The capabilities of Stevens Institute of Technology in the areas of rheology, structure formation, mathematical modeling of continuous processing of energetics

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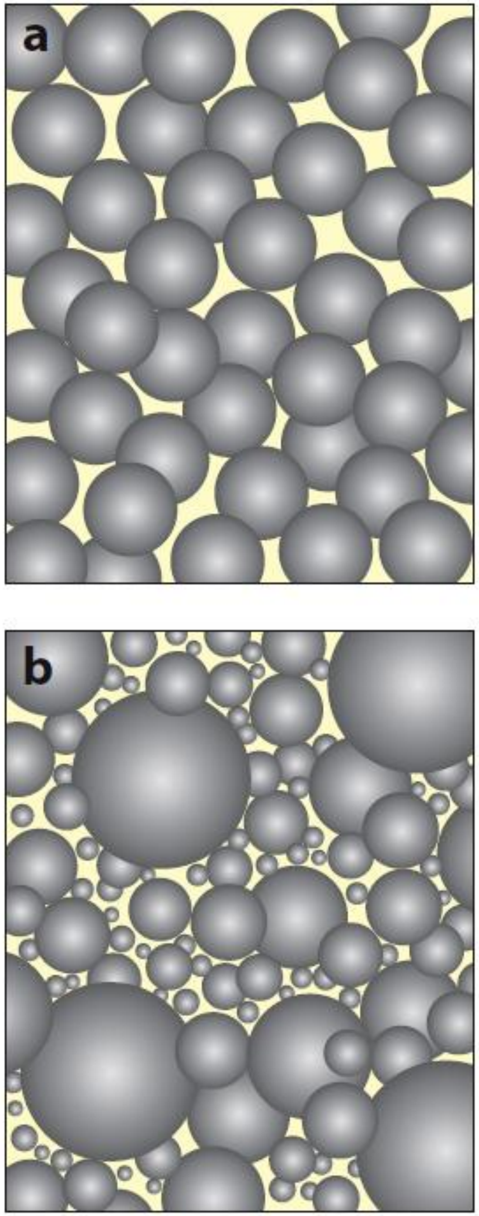
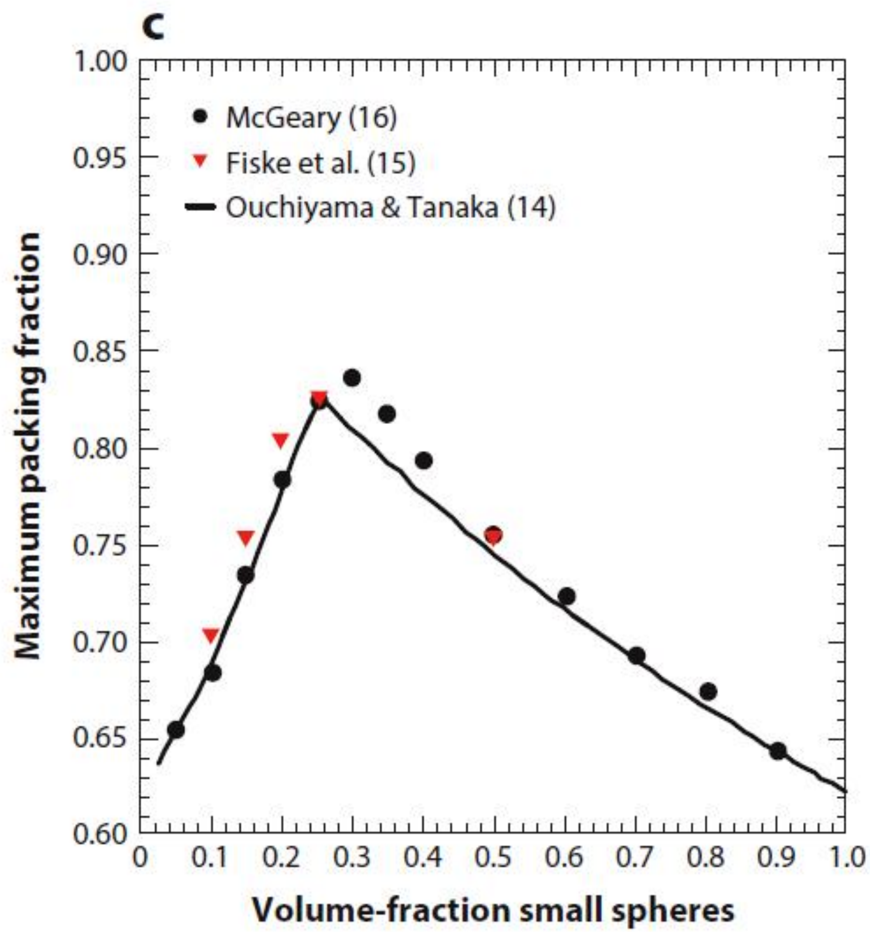
Highly Filled Materials Institute at Stevens

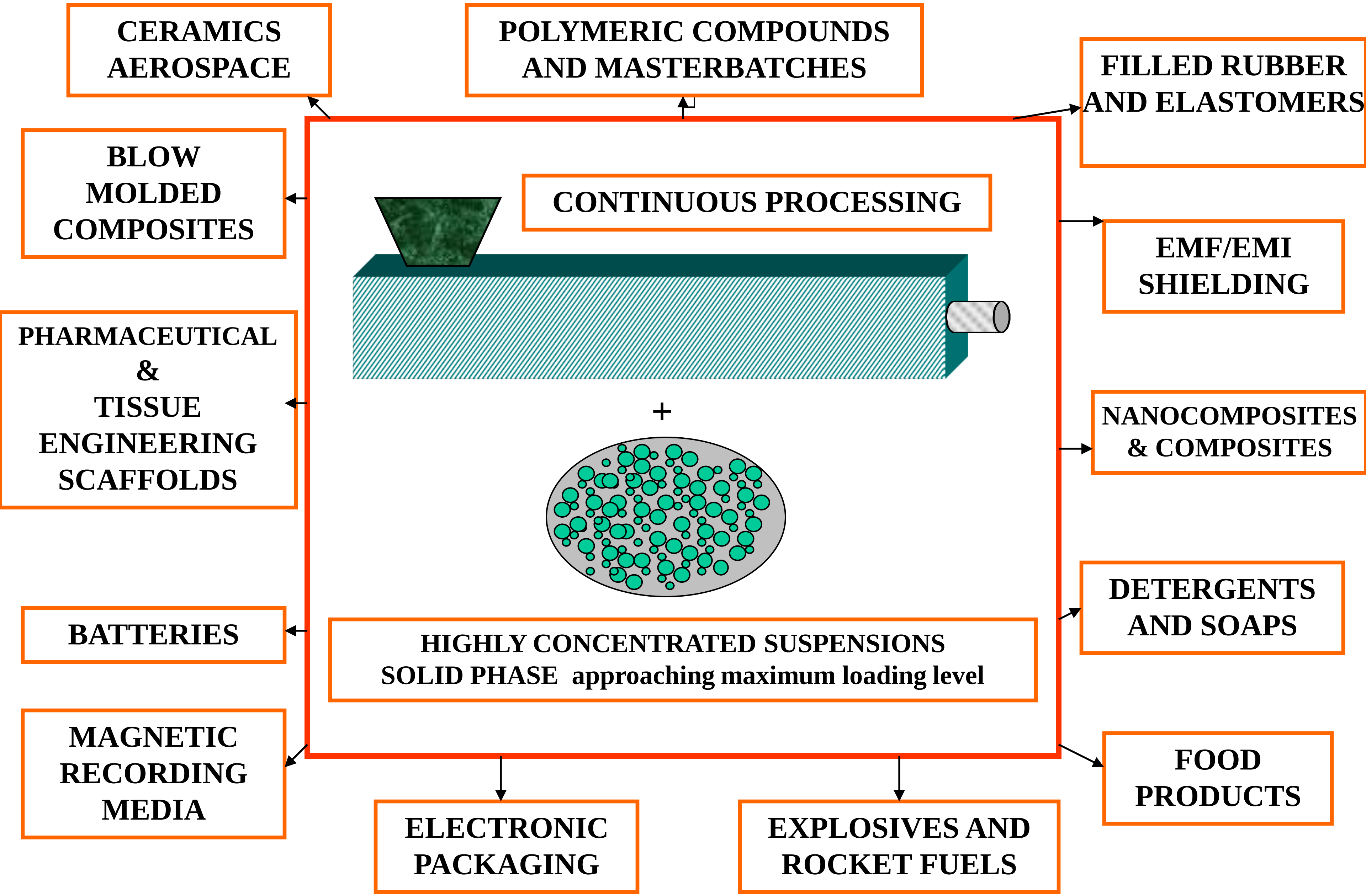
- Founded in 1989 at Stevens Institute of Technology capitalizing on the strong funding history in the area of processing of energetic materials
- HfMI focuses on the manufacturing of materials which are loaded with solids at concentrations which approach the maximum packing fraction of the solid phase. Such materials are difficult to characterize, process, simulate. Especially with energetics there is little room for experimentation.

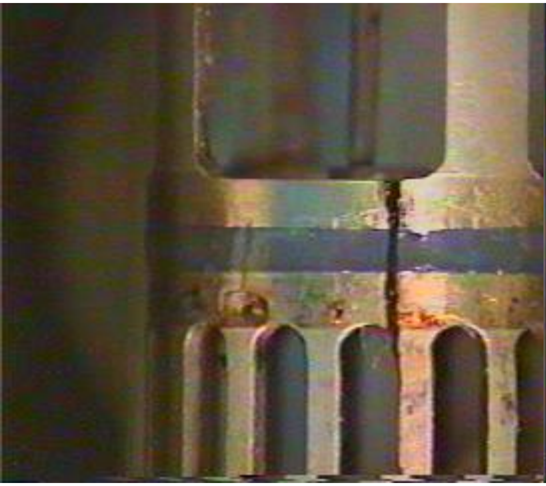


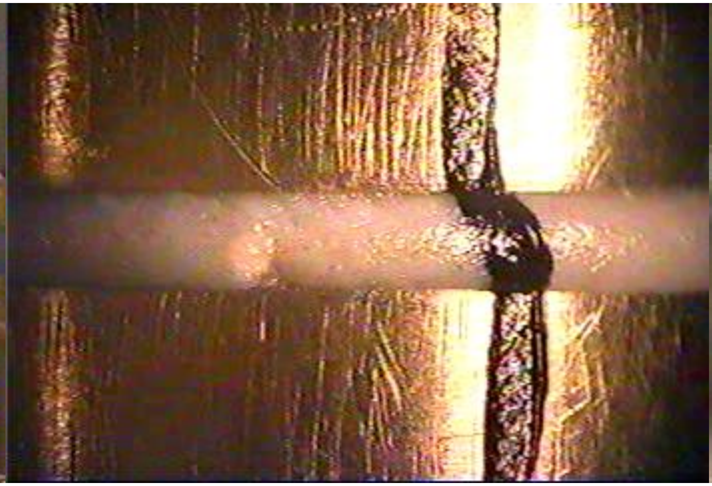


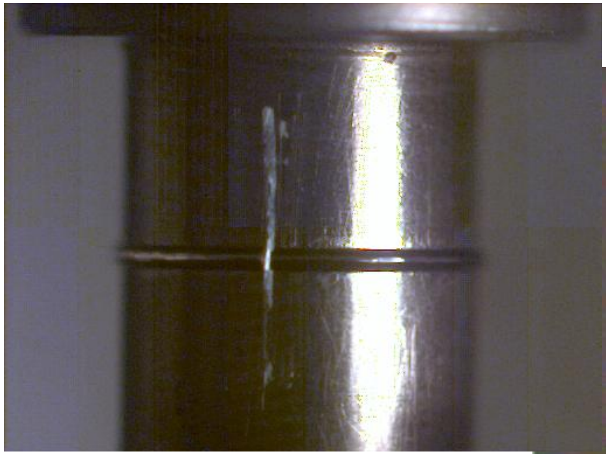
Bimodal size distribution:
Diameter Ratio= 20

Fiske , Kalyon, **Powder Technology**, 81, 57-64 (1994).


CERAMICS AEROSPACE
POLYMERIC COMPOUNDS AND MASTERBATCHES
FILLED RUBBER AND ELASTOMERS
BLOW MOLDED COMPOSITES
CONTINUOUS PROCESSING
EMF/EMI SHIELDING
PHARMACEUTICAL & TISSUE ENGINEERING SCAFFOLDS
+
NANOCOMPOSITES & COMPOSITES
DETERGENTS AND SOAPS
BATTERIES
HIGHLY CONCENTRATED SUSPENSIONS
SOLID PHASE approaching maximum loading level
MAGNETIC RECORDING MEDIA
FOOD PRODUCTS
ELECTRONIC PACKAGING
EXPLOSIVES AND ROCKET FUELS





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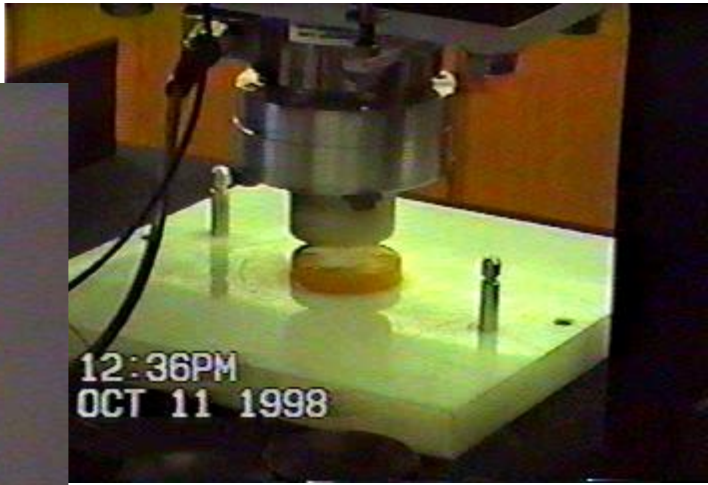
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Highly Filled Materials Institute (1989-):
From particles to products with specialization in
Highly filled suspensions

<u>Continuous Processing Lab of HfMI: Twin Screw Extruder</u> <u>Facility</u> **and the *<u>Slit Die Rheometer</u>***

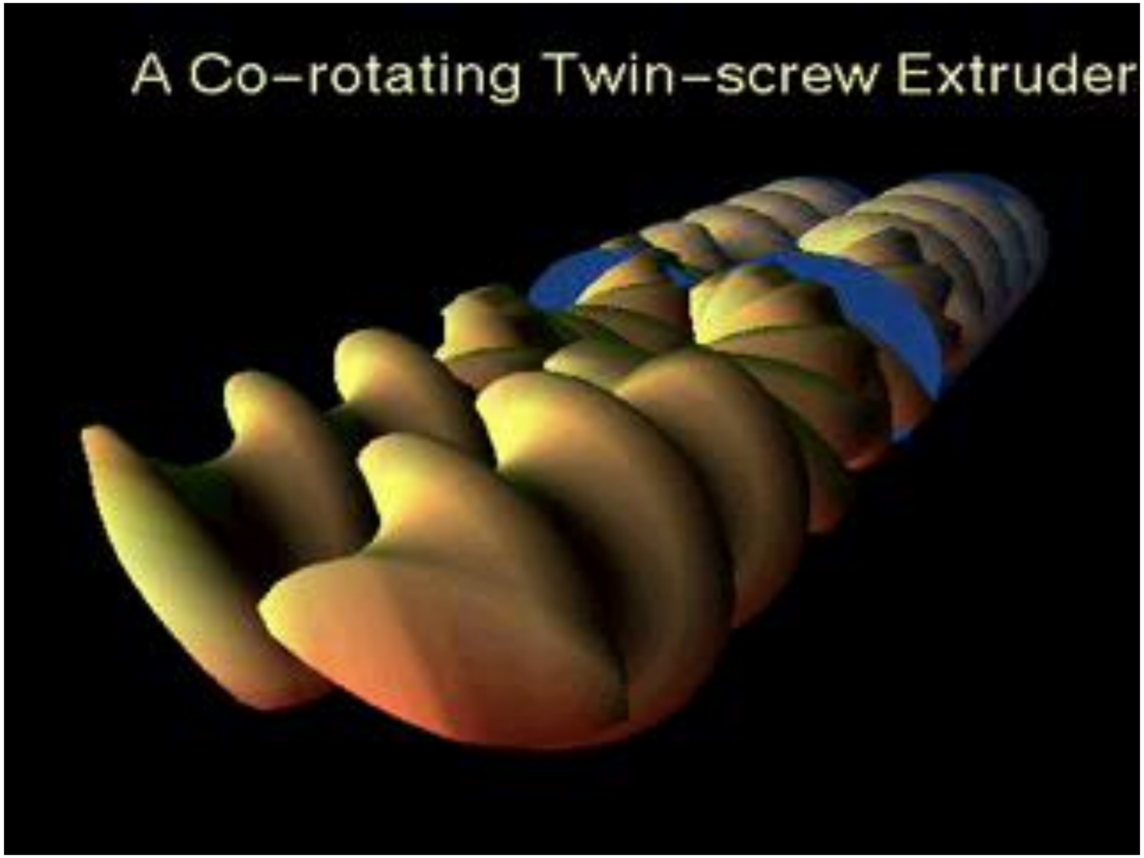
CORE STRENGTHS

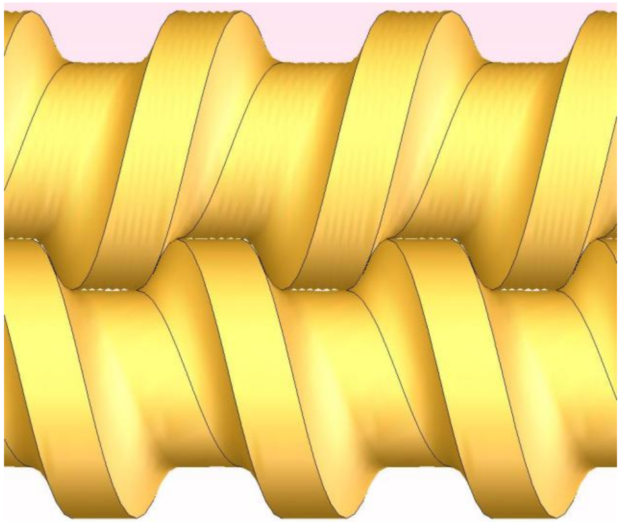
- Ability to characterize accurately the rheological behavior of highly filled materials
- Ability to simulate the processing of highly filled materials
- Ability to characterize microstructural distributions quantitatively
- Ability to design and manufacture tools for processing of highly filled materials: dies, processors, control systems.

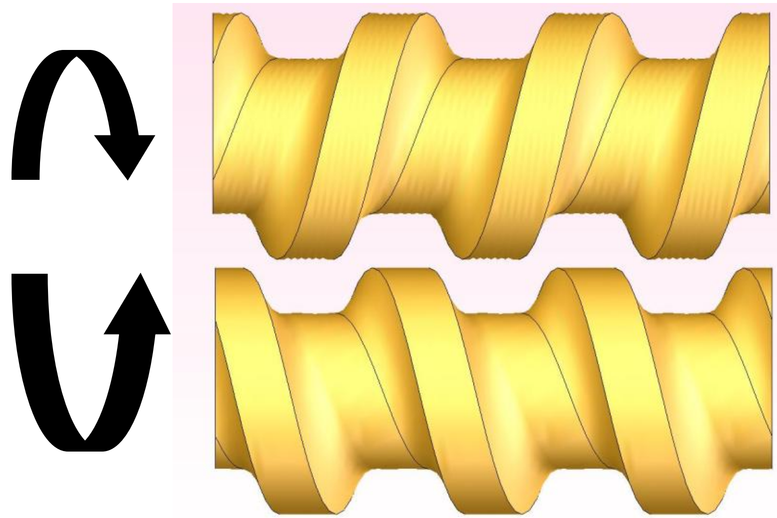
Specialized Tools

- Custom designed rheometers with remote loading and data acquisition capabilities
- Custom designed processing equipment with remote access for data acquisition and control
- Source codes (FEM, FD) with ability to run using the internet
- Structural analysis tools for degree of mixedness, particle size analysis and coating thickness

Challenge: To determine how to process-processing-structure development and ultimate properties





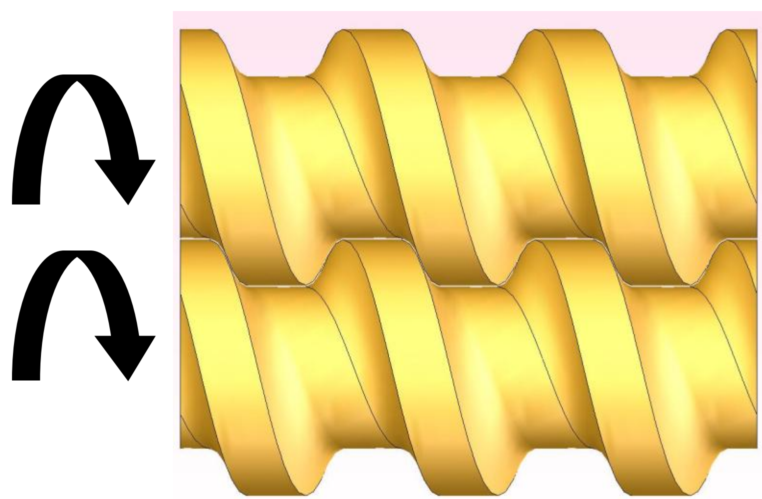


Counter-rotating fully

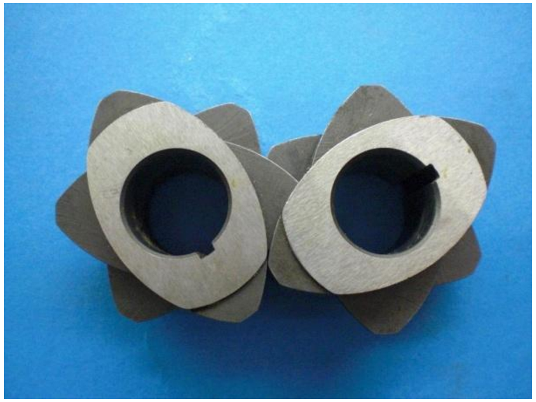
intermeshing twin screws.

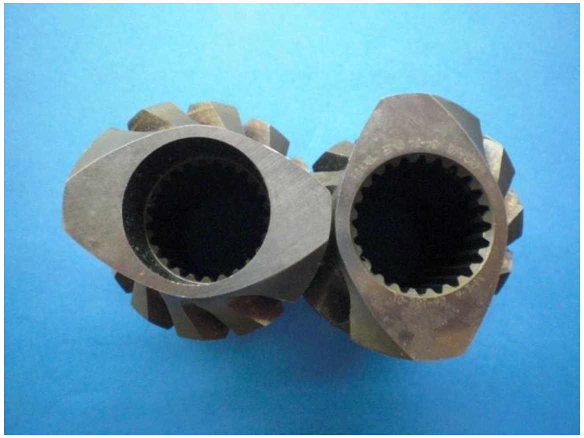
Counter-rotating tangential twin screws.

