STEVENS Institute of Technology

Overview of the Capabilities of Highly Filled Materials Institute at Stevens (20 years)

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October 22, 2008

JOCG CMEUG Meeting

Rockaway, NJ

Science and Technology Base of Synthesis, Crystallization and Compounding of Particles into Concentrated Suspensions and Shaping/Quality Control

Synthesis and Crystallization → **Wetting and Compounding of Particles/nanoparticles** → **Processing and Shaping** → **Microstructural Distributions-Ultimate Properties-Quality Control**

- Reaction Kinetics
- Simulation
- Experiments

- Rheology
- Simulation
- Interfacial Properties

- Simulation
- Pilot Scale
- Experiments

- Degree of Mixedness
- Particle Size Distribution
- Electrical/Magnetic/ Mechanical

Ability to generate samples, designs, hardware and software tools, customized products

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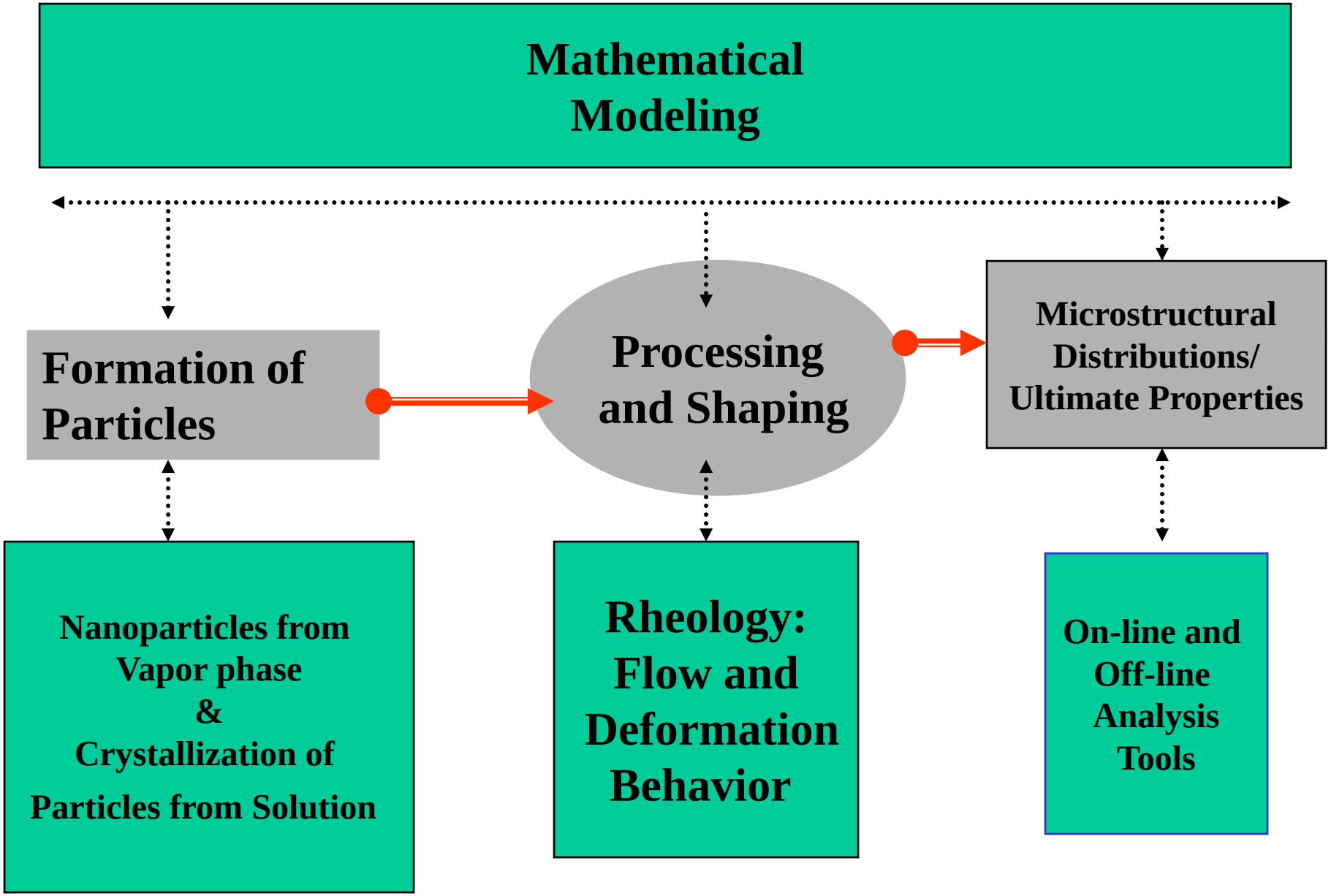
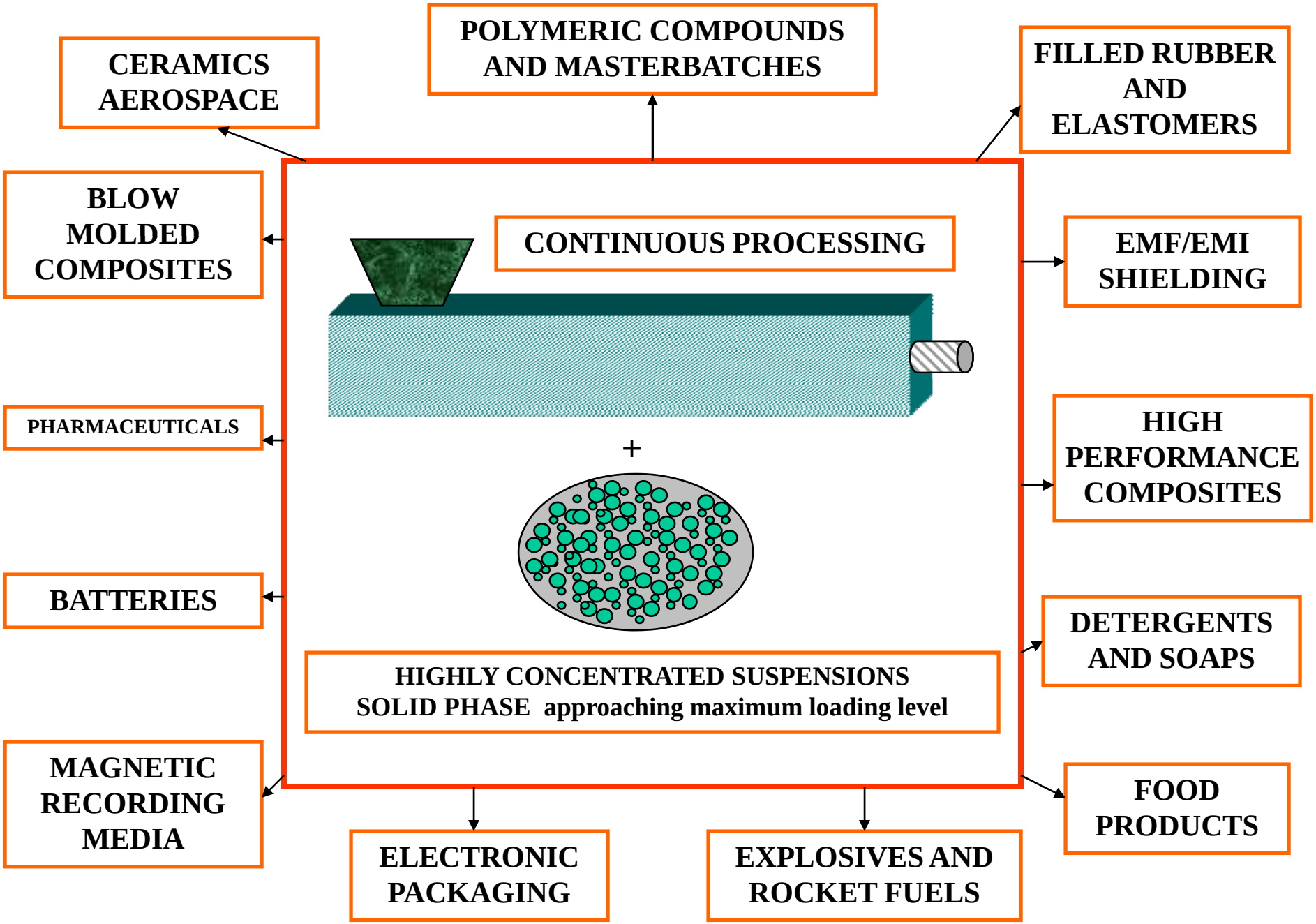
Scale-Up


Mathematical Modeling
Formation of Particles
Processing and Shaping
Microstructural Distributions/ Ultimate Properties
Nanoparticles from Vapor phase & Crystallization of Particles from Solution
Rheology: Flow and Deformation Behavior
On-line and Off-line Analysis Tools


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

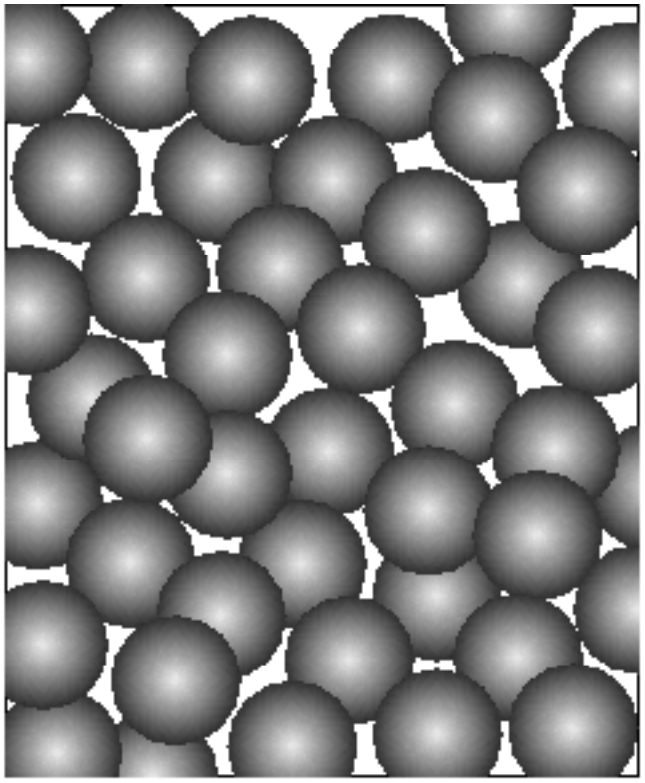


Figure 1. Packing of unimodal spherical particles and maximum packing fraction, i.e., maximum volume fraction, ϕ_m, of solids depending on the packing mode.
a) Simple cubic, $\phi_m = 0.52$
b) Body centered cubic, $\phi_m = 0.68$
c) Face centered cubic, $\phi_m = 0.74$

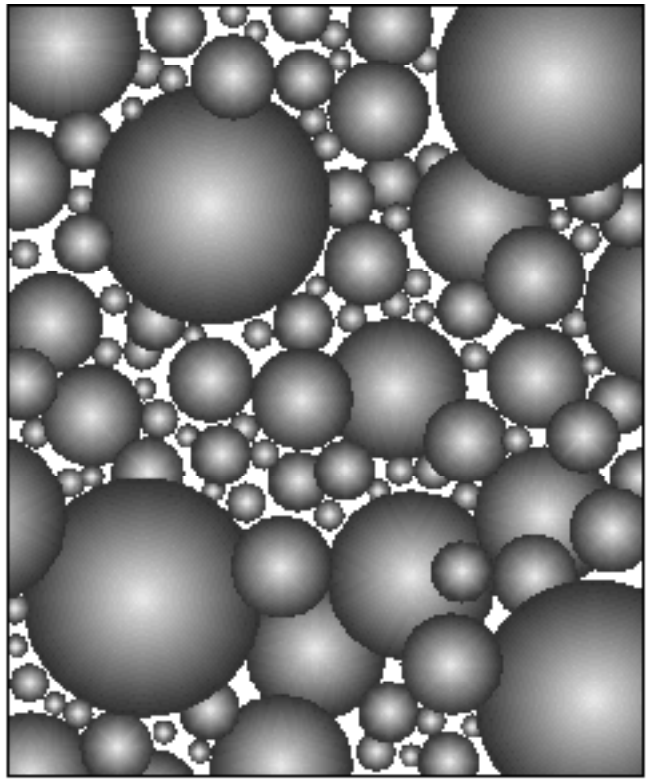
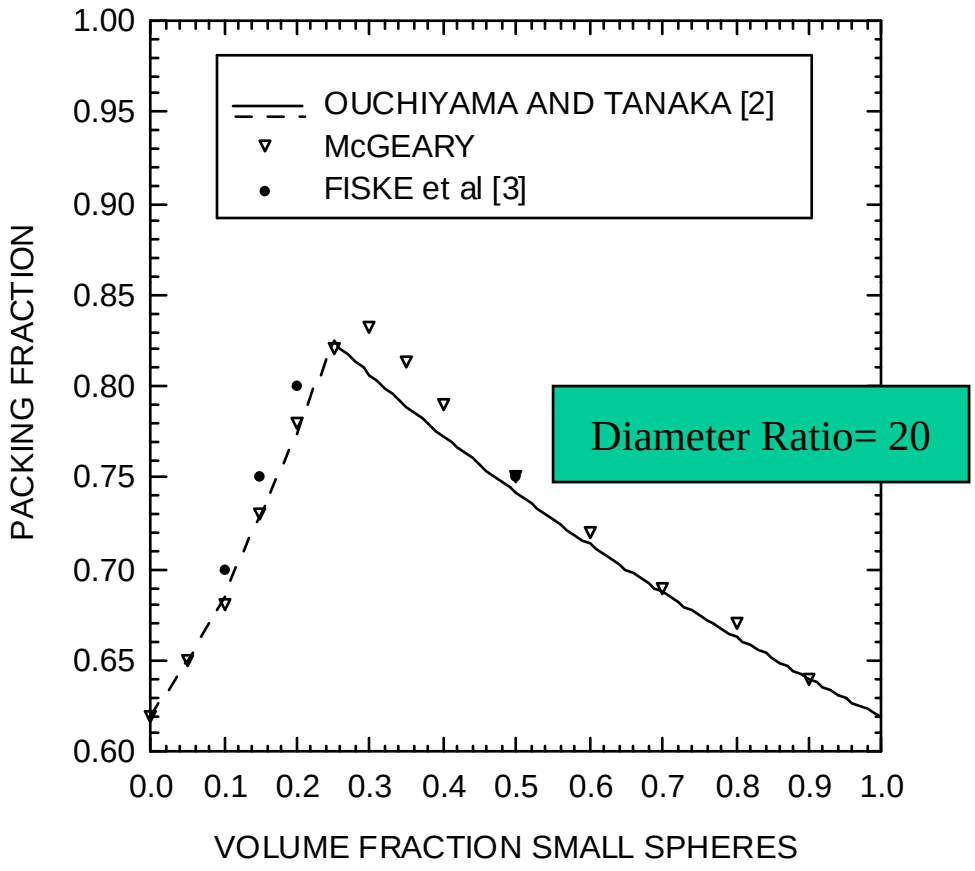


Figure 2. Packing of spherical particles with a multimodal particle size distribution $\phi_m = 0.90$.



MAXIMUM PACKING FRACTION BIMODAL DISTRIBUTION OF SPHERICAL PARTICLES

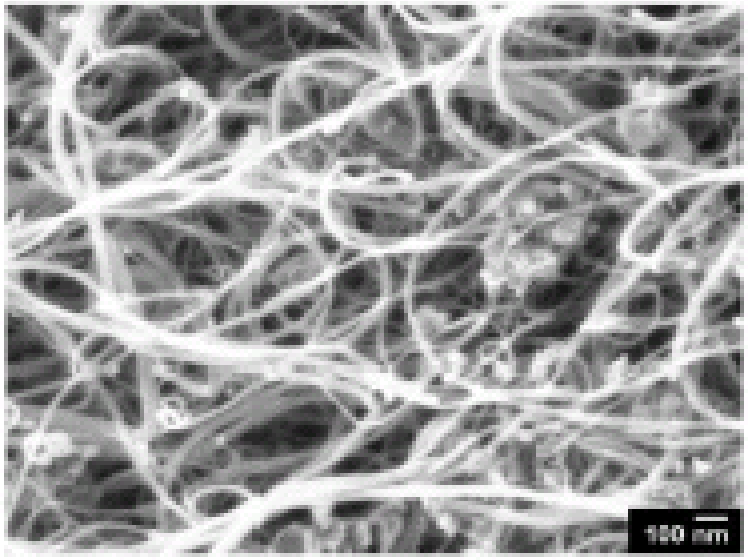


Fig. 10. Micrograph showing tangled, spaghetti-like carbon nanotubes grown with conventional CVD techniques.

Challenges keep increasing…..

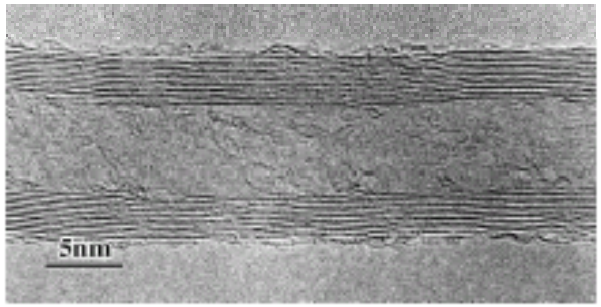


Fig. 4. TEM micrograph showing the layered structure of a multi-walled carbon nanotube.

Advances in the science and technology of carbon nanotubes and their composites: a review

Erik T. Thostenson[a], Zhifeng Ren[b], Tsu-Wei Chou[a,*]

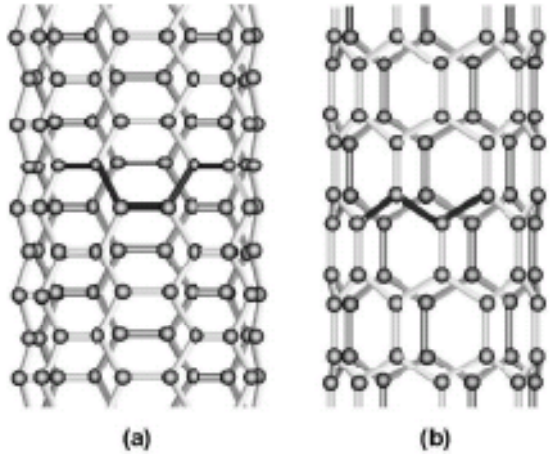
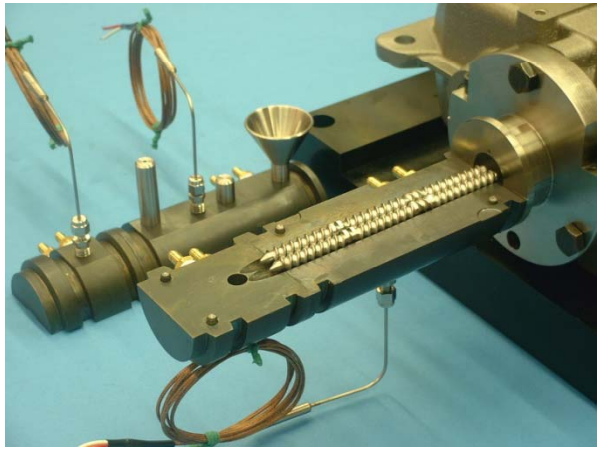


Fig. 2. Illustrations of the atomic structure of (a) an armchair and (b) a zig-zag nanotube.

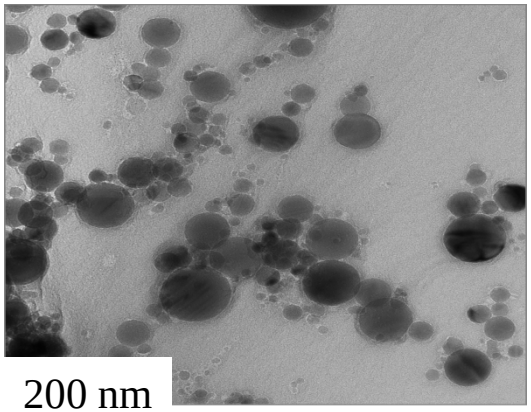
HfMI Highly Filled Materials Institute

STEVENS Institute of Technology

Specialized capabilities in particle formation, rheology, processing, simulation, structural analysis.

