Rheological Behavior of Energetic Materials: Challenges and Opportunities

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The rheological characterization of energetic materials is a challenging task.

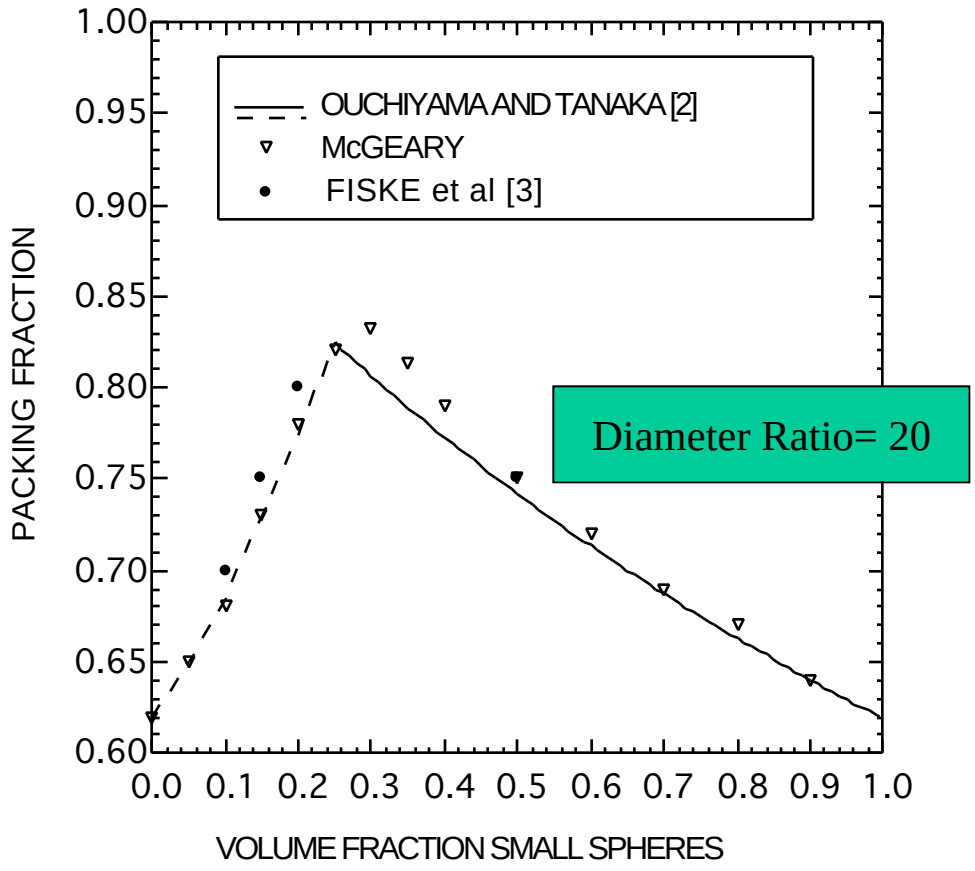
- Challenge stems from the highly solid filled nature of such materials
- Viscoplasticity
- Wall slip, which renders collecting reliable and relevant data very difficult.
- Structuring effects
- Use of high molecular weight polymers

Various Time-dependent Phenomena

- Formation of gross surface irregularities
- Development of concentration gradients for the solid and liquid ingredients upon their migration in the flow and transverse to flow directions
- Solvent evaporation
- Fibrillation and orientation effects.

Tools

- Structure characterization together with rheometry
- On-line rheometry
- Squeeze flow rheometry
- Merge extrusion with structure characterization and rheological characterization
- Use of non-linear constitutive equations for the polymer phase.



MAXIMUM PACKING FRACTION BIMODAL DISTRIBUTION OF SPHERICAL PARTICLES

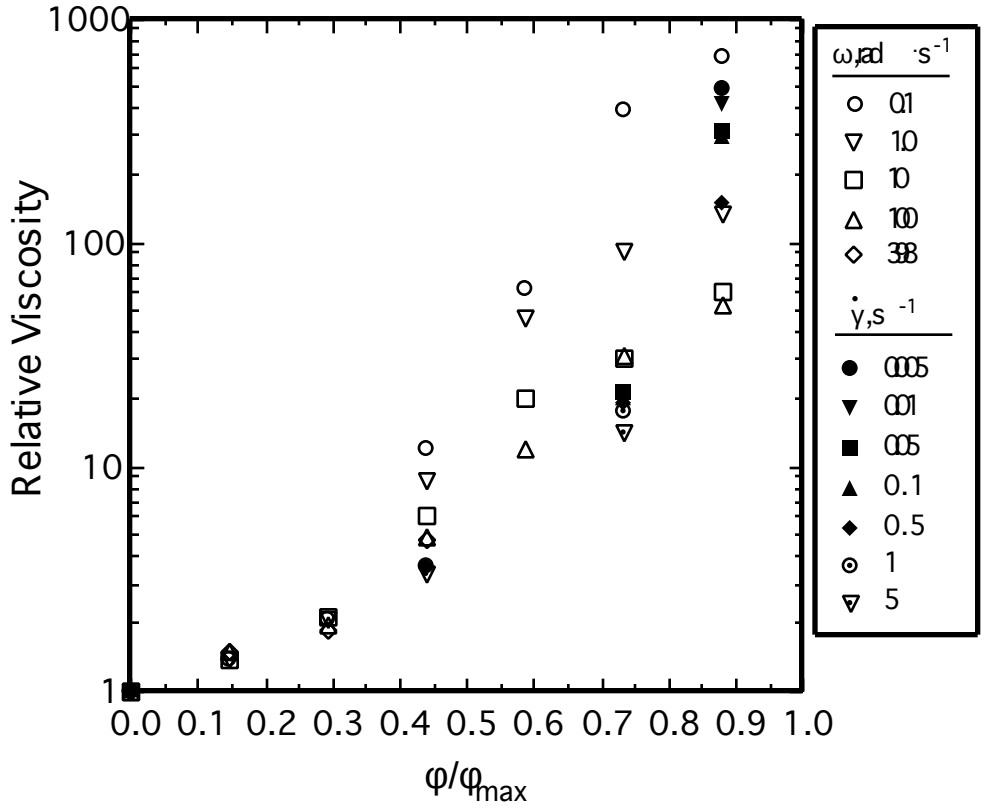


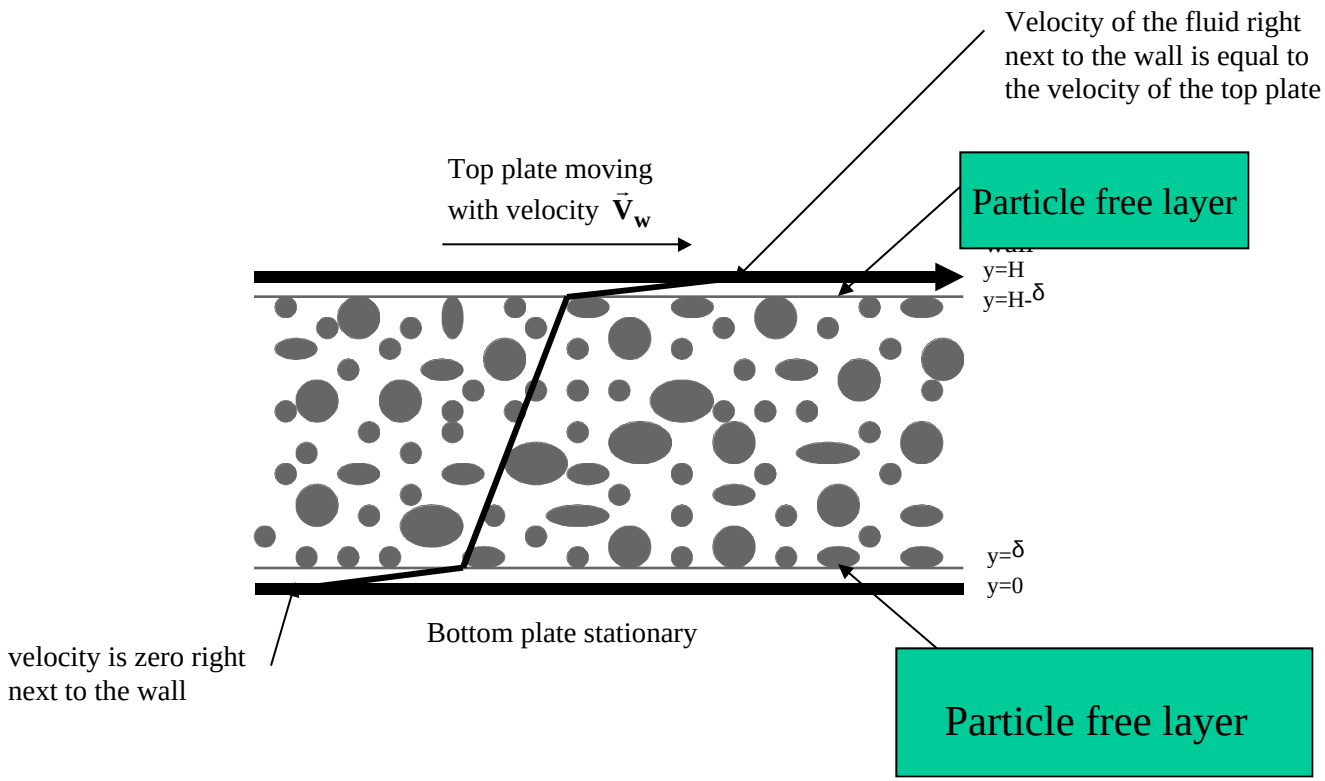
Figure 13: The effect of filler concentration on the relative viscosity of the suspensions.

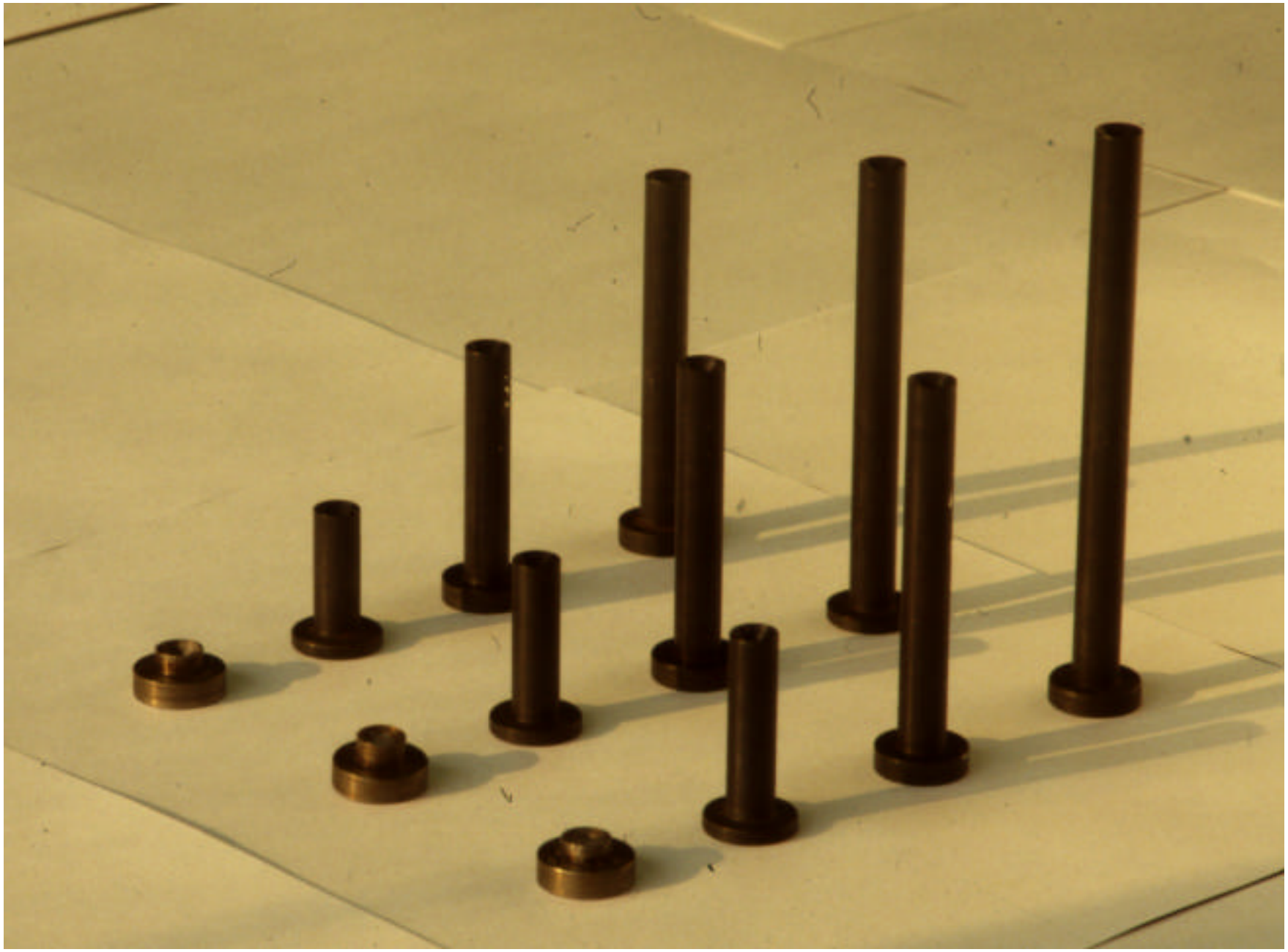
PREPARATION AND RHEOLOGICAL CHARACTERIZATION OF FILLED POLYMERS

- Apparent wall slip
- Entrainment of air and its role in shaping apparent wall slip and rheological behavior
- Migration of the particles and the binder phase, non-homogeneous suspensions
- State of the distributive and dispersive degree of mixedness of the ingredients
- Changes in physical properties of ingredients

Apparent wall slip in filled polymers

- Occurs on the basis of the formation of a particle-free apparent slip layer (Vand Layer)
- Alters apparent rheological behavior
- Needs to be incorporated into simulation as the wall boundary condition (Navier's slip condition)