•M. Malik and D. Kalyon, “Three-dimensional Finite Element Simulation of Processing of Generalized Newtonian Fluids in Counter-rotating and Tangential Twin Screw Extruder ”, Int. Polym. Processing, 20, 398- 409 (2005).
•D. M. Kalyon and M. Malik, “An integrated approach for numerical analysis of coupled flow and heat transfer in co-rotating twin screw extruders”, International Polymer Processing, 22, 293-302 (2007)
•M. Malik, D. M. Kalyon, and J. C. Golba Jr., “Simulation of co-rotating twin screw extrusion process subject to pressure-dependent wall slip at barrel and screw surfaces”, International Polymer Processing, 29, 1, 51-62 (2014).

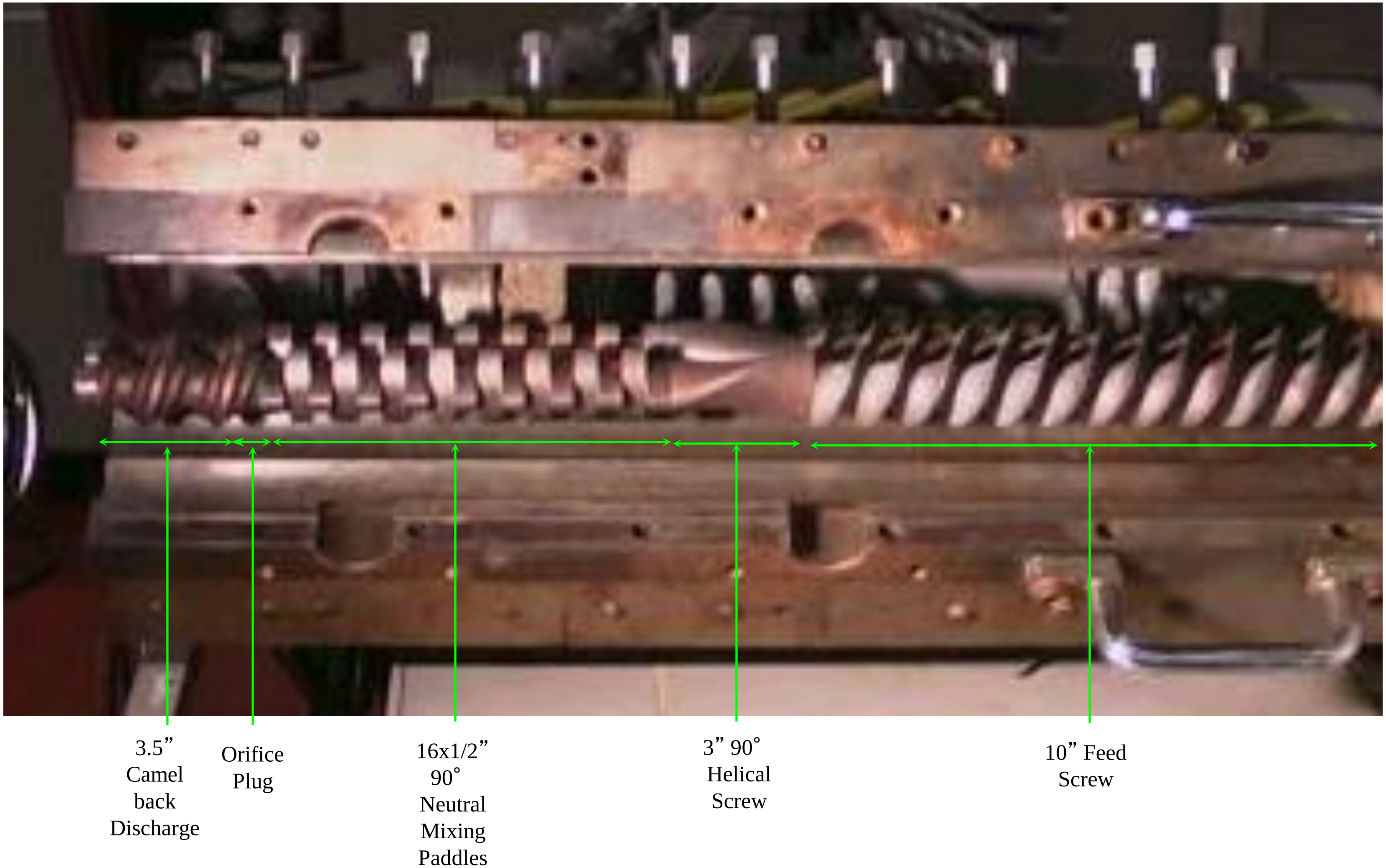


Co-rotating fully intermeshing twin screws.





Many types of flighted-screws and kneading disks: right or left handed, different stagger angles



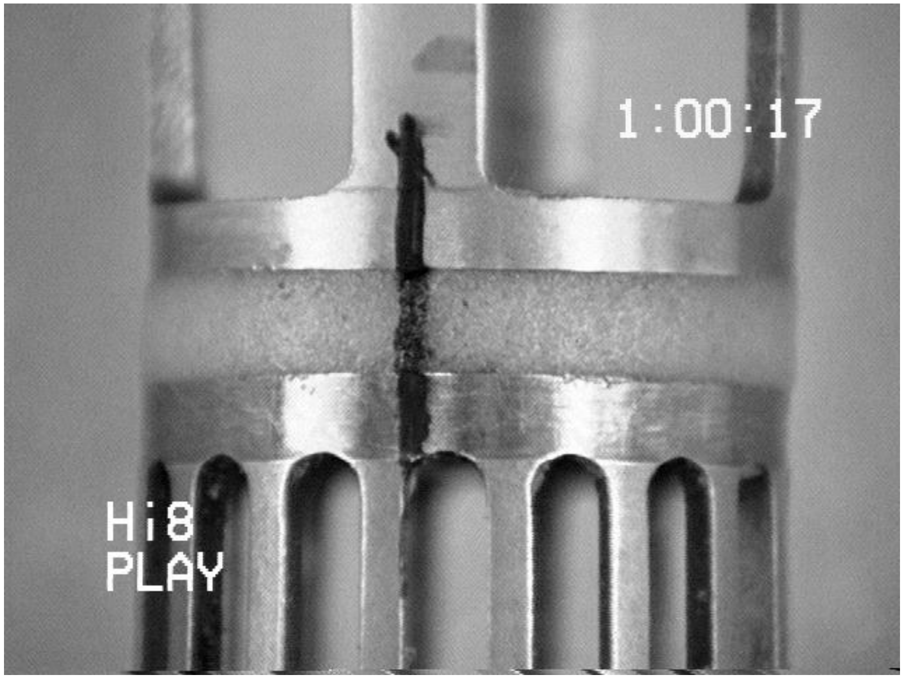
Each screw configuration is a different processor- how does one select the screw barrel configuration- given a task

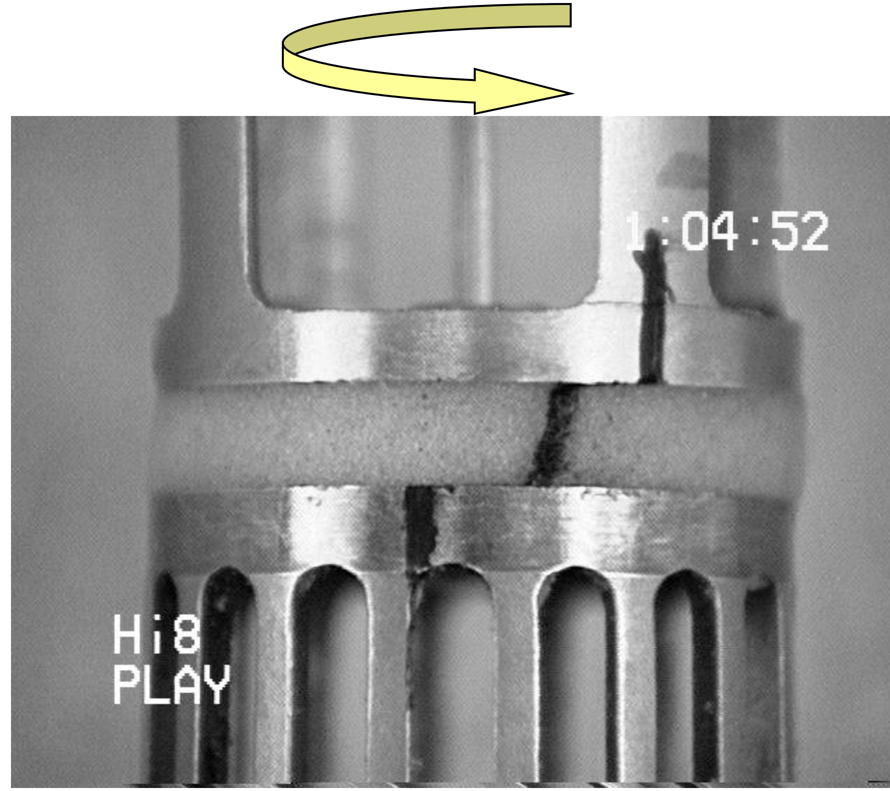
Specialized technologies

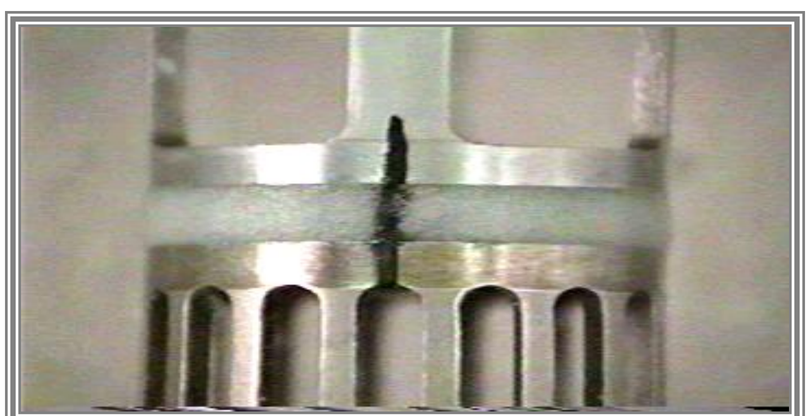
- **Rheology**
- Structure analysis using WXD
- Mathematical modeling using 3-D FEM
- Experimental validation methods
- Custom design and manufacture
  - Rheometers
  - Dies
  - Extruders

Demonstration of Apparent Wall Slip

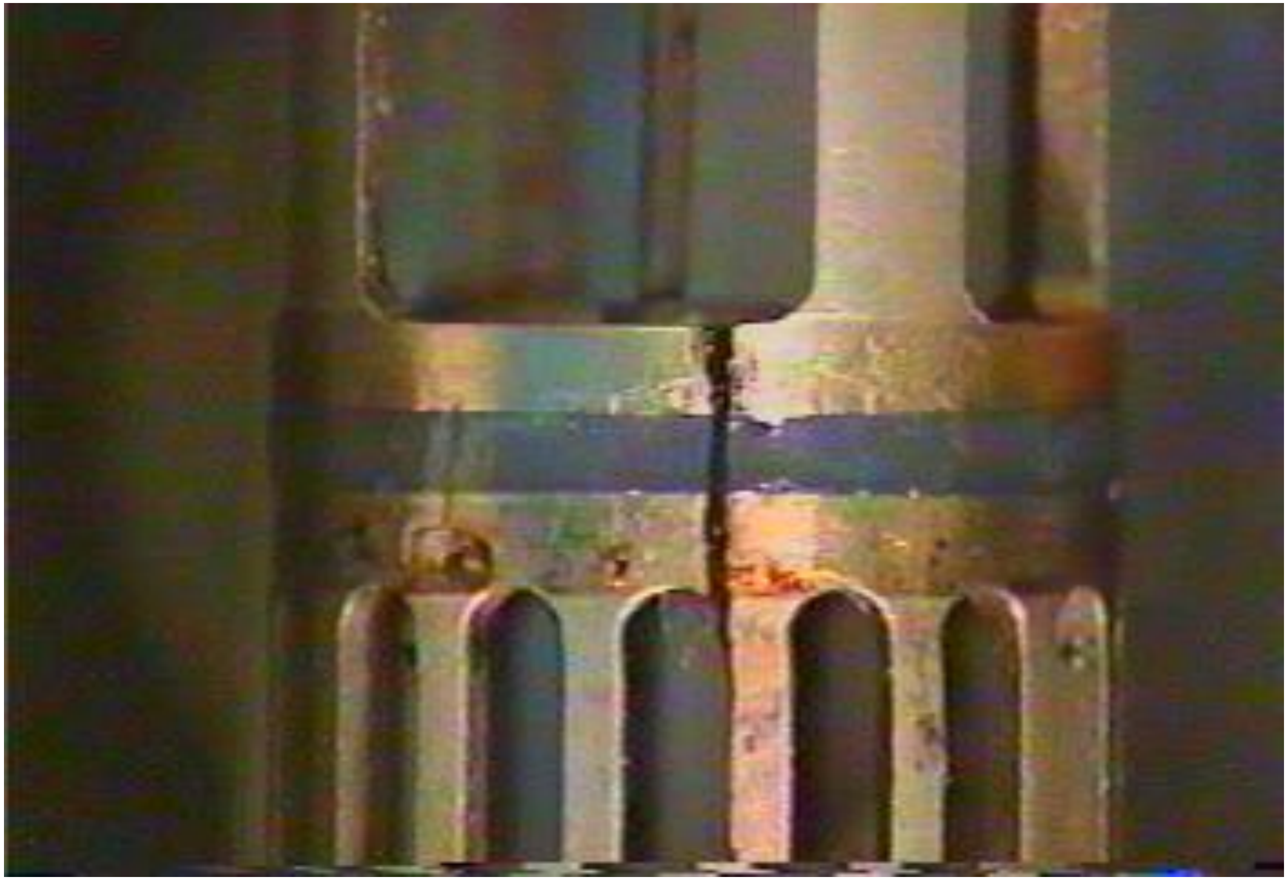
60% vol. solids





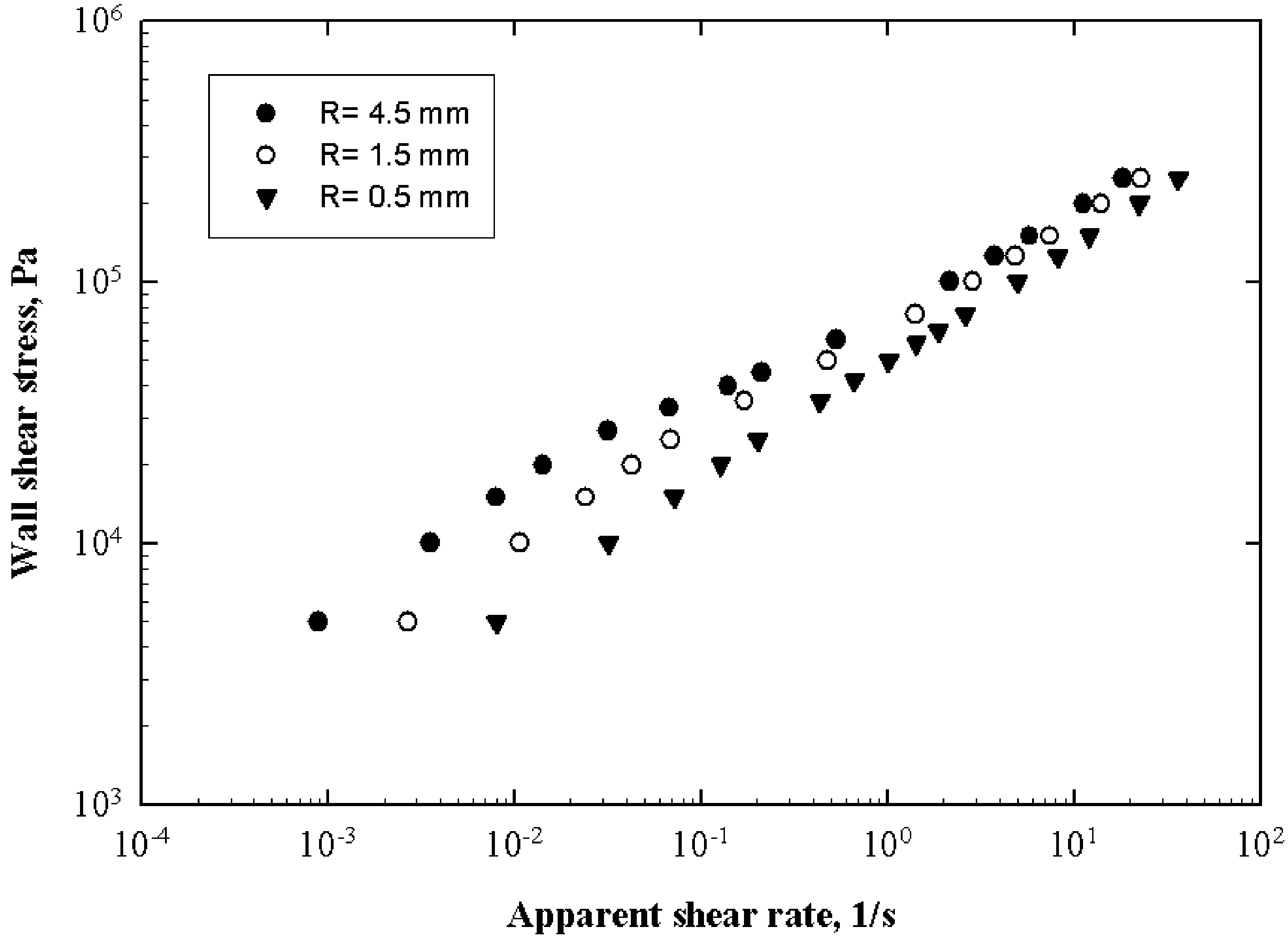


Demonstration of Viscoplasticity for Gels:



S. Aktas, D. M. Kalyon, B. M. Marín-Santibáñez and J.Pérez-González, “Shear viscosity and wall slip behavior of a viscoplastic hydrogel”, J. Rheology, 58, 2, 513-535 (2014).

With wall slip rheology data become dependent on the surface/volume ratio: Flow curves at constant capillary length/radius (L/R)



D. Kalyon, “Apparent Slip and Viscoplasticity of Concentrated Suspensions”, J. Rheology, 49, 3, 621-640 (2005).

Wall slip velocity versus shear stress behavior is characterized and used as the boundary condition in mathematical modeling

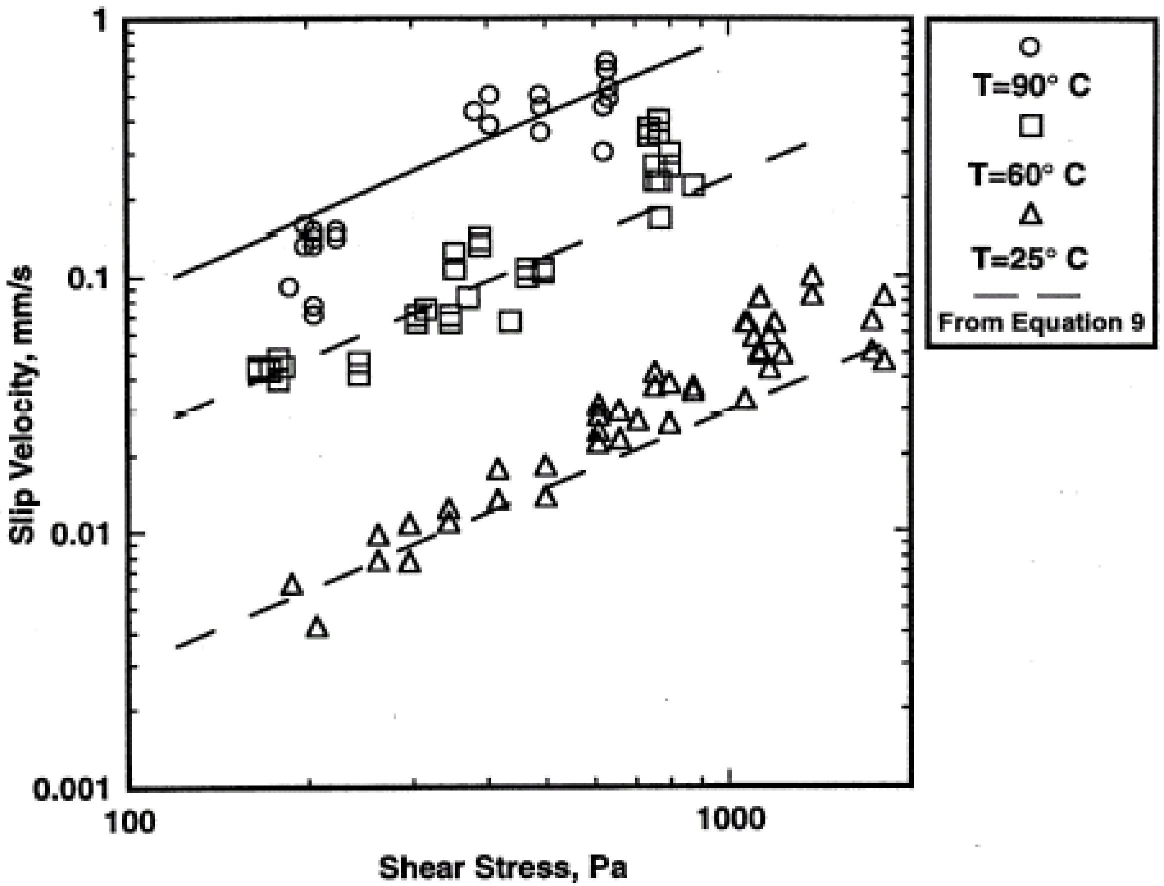
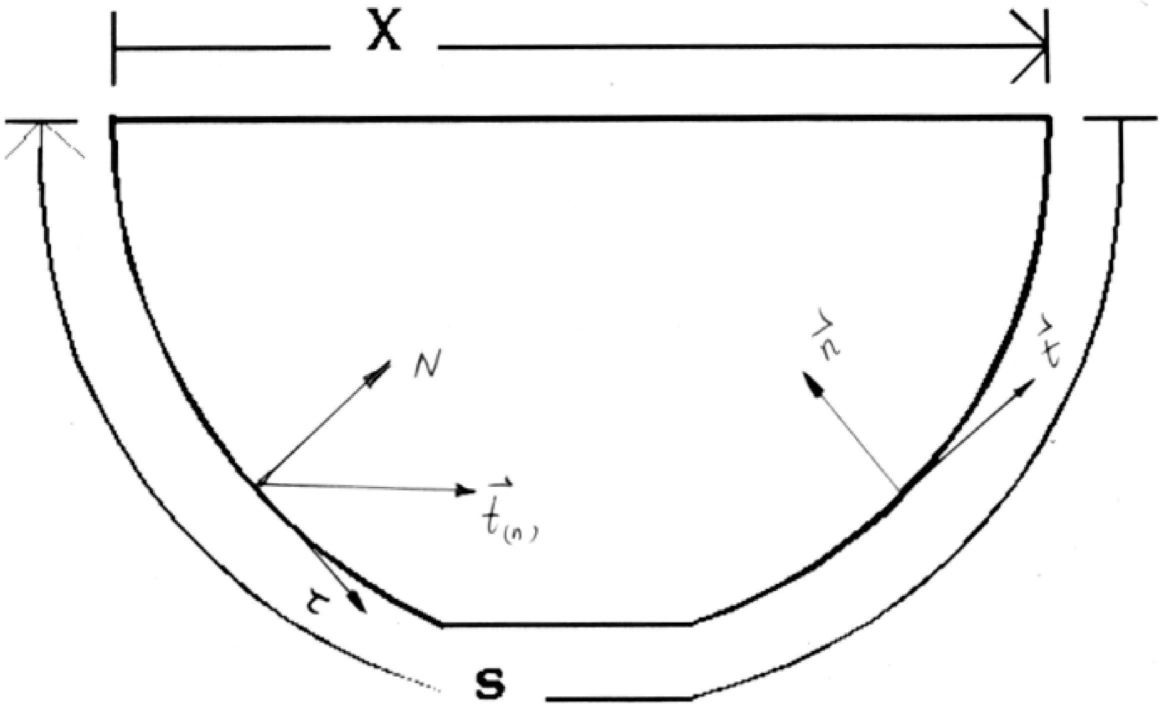
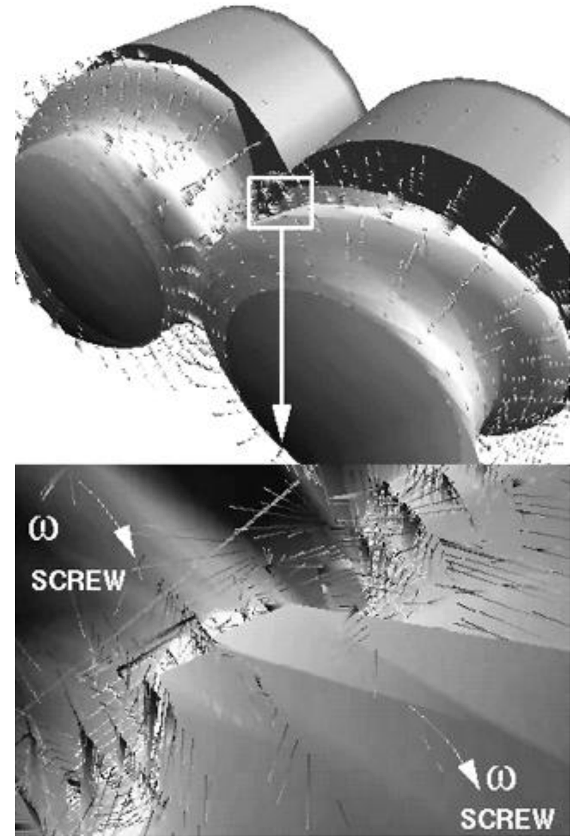


FIG. 6. Slip velocity vs shear stress at 25, 60, and 90 °C.

