ESR Cardiff
April 2009

Extreme Rheology; beyond normal boundary conditions

by
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With acknowledgement to
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Polymer Fluids

Areas of extremes!

- **Linear Viscoelasticity**

  Low viscosity, weakly viscoelastic fluids

  example; ink jet fluids.

- **Non Linear viscoelasticity**

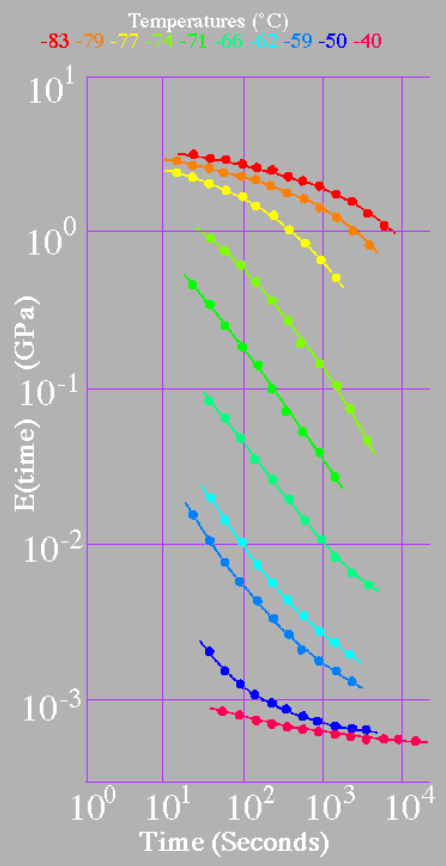
  a) Low viscosity, weakly viscoelastic fluids

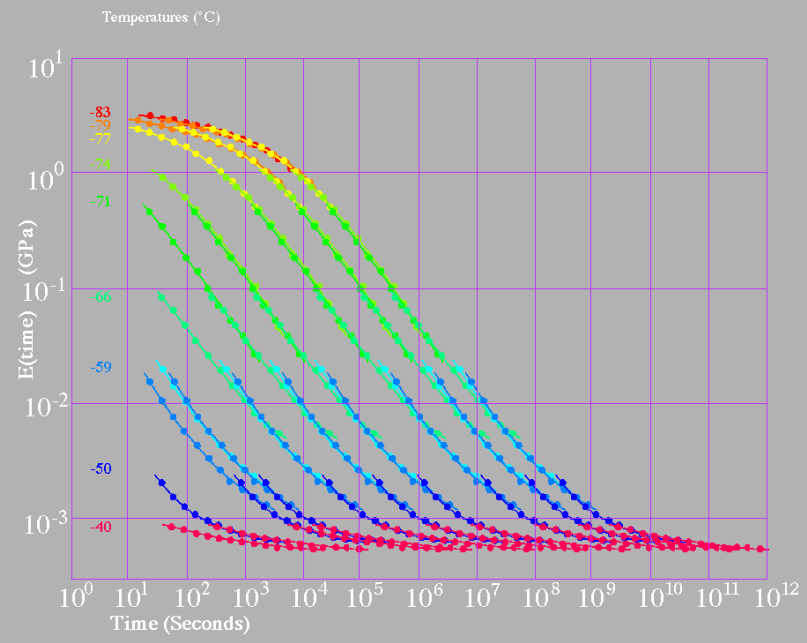
  example; ink jet fluids

  b) High viscosity, limiting large strain, extensional viscosities

  example; polymer melts

WLF; The frequency domain escape route

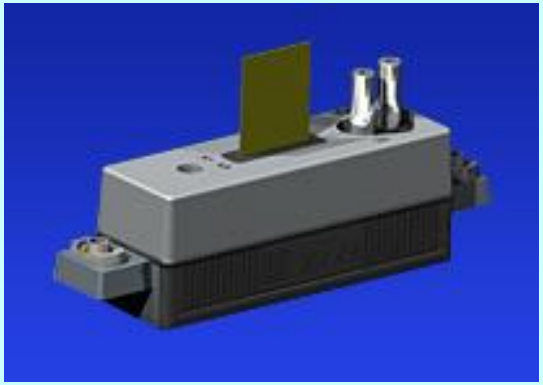




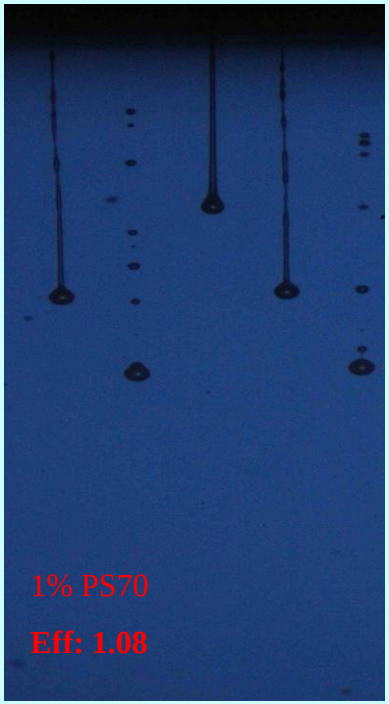
http://web.mst.edu/~wlf/Mechanical/timetemp.html

Xaar DOD Printhead

Platform III : Side shooter
Multipulse grey scale printhead (1001 series)

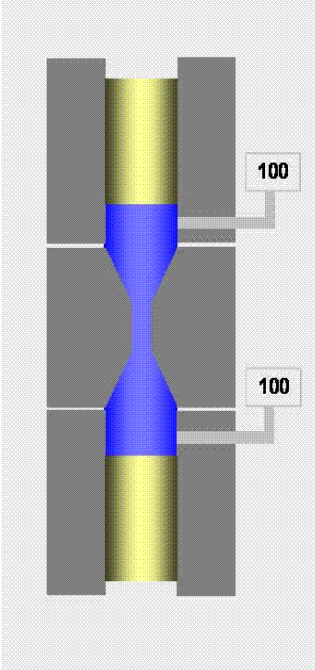


DOD drop formation

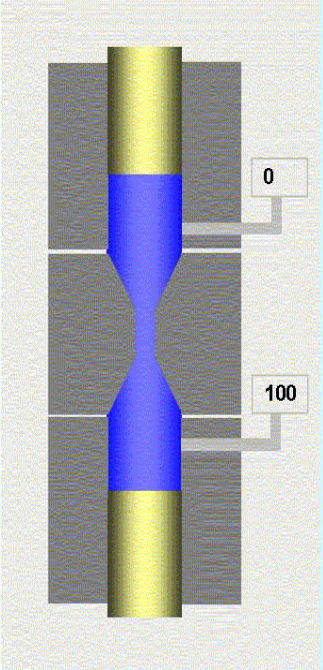


30 micron drops, ms timescale
Photo, courtesy of Dr Steve Routh

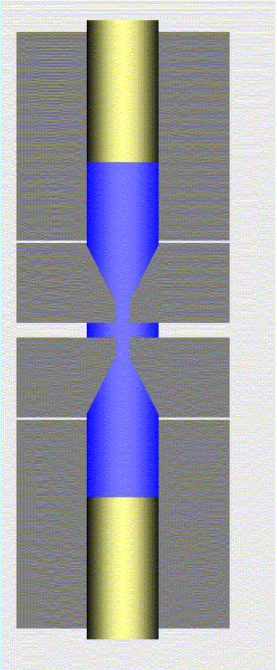
The Cambridge MultiPass Rheometer (MPR)



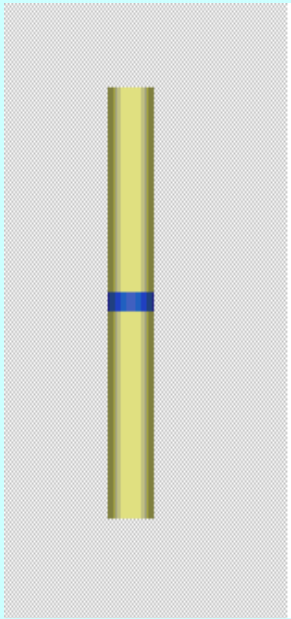
Pressure variation mode



Rheology flow mode

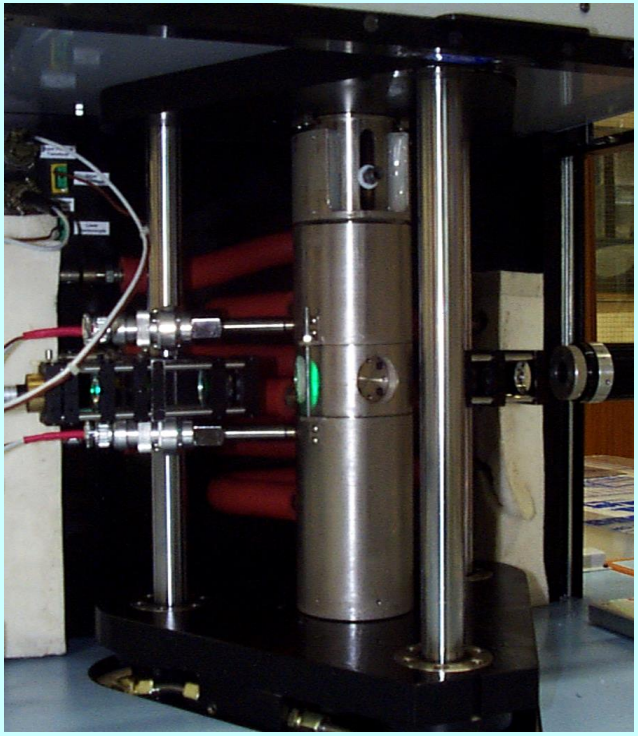


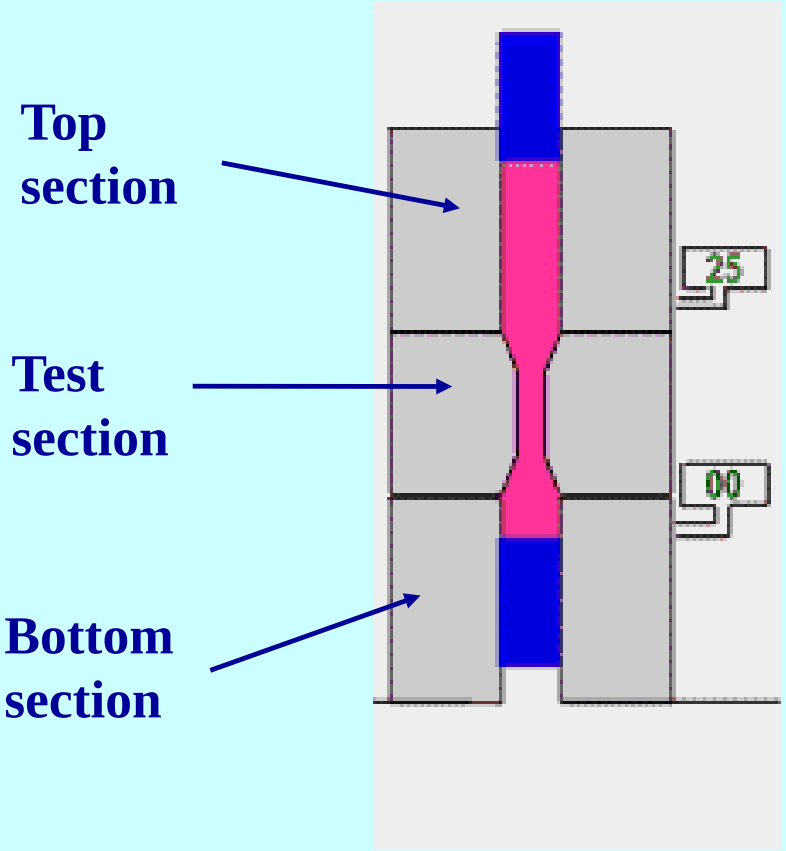
Cross-slot flow mode



Filament stretch mode

The Cambridge Multipass Rheometer (MPR4)





MPR as capillary rheometer

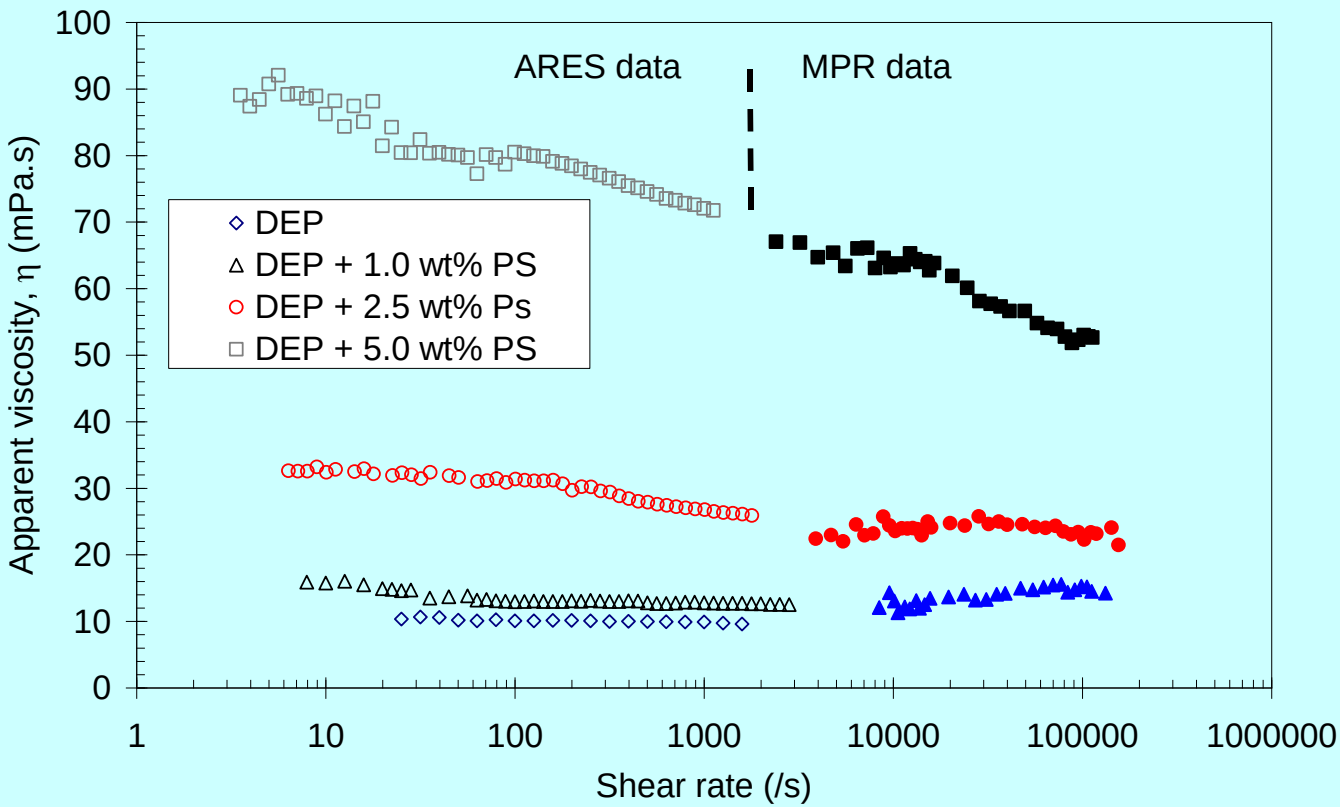
Diethyl phthalate (DEP) Supplier: Sigma Aldrich