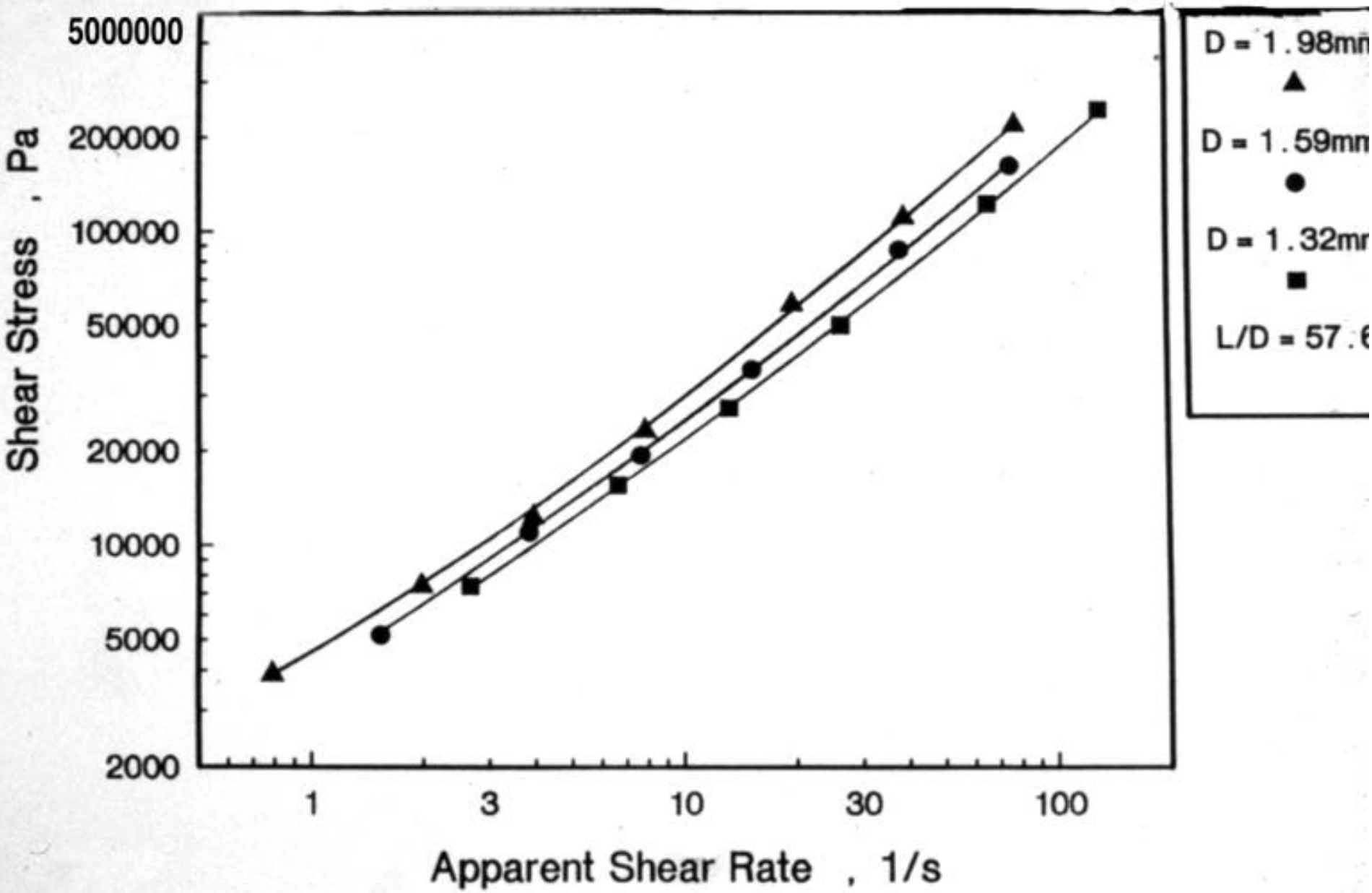

5000000
200000
100000
50000
20000
10000
5000
2000
Shear Stress , Pa
1
3
10
30
100
Apparent Shear Rate , 1/s
D = 1.98mm
D = 1.59mm
D = 1.32mm
L/D = 57.6

Figure 3

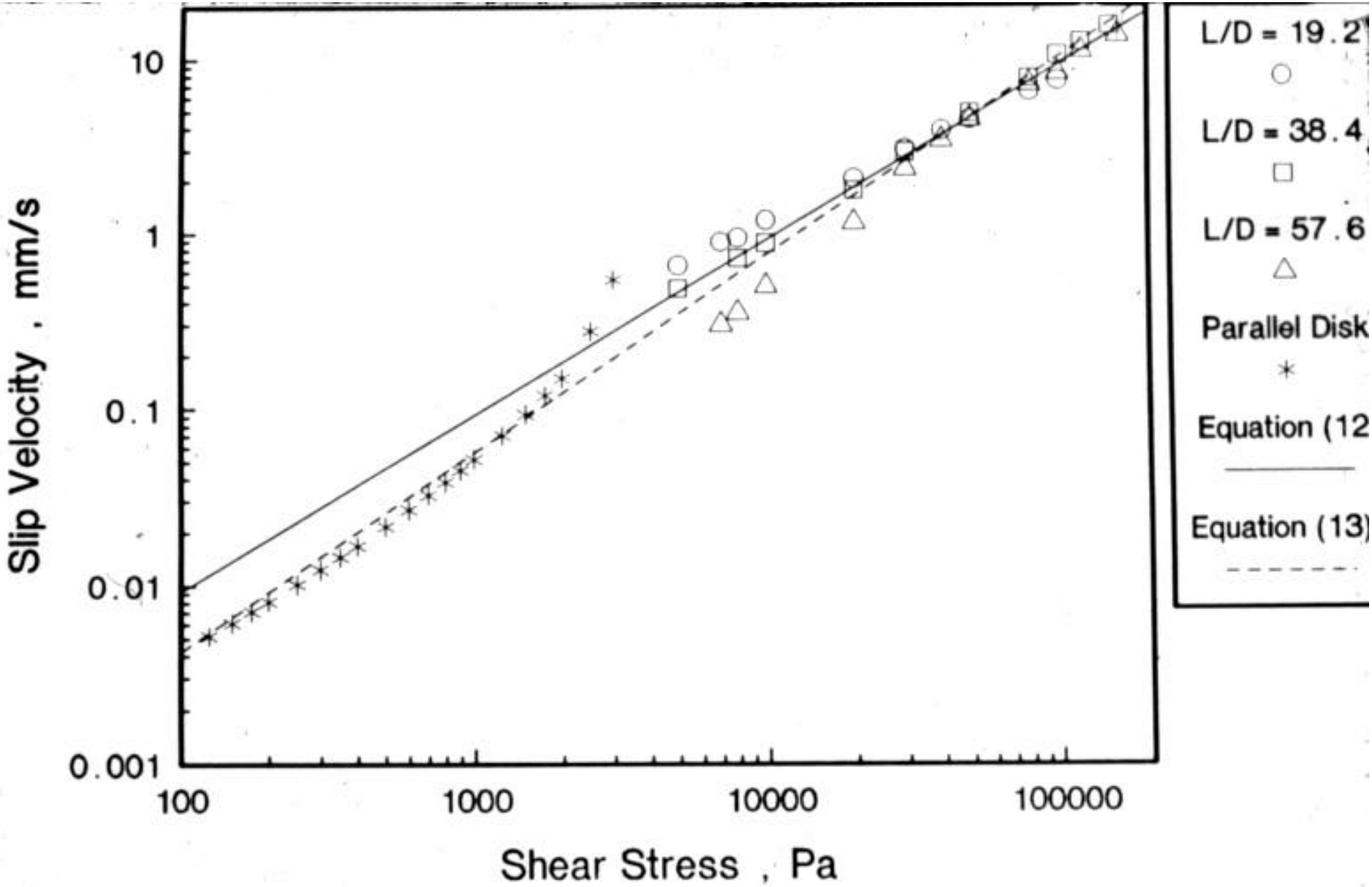
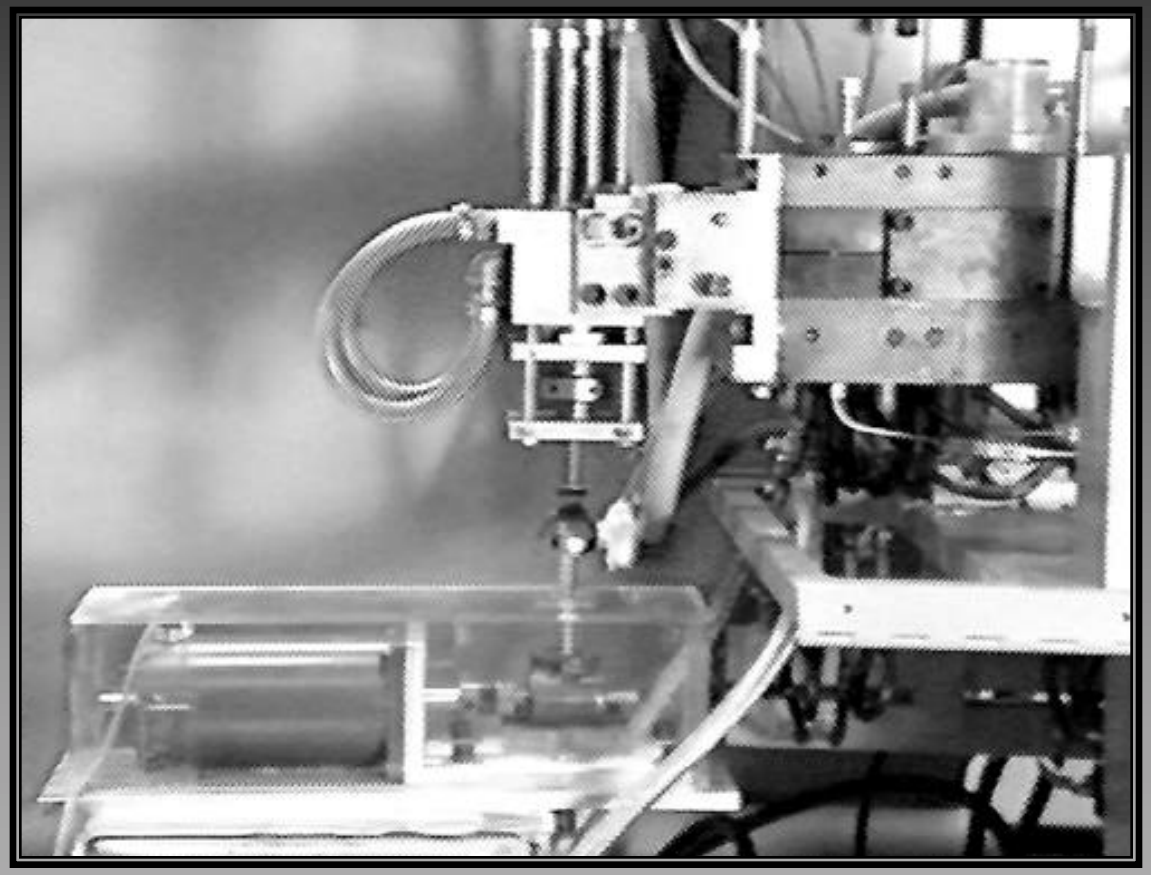

Slip Velocity , mm/s
10
1
0.1
0.01
0.001
100
1000
10000
100000
Shear Stress , Pa
L/D = 19.2
L/D = 38.4
L/D = 57.6
Parallel Disk
Equation (12
Equation (13)

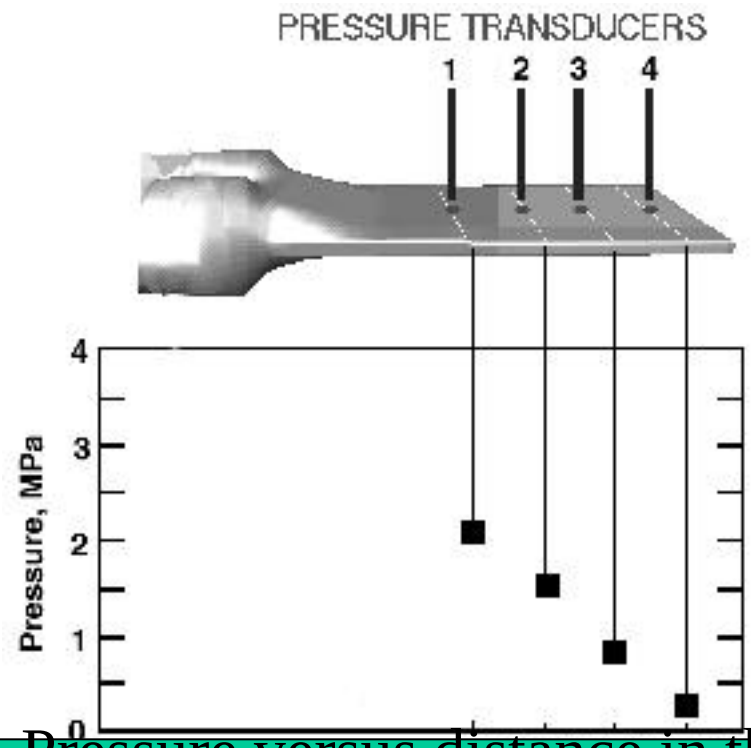
Figure 5

ADJUSTABLE GAP RHEOMETER



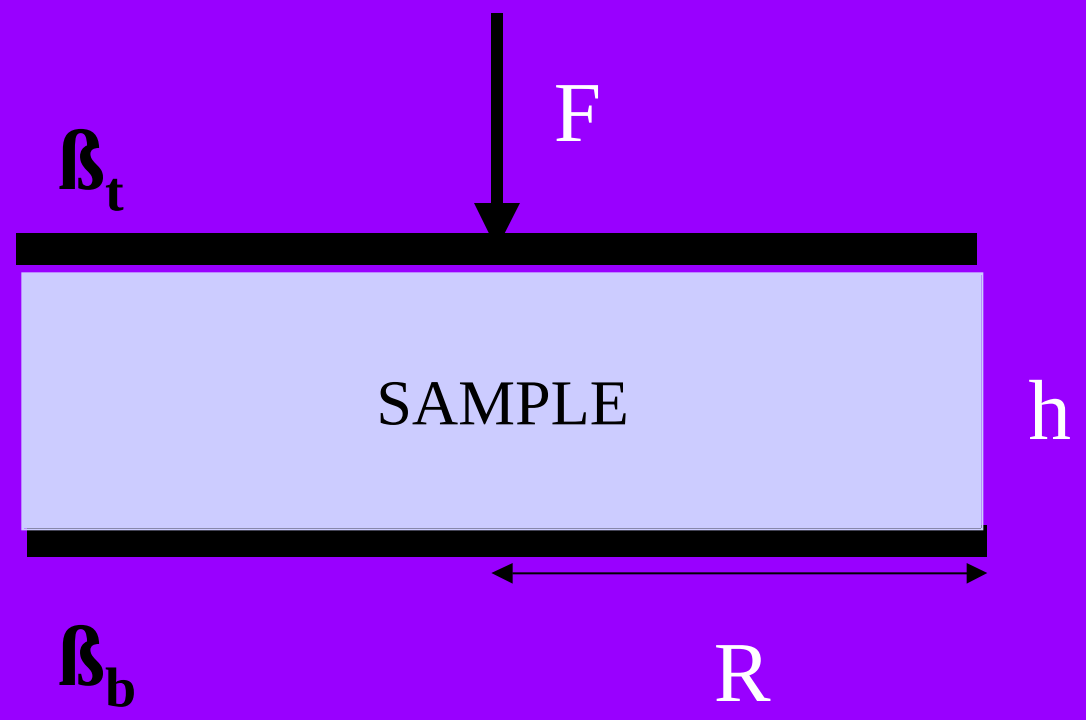
ADJUSTABLE GAP RHEOMETER

Ability to alter the flow rate and the gap of the slip independently provides the basic platform for slip correction