B. Aral and D. M. Kalyon, "Effects of Temperature and Surface Roughness on Time-Dependent Development of Wall Slip in Torsional Flow of Concentrated Suspensions," J. Rheol., 38 (4), 957-972 (1994).

Boundary condition in simulation: wall slip





Unit normal vector

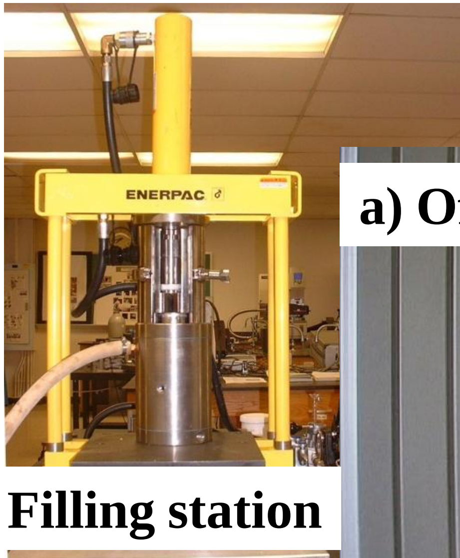
$$\underline{t} \times (\underline{u} - \underline{u}_{solid}) = b\underline{n}\,\underline{t} : \underline{\underline{T}}$$

Unit tangent vector

Total stress tensor

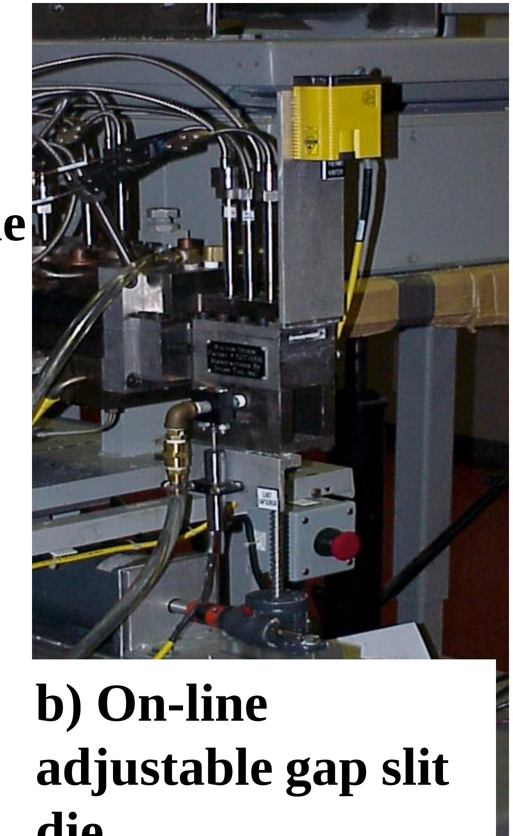
A. Lawal and D. M. Kalyon, "Non-isothermal Model of Single Screw Extrusion of Generalized Newtonian Fluids," Numerical Heat Transfer, 26 (1), 103-121 (1994).

Specialized rheometers which allow the determination of wall slip velocity as well as shear viscosity

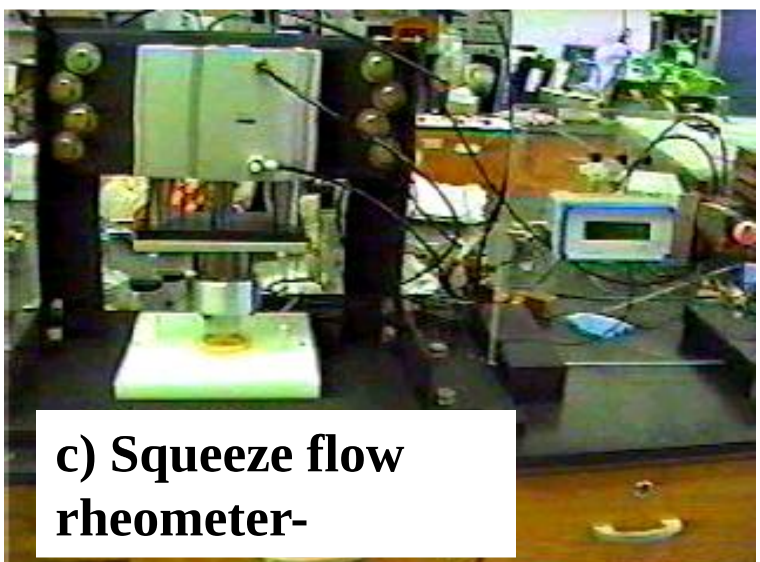


Filling station

a) Off-line adjustable gap slit die

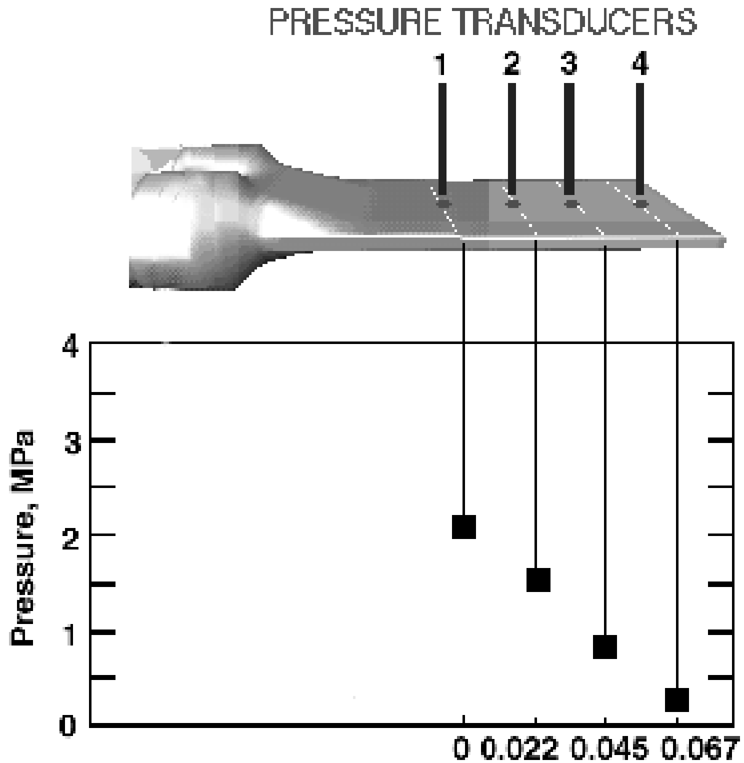


b) On-line adjustable gap slit die

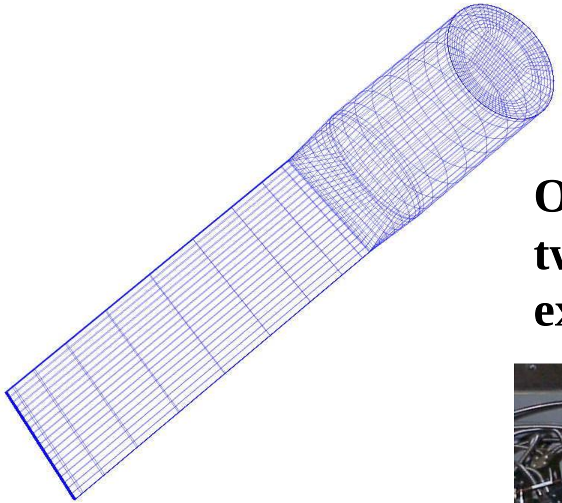


c) Squeeze flow rheometer-

ADJUSTABLE GAP RECTANGULAR SLIT DIE



Pressure versus distance

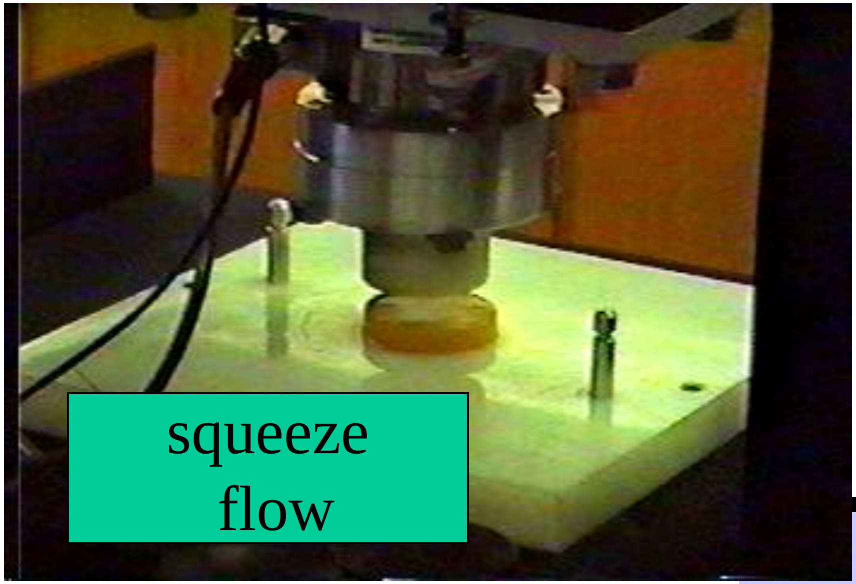


On-line, twin screw extruder

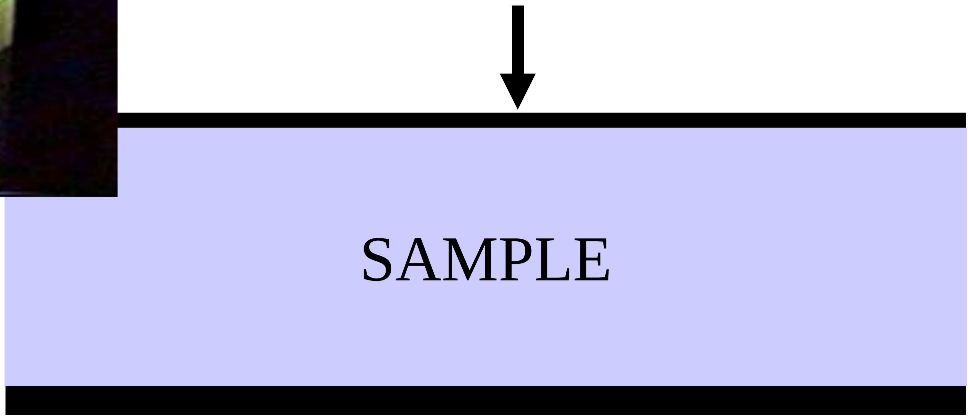
Off-line

Kalyon, Gevgilili, Kowalczyk, Prickett and Murphy, "Use of adjustable-gap on-line and off-line slit rheometers for the characterization of the wall slip and shear viscosity behavior of energetic formulations", **Journal of Energetic Materials,** 24, 175-193 (2006).

Squeeze flow rheometer

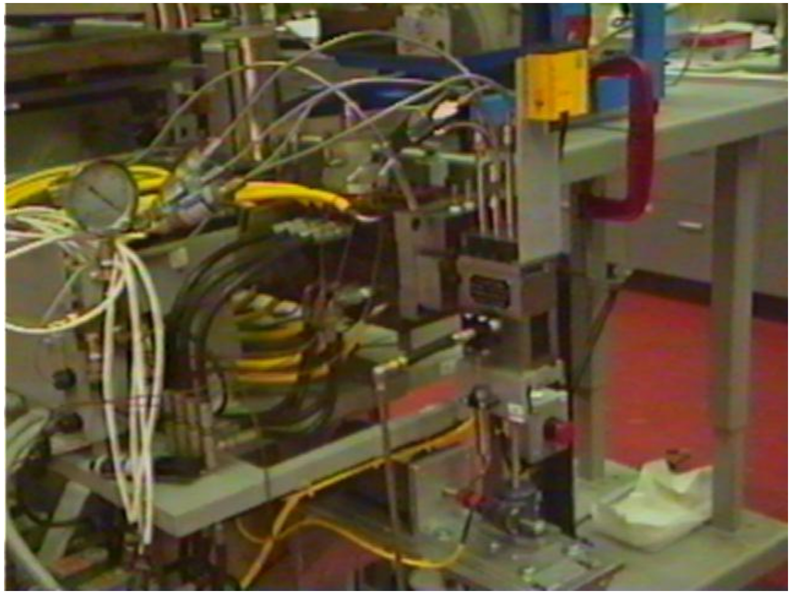


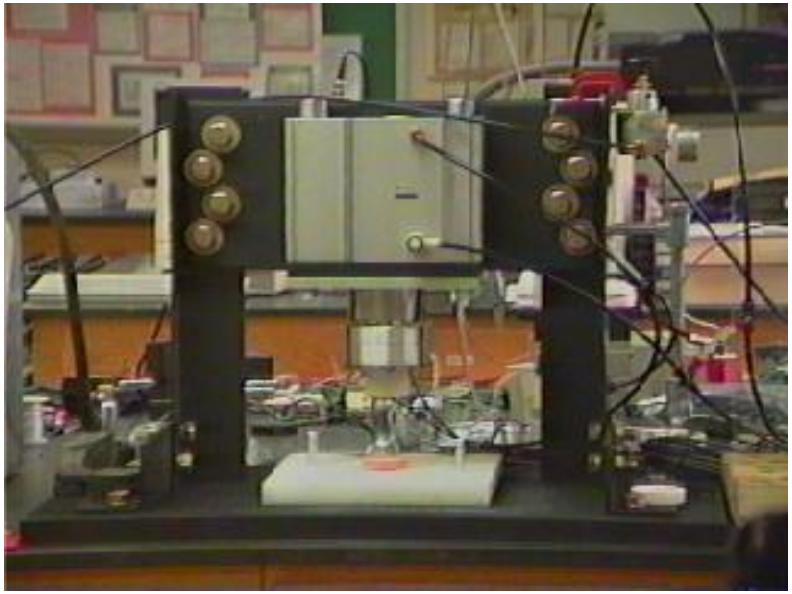
- Simple to operate
- Data analysis instantaneous
- Ideal for complex fluids
- Replaces the “finger” rheometer



D. Kalyon, H. Tang and B. Karuv, **Journal of Energetic Materials,** 24, 195-202 (2006).

NOVEL RHEOMETERS DEVELOPED, DESIGNED AND BUILT BY SIT





Adjustable Gap On-line Rheometer

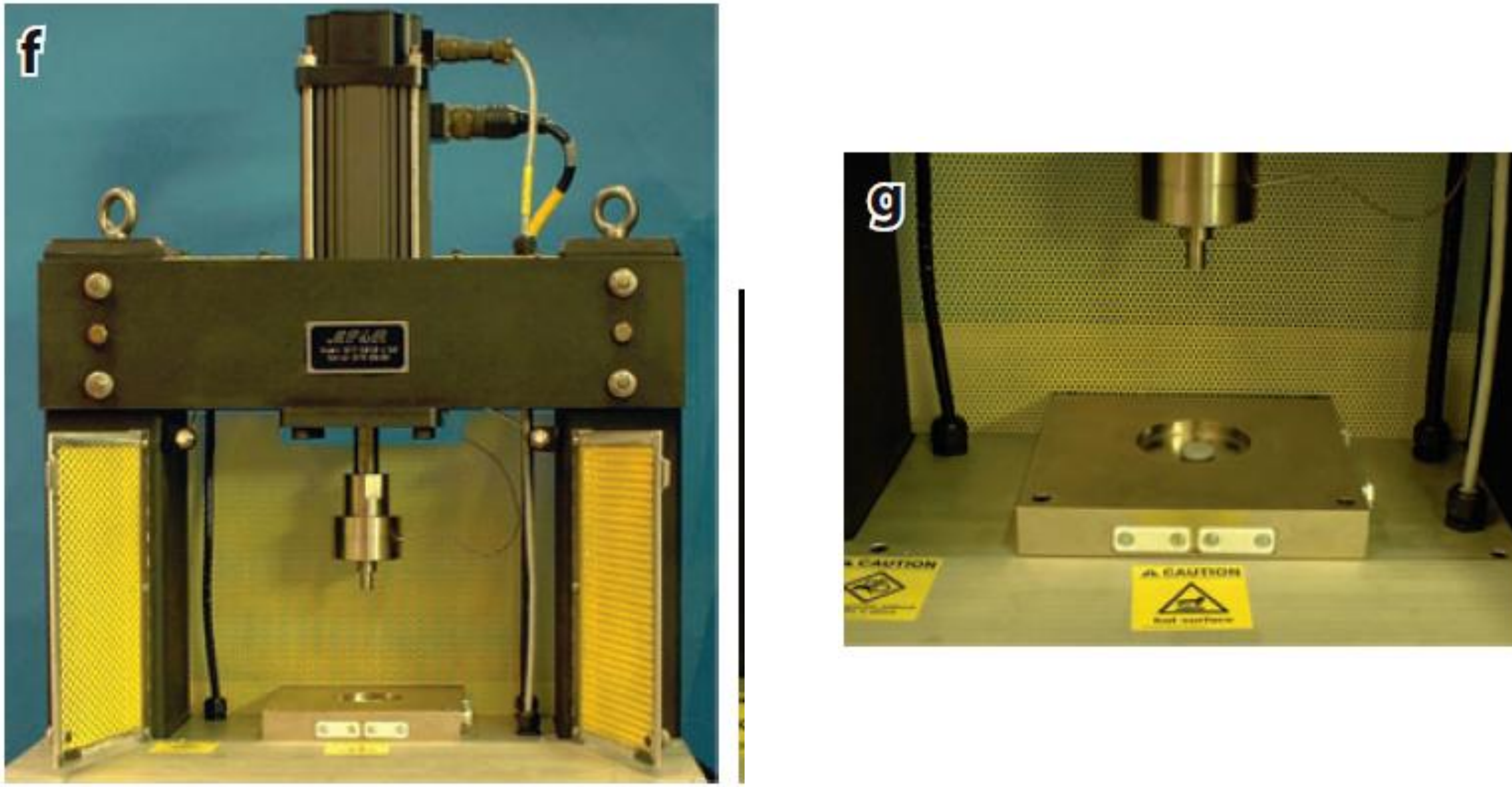
- Currently used for live energetics @ NSWC / IH

Squeeze Flow Rheometer

- Built for characterization of gun propellants @ Alliant TechSystems / Radford, VA

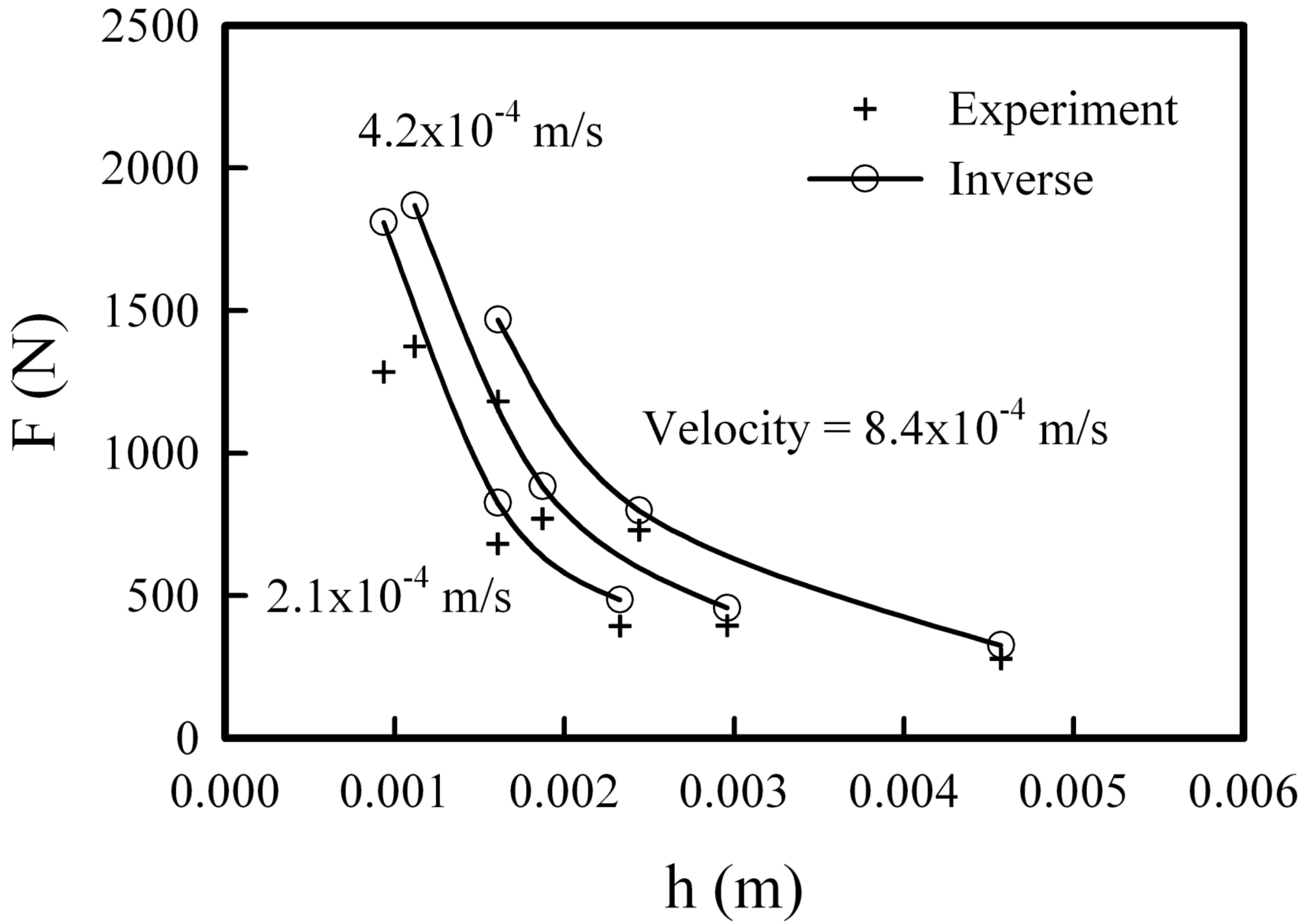
•D. Kalyon, H. Gevgilili, J. Kowalczyk, S. Prickett and C. Murphy, "Use of adjustable-gap on-line and off-line slit rheometers for the characterization of the wall slip and shear viscosity behavior of energetic formulations", Journal of Energetic Materials, 24, 175-193 (2006).

