CAPILLARY BREAKUP TO DETERMINE THE EXTENSIONAL PROPERTIES OF POLYMERIC FLUIDS

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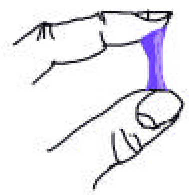
Introduction

- Industrial processing conditions always have some form of extensional deformation
  - Pumping, Filling, Spreading, Extrusion, Spinning and Ink-jets
- Biological Fluids often exposed to extensional flows
- Standard characterization techniques all shear
- Some work on extensional deformation
  - Filament Stretching Extensional Rheometer (FiSER) and similar
  - Rheometrix RME
  - RFX Opposed Jet
- Some techniques give pseudo-extensional properties
  - Capillary Rheometer
  - Fiber line tension
  - Falling ball
  - etc

References

Capillary Breakup Extensional Rheometer (CaBER™)

- Original concept by Entov and co-workers
- Fluid sets time scale
  - "Instantaneous" stretch in first case
  - Drainage governed by fluid
    - viscosity, elasticity, relaxation time, surface tension, effective extensional viscosity etc.
  - Gives measure of rheological parameters
  - Also measure of industrially relevant characteristic values
    - break-up time, stringiness etc.
- Analogous to "thumb-and-forefinger" test
  - sliding fingers gives how "slimy"
  - separating gives how "sticky"



References

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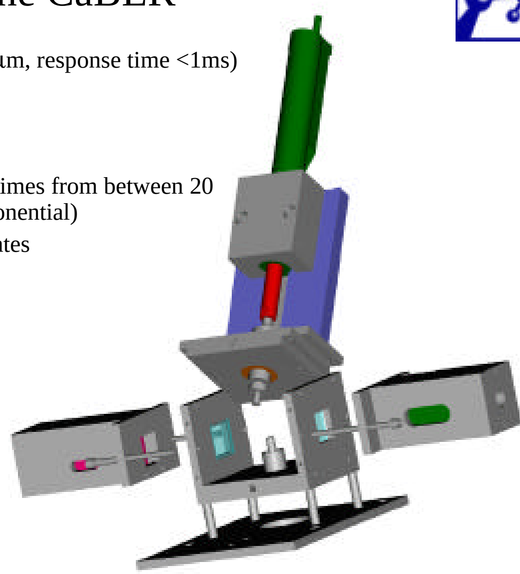
The CaBER™

- Laser Micrometer (resolution 5 µm, response time <1ms)
- Drive system:
  - Manual
  - Solenoid
  - Linear motor drive (stretch times from between 20 ms and >100s, linear or exponential)
- 6 mm diameter stainless steel plates
  - interchangeable
- Oven:
  - Low temperature to 120 ºC
  - High temperature to 300 ºC (in development)
- Force
- Camera
- Patent Pending



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CaBER™ - "Simple" Fluids

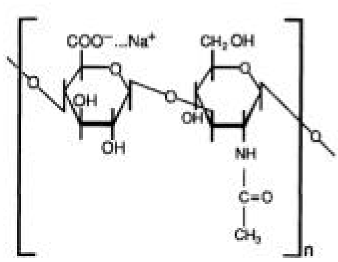
Constitutive Model	Form of Solution	Parameters found from regression to data
Newtonian, $t = h_s \dot{g}$	$D_{mid}(t) = 0.142 (s / h_s)(t_c - t)$	t_c, s / h_s
Power-Law Fluids $t = K \dot{g}^n$	$D_{mid}(t) = 2^{1-n} (0.142)(s / K)(t_c - t)^n$	t_c, s / K, n
Upper Convected Maxwell $t + l t_{(1)} = h_p \dot{g}$	$D_{mid}(t) = D_0 (G D_0 / s)^{1/3} \exp(-t / 3 l_c)$	l_c, G / s

- Newtonian
  - dynamics of the drainage of fluid column and rupture of the liquid bridge governed by viscous and elastic properties of fluid
- Viscoelasticity
  - rapid initial viscous-dominated phase, then intermediate time -scale where the filament drainage is governed by surface tension and elasticity