BP = 294-296°C; ρ = 1118 kg/m^3 ;

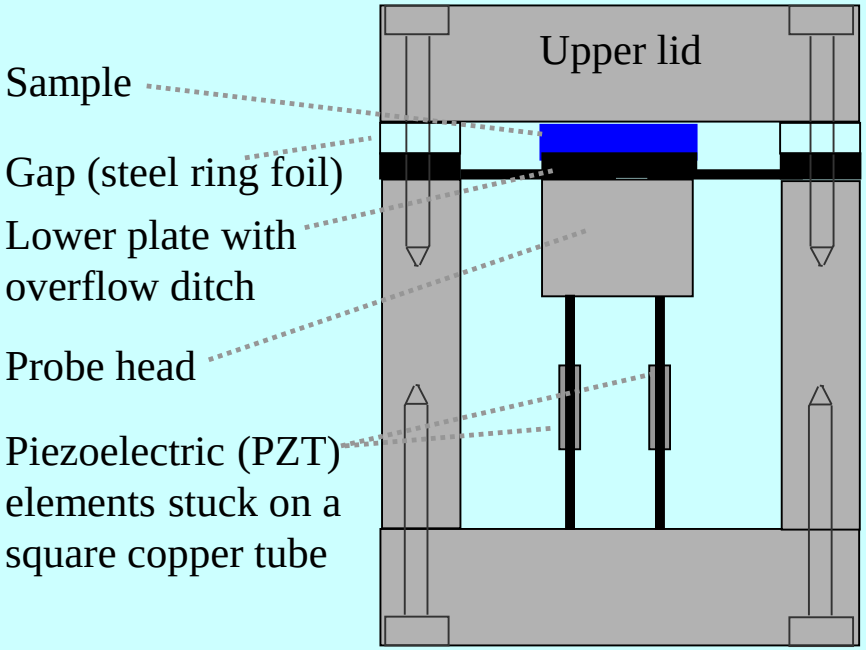
$\sigma_{20°C}$ = 36 mN/m; $\eta_{25°C}$ = 10 mPa.s

Polystyrene: Supplier: BASF – Polystyrol VPT granule

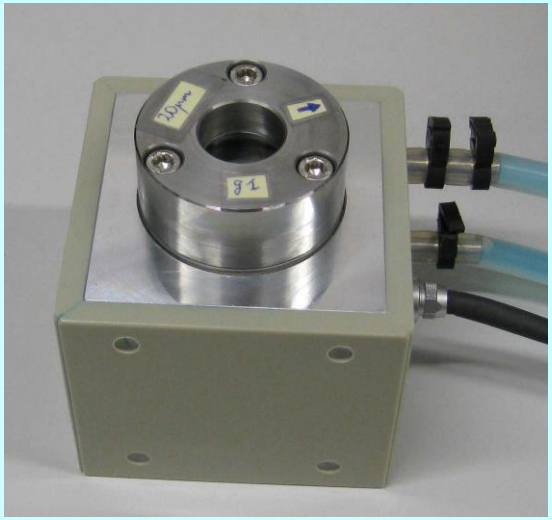
M.W ~ 195000



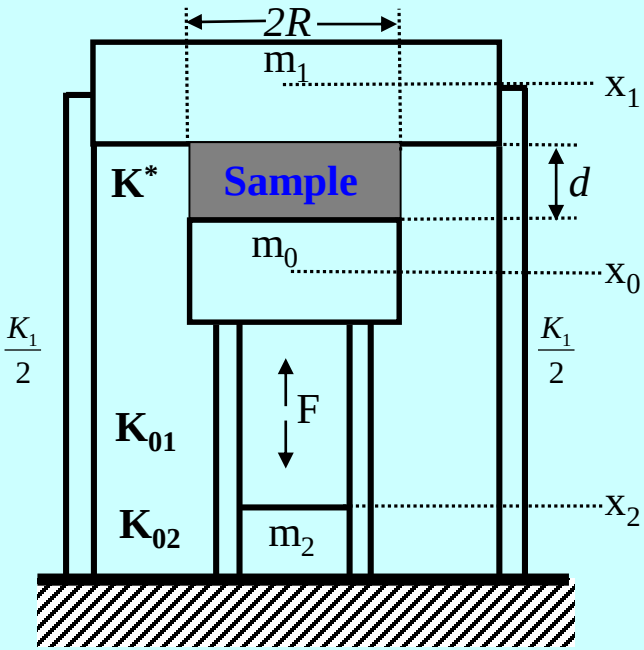
Measurement of Linear Viscoelasticity (LVE)
Piezo Axial Vibrator (PAV)
Developed by Prof Wolfgang Pechold
University of Ulm. Germany



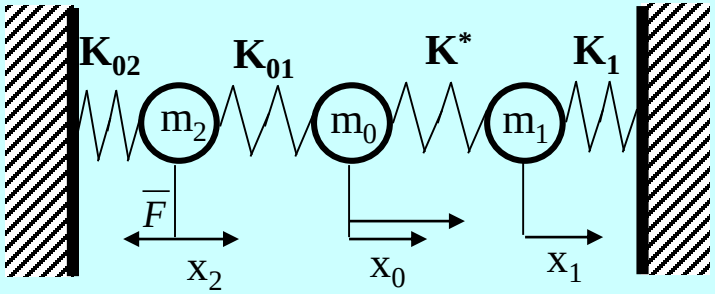
Section of PAV



Mechanical equivalent model of PAV



Mechanical equivalent model of the PAV.



Mechanical representation with springs.

The lower plate oscillates with force F ($\propto$ excitation volt U_{ref}) for a given frequency.

With blank test: Dynamic compliance of the lower plate is measured.

$$\left(\frac{\Delta x}{F}\right)_0 \sim \frac{U}{U_{ref}} e^{i\delta_0}$$

With sample: Modulated compliance of the sample is measured

$$\left(\frac{\Delta x}{F}\right)^* \sim \frac{U}{U_{ref}} e^{i\delta}$$

Complex squeeze stiffness ***K**** of the material can be calculated from the ratio of $\Delta \boldsymbol{x_0}$ and $\Delta \boldsymbol{x^*}$.

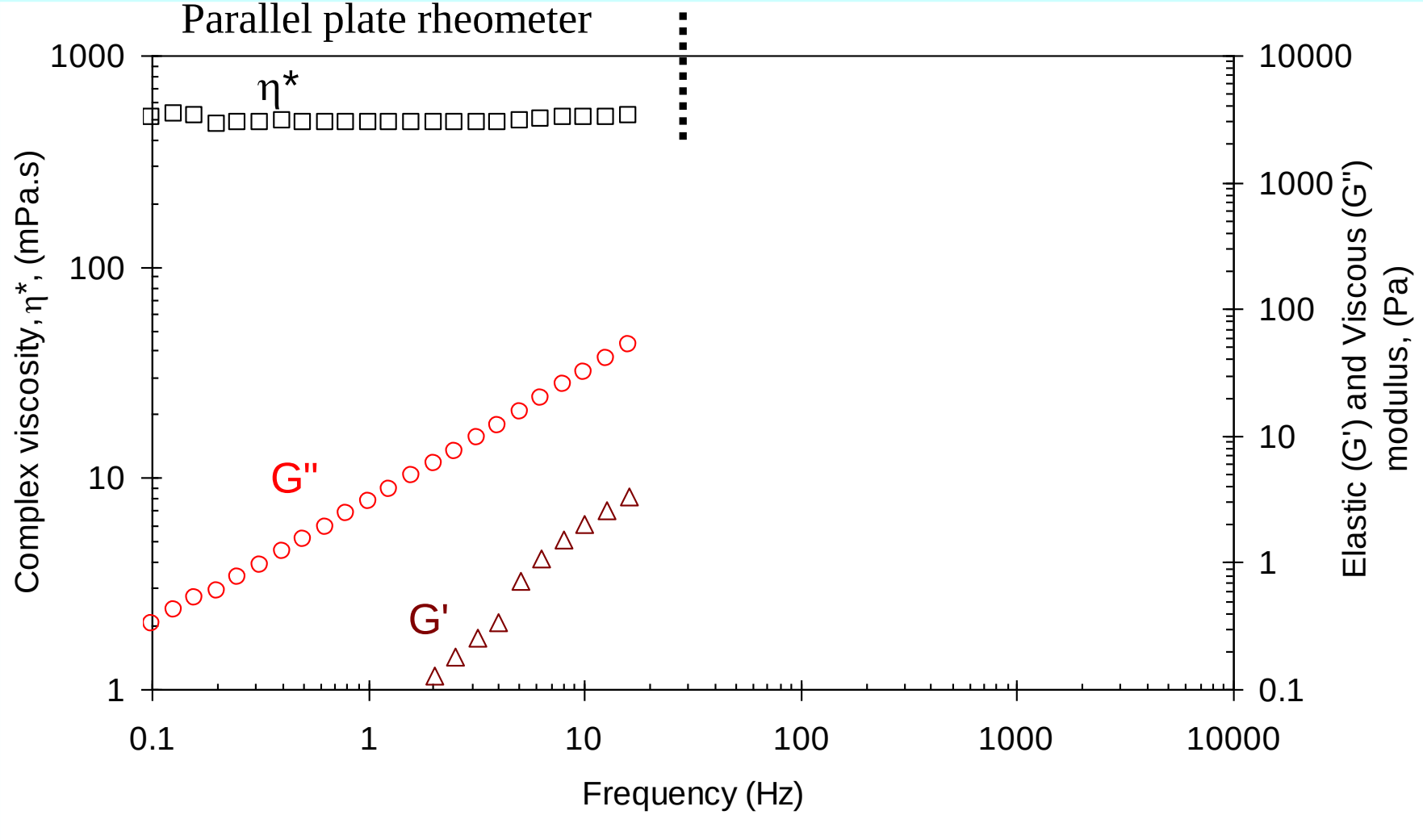
For linear viscoelasticity

$$G^* = \frac{2}{3\pi}\frac{d^3}{R^4}K^*\left(1+\frac{\rho\omega^2 d^2}{10G^*}+....\right)$$

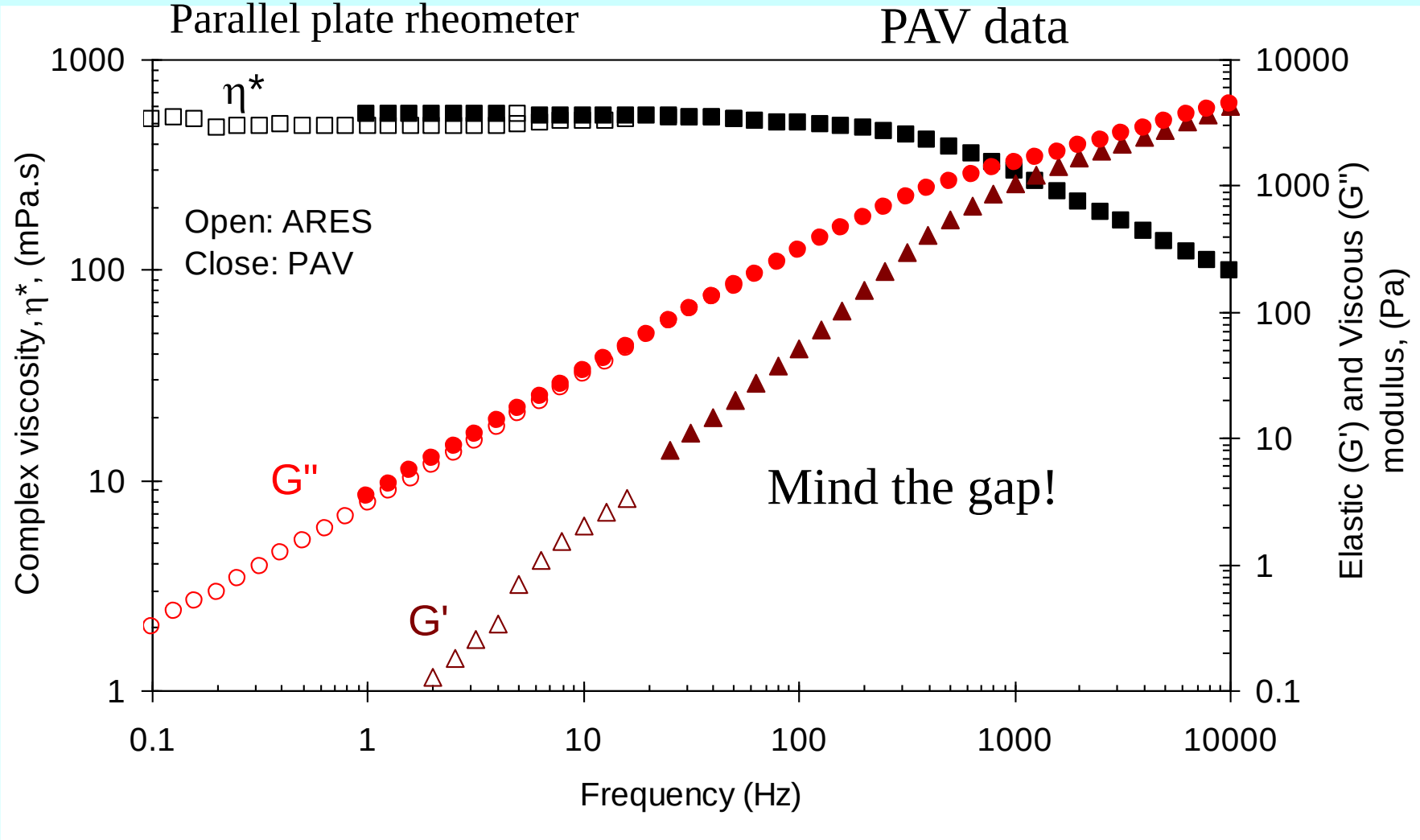
$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

