ADVANCED MATERIAL CHARACTERIZATION PERFORMING RHEOLOGICAL INVESTIGATIONS AND DYNAMIC MECHANICAL ANALYSIS WITH A DUAL MOTOR DEVICE CONCEPT

Educational Webinar

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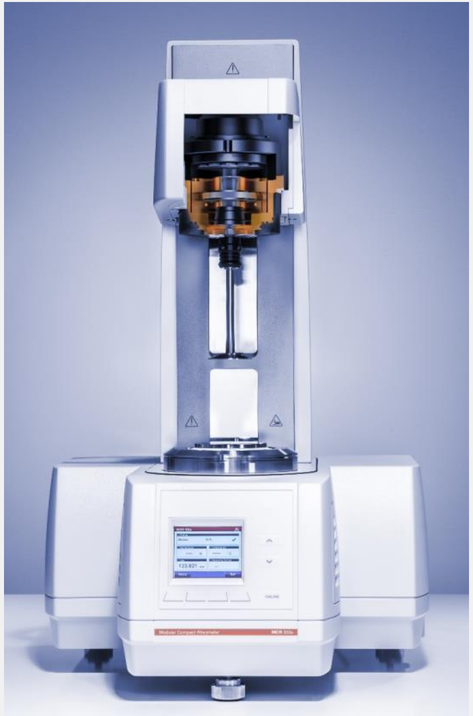
Anton Paar

Outline

- MultiDrive: Unique Design Concept with Dual Motors
- Modes: Combined Motor Transducer, Separate Motor transducer and Linear Drive
- Application examples: Liquids to solids to granular materials.

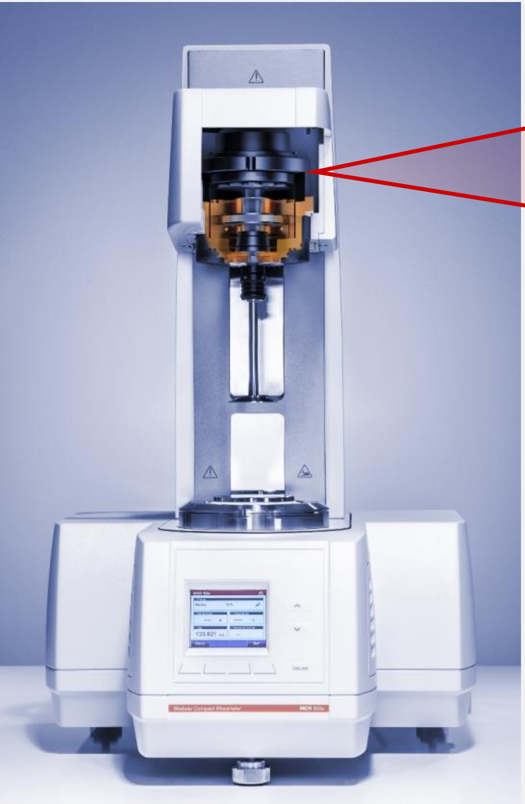
MCR 702e MultiDrive

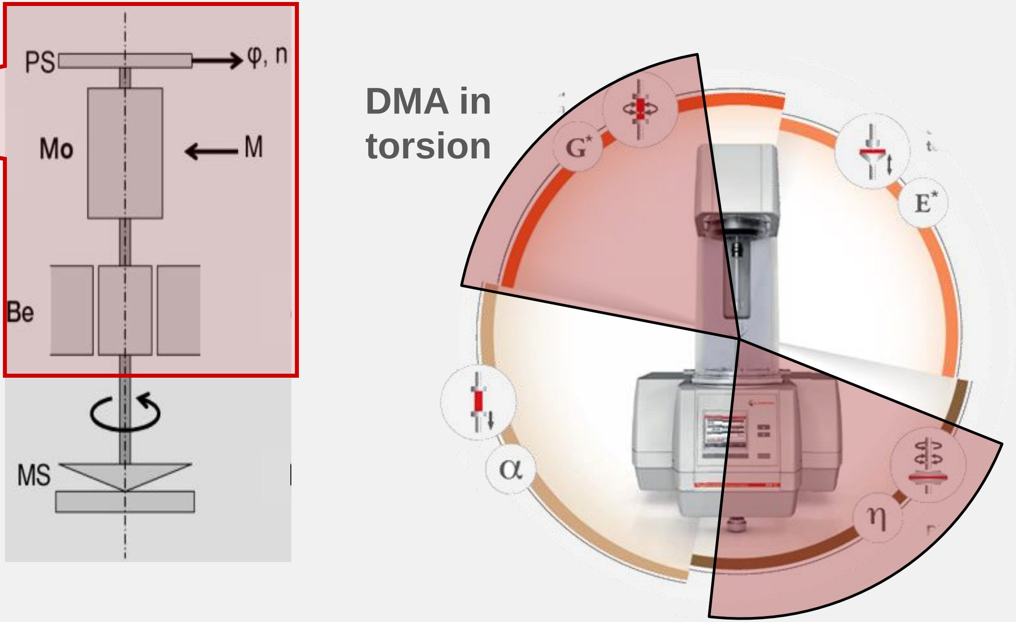
Single motor: Standard rheometer (CMT)



MCR 702e MultiDrive

1 EC-Motor: Classic **Stress Controlled Rheometer** **CMT** (Combined Motor Transducer)





MCR 702e MultiDrive

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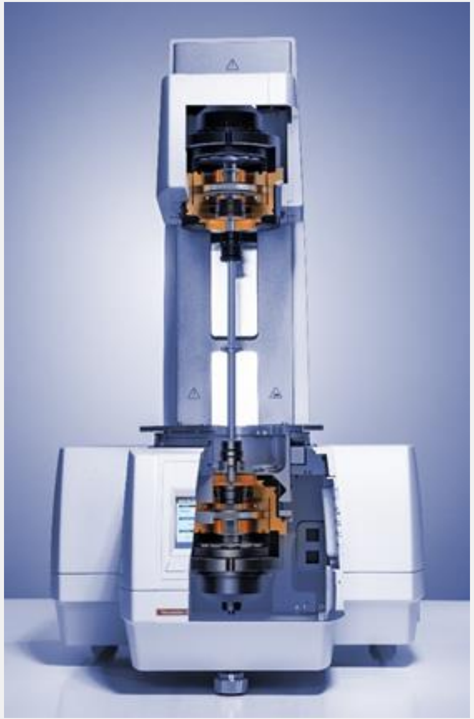
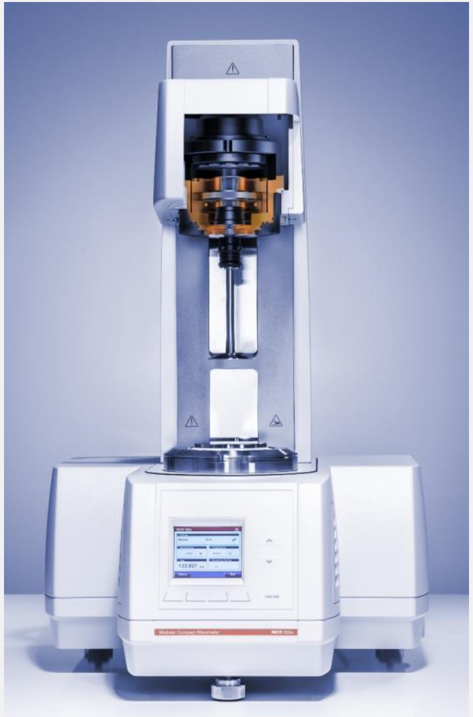
Additional rotational drive: SMT and Counter rotation (CR)



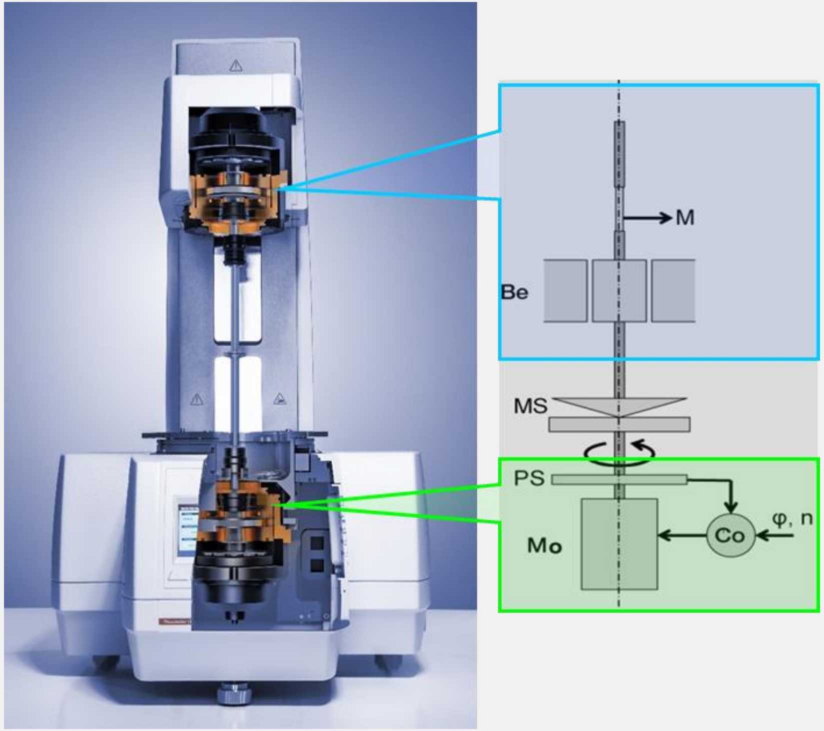
Single motor: Standard rheometer (CMT)

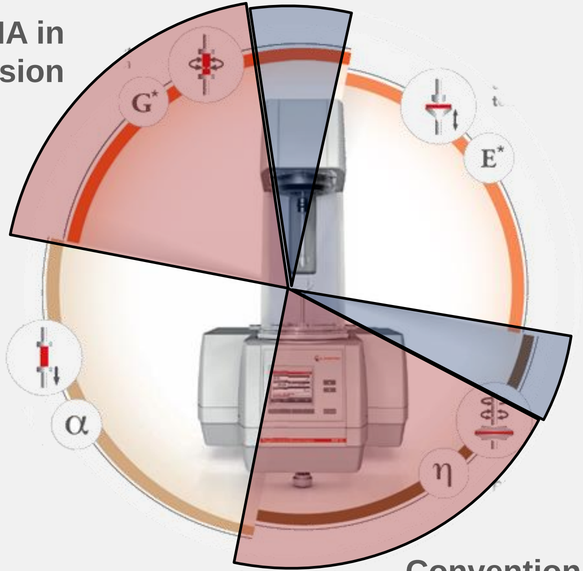


MCR 702e MultiDrive

2 EC-Motors: **TwinDrive**
(Classic Controlled Strain Rheometer)

CMT, **SMT (Separate Motor Transducer)**

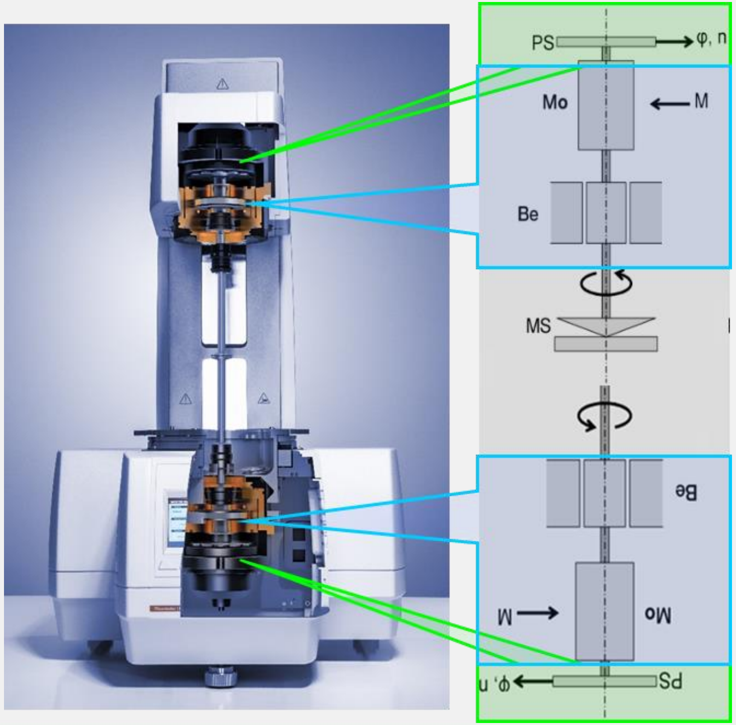




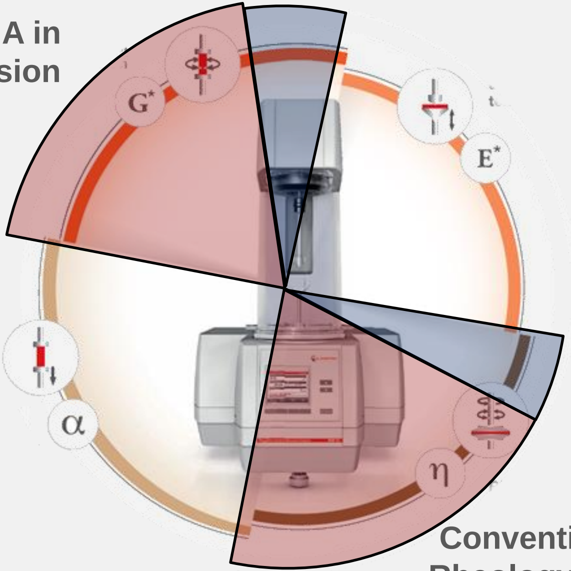
MCR 702e MultiDrive with a lower rotational drive acts as an enhanced SMT rheometer (Separate Motor Transducer)

