Effects of Polymer Concentration and Molecular Weight on the Dynamics of Visco-Elasto-Capillary Breakup

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January 30, 2004

Capillary Breakup Extensional Rheometer (CABER)

Top and Bottom Cylinders: Diameter (D_0) = 6 mm

Initial height = 3 mm

Final height = 13.2 mm

Balance of

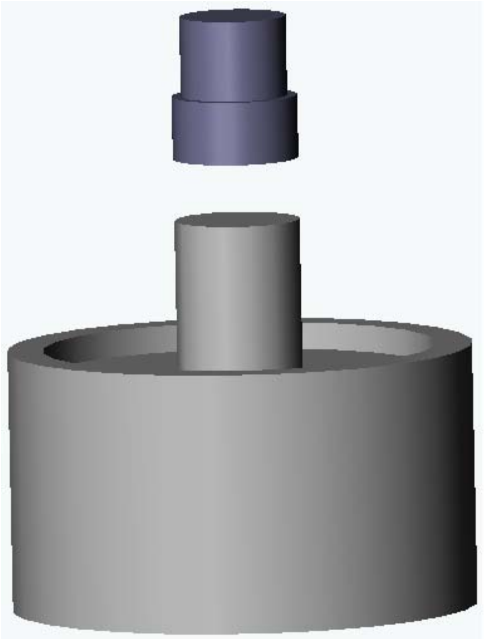
capillary, viscous, and elastic forces

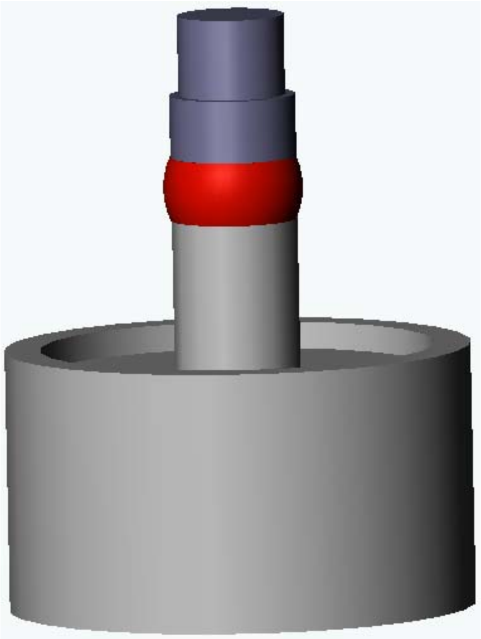
Uses ~90 μL of sample

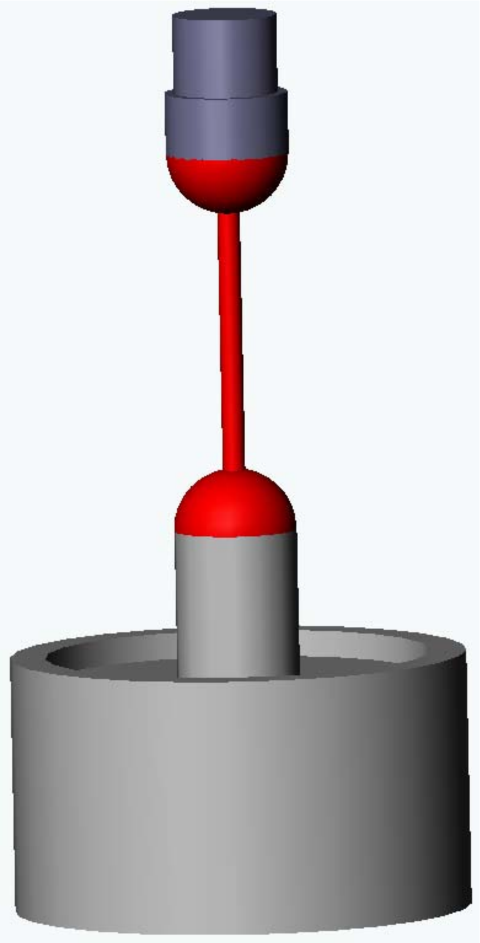
Time to open: 50 ms

Initial aspect ratio $\Lambda = \dfrac{H}{D_0} = .5$

Final aspect ratio = 2.2







Balance of Stresses

If $F_{total} = 0$

$$\frac{\sigma}{R} = 3\eta_S\left(-\frac{2}{R}\frac{dR}{dt}\right) + \left(\tau_{zz} - \tau_{rr}\right)$$

(capillary) **(viscous)** **(elastic)**

Normal stress differences:

$$\tau_p = \left[\tau_{zz} - \tau_{rr}\right] = \sum_i G_i f_i \left(A_{zz}{}^i - A_{rr}{}^i\right)$$

elastic moduli:

$$G = \frac{\eta_0 - \eta_S}{\lambda_z} \sum_i \frac{1}{i^{2+\nu}}$$

Initial conditions

• At early times, the viscous response of the solvent is not negligible for dilute polymer solutions

→ The initial value of the axial stretch is chosen to fit the curve in order to obtain a shape as good as possible.