$$\eta^* = \frac{\sqrt{G'^2+G''^2}}{\omega}$$

High frequency linear viscoelastic data of DEP-10% PS210 at 25°C

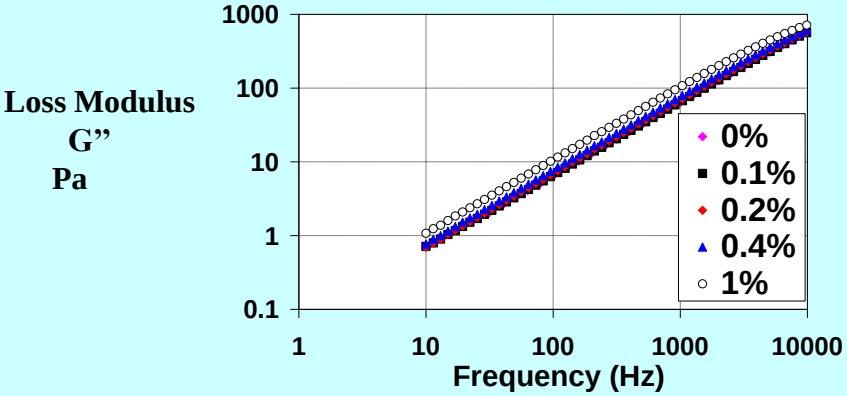


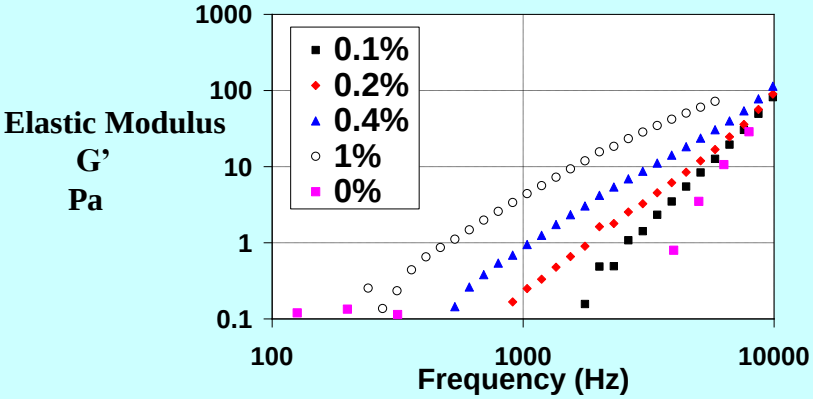
High frequency linear viscoelastic data of DEP-10% PS210 at 25°C

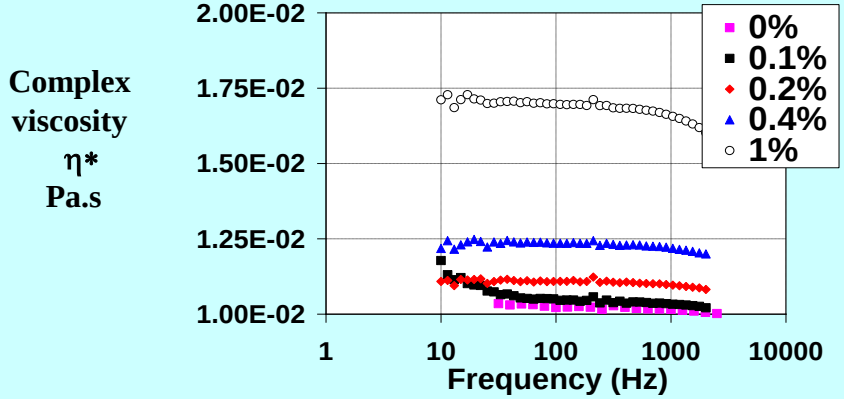


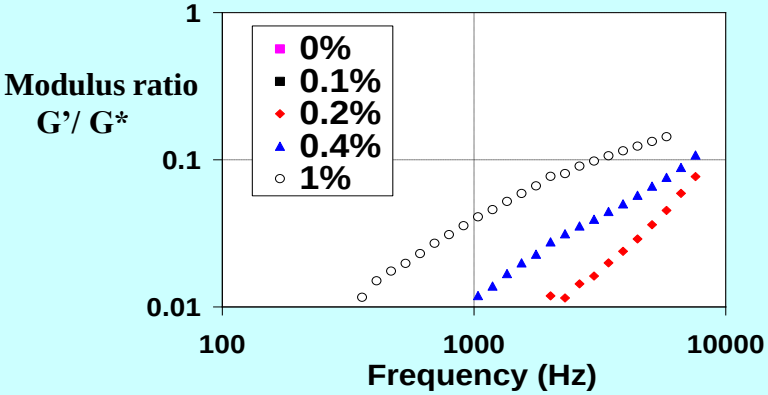
Effect of Polymer on the Linear Viscoelastic response of 'model' fluid containing different polymer concentration

Polystyrene MW = 210k in Diethyl Phthalate (DEP) solvent





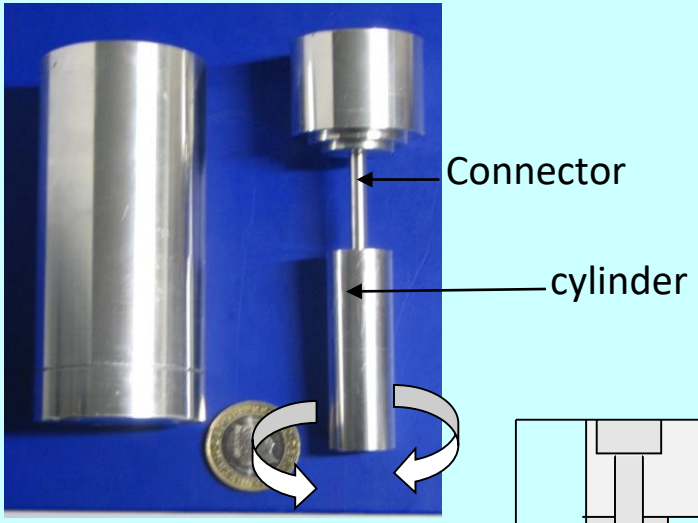




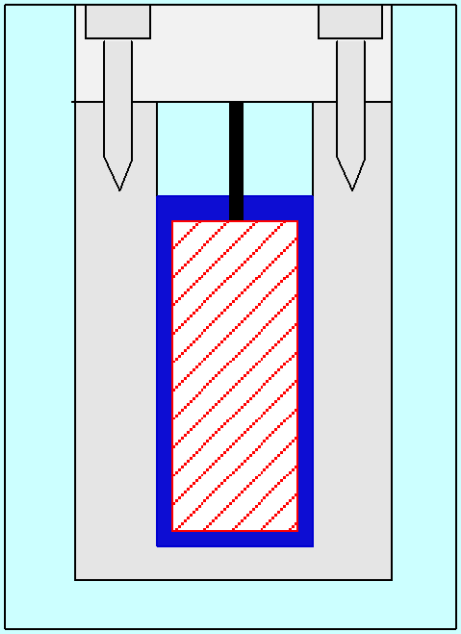
The Torsion Resonator

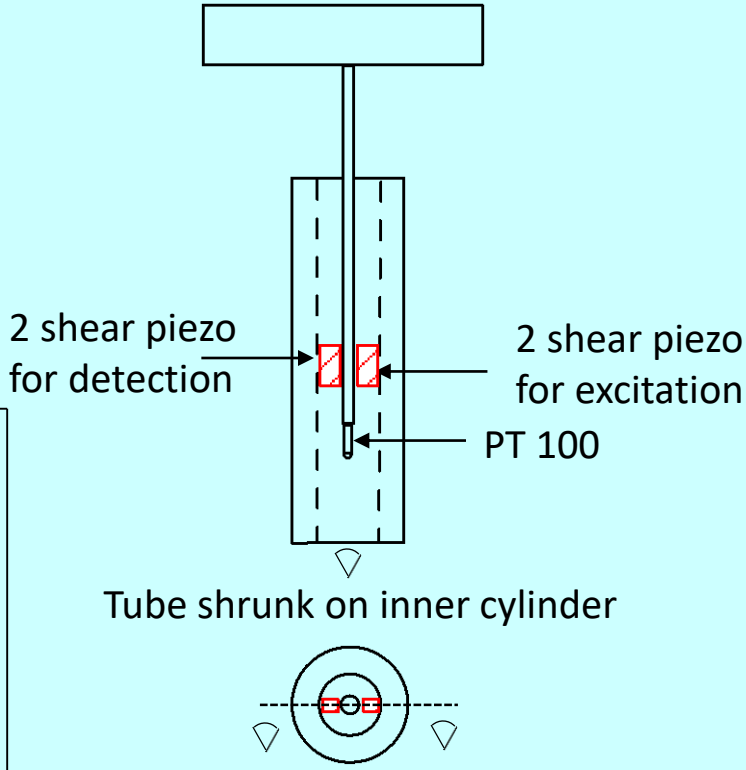
(Prof Pechold (again!) ; University of Ulm)

linear viscoelastic behaviour (LVE)



Photograph of the Torsion resonator





Schematic (side and top view) of the Torsion resonator

The Torsion Resonator

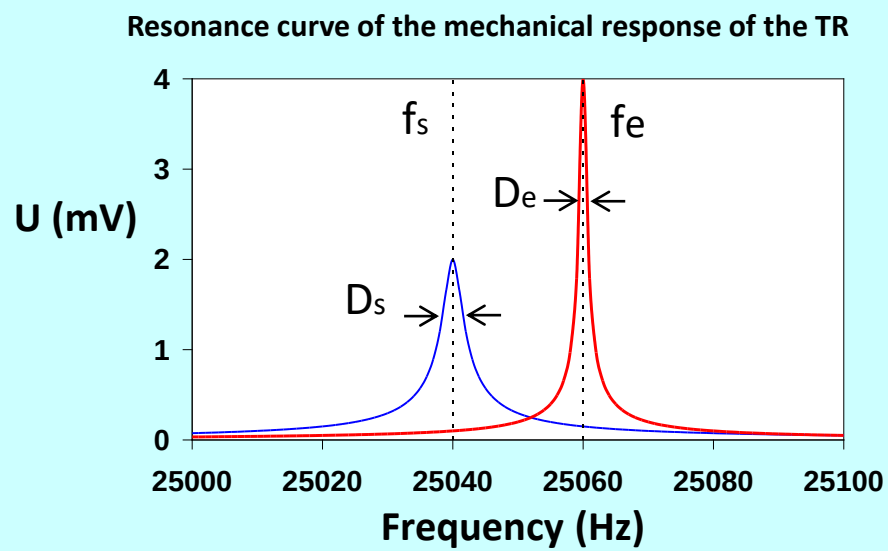
(Damien Vadillo)

The linear viscoelastic behaviour (LVE)

The piezoelectric sensor oscillates at resonance frequencies, 26kHz and 77kHz respectively.

With blank test: Determination of the apparatus constant temperature correction coefficient for each frequency

With sample: Measure the resonance frequency shift Δf (=f_s-f_e) and the damping shift ΔD (=D_s-D_e) at each resonance frequency.



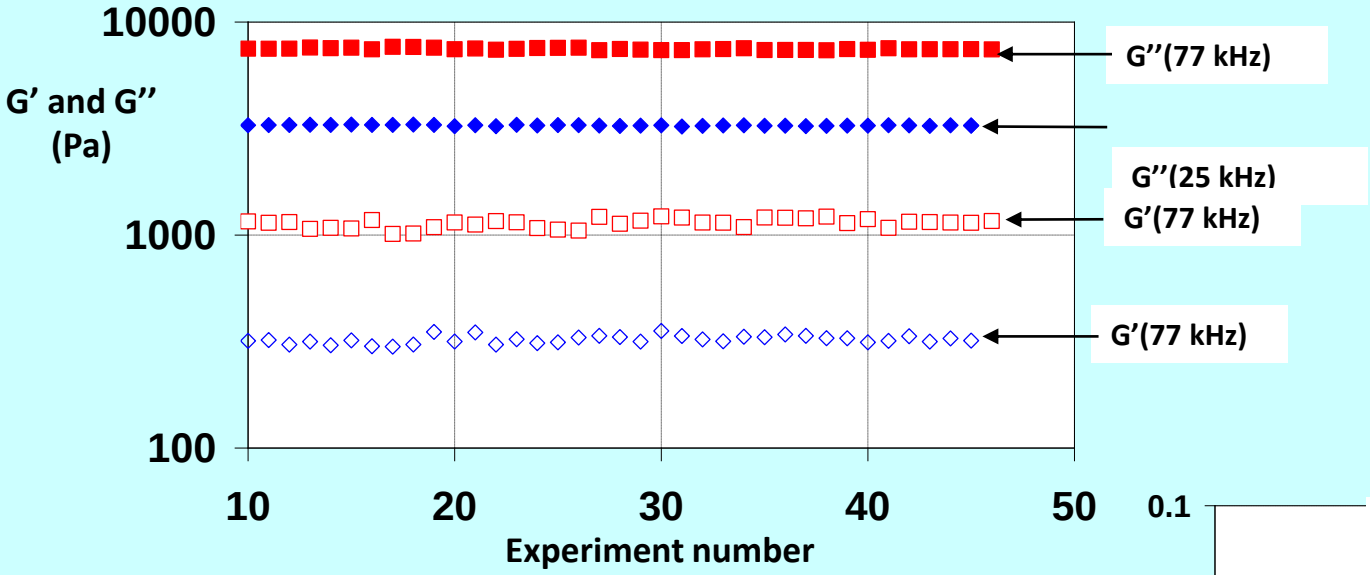
$$G' = \frac{K}{\rho_{sample}}\left[\left(\frac{\Delta D}{2}\right)^2 - (\Delta f)^2\right]$$