MCR 702e MultiDrive

2 EC-Motors: **TwinDrive (Counter Rotation Mode)**



CMT, **CR (Counter-rotation)**

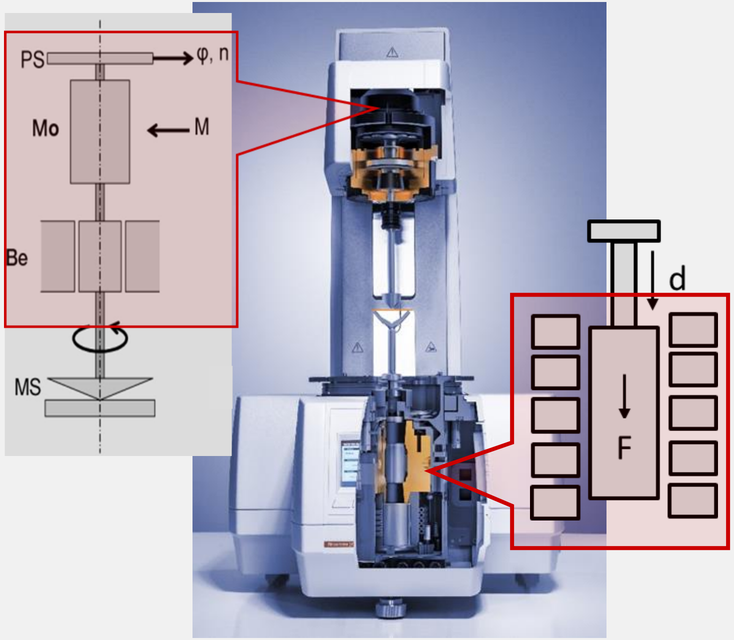


Opens up some new capability of experimentation and helps extend the range of conventional rheological measurements.

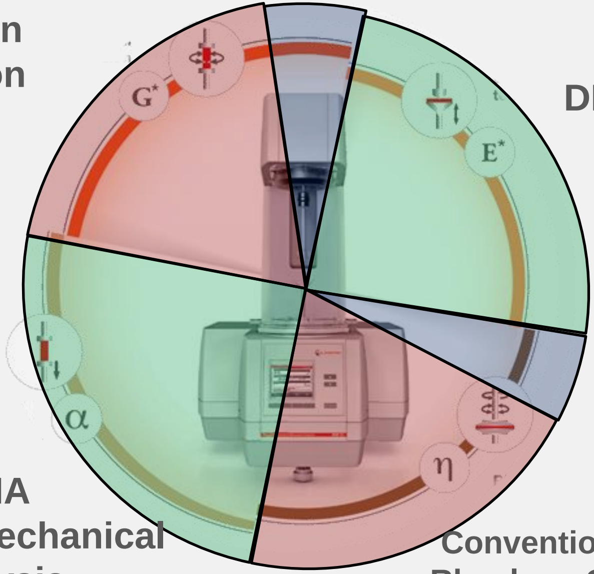
(US Patent, US 8499619)

MCR 702e MultiDrive

Top EC-Motor + Bottom Linear Motor:
DMA
(Dynamic mechanical analyzer)



CMT, **LD (Linear measuring drive)**

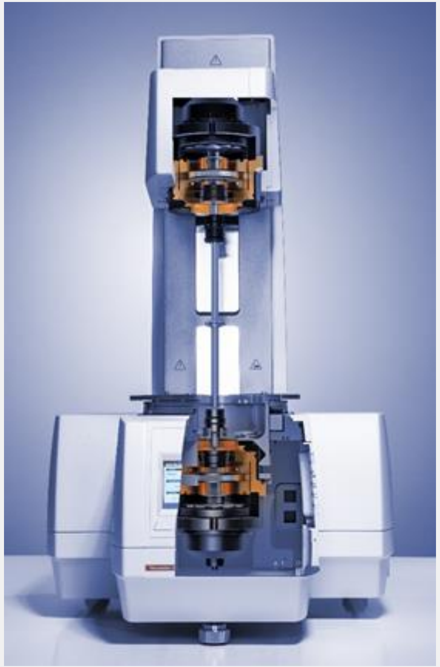


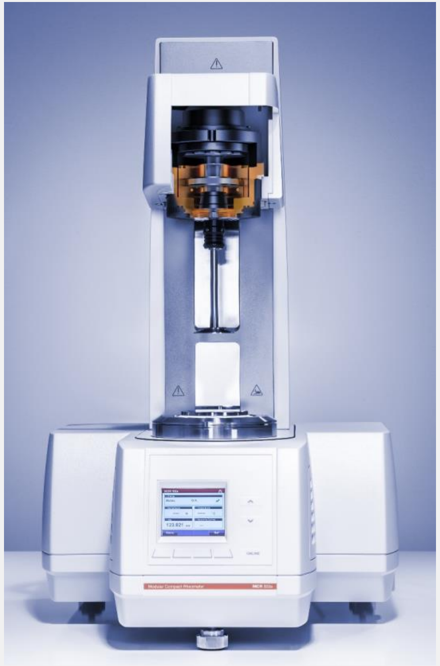
MCR 702e MultiDrive

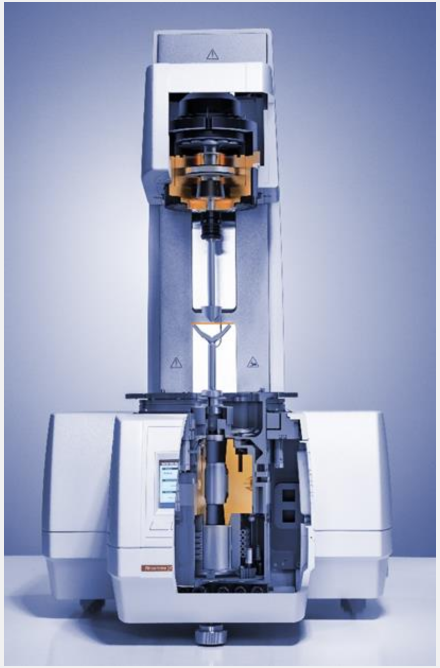
Additional rotational drive: SMT and Counter rotation (CR)

Single Motor: Standard rheometer (CMT)

Additional Linear drive: DMA and Special applications

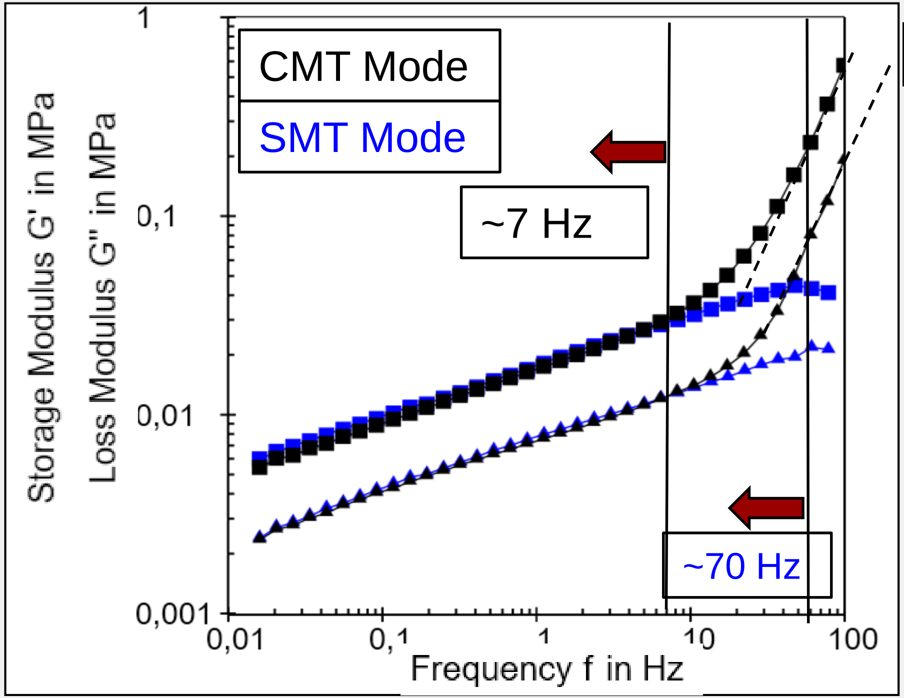






➢ **Universal Platform for Rheology and Dynamic Mechanical Analysis**

Soft materials: Extension of measurement range



$$G' \sim G'' \sim \omega^2$$

CMT Vs SMT:

- Double side tape (pressure sensitive adhesive) investigated with a PP12 at a gap of 1mm and at 90C.
- CMT: Increase in Moduli at high frequency
- SMT: One decade higher frequency possible with same sample and same geometry.
- Possible solution for CMT: Use of larger geometry: R^{-4} dependence
- At low temperature material becomes very stiff and issues with torsional compliance can occur.

CMT Mode

$$\frac{M_0}{M_S} = 1 + \frac{2h}{\pi R^4}\frac{1}{|G^*|}\mathrm{I}\,\omega^2$$

SMT Mode

$$\frac{M_0}{M_S} = 1 + \frac{2h}{\pi R^4}\frac{1}{|G^*|}\mathrm{I}\,\omega^2$$

(PP-Geometry)

Ewoldt, Randy H et al., "Experimental challenges of shear rheology: how to avoid bad data." Complex fluids in biological systems. Springer, New York, NY, 2015. 207-241.

Soft materials: Extension of measurement range

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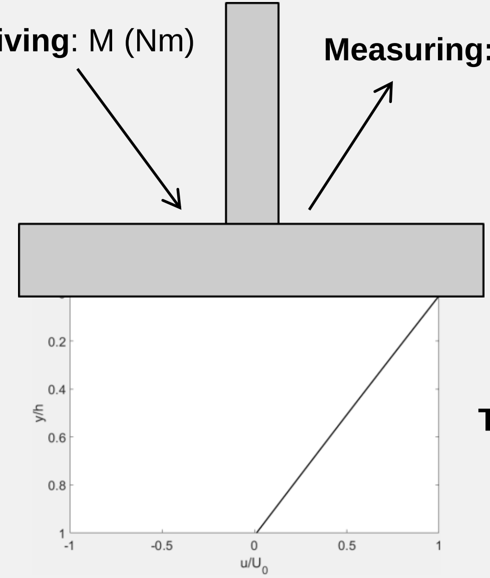
CMT (Combined Motor Transducer)

Driving: M (Nm)

Measuring: φ (rad)



CMT Mode: Total torque (M_0) not fully available for sample loading (M_S). Part of total torque required for acceleration of measuring system (M_a)

$$M_0 = M_S + M_a$$

Total torque

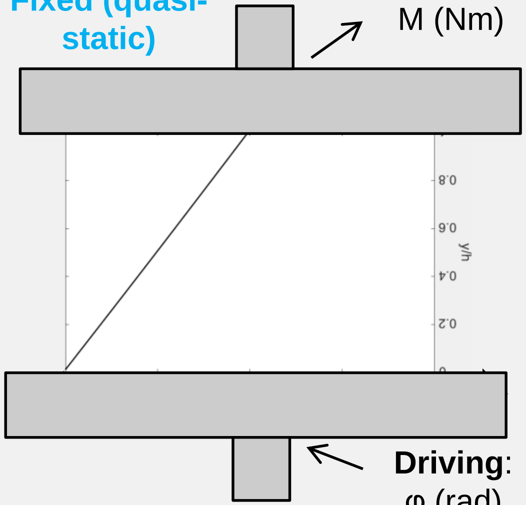
Acceleration torque

$$M_a = I\omega^2\varphi_0$$

SMT (Separate Motor Transducer)