•D. Kalyon, H. Tang and B. Karuv, "Squeeze flow rheometry for rheological characterization of energetic formulations", Journal of Energetic Materials, 24, 195-202 (2006).



New-generation of squeeze flow rheometer built for IBM and Bergquist

D. Kalyon, **Journal of Energetic Materials,** 24, 213 (2006).



Inverse problem solution in compressive squeeze flow: viscoplastic with wall slip

Kalyon and Tang, **Journal of Non-Newtonian Fluid Mechanics**, **143**, 133 (2007).

Analysis of the squeeze flow data for parameters of shear viscosity and wall slip using 2-D FEM:

$$0 = \frac{1}{r}\frac{\partial r u_r}{\partial r} + \frac{\partial u_z}{\partial z}$$

$$0 = -\frac{\partial p}{\partial r} - \left(\frac{1}{r}\frac{\partial r \tau_{rr}}{\partial r} - \frac{\tau_{\theta\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z}\right)$$

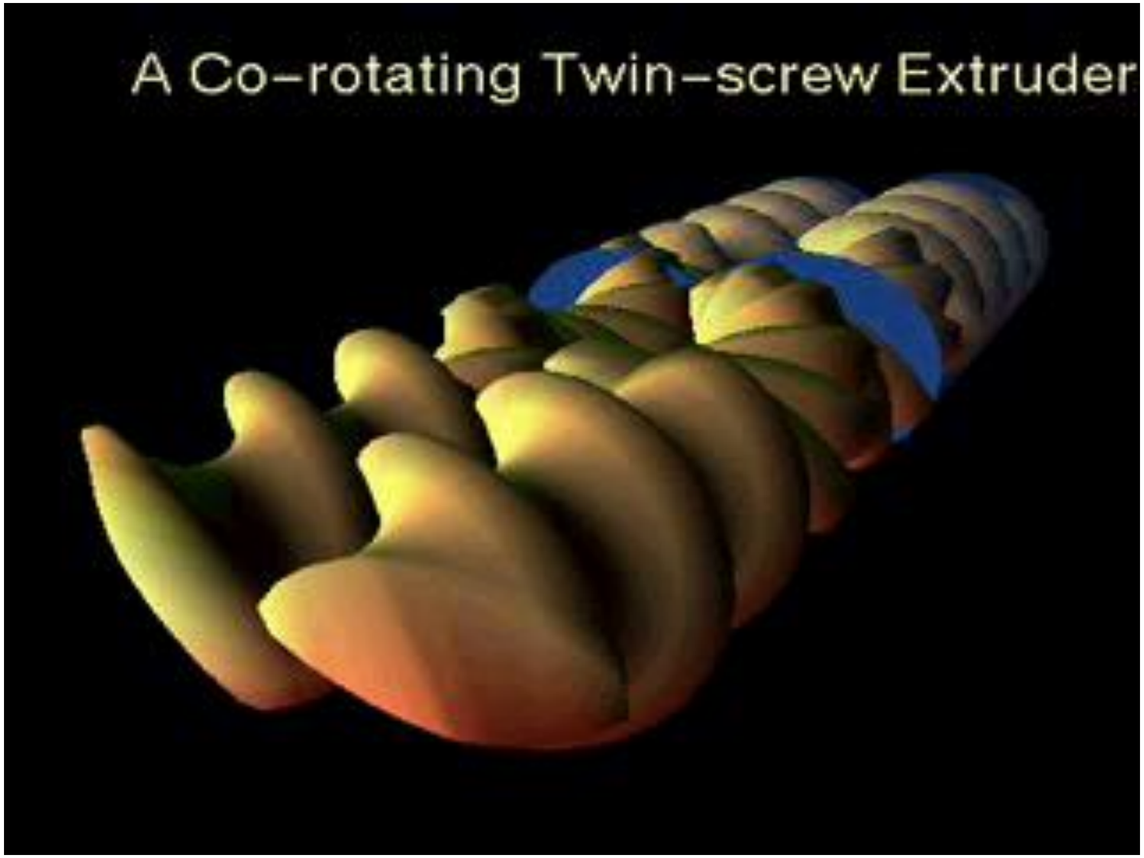
$$0 = -\frac{\partial p}{\partial z} - \left(\frac{1}{r}\frac{\partial r \tau_{rz}}{\partial r} + \frac{\partial \tau_{zz}}{\partial z}\right)$$

$$\vec{t} \cdot (\vec{V} - \vec{V}_w) = \beta \left(\mathrm{sgn}(\vec{n}\,\vec{t} : \underline{\tau})\right) \left|\vec{n}\,\vec{t} : \underline{\tau}\right|^{s_b},$$

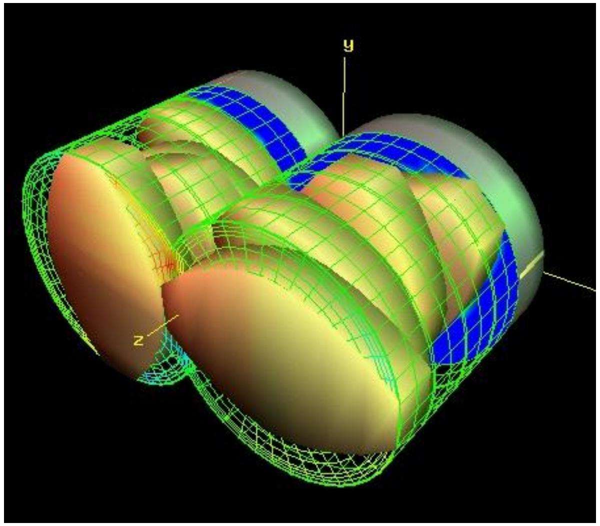
Lawal and Kalyon, **Int. Polym. Proc.**, **15**, 63 (2000).

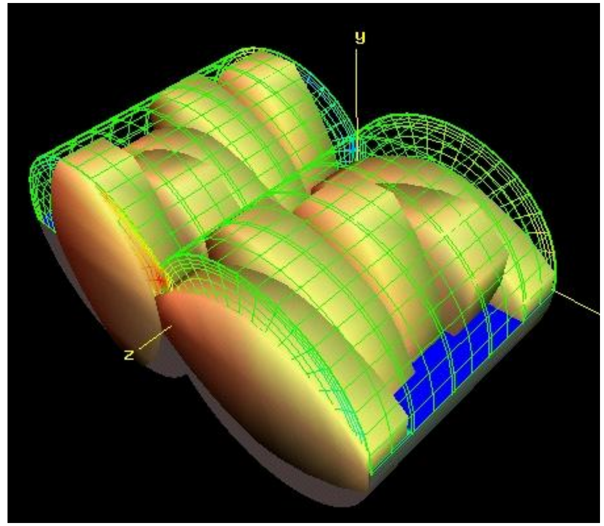
Mathematical modeling

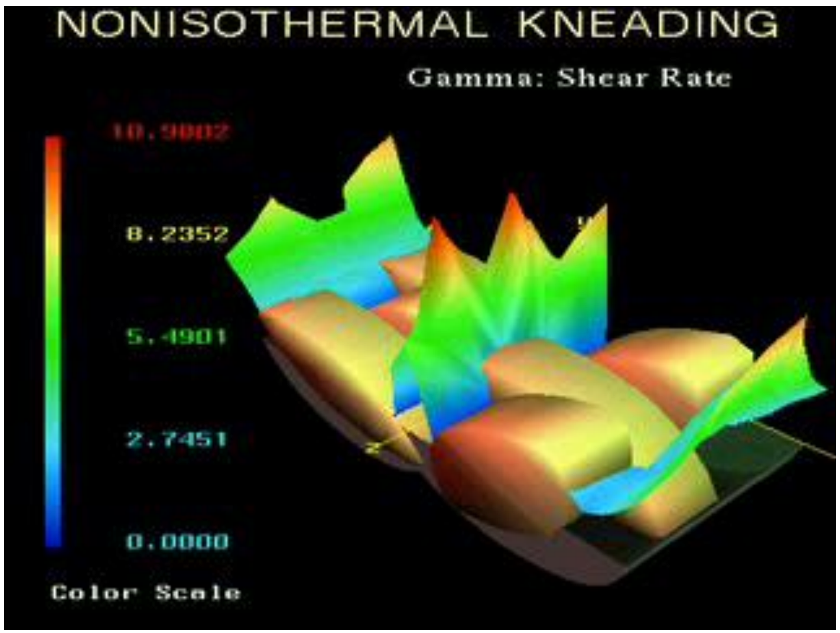
Challenge: To determine how to process-processing-structure development and ultimate properties

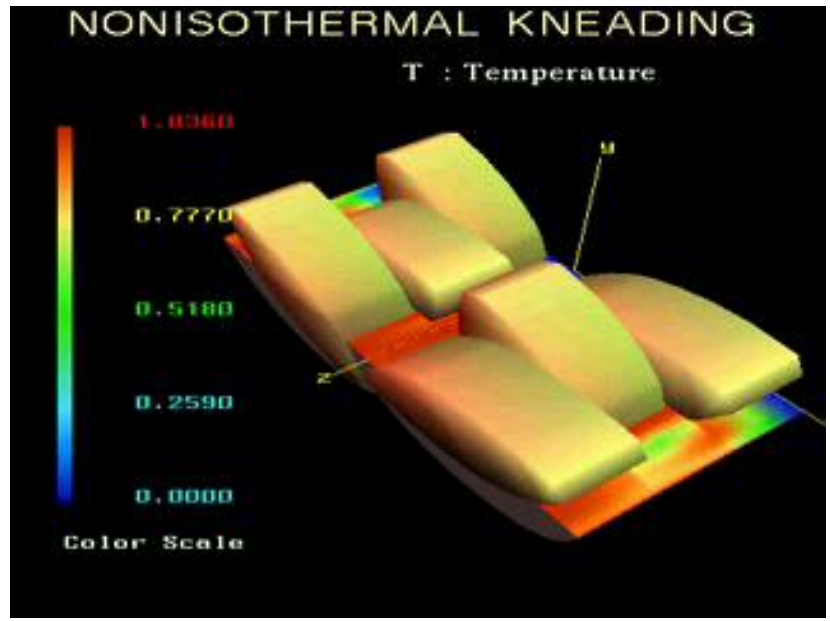


Kalyon and Malik, **International Polymer Processing,** 22, 293-302 (2007)

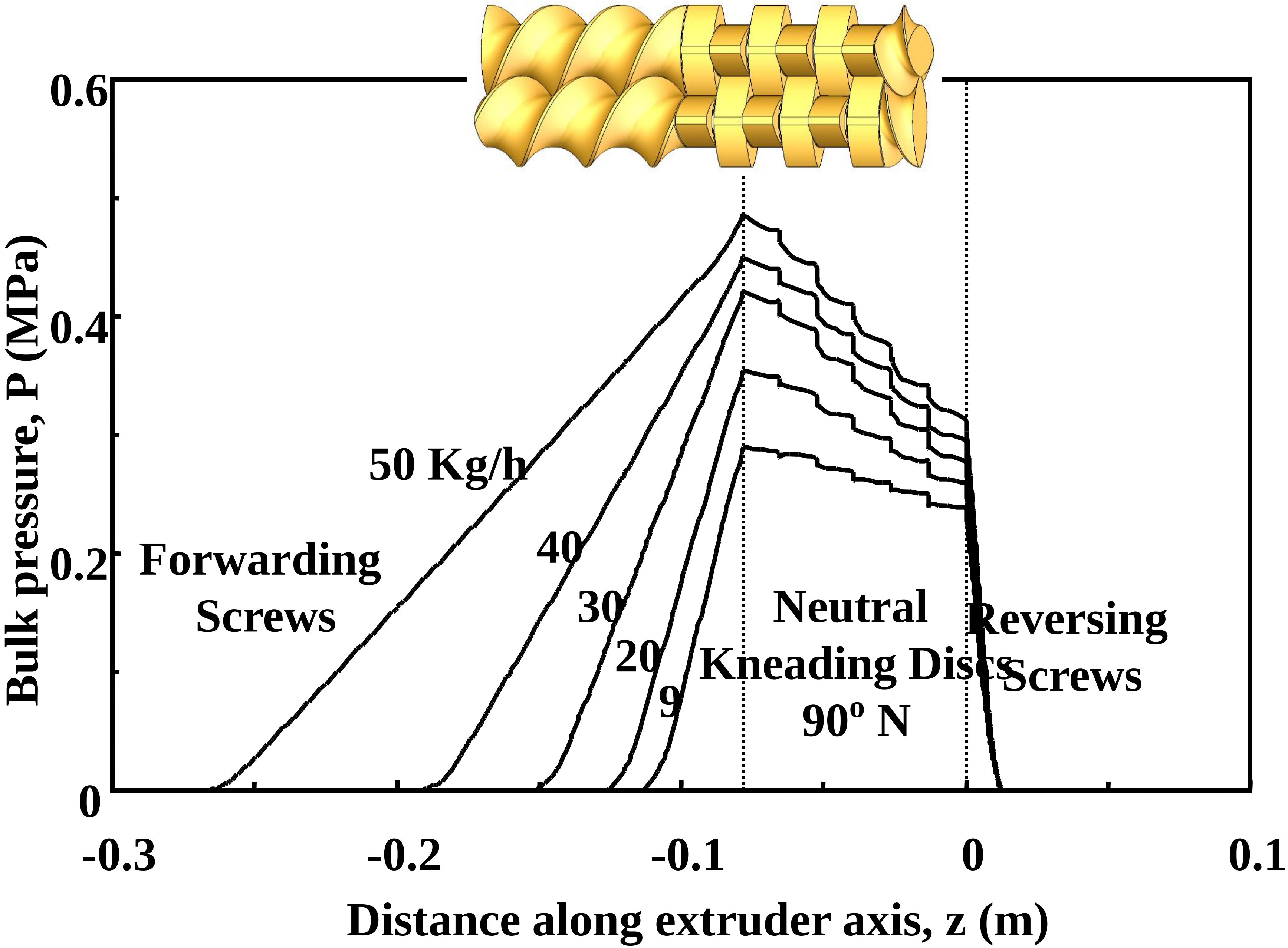




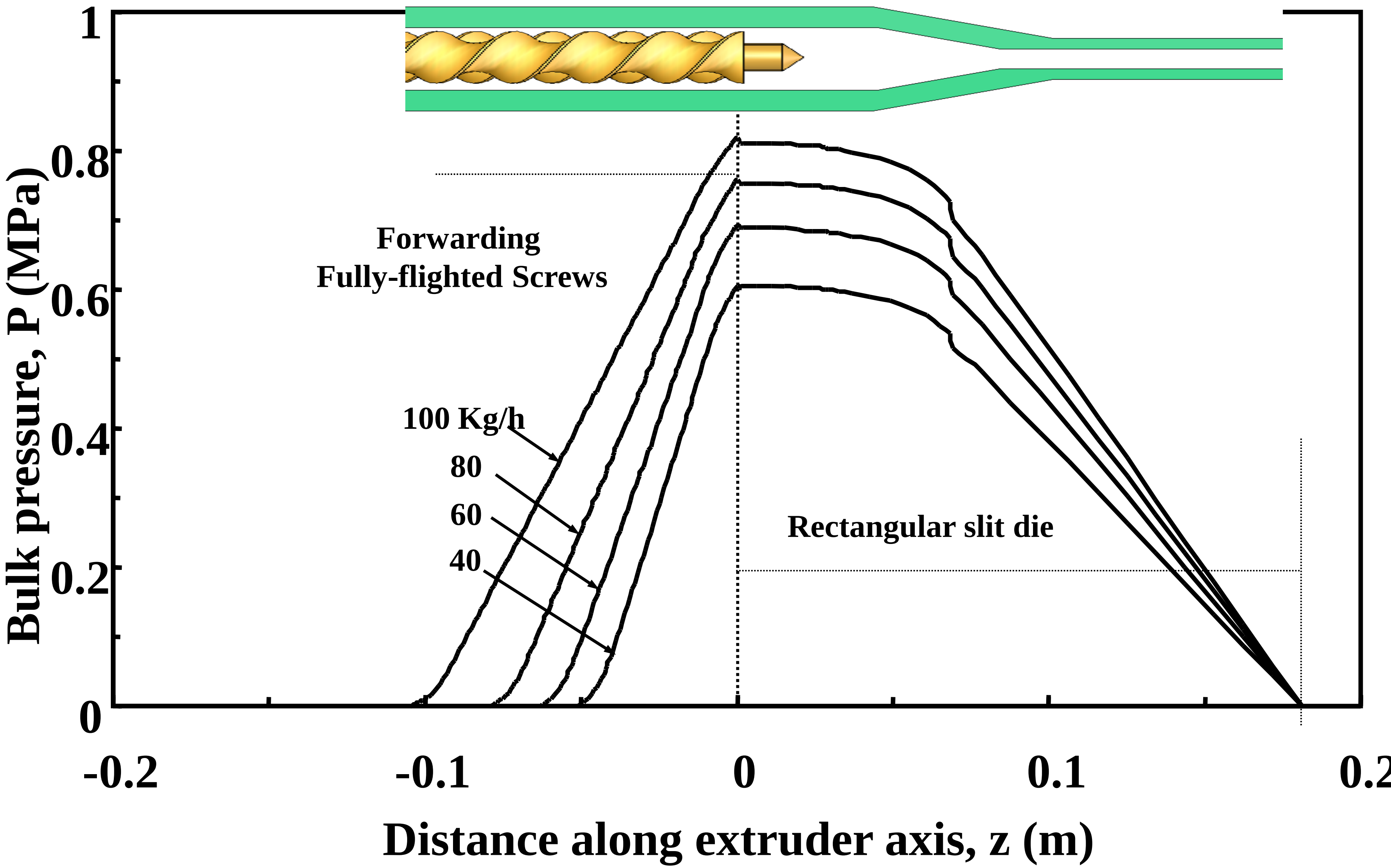




Kalyon, Lawal, Yazici, Yaras and Railkar, "Mathematical Modeling and Experimental Studies of Twin Screw Extrusion of Filled Polymers", **Polym. Eng. Sci.,** 39, 6, 1139-1151 (1999).