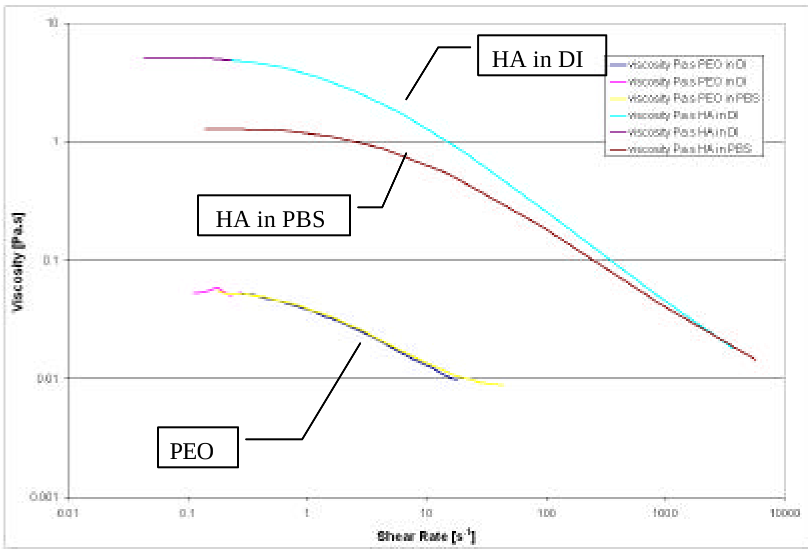
References

Test Fluids

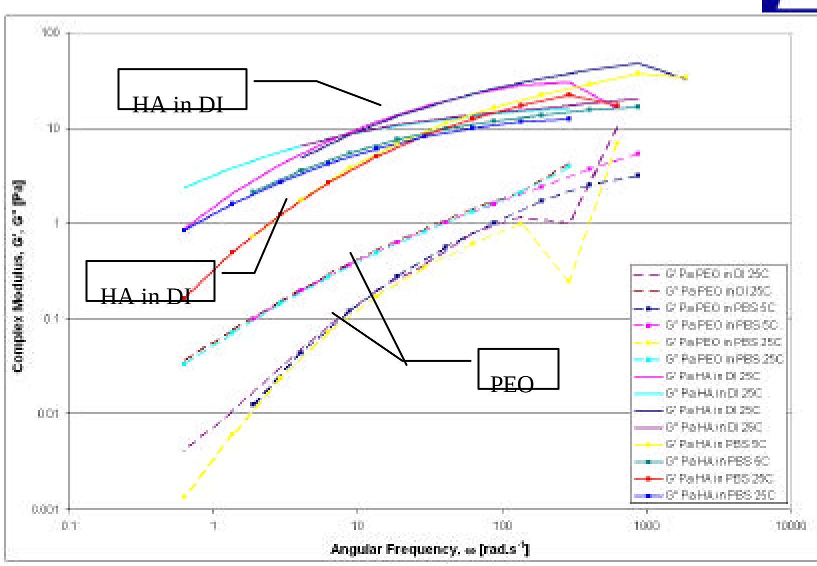
- Sodium Hyaluronate (HA)
  - 0.5 wt% in water at different salt concentrations (physiological in joint is ~0.3wt%)
  - Polysaccharide of sodium glucuronate and N-acetyl glucosamine
  - Molecular weight 1.68×10^6 g/mol
  - Known to associate in solution
- PEO from Scientific Polymer Products
  - 0.5 wt% in water at different salt concentrations
  - molecular weight 2.5×10^6 g/mol
- Cannon Instruments Newtonian Viscosity Standard N350
- Deionised water (DI) and Dulbecco's Phosphate Buffered Saline (PBS)
- Shear Rheology performed on TA Instruments AR1000N using a cone and plate geometry
- All experiments performed at 25 ºC ± 2 ºC



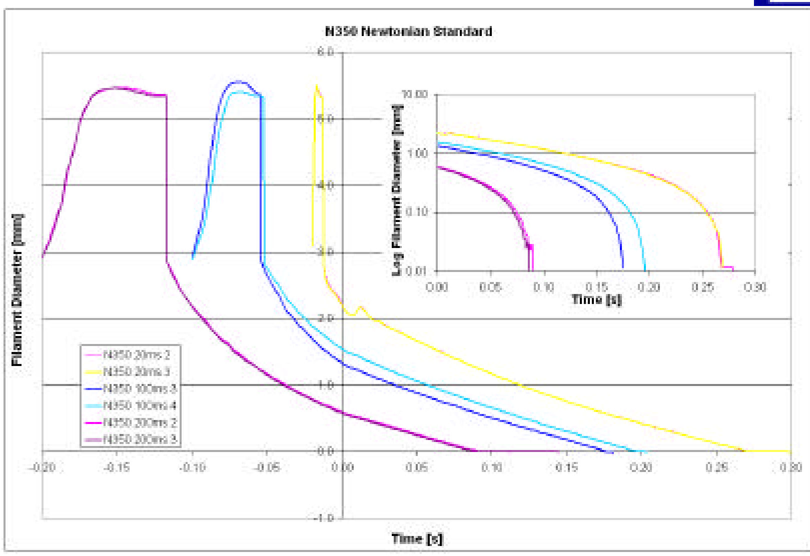
Shear Rheology (Steady)