The polymeric stretch grows as

$$A_{zz}(t) = A_{zz}{}^{0} e^{t/3\lambda_z}$$

• Other initial conditions are:

$$A_{zz}{}^{i\neq 1}(t=0) = 1 \quad \text{and} \quad A_{rr}{}^{i}(t=0) = 1$$

(undeformed material)

Ohnesorge and Deborah Numbers

The Ohnesorge Number evaluates the importance of viscous effects over inertial effects and, in our case, is defined by:

$$Oh = \frac{\eta_0}{\sqrt{\rho \sigma R}}$$

It can be seen as a Reynolds number:

$$Oh^{-2} = \frac{\rho v R}{\eta_0}$$ where the capillary velocity is $$v = \frac{\sigma}{\eta_0}$$

The Deborah Number is the dimensionless deformation rate computed as the ratio of the relaxation time of the fluid by the characteristic time of the experiment. It can be defined as:

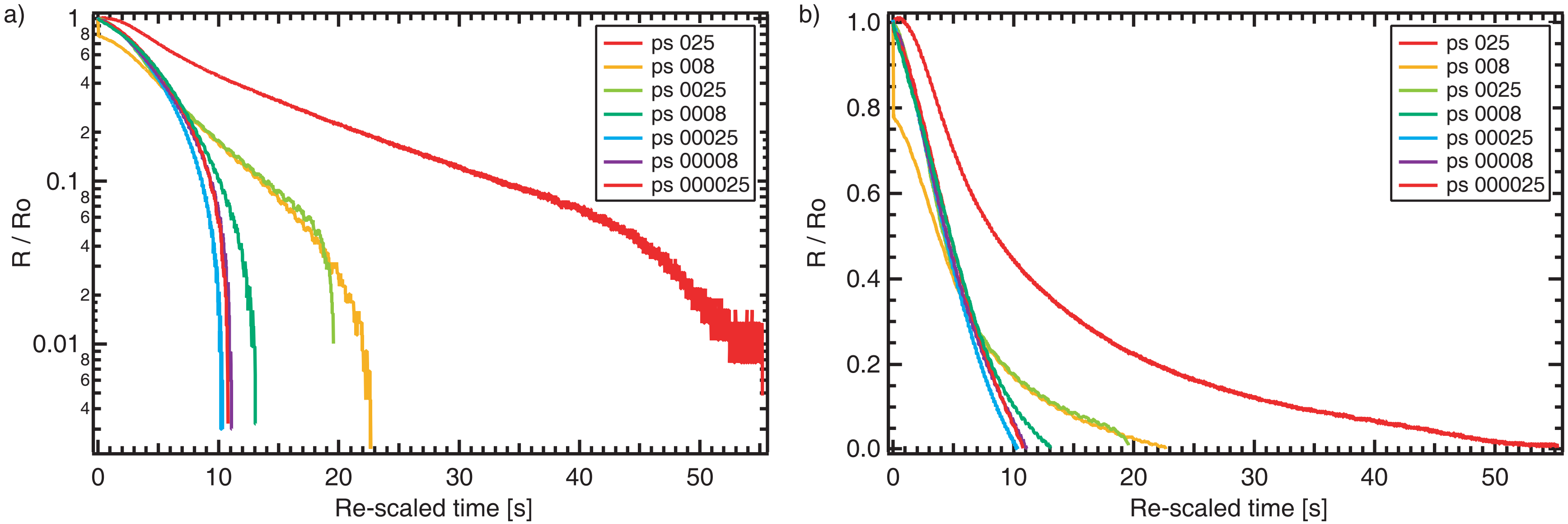
$$De = \frac{\lambda}{\sqrt{\rho R^3 / \sigma}}$$

The ratio of these two numbers is then an elasto-capillary number:

$$\frac{De}{Oh} = \frac{\lambda \sigma}{\eta_0 R}$$

Extensional Rheology: CABER experiments

Progressive dilution decreases time to breakup:

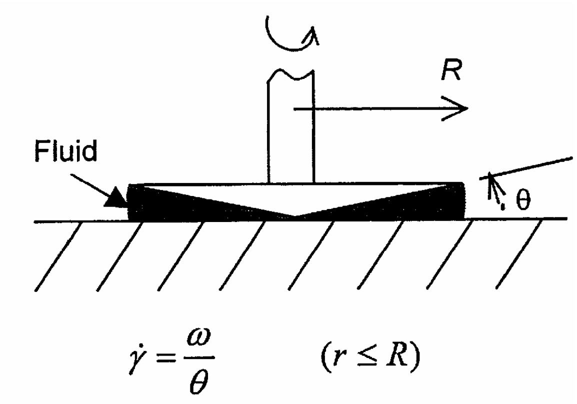


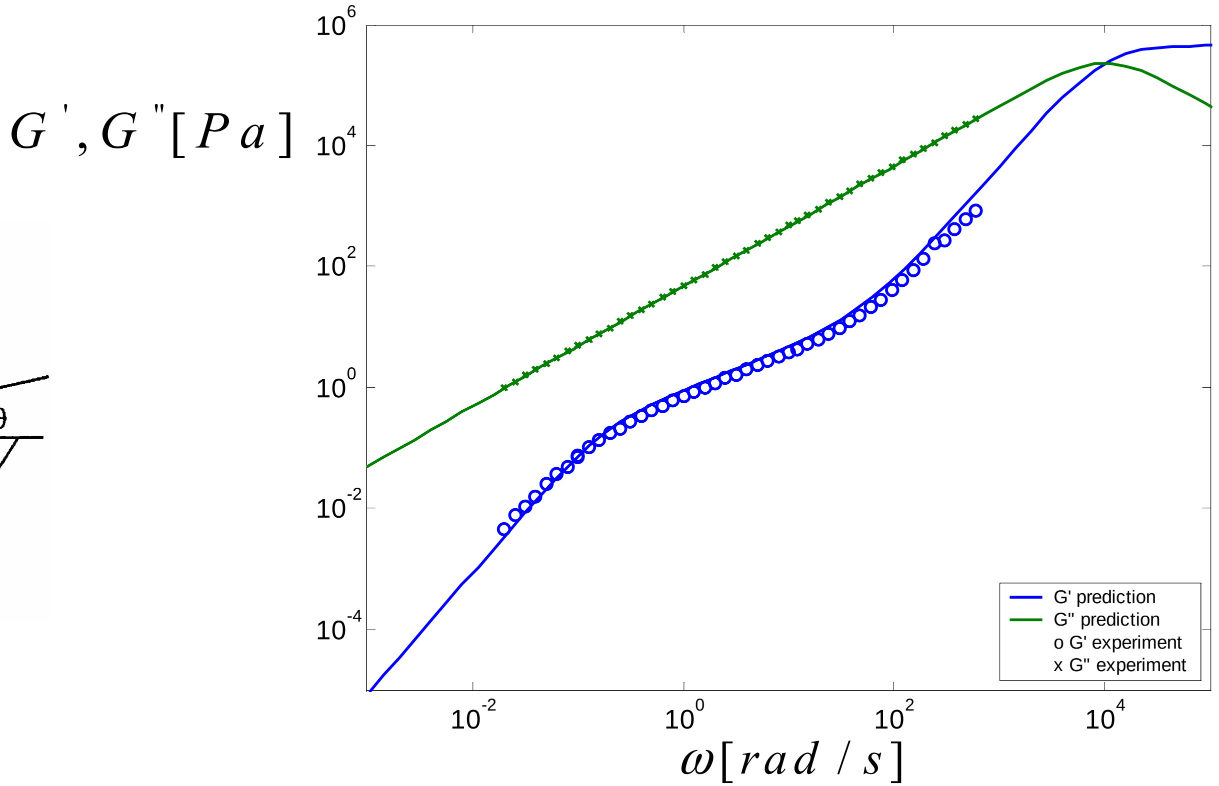
Compared to Kuhn Chain formula: $\lambda = \frac{1}{\zeta(3\upsilon)} \frac{[\eta]\eta_s M_w}{N_A k_B T}$ with $[\eta] = K.M_w^{3\upsilon-1}$

Concentration [wt.%]	0.025	0.008	0.0025	0.0008	0.00025	0.00008	0.000025
Ratio c/c*	0.273	0.0873	0.0273	0.00873	0.00273	0.000873	0.000273
Rel. Time Kuhn	3.14	3.14	3.14	3.14	3.14	3.14	3.14
Rel. Time CABER [s]	4.17	1.98	1.98	1.97	1.95	1.86	1.80

Shear Rheology: Cone and Plate Rheometer

From the data given by oscillatory shear flow with a cone and plate rheometer, one obtains the storage modulus *G*' and the loss modulus *G*". Fitting these data yields the relaxation time through Zimm theory.





Concentration [wt.%]	0.025	0.008	0.0025	0.0008
λ_{Fit} [s]	5.02	1.85	3.97	1.49

Governing equations: FENE-P model

Entov & Hinch, JNNFM 1997

The radius decreases according to

$$\dot{R} = -\frac{1}{2}\dot{\varepsilon}R$$

$\dot{\varepsilon}$: axial strain-rate of the axisymmetric extensional flow

Axial deformation

$$\dot{A}_{zz}{}^{i} = 2\dot{\varepsilon}A_{zz}{}^{i} - \frac{f_i}{\lambda_i}(A_{zz}{}^{i} - 1)$$

Radial deformation

$$\dot{A}_{rr}{}^{i} = -\dot{\varepsilon}A_{rr}{}^{i} - \frac{f_i}{\lambda_i}(A_{rr}{}^{i} - 1)$$

Finite extensibility: $L \sim M_{w}{}^{1-\upsilon}$

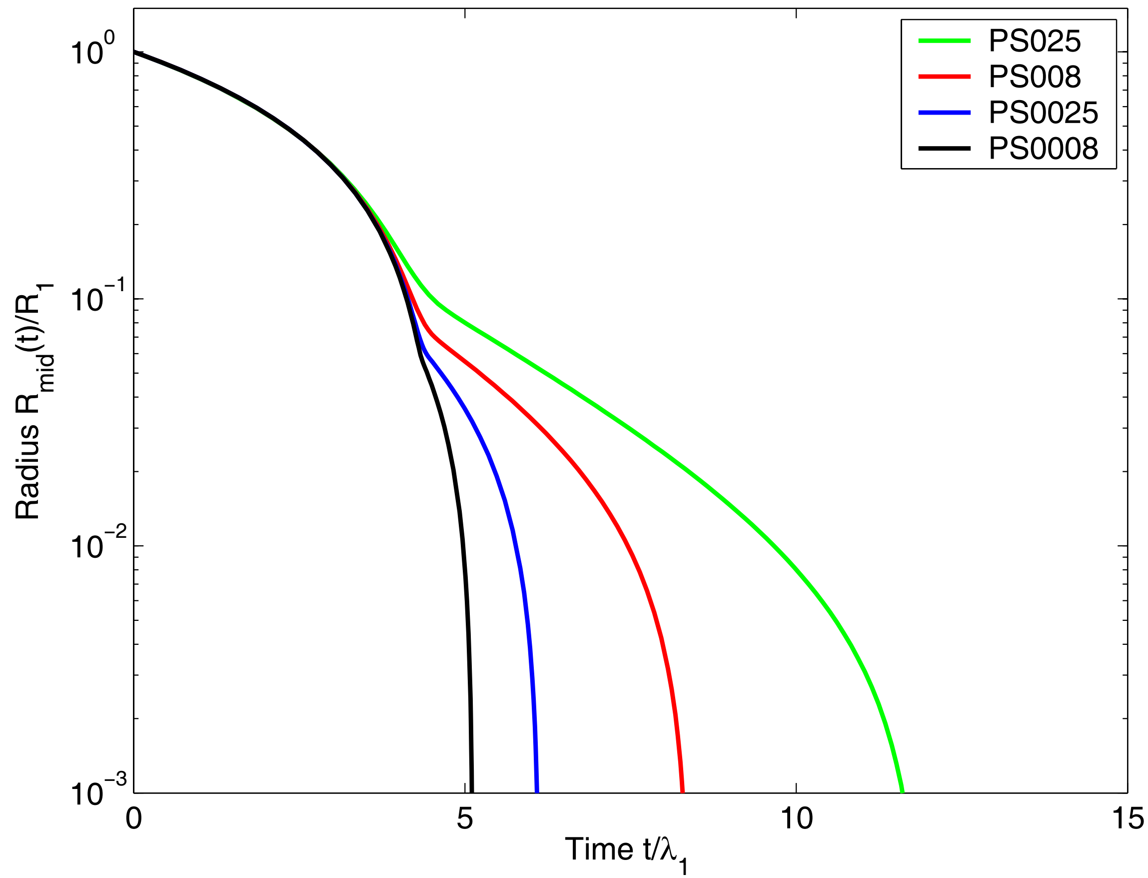
With relaxation times λ_i and FENE factors $f_i = \dfrac{1}{1 - trA^i / L_i{}^2}$, $L_i = \dfrac{L}{i^{\nu}}$