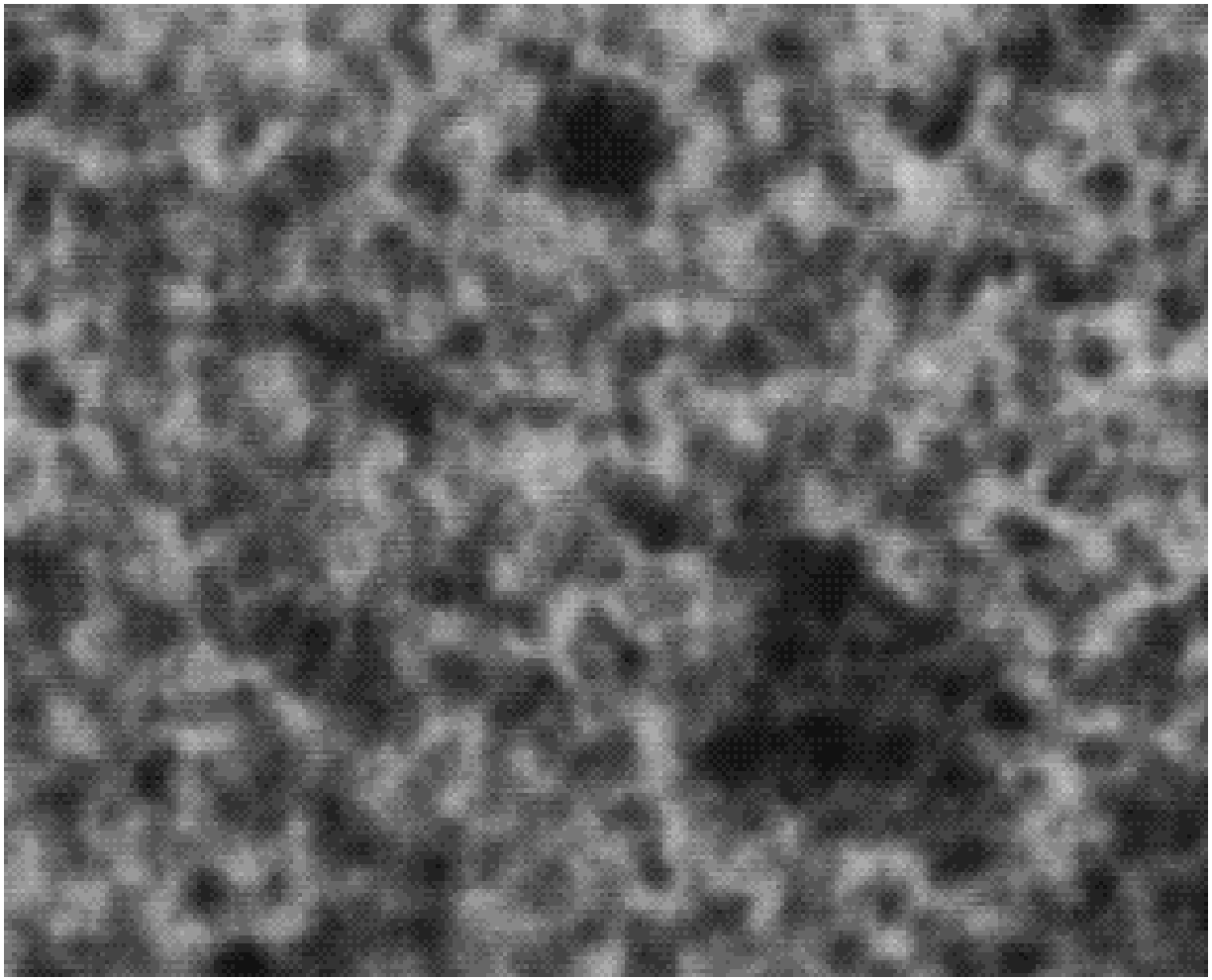


Pressure versus distance in the die

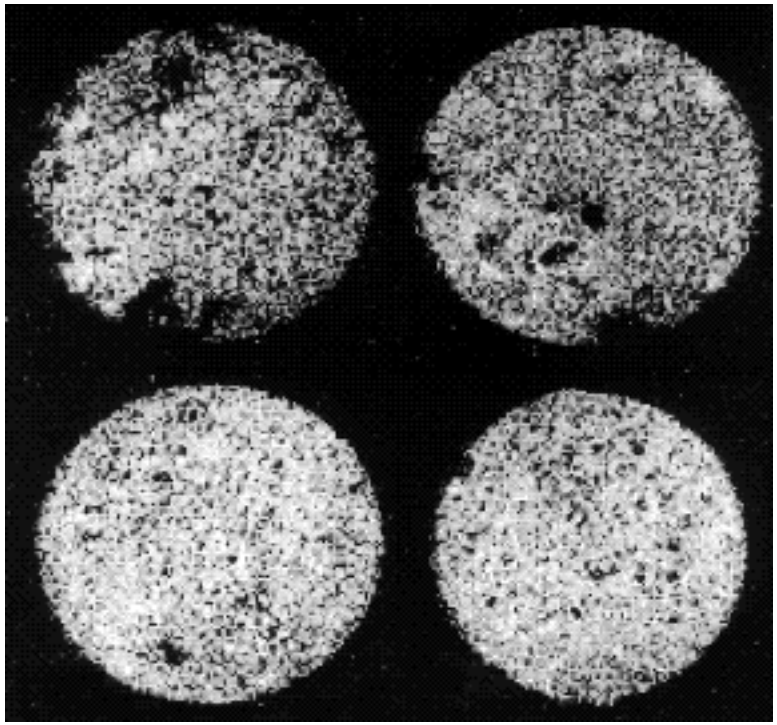
Compressive Squeeze Flow



Entrainment of Air into Suspensions: Demo using x-ray Radiography, darker regions are air in Al/Amm.Sulfate suspension in PBAN

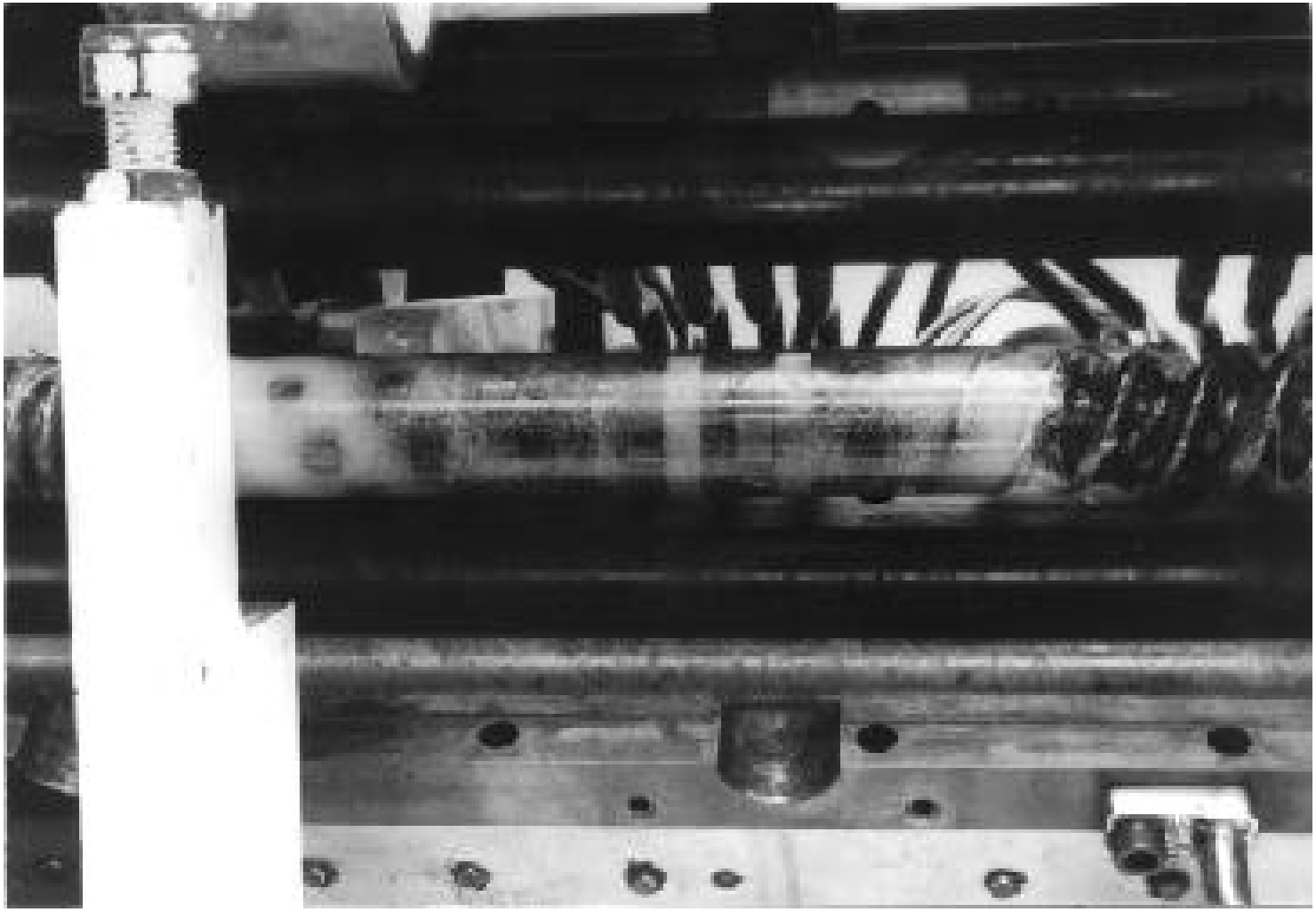


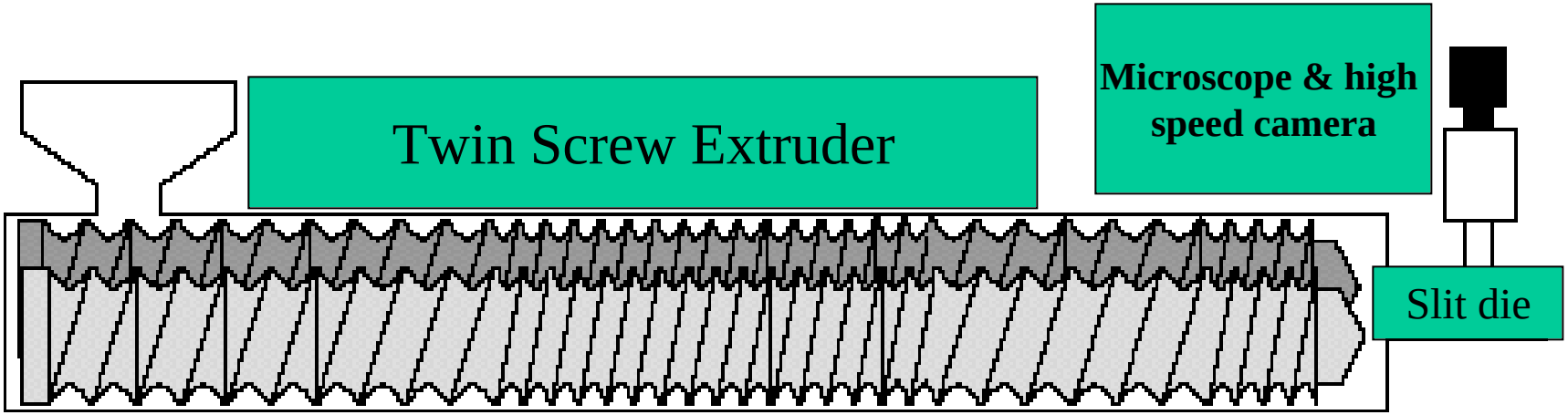
Air Entrainment into Filled Polymers: Demo using MRI



Lockheed results on the same suspension

The elastomer is opaque when significant air is introduced in the extruder

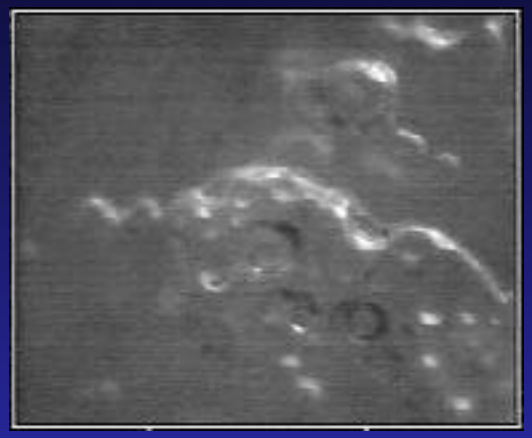




Experimental set-up to investigate
the velocity distribution in the slit die

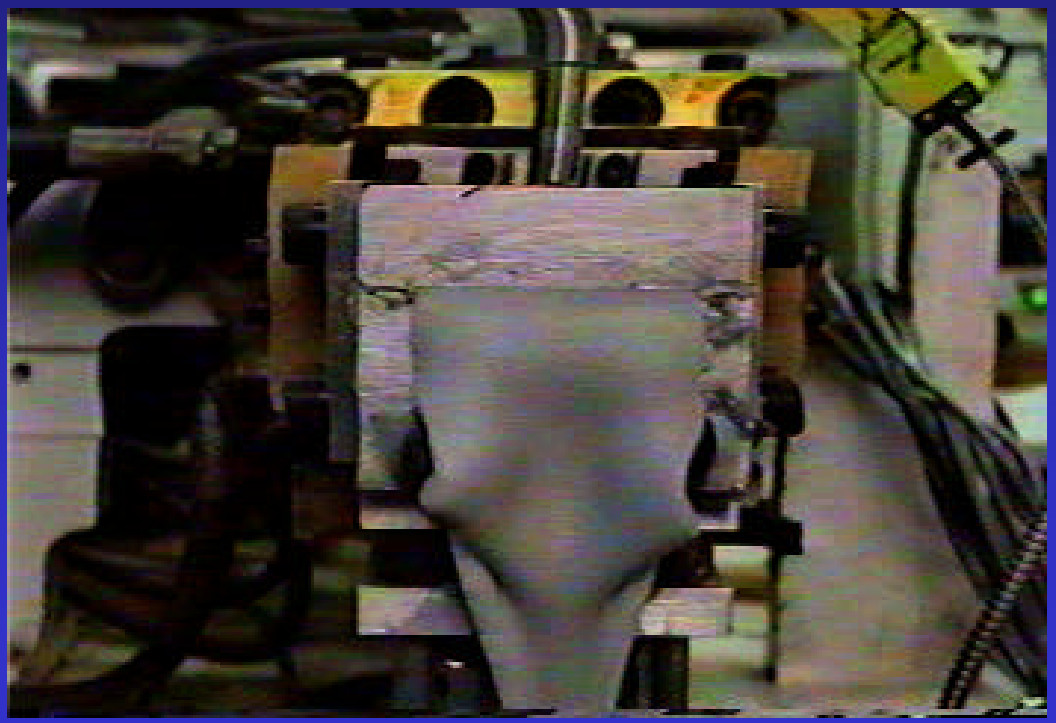
Air lubricates the wall of the die at exit of the die