Fixed (quasi-static)

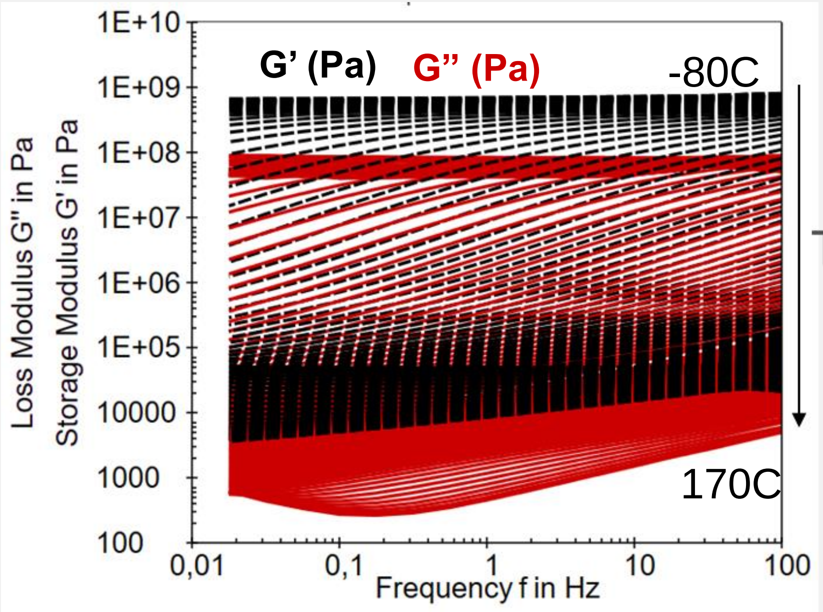
Measuring: M (Nm)

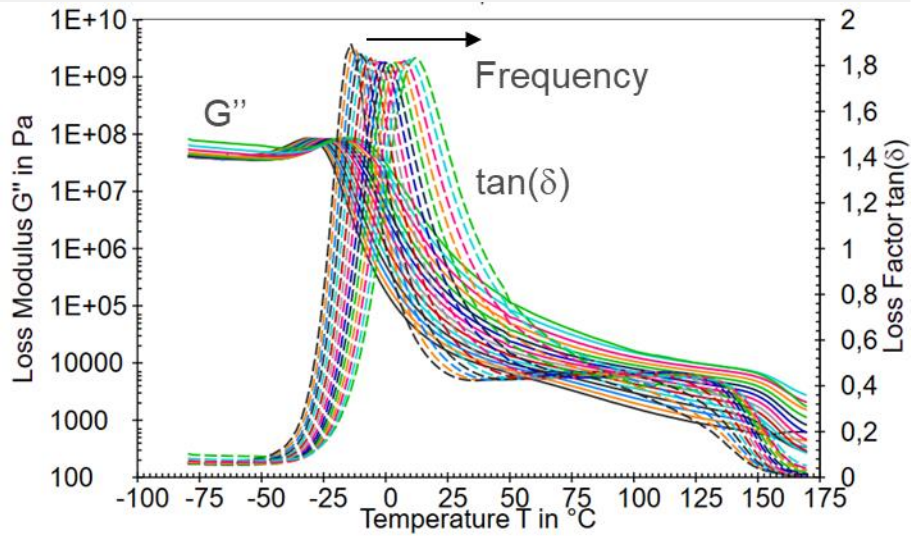


Driving: φ (rad)

As the upper measuring system is not moving **in SMT mode** the **torque** required **for acceleration** can be **neglected**. This **reduces inertia effects** dramatically

Soft materials: Extension of measurement range





- PP12 frequency sweeps (0.01-100Hz) at different temperatures (-80C to +170C; *ΔT = 2°C)*
- Large ranges in moduli and frequency during one measurement. (5 decades in a single test)
- Using the **SMT mode** and an accurate compensation of the torsional compliance allow precise characterization over the **widest temperature and frequency range.**

Soft materials: Extension of measurement range

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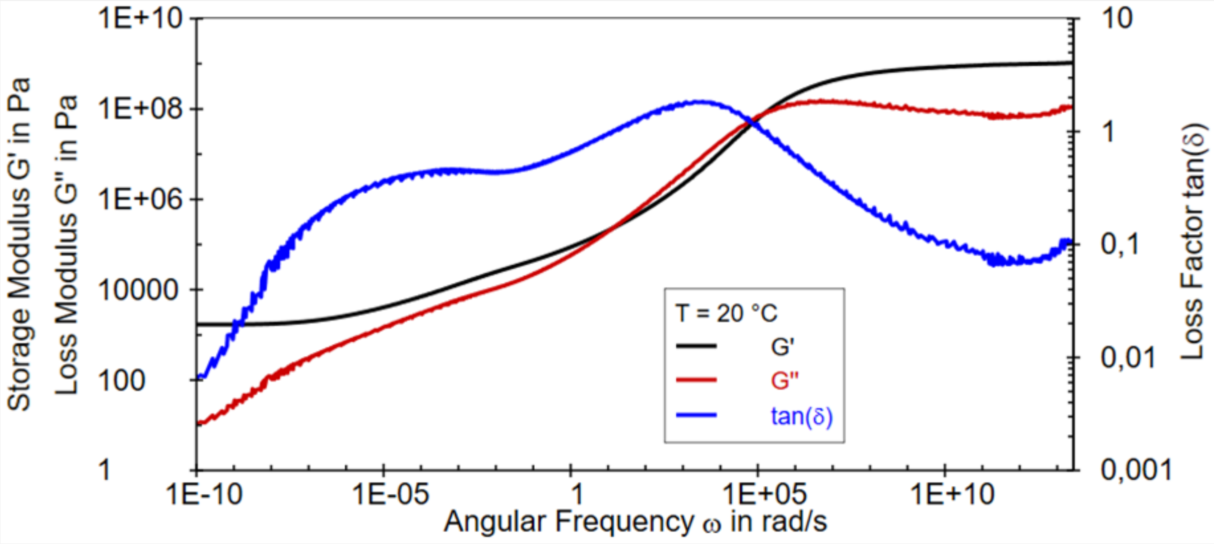
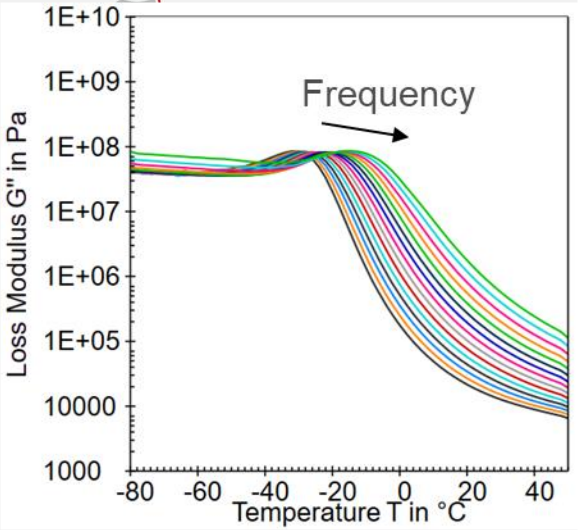
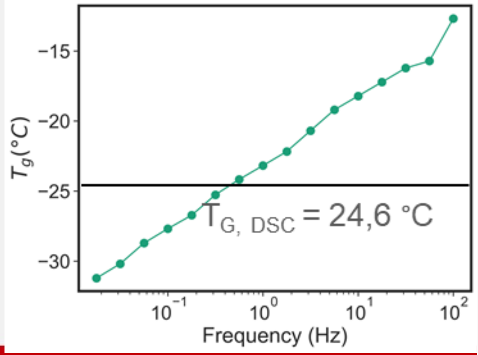




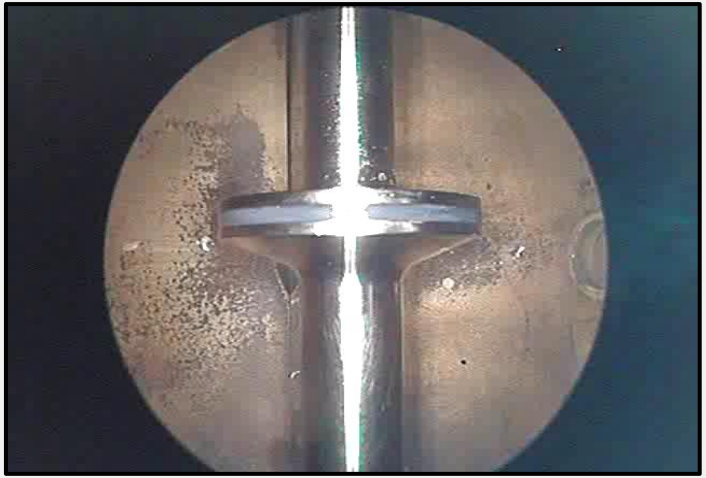


- Master Curve Data at 20C for a PSA covers more than 25 decades in frequency.
- Allows to analyze performance of PSA at reference temperature
- PSA performance correlates to: Viscoelastic properties of the bulk adhesive.
- Study of glass transition as a function of frequency Vs measured by DSC

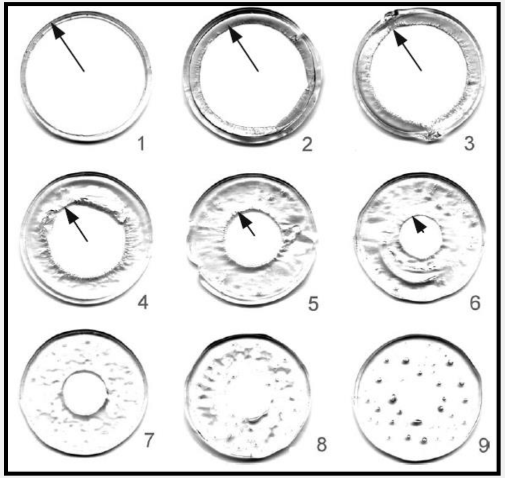
Edge fracture in viscoelastic samples

- Commonly seen in traditional PP and CP rheometric configurations.
- Deformation of the sample surface
- Propagates radially
  - Function of time
  - Function of deformation
- Limits accuracy of start up shear measurements, Flow curves and LAOS measurements.
- Flows relevant to polymer processing involve higher deformations.

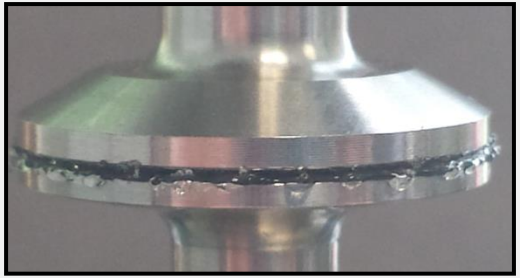
How can we extend measurements!

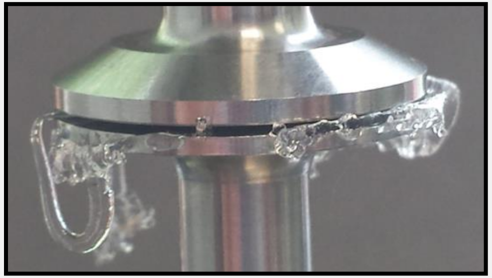


Edge fracture effects in Polypropylene polymer.



Mattes et al., Rheo Acta 47 929-942(2008)





Edge fracture effects in PDMS as a function of the set deformation.

SMT Setup: Cone Partitioned Plate

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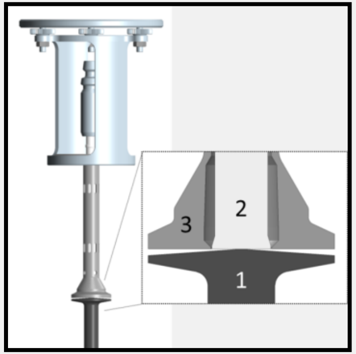
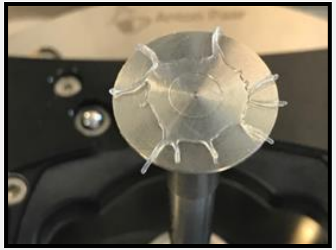
Operation:

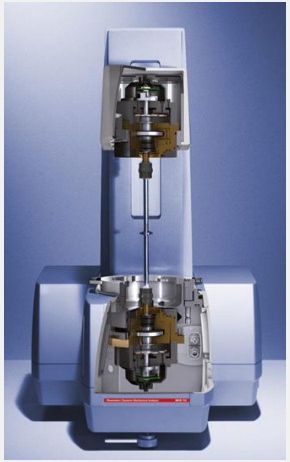
- Upper geometry: Partitioned Plate
- Lower geometry: Cone
- Only sample volume below the inner plate used for characterizing sample behavior.