Numerical Simulations

Decrease of the radius as a function of time.

Inputs of the simulation:

$$\eta_0,\ \eta_S\ ,\ \lambda_{Zimm}\ ,\ A_{zz}{}^{0}$$



Asymptotic Behaviors

1- Early viscous times:

For a strong surface tension with no elastic stress…

Stress balance:
$$\frac{\sigma}{R} = 3\eta_S \dot{\varepsilon}$$

$$\Rightarrow \quad \boxed{R = R_1 - \frac{\sigma}{6\eta_S} t}$$

2- Middle elastic times:

Elastic stress grows. Viscous stress drops with the strain-rate. Balance between capillary pressure and elastic stress.

Assumption: $A_{zz}{}^{i} >> 1 > A_{rr}{}^{i}$

The deformation is smaller than the finite extension limit: $A_{zz}{}^{i} << L_i{}^{2} \qquad (f_i = 1)$

Asymptotic Behaviors (2)

The radius decreases exponentially:

$$R(t) = R_1 \left(\frac{R_1 G(t)}{\sigma} \right)^{\frac{1}{3}} \qquad \text{with} \qquad G(t) = \sum_i G_i e^{-\frac{t}{\lambda_i}}$$

3- Late times limited by finite extension:

Viscous stress is the difference of large numbers. The system of equations is very stiff.

Balance capillary pressure/elastic stress:

$$\frac{\sigma}{R} = \sum_i G_i f_i \left(A_{zz}^{\ i} - A_{rr}^{\ i} \right)$$

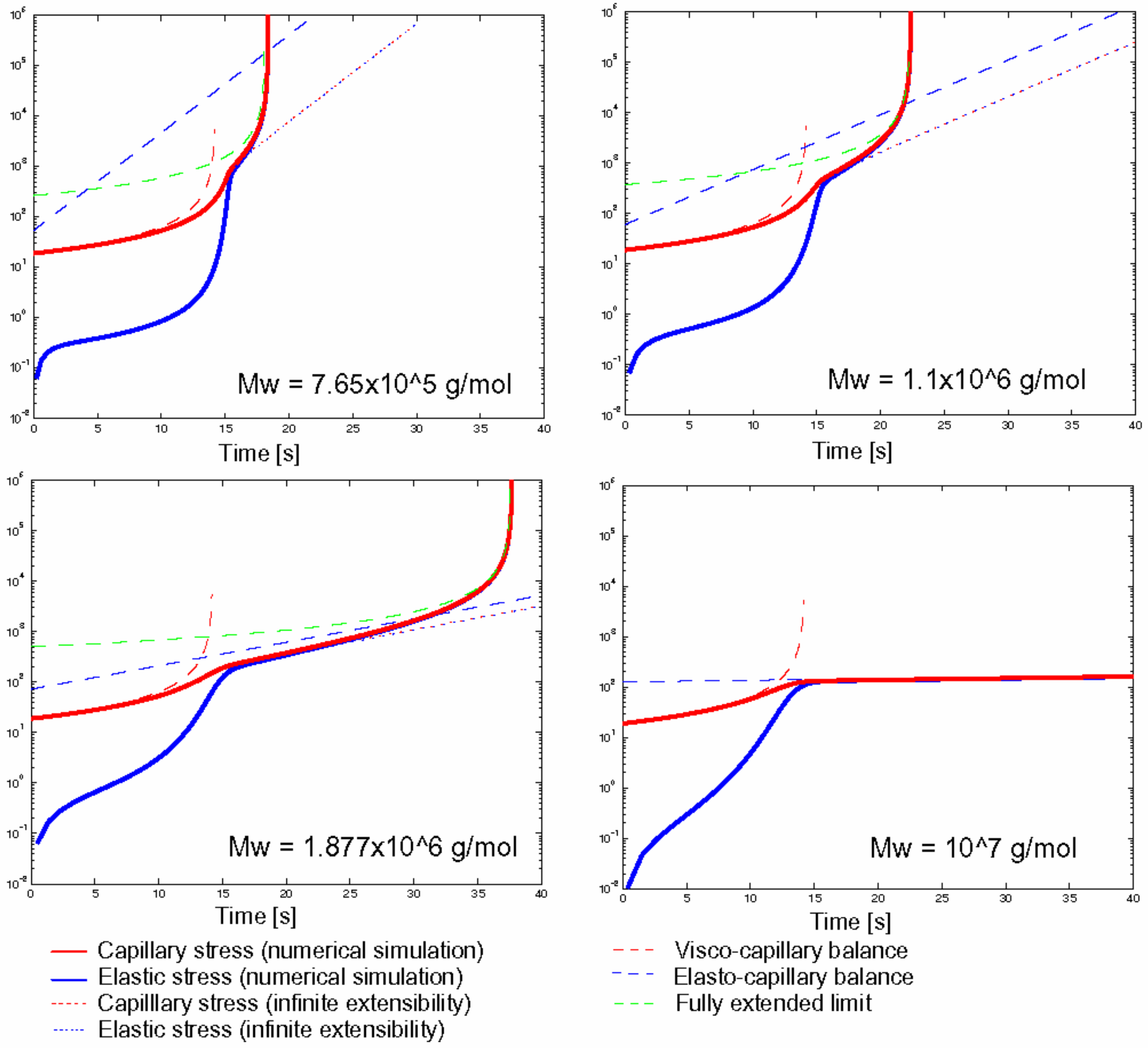
The FENE fluid is now behaving like a suspension of rigid rods, with an effective viscosity