Camera at 500-1000 fps

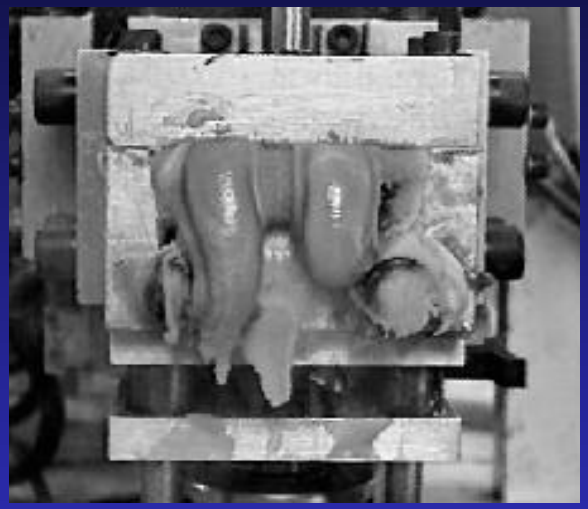


Reduction of the air content of a filled polymer alters its processability in the extruder (a)

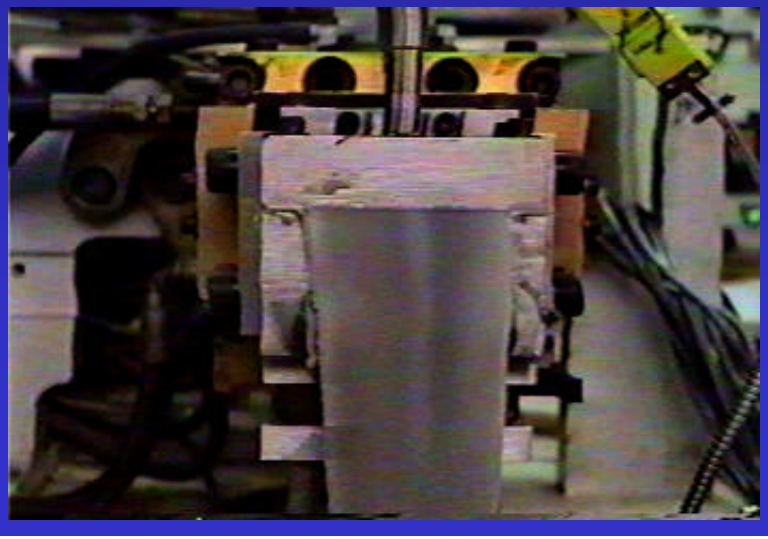
No vacuum



Reduction of the air content of a filled polymer alters its processability in the extruder (b)



Upon the application of vacuum



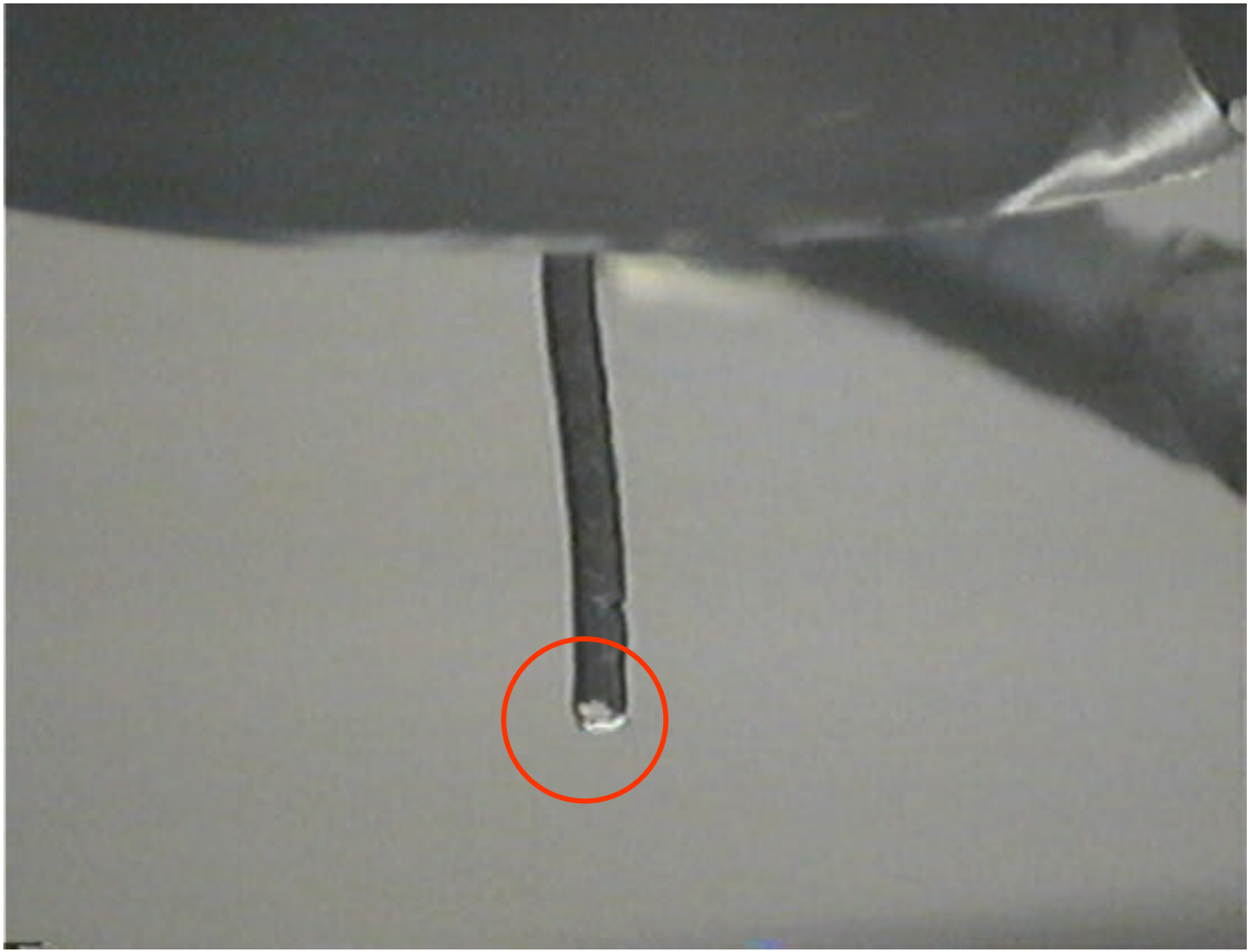
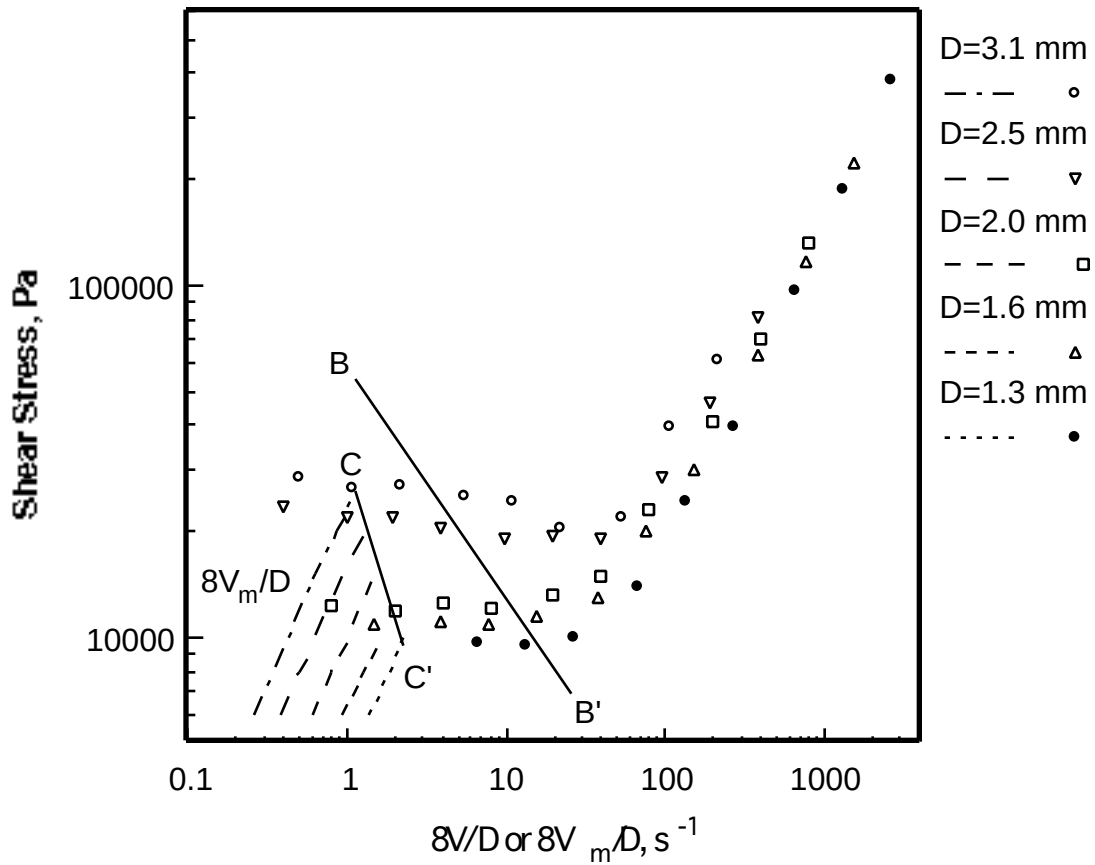
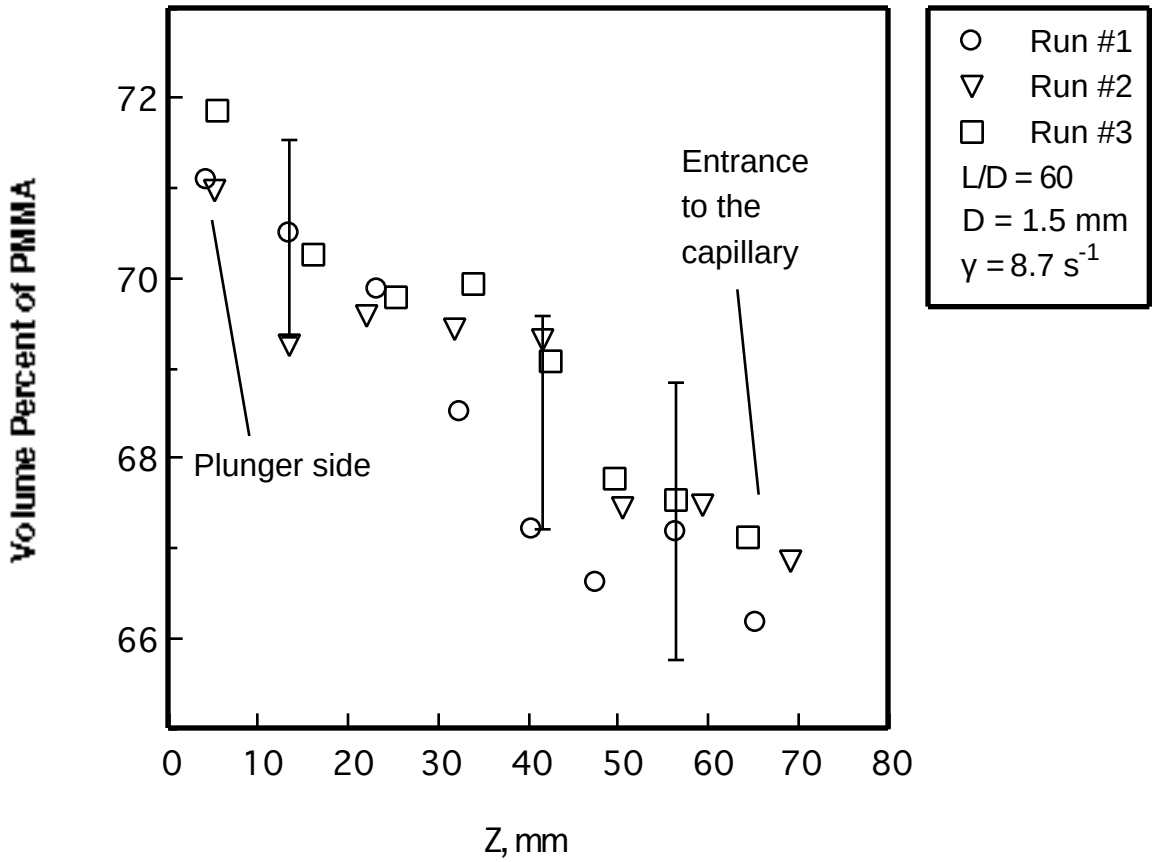


Figure 2: Pure lubricant is seen to filter out of the suspension as the extrusion takes place
L/D=33.2 D=0.0591”

Filtration of the Binder occurs in the low shear rate region



Development of Concentration Profile in the Reservoir during Capillary Flow upon Axial Migration of the Polymer

