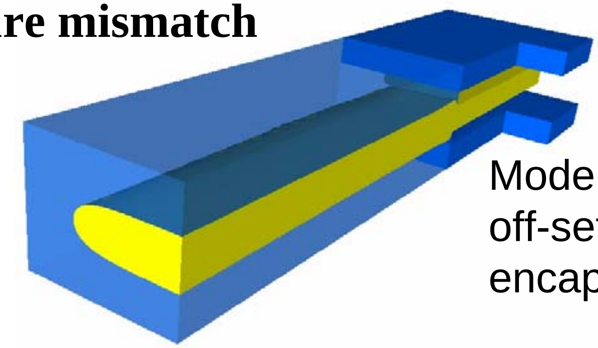
SEM 50X
X-section
Unequal,
slow flow



SEM 500X
Partial
X-section
Unequal,
slow flow

Conclusions and Future Work

- **Filled polymers offer ability to make multifunctional co-extruded layered materials**
- **Proof-of-Principle experiment "was not pretty" but materials were not ideal**
- **Rheology and modeling will help us improve the product!**
- **Finite element modeling has been used to better understand a multilayer coextrusion process for manufacturing composite materials with filled polymers**
  - **Effects of viscosity/pressure mismatch**
  - **Effects of geometry**



Modeling used to design an off-set die to create an encapsulated layer

For future work, we would like to look at

- Redesigning splitter dies, adding quieting regions, etc
- Finer mesh/more layers
- Slip boundary conditions on solid surfaces/ Blake wetting condition
- Continue linear stability analysis to create an operating window
- Shear rheology in capillary viscometer with nanoparticle filled PS
- More complex fluids, particle filled, viscoelastic effects?