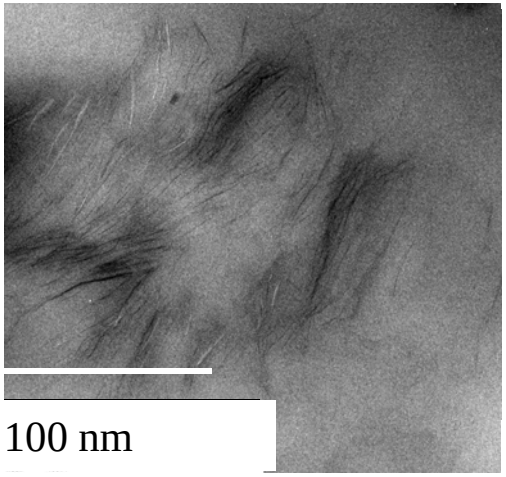


Processing of nanoparticles: Examples



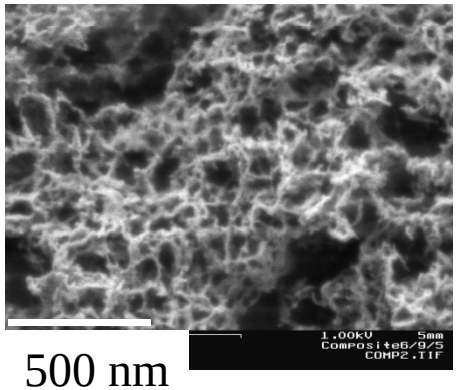
200 nm

Processing of Al nanoparticles



100 nm

Intercalation and exfoliation of clay tactoids into nanoclays

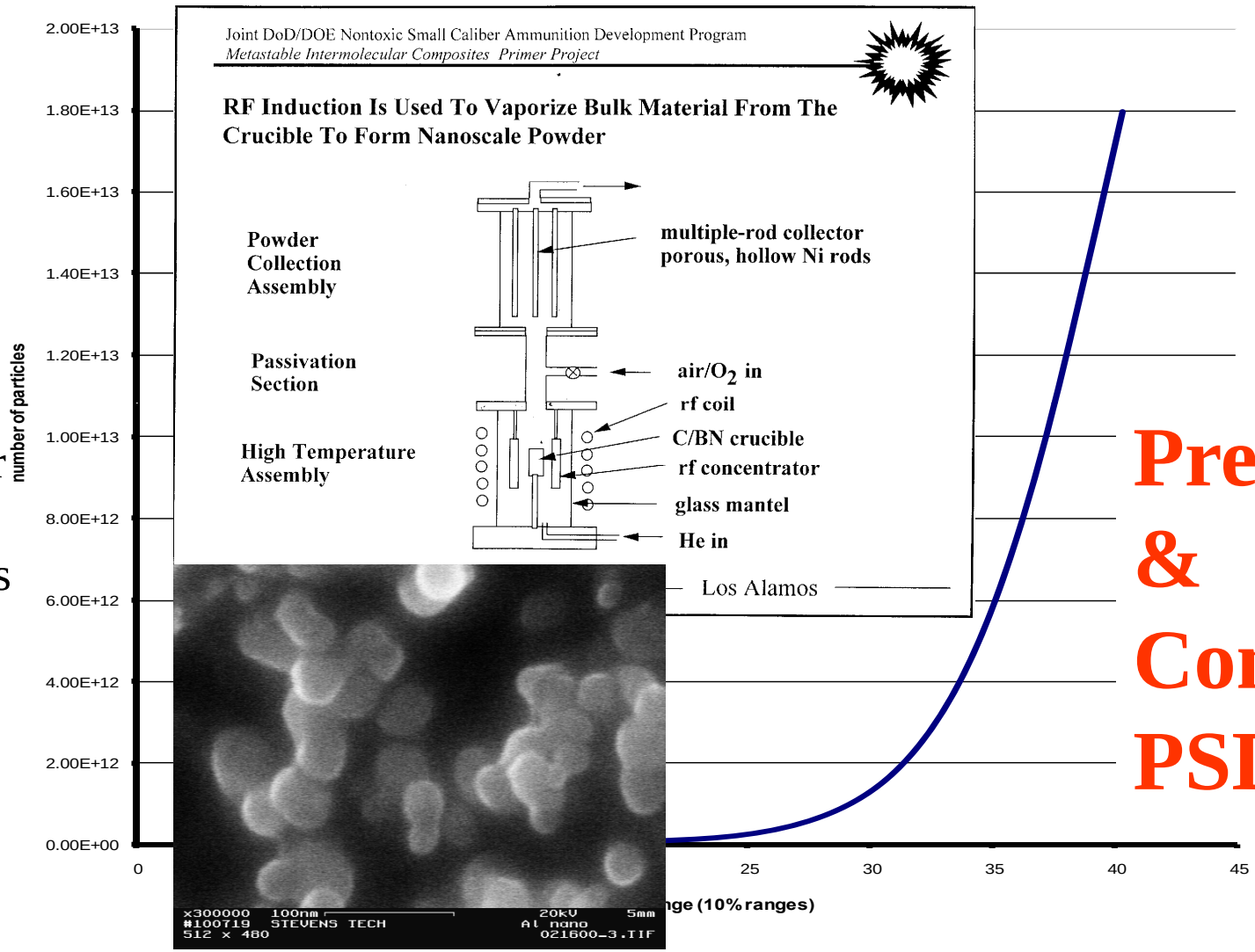


500 nm

In situ synthesis of hydroxyapatite

Particle formation: Synthesis and crystallization

Need to consider upstream equipment

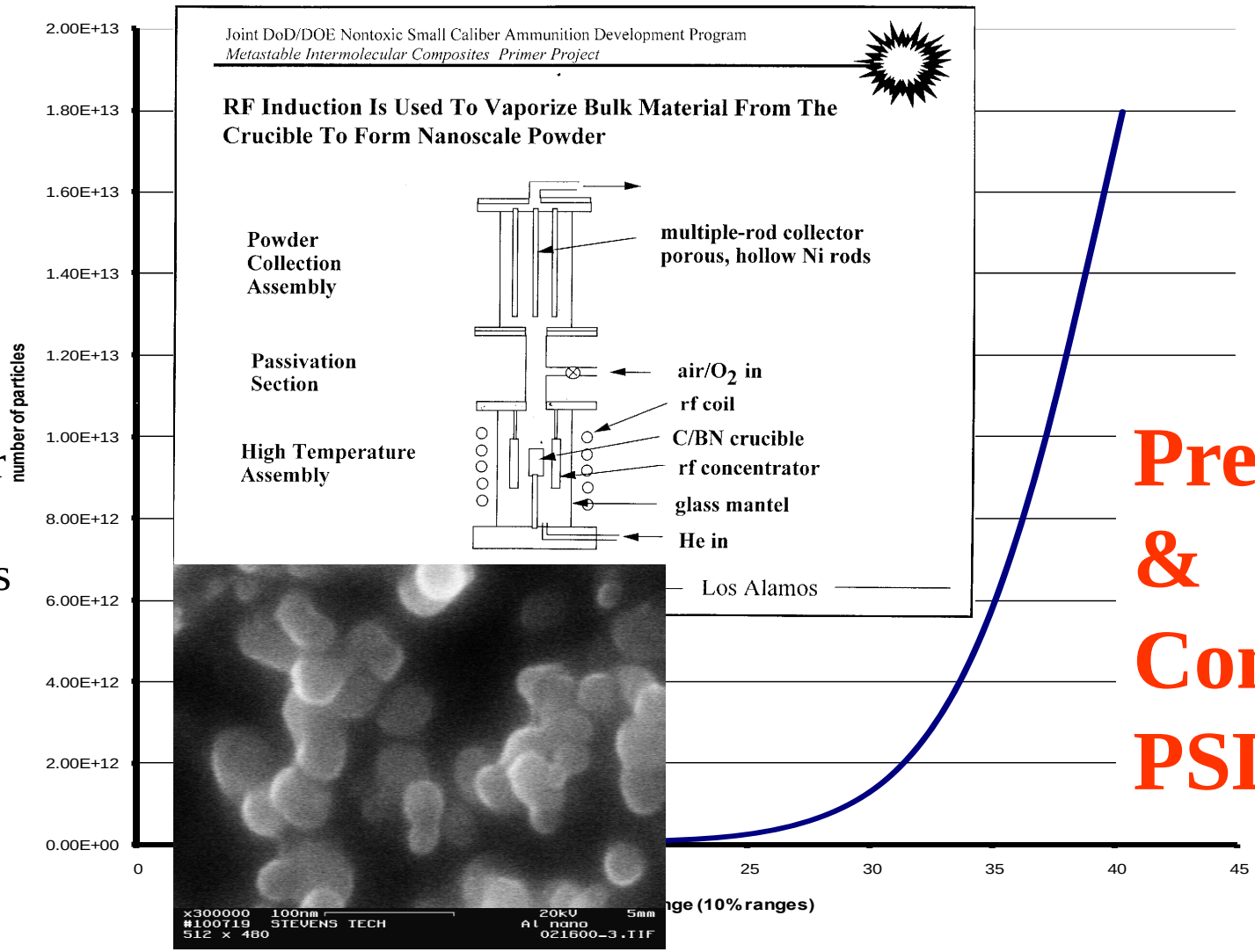


Number of particles

Predict & Control PSD

Particle size, nm

Need to consider upstream equipment



Number of particles

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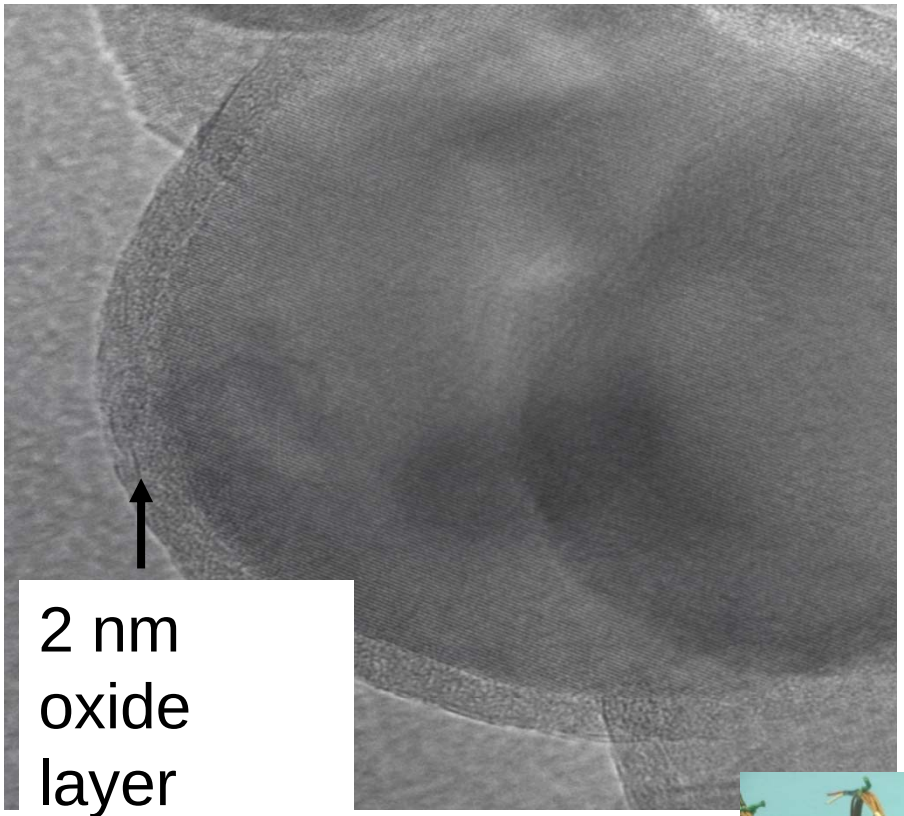
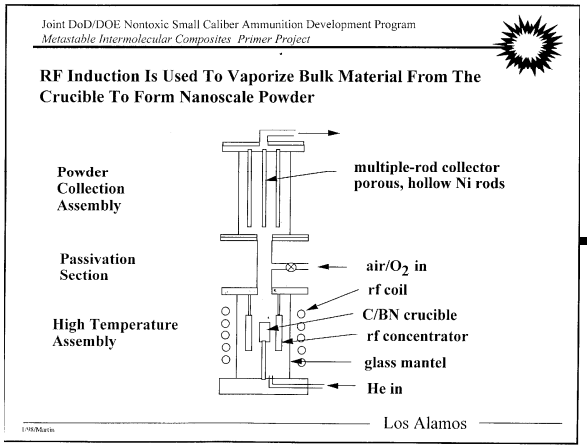
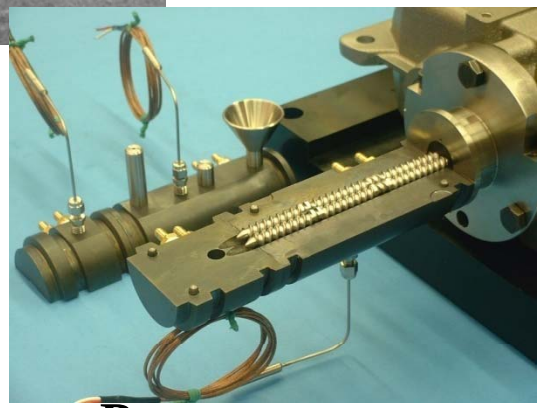


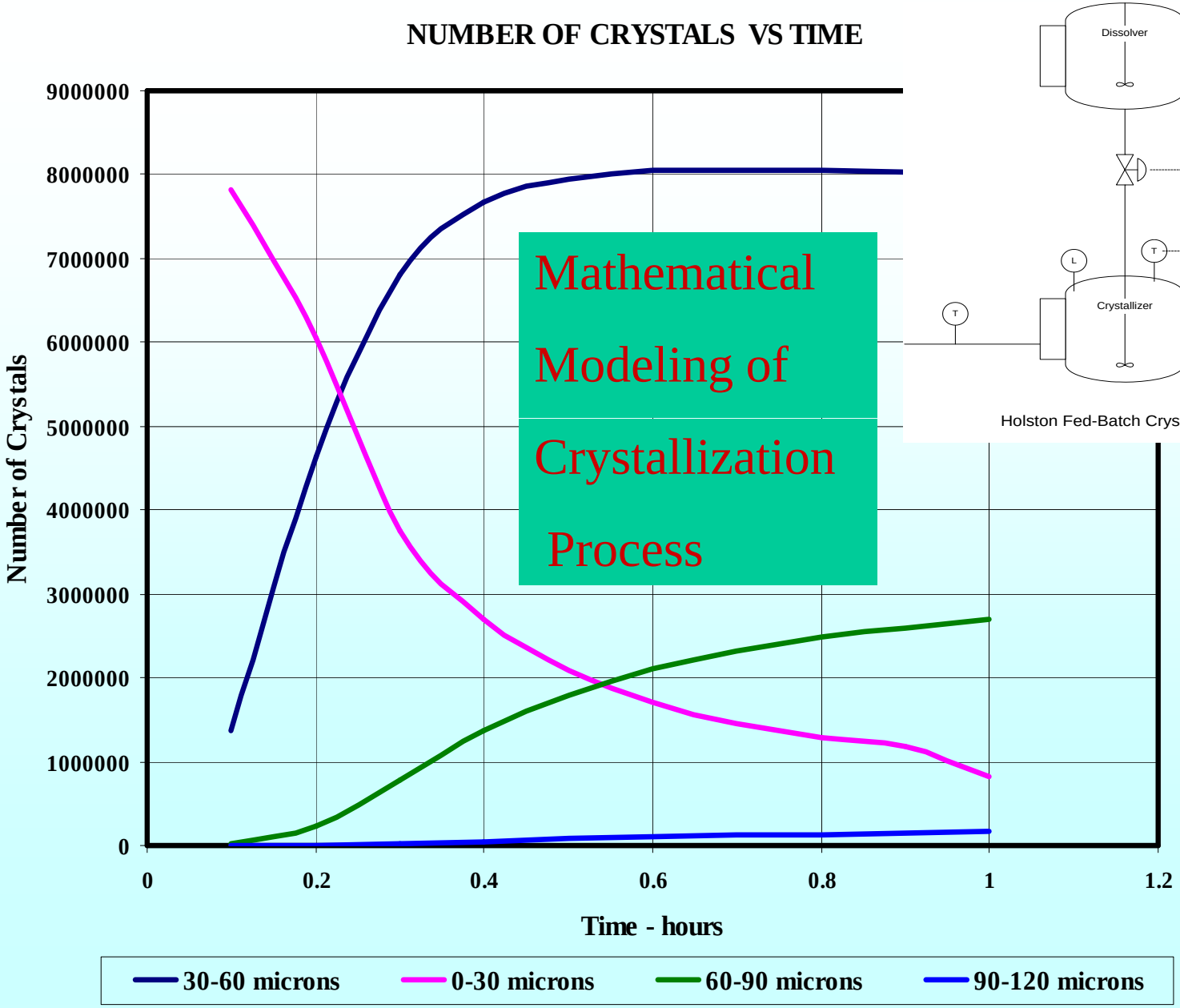
Al nanoparticles

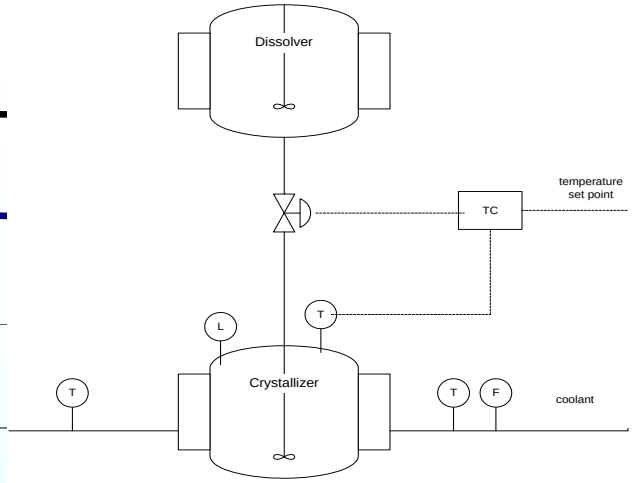




From Reactor to Continuous Processor

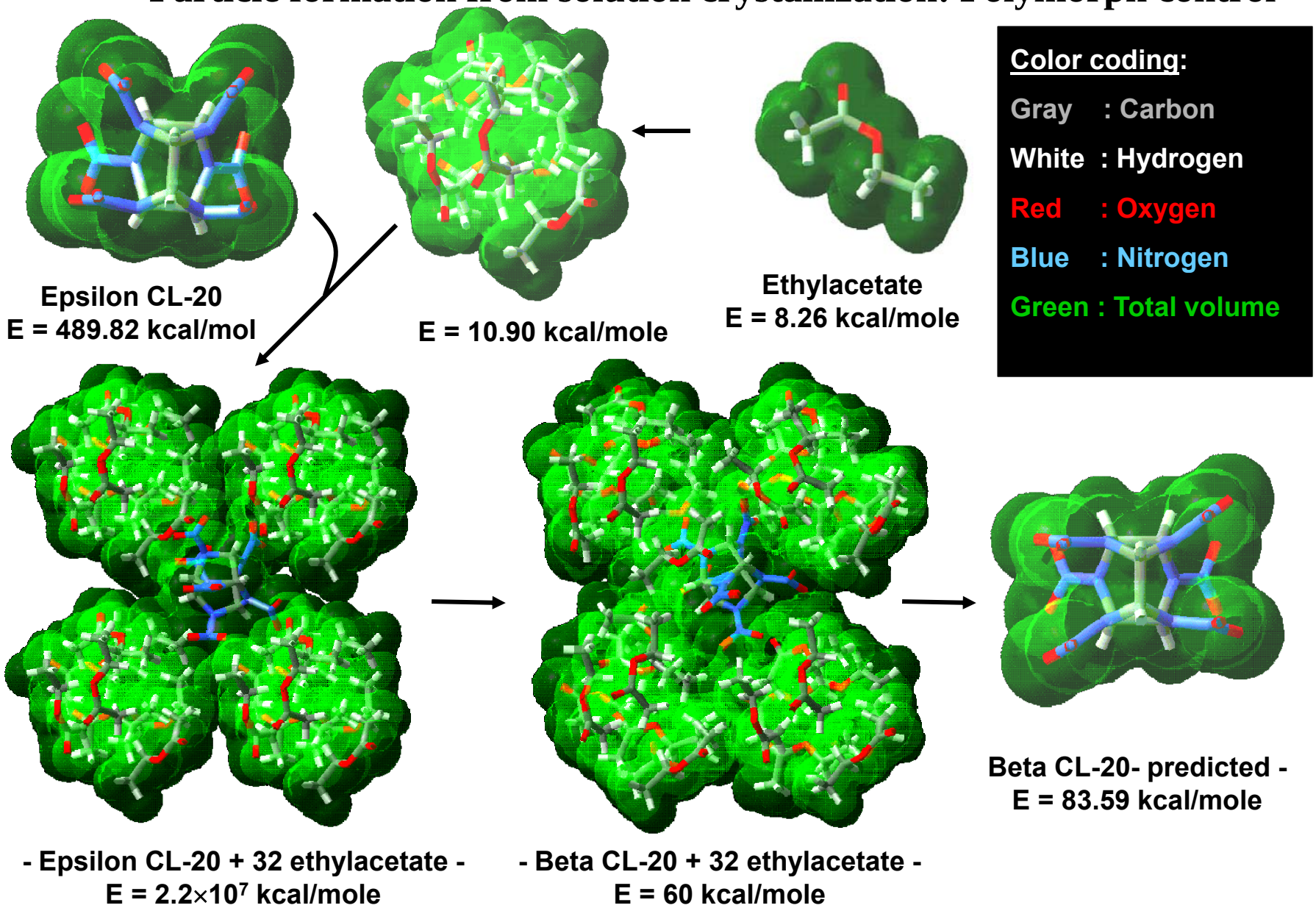
Mathematical Modeling of Crystallization Process



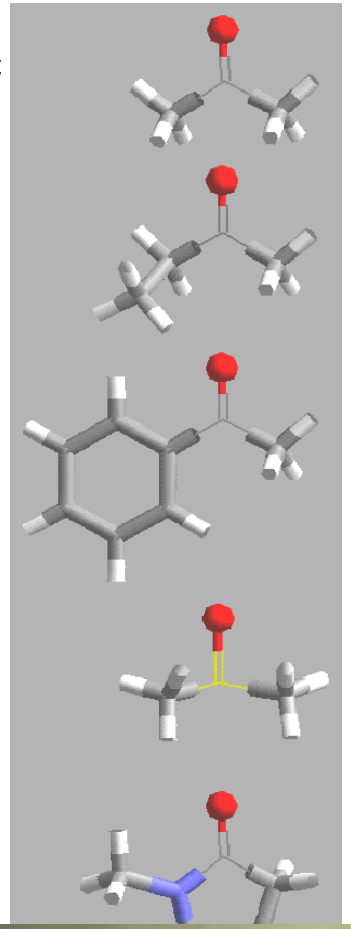


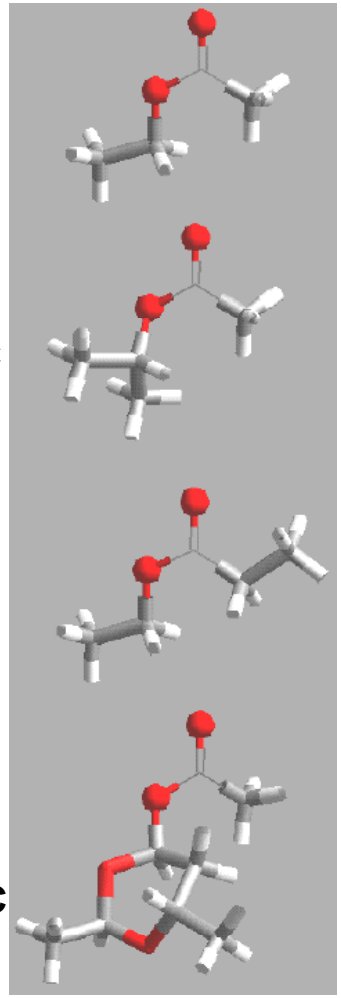
Holston Fed-Batch Crystallizer System

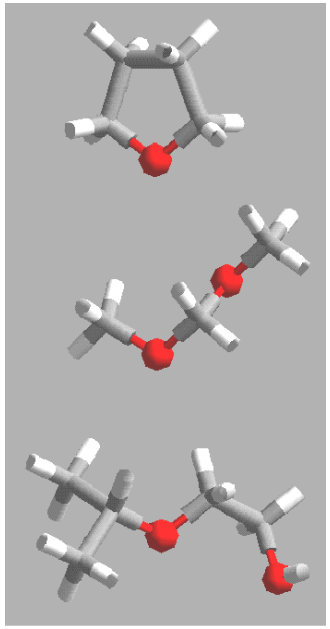
Particle formation from solution crystallization: Polymorph control

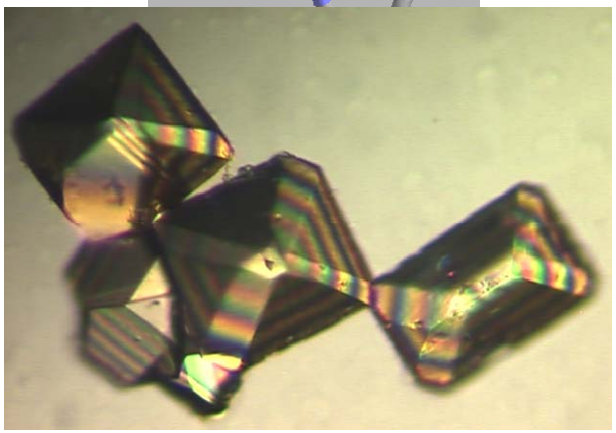


Energy minimization of CL-20 in solution and polymorph prediction.







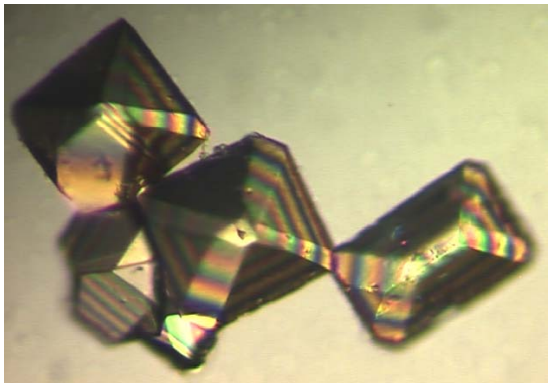


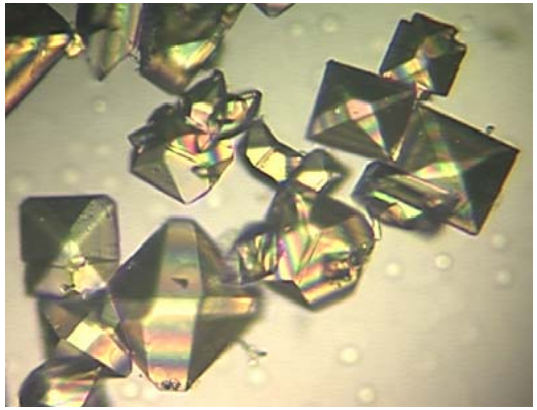
AC- Acetone
MEK- Methyl ethyl ketone
A- Acetophenone
DMSO- Dimethyl sulfoxide
NMP- N-Methyl-pyrrolidone
ETAC- Ethyl acetate
IPAC- Isopropyl acetate

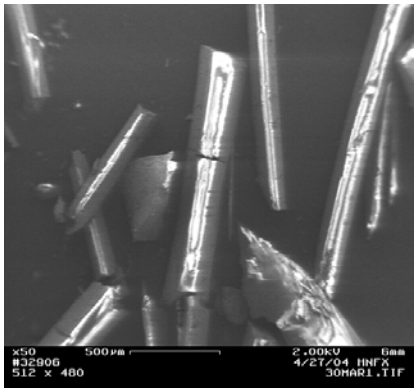
ETPR- Ethyl propionate
DDAC- 2,6-Dimethyl-1,3-dioxane-4-ol acetate
THF- Tetrahydrofurane
DMM- Dimethoxy methane
IPOETOH- 2-Isopropoxyethanol

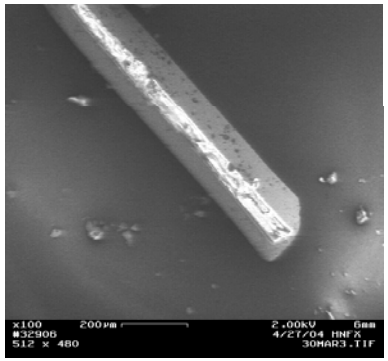
Predicted polymorph types of CL-20 for various solvent molecules.

For acceptable processability: Need low aspect ratio particles

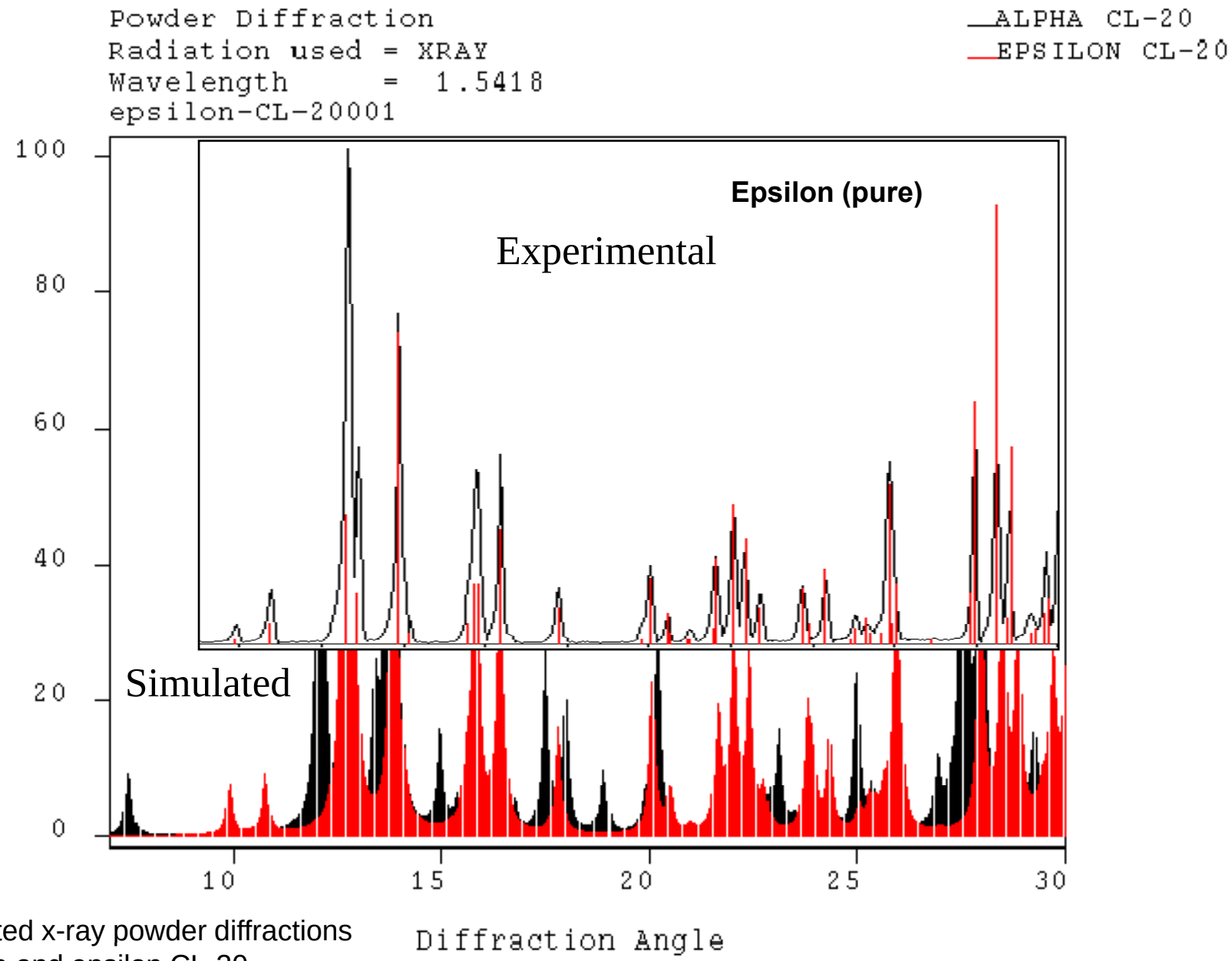








What happens to packing density of the energetic suspension if the polymorph type changes (due to the solvents used) in the continuous mixer?