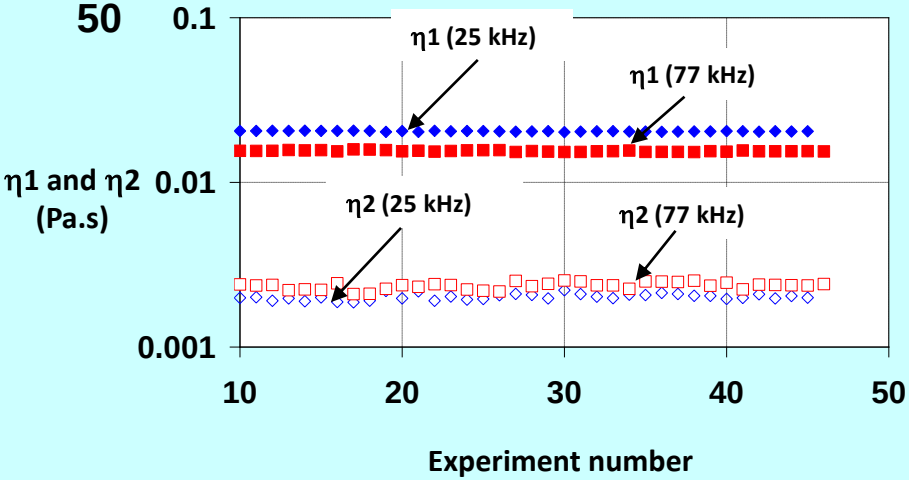
$$G'' = \frac{K}{\rho_{sample}}\Delta D.\Delta f$$

The Torsion Resonator (TR)

(Damien Vadillo)

Proof of concept (DEP + 2.5%wt PS110)

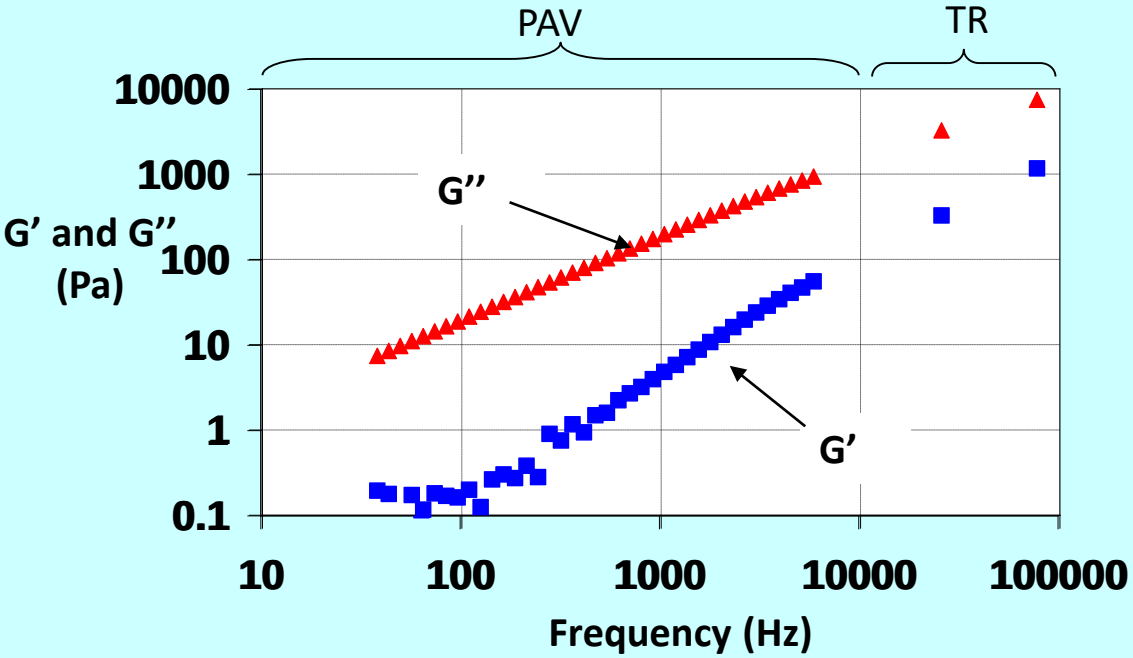


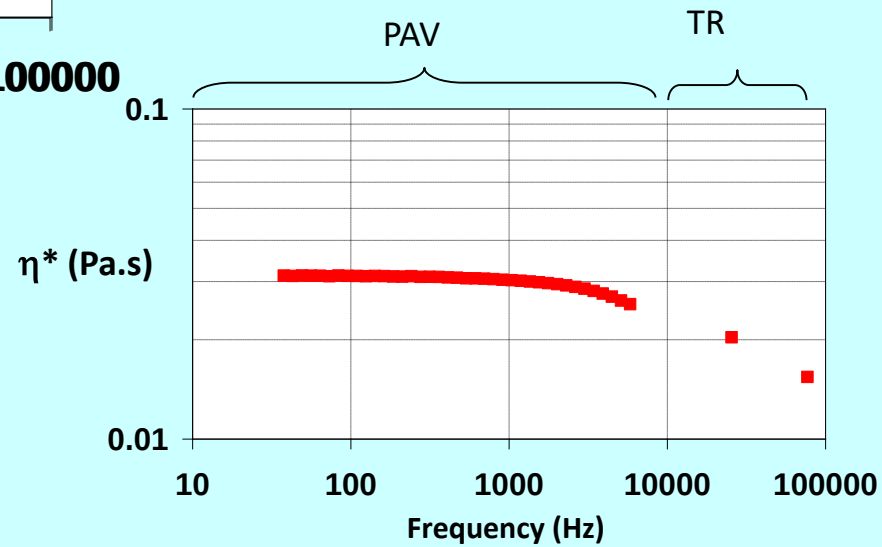


The Torsion Resonator

(Damien Vadillo)

Proof of concept (DEP + 2.5%wt PS110)





- **PAV and TR match**
- **"Shear thinning" at high frequency**

Extensional non linear measurements

a) Medium viscosity fluids

Filament thinning

A.V.Bazilevsky, V.M. Entov and A.N.Rozhkov
3rd European Rheology Conference 1990 Ed D.R.Oliver

ELSEVIER

J. Non-Newtonian Fluid Mech., 52 (1994) 387–405

Journal of Non-Newtonian Fluid Mechanics

Rheological characterization of the time and strain dependence for polyisobutylene solutions

R.F. Liang [1], M.R. Mackley *

Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK

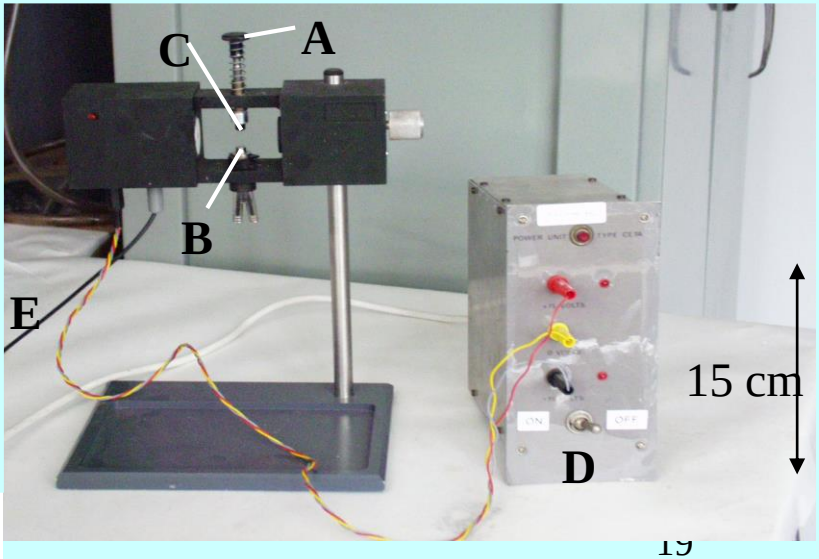
(Received March 4, 1994)

Abstract

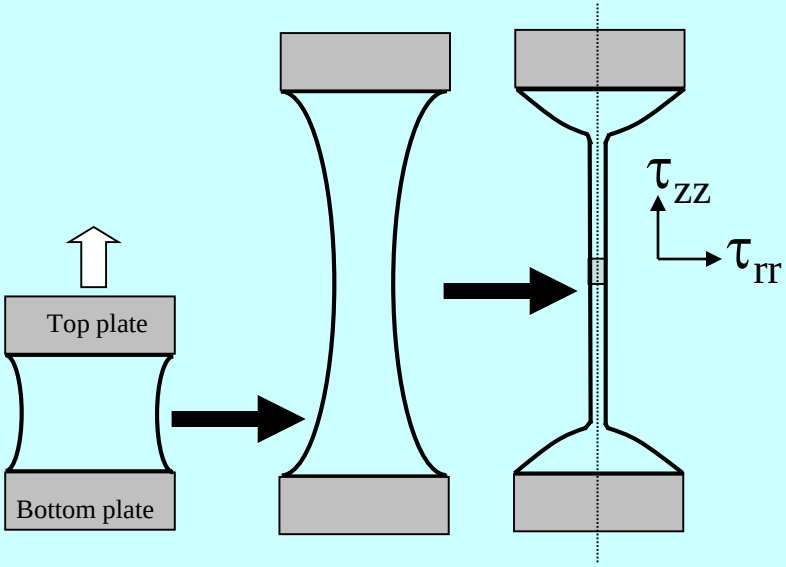
The rheological response of polyisobutylene (PIB) solutions in Decalin and a related standard fluid S1 has been characterized in dynamic oscillatory flow, step strain, step-shear rate and steady shear using a Rheometrics RDSII rheometer. The time dependence represented as a discrete spectrum of relaxation times and the strain dependence characterized as an exponential damping function have been presented as a function of PIB concentration. The relaxation spectrum was calculated from the dynamic storage modulus and loss modulus. The damping function was determined from the non-linear relaxation modulus in a step-strain experiment. The Wagner integral viscoelastic model incorporated with the relaxation and the damping function has been used to predict the stress growth and the steady-shear behaviour, which were compared with the experimental data. A novel extensional rheotester was also used in this study to measure the stretching response of polymer solutions. The data gave a near single relaxation time for each solution, and this single relaxation time obtained from uniaxial extension was correlated to the relaxation spectrum obtained in simple shear.

Keywords: Relaxation spectrum; Damping function; Filament stretching; Wagner integral viscoelastic model; Polyisobutylene solutions

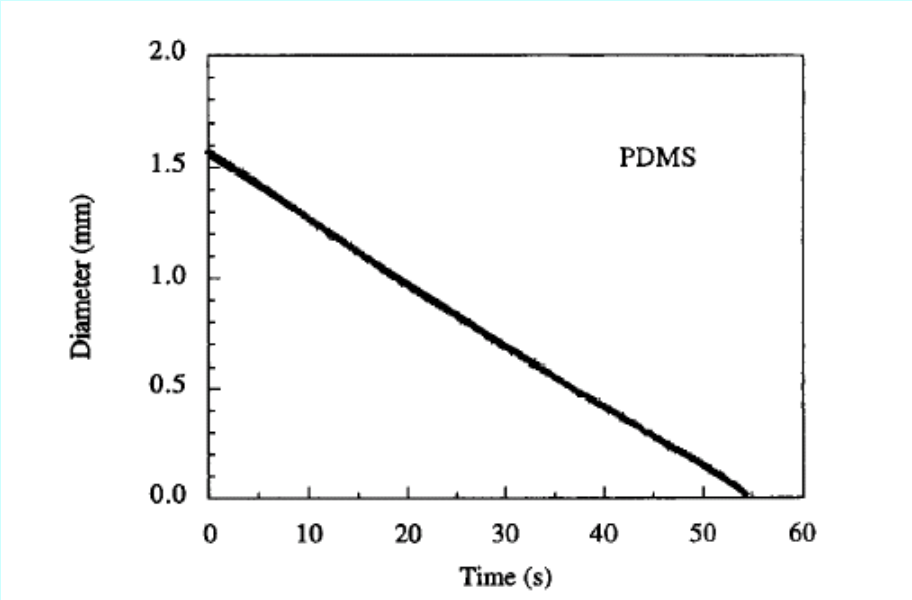
The "Russian Rheotester"



Liang and Mackley (1994)- Extensional Rheotester



Extensional rheotester



Newtonian modelling

$$\tau_{zz} = -p_0 + 2\eta\dot{\gamma}_{zz} = 0 \quad (11)$$

$$\tau_{rr} = -p_0 + 2\eta\dot{\gamma}rr = -2\sigma / D \quad (12)$$

$$\dot{D} = \frac{1}{2}\dot{\varepsilon}D \quad (13)$$

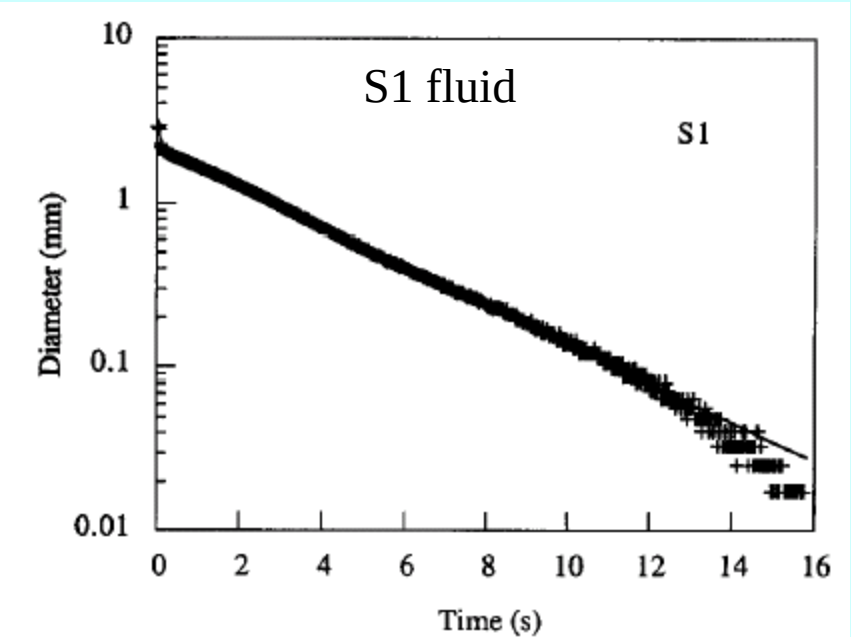
$$\tau_E = \tau_{zz} - \tau_{rr} = 3\eta\dot{\varepsilon} = 2\sigma / D \quad (14)$$

