A Technique for Characterizing Complex Polymer Solutions in Extensional Flows

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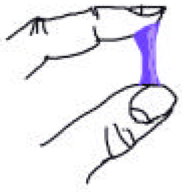
Introduction

- Industrial processing conditions always have some form of extensional deformation
  - Pumping, Filling, Spreading, Extrusion, Spinning and Ink-jets
- Standard characterization techniques all shear
- Some work on extensional deformation
  - Filament Stretching Extensional Rheometer (FiSER) and similar
  - Rheometrix RME
  - RFX Opposed Jet

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

Motivation

- Clearly an experimental niche is open that requires an instrument that is:
  - compact (suitable for shop floor or lab bench operation)
  - robust (capable of fast turn around)
  - simple design (to allow easy operation and modification)
  - easy characterization (capable of rapidly yielding characteristic material parameters).
- Simplest intuitive test is “thumb-and-forefinger”



Motivation

- Polymeric solutions common in industry
- In particular polymers derived from bio-materials common as process aids and rheological modifiers
- Materials such as those based on cellulose extremely common, finding uses in fields such as:
  - cosmetics (toothpastes, shampoos, lotions, adhesives,….)
  - foods (sauces, beverages,…)
  - pharmaceuticals (suspensions, creams, tablets,…)
  - paper/textiles (binders, thickeners,…)
  - ceramics (binders, thickeners,…)

- Hydroxy propyl methyl cellulose

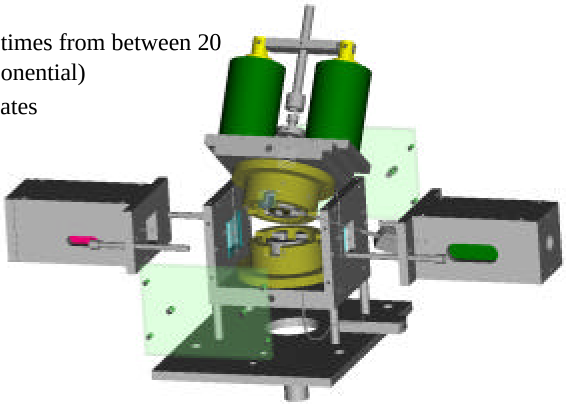
Capillary Breakup
Extensional Rheometer (CaBER™)

- Original concept by Entov and co-workers
- Fluid sets time scale
  - “Instantaneous” stretch
  - 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.

References:
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

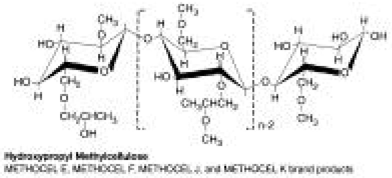
The CaBER™

- 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



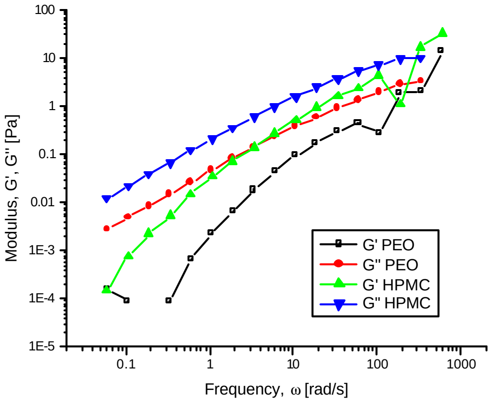
Test Fluids

- HPMC Methocel K100M from Dow Chemical
  - 0.5 wt% in water
  - Degree of substitution 1.4 (22% Methoxyl, 8.1% Hydroxypropyl)
  - approximate molecular weight 10^5 g/mol
  - Known to weakly gel under correct conditions
- PEO from Scientific Polymer Products
  - 0.5 wt% in water
  - molecular weight 2.5×10^6 g/mol
- Shear Rheology performed on TA Instruments AR1000N using a cone and plate geometry
- All experiments performed at 25 ºC ± 2 ºC