$$\eta^* = \frac{2}{3} \sum_i G_i \lambda_i L_i^{\ 2}$$

The decrease of radius is then linear:

$$R(t) = \frac{\sigma}{6\eta^*} \left(t_b - t \right)$$

Correspondence between numerics and asymptotes



Importance of Gravity: New Test Fluid (MV1)

Competition between gravitational and viscous forces: Bo/Ca

$$\frac{Bo}{Ca} = \frac{\rho g R_0}{\eta_0 \dot{\varepsilon}} \longrightarrow \dot{\varepsilon}_{sag} = \frac{\rho g R_0}{\eta_0}$$

$$De_{sag} = \frac{\lambda \rho g R_0}{\eta_0} = \frac{[\eta] M_w \rho g R_0}{\zeta(3\upsilon) N_A k_B T (1 + c[\eta])} \leq 0.5 \longrightarrow 1.3\times10^{-5} M_w^{1.59} \leq 0.5$$

$$M_w \leq 765000 g/mol$$

$$M_w = 750000 g/mol$$

Experimental Results:

Fluid	PS 025	MV1
Ratio c/c*	0.273	0.50
Zero-shear viscosity [Pa.s]	49	53.5
Solvent viscosity [Pa.s]	45.5	48.5
Relaxation time Kuhn Chain [s]	3.14	0.78
Relaxation time by fitting with Zimm theory [s]	5.02	1.04
Relaxation time CABER [s]	4.17	1.09