Simulated x-ray powder diffractions of alpha and epsilon CL-20

compared to experimental data of pure epsilon.

.TECHNOLOGY FOR IDENTIFICATION OF POLYMORPH IMPURITIES

Rheology and Processing

Specialized Tools

- Custom designed rheometers with remote loading and data acquisition capabilities
- Custom designed processing equipment with remote access for data acquisition and control-
  - Example: Twin screw extrusion/electrospinning process for the manufacture of nanofibers with nanoparticles
- Specialized source codes (FEM, FD)
- Structural analysis tools for degree of mixedness, particle size analysis and coating thickness

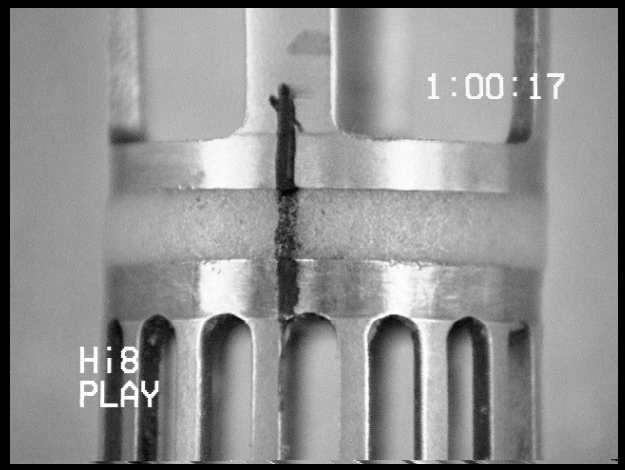
Why is the rheological characterization of highly filled materials such a challenge?

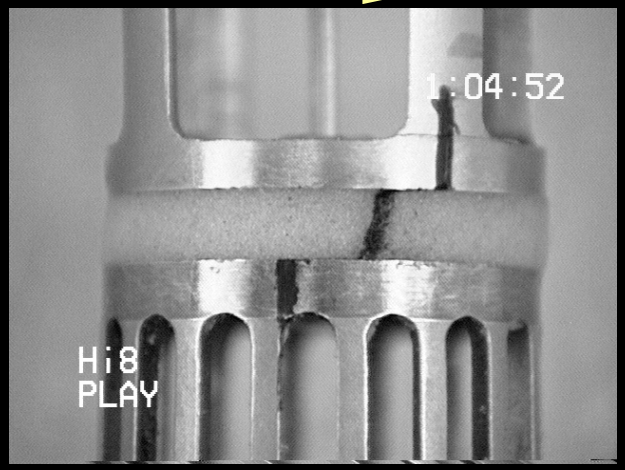
Wall slip Dependence on the surface/volume ratio
Viscoplasticity Dilatancy
Role of air
Binder migration
Particle migration in the transverse to flow direction

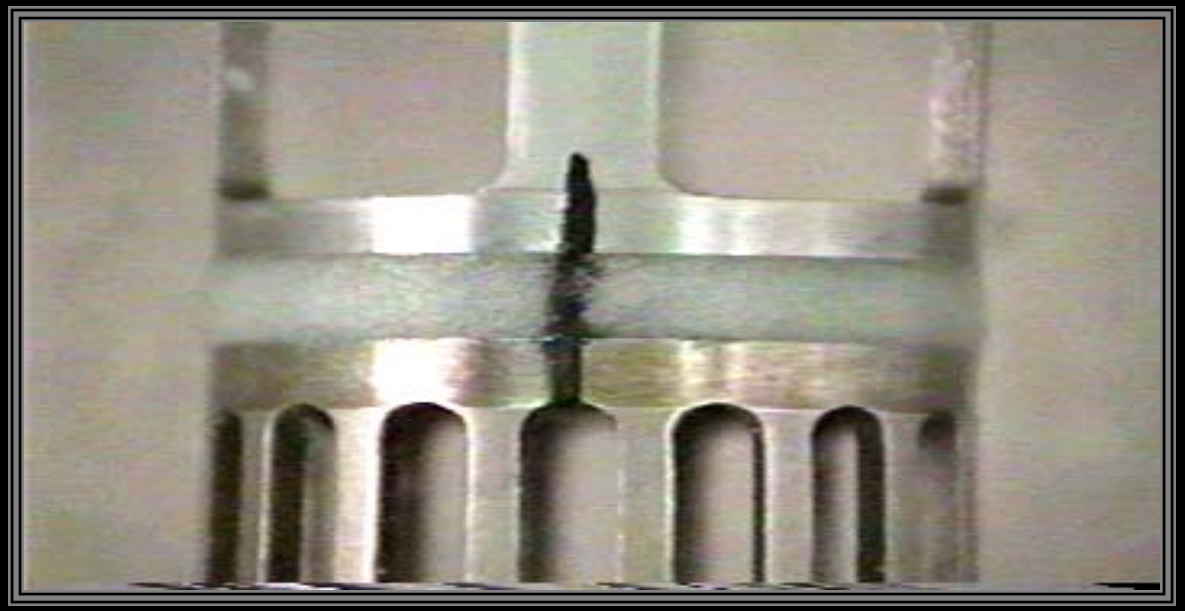
Special tools are necessary plus modified utilization of Conventional rheometers

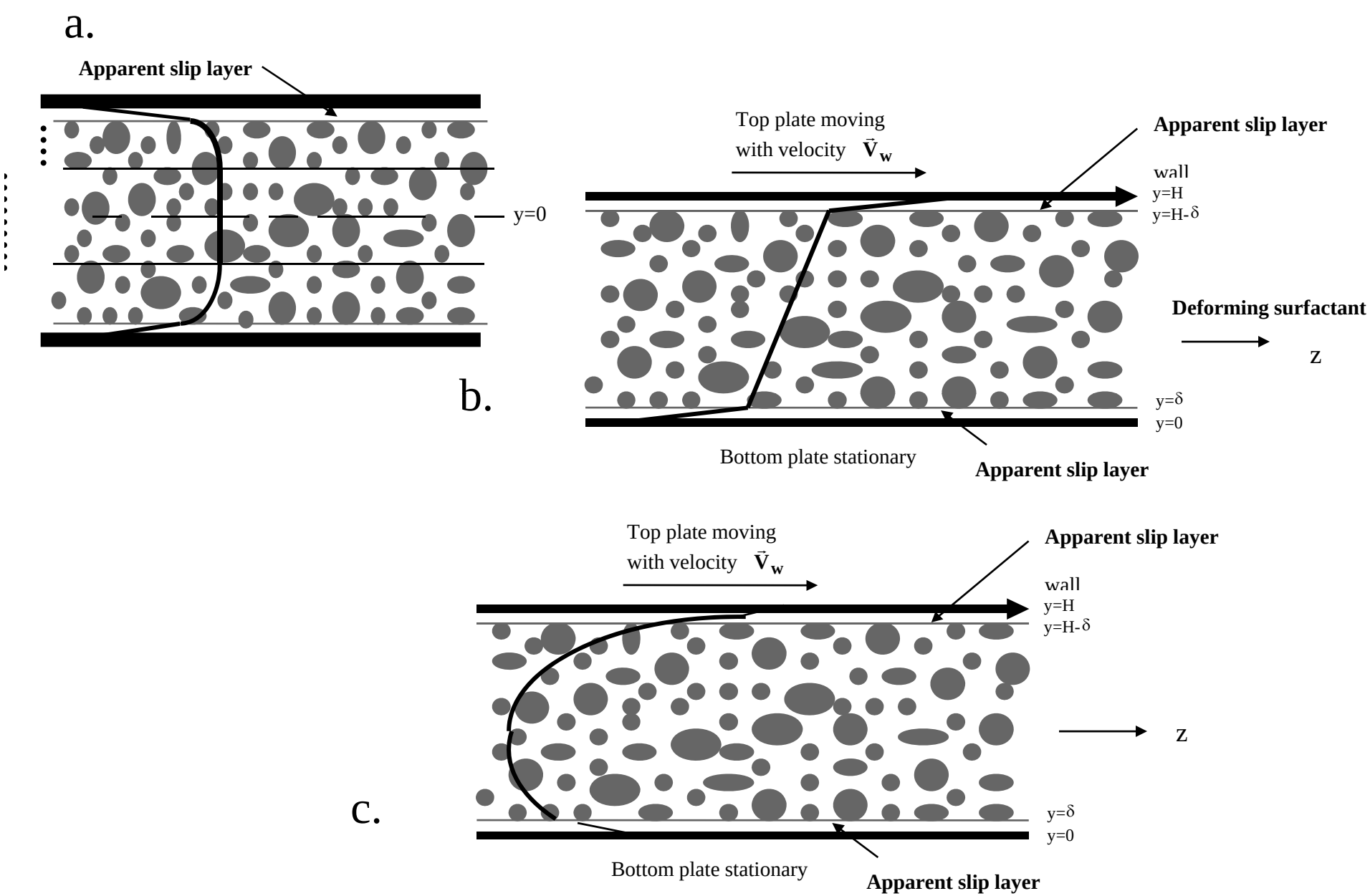
Demonstration of Apparent Wall Slip

60% vol. solids









Three types of deformation with slip

Why was wall slip during flow so important for us so that we had to study it over 23 years?

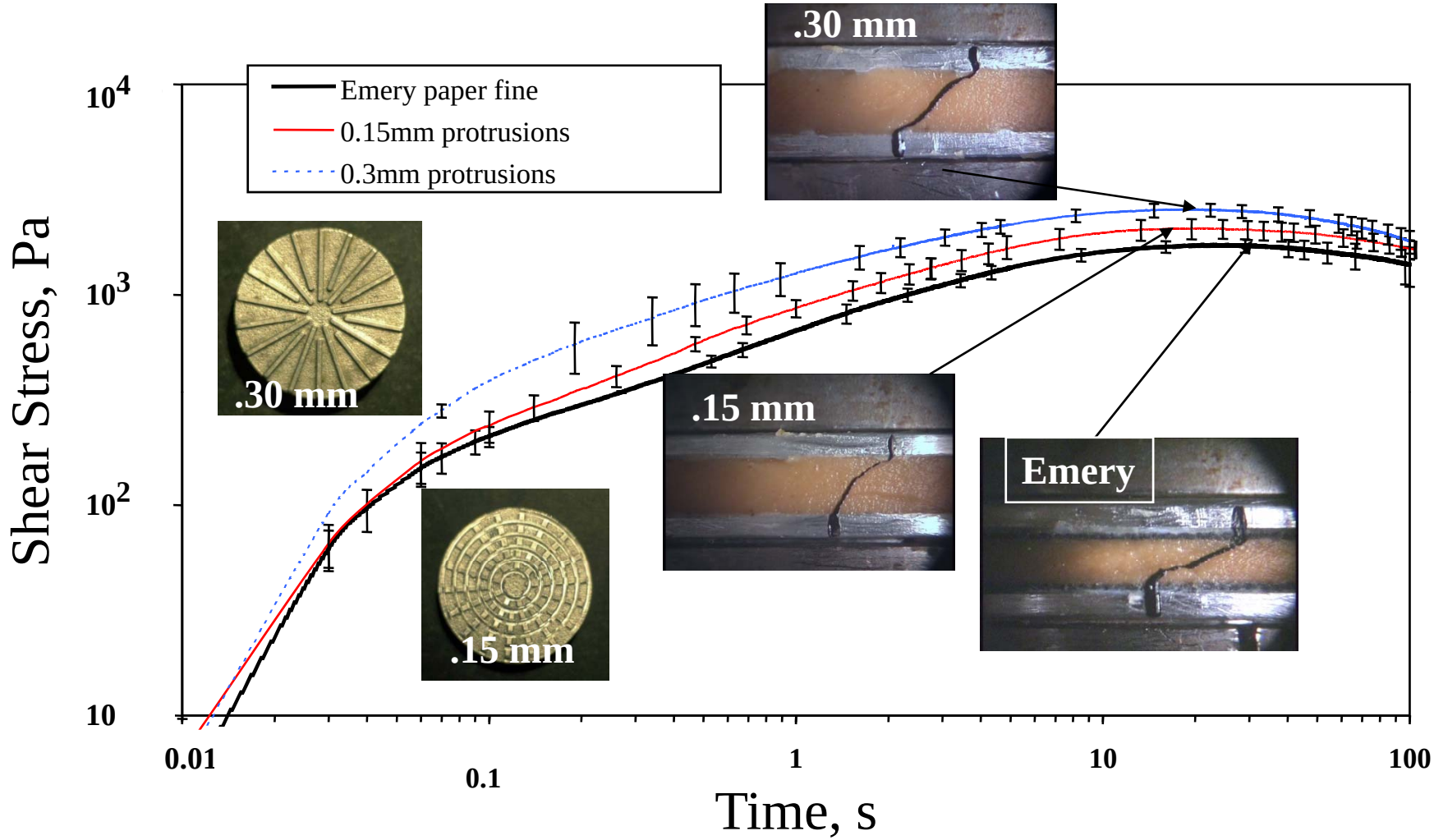
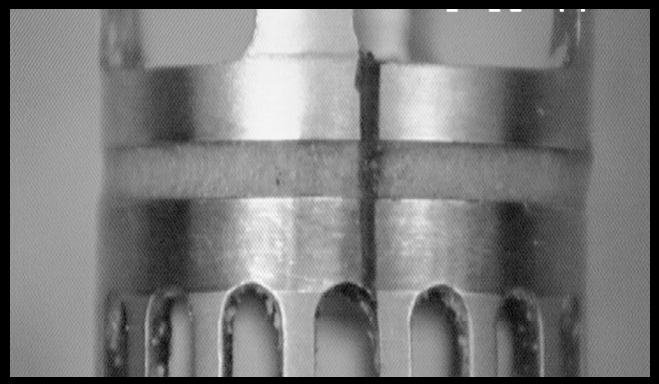
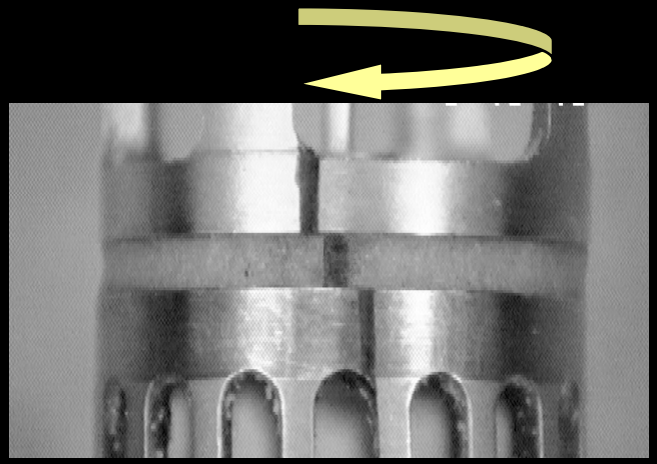
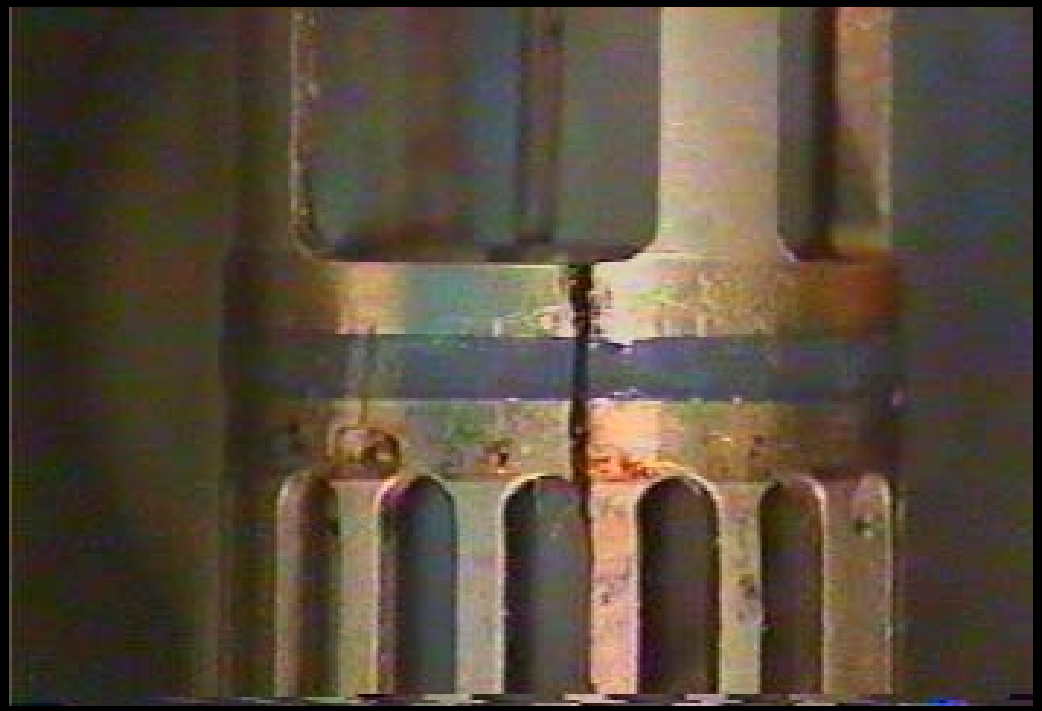


Figure 1: Development of nonhomogeneous shear rate distributions in steady torsional flow with three different types of surface protrusions/asperities.

Demonstration of Viscoplasticity



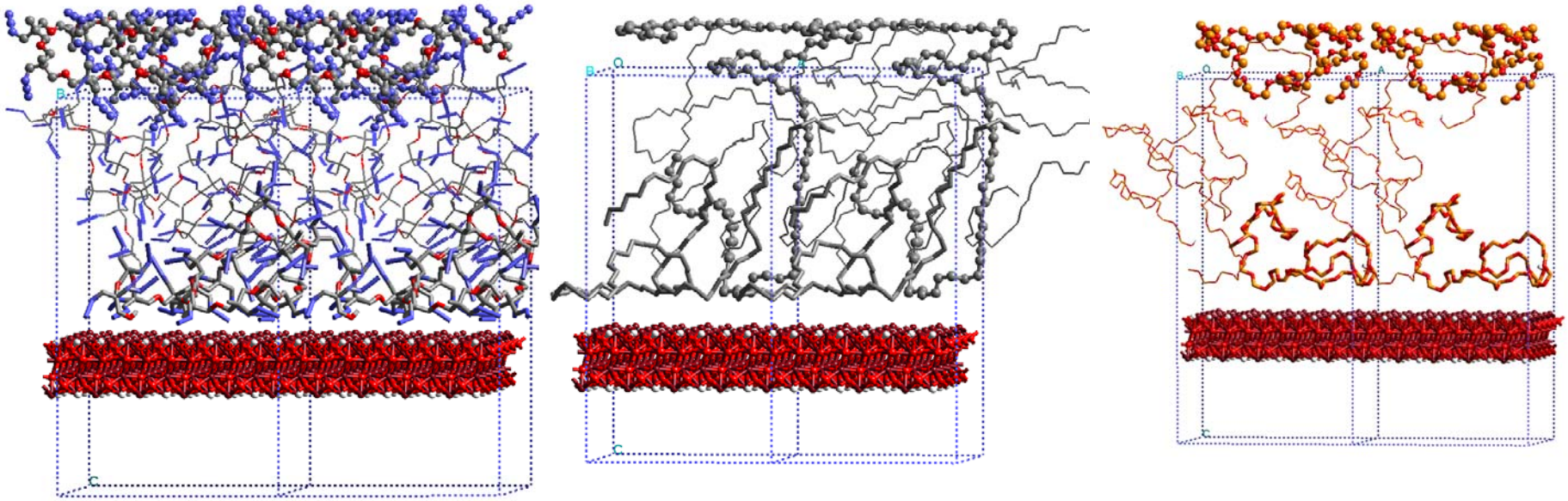




Critical wall shear stress values

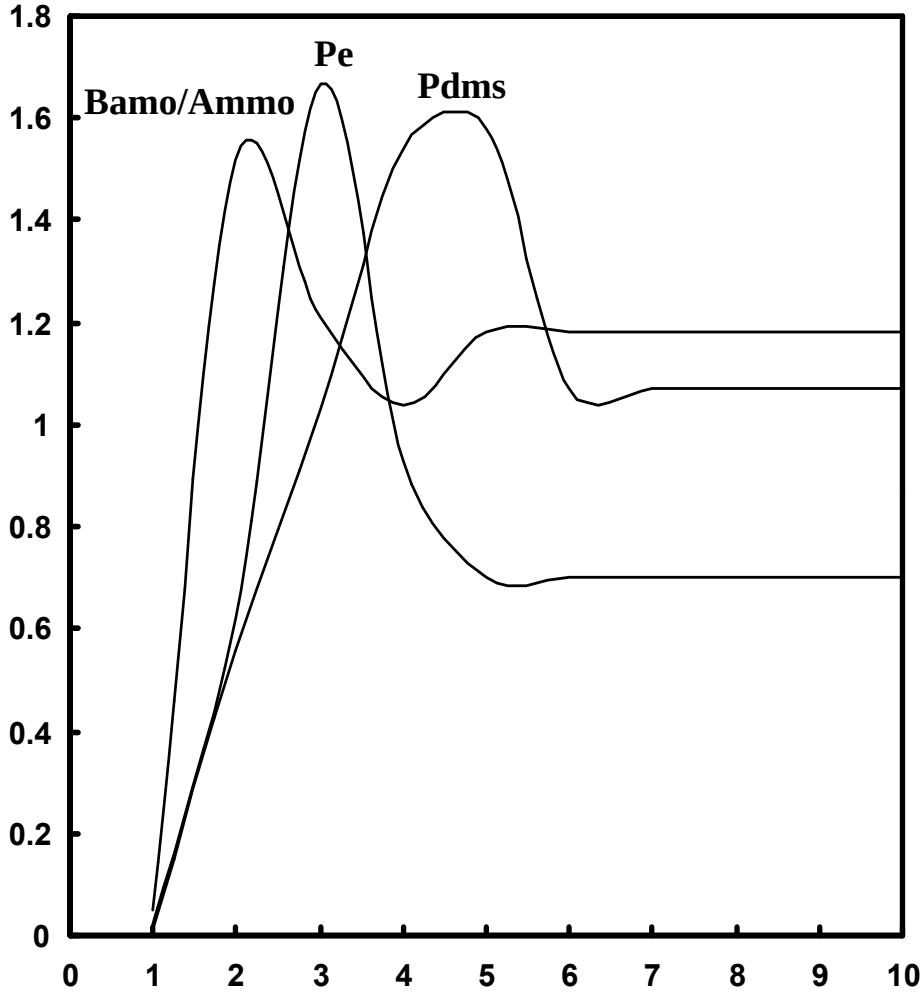
- BAMO/AMMO: No slip condition
- High density polyethylene: Slip at 0.2MPa
- Poly(dimethylsiloxane): Slip at 0.07 MPa

Are molecular dynamics calculations capable of predicting the relative slip behavior of the three polymeric binders?



BAMO/AMMO-Fe **HDPE-Fe** **PDMS-Fe**

Simulated BAMO/AMMO, HDPE and PDMS melt flows and interfaces with Fe surface.