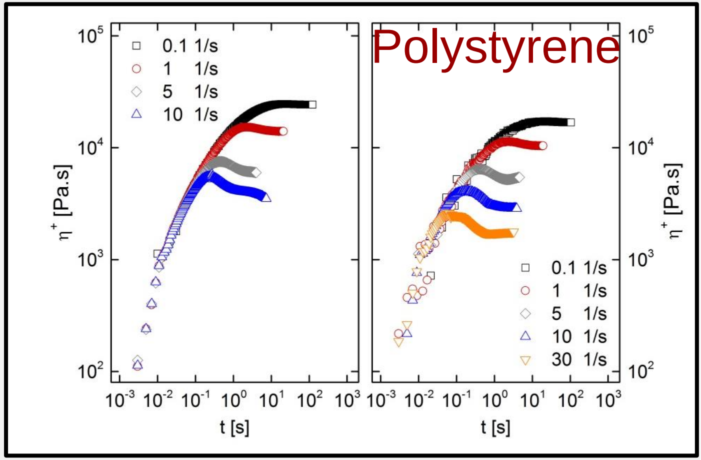
Benefits:

- Instabilities arising at the edge don’t have any effect.
- Reduces effect of trimming.
- Measurements at larger deformations than conventional geometries.



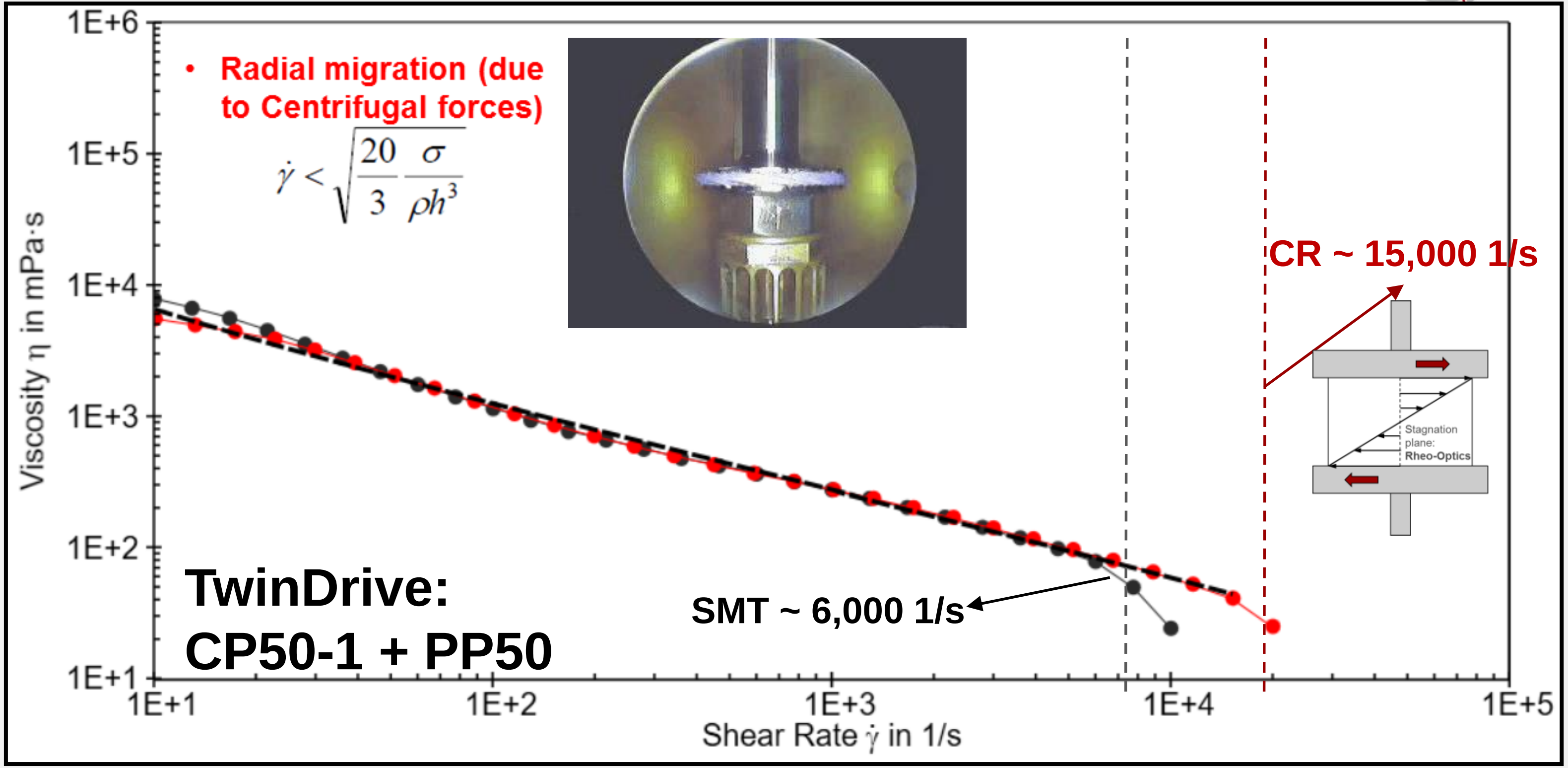






Schweizer et al, J. Rheol. 47, 1071-1085(2003), Schweizer et al, Rheol. Acta 41, 337–344(2002), Snijkers et al, J. Rheol. 55, 1167-1186 (2011).

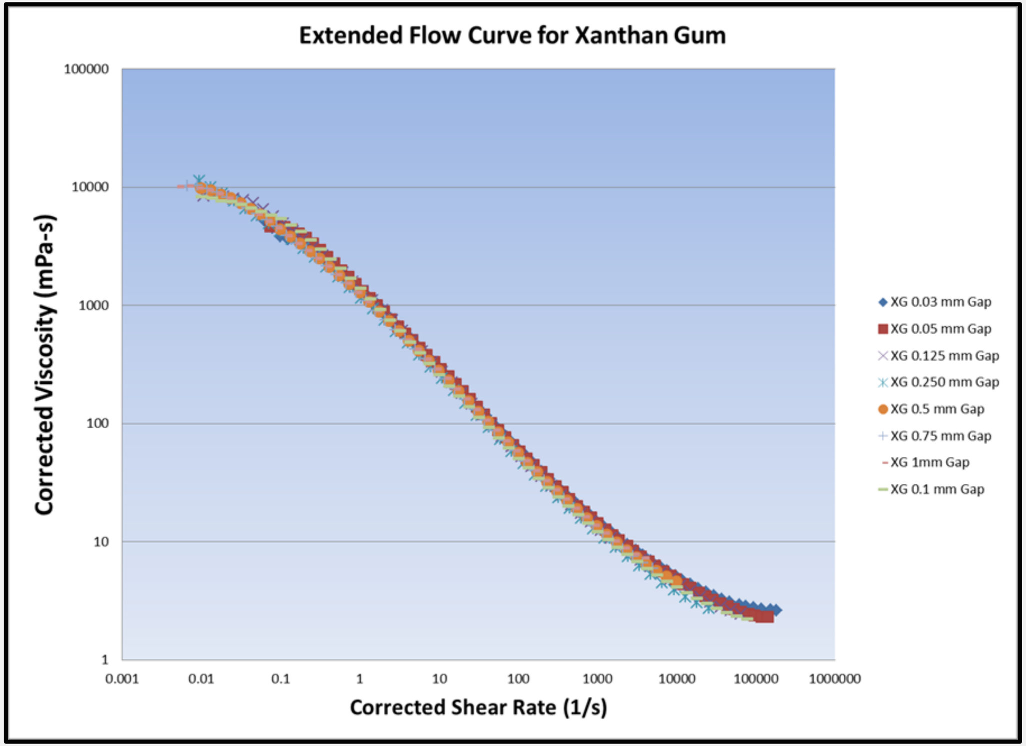
Soft materials: Extension of shear rates (CR)



G.A Davies et al., J Non-Newtonian Fluid Mech 148 (2008)

- Counter rotation extends the range of achievable shear rates compared.
- Extending flow curves (CR) beyond what is possible on a conventional rheometer.

Polymer solutions: Extending flow curves (CR)



- Using CR and narrow PP gap rheometry (Xanthan Gum).
- Errors in narrow gap rheometry: a)Viscous Shear Heating b) Edge Fracture c)Secondary Flows d) **Gap Parallelism Errors.**
- Formalism of Davies etal., applied to correct for gap parallelism errors.

$$\dot{\gamma}_R = \dot{\gamma}_{actual} = \dot{\gamma}_M \frac{\delta}{\delta + \varepsilon}$$

$$\eta = \eta_{actual} = \eta_M \frac{\delta + \varepsilon}{\delta}$$

$$R_E = \frac{\rho \dot{\gamma}_R h^2}{\eta}$$

G.A Davies et al., J Non-Newtonian Fluid Mech 148 (2008)

Narrow gap PP rheometry in conjunction with Counter Rotation can be used to extend the flow curve to shear rates in excess of 100000 (1/s)

Soft Materials: Increase the Measurable Strain range using CO

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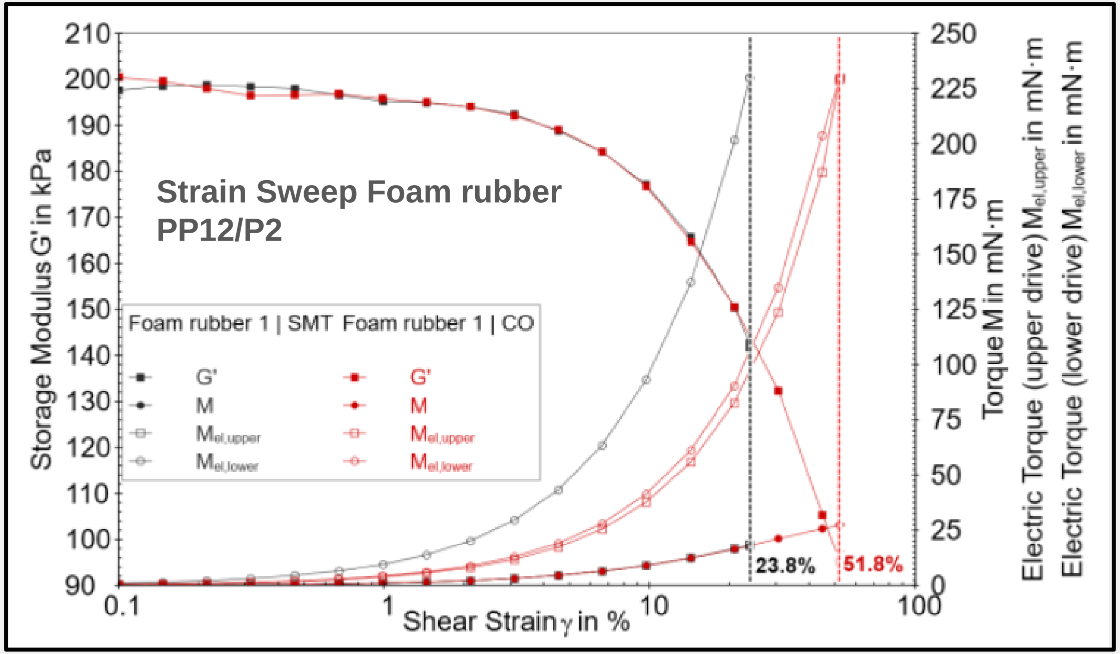
Counter-Oscillation Mode