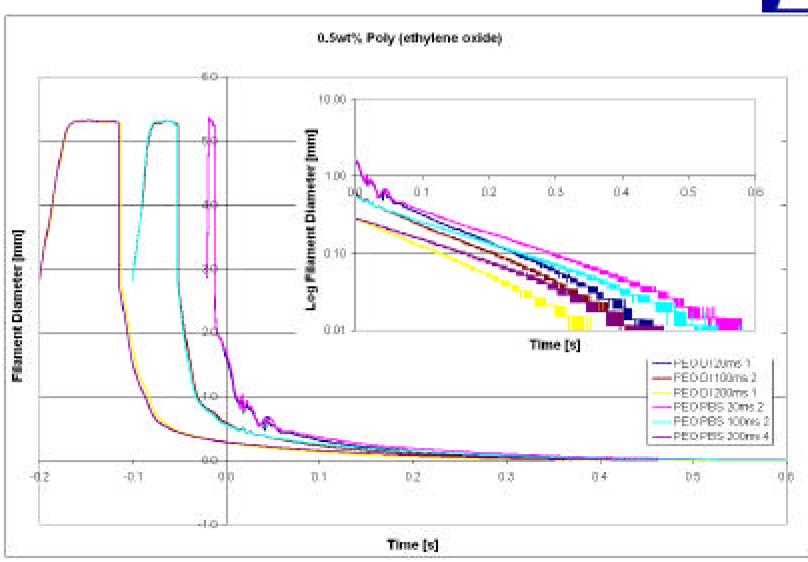
Shear Rheology (Dynamic)