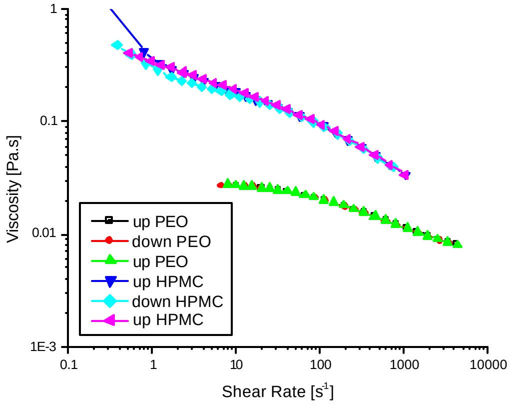


From Methocel Cellulose Ethers Technical Handbook. Dow Chemical Company

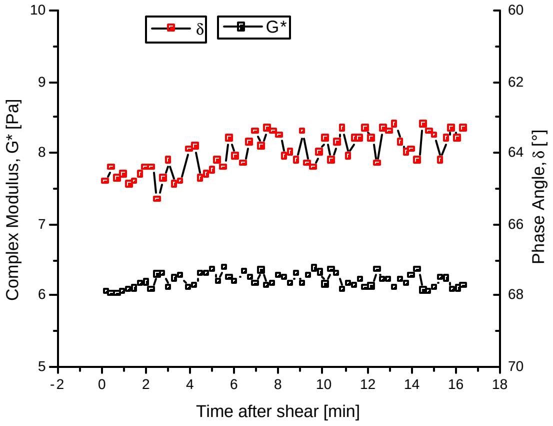
Shear Rheology



Shear Rheology

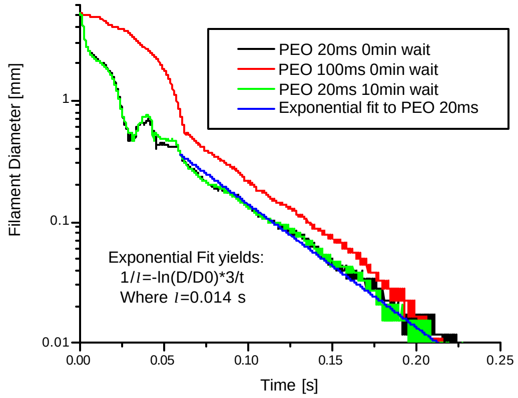


Relaxation after steady shear



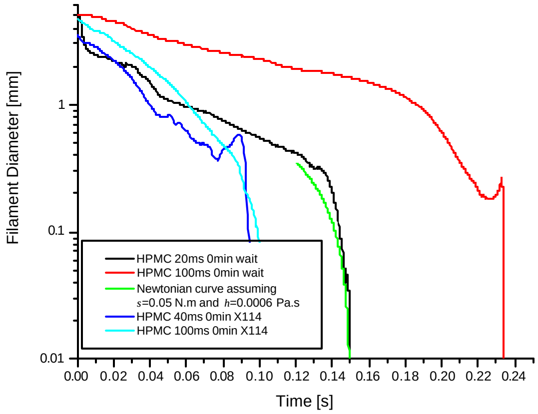
Data collected at 60 rad/s after a steady shear for 2 minutes of 2000 Pa

Capillary Breakup



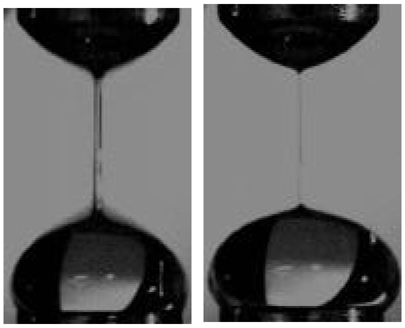
PEO in water

Capillary Breakup

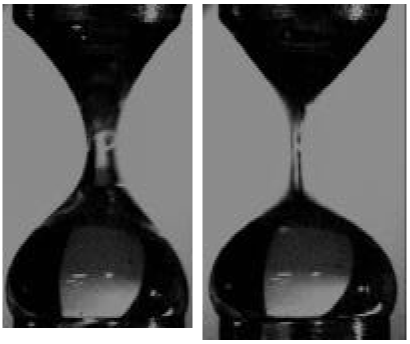


HPMC in water with and without Triton X114 surfactant (Union Carbide)

Images

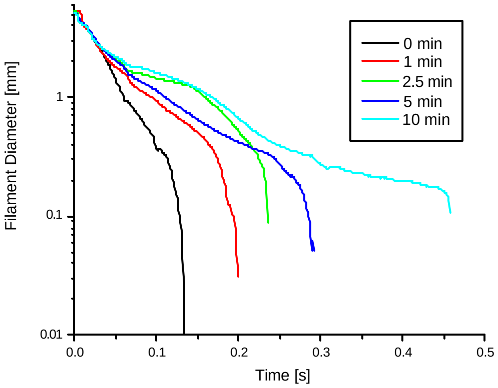


PEO



HPMC

Capillary breakup with time



Note: representative data show repeatability extremely difficult

Summary

- PEO solution is a weakly elastic solution
  - CaBER relaxation time consistent with oscillatory data
  - breakup independent of stretch rate
- HPMC
  - oscillatory rheology resembles PEO data
  - shear rheology hints at more complexity (hysterisis, no plateau)
  - breakup appears to be rate sensitive
  - response time dependant
  - behavior strongly modified by surfactant
    - aggregates
    - structure
    - dehydration
  - Environment may be an issue

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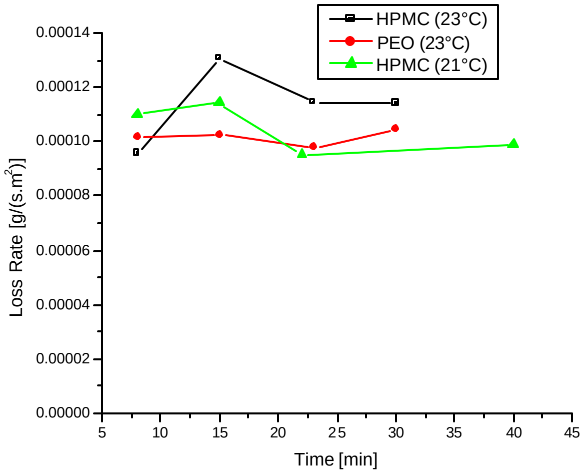
Conclusions