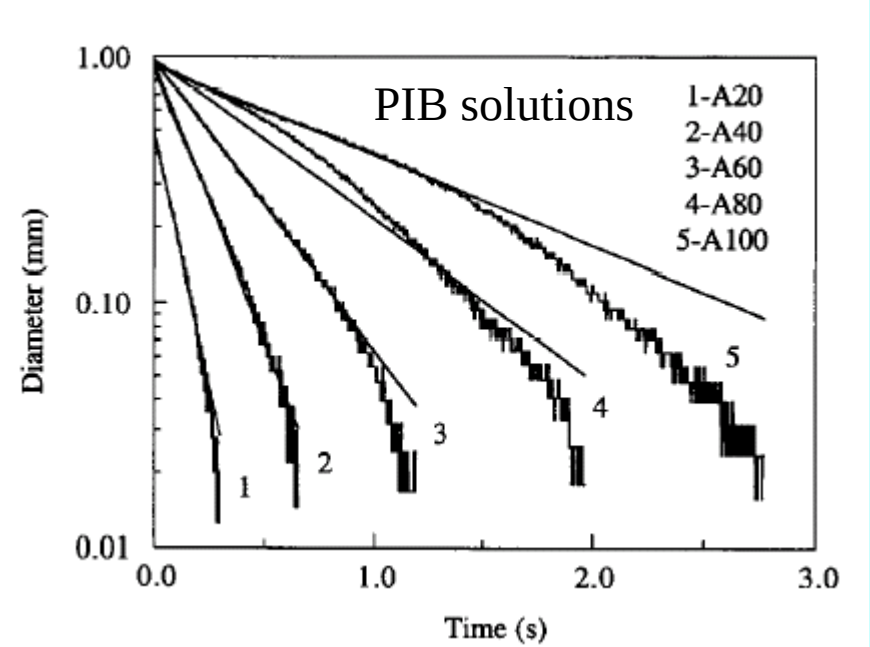
$$\dot{\varepsilon} = \frac{2\sigma}{3\eta D} \quad (15)$$

$$\eta_E = \tau_E / \dot{\varepsilon} = 3\eta \quad (16)$$

$$D(t) = D_0 - \frac{\sigma}{3\eta}t \quad (17)$$

Liang and Mackley (1994)- Viscoelastic fluid





First approximation

$$D(t) = D_0 \exp\left(-\frac{1}{3\lambda_R} t\right) \tag{18}$$

Viscoelastic modelling

$$\tau_E = 3\eta \dot{\varepsilon}_d = 2\sigma / D \tag{19}$$

$$\dot{\tau}_E = g \dot{\varepsilon}_s = -2\sigma \dot{D} / D^2 \tag{20}$$

$$\dot{\varepsilon}_d = \dot{\varepsilon}_s \tag{21}$$

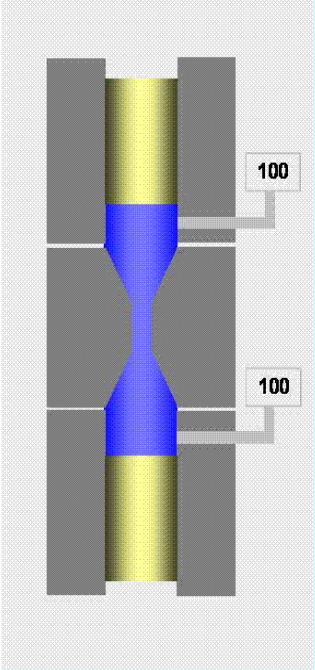
$$\dot{D} / D = -g / 3\eta \tag{22}$$

$$D(t) = D_0 \exp\left(-\frac{g}{3\eta} t\right) \tag{23}$$

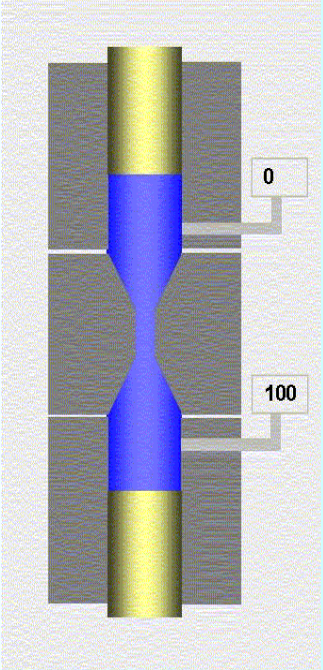
Extensional non linear measurements

b) Low viscosity fluids

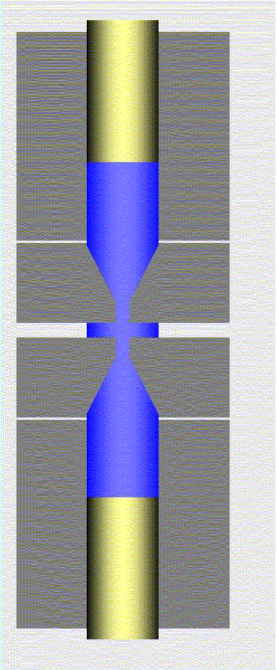
The Cambridge MultiPass Rheometer (MPR)



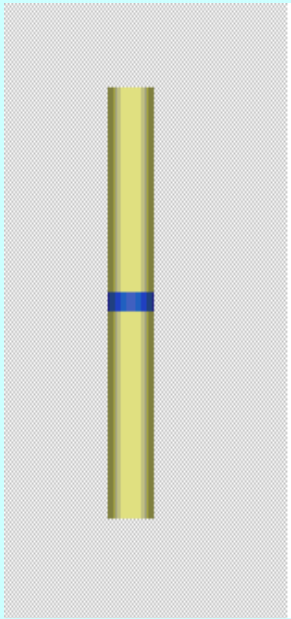
Pressure variation mode



Rheology flow mode

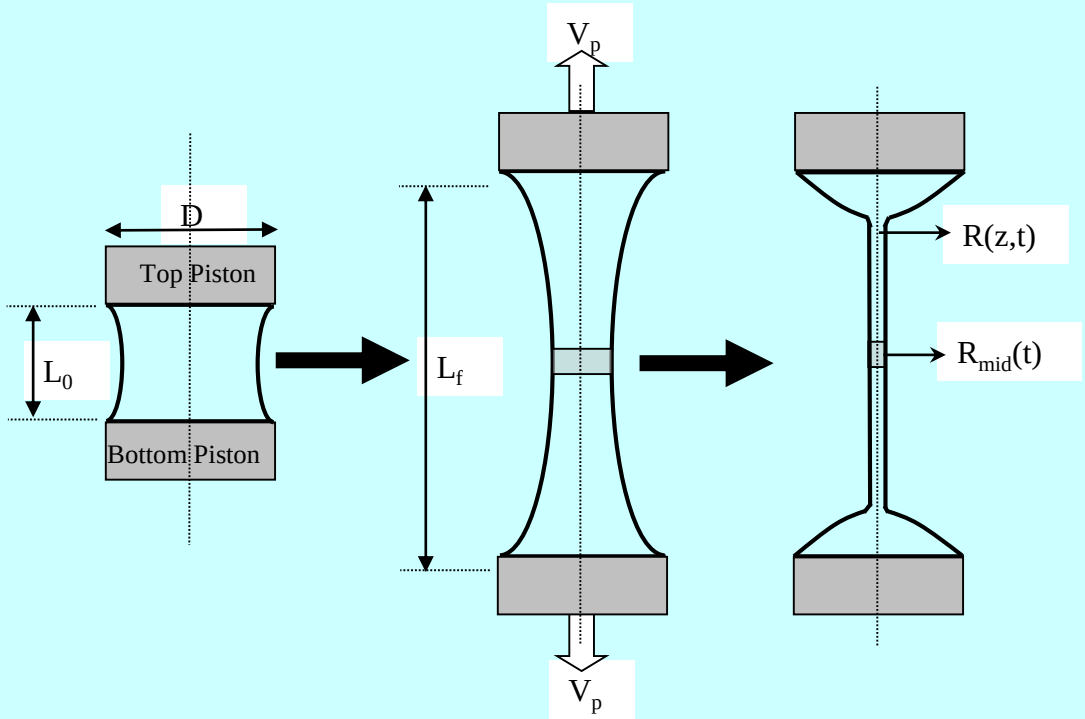


Cross-slot flow mode



Filament stretch mode

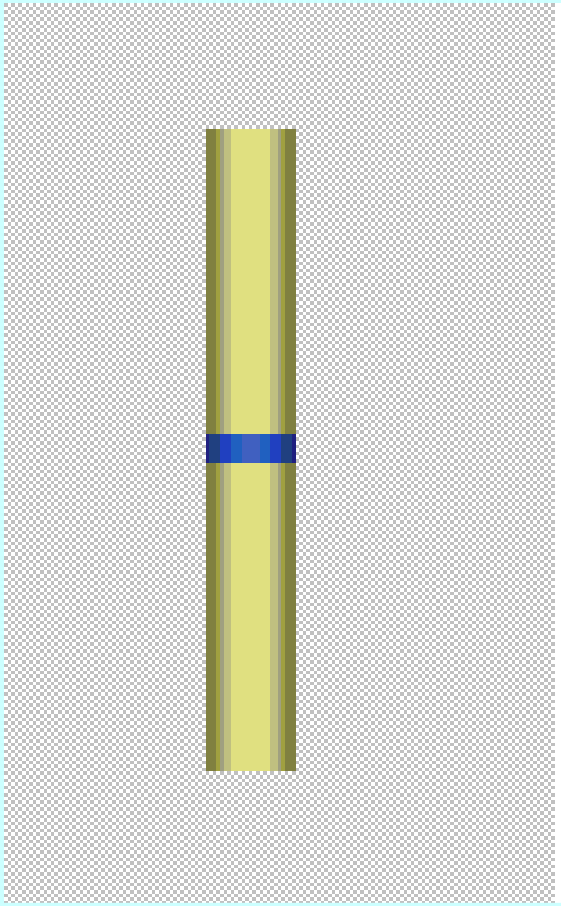
MPR Filament stretch Rheometer



(a) Test fluid positioned between two pistons.

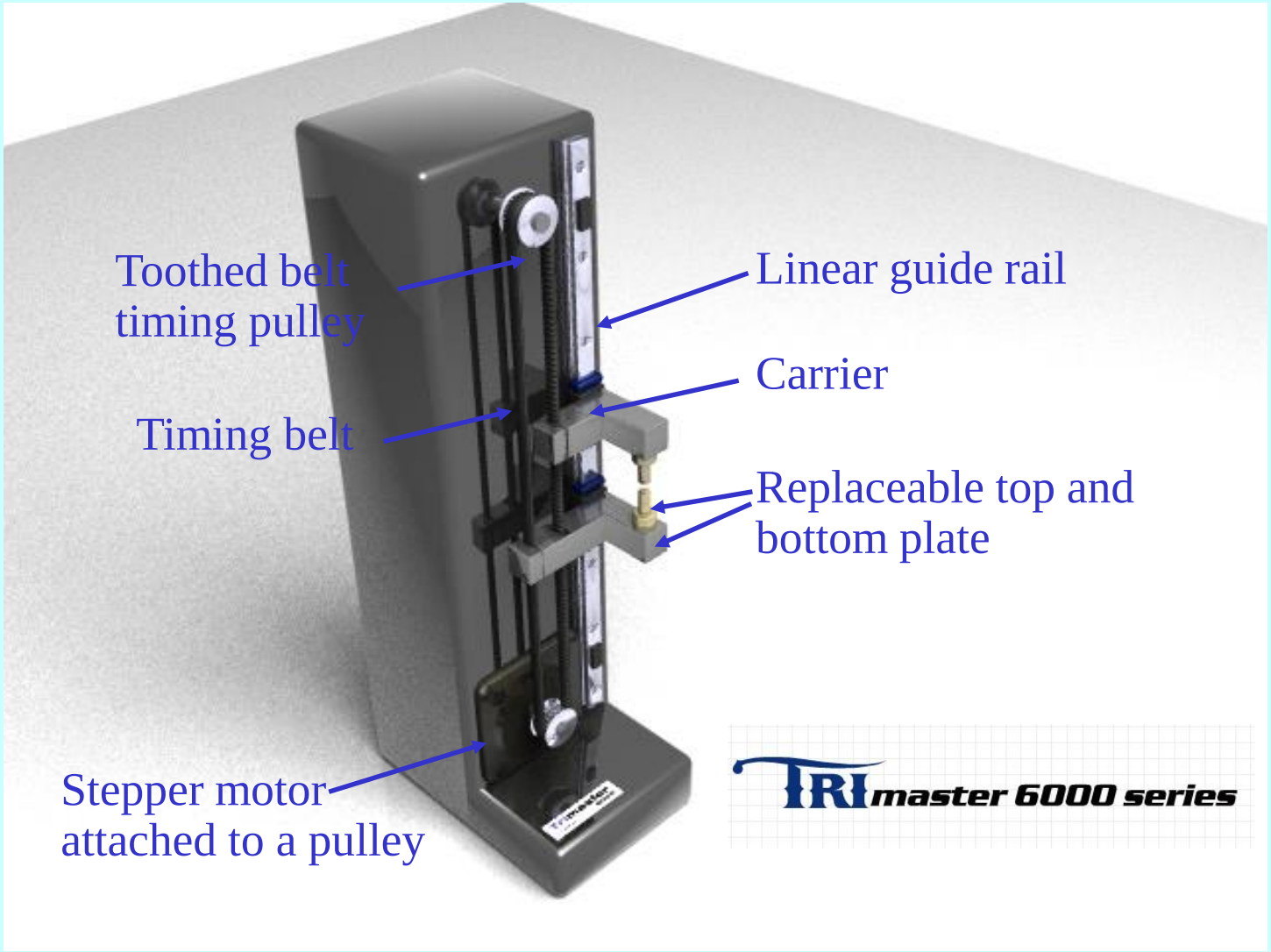
(b) Test fluid stretched uniaxially at a uniform velocity.
$t < 0$