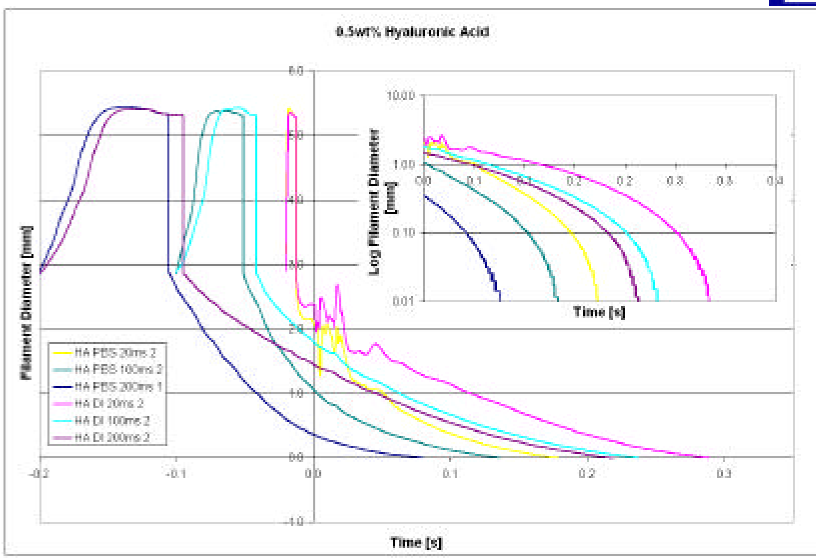
N350 Newtonian Standard Fluid



pEO Elastic Fluid



Hyaluronic Acid



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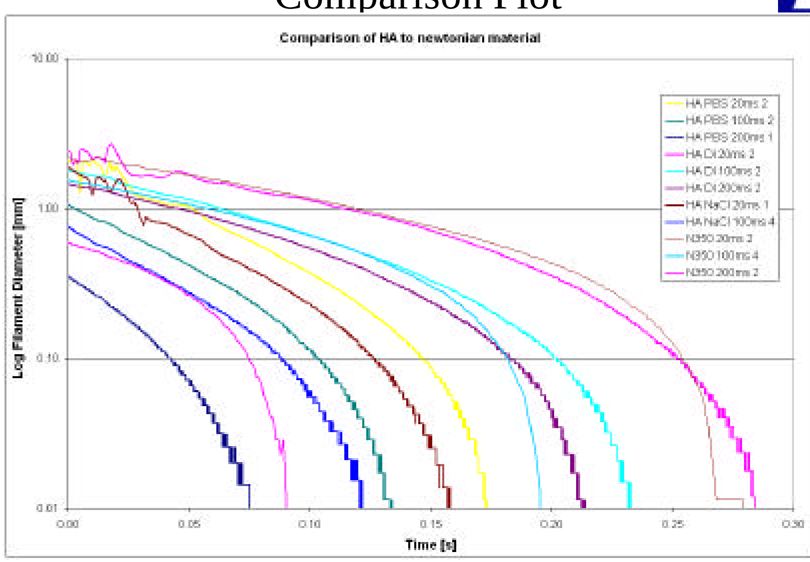
Comparison Plot



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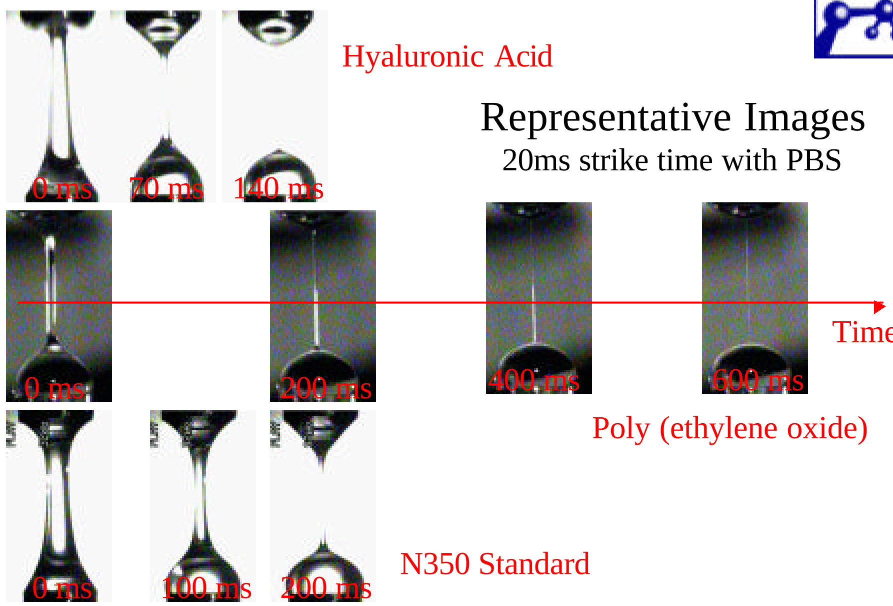
Representative Images

20ms strike time with PBS



Calculated rheological parameters

Fluid	Determined Viscosity [Pa.s]	Determined Relaxation Time [s]	Actual Viscosity [Pa.s] [3]	Actual relaxation time [s] [3]
N350	0.77 [1]	N/A	0.75 [2]	N/A
0.5 wt% PEO in DI	N/A	0.040	0.05	<0.05
0.5wt% PEO in PBS	N/A	0.045	0.05	<0.05
0.5 wt% HA in DI	N/A	N/A	5.1	1
0.5 wt% HA in PBS	N/A	N/A	1.3	0.3

[1] Assuming Surface Tension of 36 mN.m of Poly(butene)
[2] From Cannon Fluid Specifications @ 25 °C
[3] From Shear Rheology

Summary

- Demonstrated an instrument capable of studying capillary breakup of simple and complex fluids
  - Leads directly to information on the extensional properties of fluids
  - Fluid sets timescale
  - Complementary to shear data
- Presented data for three different fluids
  - Model Newtonian
  - Elastic
  - Associative (note rates)

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Conclusions

- Physiological fluids increasingly studied
  - Hyaluronic acid is clearly not a simple Newtonian liquid, nor is it a simple elastic fluid.
    - Shear rheology suggests a polymeric solution
    - Extensional rheology clearly indicates more complex
  - Salt subtle effect on PEO, strong effect on HA
    - Disruption of water "cage" around PEO?
      - Implication is PEO is less flexible in salt
    - Charge Screening on HA (but no effect on character of flow)
      - HA more flexible in salt or smaller "molecules"
    - HA is strike rate dependent – perhaps evidence for association
      - Rate dependence due to elasticity of fluid
    - "Shear Thinning" for HA suggest structure