- Demonstrated an instrument capable of studying capillary breakup of simple and complex fluids
- Showed comparison of polymeric solutions where polymers are interacting and associating
- Observed effects not obvious in shear rheology
- Clearly question mark over environmental conditioning of samples

Evaporation



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 $t = K \dot{g}^n$	$D_{mid}(t) = 2^{1-n} (0.142)(s / \mathrm{K})(t_c - t)^n$	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

    J. Eggers, *Review of Modern Physics*, **1997**, 69, 3, 865-929
    G. H. McKinley and A. Tripathi, *Journal of Rheology*, **2000**, 44, 3
    D. Papageorgiou, *Physics of Fluids*, **1995**, 7, 7, 1529-1544

- Viscoelasticity
  - rapid initial viscous-dominated phase, then intermediate time-scale where the filament drainage is governed by surface tension and elasticity

    M. Renardy, *Journal of Non-Newtonian Fluid Mechanics*, **1994**, 51, 97-107
    V. M. Entov and E. J. Hinch, *J. Non-Newtonian Fluid Mech.*, **1997**, 72, 31-53

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

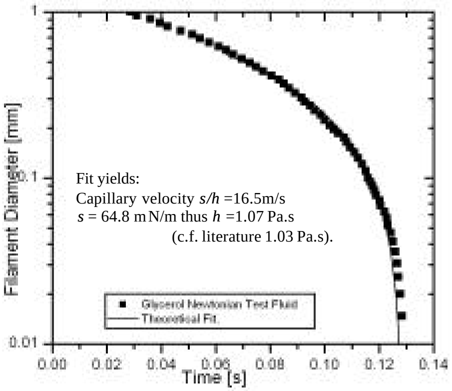
$$\underbrace{3h_s\left(-\frac{2}{D_m}\frac{dD_m}{dt}\right)}_{\text{Viscous Stress}} = 3h_s\dot{e} = \underbrace{\frac{4F_z}{p D_m^{\,2}}}_{\text{Tensile Stress}} - \underbrace{\left[t_{zz} - t_{rr}\right]}_{\text{Elastic/ Non-Newtonian Stress}} - \underbrace{\frac{2s}{D_m}}_{\text{Capillary Pressure}}$$

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

Example Data

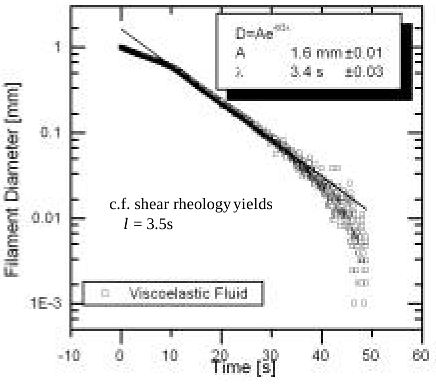
$$D_{mid}(t) = D_1 - \frac{(2X(t)-1)}{3}\frac{s}{h_s}t$$

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



Fit yields:
Capillary velocity s/h =16.5m/s
s = 64.8 mN/m thus h =1.07 Pa.s
(c.f. literature 1.03 Pa.s).

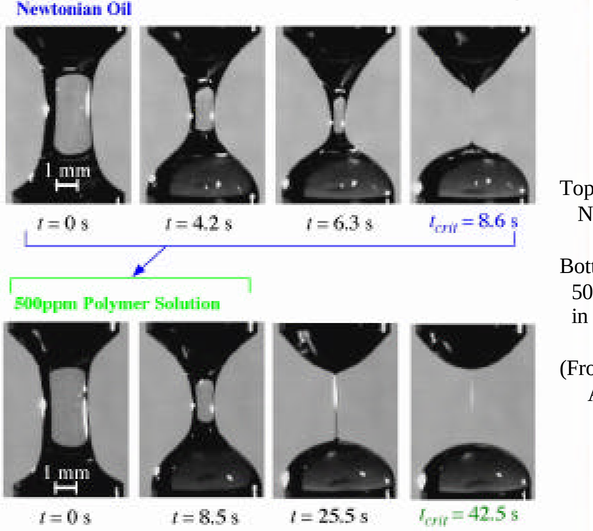
Glycerol



c.f. shear rheology yields
l = 3.5s

0.025 wt% 2.5×10⁶ Mw
PS in Styrene oligomer

Example Images



Top Images:
Newtonian oil (styrene oligomer)

Bottom Images:
500 ppm Polystyrene (2.5×10^6 Mw)
in styrene oligomer

(From G. H. McKinley and
A. Tripathi, *J. Rheol.*, **2000,**.44, 3)

Sample Images