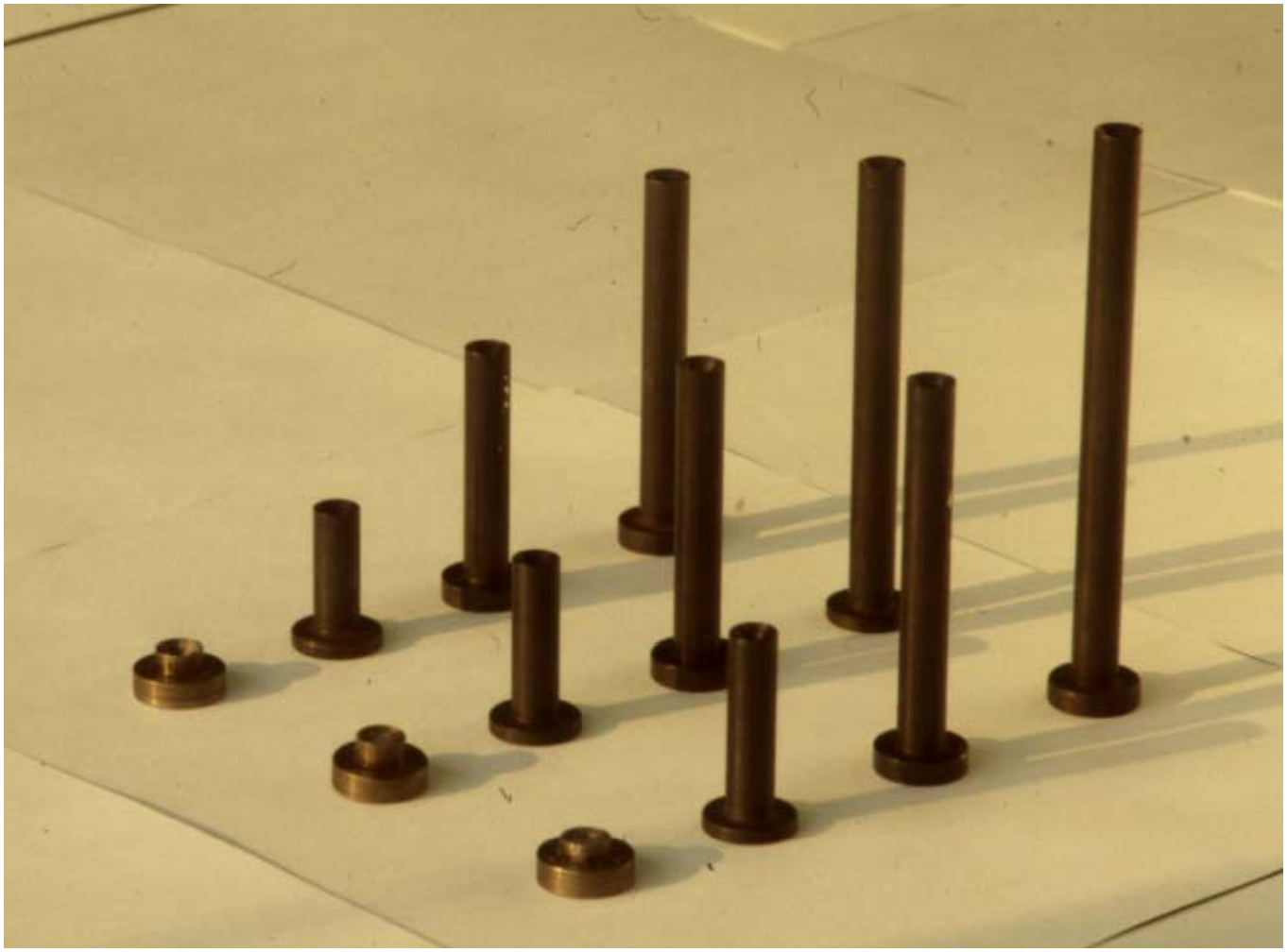
Polymer density versus distance from the metal surface.

Calculated cohesive energy values of BAMO/AMMO, HDPE and PDMS.

Polymer	Simulation Density (g/cm^3)	Coulomb Energy (cal/cm^3)	VDW Energy (cal/cm^3)	**Cohesive Energy (cal/cm^3)**
BAMO/AMMO	1.2	-43	-38	**-81**
HDPE	0.9	-67	-2	**-69**
PDMS	1.2	-58	-3	**-61**

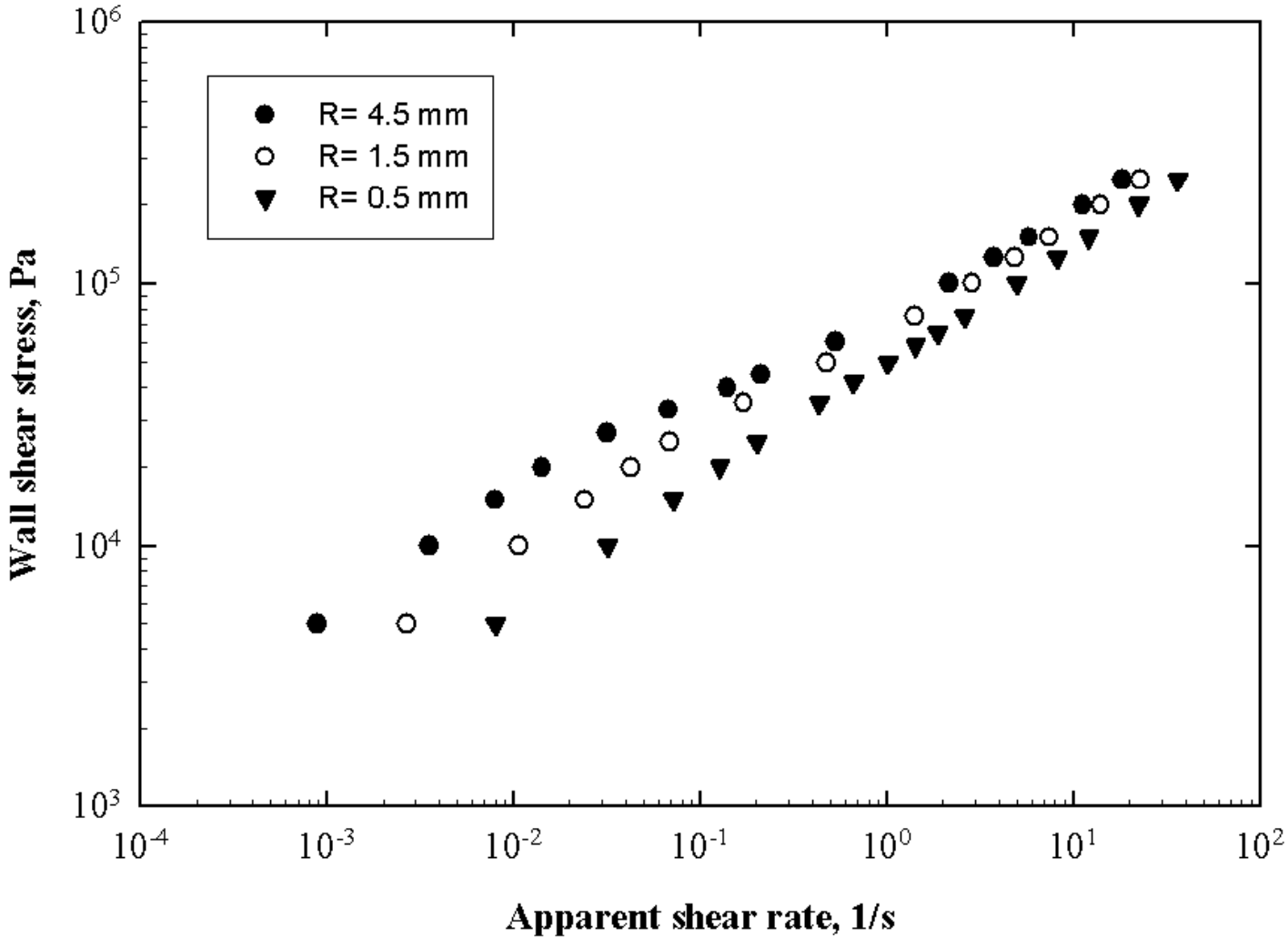
Table 2. Calculated adhesive energy values of BAMO/AMMO, HDPE and PDMS melts with the iron wall.

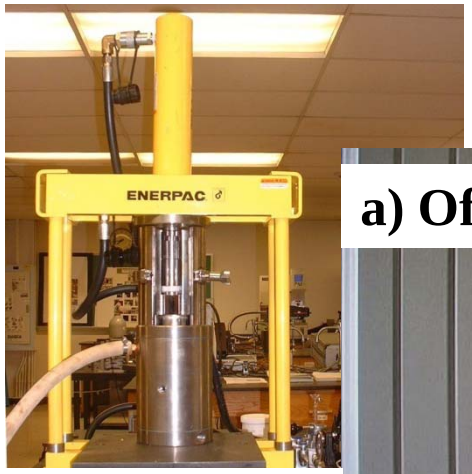
Polymer-Fe Interface	Simulation Density[a] (g/cm^3)	Coulomb Energy (cal/cm^3)	VDW Energy (cal/cm^3)	Adhesive Energy (cal/cm^3)
BAMO/AMMO-Fe	2.1 (1.2)	-132	-7	**-140**
HDPE-Fe	1.9 (0.9)	-47	-13	**-60**
PDMS-Fe	1.9 (1.1)	-60	-8	**-68**



Capillary rheometry- wall slip and wall shear stress corrections
Require multiple capillaries with differing diameters and L/D ratios

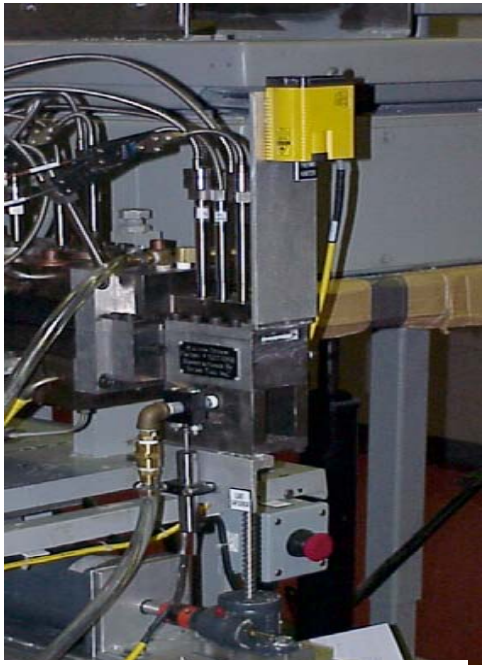
With wall slip rheology data become dependent on the surface/volume ratio: Flow curves at constant capillary length/radius (L/R)



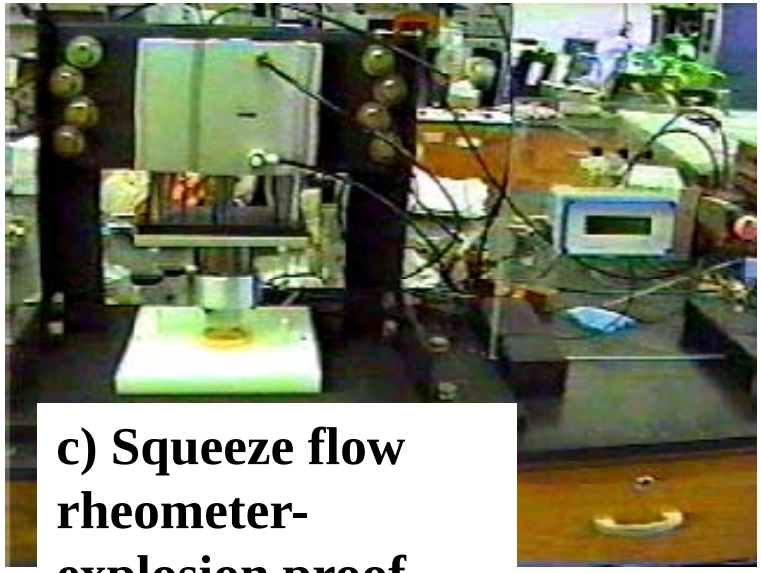


Filling station

a) Off-line adjustable gap slit die



b) On-line adjustable gap slit die

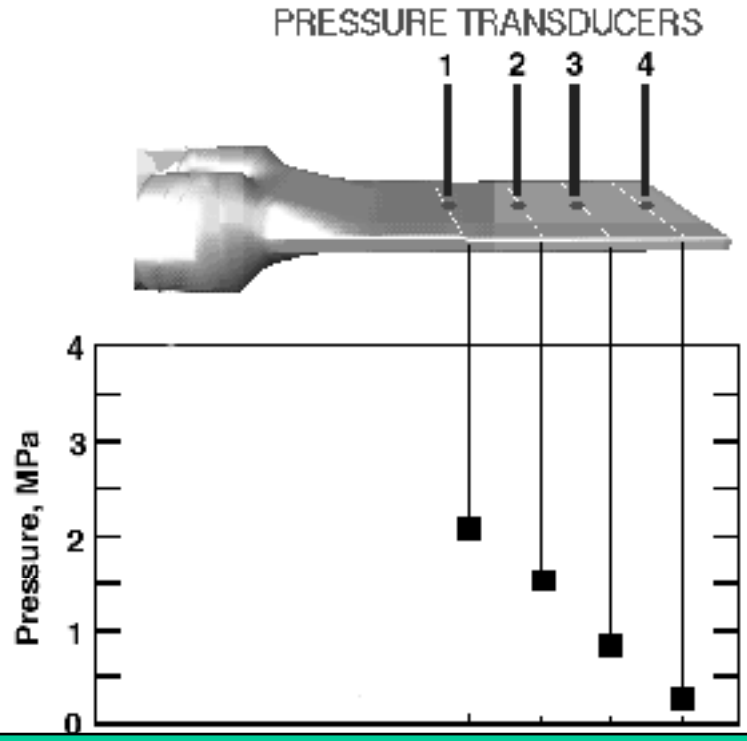


c) Squeeze flow rheometer-explosion proof

Patented adjustable gap rheometer
of HfMI capable of
In-line characterization of wall slip
and shear viscosity
In conjunction with extrusion
processing

Special tool for faster and more accurate characterization:
In line slit rheometer with adjustable gap.

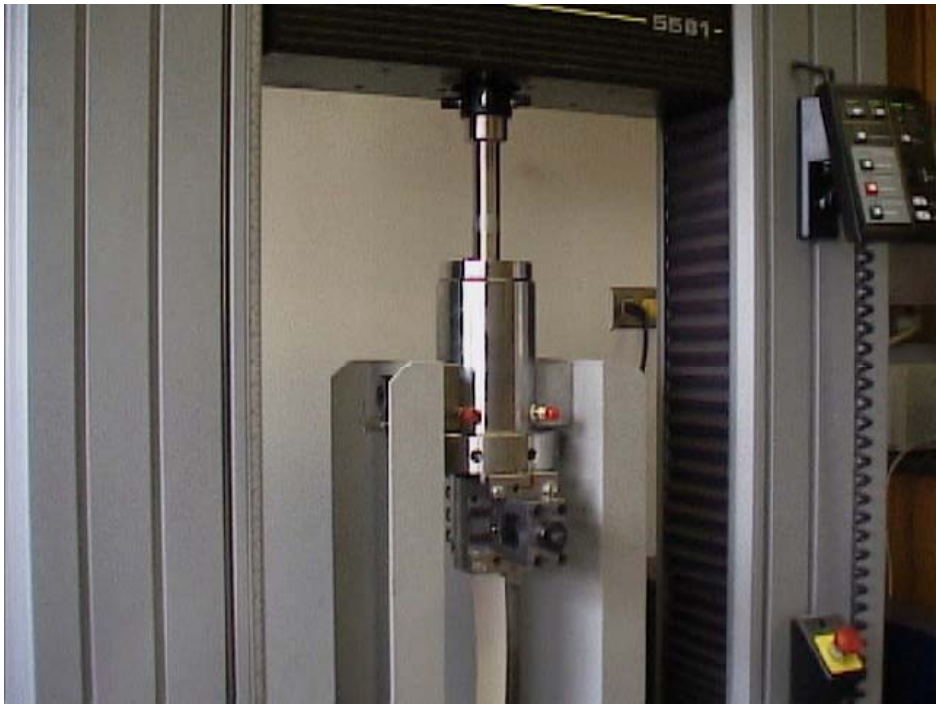
ADJUSTABLE GAP RHEOMETER



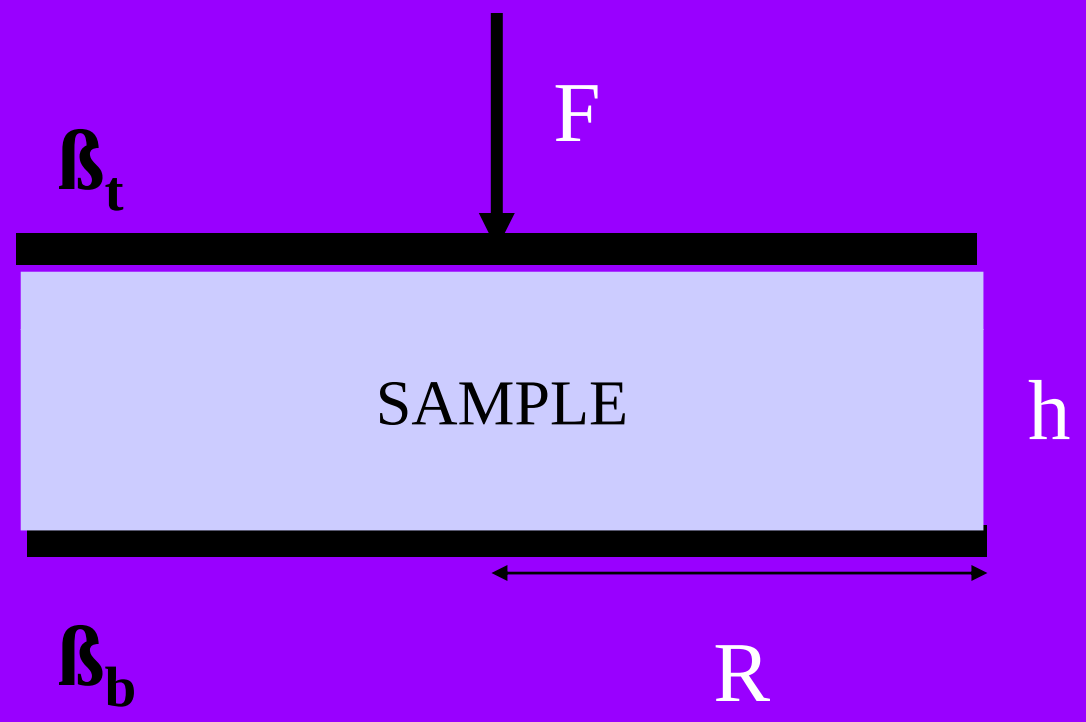
Pressure versus distance in the die

Off-line adjustable gap slit die

Filling station

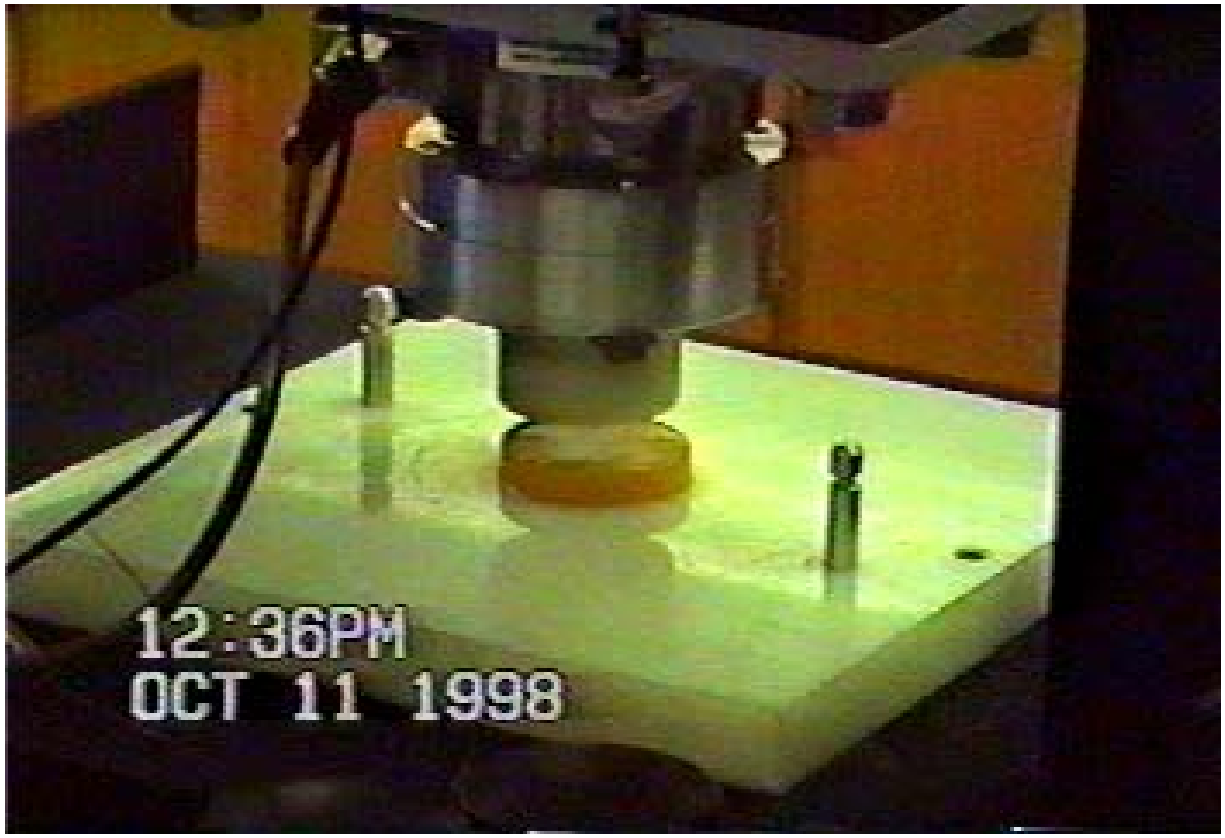


Compressive Squeeze Flow



Special tool for faster and more accurate characterization:
In line slit rheometer with adjustable gap.

SIT Squeeze Flow Rheometer

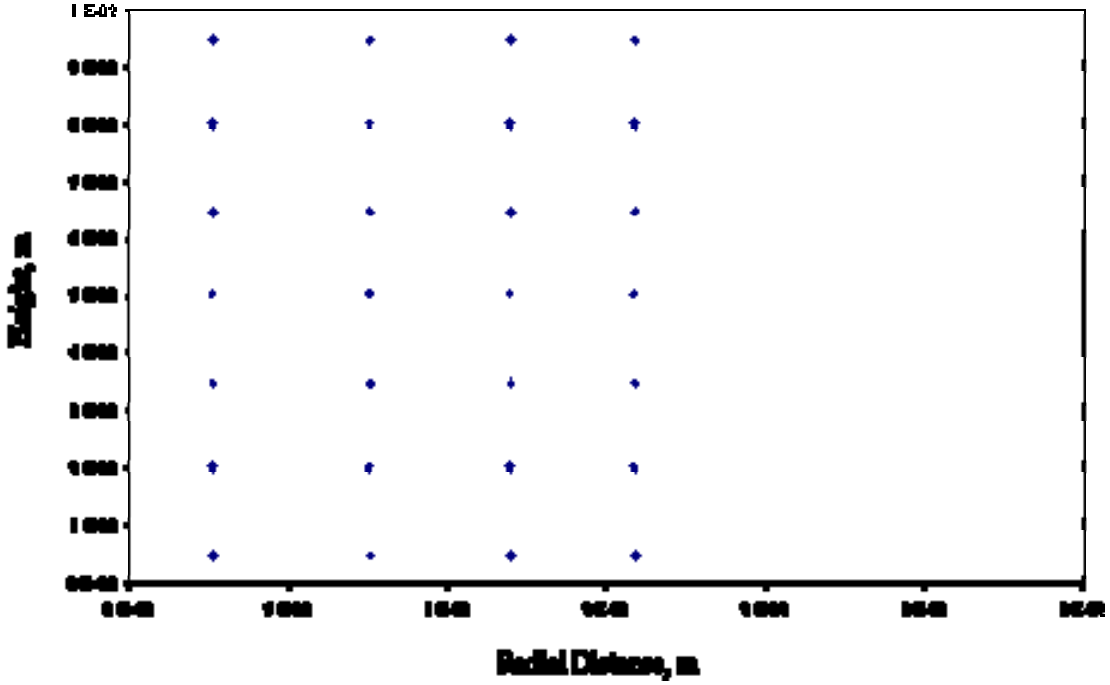


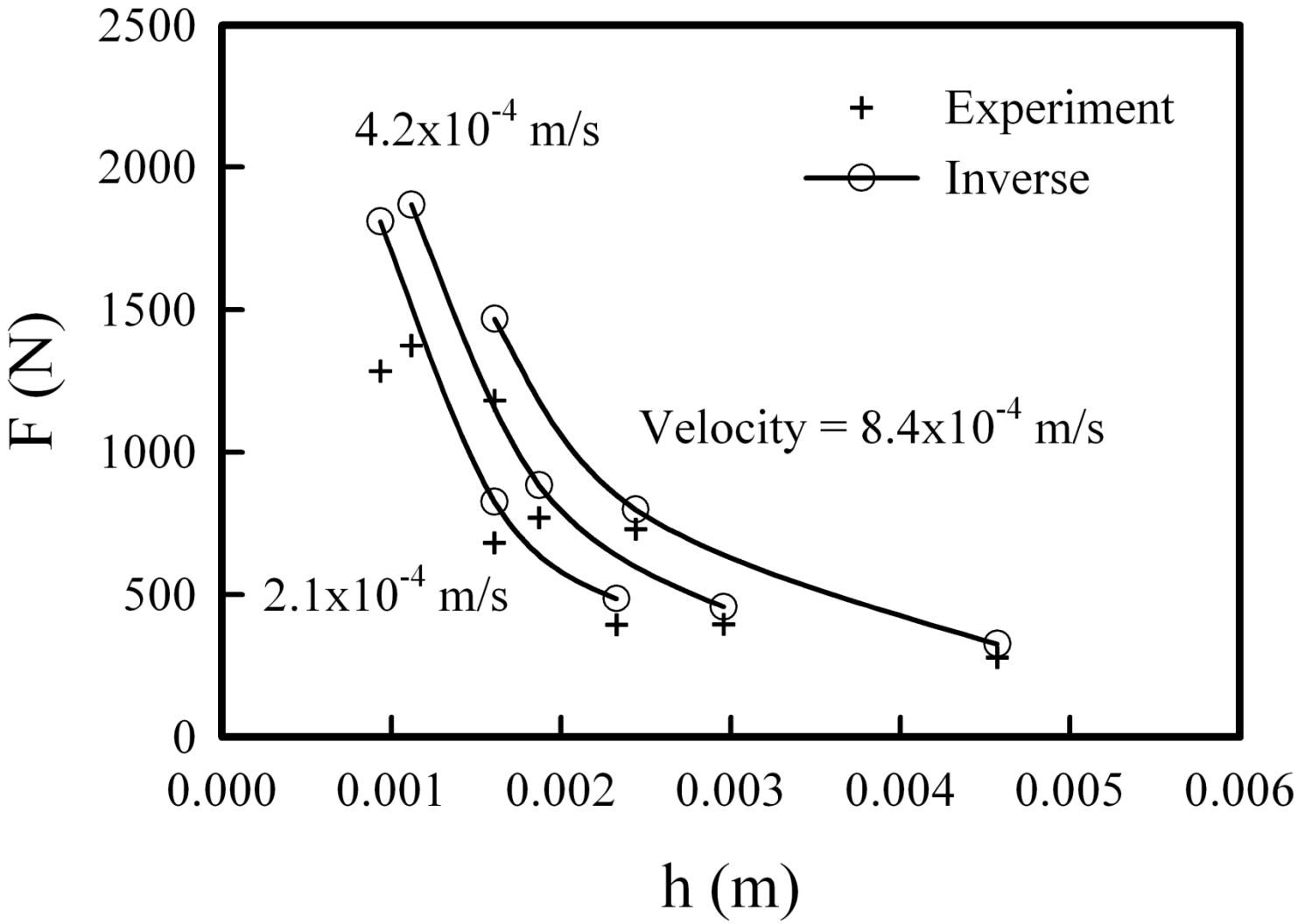
Special tool for faster and more accurate characterization:
In line slit rheometer with adjustable gap.