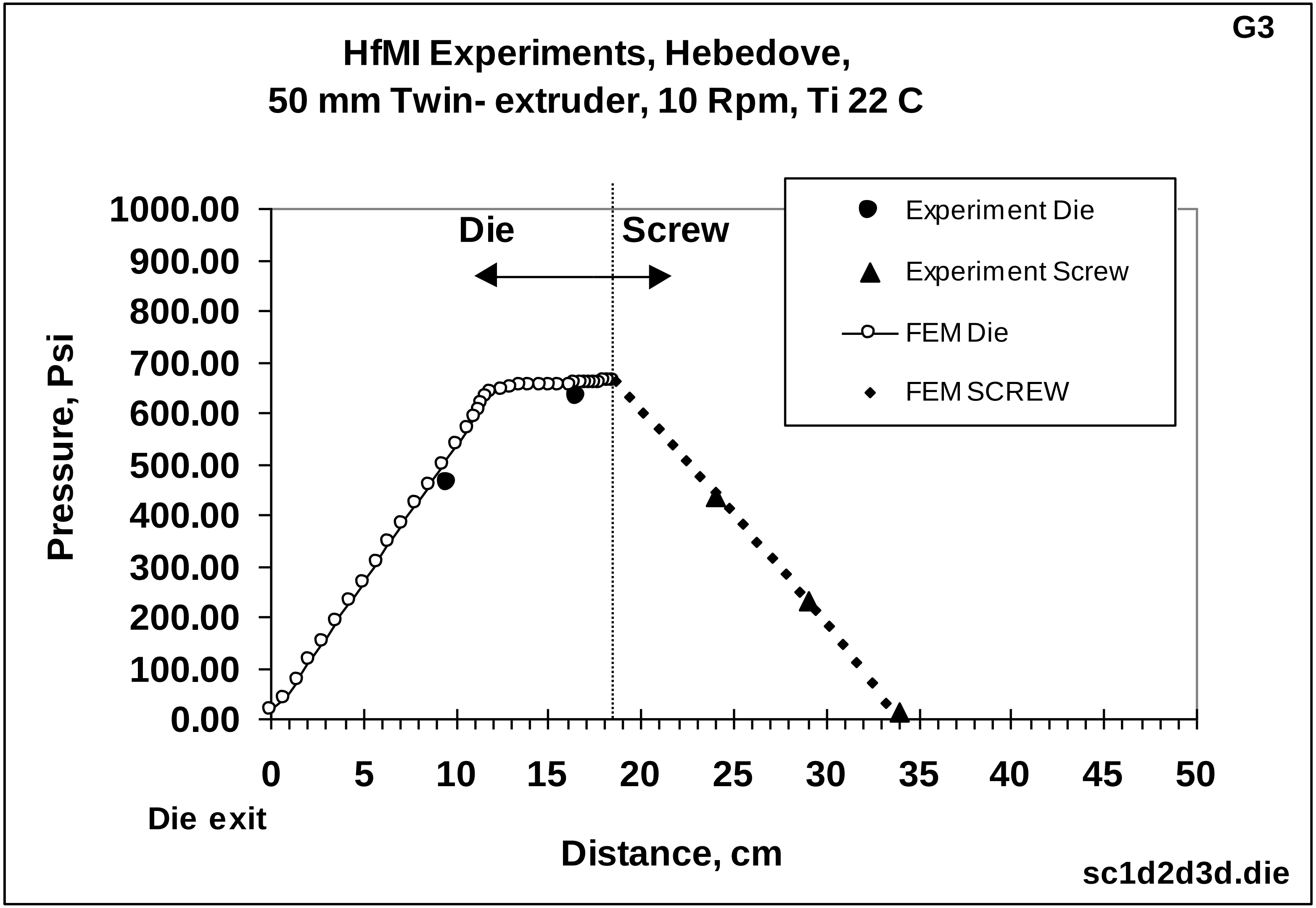


Kalyon and Malik, **International Polymer Processing,** 22, 293-302 (2007)



Kalyon and Malik, **International Polymer Processing,** 22, 293-302 (2007)

Experimental validation


G3
HfMI Experiments, Hebedove,
50 mm Twin- extruder, 10 Rpm, Ti 22 C
Die
Screw
Experiment Die
Experiment Screw
FEM Die
FEM SCREW
Pressure, Psi
1000.00
900.00
800.00
700.00
600.00
500.00
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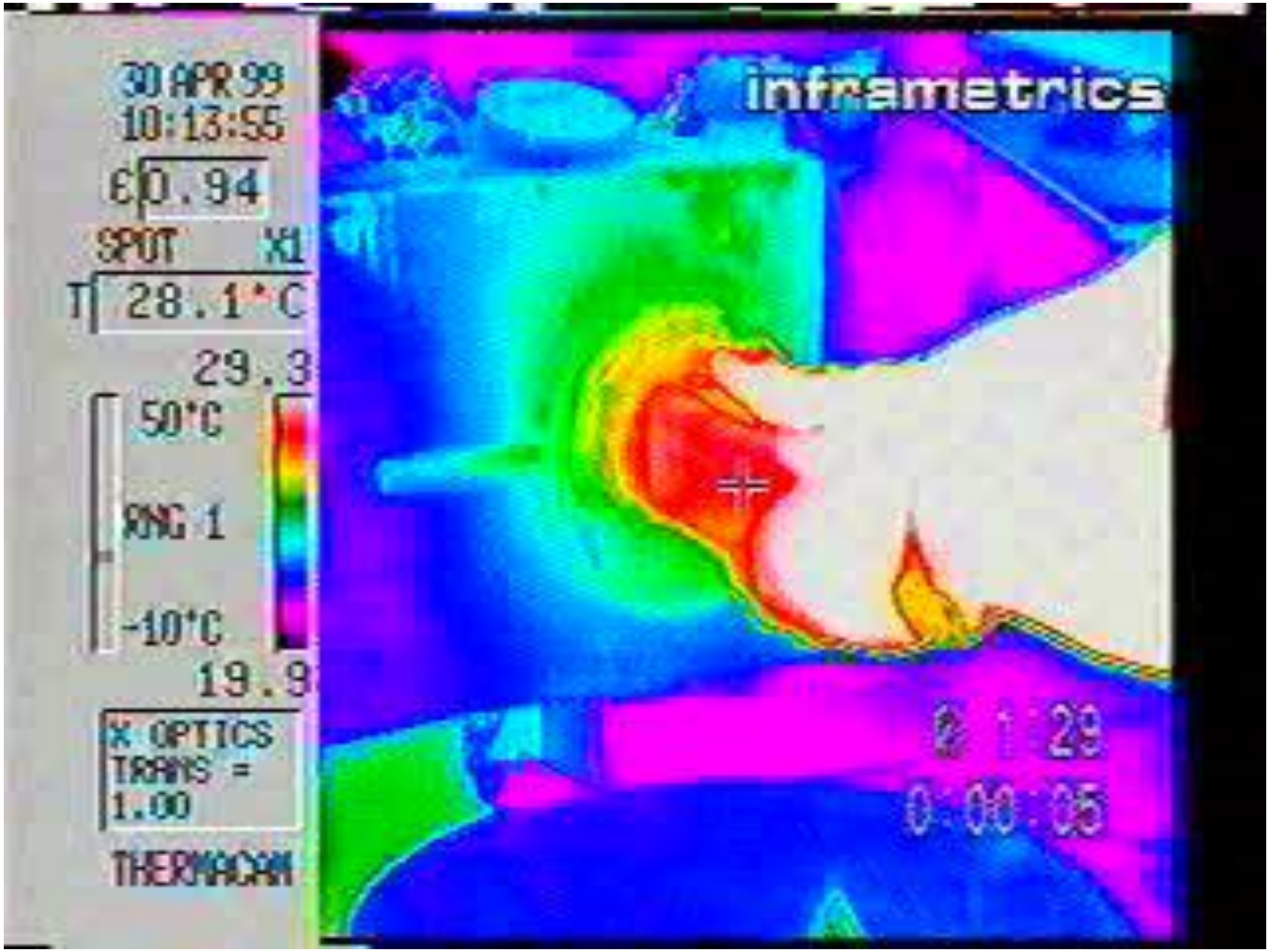
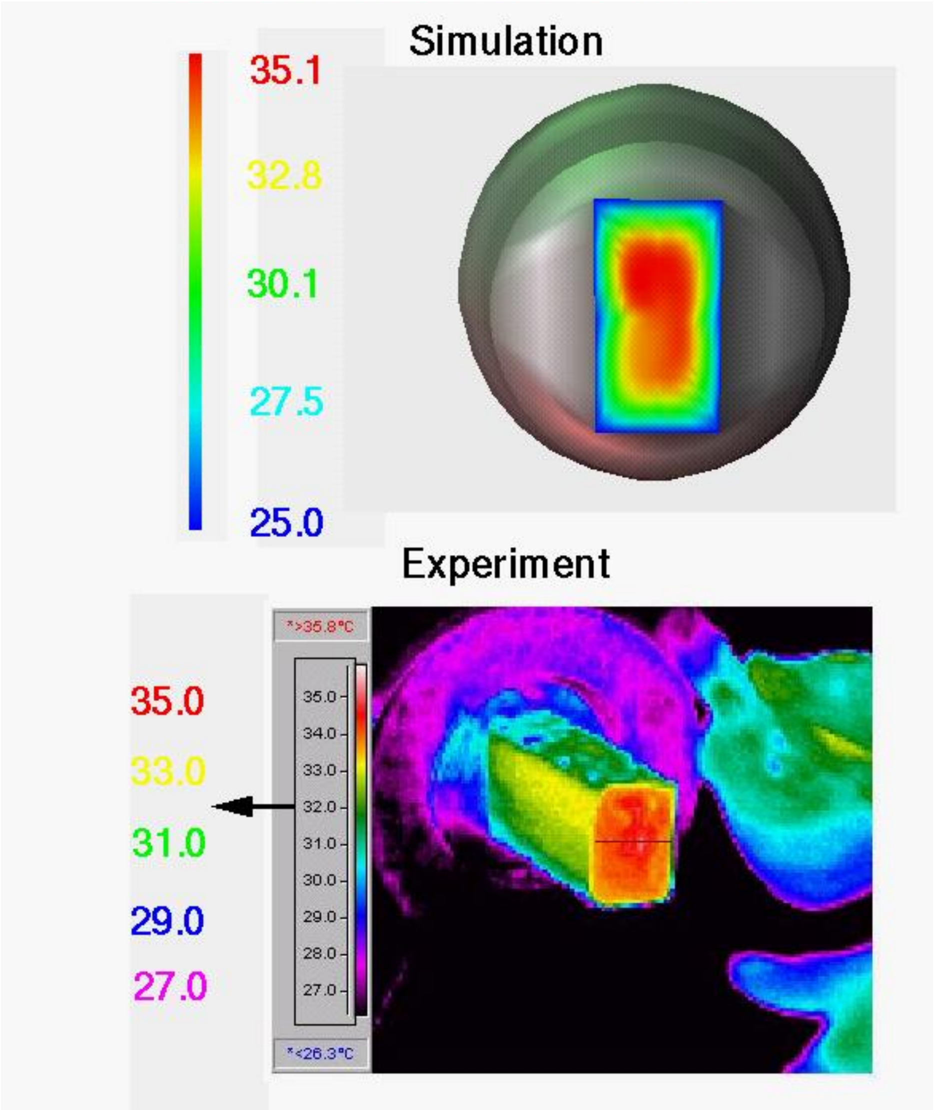
Die exit
Distance, cm
sc1d2d3d.die



Thermal imaging camera: extrusion

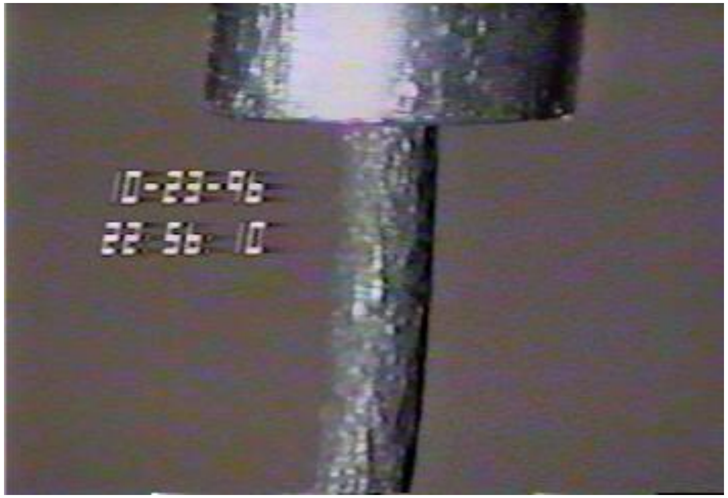
Temperature distribution: experimental versus simulation



Challenges

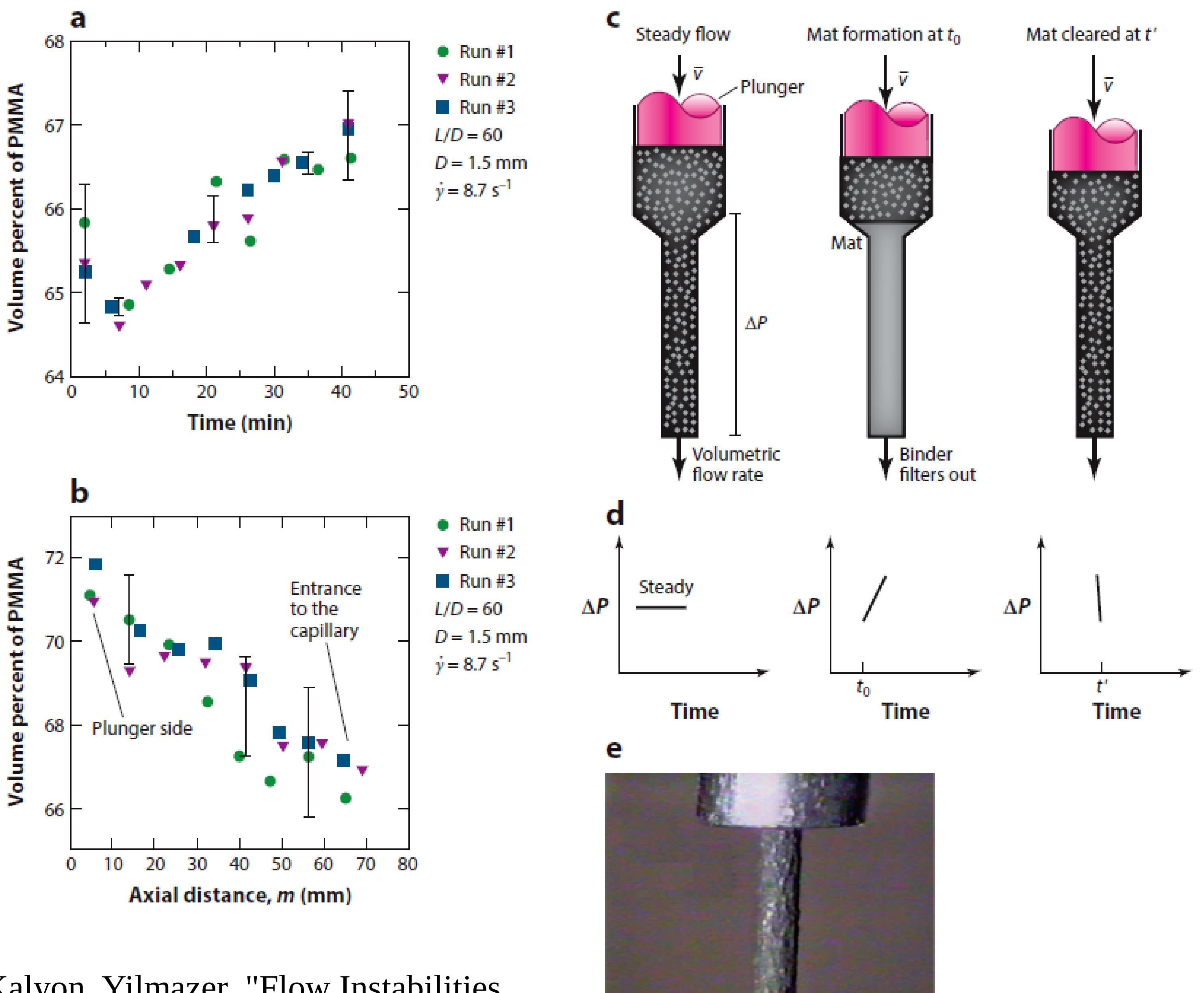
Extrudate with 76.5% solids prior to axial migration of binder

Unstable flow



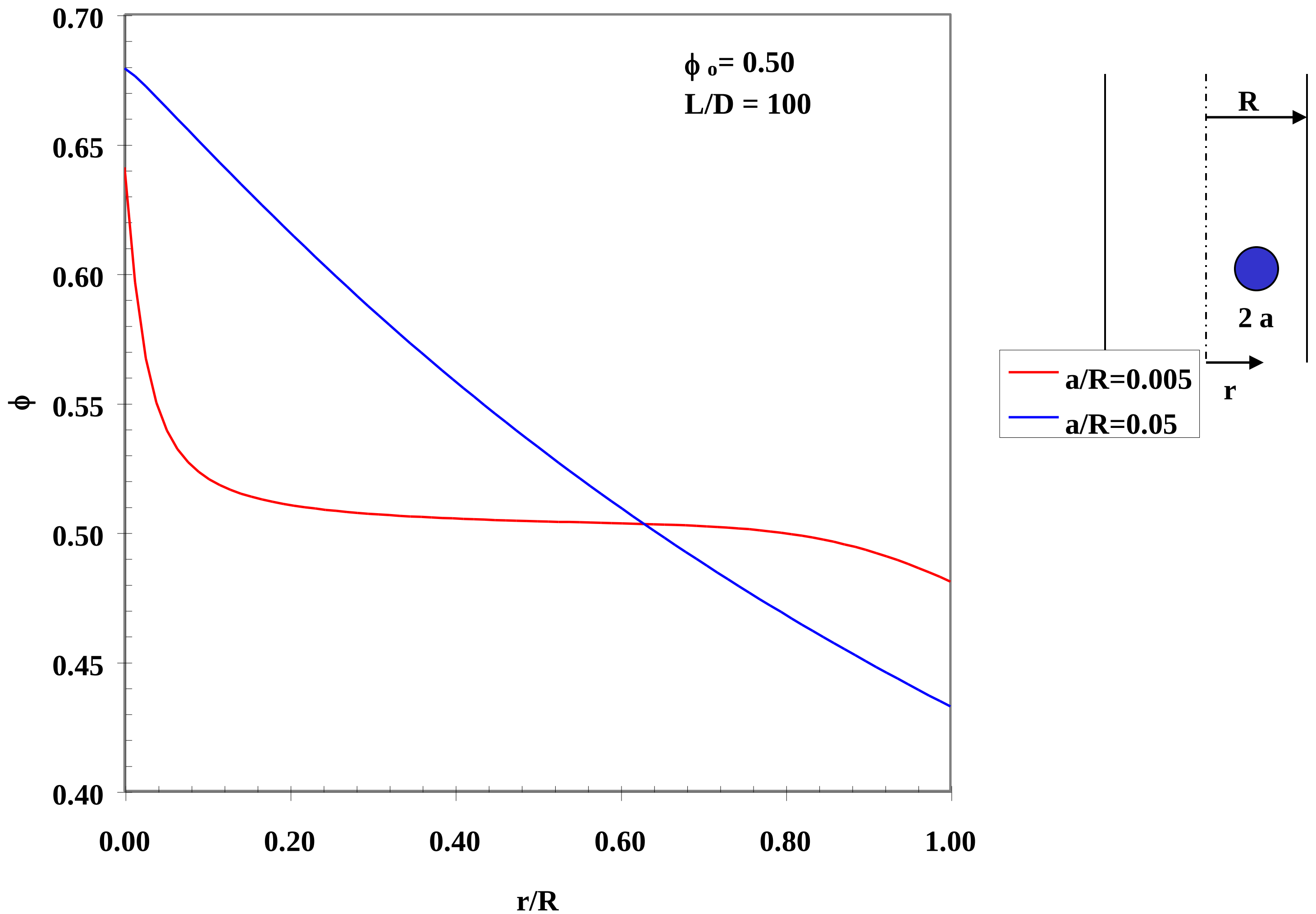
Filtration of the binder phase

U. Yilmazer , C. Gogos and D. M. Kalyon, "Mat Formation and Unstable Flows of Highly Filled Suspensions in Capillaries and Continuous Processors," Polymer Composites, 10 (4), 242-248(1989).



Yaras, Kalyon, Yilmazer, "Flow Instabilities in Capillary Flow of Concentrated Suspensions, " **Rheologica Acta, 33**, 48-59 (1994).

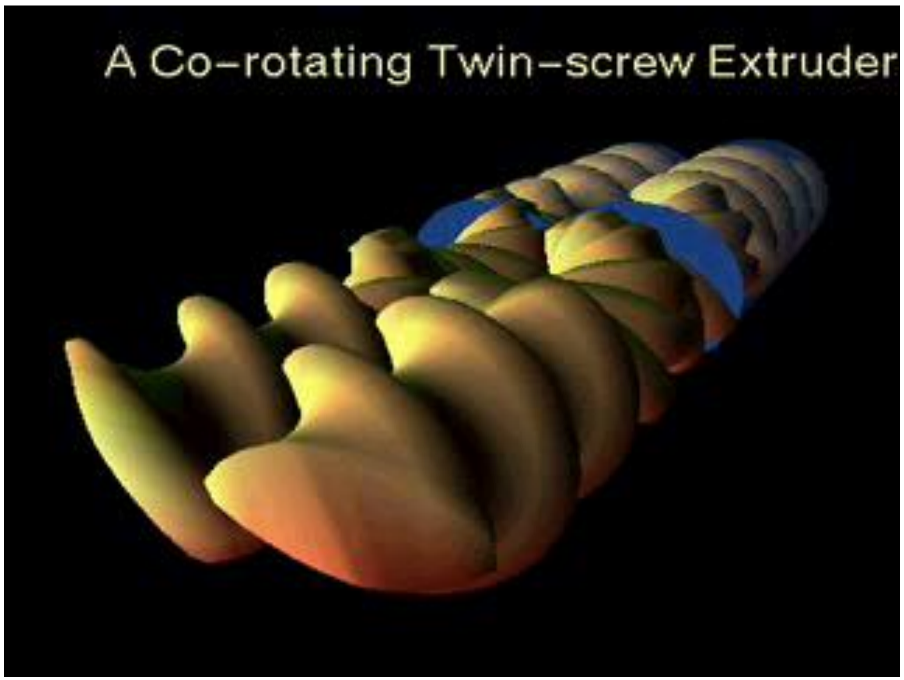
Concentration Distribution

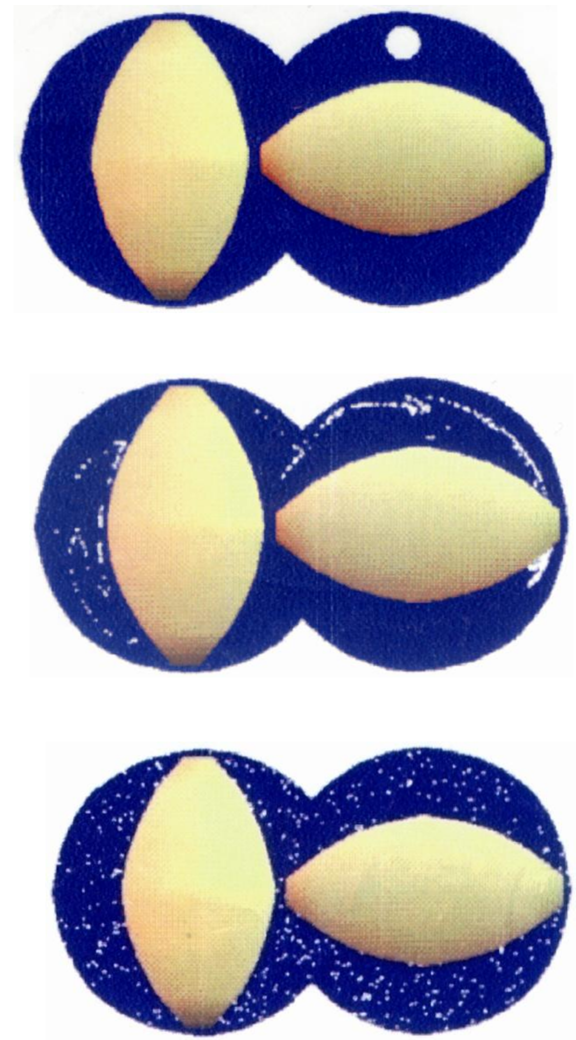


M. Allende, D. Fair, D. M. Kalyon, D. Chiu and S. Moy,
"Development of particle concentration distributions and burn rate gradients upon shear-induced particle migration during processing of energetic suspensions", Journal of Energetic Materials, 25, 49- 67 (2007).