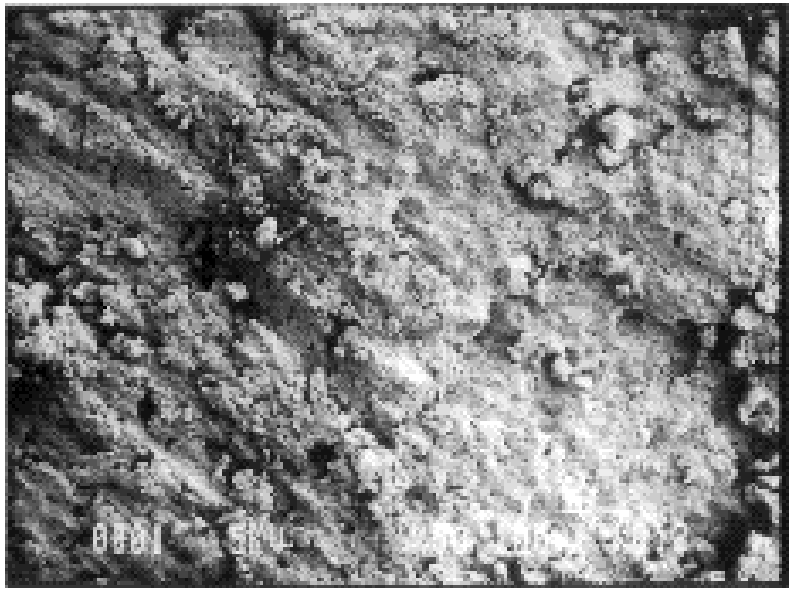


UPON FILTRATION OF THE BINDER THE REMAINDER IS SOLID-LIKE

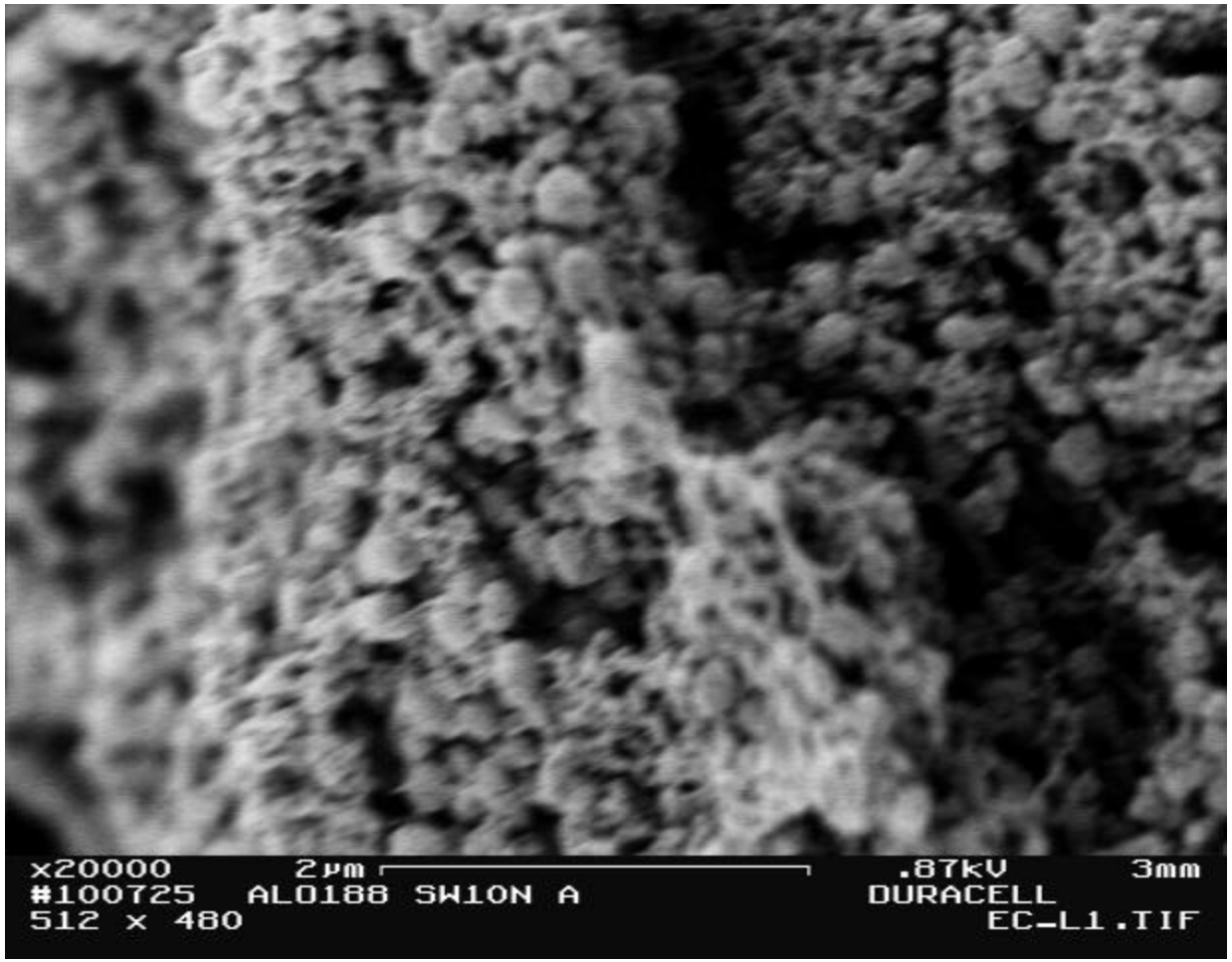
The Grinding of the Powder in the Extruder upon the Filtration of the Binder and Mat Formation

=0.765

Ammonium sulfate into the extruder



Ammonium sulfate ground in the extruder (same scale)



Extruded calendered longitudinal cryogenic fracture

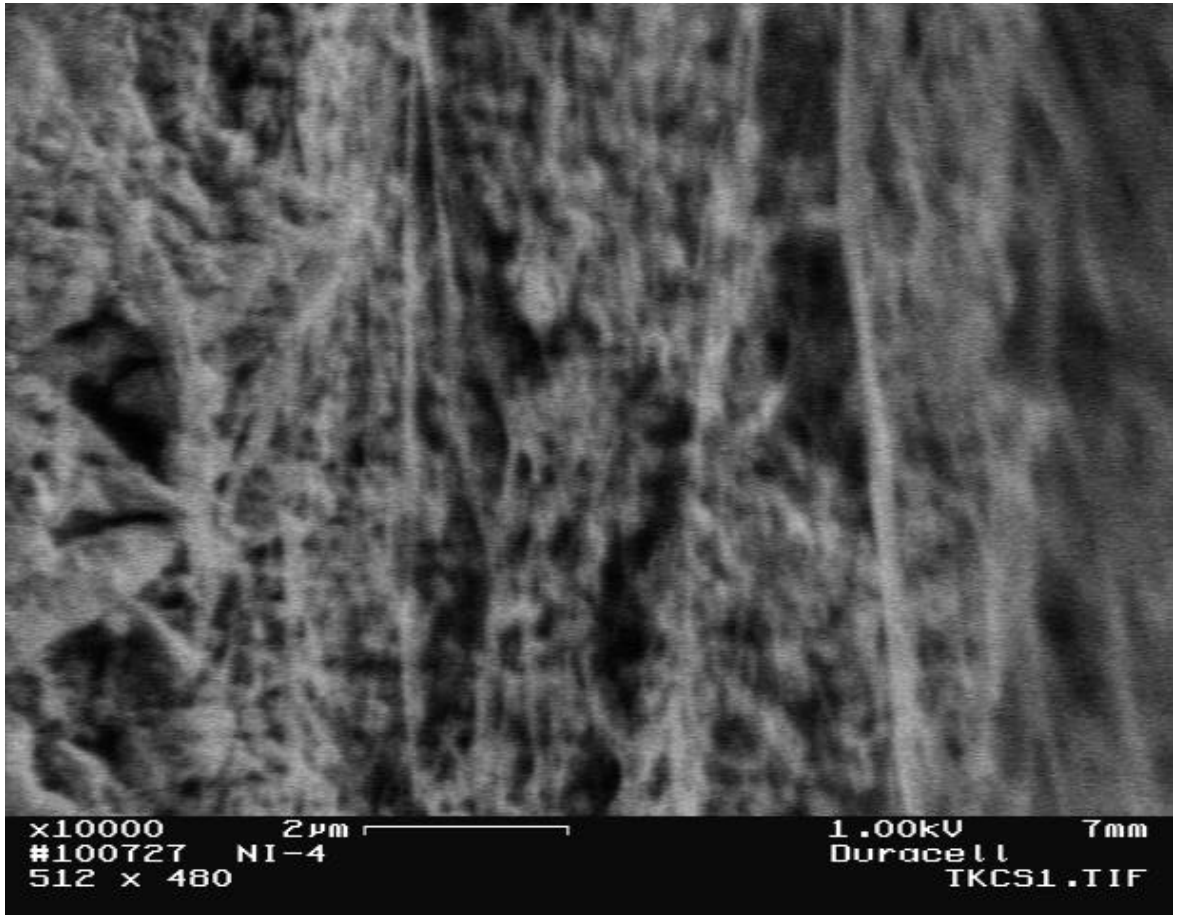
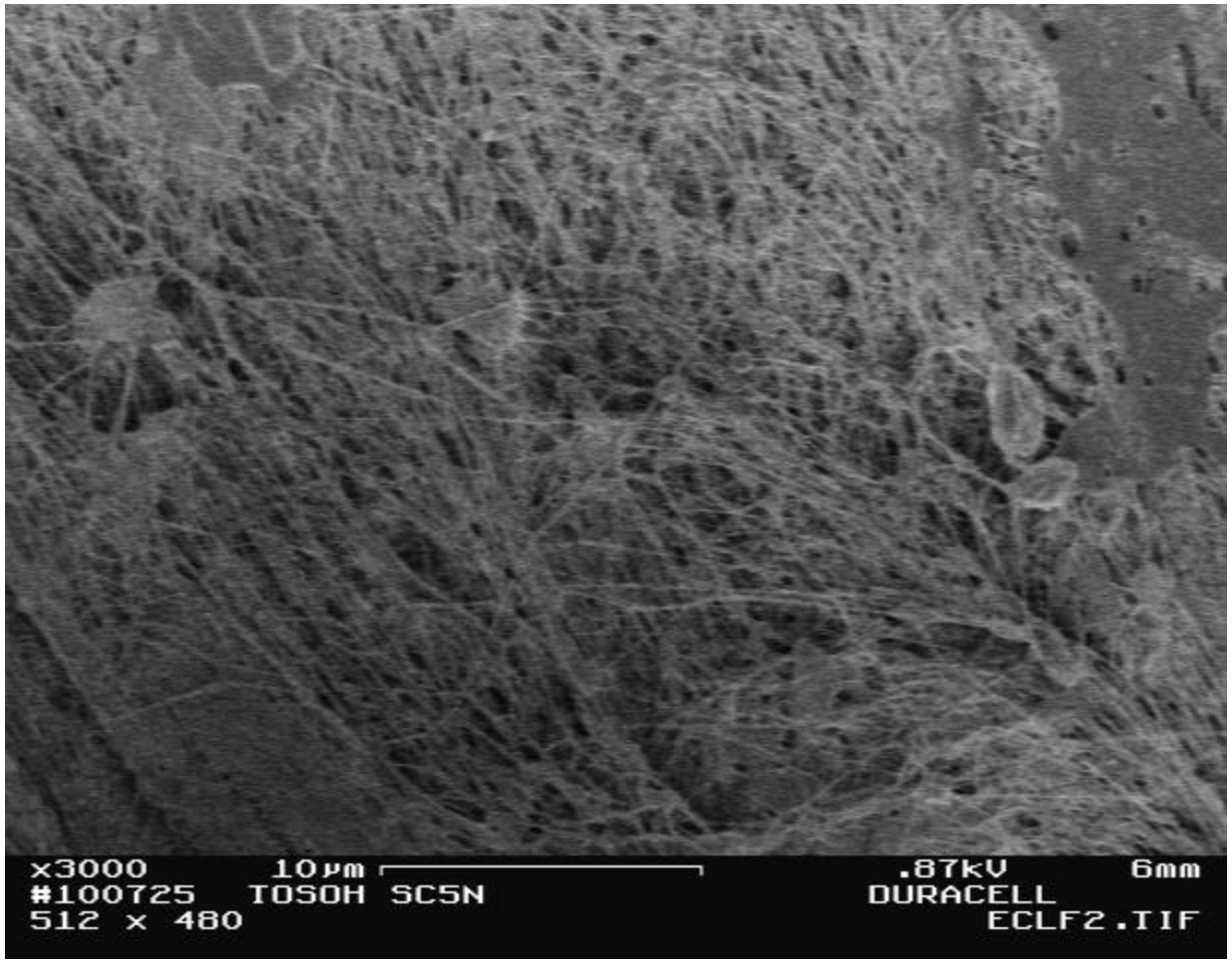
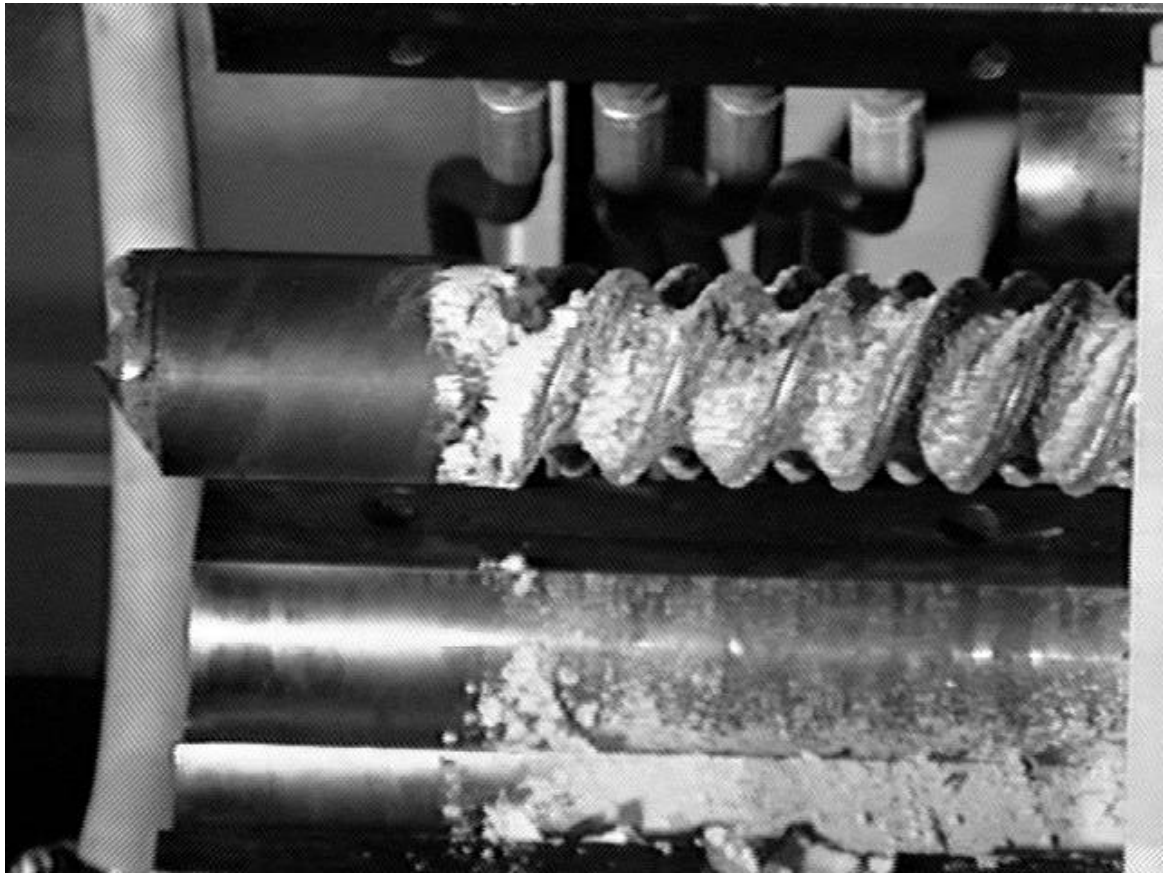