Squeeze Flow Rheometer

Explosion proof v

Ability to solve the flow field and to determine parameters from the inverse problem.



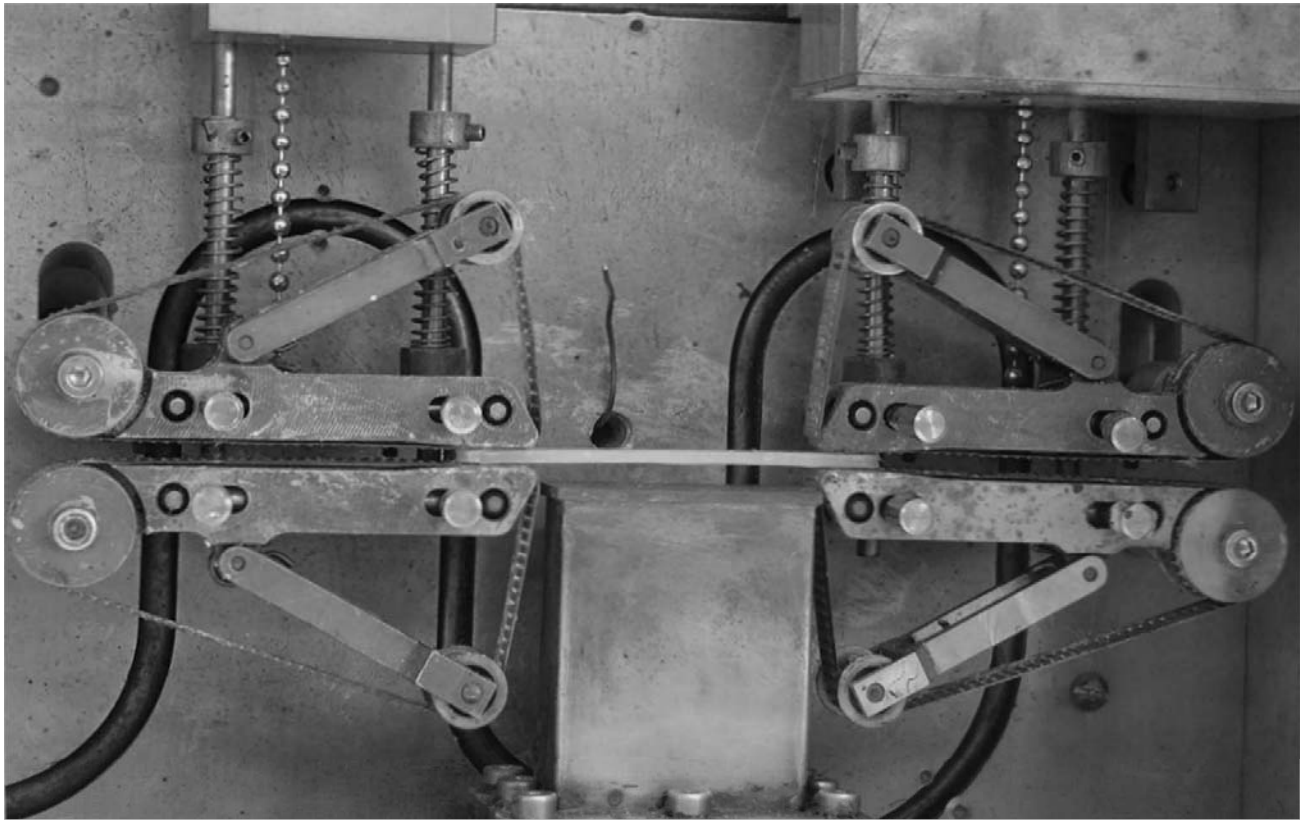


Normal force, F, versus gap, h, during squeeze flow of suspension of PDMS with glass spheres (ϕ=0.1) as a function of the plate velocity.

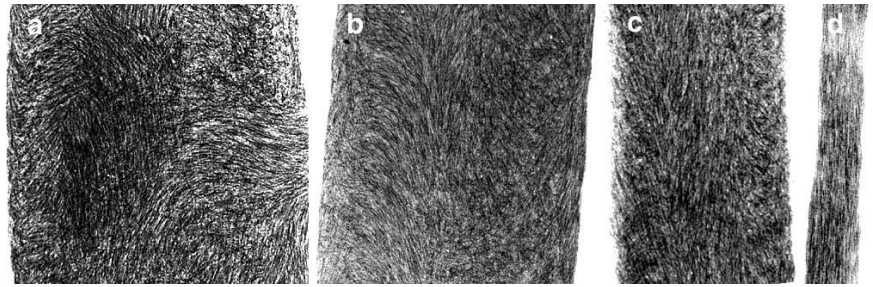
Specialized capabilities for rheological analysis and design

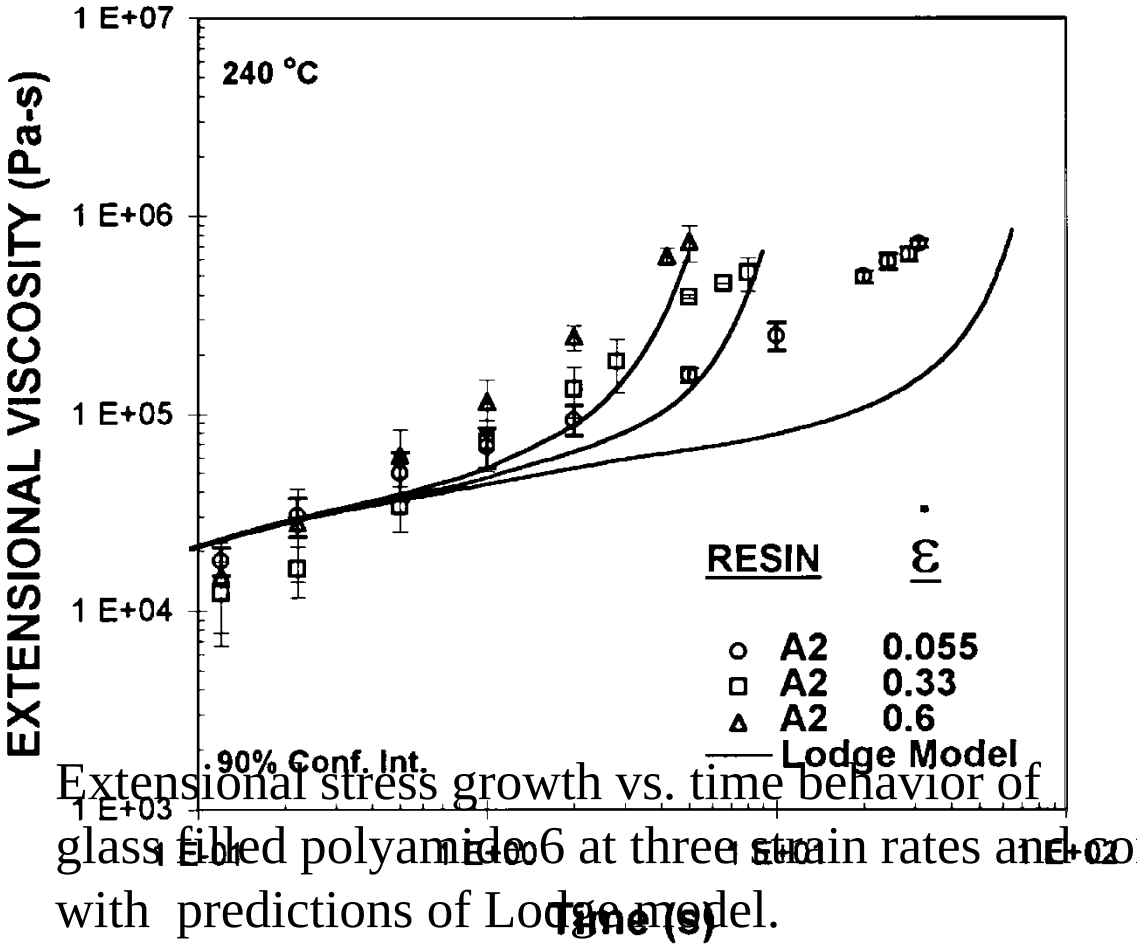
Extensional flow behavior analysis of suspensions

Uniaxial extensional rheometer



Rotary clamp system of the rheometer

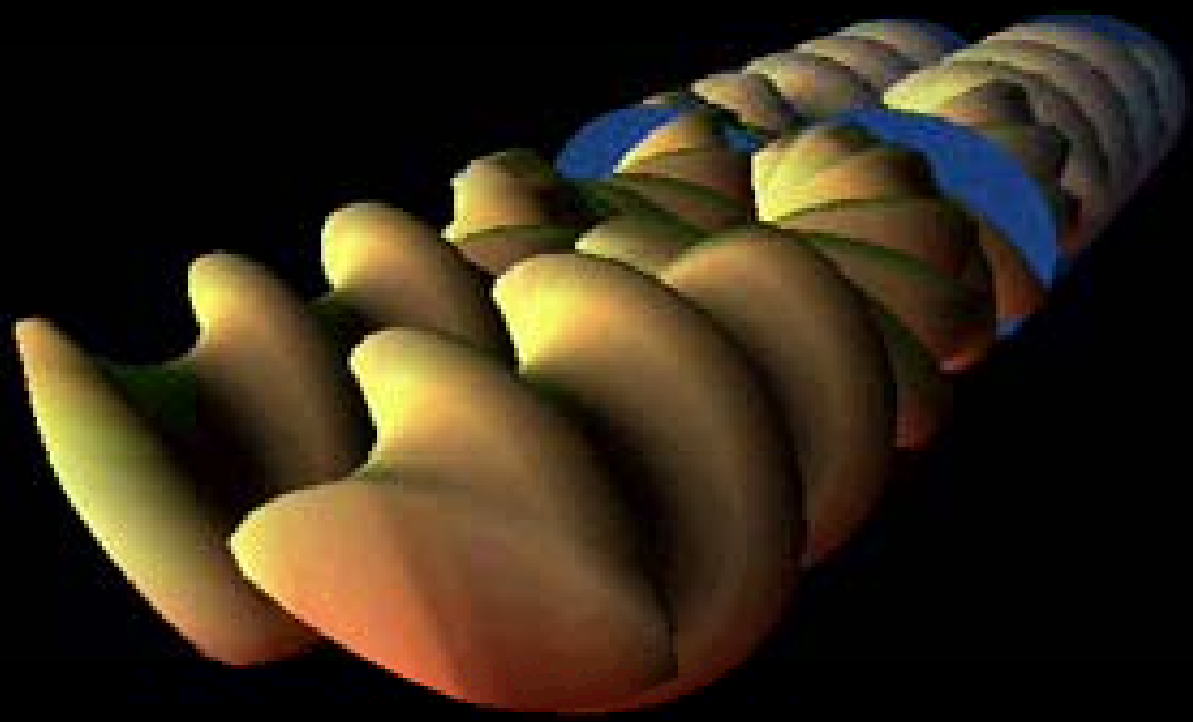


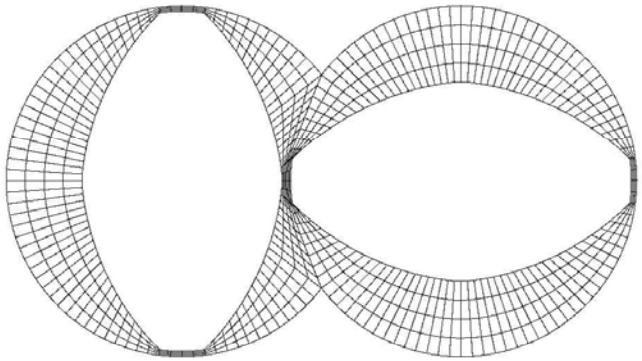


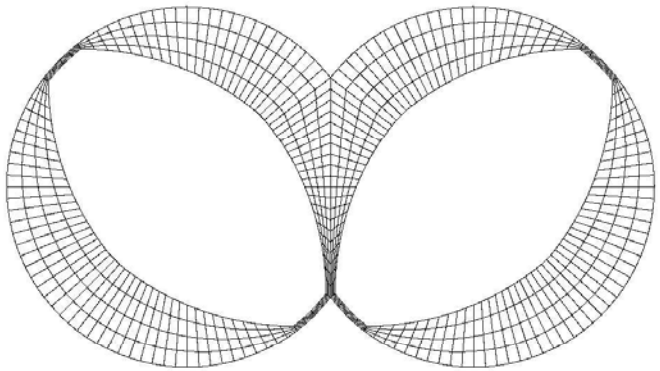
Extensional stress growth vs. time behavior of glass filled polyamide 6 at three strain rates and comparisons with predictions of Lodge model.

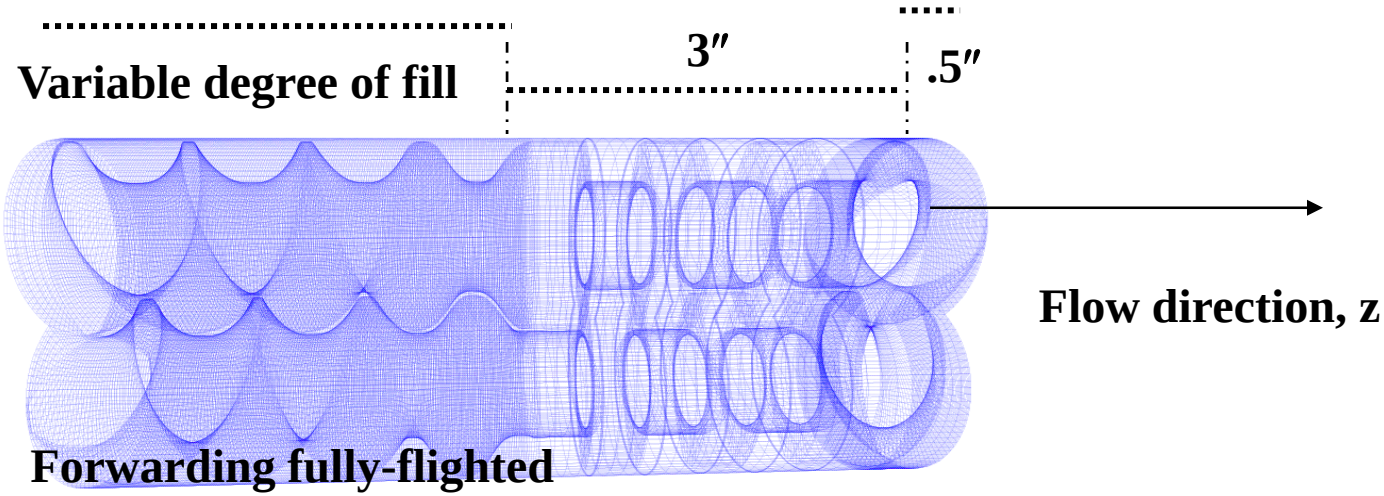
Mathematical modeling of flow and heat transfer occurring in single/twin screw extrusion and validation of the results