(c) Filament thinning and break up occurrence after pistons has stopped.
$t \geq 0$

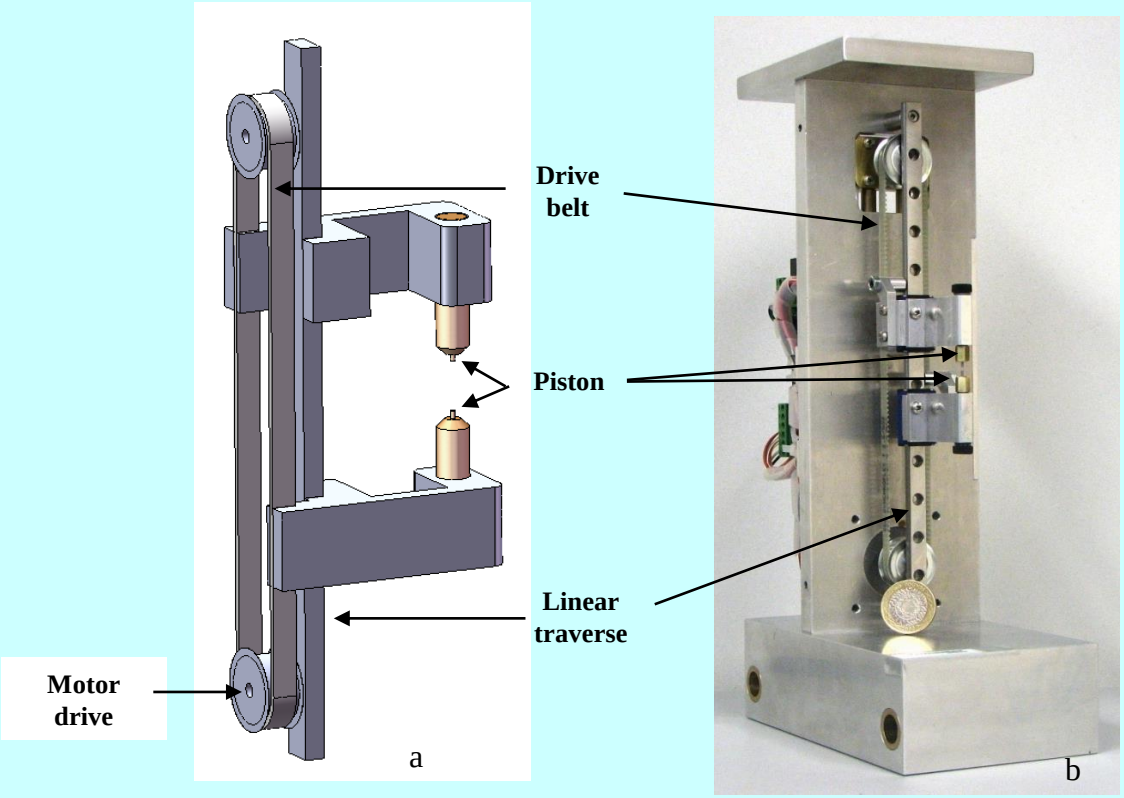


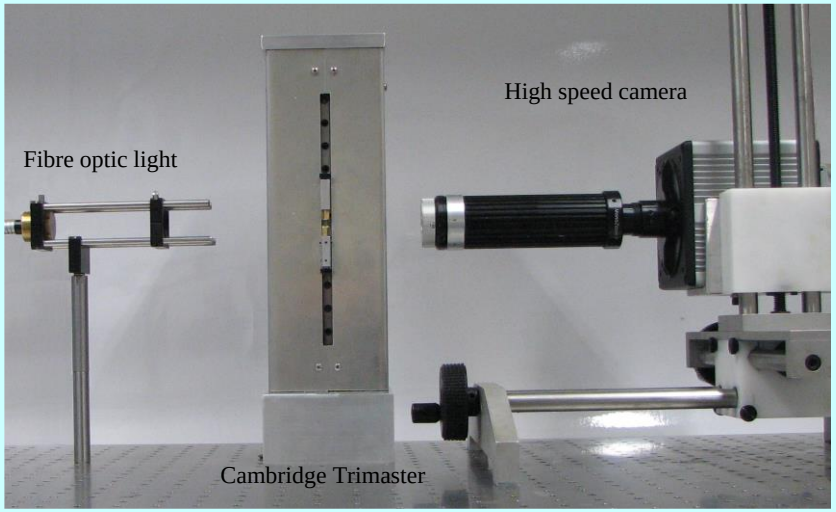
The CambridgeTrimaster

A dream turning into a reality

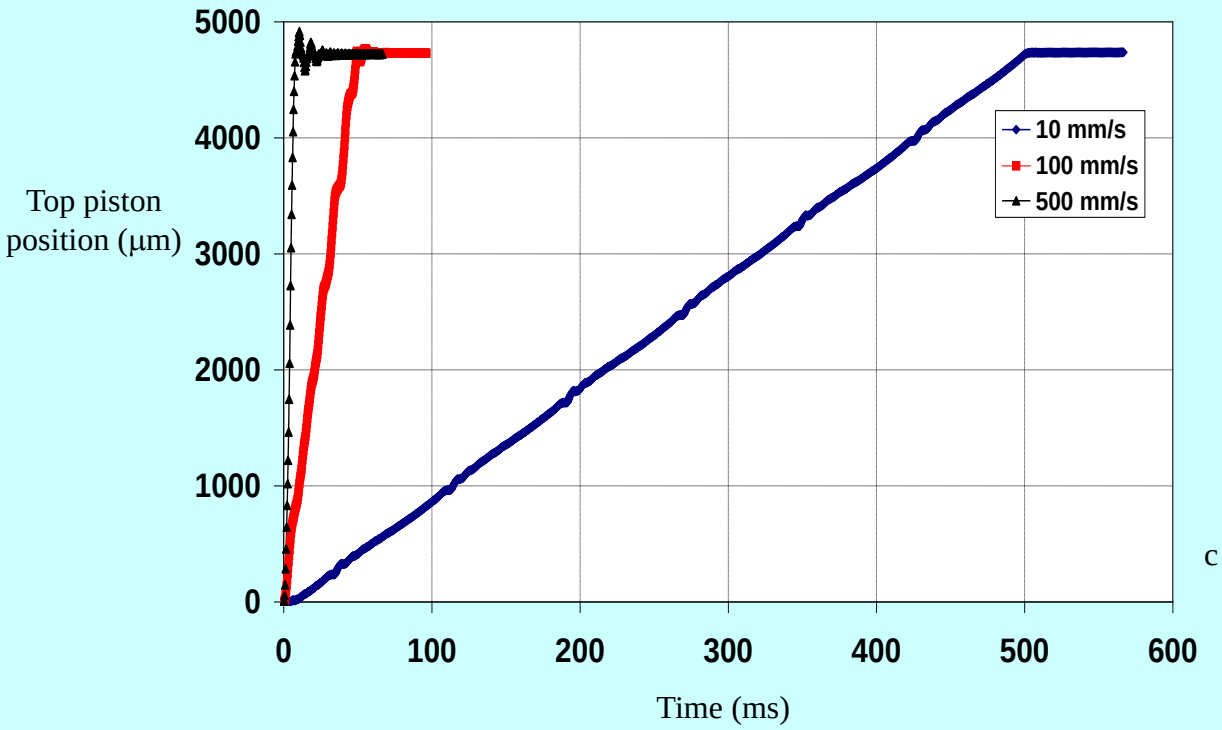


Graphics courtesy of James Waldmeyer


Drive belt
Piston
Linear traverse
Motor drive
a
b

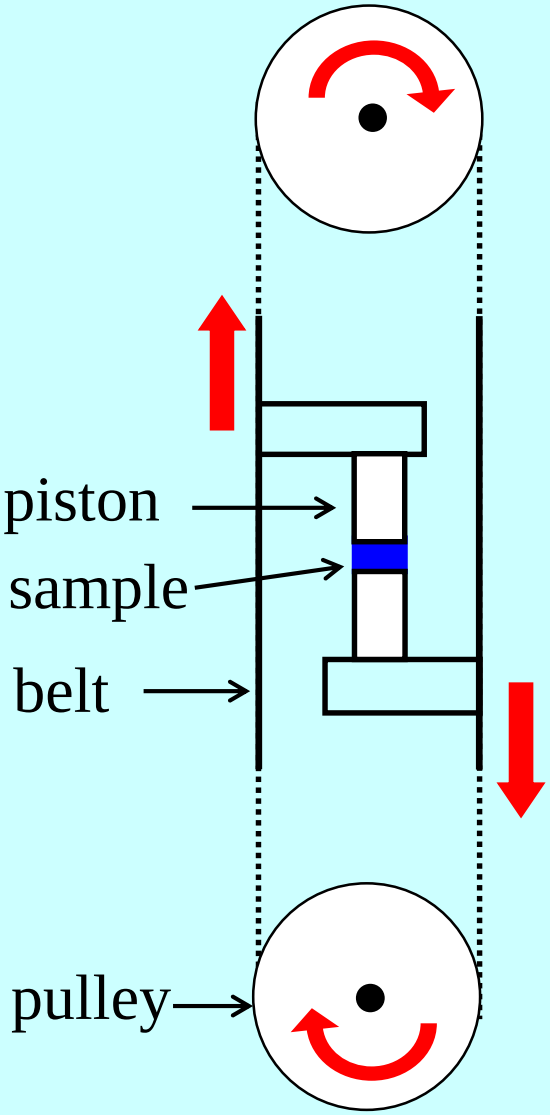

High speed camera
Fibre optic light
Cambridge Trimaster

Piston response



c

The 'TriMaster' Filament stretch and break up apparatus



Initial gap ≈ 0.2 mm, Final gap ≈ 1.2 mm

Piston diameter ≈ 1.2 mm, Piston velocity ≈ 1 m/s

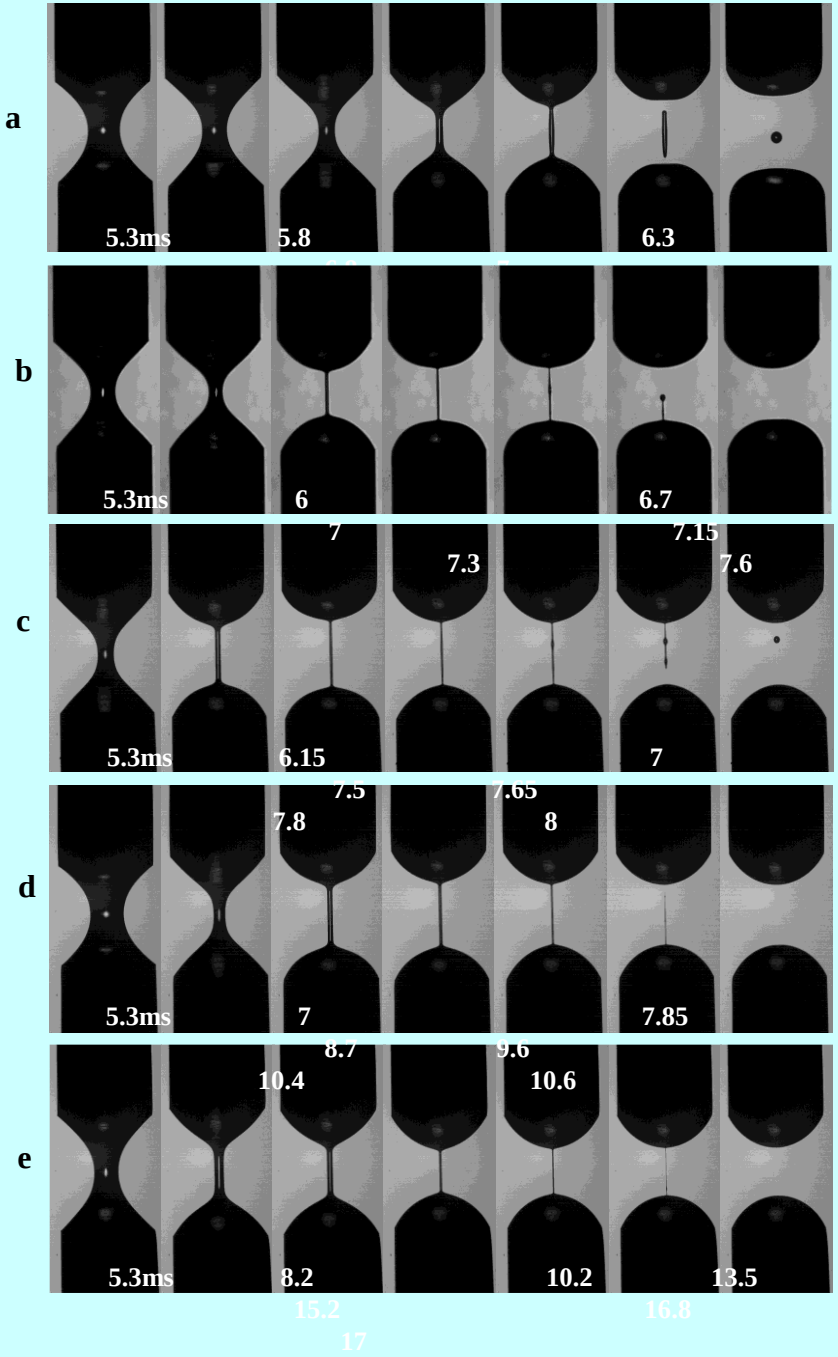
Filament thinning

(a) DEP,
(b) DEP + 0.2% PS110,
(c) DEP + 0.5% PS110,
(d) DEP + 1% PS110,
(e) DEP + 2.5% PS110.