$$\gamma = \frac{R \cdot \Delta\varphi}{D}$$

$$\Delta\varphi = |\varphi_{upper}| + |\varphi_{lower}|$$

$$\frac{R}{D}\Delta\varphi_{CO} = \frac{R}{D}\Delta\varphi_{SMT}$$

$$\varphi_{CO,lower} = \frac{1}{2}\varphi_{SMT,lower}$$

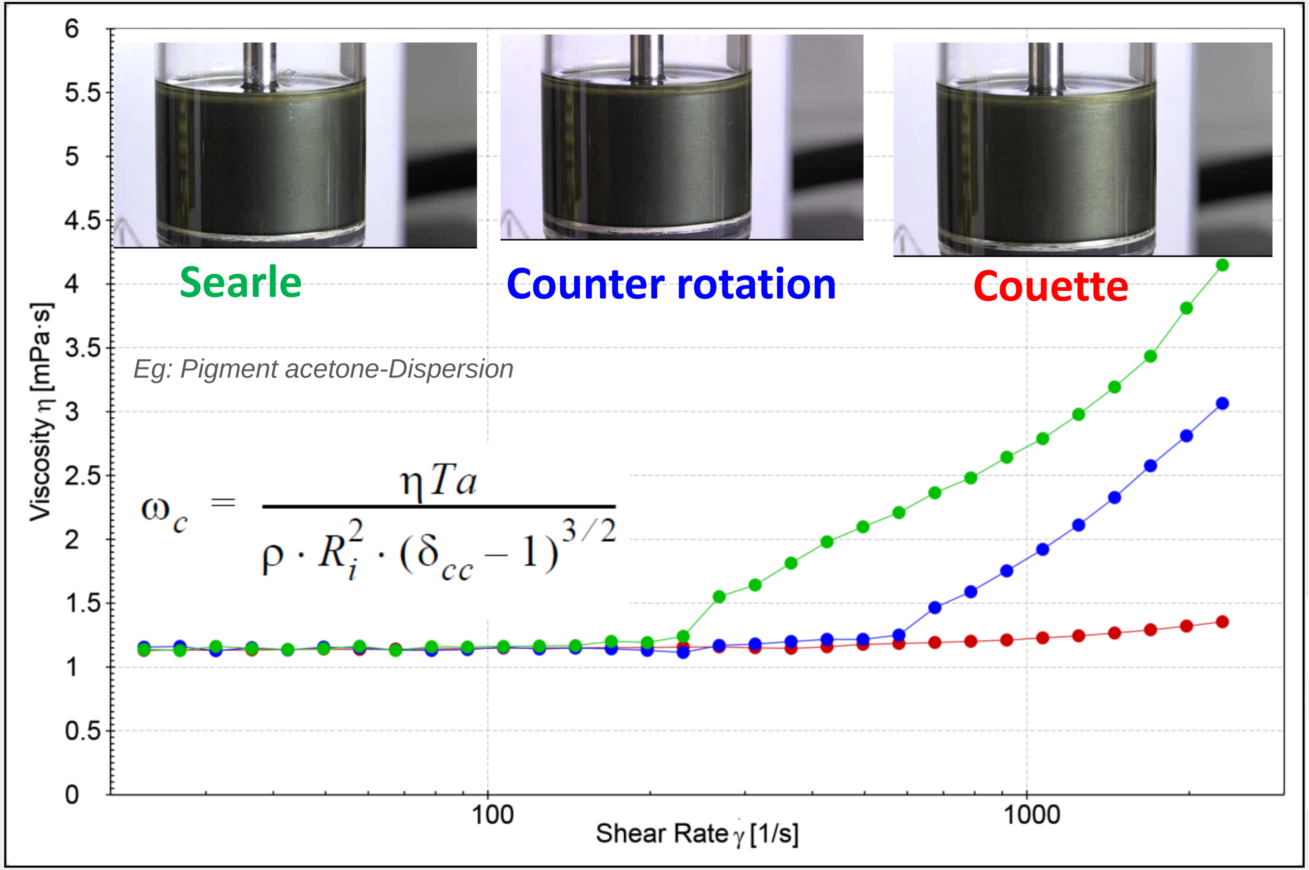
$$I\omega^2\Delta\varphi_{CO} = I\omega^2\varphi_{SMT}$$

$$I\omega^2(\varphi_{CO,upper} + \varphi_{CO,lower}) = I\omega^2\varphi_{SMT,lower}$$

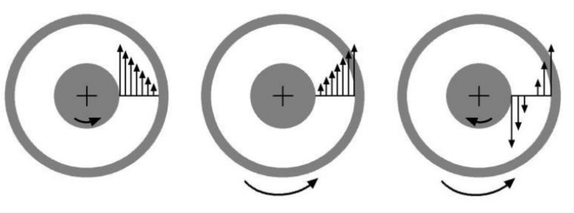
$$\Rightarrow M_{a,CO,lower} = M_{a,CO,upper} = \frac{1}{2}M_{a,SMT} = \frac{1}{2}M_{a,CMT}$$

- The maximum strain amplitude that can be reached in an oscillatory rheological measurement using the CO mode is almost twice that seen with single drive modes (SMT/CMT).
- CO mode, the total deflection angle of the measurement system was distributed onto the two individual motor drives.

Effect of CMT, SMT and CR on Low Viscosity Fluids

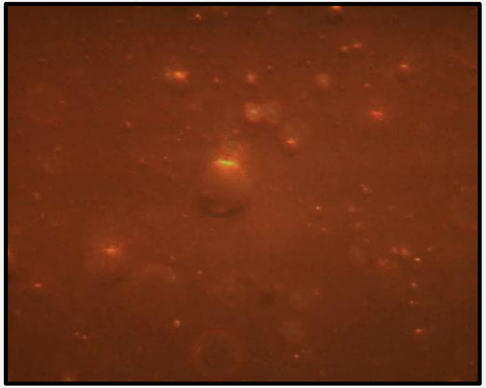


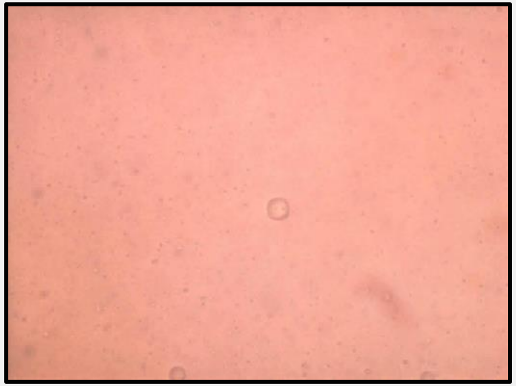
- Three different modes can be investigated using the same geometry.
- Searle: Taylor vortices observed.
- Counter Rotation: These instabilities are shifted to higher shear rates.
- SMT: No Taylor vortices form but some secondary flows still exist.

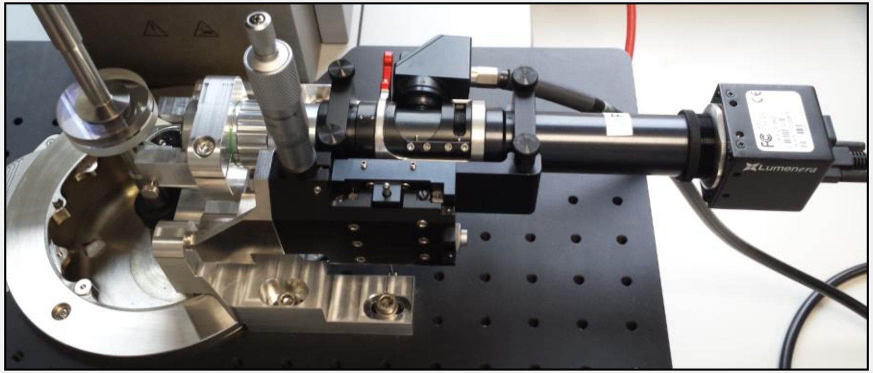


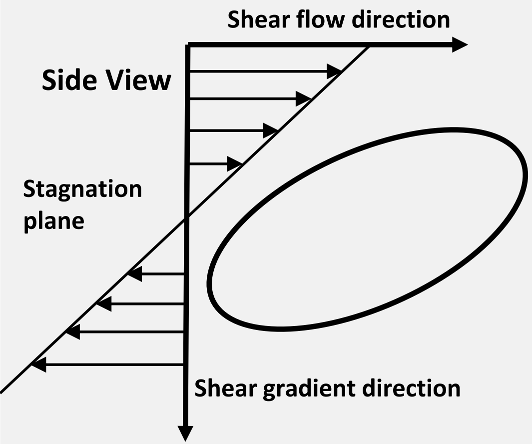
Counter Rotation for Microscopy

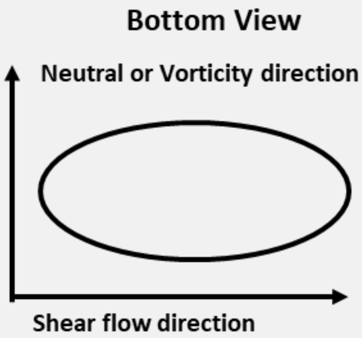
PIB in PDMS





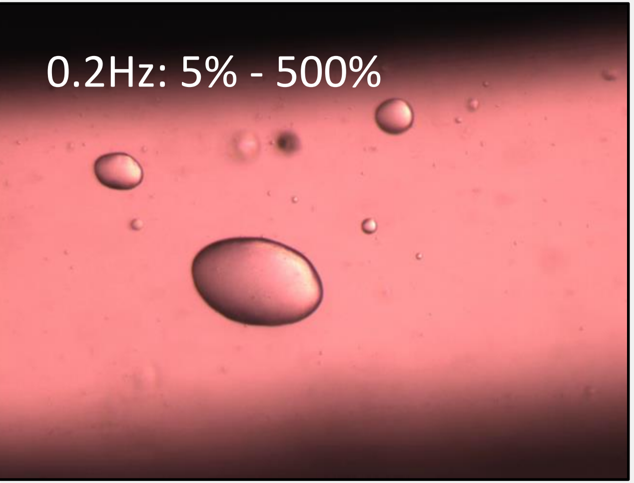


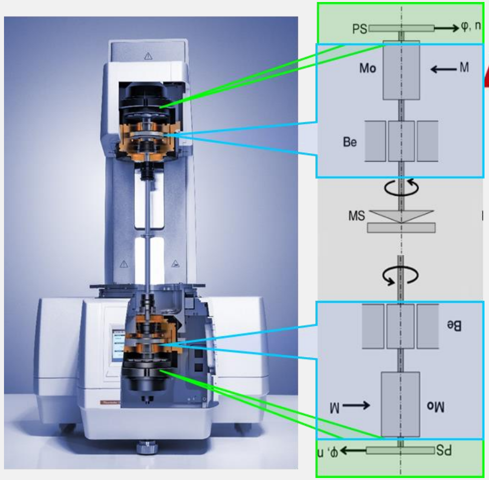




- CMT Mode: Challenging to keep the sample elements in the field of view.
- Counter rotation creates a stagnation plane in the sample.
- Better for microscopic investigations since the material of interest can be locked in the stagnation plane.
- Stretched particles or droplets can be followed much more easily in the stagnation plane.
- Investigation limited to room temperature

Counter Oscillation Microscopy: PIV-Cell





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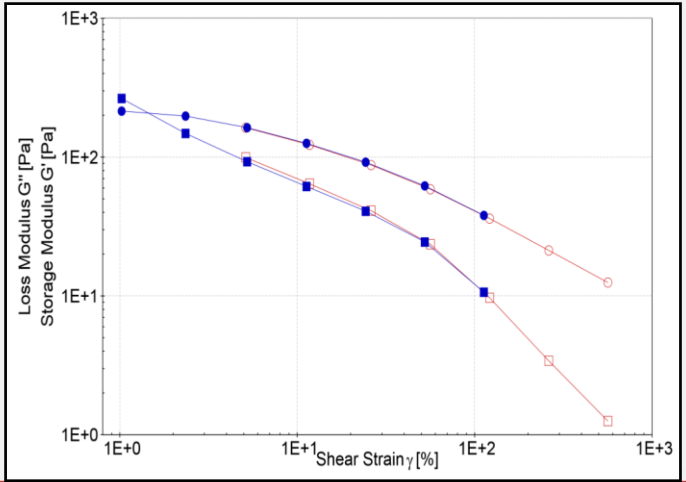
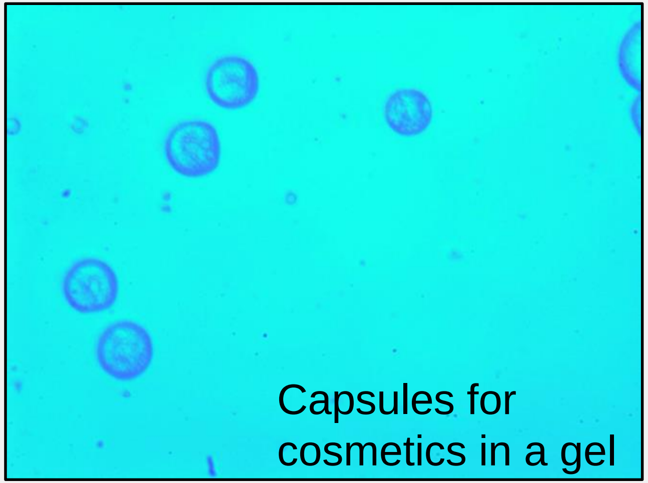
- Rheological data coupled with structural changes.
- Intra-cycle information for LAOS-analysis is available