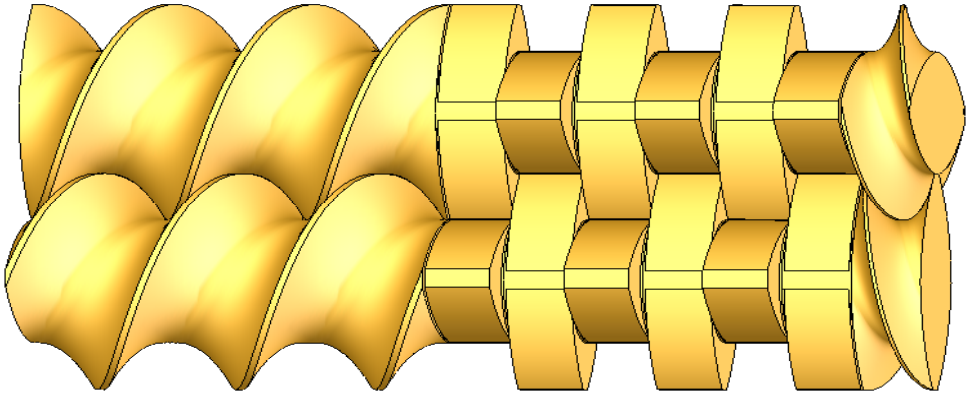
A Co-rotating Twin-screw Extruder

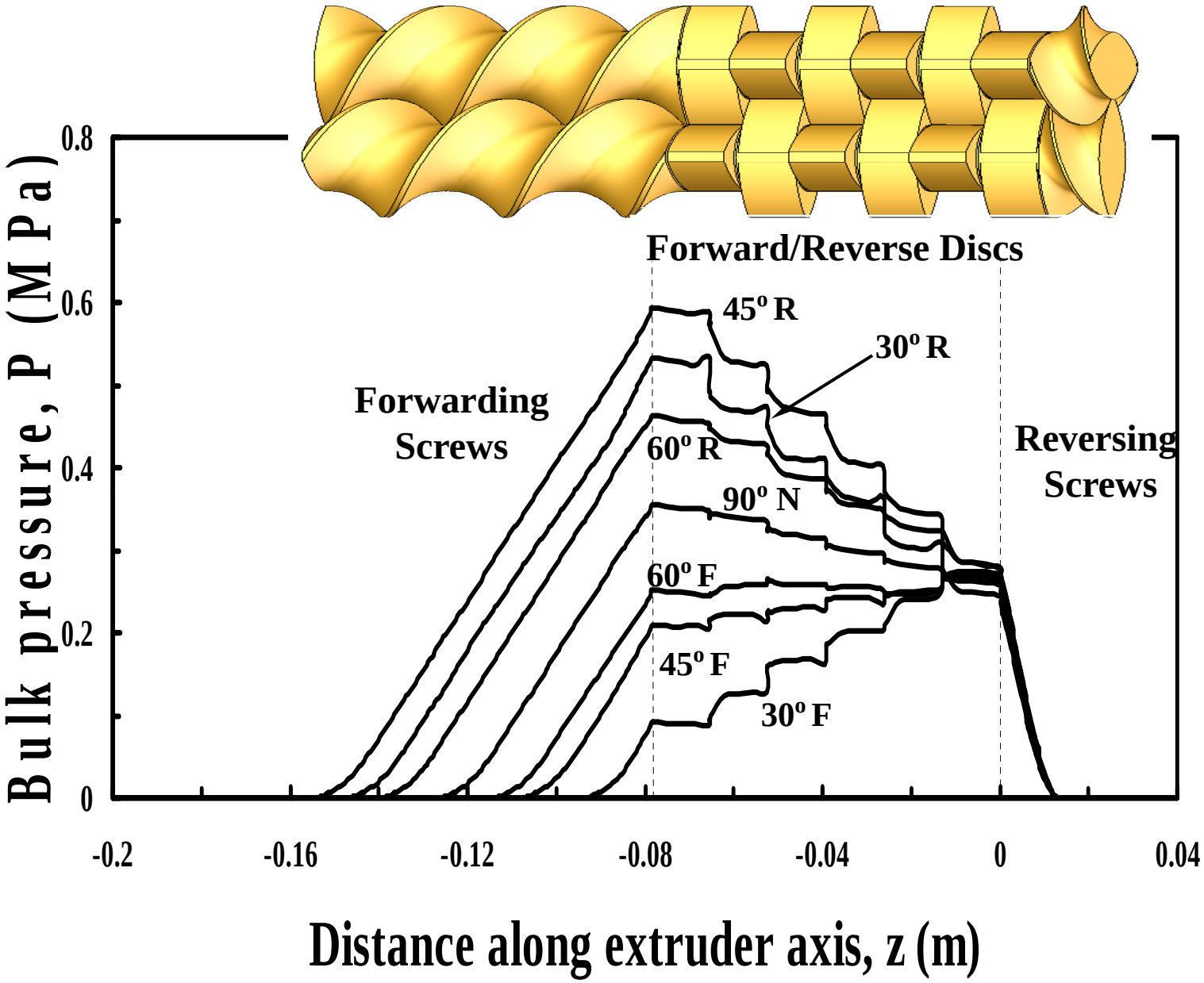


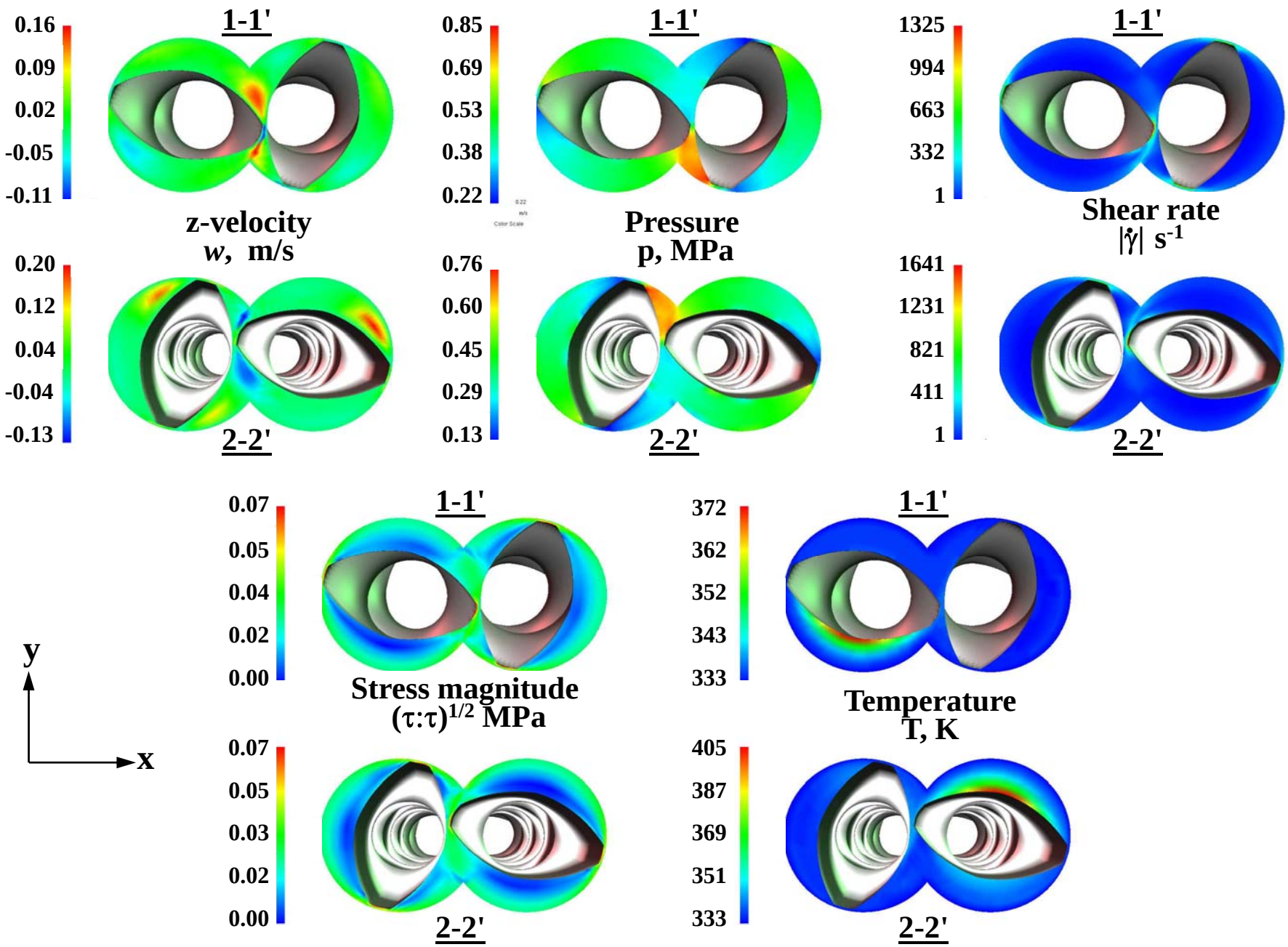


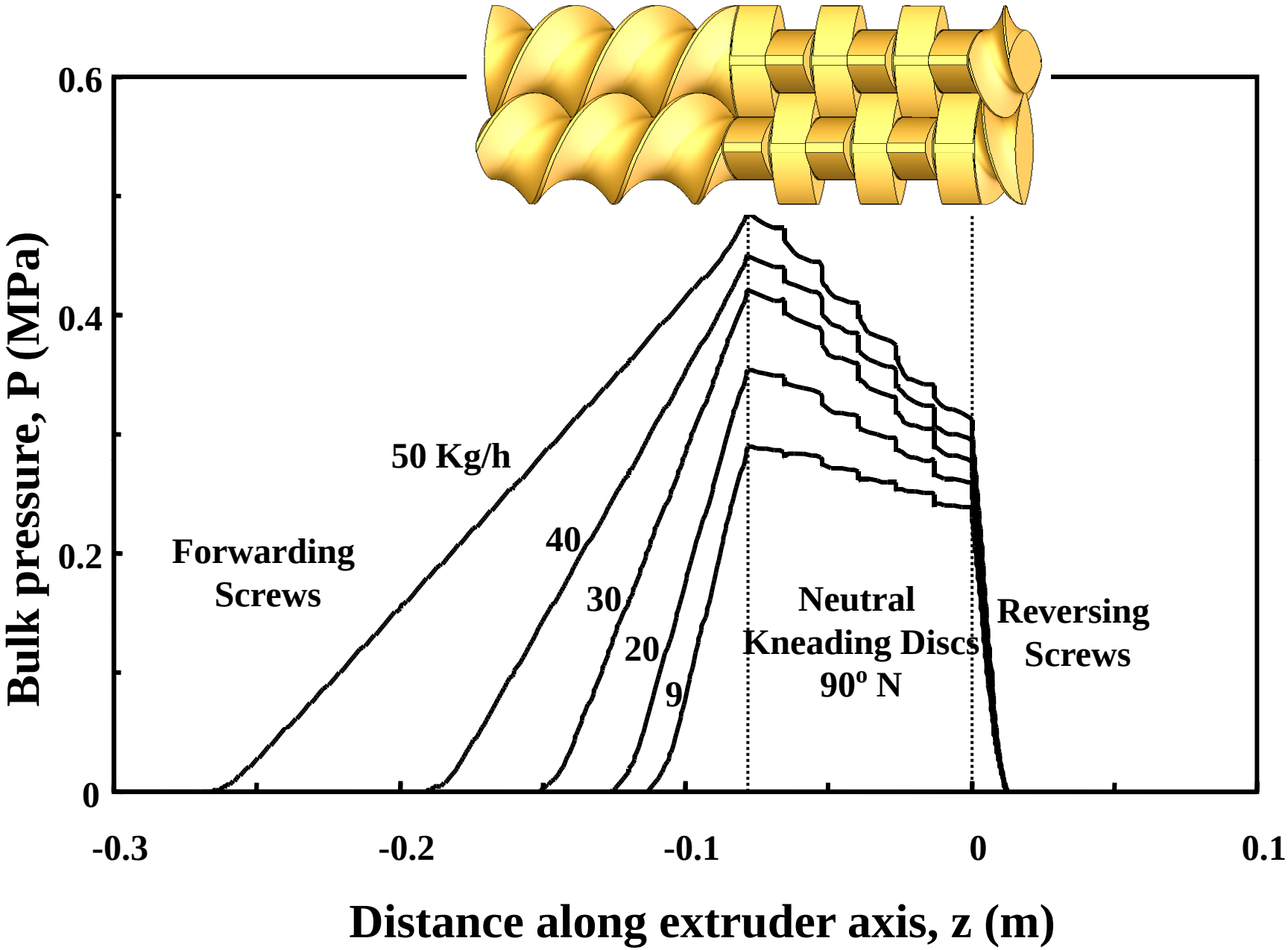


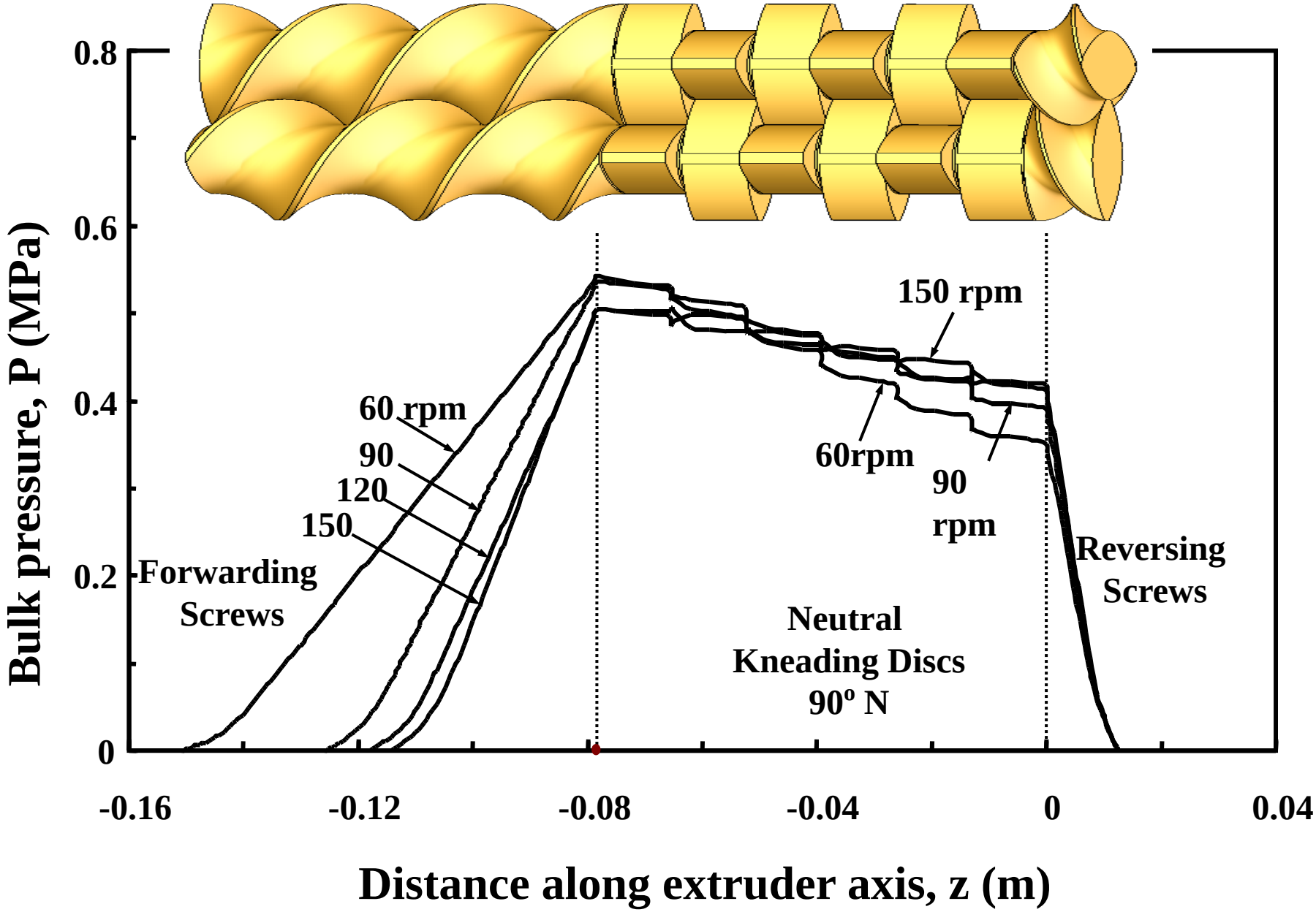

Variable degree of fill
3″
.5″
Flow direction, z
Forwarding fully-flighted screws
Kneading discs
Reversing screws

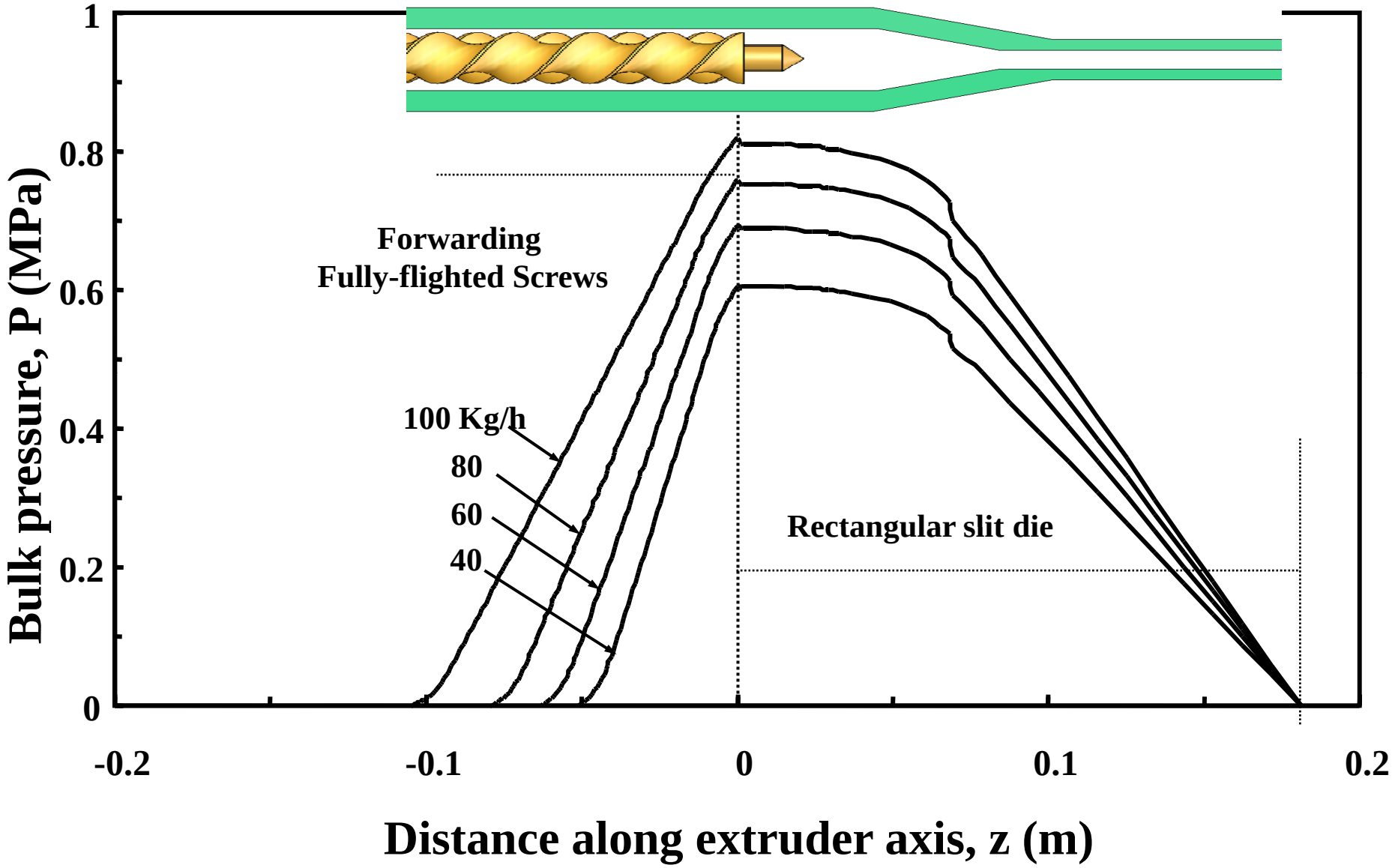


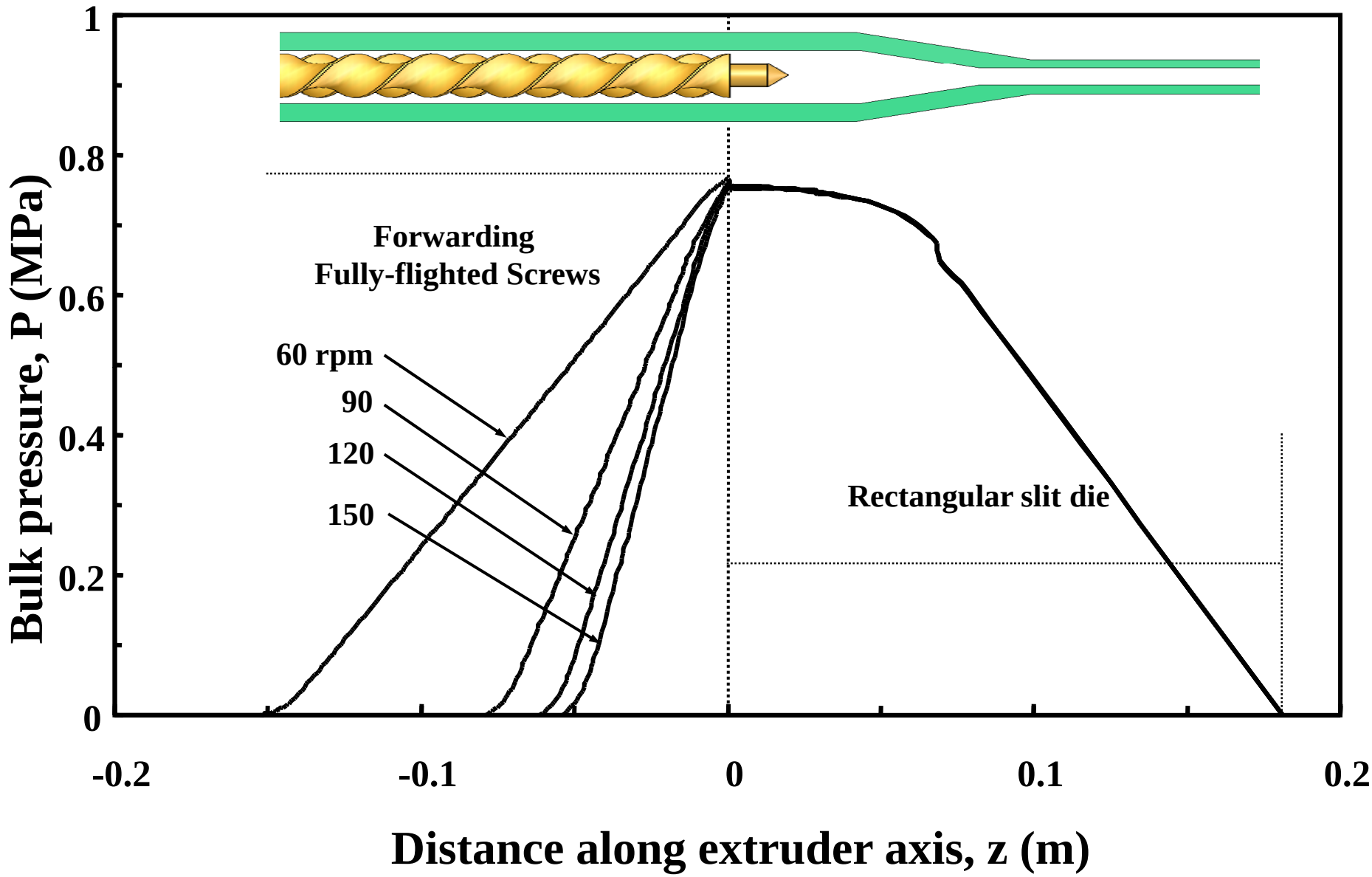

Forward/Reverse Discs
45° R
30° R
Forwarding Screws
60° R
90° N
Reversing Screws
60° F
45° F
30° F
0.8
0.6
0.4
0.2
0
Bulk pressure, P (MPa)
-0.2
-0.16
-0.12
-0.08
-0.04
0
0.04
Distance along extruder axis, z (m)


1-1'
0.16
0.09
0.02
-0.05
-0.11
z-velocity
w, m/s
0.20
0.12
0.04
-0.04
-0.13
2-2'
1-1'
0.85
0.69
0.53
0.38
0.22
Pressure
p, MPa
0.76
0.60
0.45
0.29
0.13
2-2'
1-1'
1325
994
663
332
1
Shear rate
|γ̇| s-1
1641
1231
821
411
1
2-2'
y
x
1-1'
0.07
0.05
0.04
0.02
0.00
Stress magnitude
(τ:τ)1/2 MPa
0.07
0.05
0.03
0.02
0.00
2-2'
1-1'
372
362
352
343
333
Temperature
T, K
405
387
369
351
333
2-2'

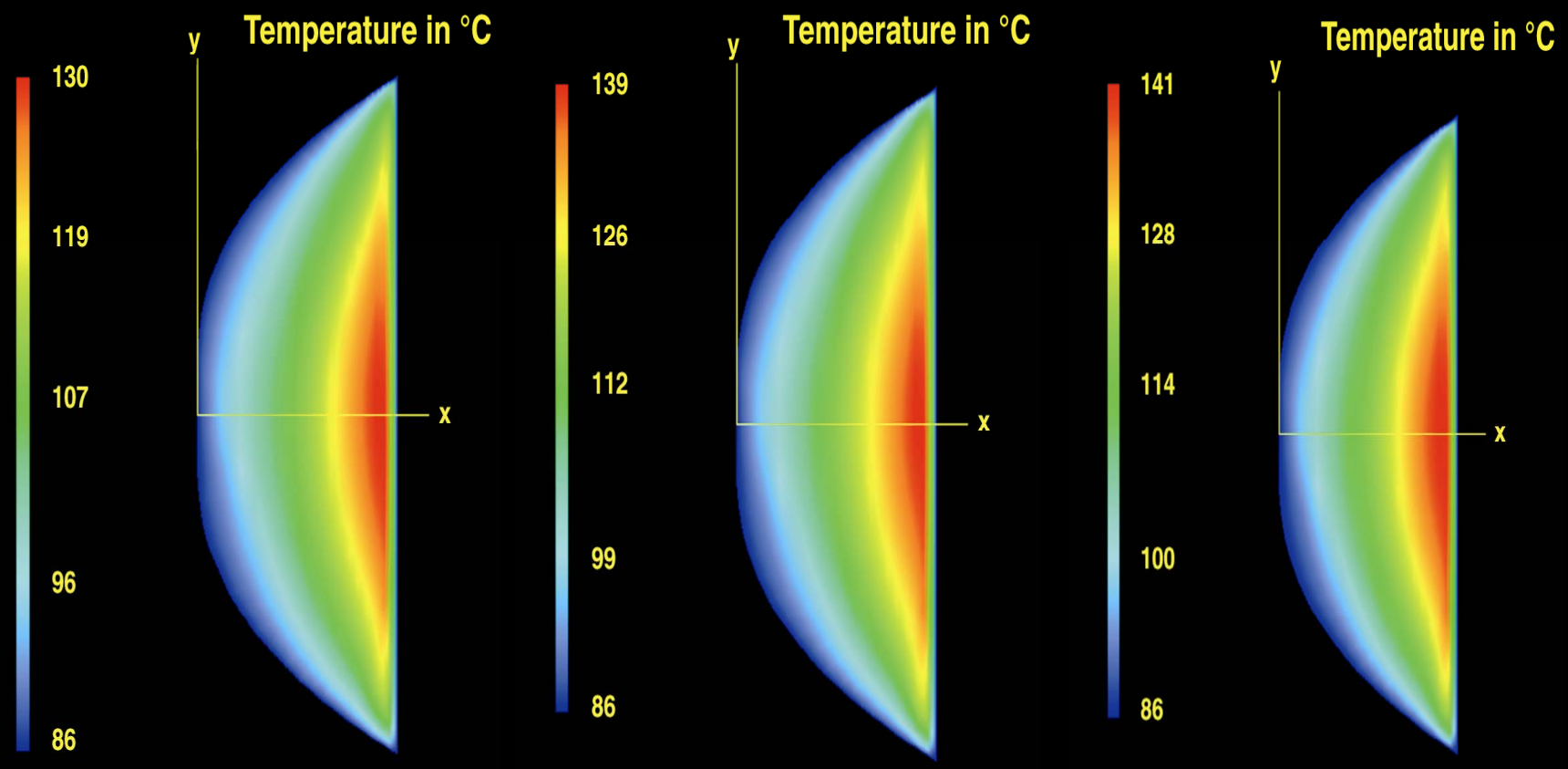

0.6
0.4
0.2
0
Bulk pressure, P (MPa)
-0.3
-0.2
-0.1
0
0.1
Distance along extruder axis, z (m)
50 Kg/h
40
30
20
9
Forwarding
Screws
Neutral
Kneading Discs
90º N
Reversing
Screws


0.8
0.6
0.4
0.2
0
Bulk pressure, P (MPa)
-0.16
-0.12
-0.08
-0.04
0
0.04
Distance along extruder axis, z (m)
60 rpm
90
120
150
Forwarding Screws
150 rpm
60rpm
90 rpm
Neutral Kneading Discs 90º N
Reversing Screws

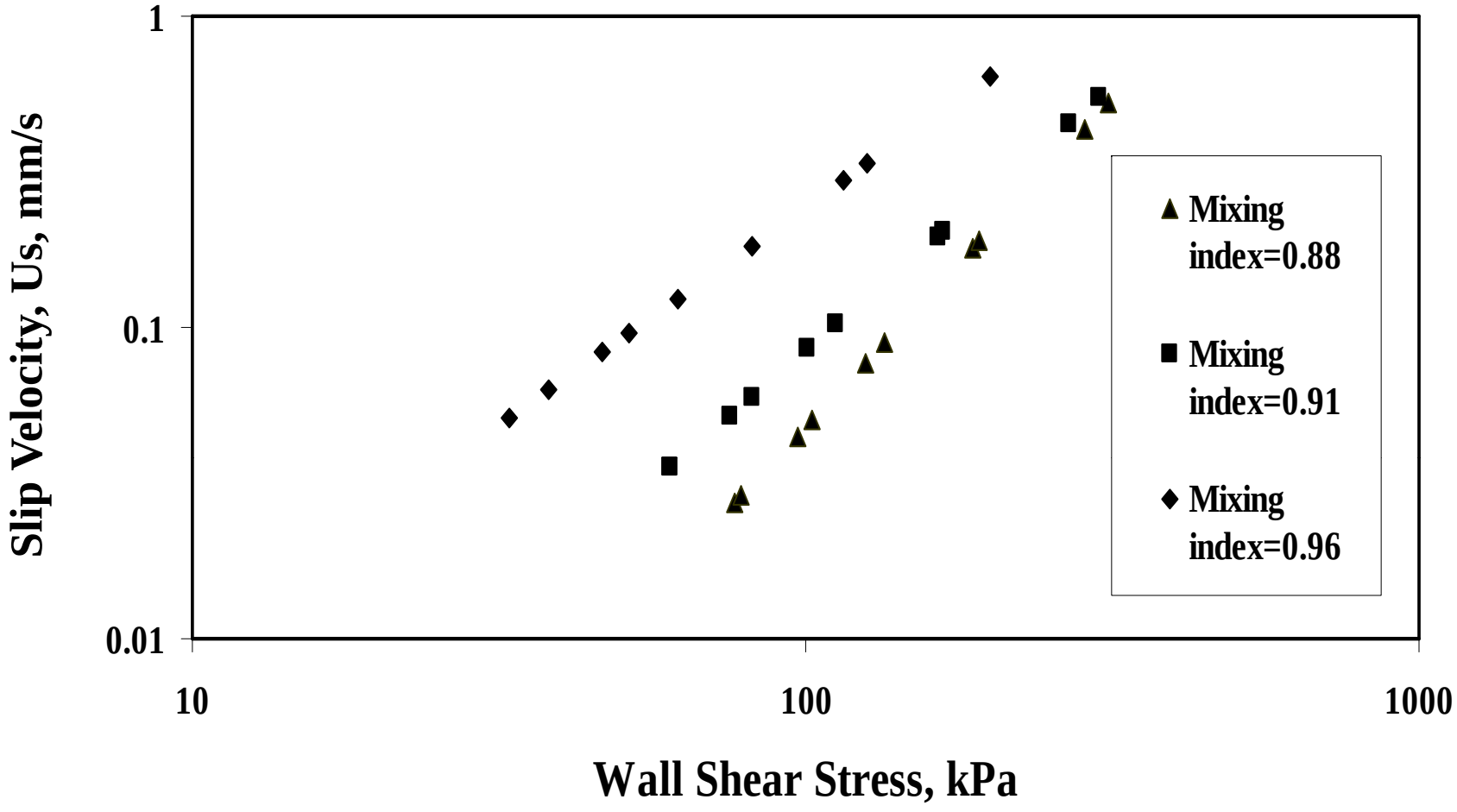

Bulk pressure, P (MPa)
1
0.8
0.6
0.4
0.2
0
-0.2
-0.1
0
0.1
0.2
Distance along extruder axis, z (m)
Forwarding
Fully-flighted Screws
100 Kg/h
80
60
40
Rectangular slit die


Bulk pressure, P (MPa)
1
0.8
0.6
0.4
0.2
0
-0.2
-0.1
0
0.1
0.2
Distance along extruder axis, z (m)
Forwarding
Fully-flighted Screws
60 rpm
90
120
150
Rectangular slit die