Mixing- degree of mixedness

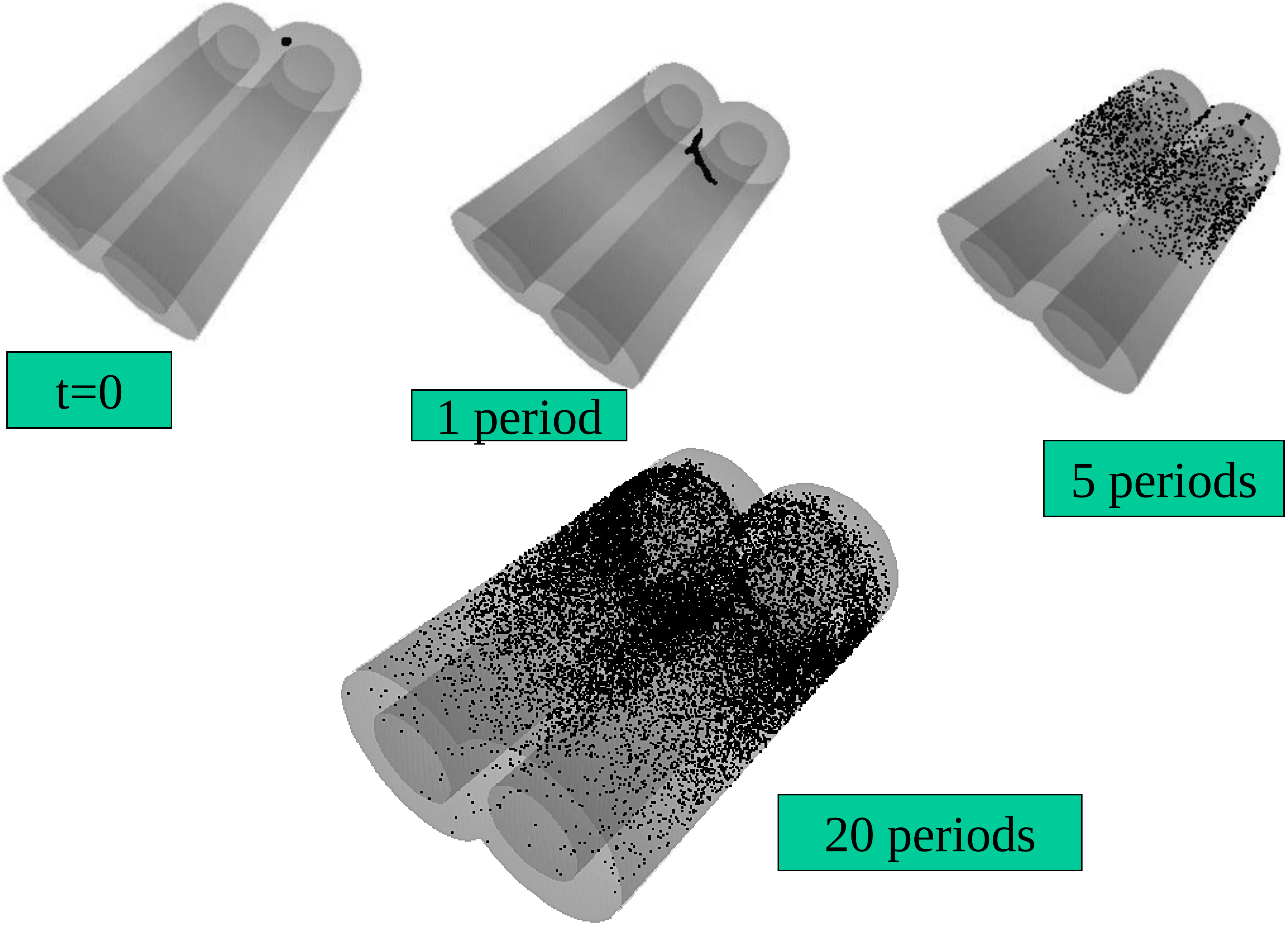
Ability to mathematically model the processing/mixing process





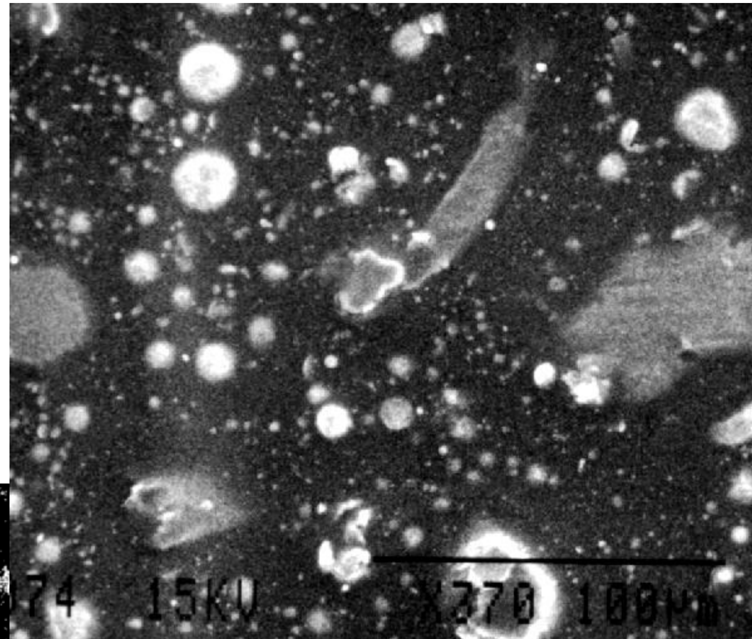
A. Lawal and D. M. Kalyon, Polym. Eng. Sci., 35, 1325-1338 (1995).

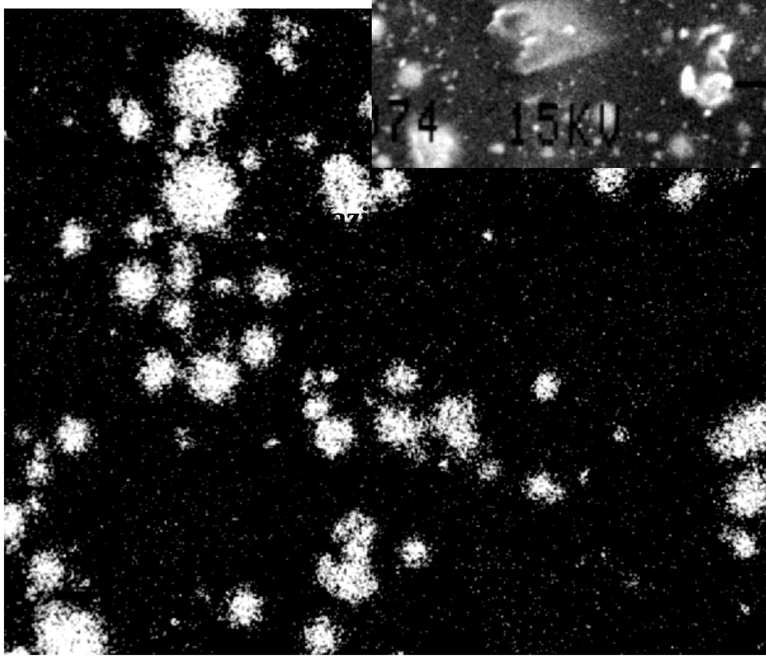
Analysis of Kneading Disks staggered at 30 forward



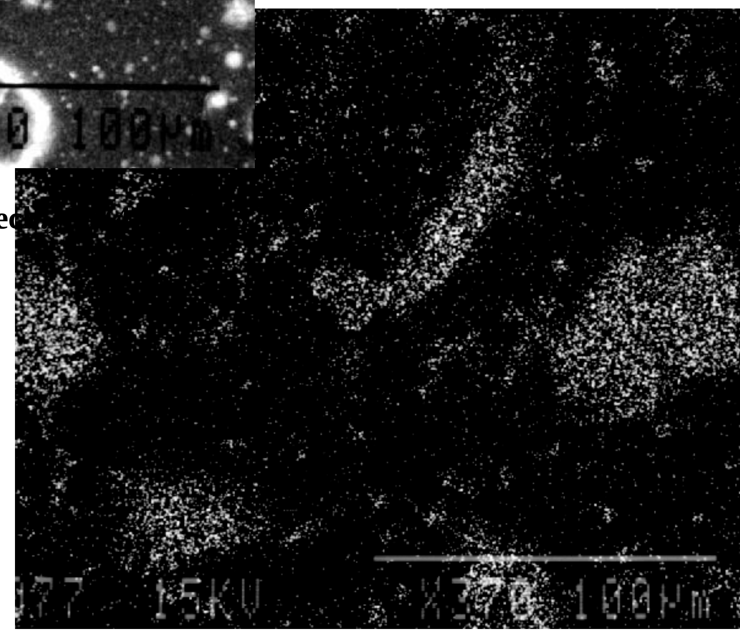
A. Lawal and D. M. Kalyon, "Mechanisms of Mixing in Single and Co-rotating Twin Screw Extruders,“ Polym. Eng. Sci., 35 (17) 1325-1338 (1995).

SEM and EDX for mixing analysis





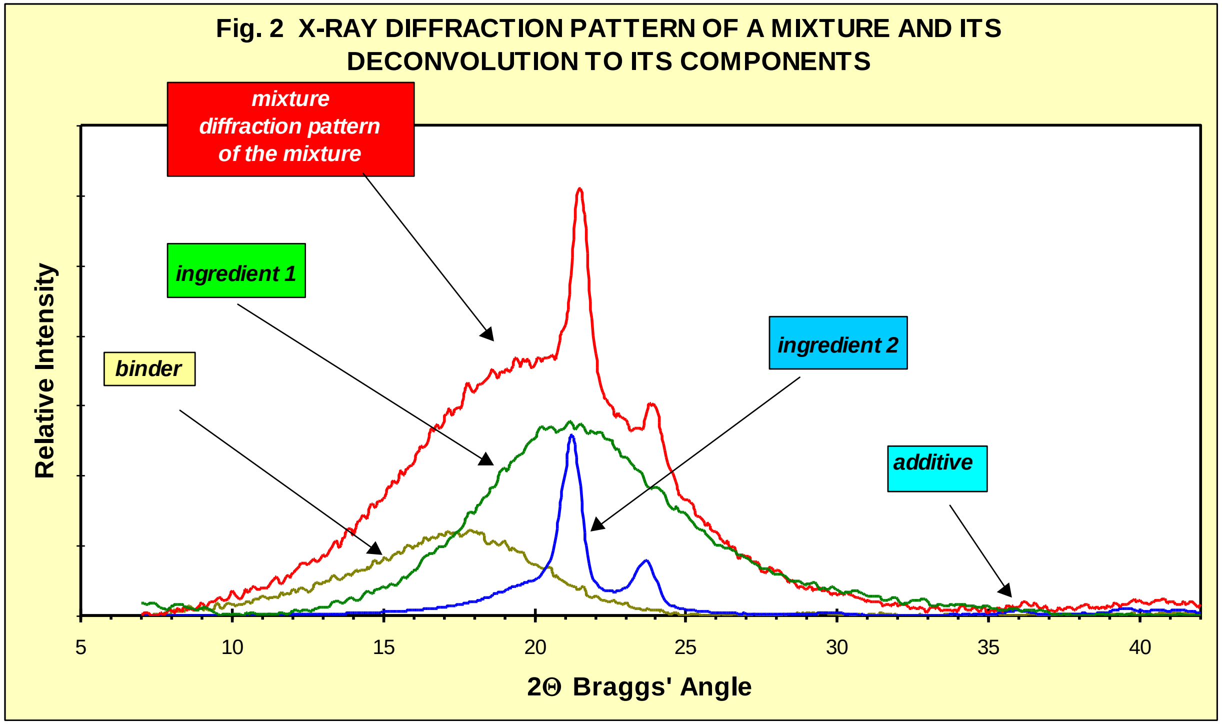
Aluminum Scan



Sulfur scan

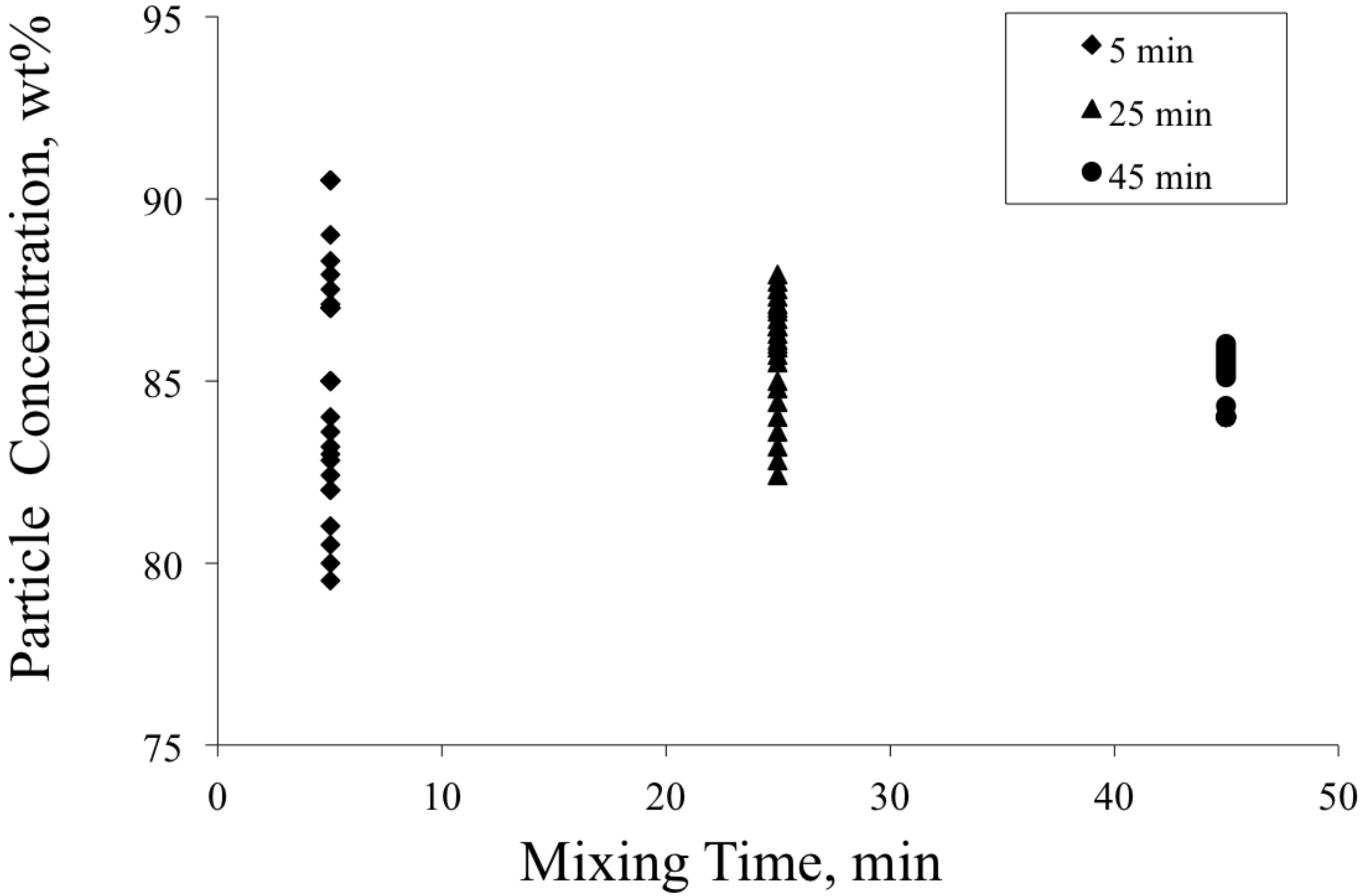
Yazici and Kalyon, Rubber Chem. and Tech., 66 (4), 527-537 (1993).

To quantitatively characterize the degree of mixedness of the ingredients

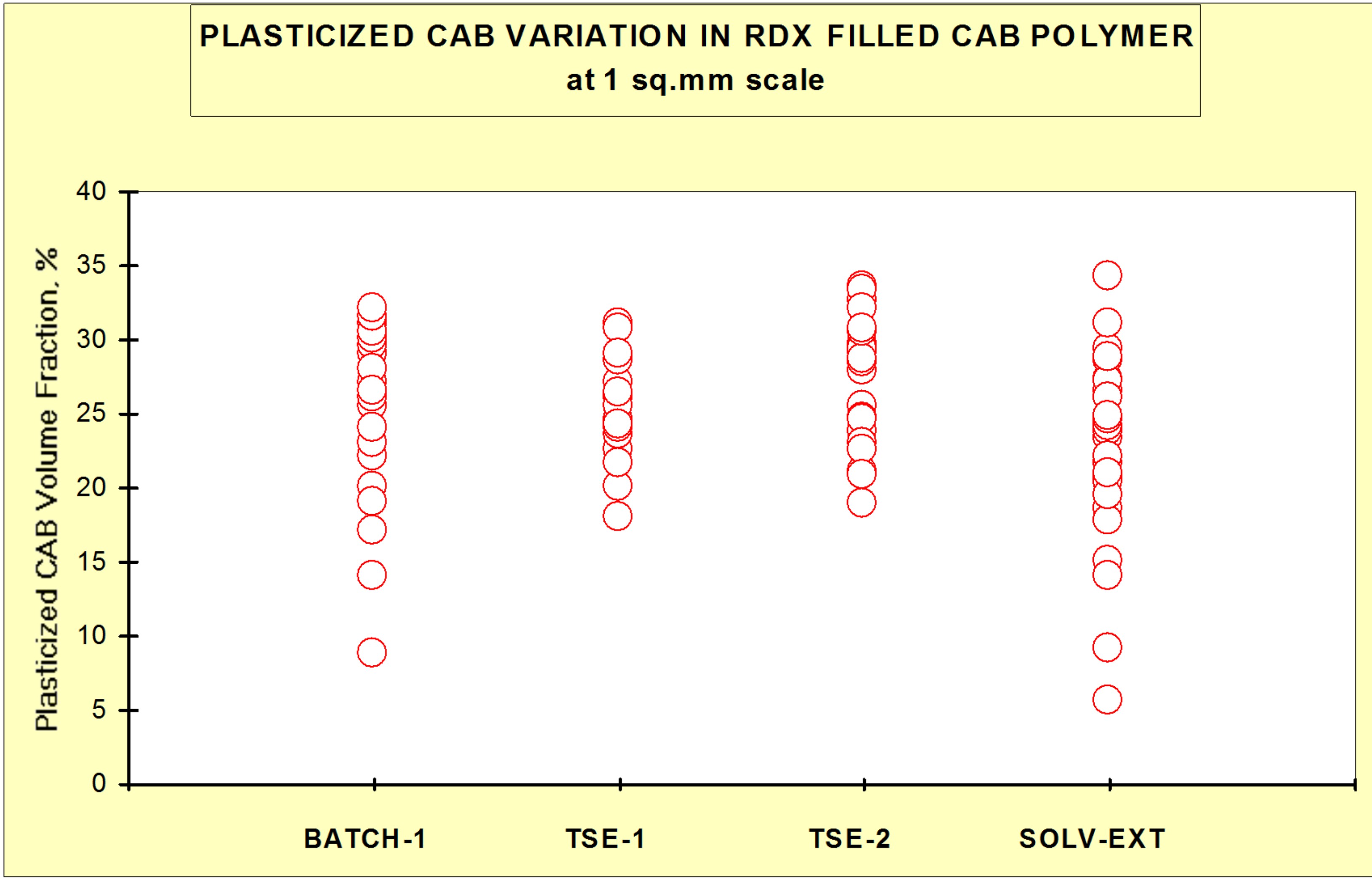


Yazici and Kalyon, Rubber Chem. and Tech., 66 (4), 527-537 (1993).

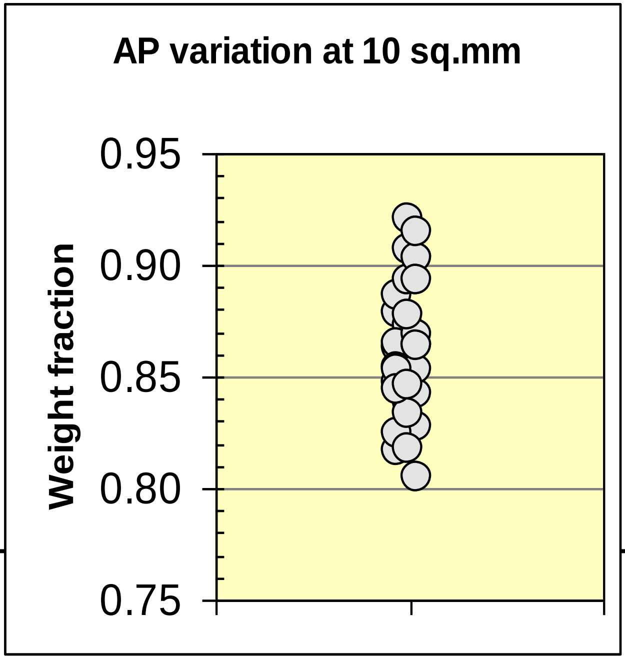
Effects of mixing time on distribution of particle concentration in the mixture

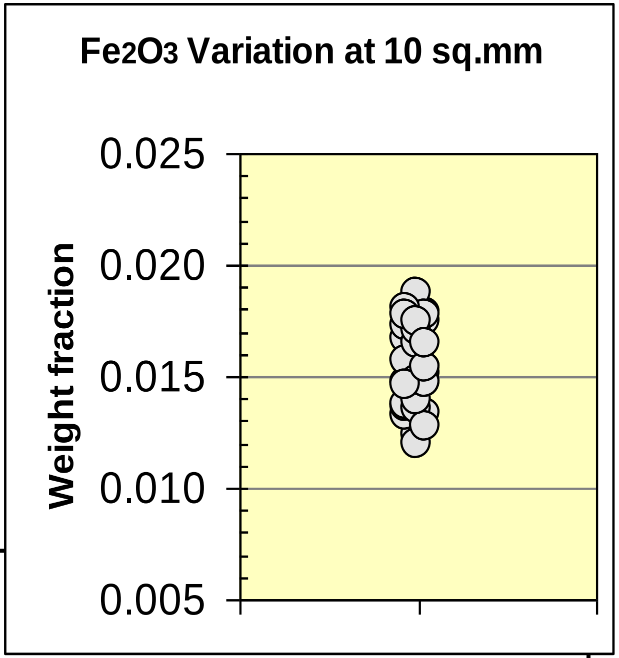


Erol and Kalyon, International Polymer Processing, 20, 228-237 (2005).



R. Yazici and D. M. Kalyon, "Quantitative Characterization of Degree of Mixedness of LOVA Grains," Journal of Energetic Materials, 14 (1), 57-73(1996).