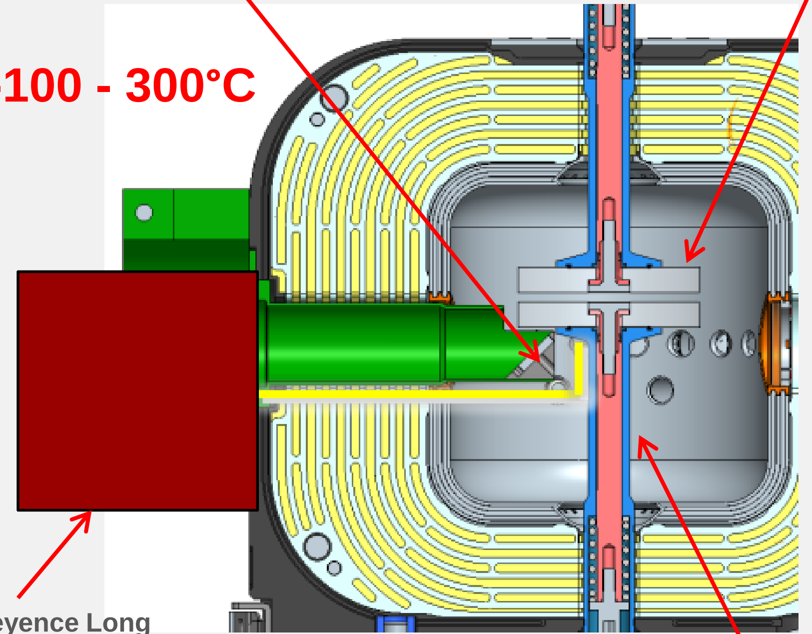


Counter Rotation: High (Low)Temperature

High Temperature Mirror (300°C)

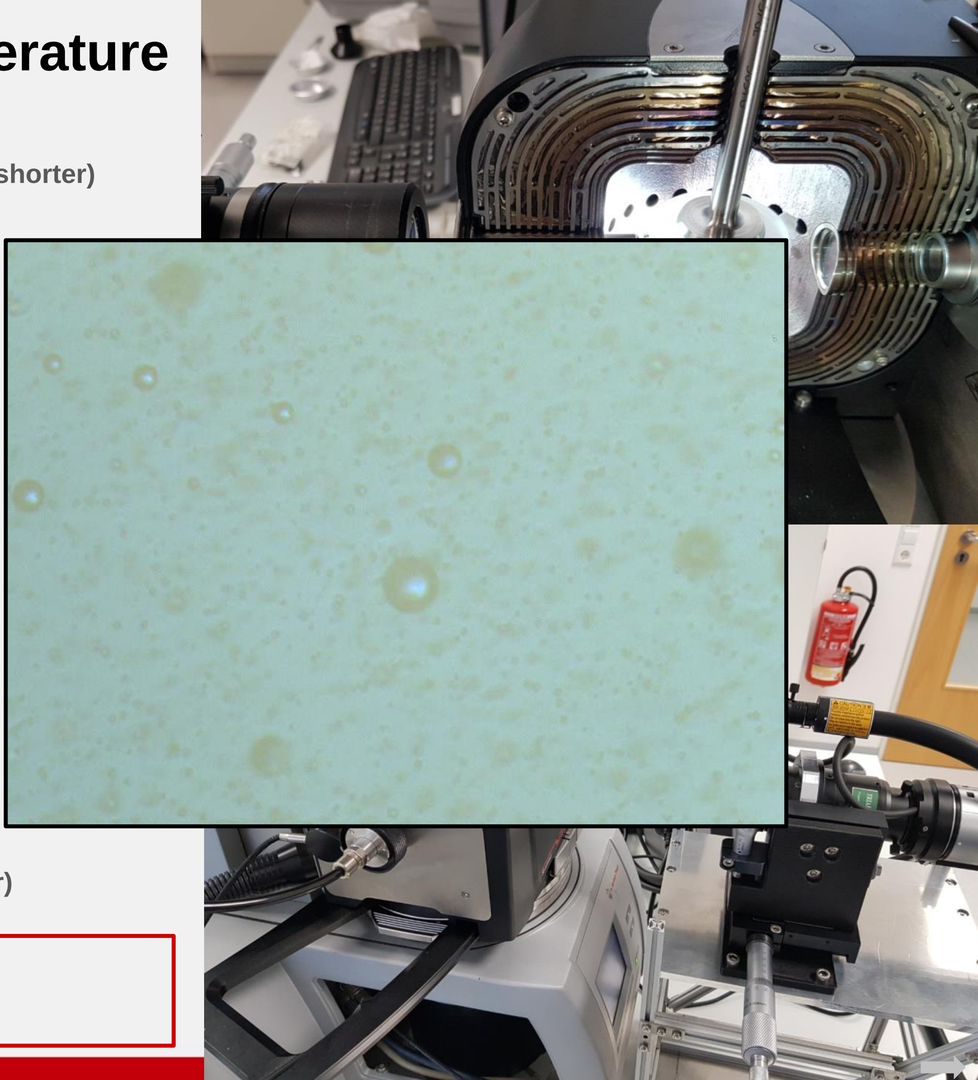
Upper geometry (shorter)

-100 - 300°C



Keyence Long Distance Microscope

Lower geometry (longer)



Combination with a convection oven and long distance microscope increases range of measurements in CR.

Flow instabilities in rheometric flows

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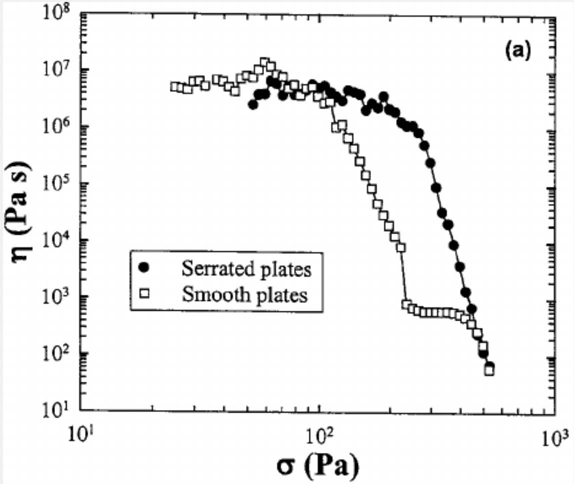
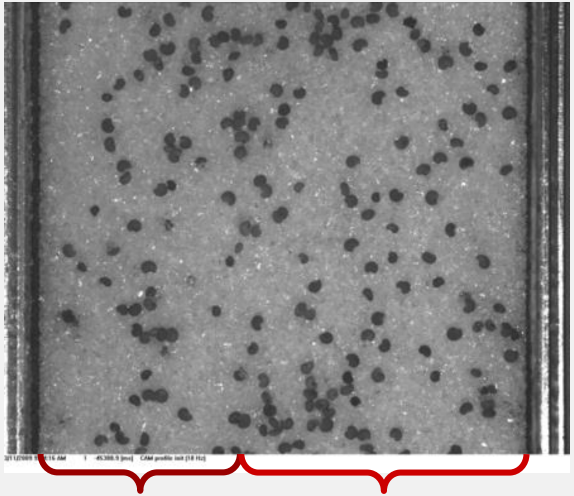
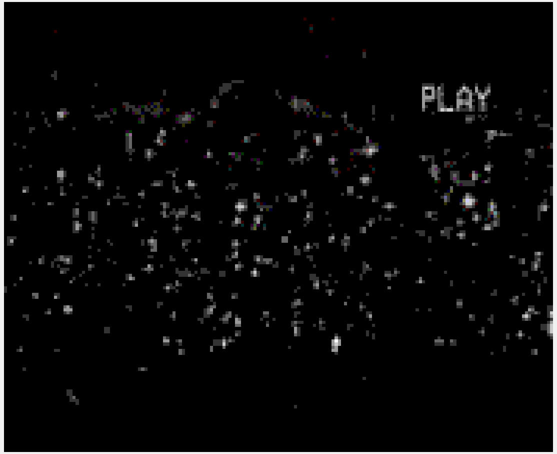
Wall slip[1]	*Strain localization (solids)*[2]	*Shear banding (liquids)*[3]





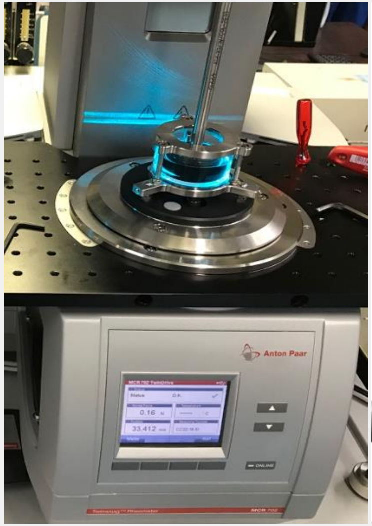


Flow instabilities complicate processing, confound interpretation of rheological data, and hide important information about fluid physics.

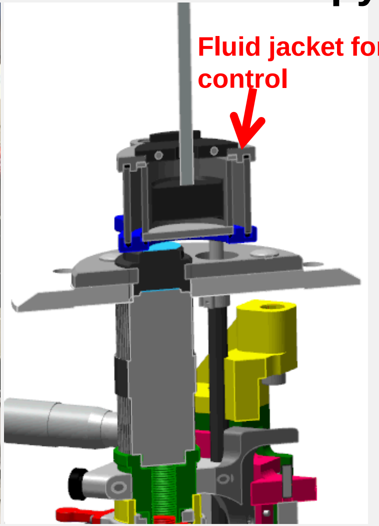
[1] H.J. Walls et al., J Rheology, 2003 47(4): 847-868. [2] T. Börzsönyi et al., Phys Rev E, 2009, 80(6): 060302. [3] S. Ravindranath et al., Macromolecules, 2008, 41(7): 2663-2670.