DEVELOPMENT OF TEMPERATURE DISTRIBUTIONS



Subtle effects can play a significant role in processing of highly filled suspensions



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

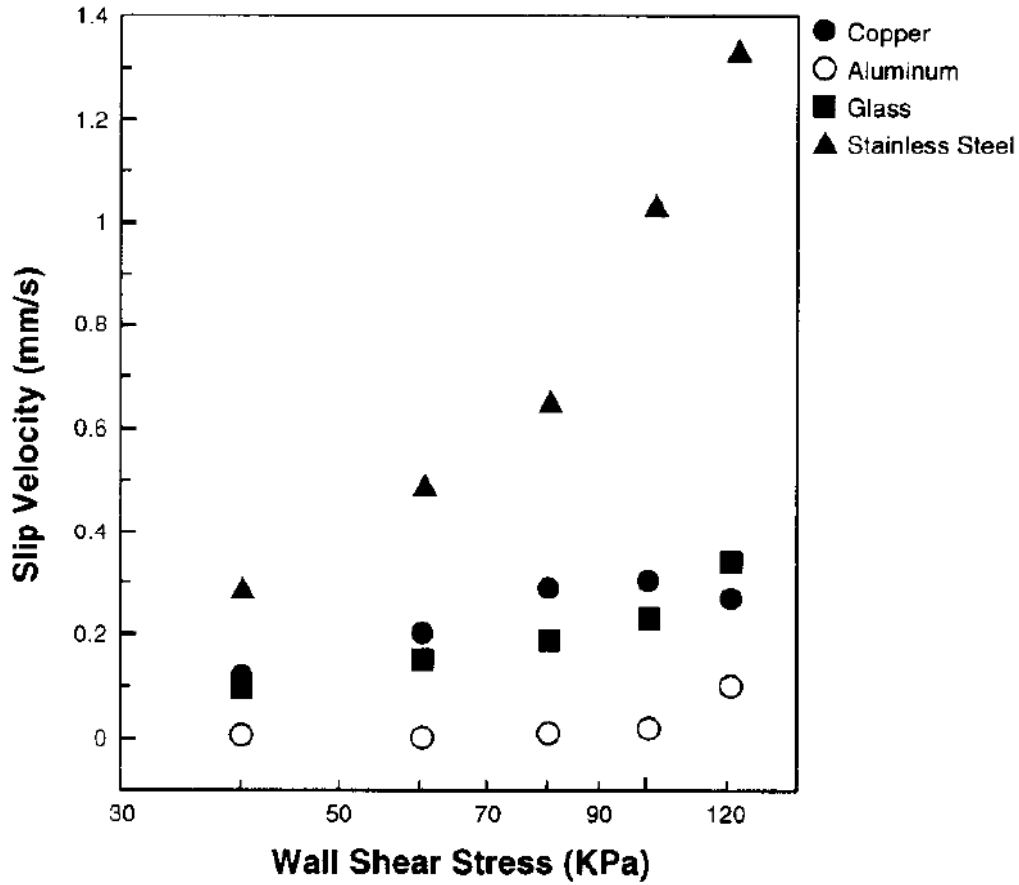
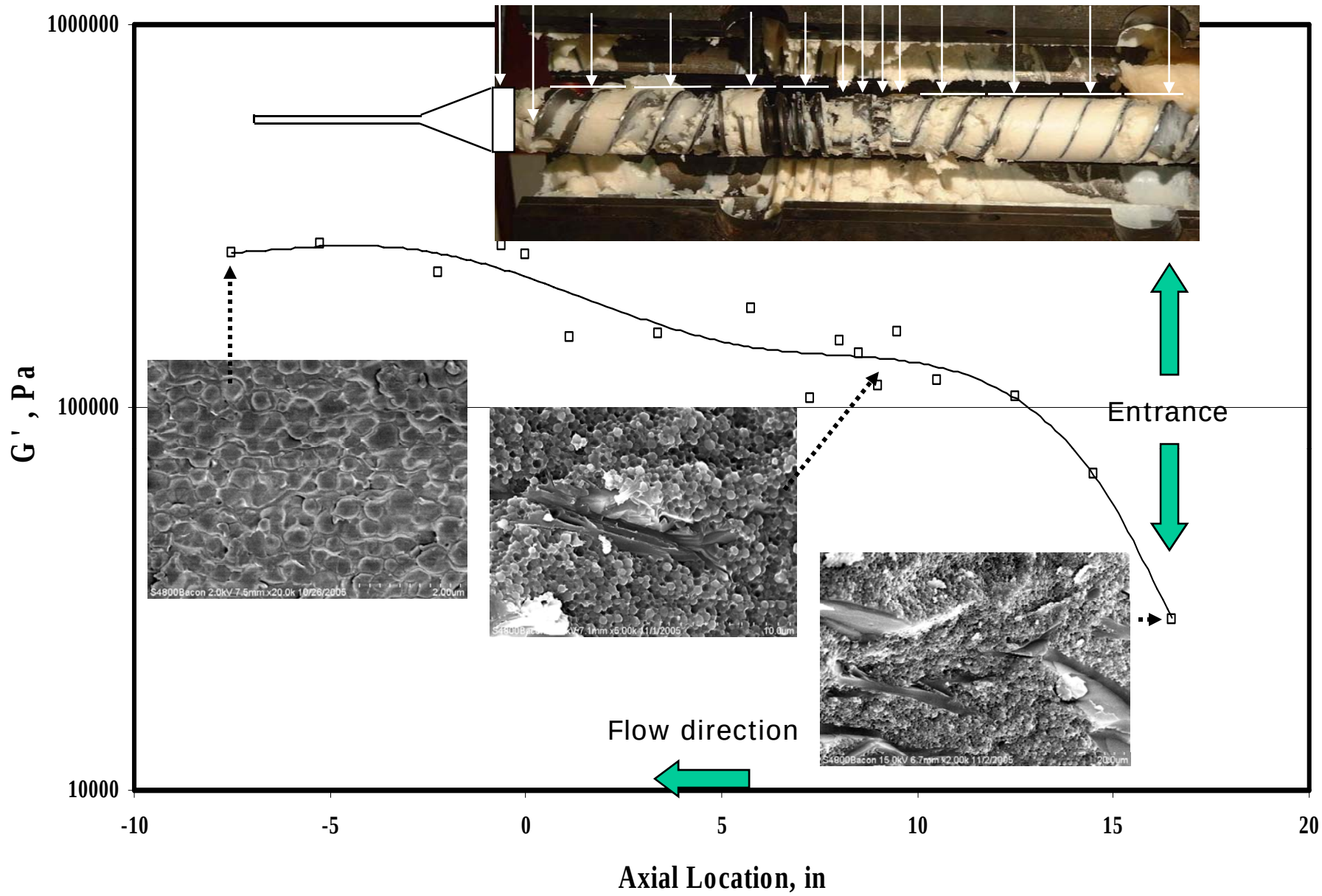
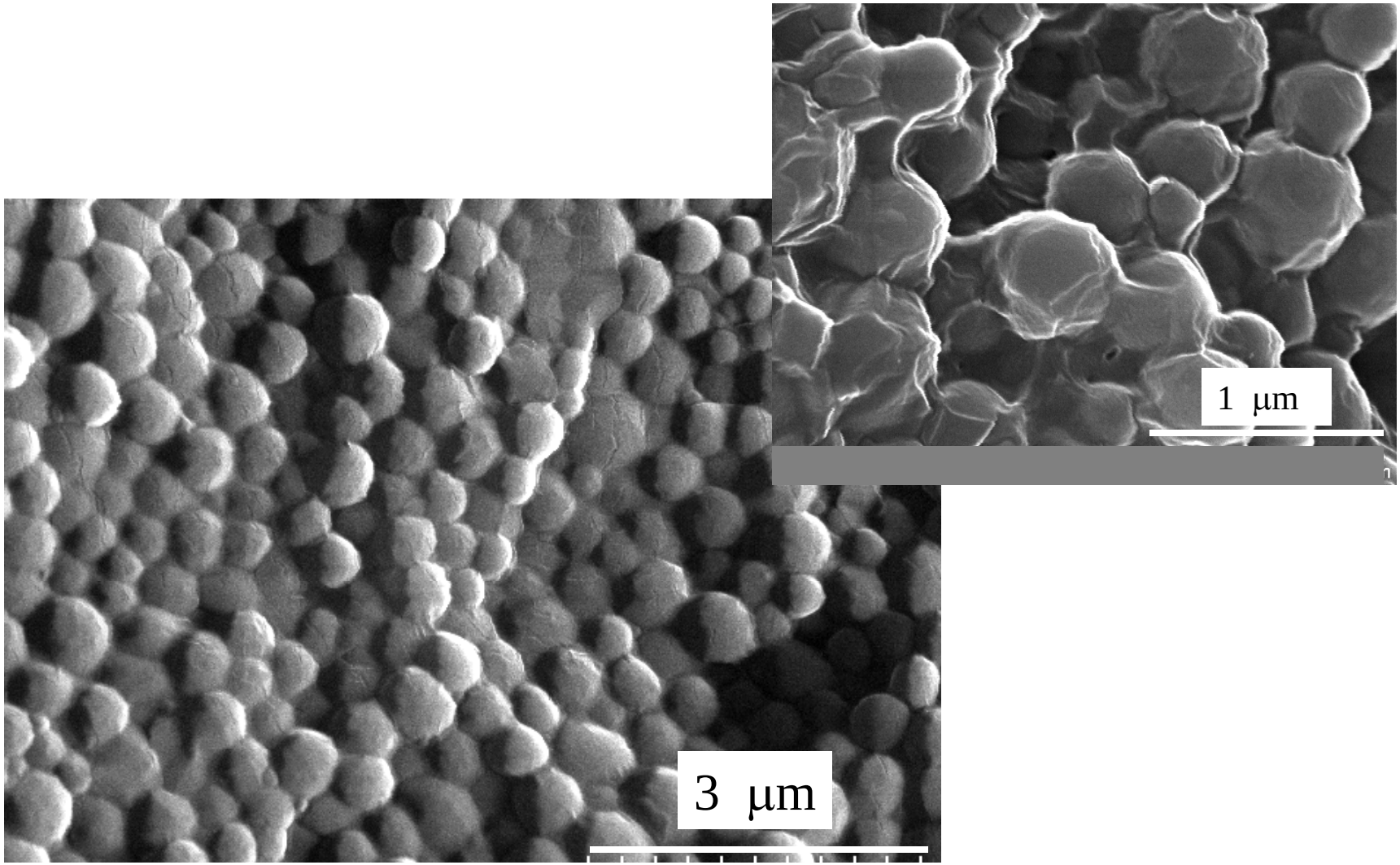


Figure 2 The slip velocity vs. shear stress of LLDPE melt, flow through various capillaries at 170°C with L/D of 57.6.

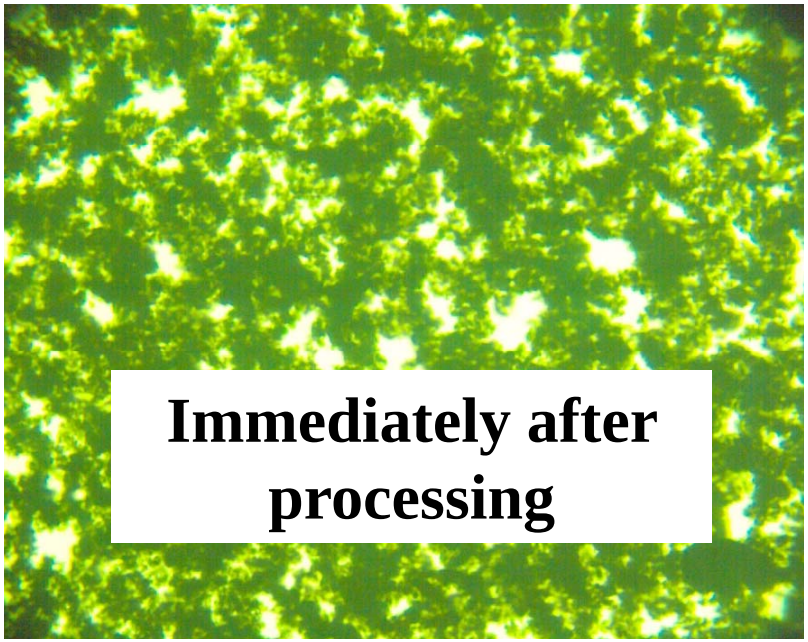


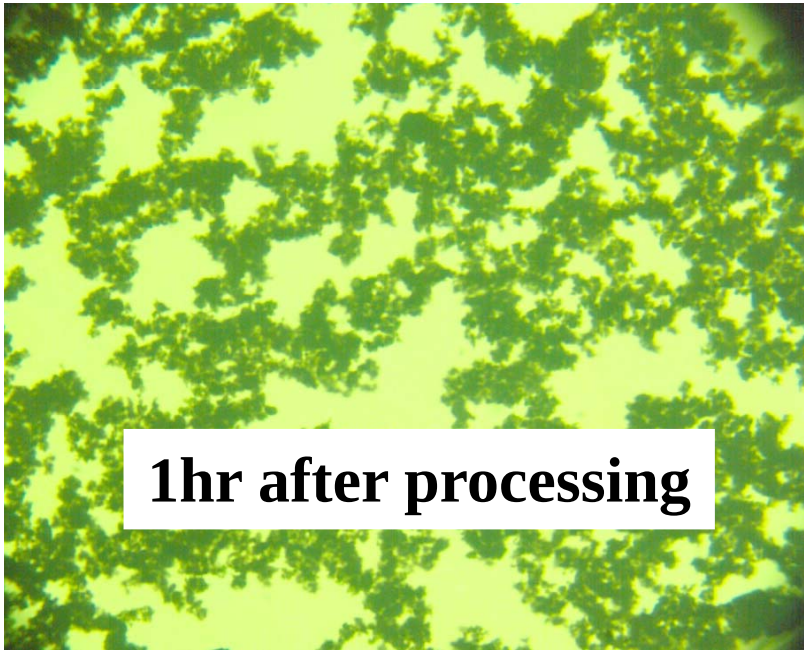
Development of the elasticity of the paste (represented by the storage modulus, G') upon pressurization and shearing based self-assembly in the twin screw extruder



Formation of multi-layered vesicles of LAS paste upon the drag and pressure induced deformation in the twin screw extrusion flow.

Time matters!

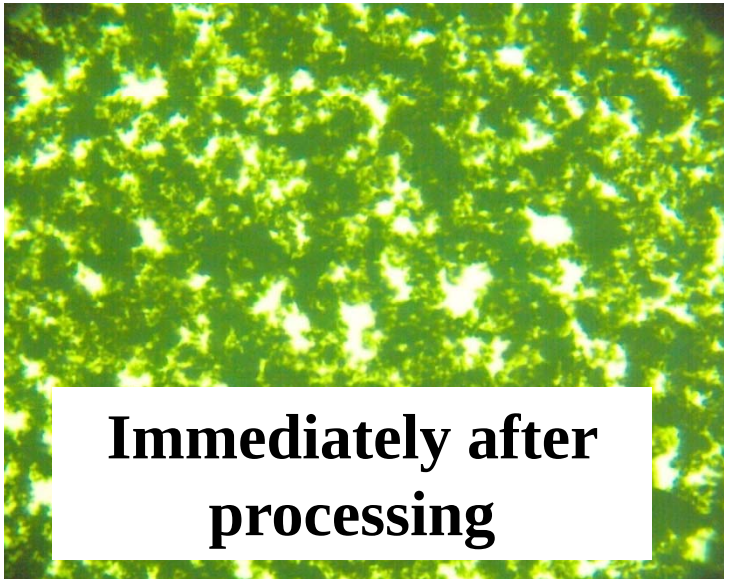


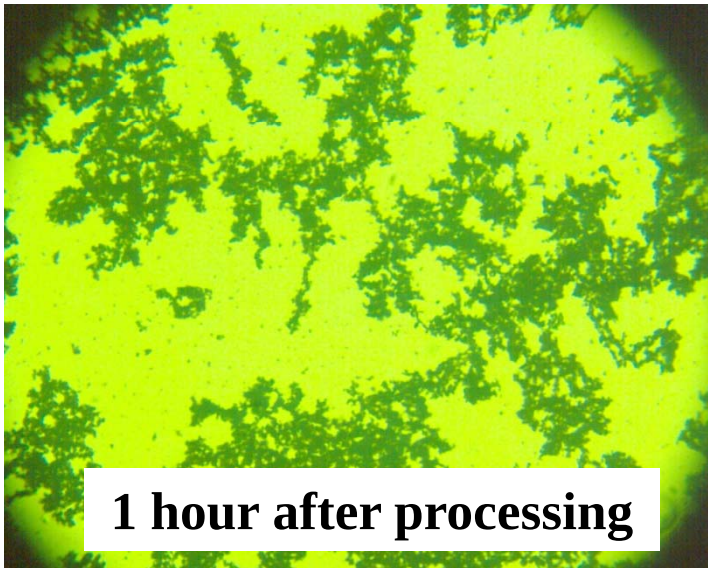


1% C nanotubes

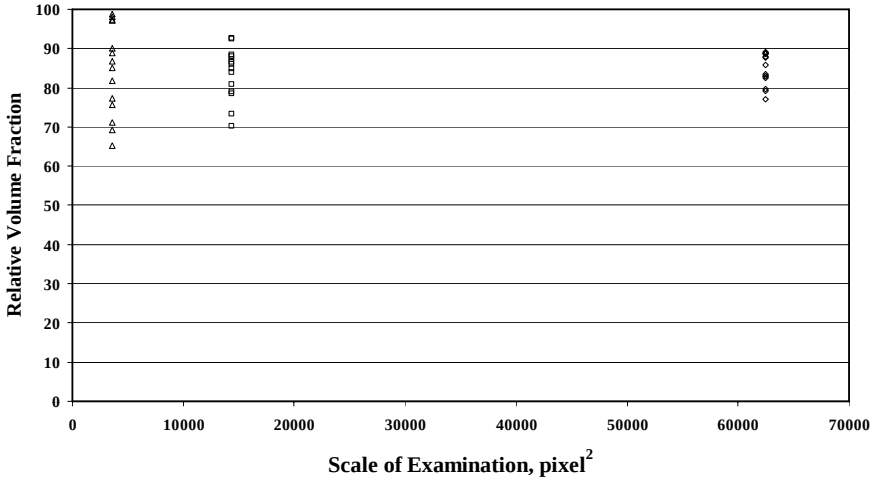
-99% PEG 600

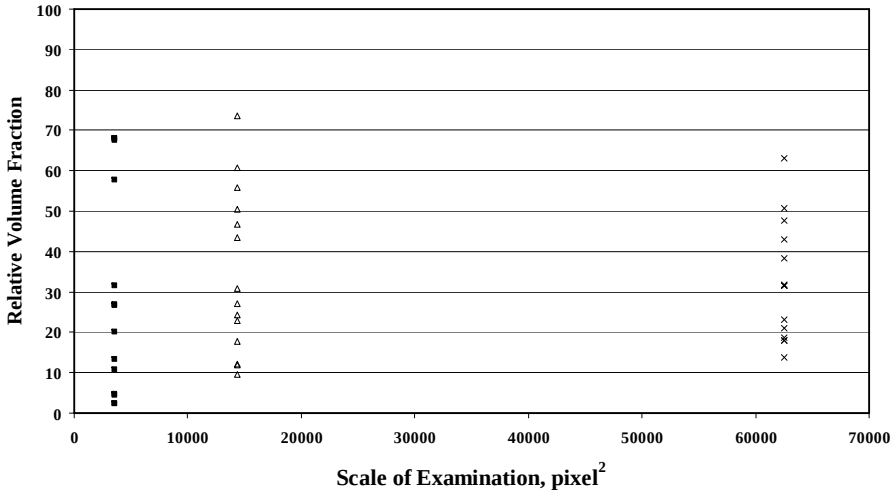
Degree of mix changes!



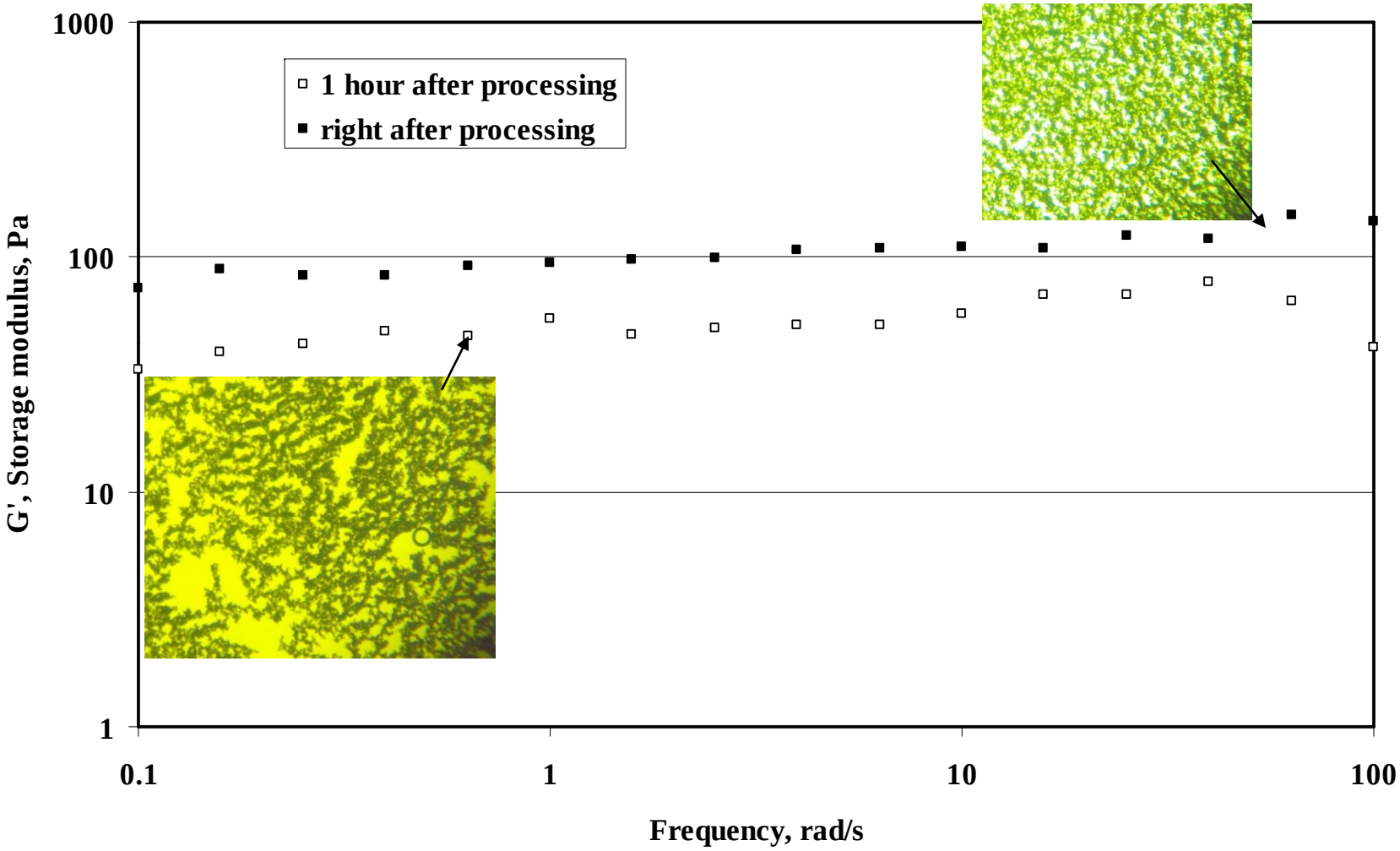


1%CNT-99% PEG 600



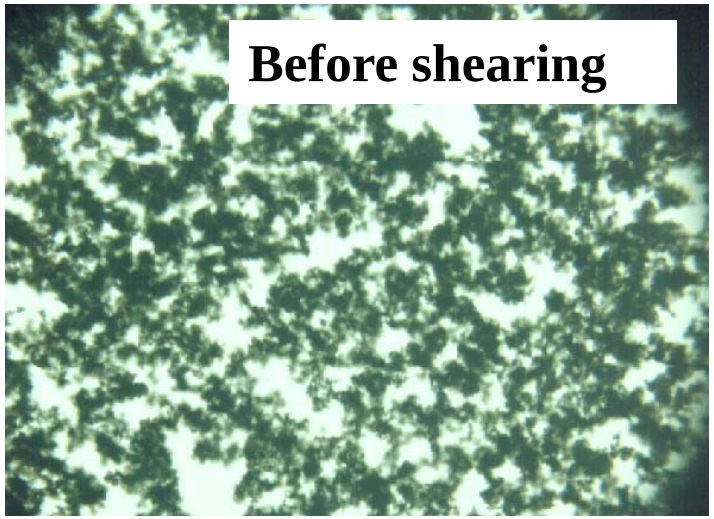


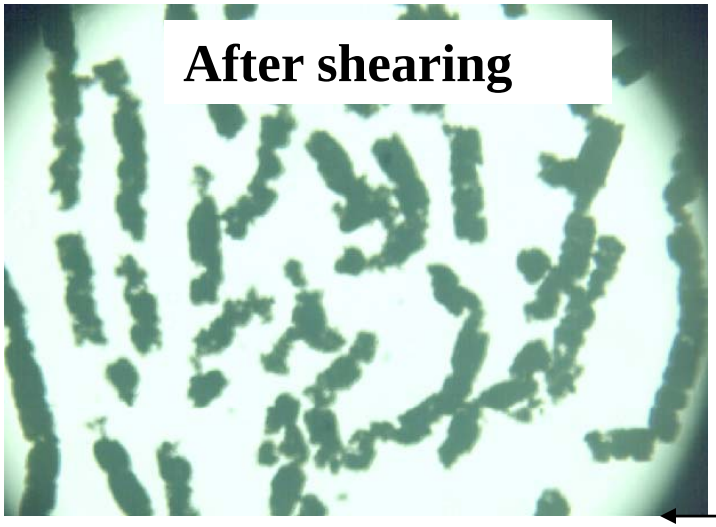
Rheological behavior changes!