Filament Thinning and Gravitational Sagging

Newtonian Fluid: Glycerol


t = 0.01s


t = 0.06s


t = 0.11s


t = 0.18s

New test fluid: MV1


t = 0.01s


t = 9.00s


t = 18.00s


t = 27.00s

Viscoelastic Fluid: PS 025

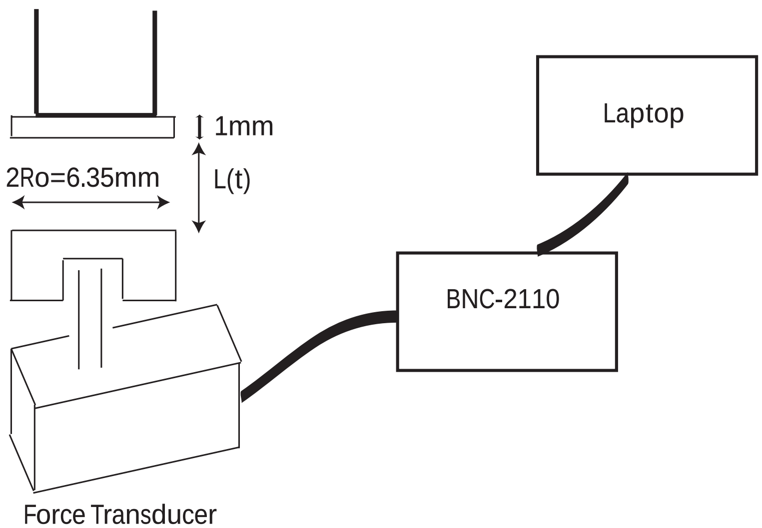

t = 0.01s

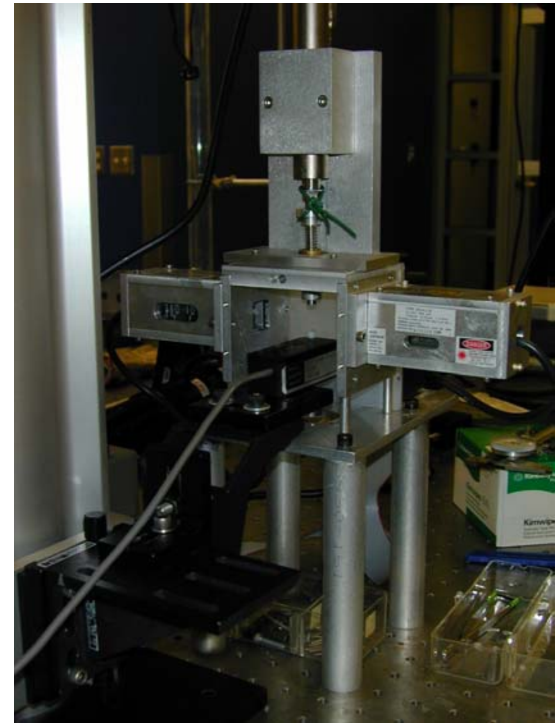

t = 11.71s


t = 22.70s

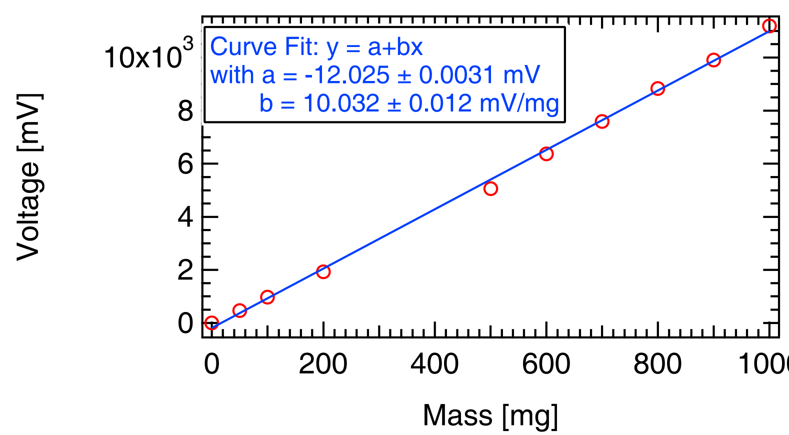

t = 34.00s

Force Transducer: Experimental Setup





Calibration:



Gain = 10 V/g

Maximal force =0.01 N = 1 g

Force measured on the bottom plate of the CABER

Force Balance:

$$F_N = 3\eta_S\dot{\varepsilon}\pi R^2(t) + \pi\sigma R(t) + \Delta\tau_p \pi R^2(t) - \rho g \pi \frac{R_0{}^2 L_0}{2}$$

Elongation:

$$\dot{\varepsilon} = \frac{v_{plate}}{L} \longrightarrow \dot{\varepsilon}(0^-) = 15.38 s^{-1} \quad \text{and} \quad R(0^-) = R_0 e^{-3/4\,\dot{\varepsilon}t}$$

$$\longrightarrow \begin{array}{l} F_V(0^-) = 2.07\times10^{-2}\,N \\ F_\sigma(0^-) = 2.12\times10^{-4}\,N \end{array}$$

Stress Relaxation:

Visco-Capillary part: $\dot{\varepsilon} = -\frac{2}{R}\frac{dR}{dt} = \frac{\sigma}{3\eta_S R} \longrightarrow \dot{\varepsilon}(0^+) = .158 s^{-1}$

$$F_N = 2\pi\sigma\left(R(0^+) - \frac{\sigma t}{6\eta_S}\right)$$

Force measured on the bottom plate of the CABER (2)

Elasto-Capillary part:

$$R(t) = R_i \left(\frac{G A_{zz}{}^0 R_i}{\sigma} \right) e^{-t/3\lambda}$$

$$F_V = \frac{2\pi\eta_S}{\lambda} R_i{}^2 \left(\frac{G A_{zz}{}^0 R_i}{\sigma} \right)^{2/3} e^{-2t/3\lambda}$$

$$F_\sigma = \pi\sigma R_i \left(\frac{G A_{zz}{}^0 R_i}{\sigma} \right)^{2/3} e^{-t/3\lambda}$$

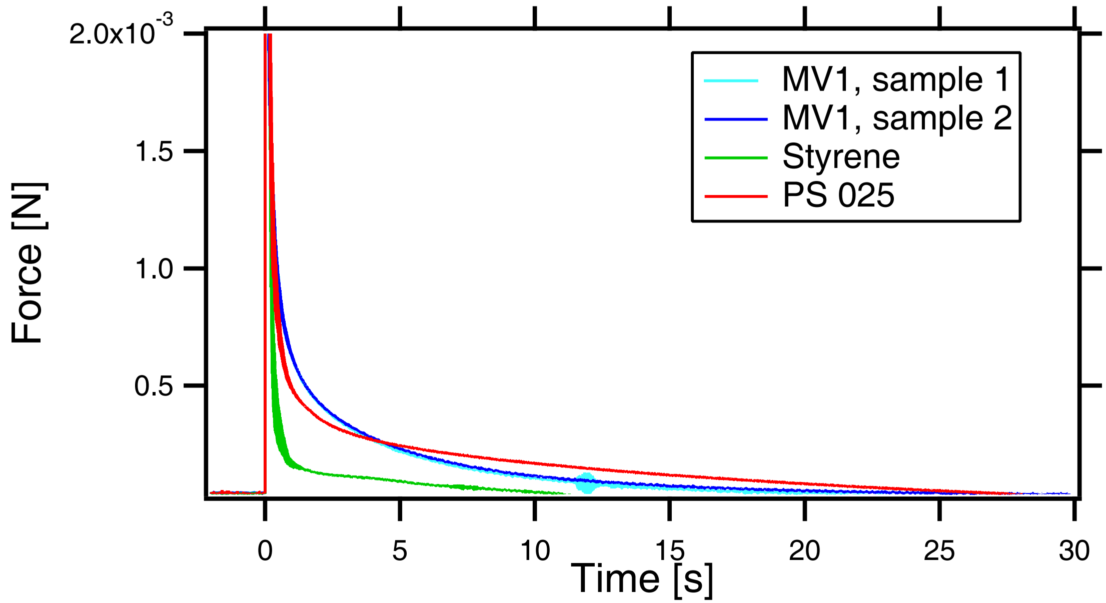
$$F_E = \pi G A_{zz}{}^0 R_i{}^2 \left(\frac{G A_{zz}{}^0 R_i}{\sigma} \right)^{2/3} e^{-t/3\lambda}$$