CMT: Rheo-PTV and Microscopy to identify mechanisms of banding

Rheo-PTV cell

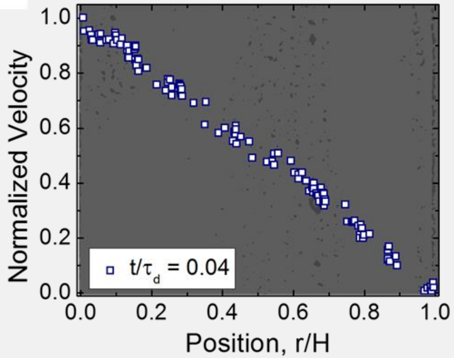


Rheo-microscopy optical train



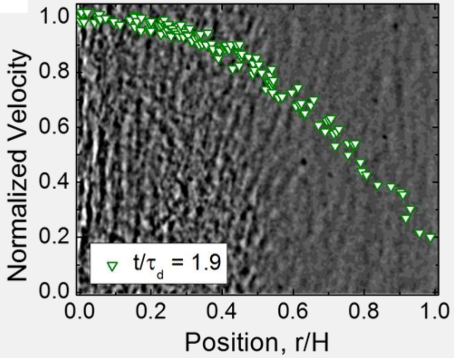
Short times

No banding, no turbidity



Moderate times

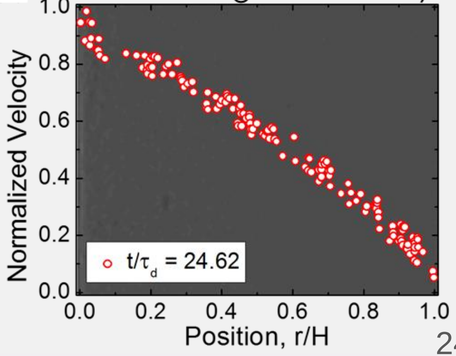
Banding/slip, turbidity



16wt%PS (3.84M)/DOP;
Wi=11.1

Long times

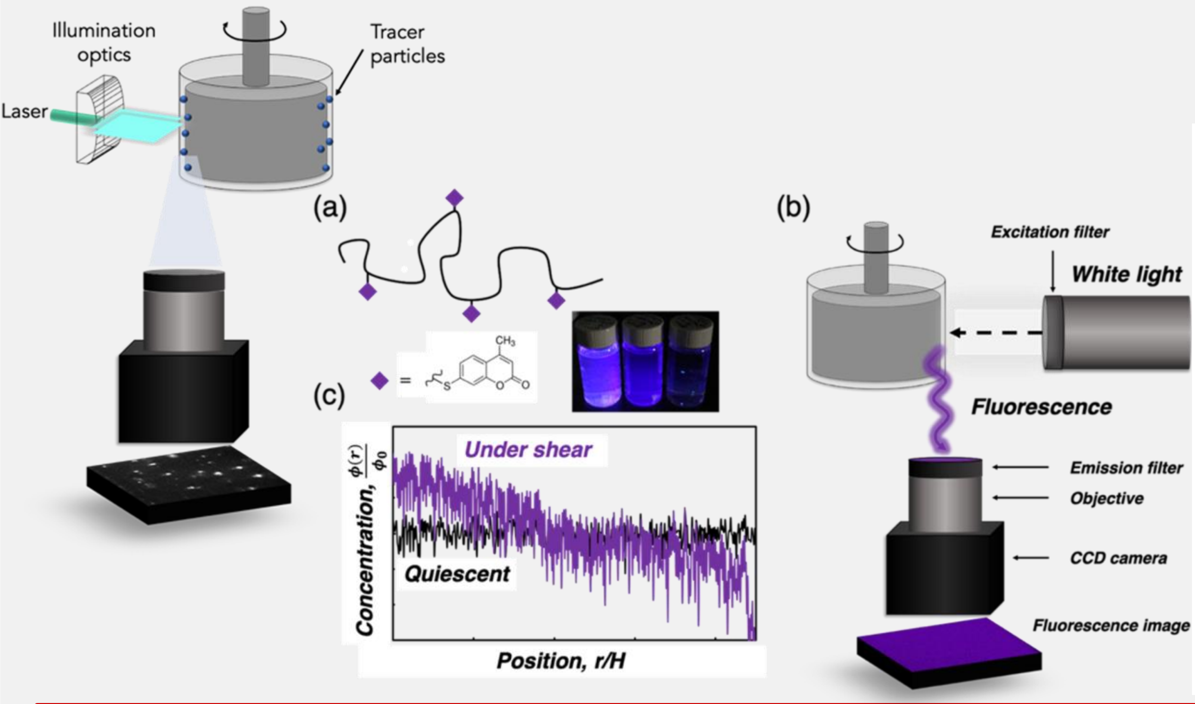
No banding, no turbidity

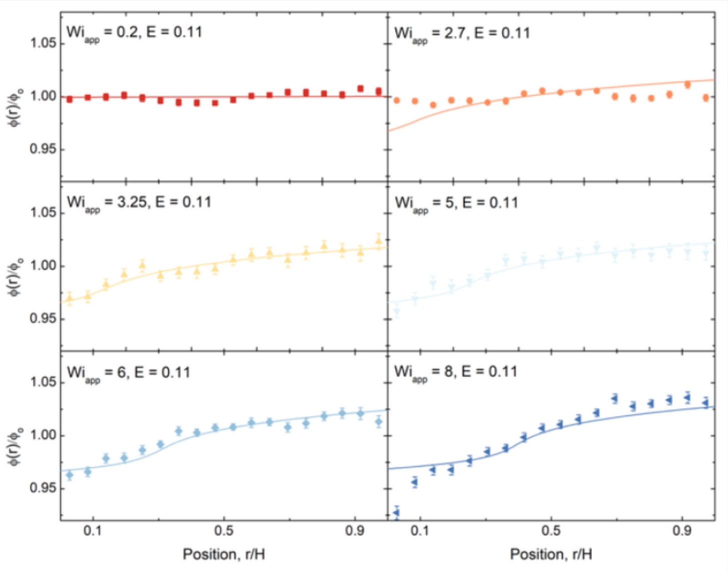


Combining rheo-PTV and rheo-microscopy gives insight into the microstructural origins of non-homogeneous flow (shear-enhanced concentration fluctuations

Burroughs, Michael C., Abhishek M. Shetty, L. Gary Leal, and Matthew E. Helgeson, Physical Review Fluids 5, no. 4 (2020): 043301.

Rheo-PTV and Rheo-Fluorescence to identify mechanisms of banding





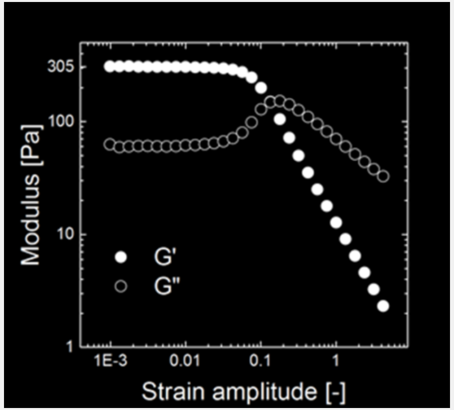
First experimental probe of the *in situ* concentration and velocity profiles of entangled polymer solutions under shear.

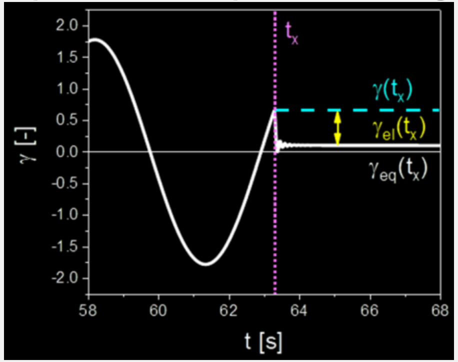
Burroughs, Michael C., Yuanyi Zhang, Abhishek M. Shetty, Christopher M. Bates, L. Gary Leal, and Matthew E. Helgeson, Physical Review Letters 126, no. 20 (2021): 207801.

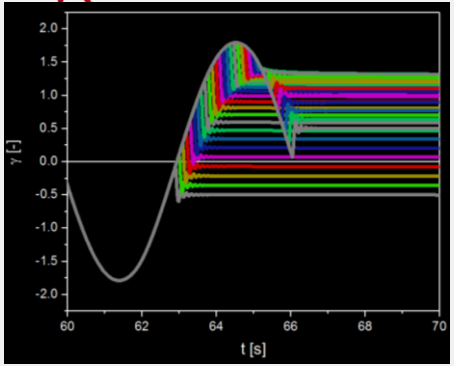
Time resolved Oscillatory Shear/Recovery to study Yielding

Hybrid Stress/Strain Experiments

Traditional Amplitude Sweep







The overshoot in G" in soft yielding materials is due to the increase in the amount of strain acquired unrecoverably at large amplitudes

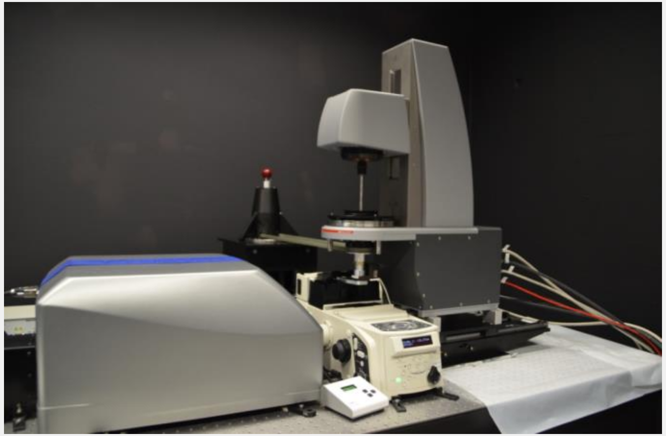
New hybrid tests shed light on sequence of physical processes which occur during yielding

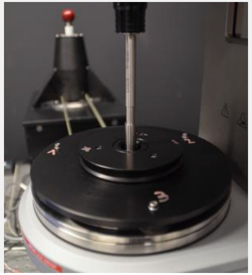
<u>Hybrid Protocols:</u>

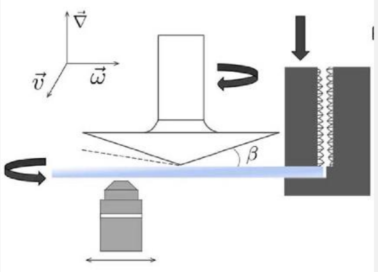
- Apply oscillatory strain till steady alternance is reached.
- Continue oscillating for a portion of a cycle.
- Apply zero stress until the strain in the material completely relaxes
- Use of the MCR-702 –EC Motor allows for controlled stress and controlled strain measurements on one device.

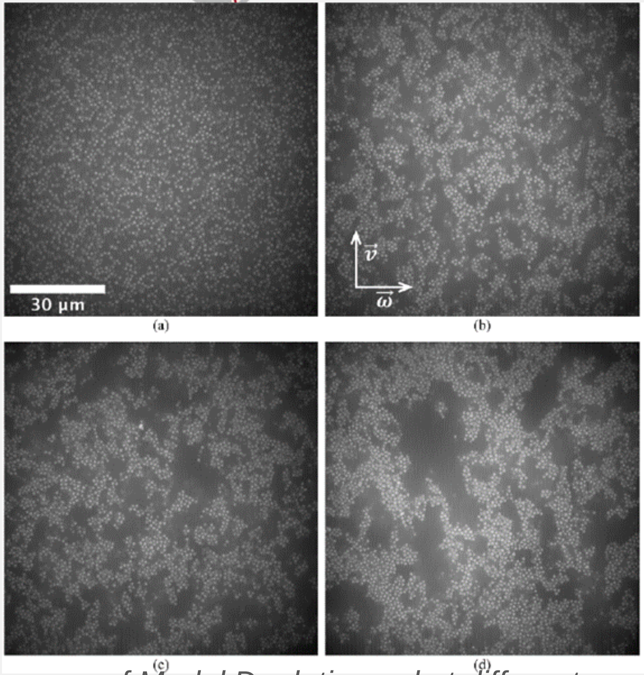
Donley, G. J., Singh, P. K., Shetty, A., & Rogers, S. A. (2020). Proceedings of the National Academy of Sciences, 117(36), 21945-21952.

Confocal Rheo-Microscopy in Counter rotation







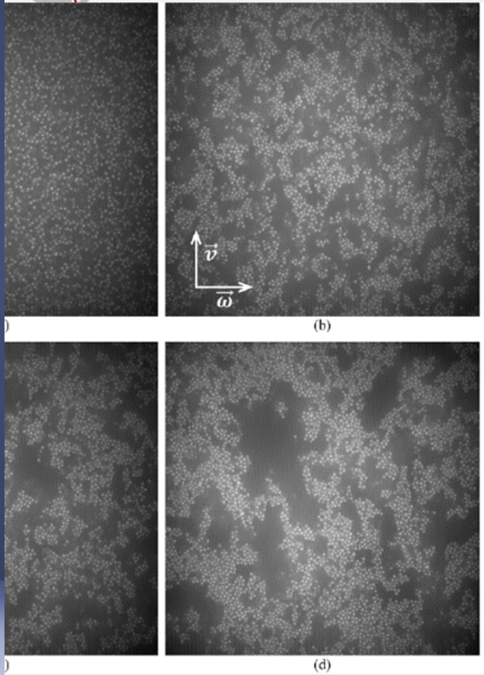


Images of Model Depletion gel at different shear rates

- Dual motor stress controlled rheometer coupled with Rheo-Confocal.
- Rotation of the second motor via a toothed belt to the shear cell assembly.
- Imaging in the velocity-vorticity plane.
- Possibility to study structural evolutions with higher resolution and for longer times at the stagnation plane.