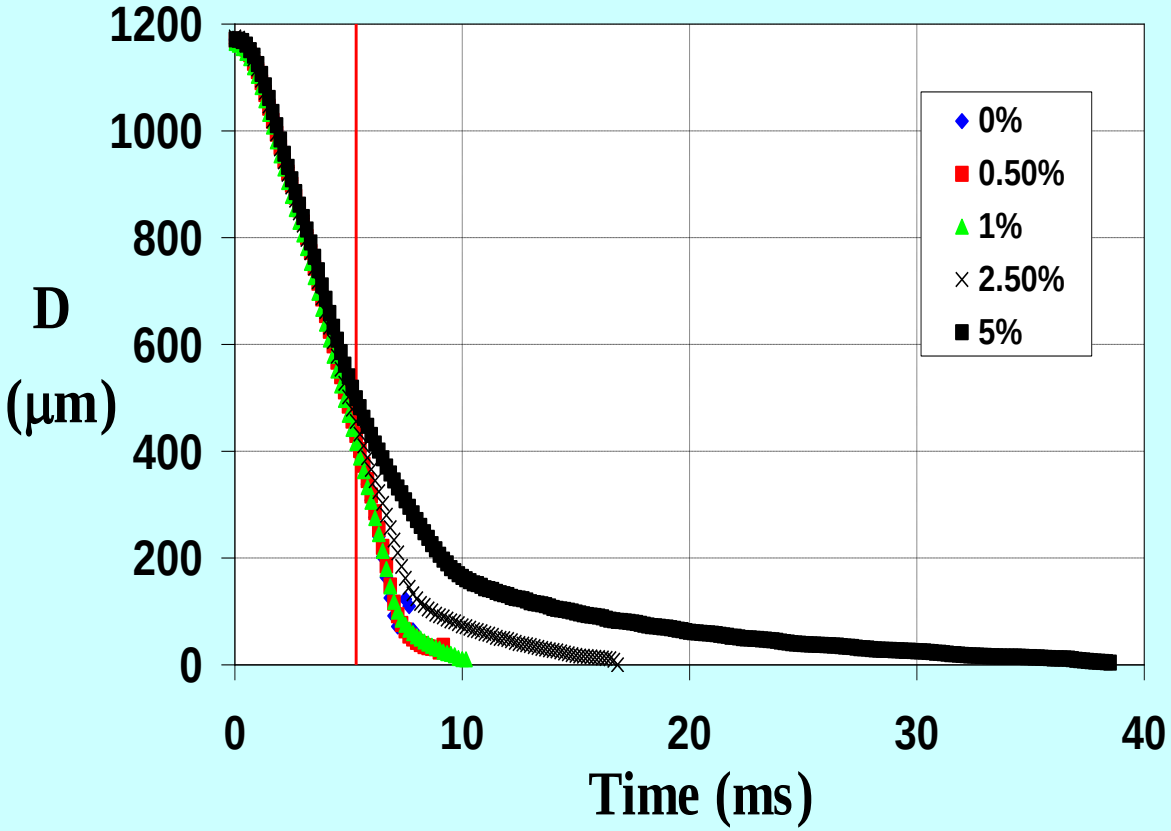
Initial gap size: 0.6mm,

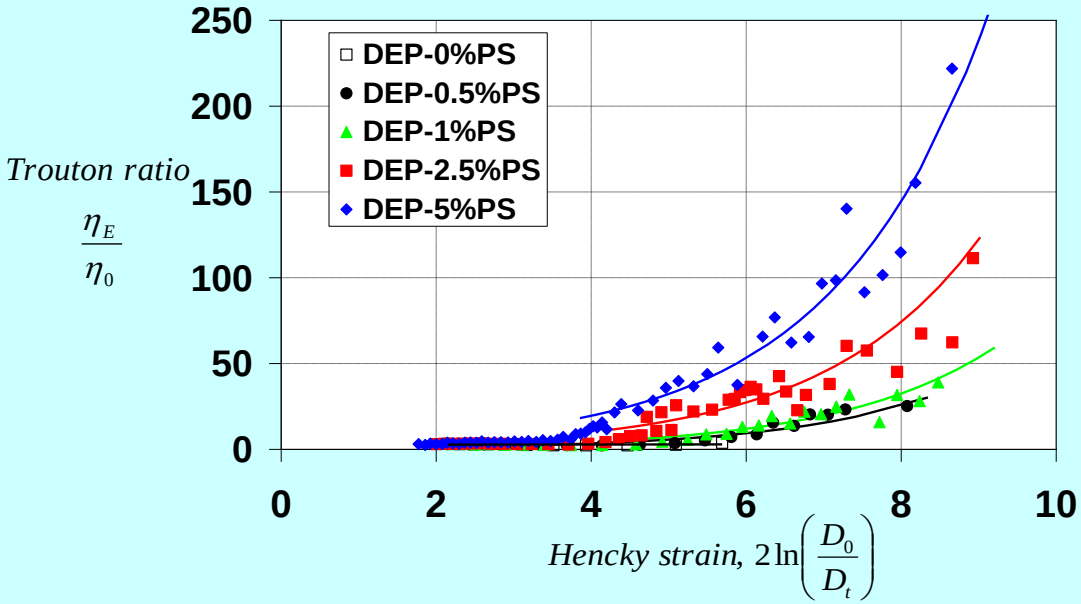
Stretching distance:0.8mm,

Stretching velocity:150mm/s



Mid filament diameter time evolution





The transient extensional rheology of DEP solutions as a function of relaxation Hencky strain for different PS concentrations.

Initial distance 0.6mm, final distance: 1.4mm.

The line represent are obtained from the exponential fitting of the evolution of the thinning of the diameter.

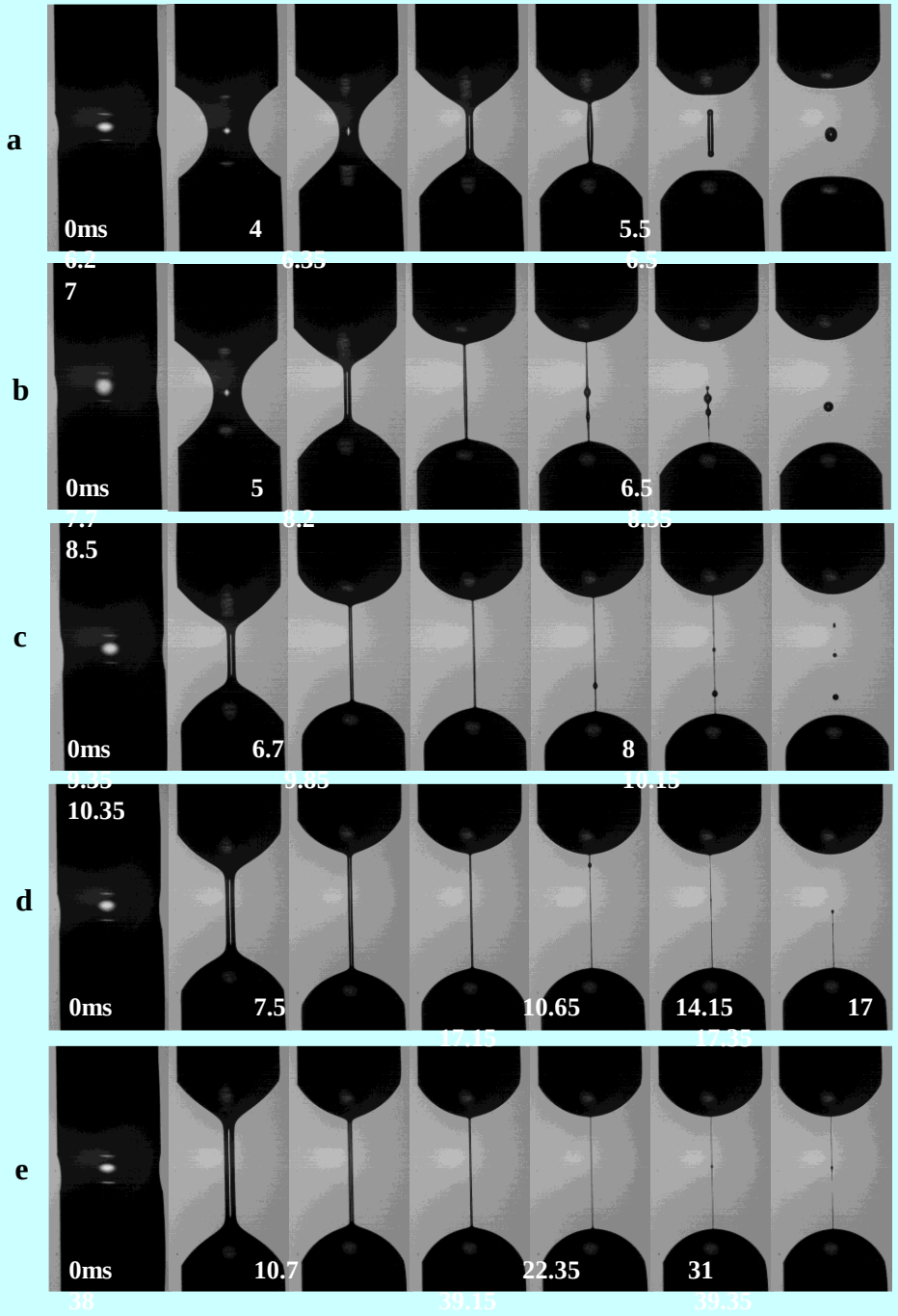
The geometrical factor “X” is fitted using the experimental data at low Hencky strain.

Breakup

(a) DEP,
(b) DEP + 0.5% PS110,

(c) DEP + 1% PS110,
(d) DEP + 2.5% PS110,
(e) DEP + 5% PS110.

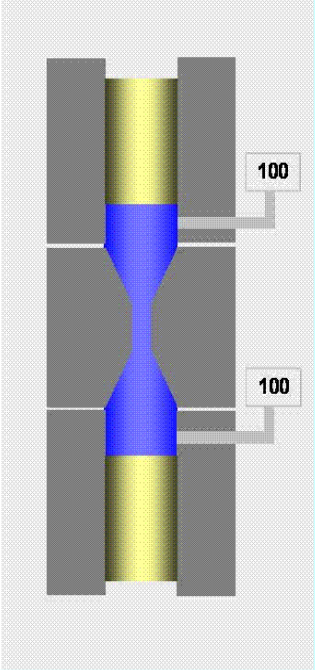
Initial gap size: 0.6mm,
stretching distance: 1.6mm,
stretching velocity: 150mm/s



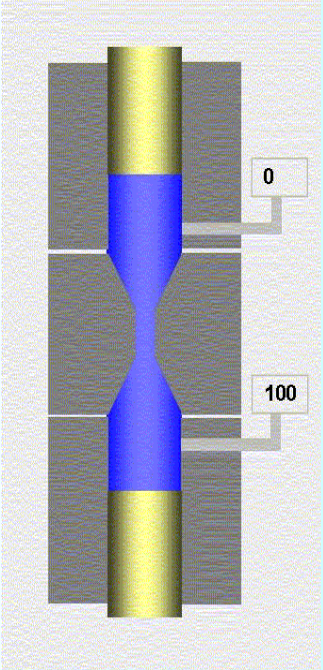
Extensional non linear measurements

c) High viscosity fluids

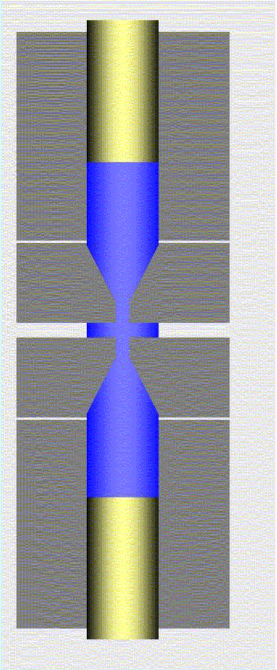
The Cambridge MultiPass Rheometer (MPR)



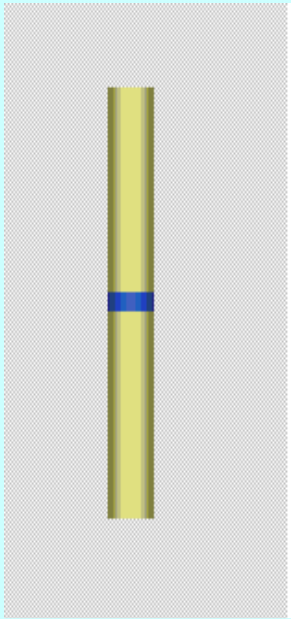
Pressure variation mode



Rheology flow mode



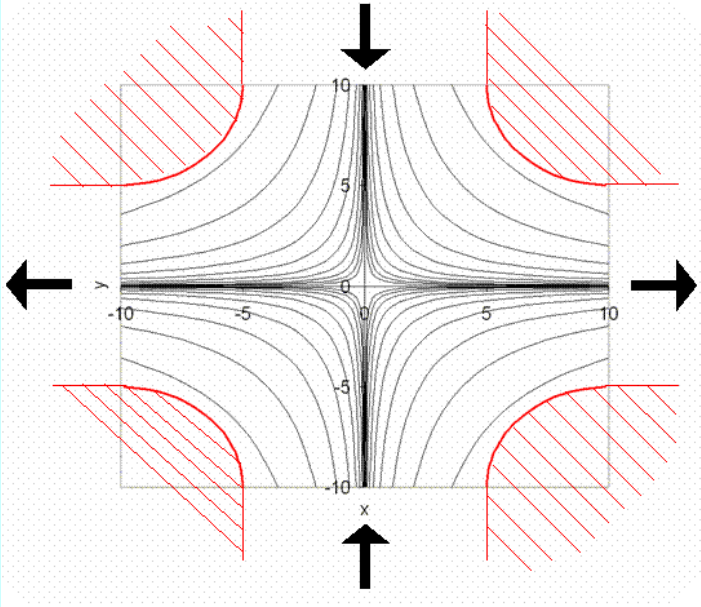
Cross-slot flow mode

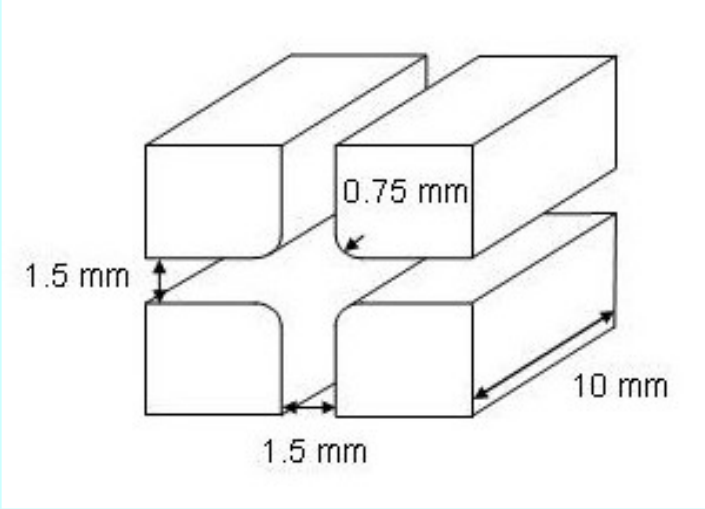


Filament stretch mode

The Cross-Slot

- Generates a hyperbolic
- pure shear flow pattern
- as shown.
- Near centre.
- Essentially uniform extensional
- flow with residence time, which is equivalent to strain, inversely dependant on distance from the exit symmetry axis