Figure 11: D= 0.0591”, 10”/min, L/D=22, at circular cross-section



Extruded calendered longitudinal fracture

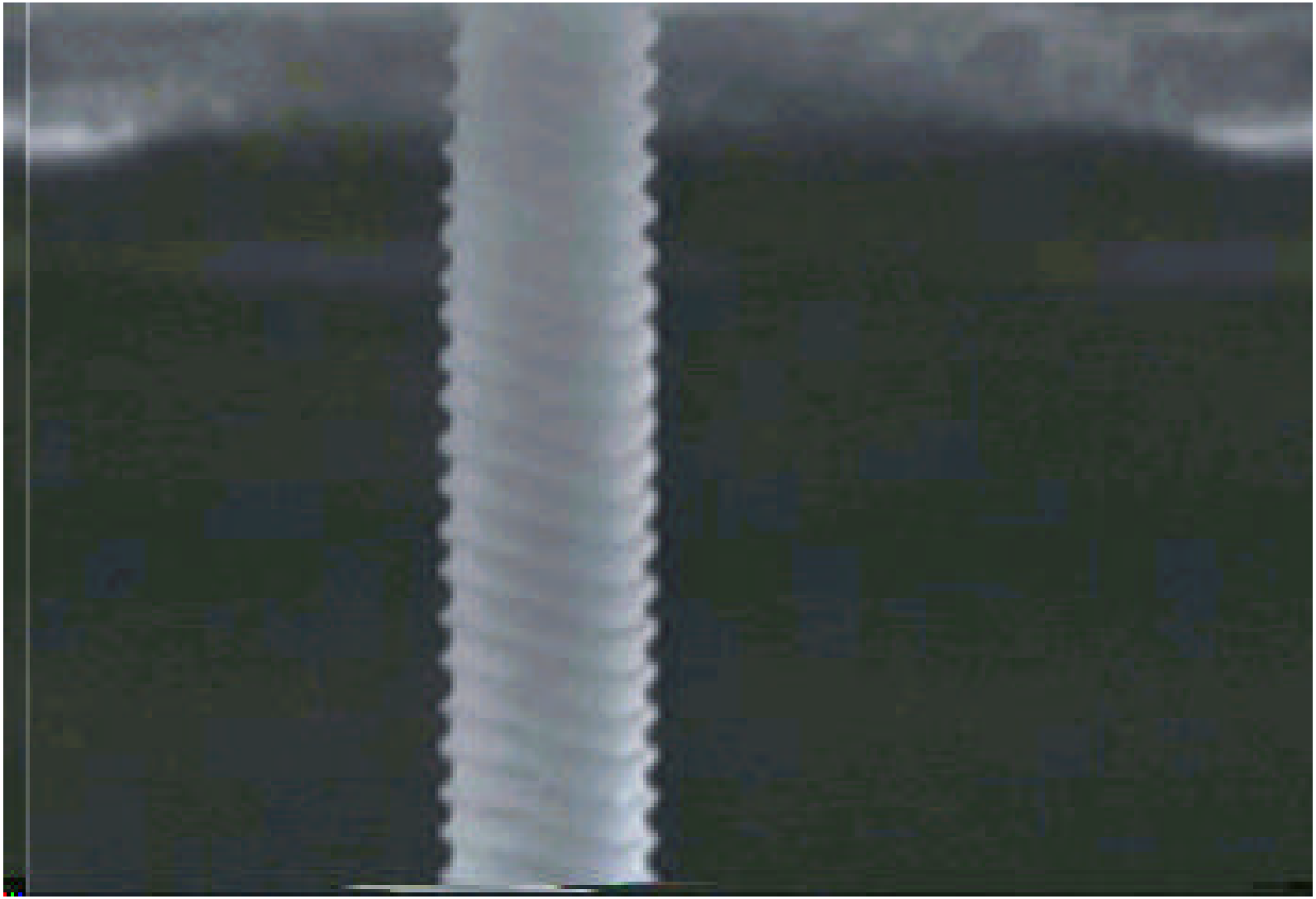
How does one define Degree of Mixedness in Filled Polymers?



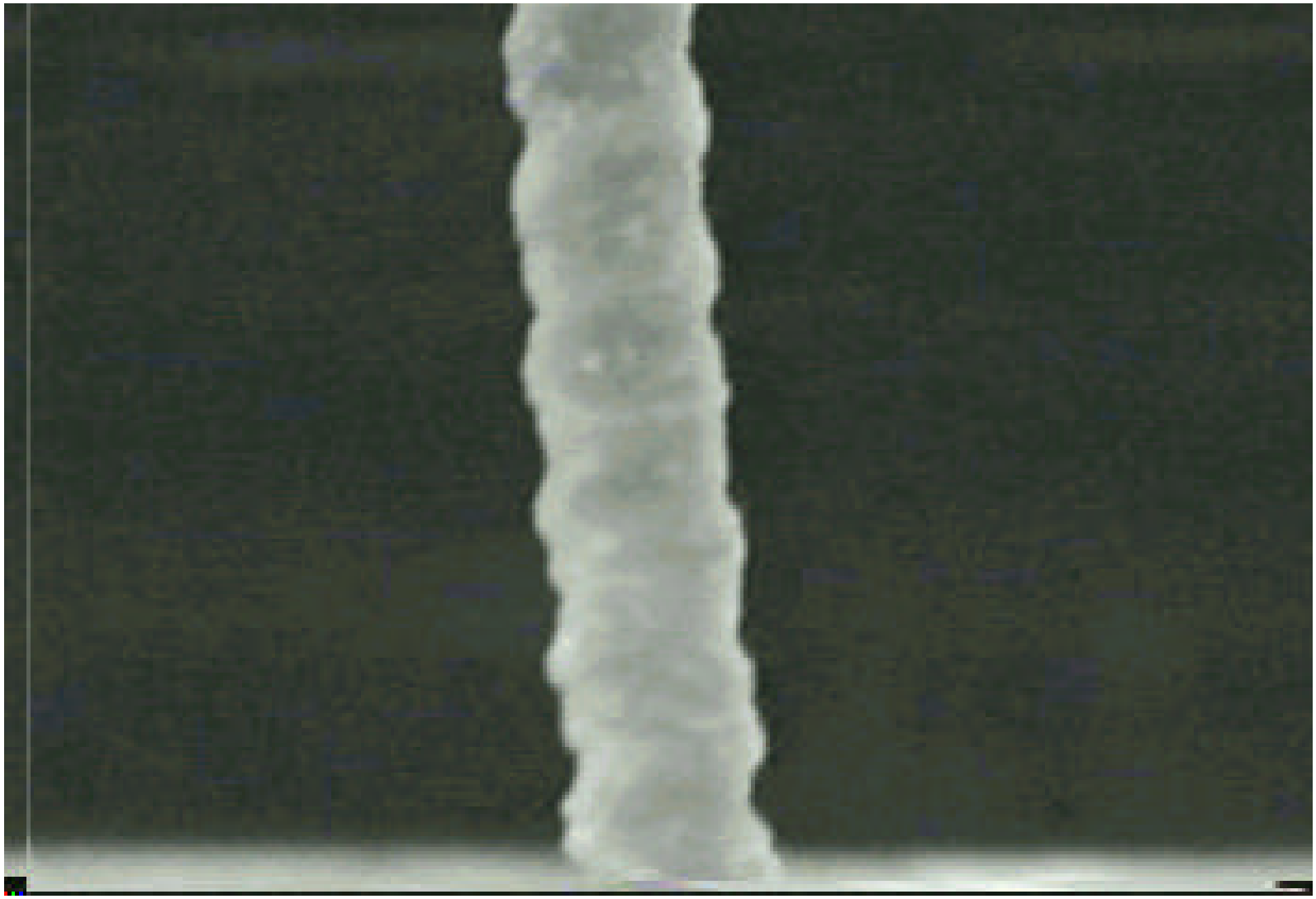
New Considerations with High Molecular Weight Polymeric Binders

- Flow instabilities and gross surface irregularities
- Extrudate swell, time dependence
- Viscous energy dissipation
- Wall slip is more complicated
- Use of non-linear constitutive equations is necessary for describing the rheological behavior

PDMS Instron Capillary Extrusion
Diameter=0.0984” L/D=60 T=30°C Vc



PDMS Instron Capillary Extrusion
Diameter=0.0984” L/D=60 T=30°C Vc=1”/min
Shark Skin



PDMS Instron Capillary Extrusion
Diameter=0.0984” L/D=60 T=30°C Vc=2”/min
Gross Melt Fracture

$$\tau = \int_0^{\infty} [M_1(s, I_1, I_2) C_t^{-1} + M_2(s, I_1, I_2) C_t] ds$$

where τ is the stress tensor,

- M1 and M2 are the
- memory functions which describe the fading memory of the polymer melt,
- C is the strain tensor,
- s is the elapsed time

$$M(s) = M_0(s)\, h(\gamma_0) \qquad h(\gamma) = f \exp(-n_1 \gamma) + (1-f) \exp(-n_2 \gamma)$$

$$h(\gamma_0) = G(t, \gamma_0) / G(t)$$

$$G'(w) = \sum_i \frac{G_i \lambda_i^2 w^2}{1+\lambda_i^2 w^2} \qquad G''(w) = \sum_i \frac{G_i \lambda_i w}{1+\lambda_i^2 w^2}$$

$$\eta(\gamma) = f \sum_i \frac{G_{oi}\lambda_i}{(1+n_1\gamma\lambda_i)^2} + (1-f)\sum_i \frac{G_{oi}\lambda_i}{(1+n_2\gamma\lambda_i)^2}$$

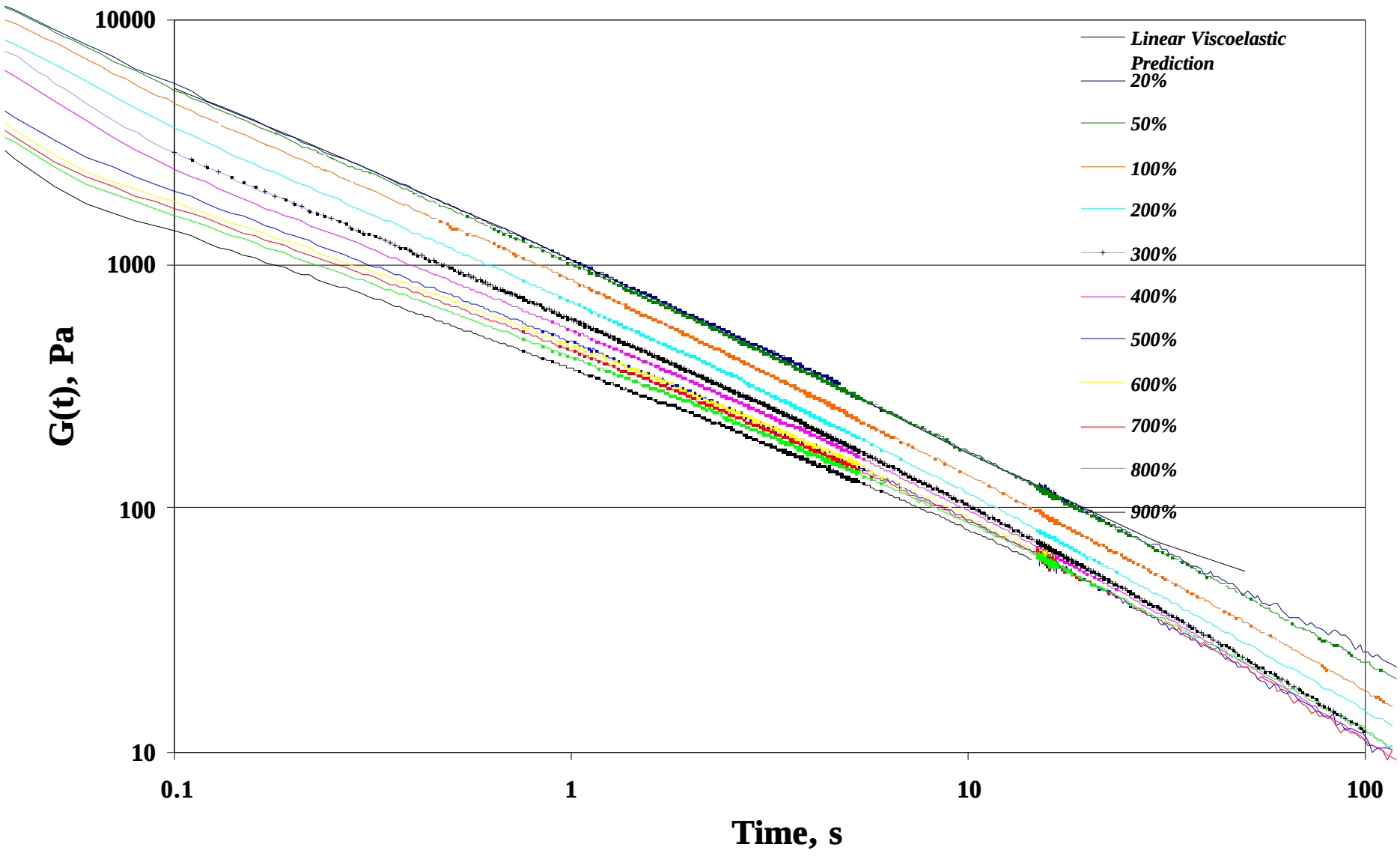
$$\psi_1(\gamma) = f \sum_i \frac{2G_{oi}\lambda_i^2}{(1+n_1\gamma\lambda_i)^3} + (1-f)\sum_i \frac{2G_{oi}\lambda_i^2}{(1+n_2\gamma\lambda_i)^3}$$