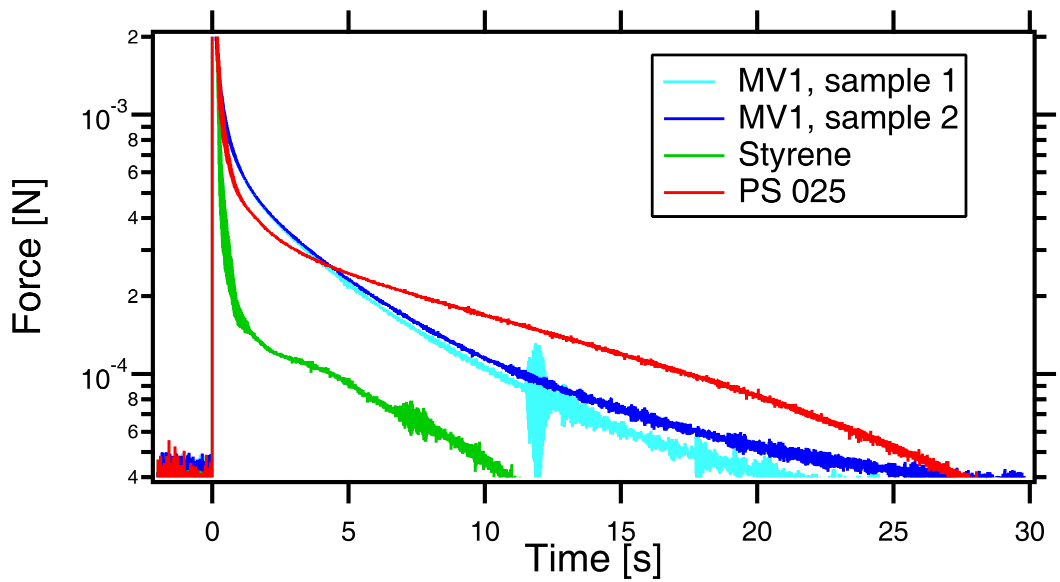
Measure of Azz0: exponential fit of the force data $F_\sigma + F_E = \alpha e^{-\beta t}$

Fluid	PS 025	MV1
$A_{zz}{}^0$	49.7	8.09
λ [s]	4.83	1.82

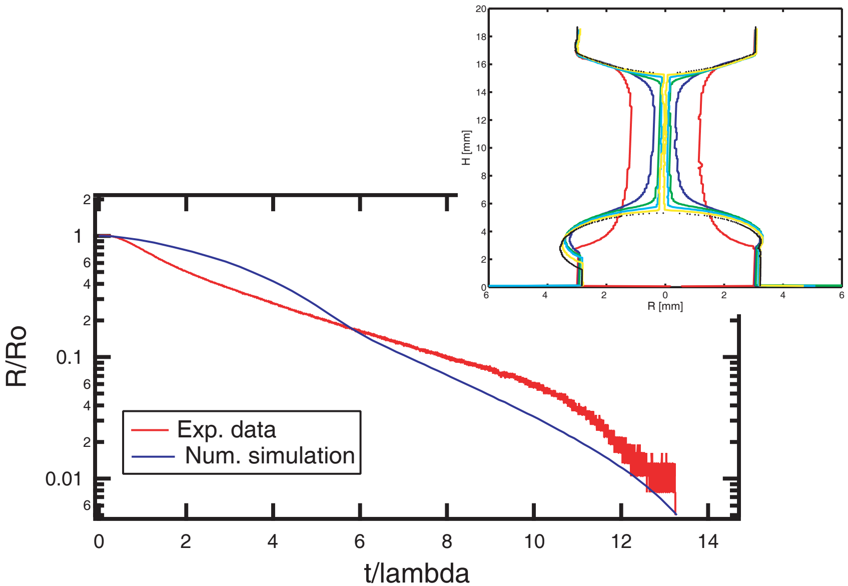
Fluid	PS 025	MV1
F_exp [N]	4.64×10^{-4}	4.49×10^{-4}
F_num [N]	4.25×10^{-4}	4.26×10^{-4}
F_an [N]	4.25×10^{-4}	4.25×10^{-4}