TSE Extrudate	HyTe+DOA	Gr	Fe2O3	ZrC	AP
MEAN	0.123	0.003	0.020	0.005	0.849
STDEV	0.028	0.002	0.007	0.002	0.037
COEF.VAR	0.23	0.46	0.35	0.39	0.04
MIX.INDX.	0.91	0.97	0.95	0.97	0.90

Degree of mixing parameters of the twin screw extruded grains (SIT/ARDEC study).

$$s^2 = \frac{1}{(N-1)} \sum_{i=1}^{N} \left(c_i - \bar{c}\right)^2$$

S is the standard deviation, C_i is the concentration, C is the average, N is the number of specimens

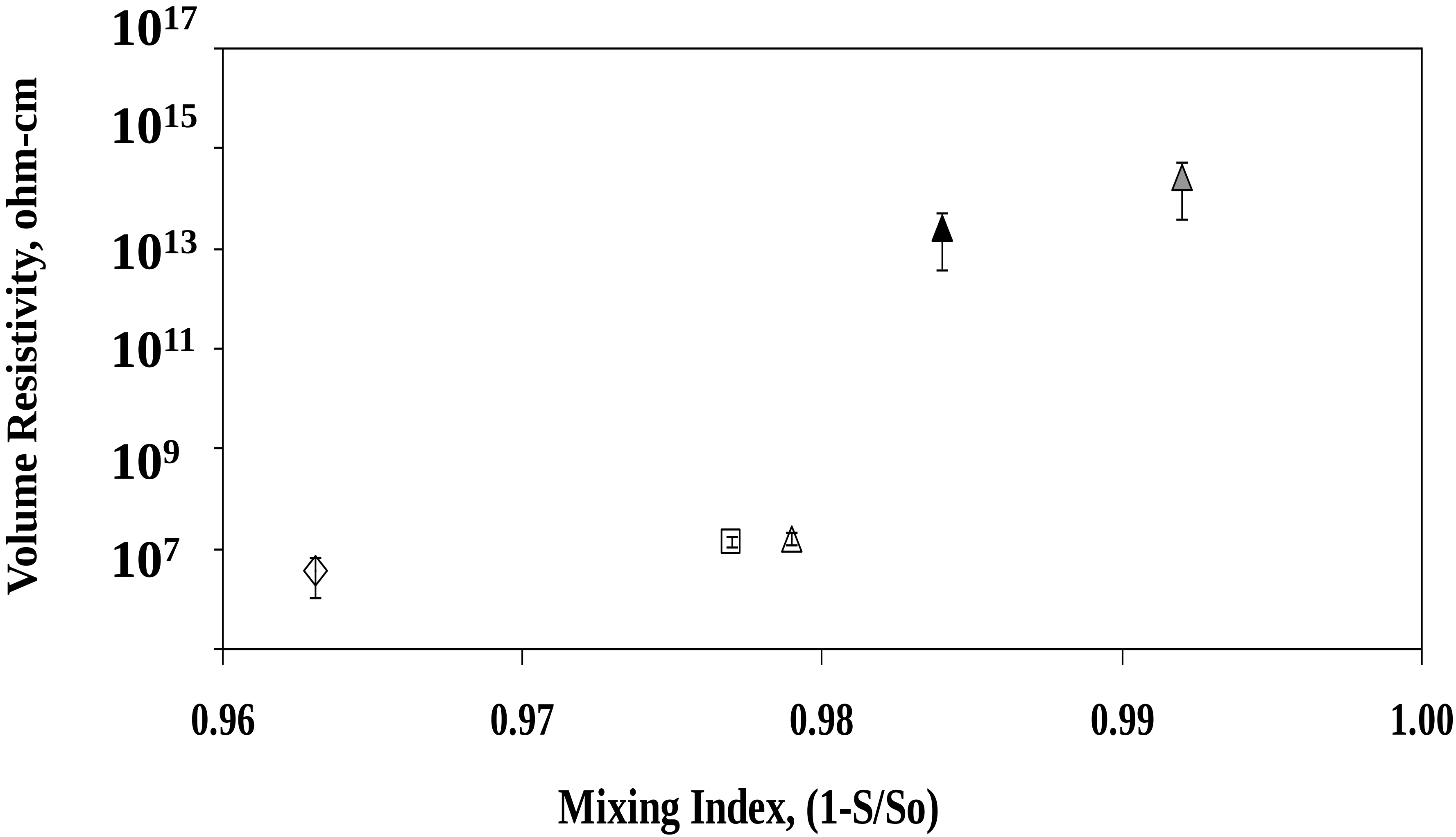
$$s_0^2 = \bar{c}\left(1 - \bar{c}\right)$$

Variance for the completely segregated sample

—

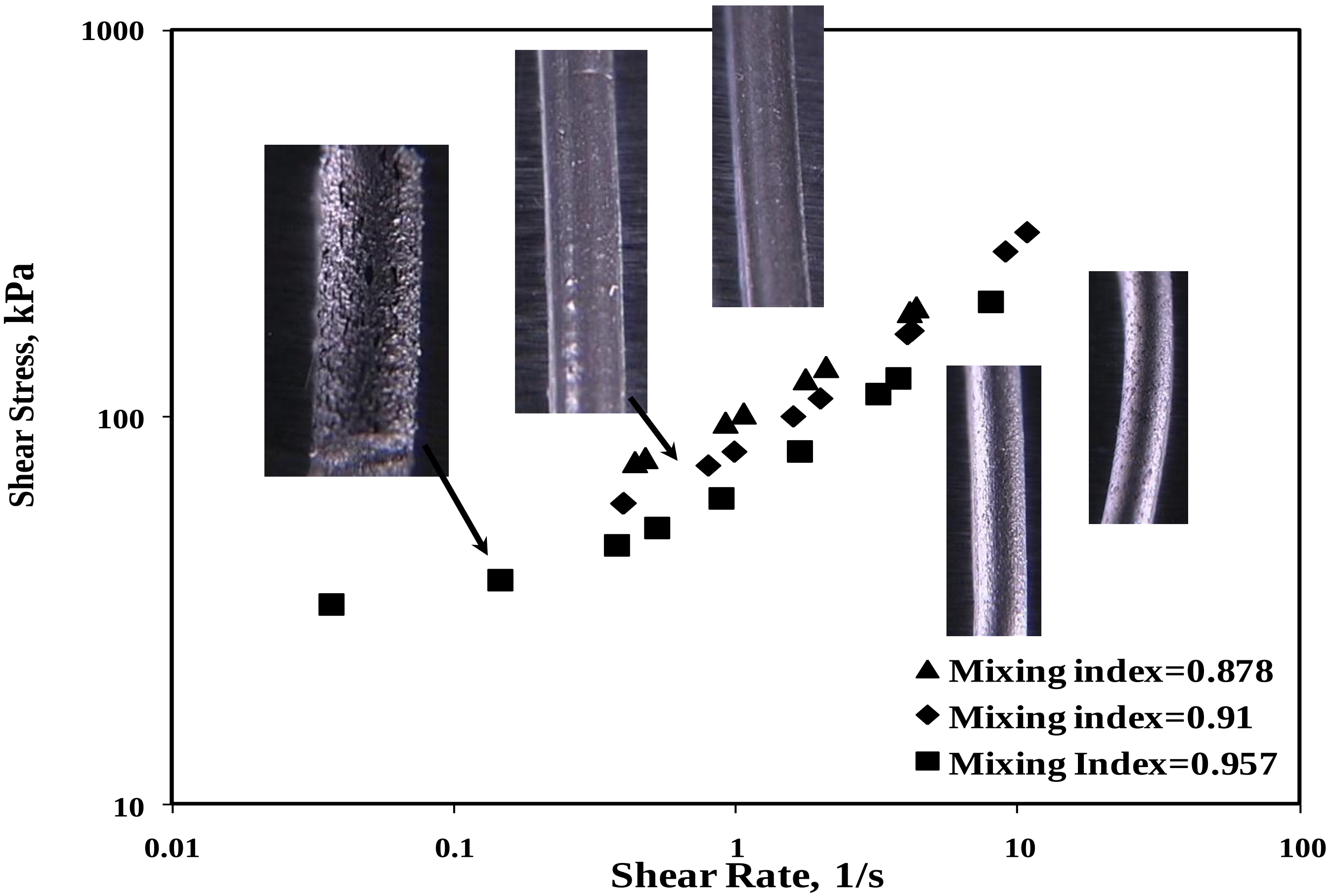
Mixing Index, MI = 1 – *s/s*$_o$

Conductive particles in insulating binder



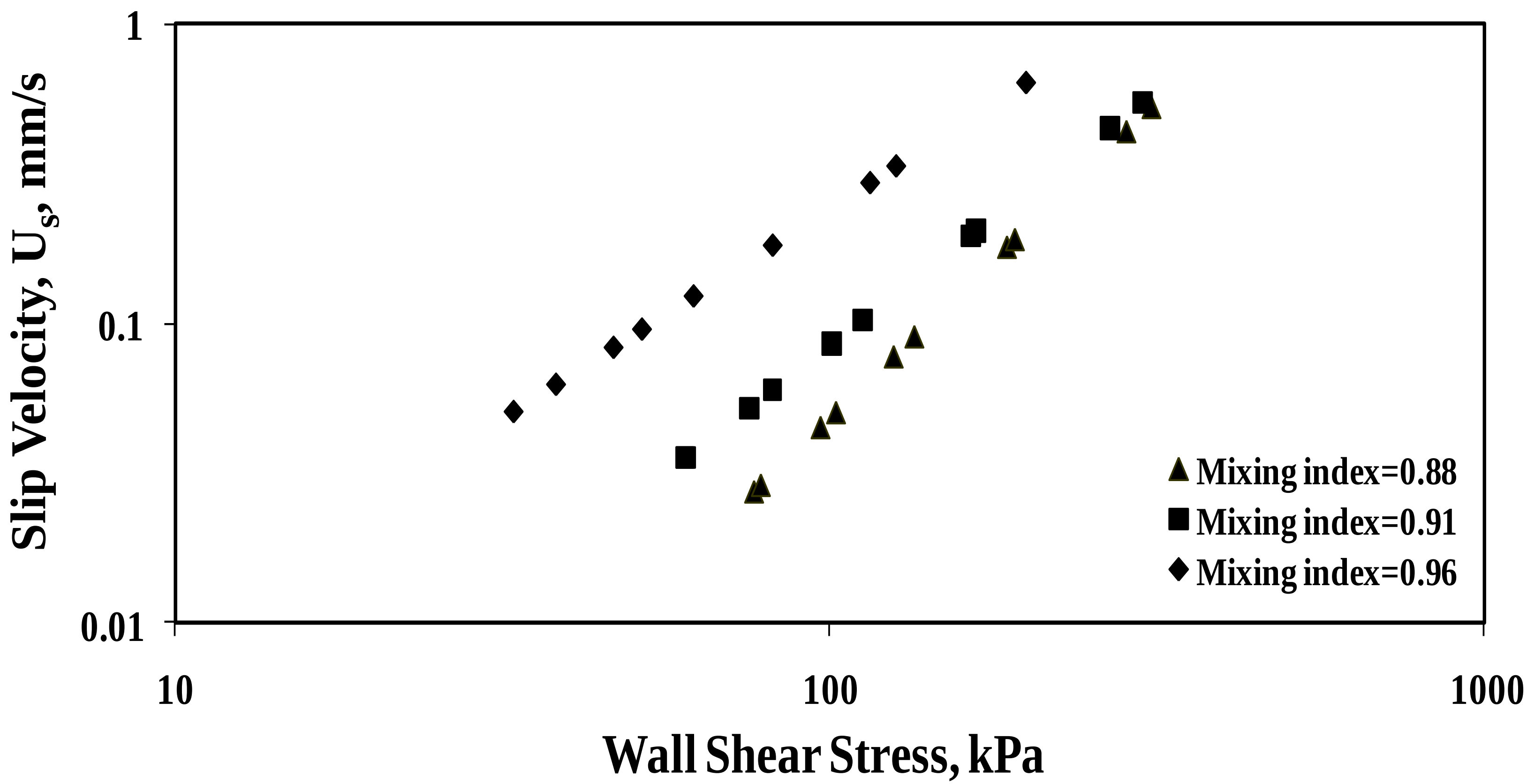
Volume resistivity versus the mixing index

Erol and Kalyon, International Polymer Processing, 20, 228-237 (2005).



Comparison of flow curves for the suspension specimens
with different mixing indices and extruded through a capillary di

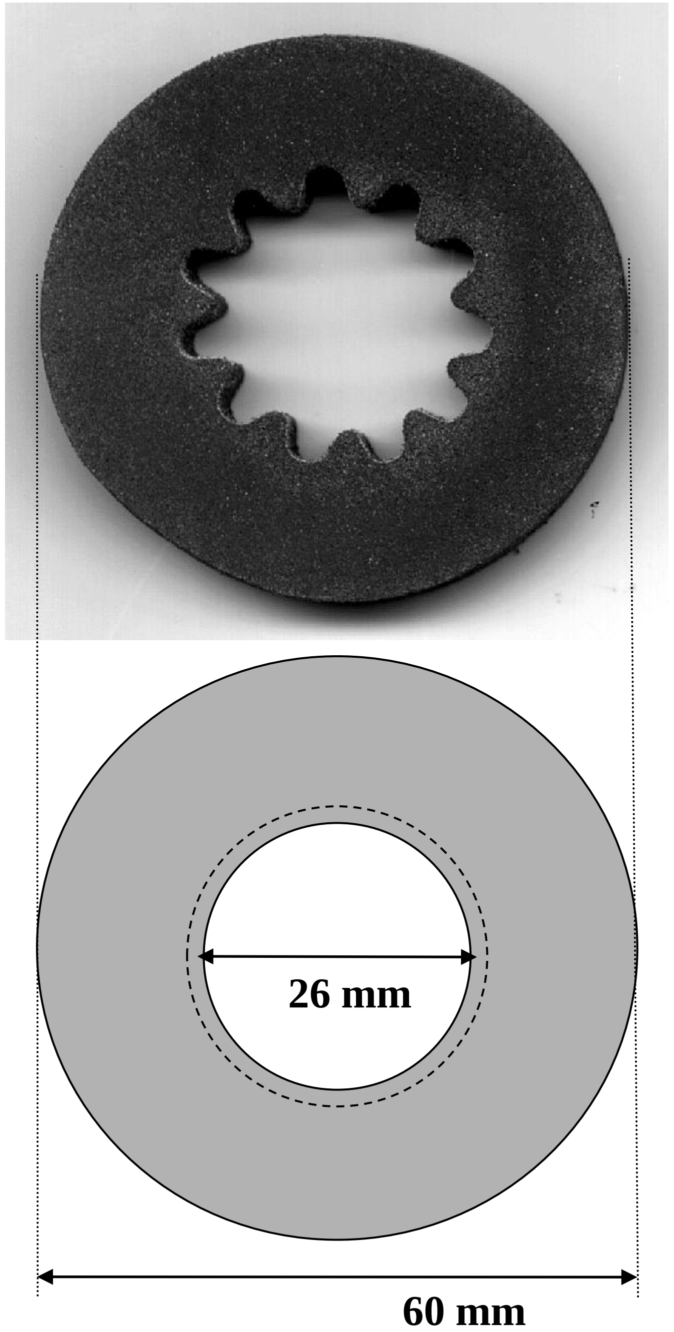
Kalyon et al. Rheologica Acta, 45, 641-658 (2006).

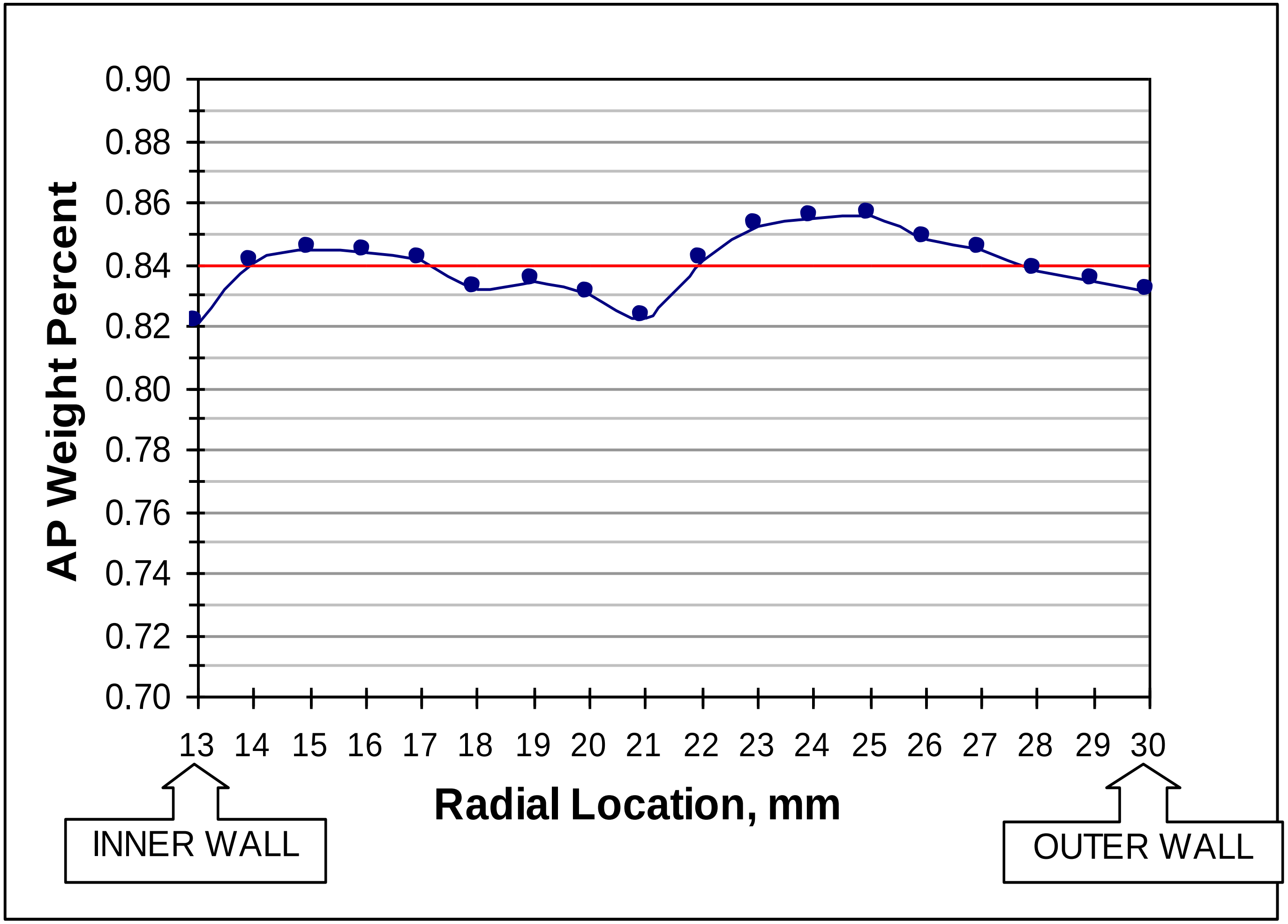


Comparison of slip velocity vs wall shear stress data for the suspension specimens batch mixed for different durations

Kalyon et al. Rheologica Acta, 45, 641-658 (2006).

Annular extrudate cross section

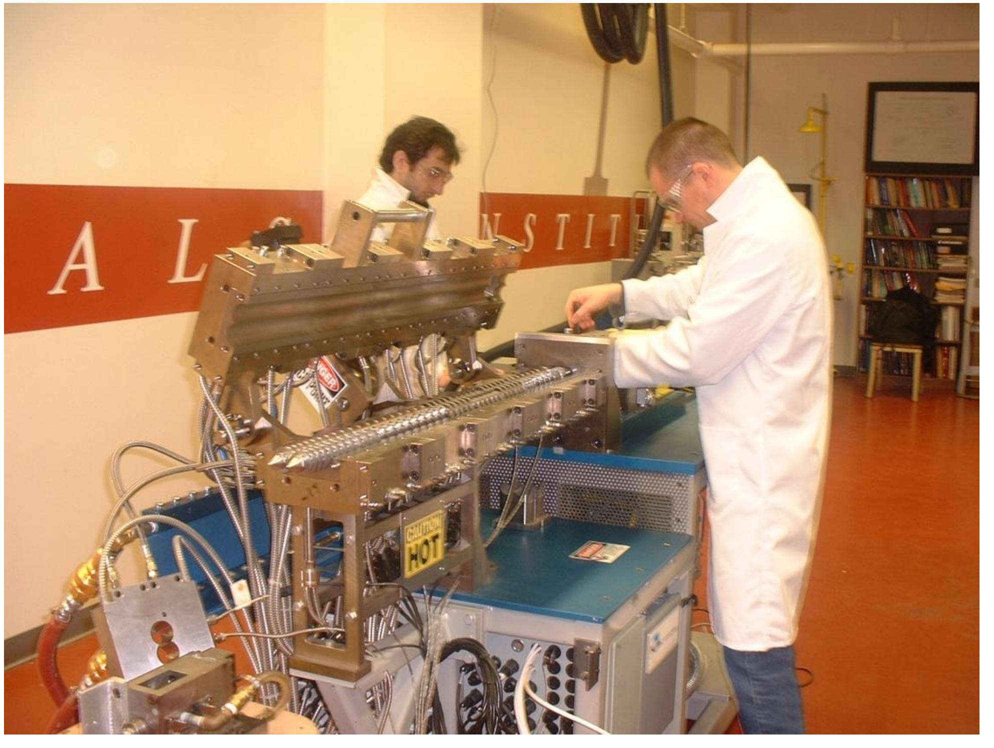


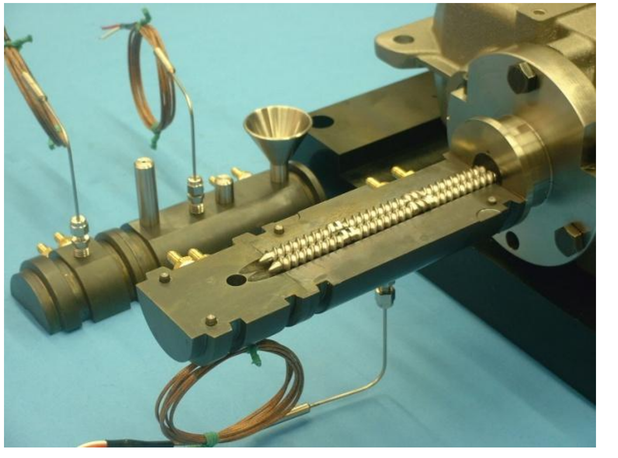


Mixing distribution of ammonium peroxide (AP) in filled elastomer extrudate as a function of radial location on the annular cross section.