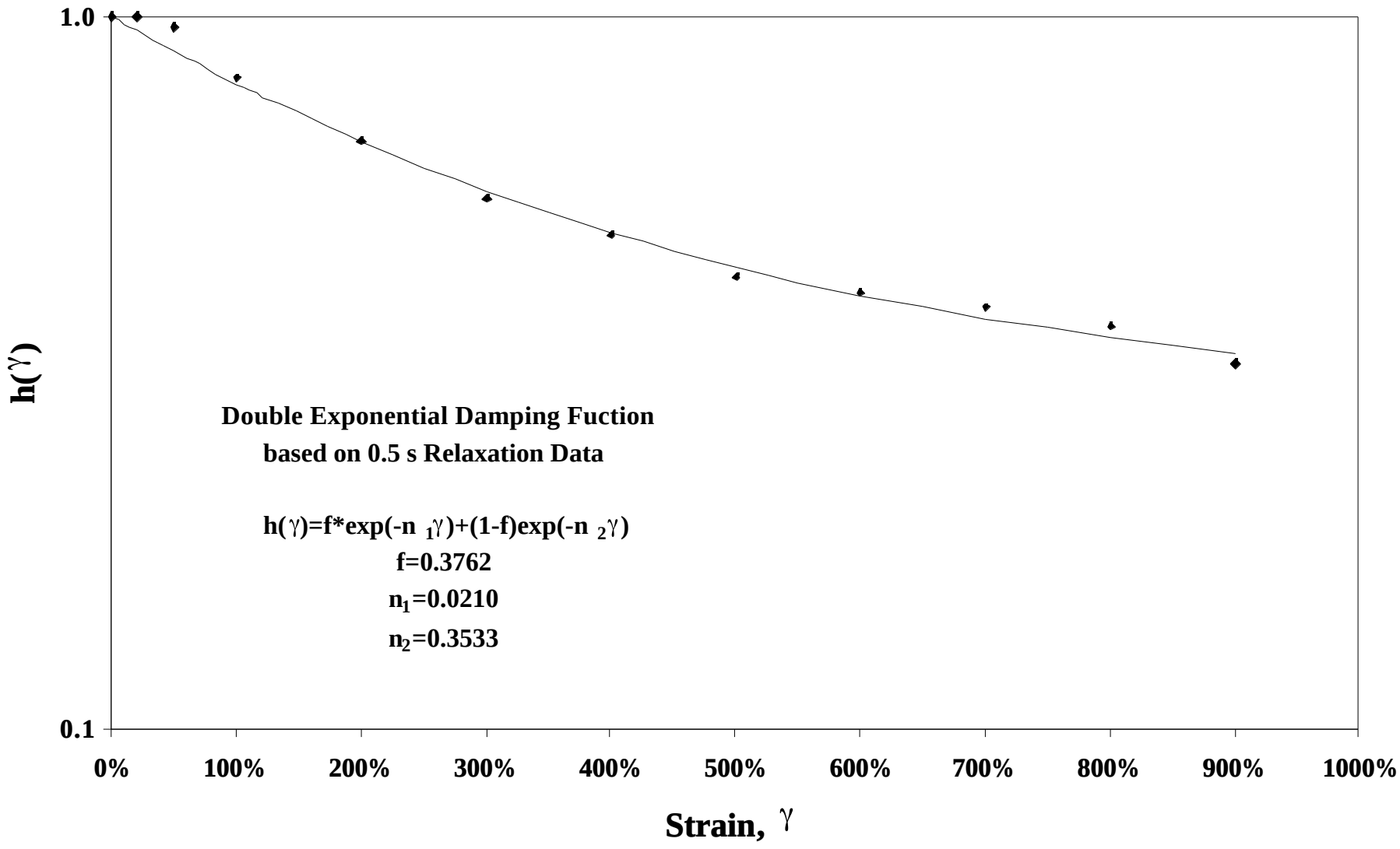
$$\left[\tau_{11} - \tau_{22}\right](t) = \int_0^t \sum \frac{G_{oi}}{\lambda i} \exp\left(-\frac{s}{\lambda_i}\right) h(s) \left[e^{2\varepsilon(s)} - e^{-\varepsilon(s)}\right] ds$$

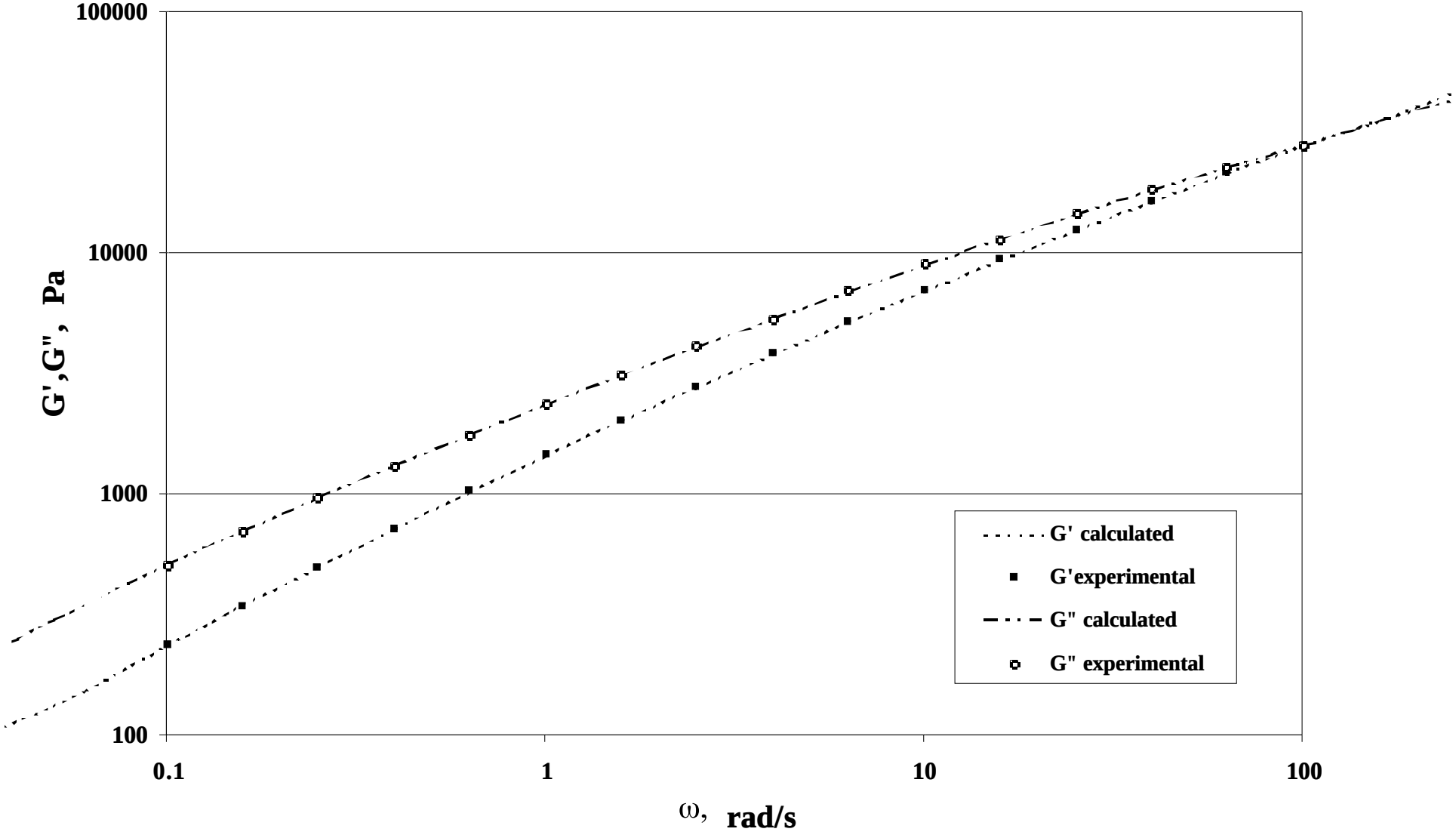
$$+ \sum G_{oi} \exp\left(-\frac{t}{\lambda_i}\right) h(t)\left(e^{2\dot{\varepsilon}t} - e^{-\dot{\varepsilon}t}\right)$$

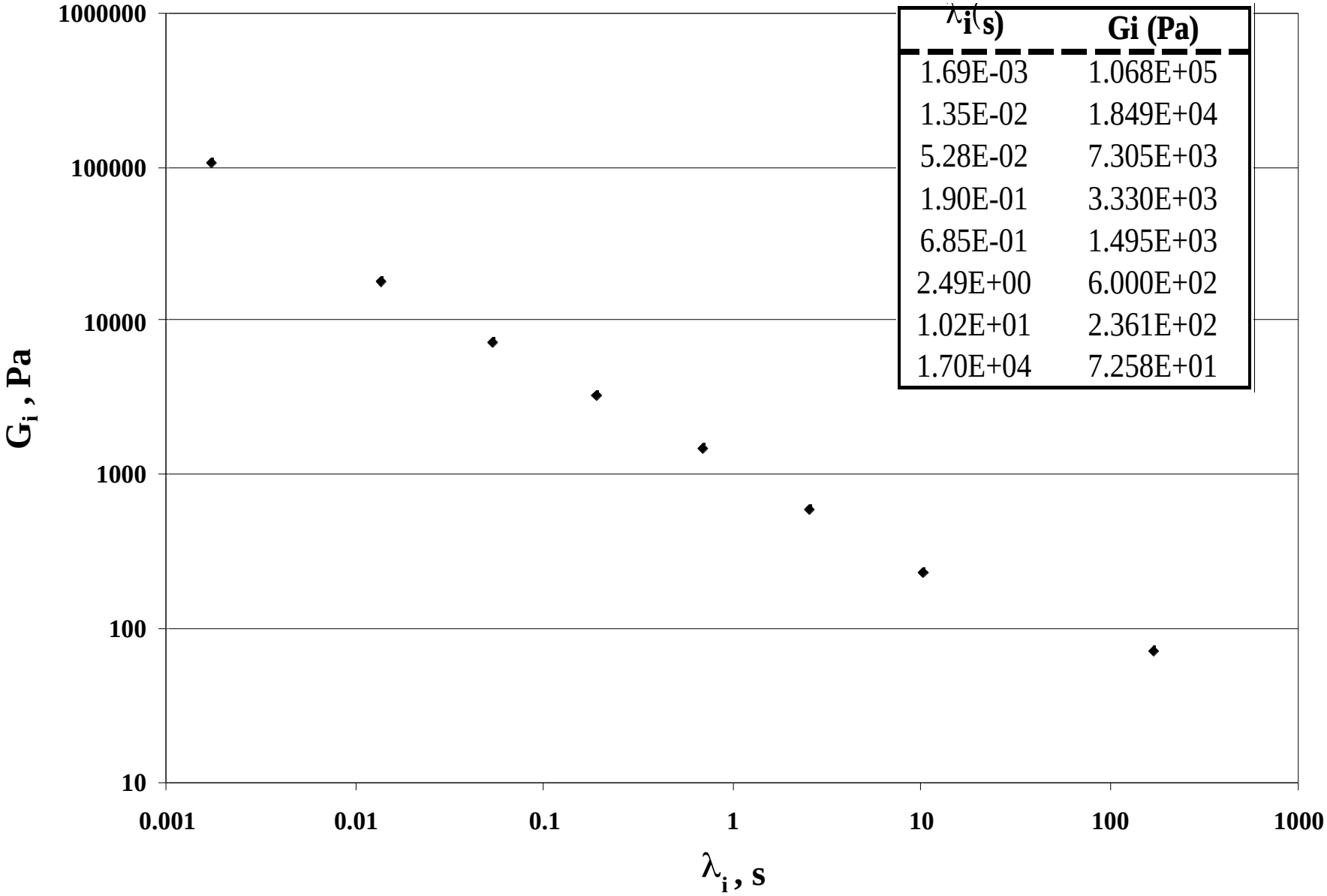
Typical results for 35/65 BAMO/AMMO TPE

- Relaxation modulus
- Dynamic properties
- Stress growth
- Stress relaxation
- Shear Viscosity
- First normal stress difference
- Uniaxial extensional viscosity

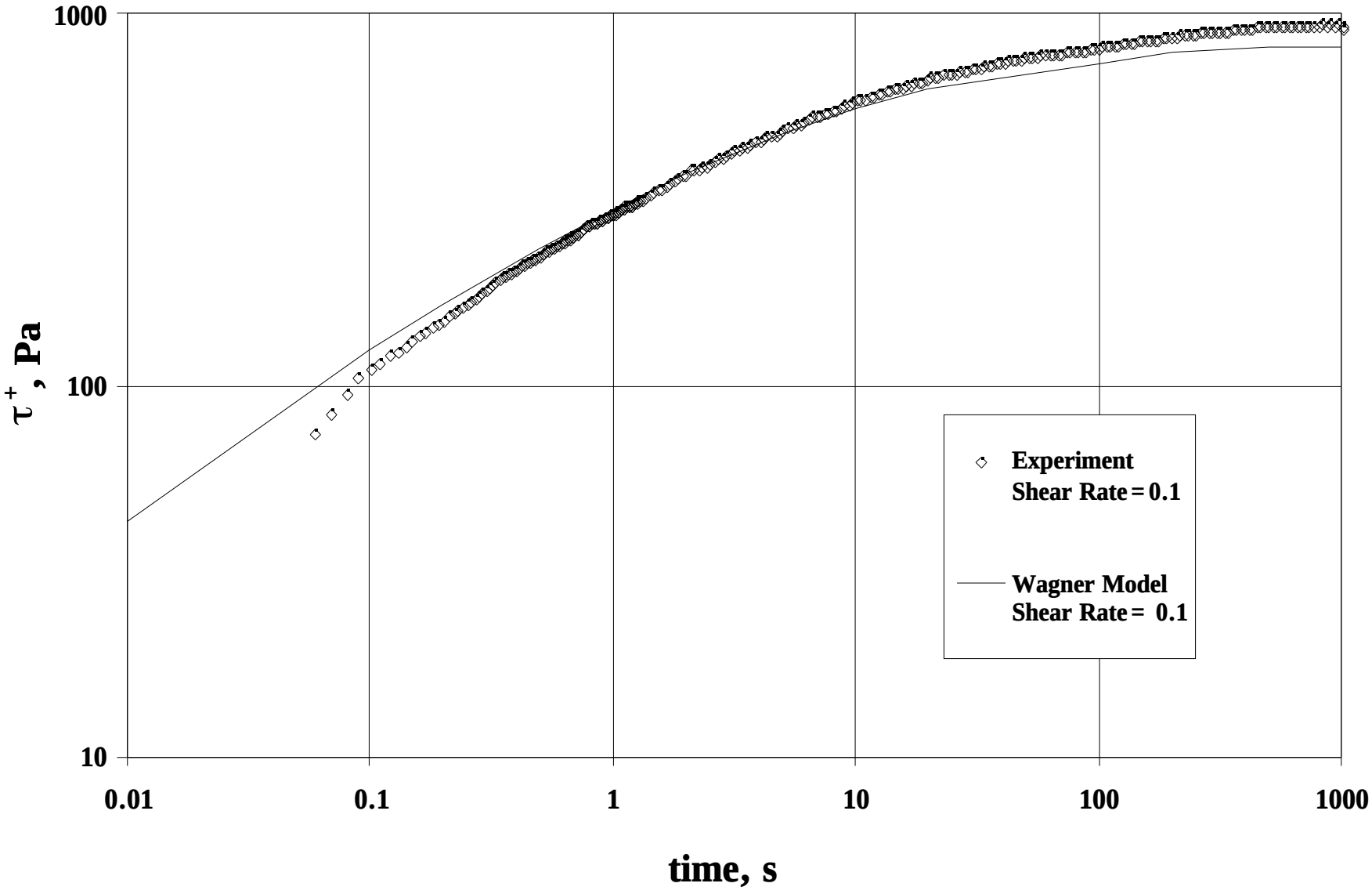

10000
1000
100
10
G(t), Pa
0.1
1
10
100
Time, s
Linear Viscoelastic Prediction
20%
50%
100%
200%
300%
400%
500%
600%
700%
800%
900%