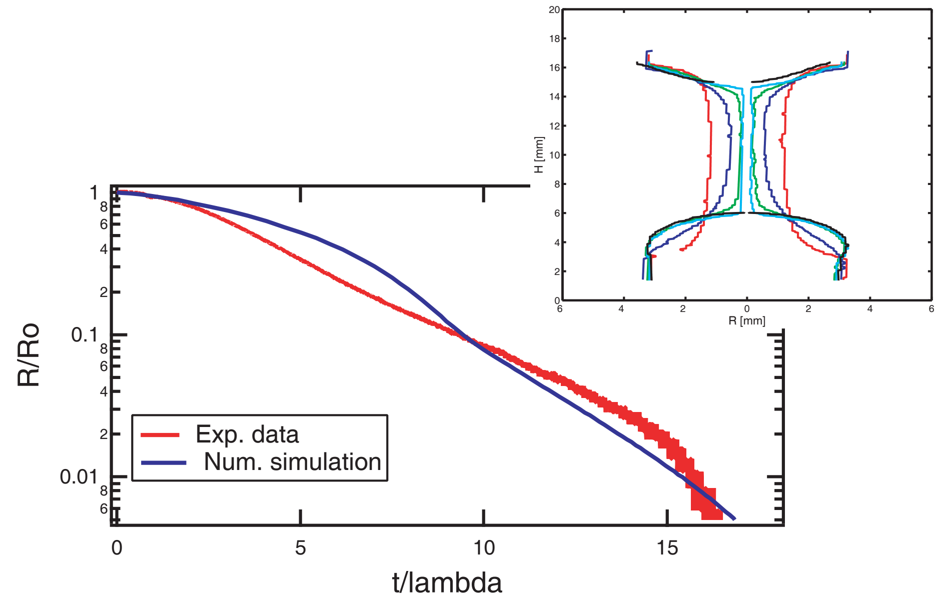
Experimental Results

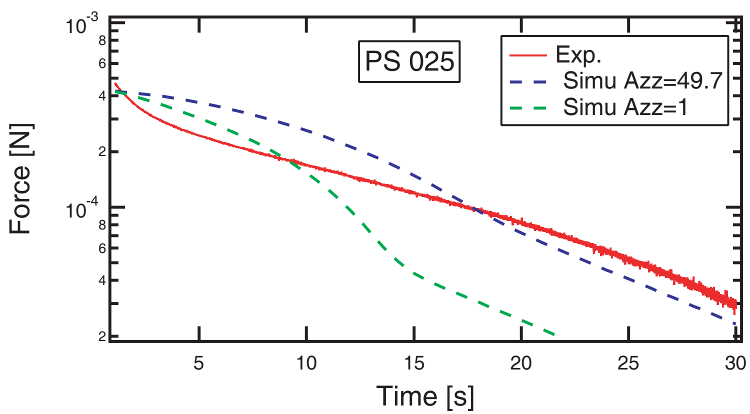


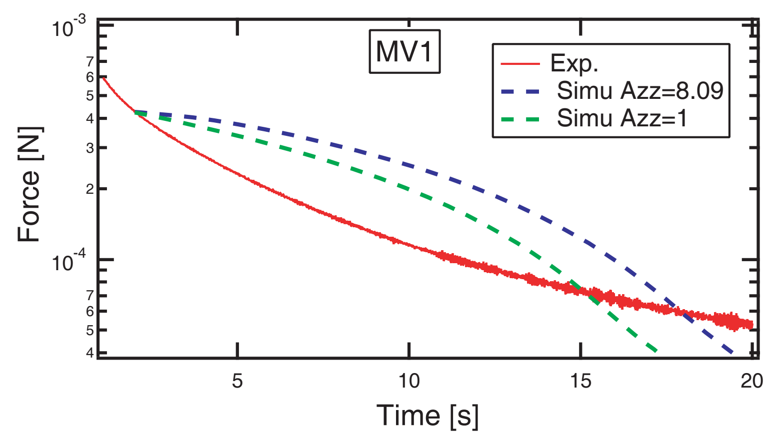


Comparison to the Simulations









Conclusion and Future Work

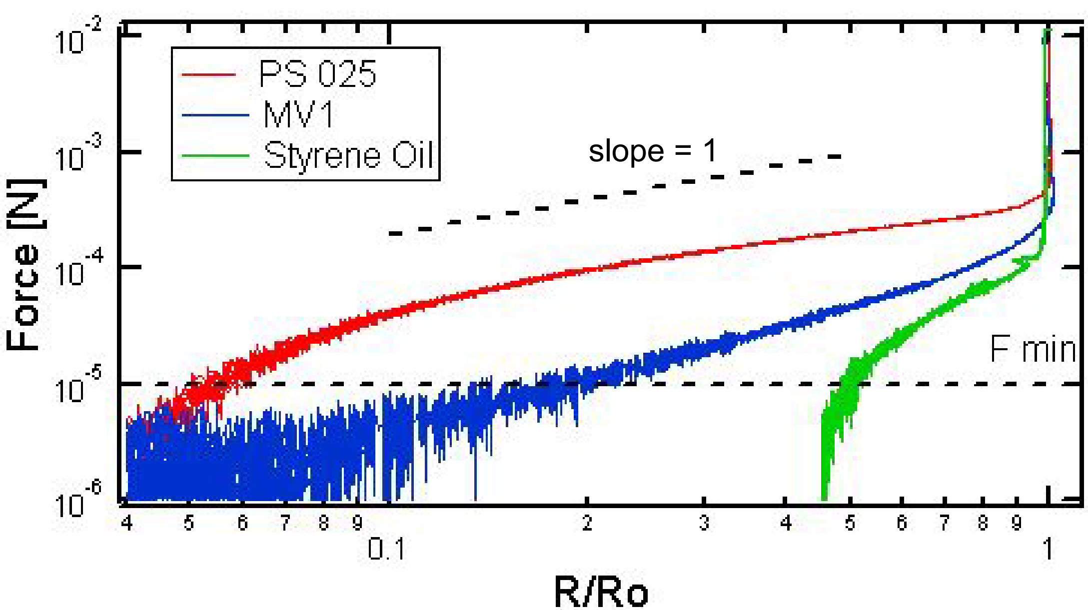
•Experimental and numerical demonstration of the concentration dependence for relaxation times.

•Breakdown of the necking in three asymptotic behaviors.

•Fabrication of a new viscoelastic fluid.

•Measure of the force on the bottom plate of the CABER: measure of Azz0.

•Simulation of the evolution of the force and comparison with experimental data.



QUESTIONS?