CaBER™ - "Complex" Fluids

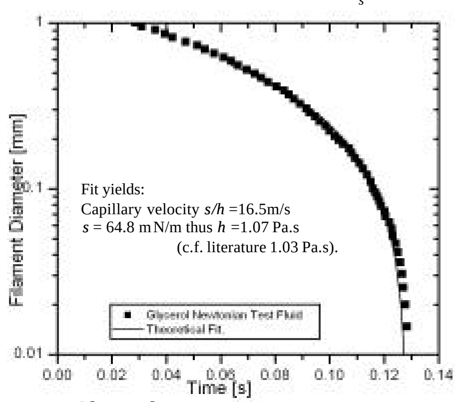
- Complex fluids
- A balance of forces on the fluid filament governs the evolution in the midpoint profile of the liquid bridge
- Allows derivation of an "apparent" extensional viscosity

$$\underbrace{3h_s\left(-\frac{2}{D_m}\frac{dD_m}{dt}\right)}_{\text{Viscous Stress}} = 3h_s\dot{e} = \underbrace{\frac{4F_z}{pD_m^2}}_{\text{Tensile Stress}} - \underbrace{[t_{zz}-t_{rr}]}_{\text{Elastic/ Non-Newtonian Stress}} - \underbrace{\frac{2s}{D_m}}_{\text{Capillary Pressure}}$$

$$\bar{h}_{app}(e) = \frac{2s/D_{mid}(t)}{\left\{-\frac{2}{D_{mid}}\frac{d\,D_{mid}}{d\,t}\right\}} = \frac{s}{\frac{d\,D_{mid}}{d\,t}}$$

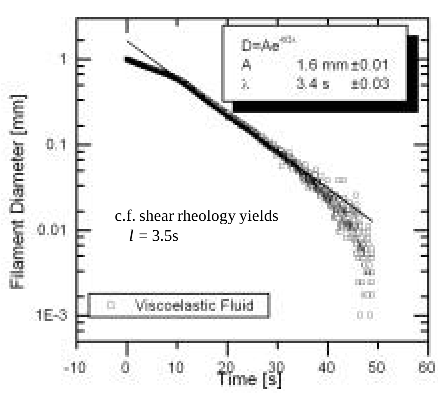
Example Data

$$D_{mid}(t) = D_1 - \frac{(2X(t)-1)}{3}\frac{s}{h_s}t$$



Glycerol

$$D_{mid}(t) = \frac{GD_0}{s}\exp(-t/3l_c)$$



0.025 wt% 2.5×10^6 Mw PS in Styrene oligomer

References

V. Tirtaatmadja and T. Sridhar, *Journal of Rheology*, **1993,**.36, 3, 277-284

S. Spiegelberg, D. Ables, and G. McKinley, *Journal of Non-Newtonian Fluid Mechanics*, **1996,**.64, 2-3, 229-267

A. V. Bazilevsky , V. M. Entov, and A. N. Rozhkov, "Liquid filament microrheometer and some of its applications," presented at Proceedings of the 3rd European Rheology Conference, 1990.

M. Renardy , *Journal of Non-Newtonian Fluid Mechanics*, **1994,**.51, 97-107

D. Papageorgiou, *Physics of Fluids*, **1995,**.7, 7, 1529-1544

V. M. Entov and E. J. Hinch, *J. Non-Newtonian Fluid Mech.*, **1997,**.72, 31-53

A. V. Bazilevskii, V. M. Entov, M. M. Lerner, and A. N. Rozhkov, *Polym. Sci., Ser. A*, **1997,**.39, 3, 316-324

J. Eggers, *Review of Modern Physics*, **1997,**.69, 3, 865-929

V. M. Entov and E. J. Hinch, *J. Non-Newtonian Fluid Mech.*, **1997,**.72, 31-53

A. Tripathi, P. Whittingstall, and G. H. McKinley, *Rheol. Acta*, **2000,**.39, 321-337

G. H. McKinley and A. Tripathi, *Journal of Rheology*, 2000,.44, 3

W. E. Krause, E. G. Bellemo, and R. H. Colby, *Biomacromolecules*, **2001,**.2, 1, 2001