Typical Result

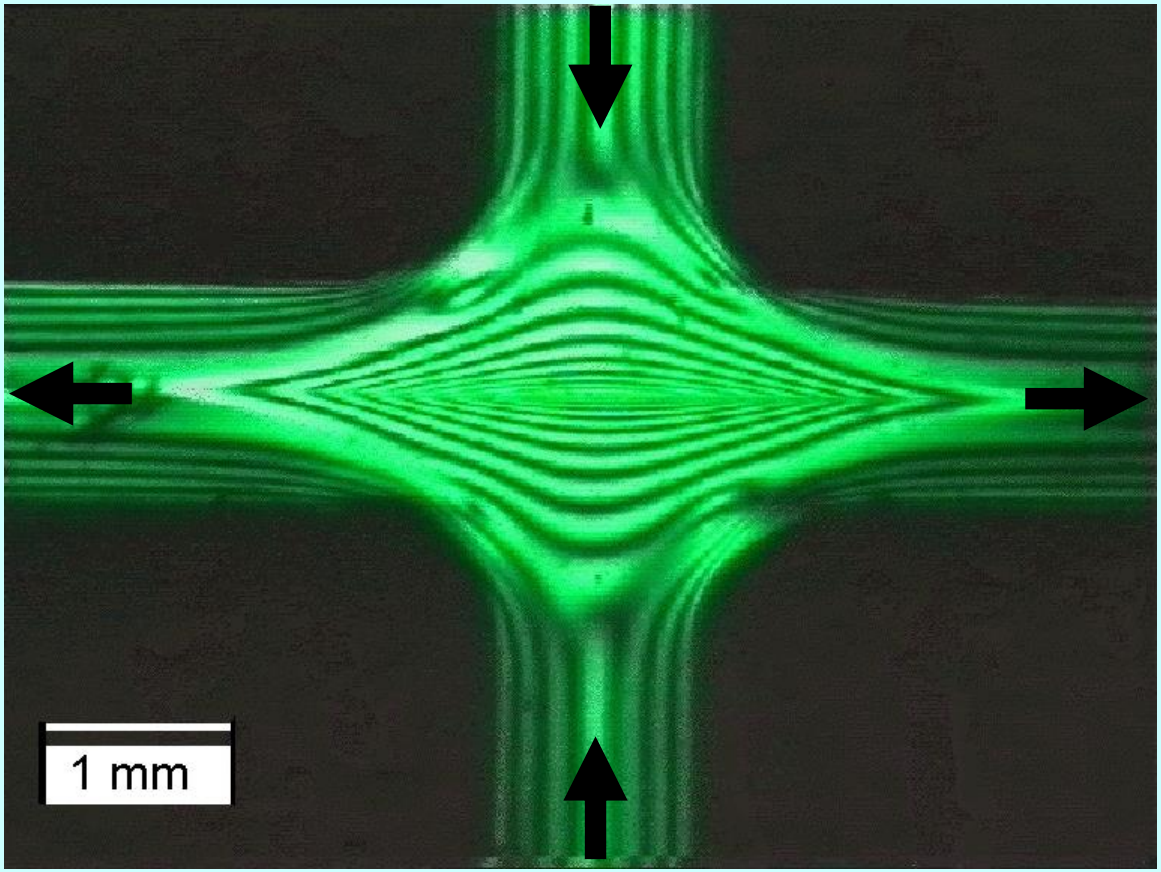
-Dow PS680E

-Piston velocity of 0.5 mm/s (maximum extension rate =4.3/s).

-Inlet slit width=1.5mm

-Section depth=10mm

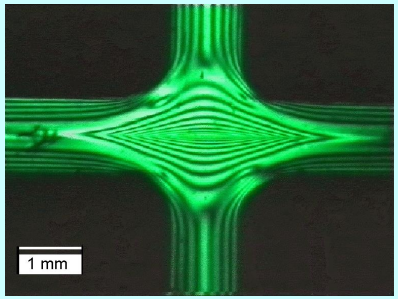
- T=180°C.

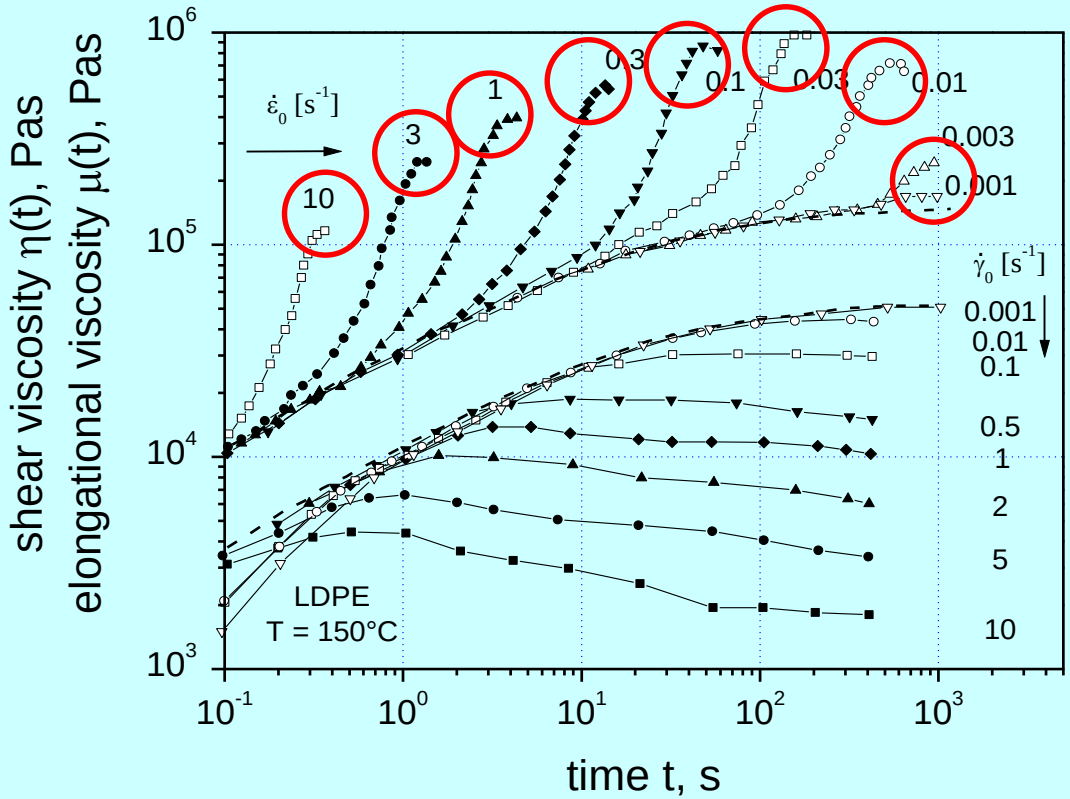


Stagnation Point flows as rheometers

Dr Dietmar Auhl et al,

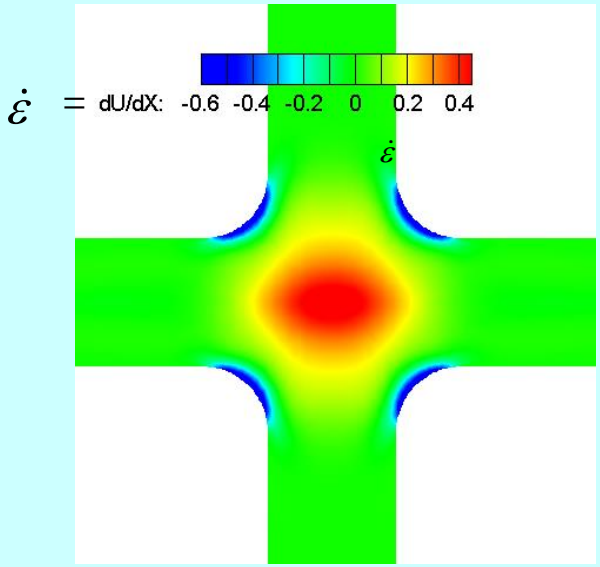
Leeds University 2008

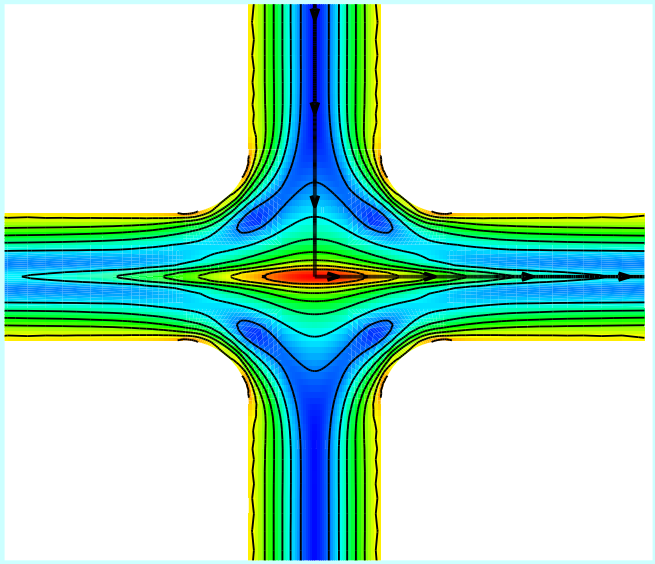




$$\eta_{E,st}(\dot{\varepsilon}) = \left(\sigma_{xx} - \sigma_{yy}\right)_{st} / \dot{\varepsilon}_{st}$$

steady-state elongational viscosity at the stagnation point

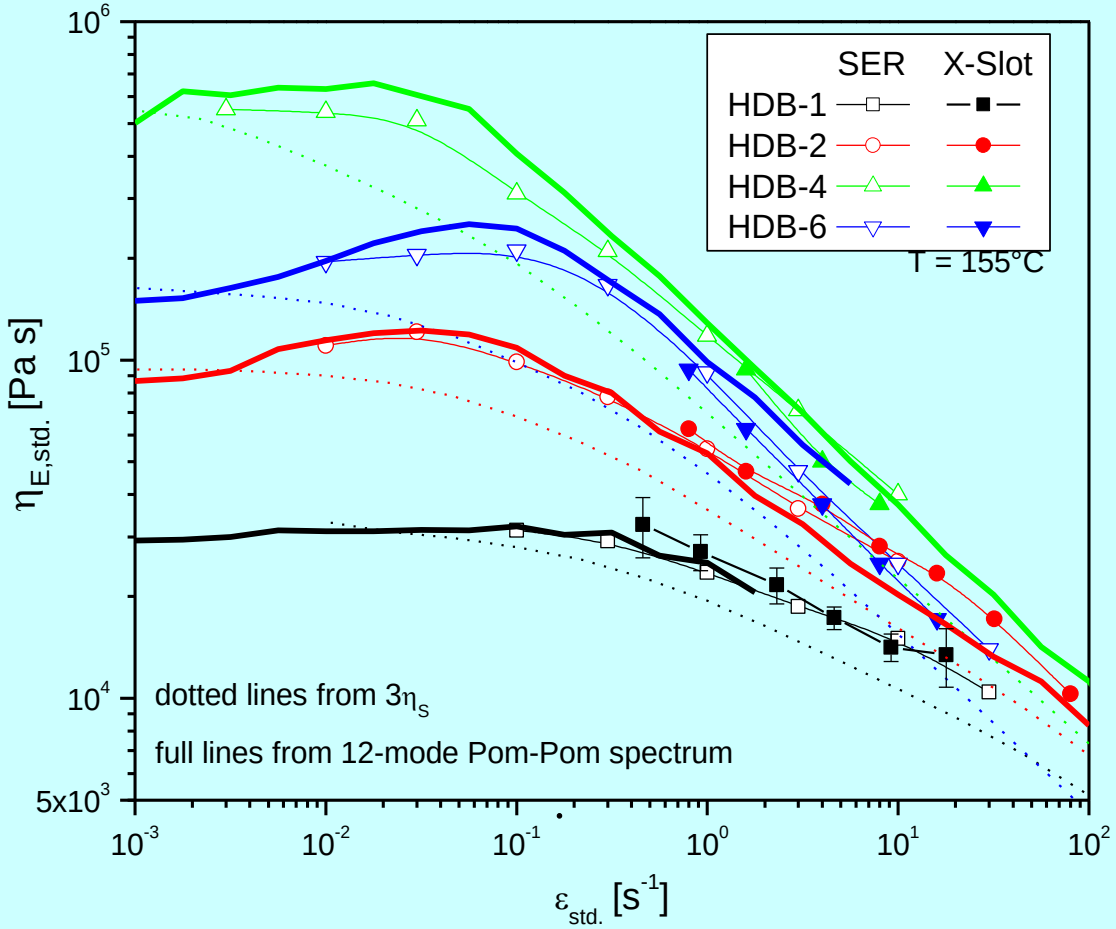




$$\dot{\varepsilon}_{st} = A \; x \; V_{piston}$$

$$\Delta n = SOC\sqrt{\left(\sigma_{xx} - \sigma_{yy}\right)^2 + 4\sigma_{xy}^{\;2}}$$

Dr Dietmar Auhl et al , Leeds University



Conclusions

Piezo Axial Vibrator (PAV) and Torsion Resonator (TR)

Can quantify LVE high frequency response of low viscosity viscoelastic fluids

Cambridge Trimaster

Can follow transient extensional viscosity and filament break up process of low viscosity fluids

MPR Cross slot

Can measure limiting extensional viscosities of polymer melts

Acknowledgments

EPSRC and industrial partners in Next Generation Ink Jet Consortium