Dynamic properties decrease over time

as the CNT particles flocculate





Shear matters!

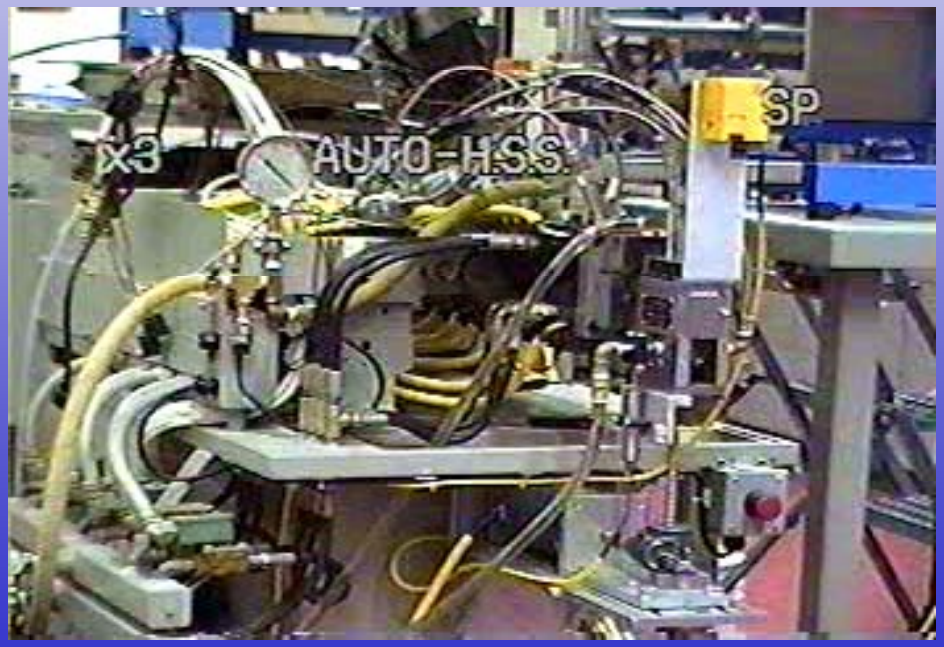
1% CNT+99% PEG600

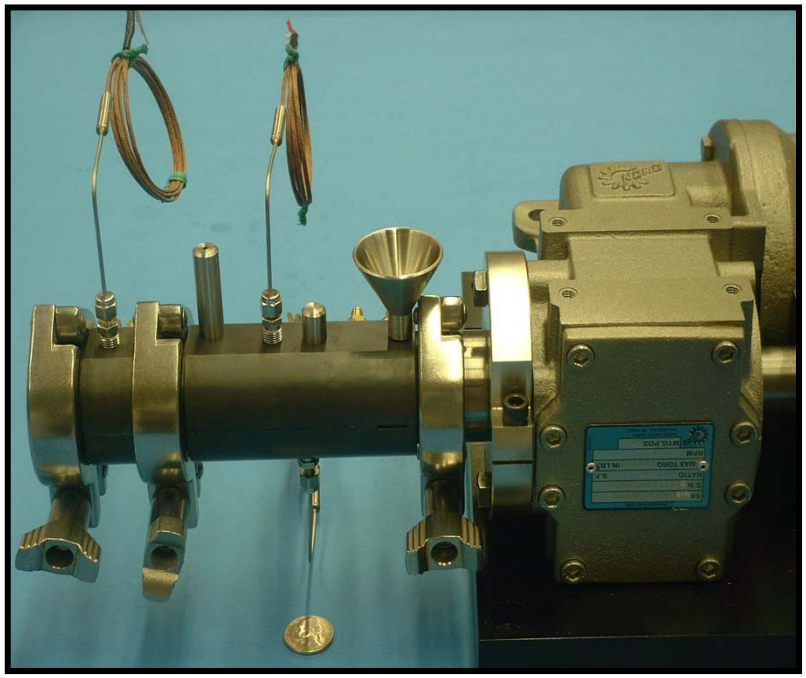
Particles flocculate

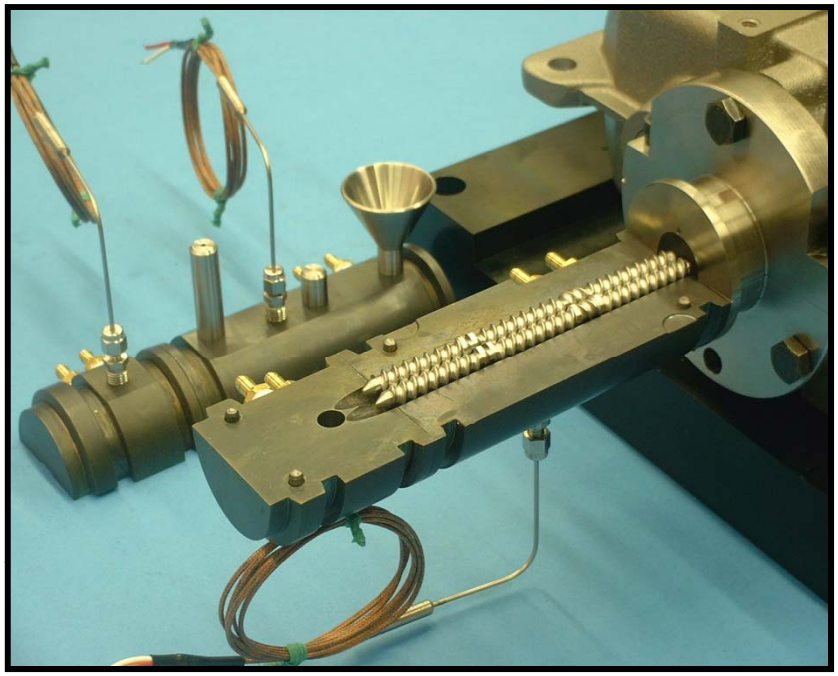
and orient upon shearing

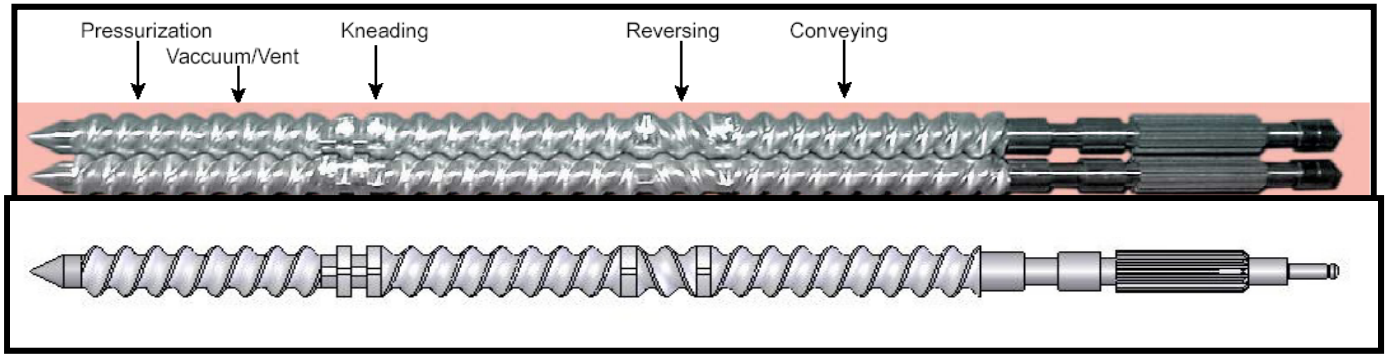
How do we validate the rheological/thermal behavior and modeling?

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









MPR 7.5 mm twin screw extruder used at HfMI for the processing of nanocomposites

Continuous mixer facility

Universal twin screw extruder

Single Screw

Twin Screw

Shear Roll Mill

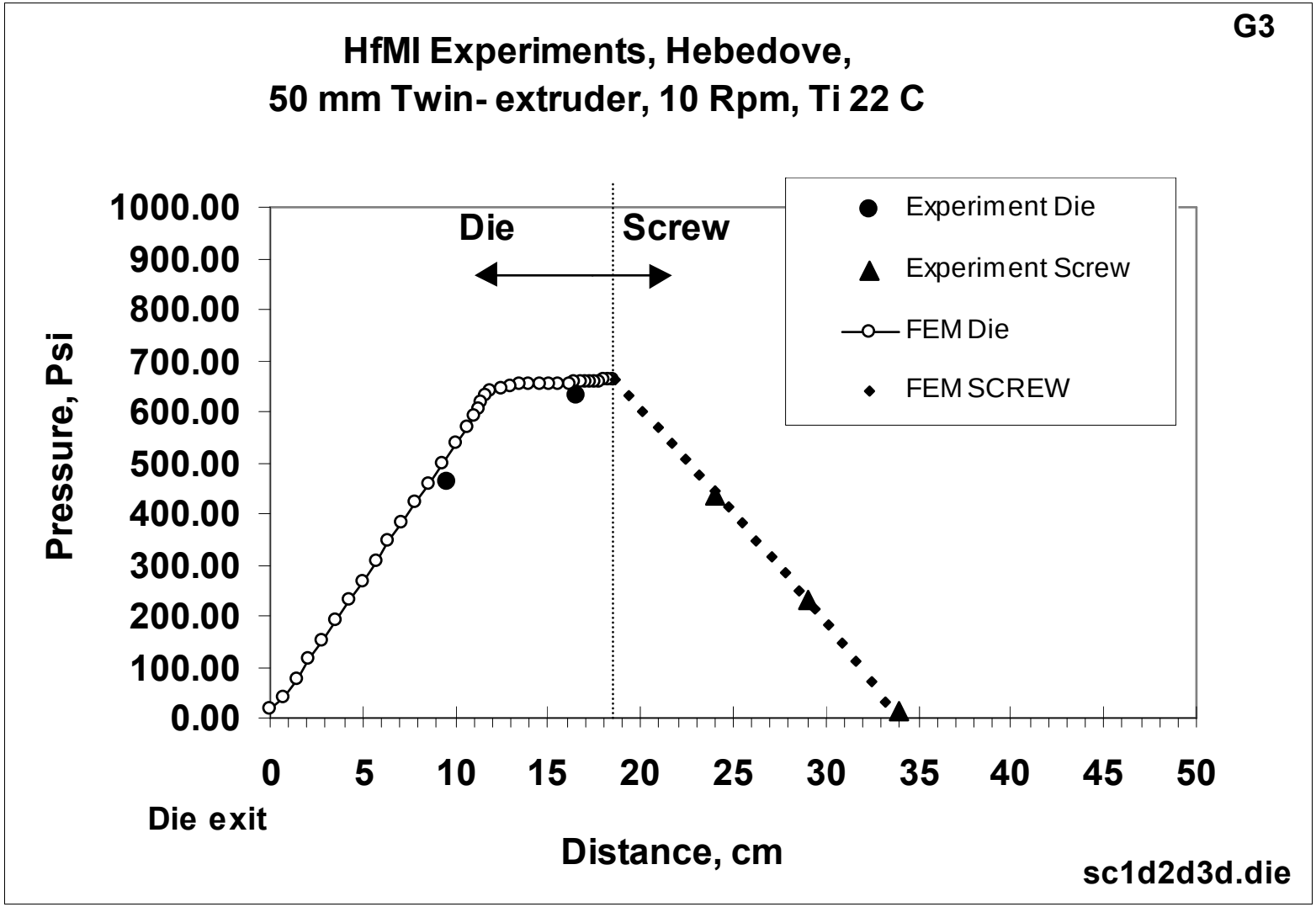
Co-rotating

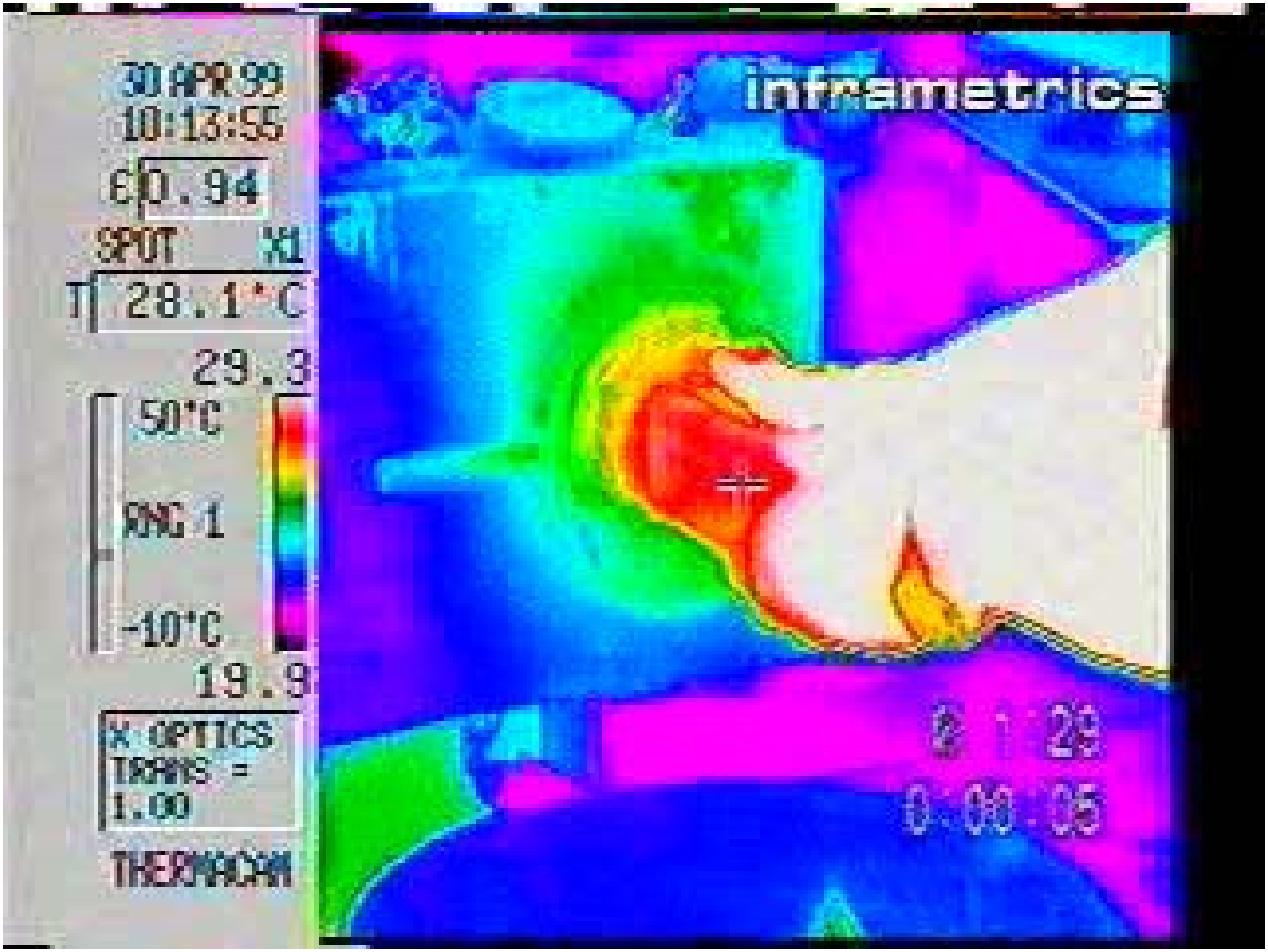
Counter-rotating

Fully-Intermeshing

Tangential

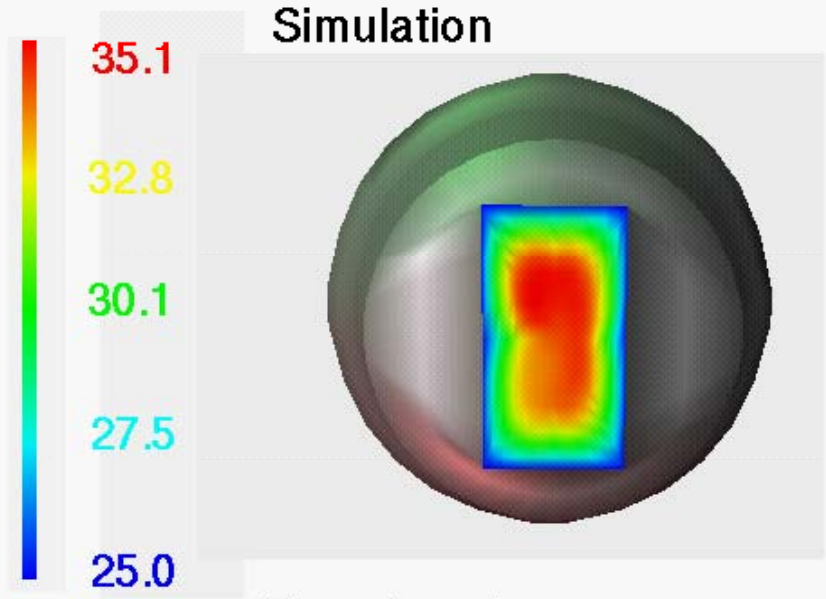
SIT Universal twin screw extruder: Co, counter, tangential, fully-intermeshing, Adjustable length, split barrel with hydraulic opening, field point based data acquisition.and process control.


G3
HfMI Experiments, Hebedove,
50 mm Twin- extruder, 10 Rpm, Ti 22 C
Pressure, Psi
1000.00
900.00
800.00
700.00
600.00
500.00
400.00
300.00
200.00
100.00
0.00
Die
Screw
Experiment Die
Experiment Screw
FEM Die
FEM SCREW
0
5
10
15
20
25
30
35
40
45
50
Die exit
Distance, cm
sc1d2d3d.die

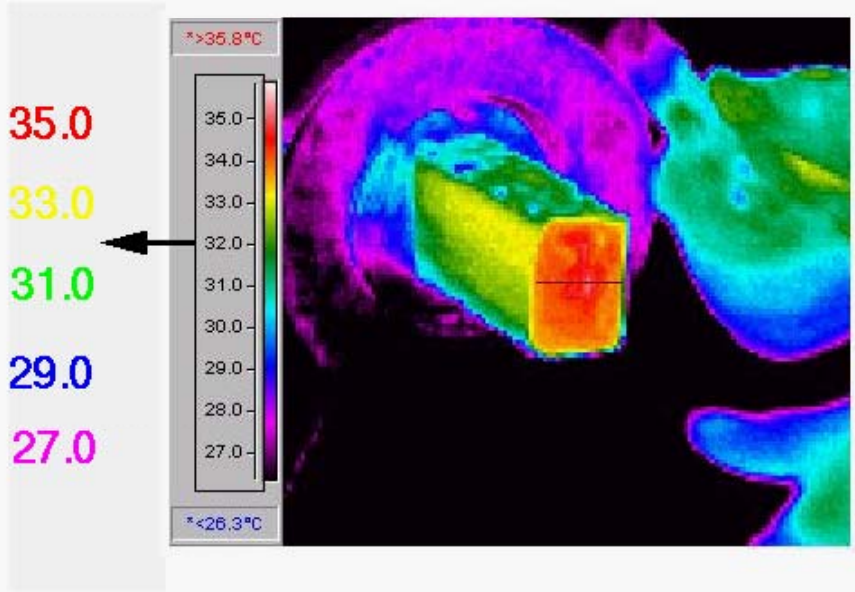

30 APR 99
10:13:55
ε 0.94
SPOT X1
T 28.1°C
29.3
50°C
RNG 1
-10°C
19.9
X OPTICS
TRANS =
1.00
THERMACAM
inframetrics

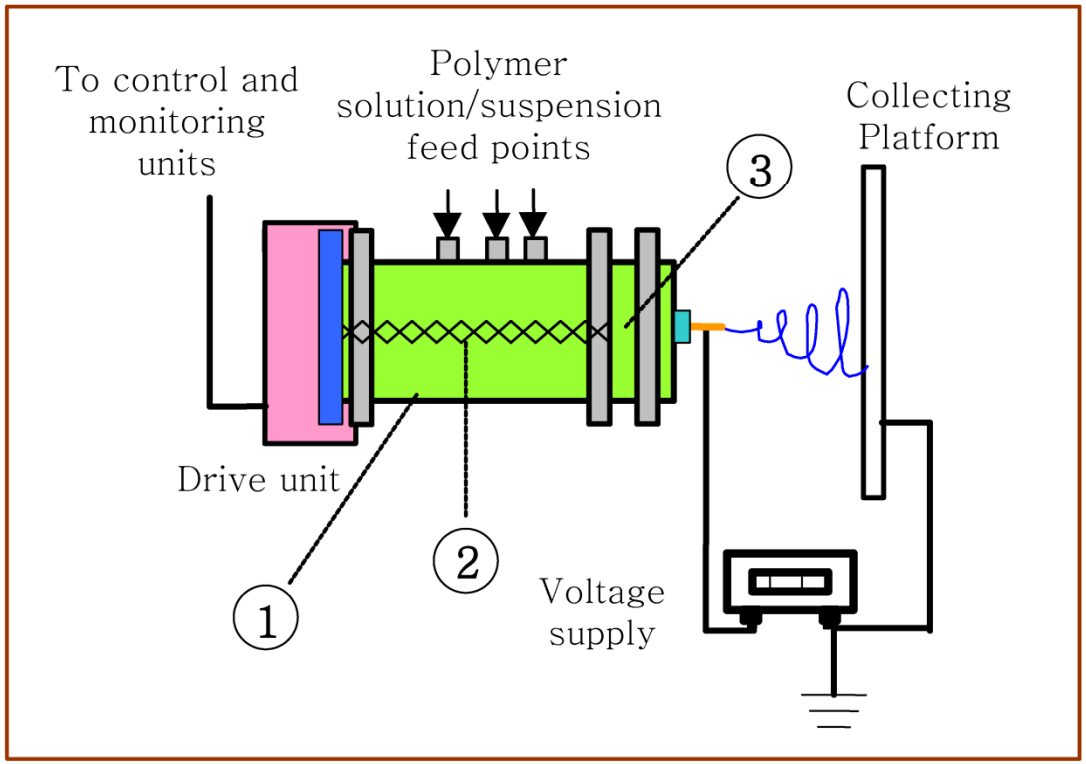
UNILEVER, MAZZONI EXTRUDER AND DIE

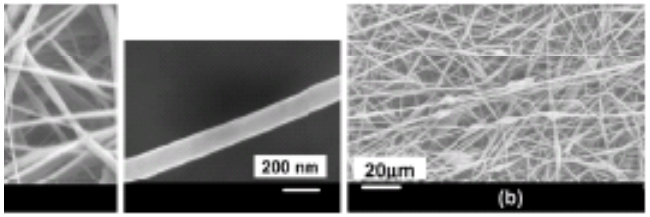
Simulation

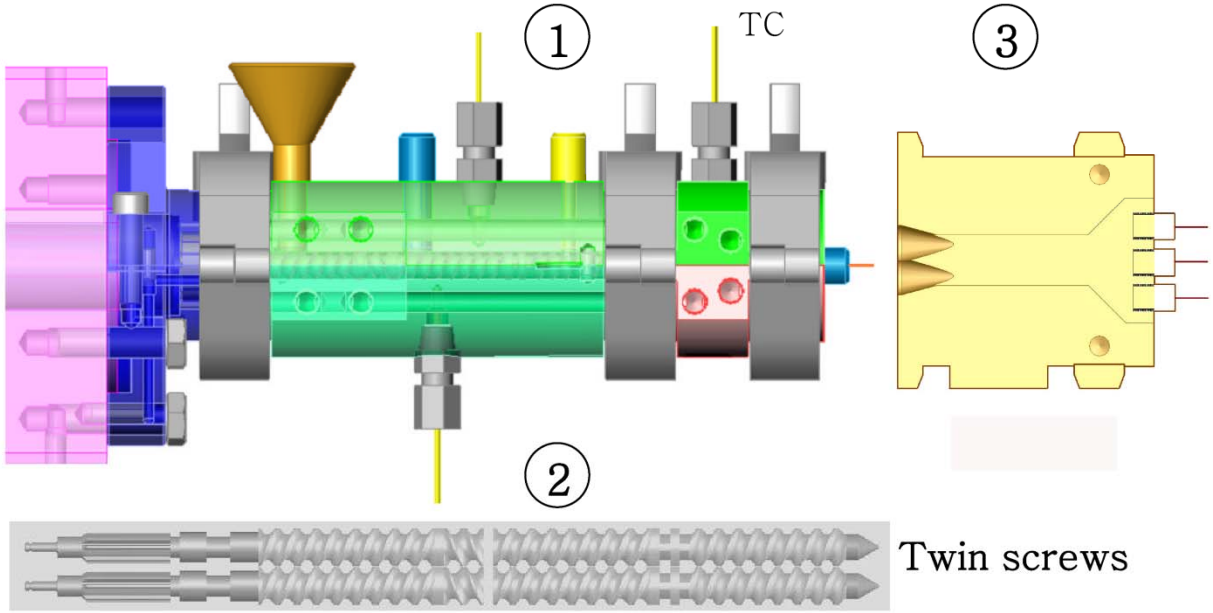


Experiment









Generation of nanofibers with nanoparticles

HfMI technology:
TSE with electrospinning

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