Capabilities with industrial impact:

- Dies
- New rheometers
- New extruders- Universal and the mini
- New screw elements
- New technologies based on extrusion





Continuous processing platforms: Universal and the Mini

Extrusion Facility to probe all types of extruders

Universal twin screw extruder

Shear Roll Mill

Single Screw

Twin Screw

Co-rotating

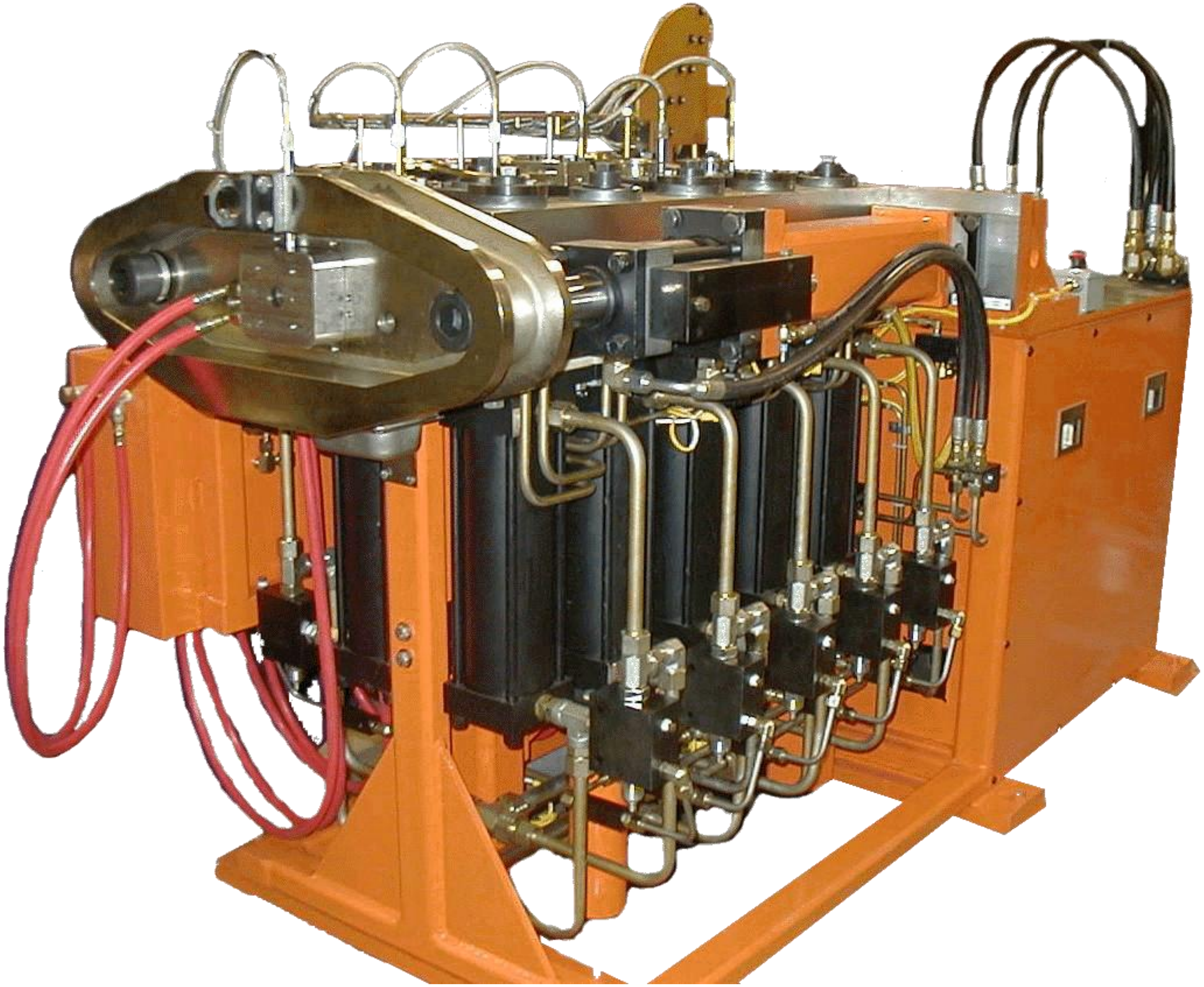
Counter-rotating

Fully-Intermeshing

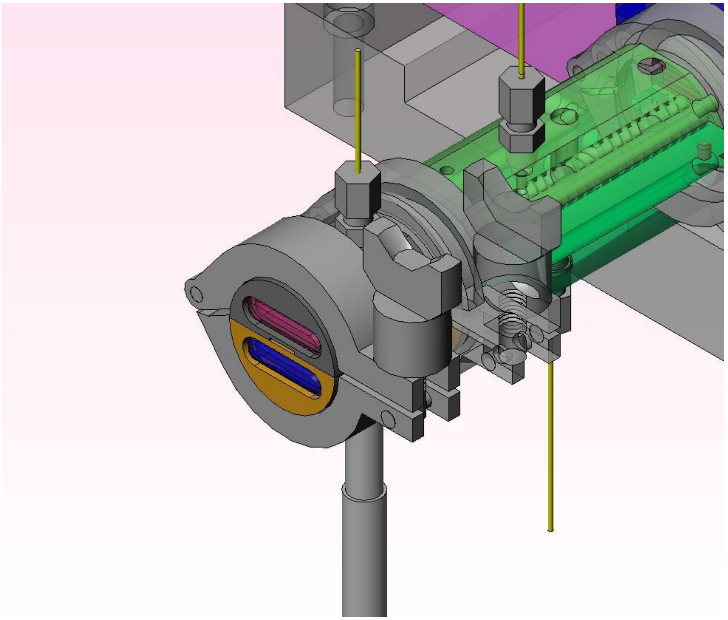
Tangential

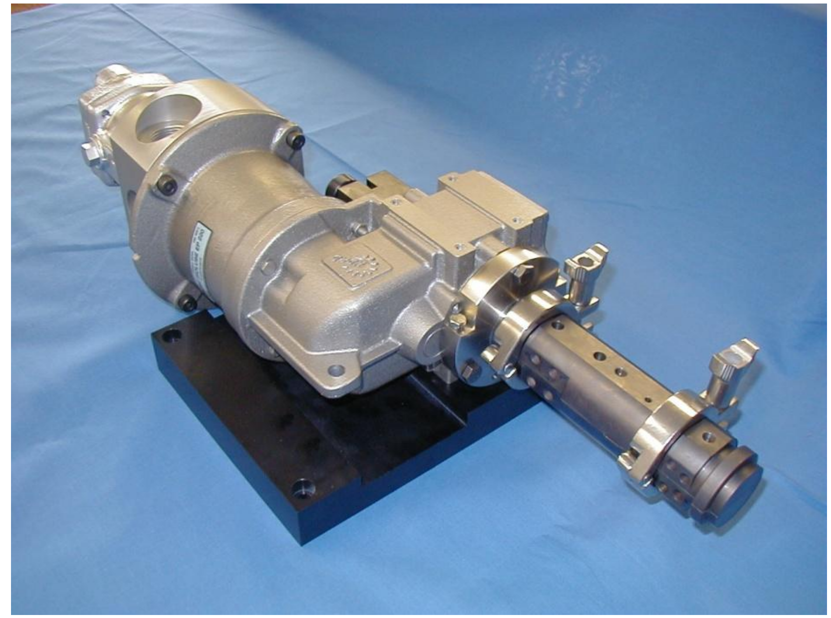
Remote running using the internet and wireless

Universal extrusion system for energetic materials processing



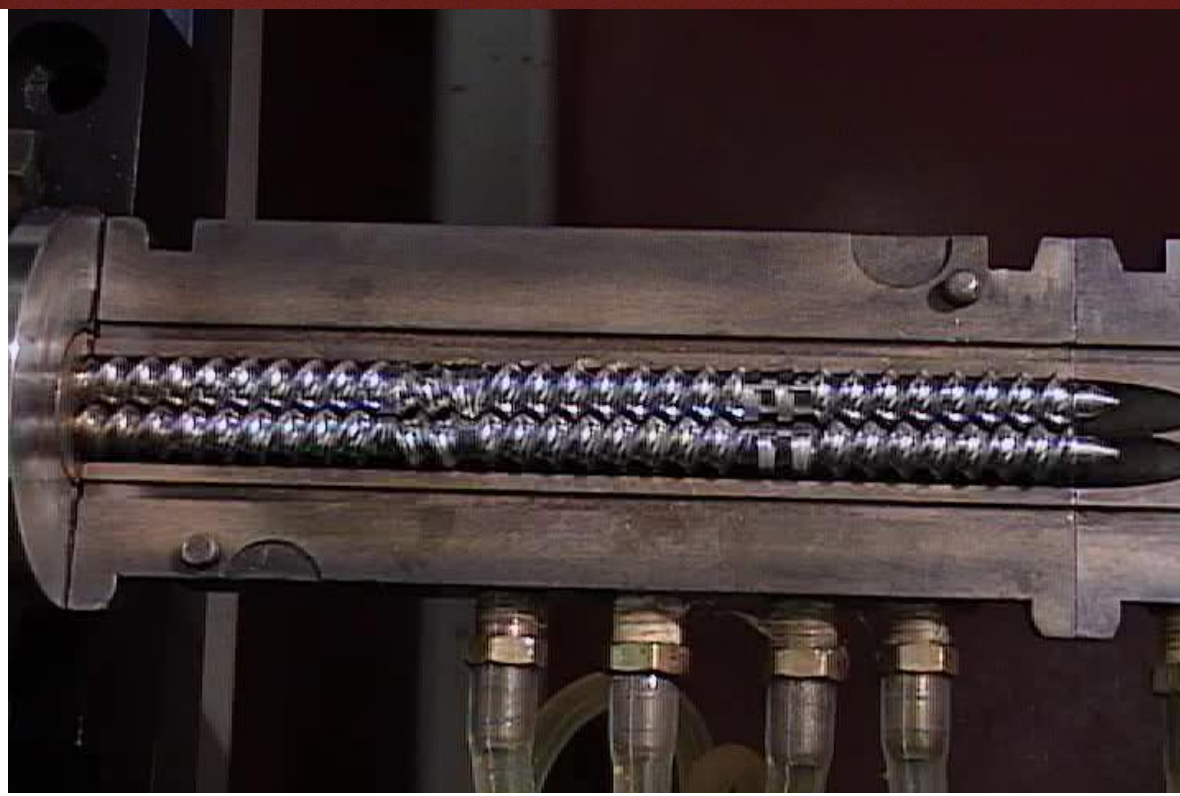
J. E. Kowalczyk, M. Malik, D. M. Kalyon, H. Gevgilili, D. F. Fair, M. Mezger and M. Fair,
“Safety in Design and Manufacturing of Extruders used for the Continuous Processing of Energetic Formulations”,
Journal of Energetics Materials, 25, 247-271 (2007).



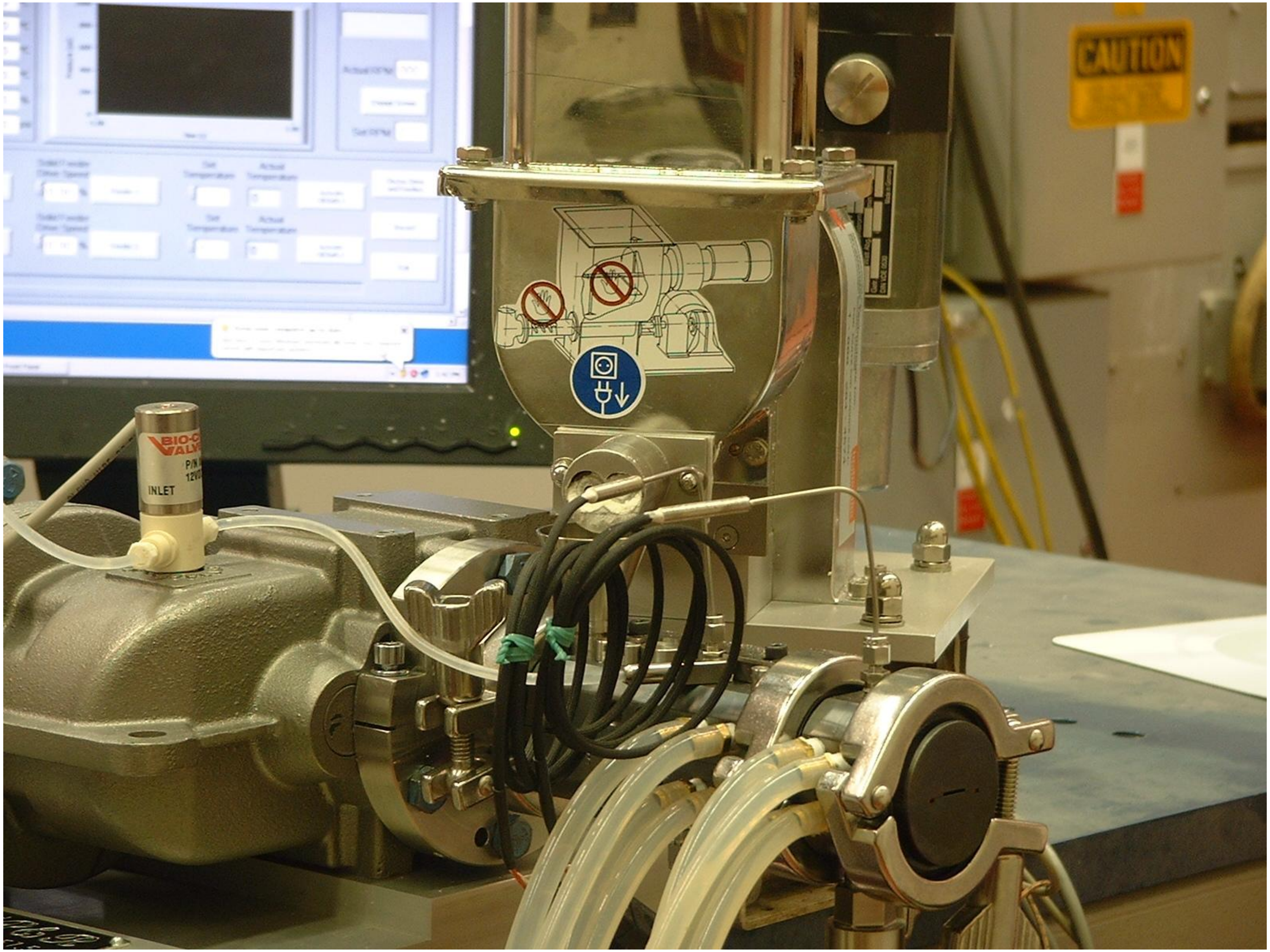


The smallest twin screw extruder in the World: 7.5 mm

62. S. Ozkan, H. Gevgilili, D.M. Kalyon, J. Kowalczyk, and Mark Mezger, "Twin screw extrusion of nano-alumina
63. based simulants of energetic formulations involving gel based binders", Journal of Energetics Materials, 25, 3, 173-201 (2007).



Complex Screw Configuration

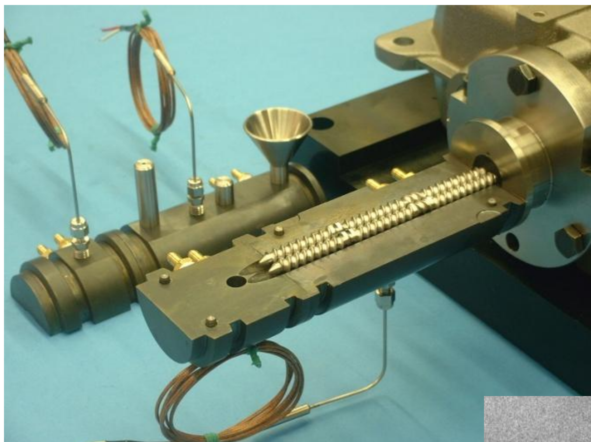


Brabender SR12-05 Feeder with the mini-TSE

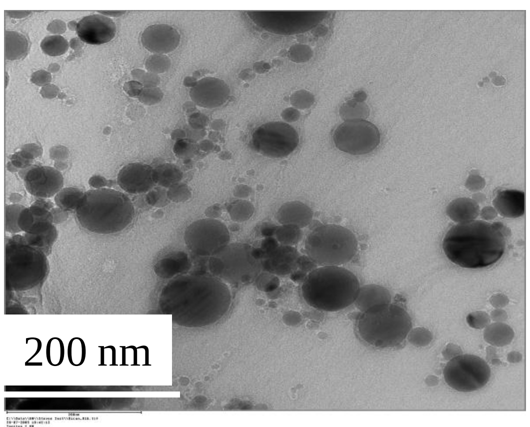
HfMI Highly Filled Materials Institute

STEVENS Institute of Technology

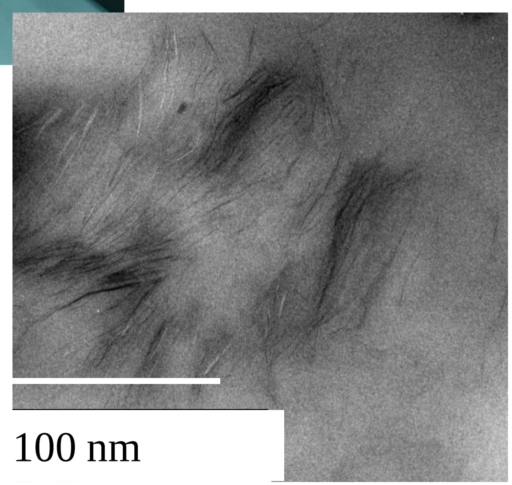
Specialized capabilities in particle formation, rheology, processing, simulation, structural analysis.
Sources of funding used in 2005: ONR, ARDEC, P&G, MPR, IBM (750K for 7 staff and 8 students)



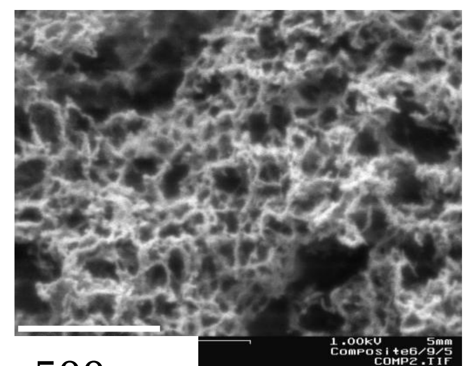
Processing of nanoparticles: Examples



Processing of nanoparticles for energetic applications

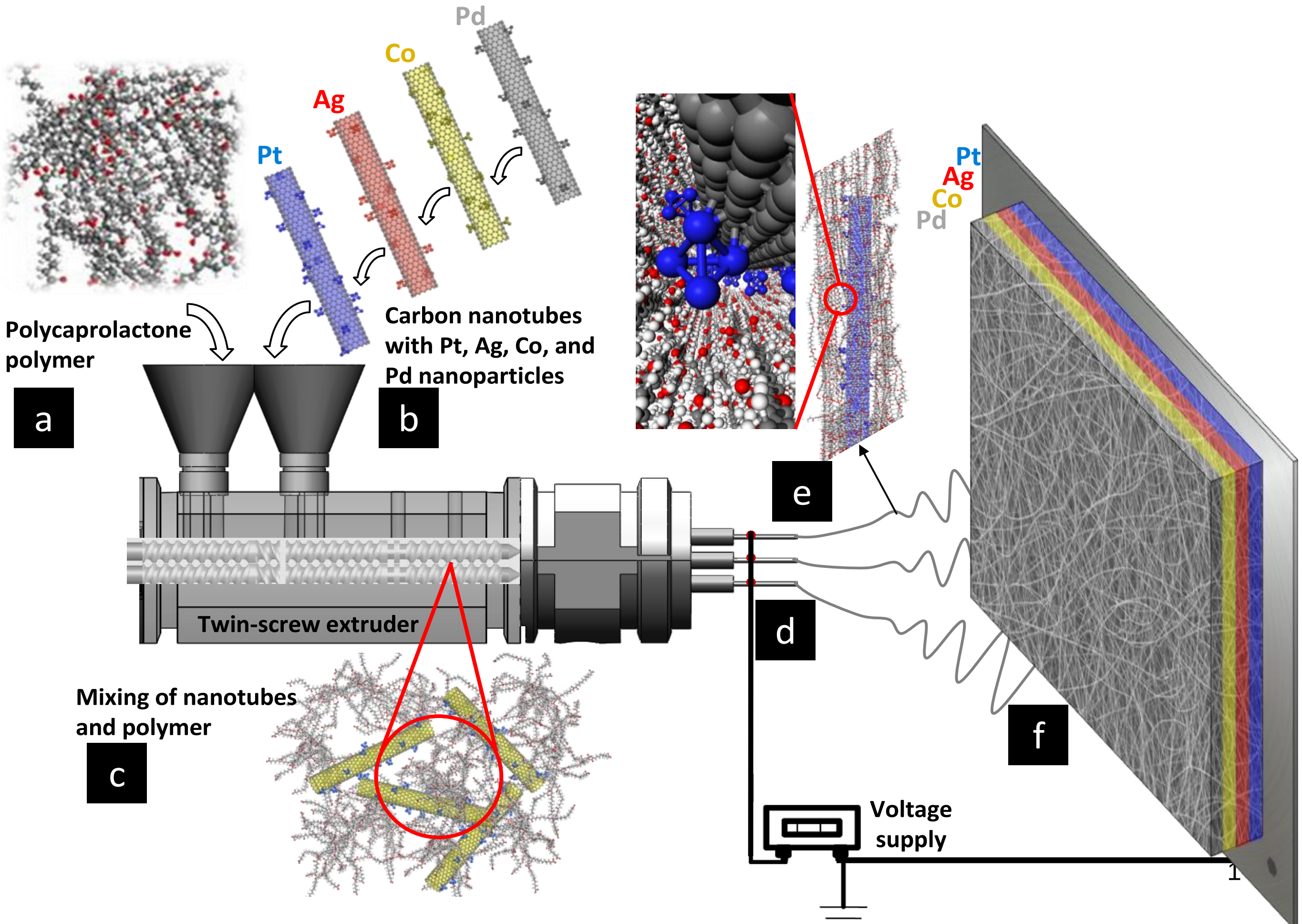


Intercalation and exfoliation of clay tactoids into nanoclays



In situ synthesis of hydroxyapatite for tissue engineering

A recent example of development of a novel processing method



Production of a nano*bursa* mesh material with a newly-developed hybrid process of twin-screw extrusion and electrospinning: (a) Feeding of the polymer and metal-functionalized CNTs, (b) Continuous mixing of the polymer with CNTs, (c) Electrospinning via a spinneret with multiple nozzles, (d) Encapsulation of the nanotubes into polymer nanofibres, (e) Graded nano*bursa* mesh with consecutive layers of CNTs functionalized with Pd, Co, Ag, and Pt nanoparticles.

S. Senturk-Ozer, T. Chen, N. Degirmenbasi, H. Gevgilili, S. G. Podkolzin, D. M. Kalyon, "Nano*bursa* mesh: Graded electrospun nanofiber mesh with metal nanoparticles on carbon nanotubes", Nanoscale, 6, 8527-8530 (2014).

Ramifications of capabilities on additive manufacturing

- Rheology, viscoplasticity, viscoelasticity, wall slip
- Microstructure formation
- Modeling - time dependence- functional grading
- Capabilities in hardware design and fabrication

Government Sponsors

- **BMDO/IST**
- **DARPA**
- **DURIP**
- **ONR**
- **NAWC**
- **NSF**

- **NSWC**
- **SDI**
- **SERDP**
- **US Army RO**
- **US Army PBMA**
- **US Army TACOM/TARDEC**


Thanks for listening