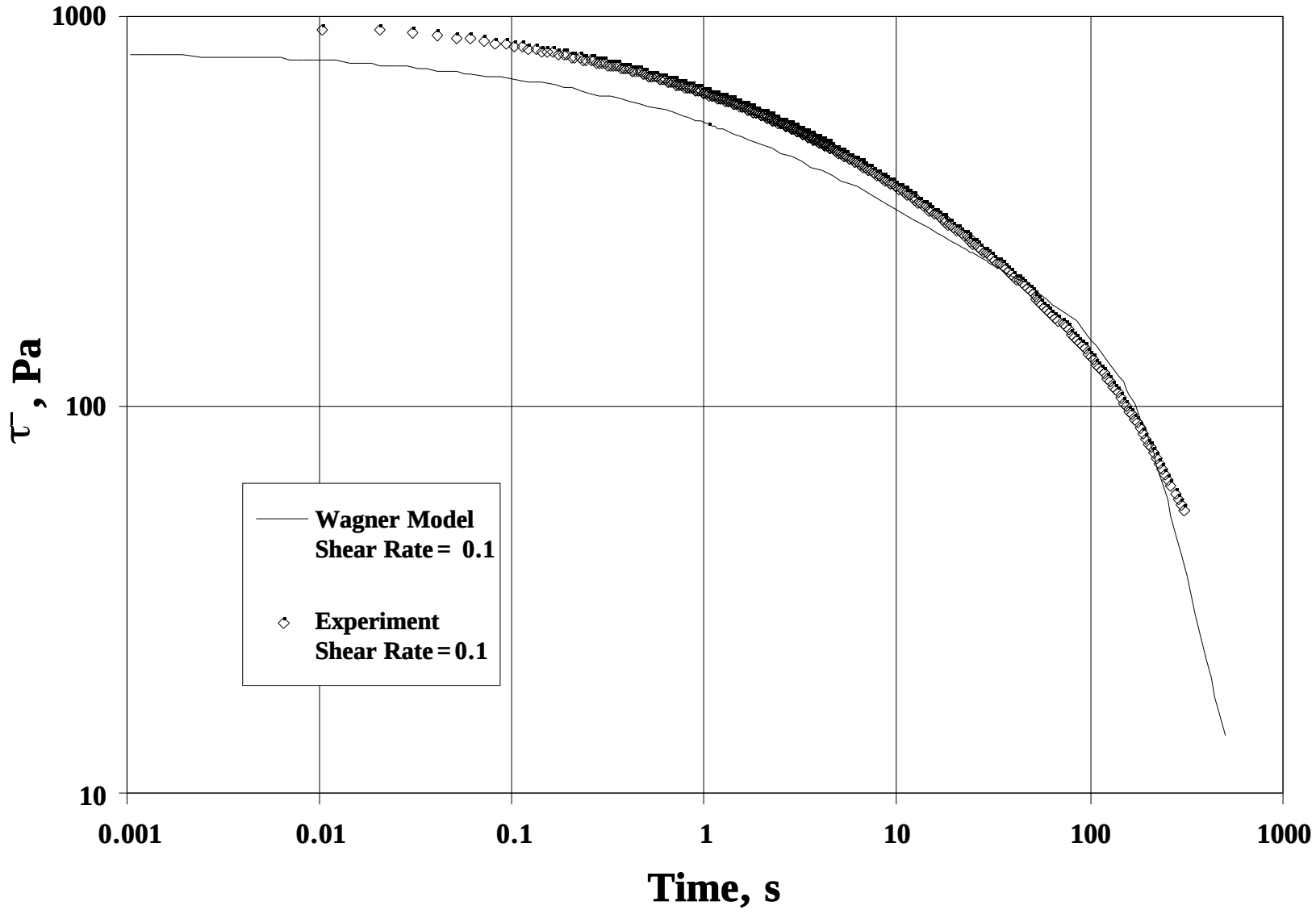

1.0
0.1
h(γ)
Double Exponential Damping Fuction
based on 0.5 s Relaxation Data
h(γ)=f*exp(-n 1γ)+(1-f)exp(-n 2γ)
f=0.3762
n1=0.0210
n2=0.3533
0%
100%
200%
300%
400%
500%
600%
700%
800%
900%
1000%
Strain, γ

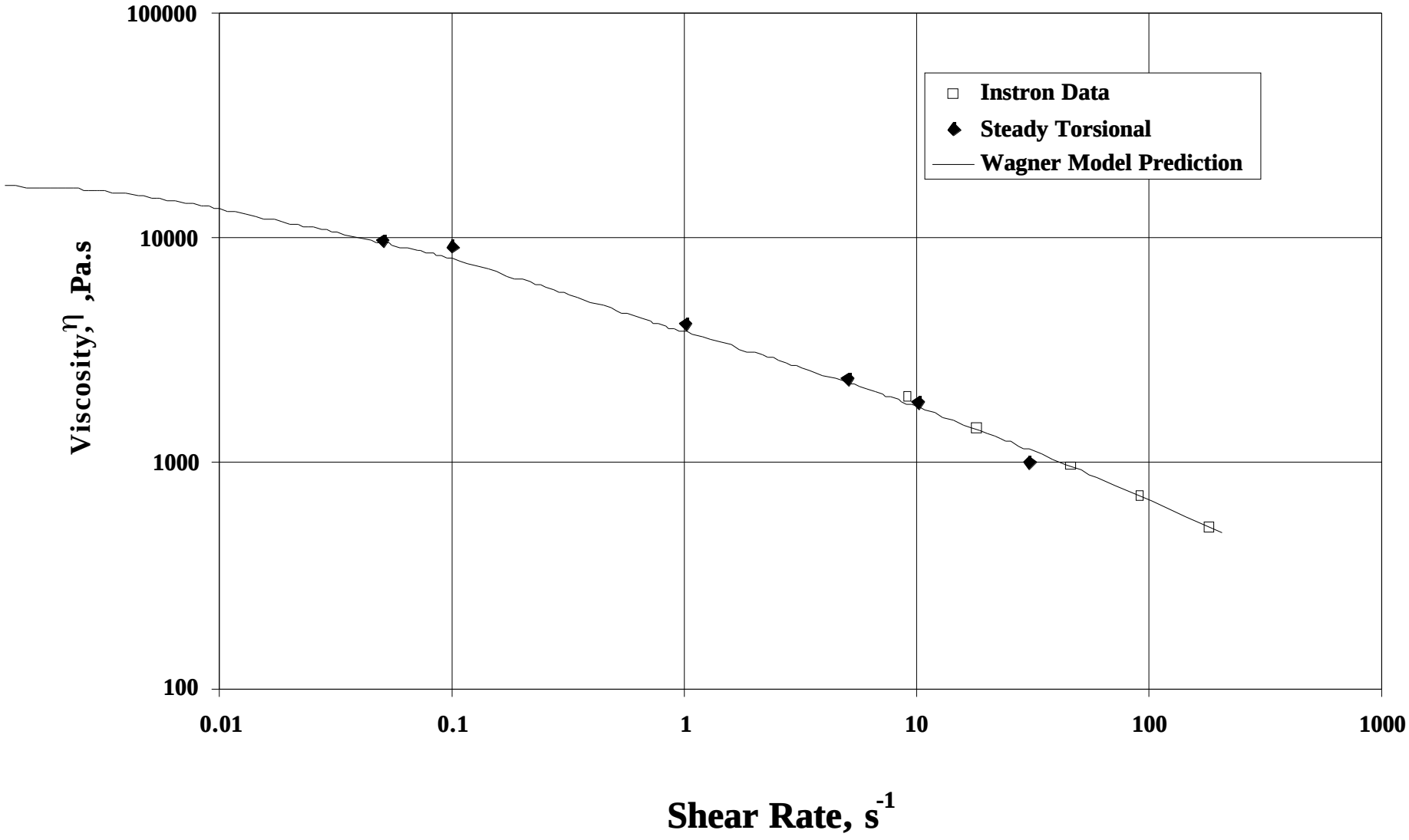

100000
10000
1000
100
G',G", Pa
0.1
1
10
100
ω, rad/s
G' calculated
G'experimental
G" calculated
G" experimental

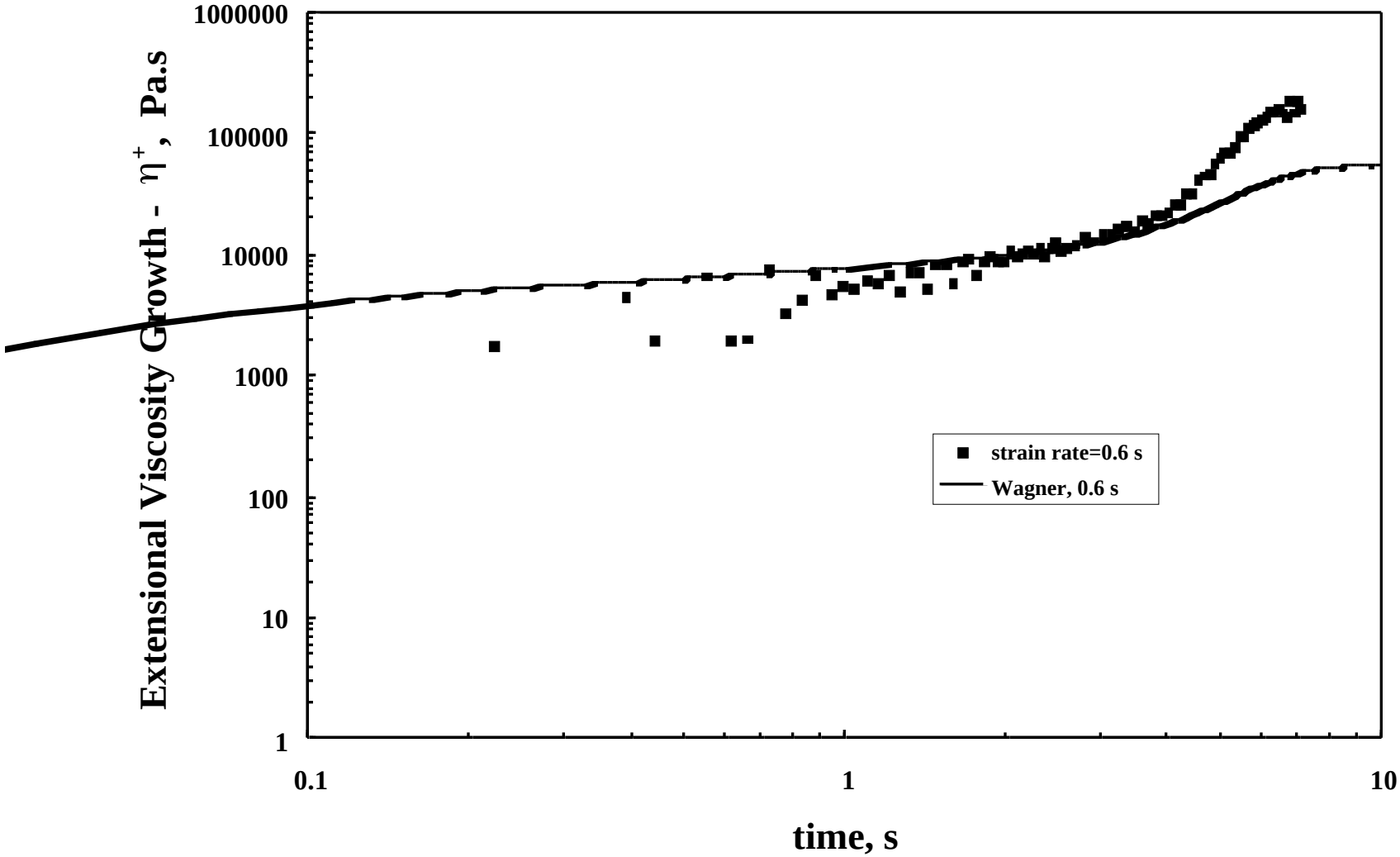


λ_i (s)	Gi (Pa)
1.69E-03	1.068E+05
1.35E-02	1.849E+04
5.28E-02	7.305E+03
1.90E-01	3.330E+03
6.85E-01	1.495E+03
2.49E+00	6.000E+02
1.02E+01	2.361E+02
1.70E+04	7.258E+01


1000
100
10
0.01
0.1
1
10
100
1000
τ+, Pa
time, s
Experiment
Shear Rate = 0.1
Wagner Model
Shear Rate = 0.1


1000
100
10
τ, Pa
0.001
0.01
0.1
1
10
100
1000
Time, s
Wagner Model
Shear Rate = 0.1
Experiment
Shear Rate = 0.1


100000
10000
1000
100
Viscosity, η ,Pa.s
0.01
0.1
1
10
100
1000
Shear Rate, s-1
Instron Data
Steady Torsional
Wagner Model Prediction


1000000
100000
10000
1000
100
10
1
0.1
1
10
Extensional Viscosity Growth - η^+, Pa.s
time, s
strain rate=0.6 s
Wagner, 0.6 s

Conclusions

- Characterization of energetic materials is a challenge
- The structuring effects need to be continuously considered
- Multiple rheometers are recommended
- Special techniques are necessary to analyze the data especially for high molecular weight polymeric binders.

One last point

- BAMO/AMMO thermoplastic elastomers are not inert but will initiate under pressure
- Treat it as other energetic materials