G. Colombo, R. Massaro, S. Coleman, J. Läuger, P. Van Puyvelde, J. Vermant , Ultra fast imaging of soft materials during shear flow Korean-Australian Rheology Journal, 31(4), 229-240 (2019)

Confocal Rheo-Microscopy in Counter rotation



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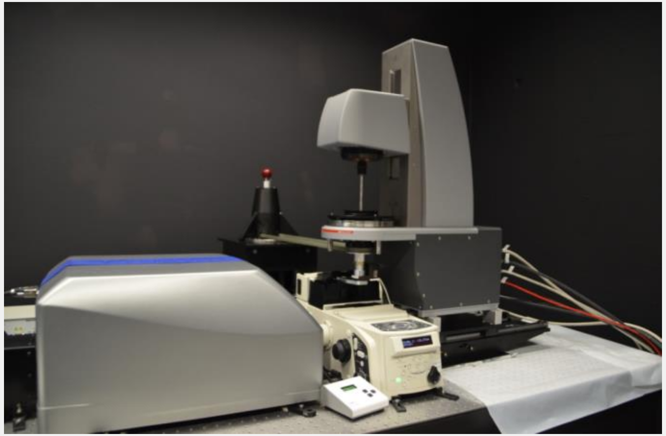

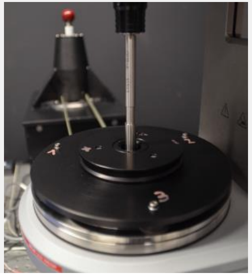

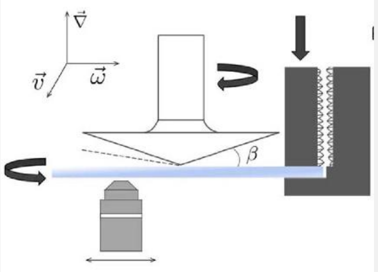

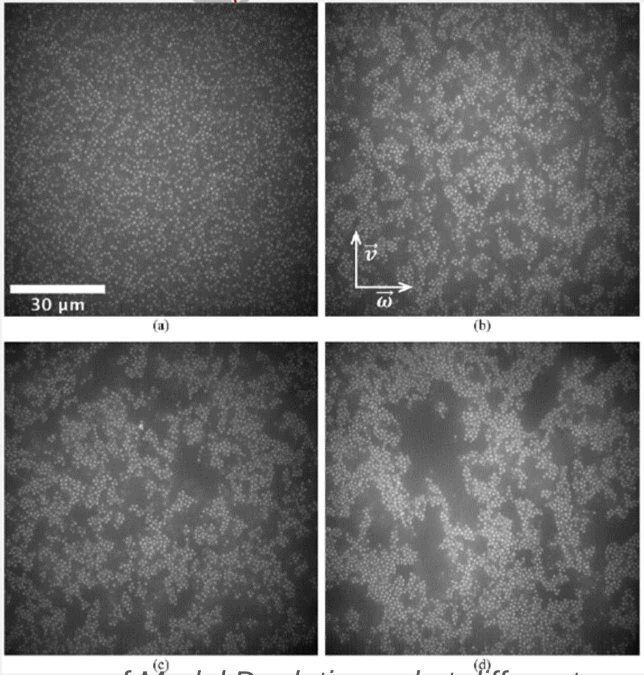

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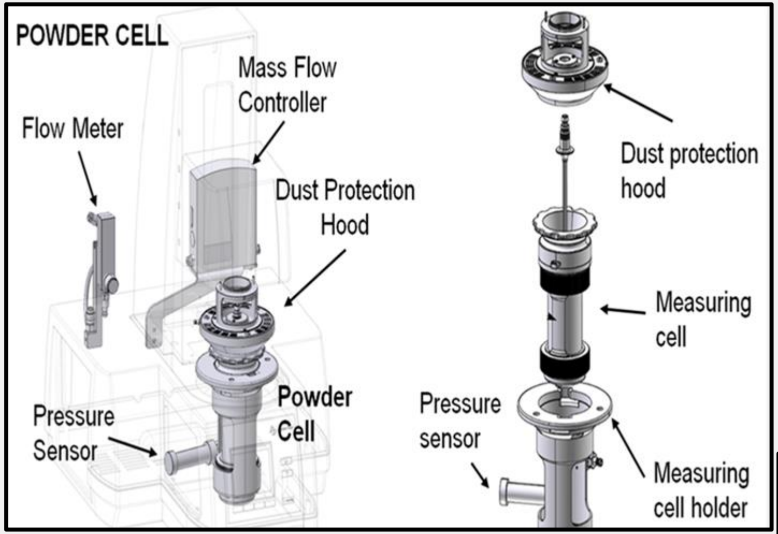
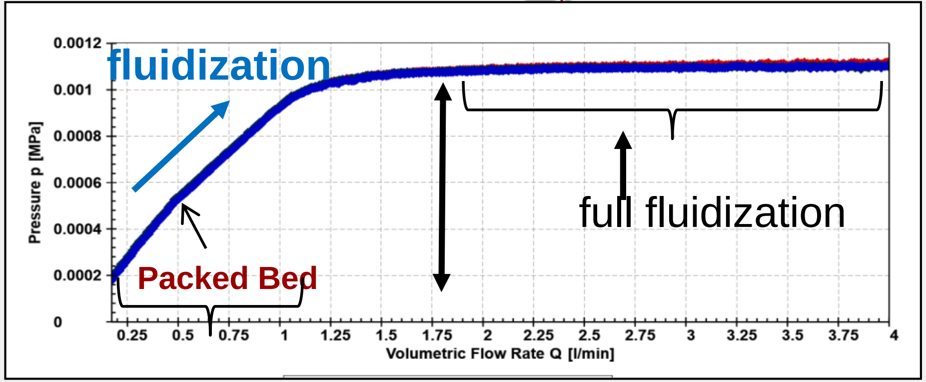
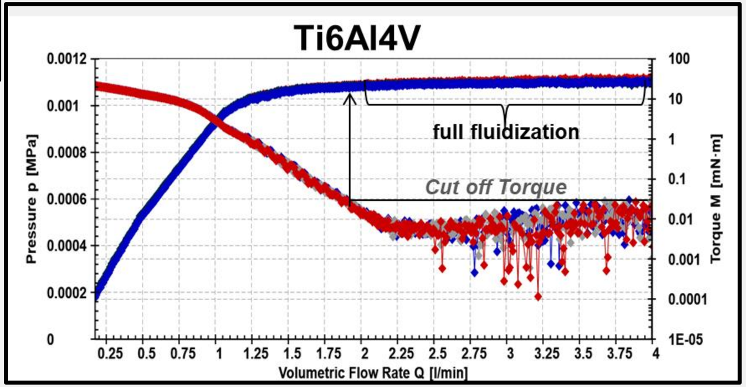
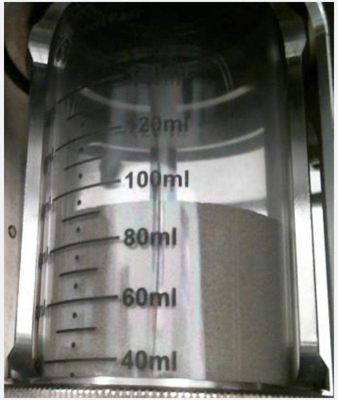
CMT: Fluidized Bed Powder rheology





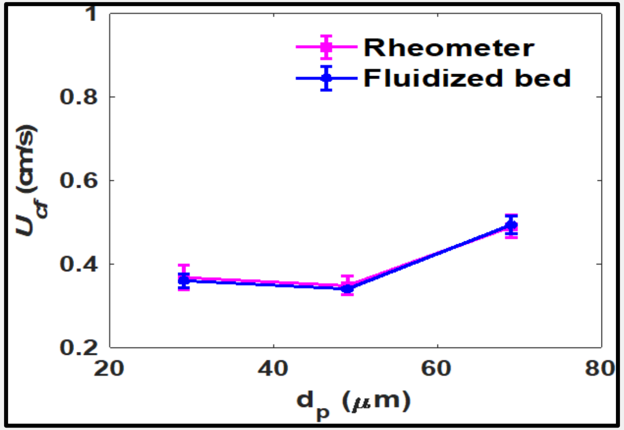
- Controlled gas flow through a powder bed.
- Gauge fluidization by monitoring pressure drop and torque.
- Determination of minimum and complete fluidization points as with classic fluidized beds.
- Ability to measure extremely low torques.
- Characterization of hazardous powders-sealed cell concept.

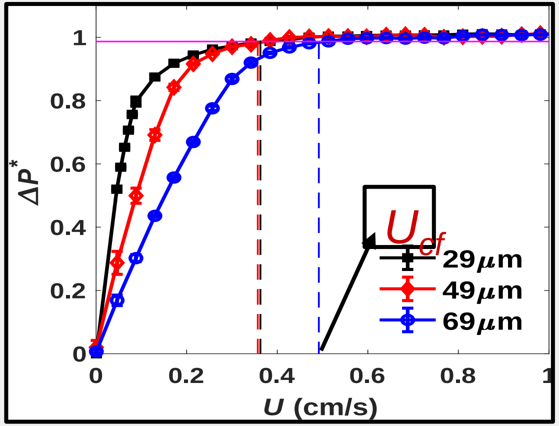


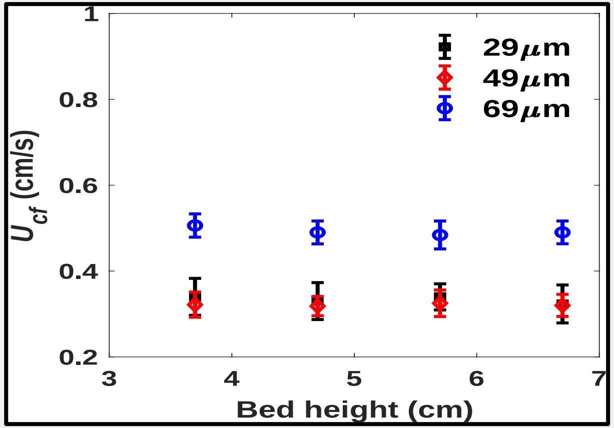


FCC Sample

CMT: Fluidized Bed Powder rheology





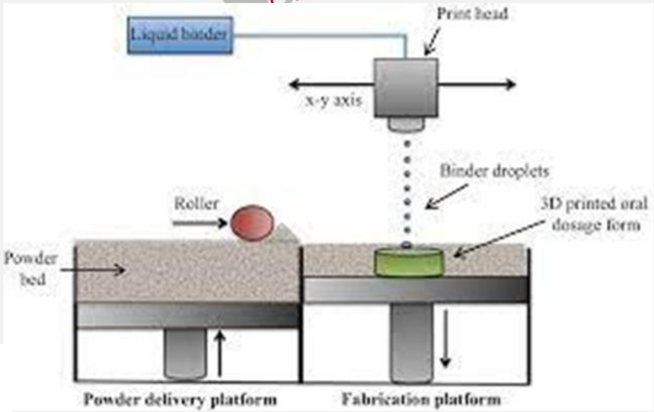


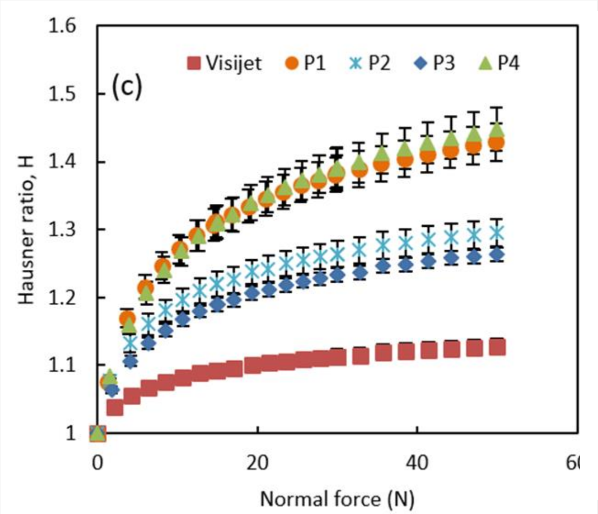
- Defluidization experiments on glass beads (mildly cohesive) showed system size independence.
- Results found to be insensitive to bed diameter and static bed height.
- System able to fluidize cohesive particles as well which would show channeling in a conventional bed.
- Feasibility to directly couple experiments with smaller DEM simulations.

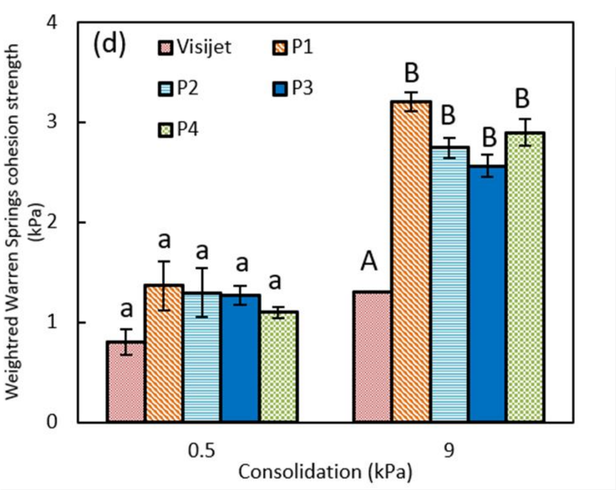
Mishra I, Liu P, Shetty A, Hrenya CM, Chemical Engineering Science. 2020 Mar 16;214:115422.

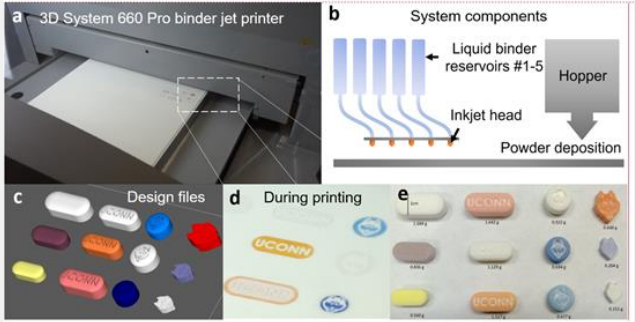
Binder-jet 3D printing of pharmaceutical dosage forms

- Characterization of powder flow properties important.
- Need to explore new types of pharmaceutical excipient powder-binder combinations that can be effectively used in binder jet printing.
- Quasi-static characterization and empirical flow indices characterized.
- Useful tool for benchmarking formulations.





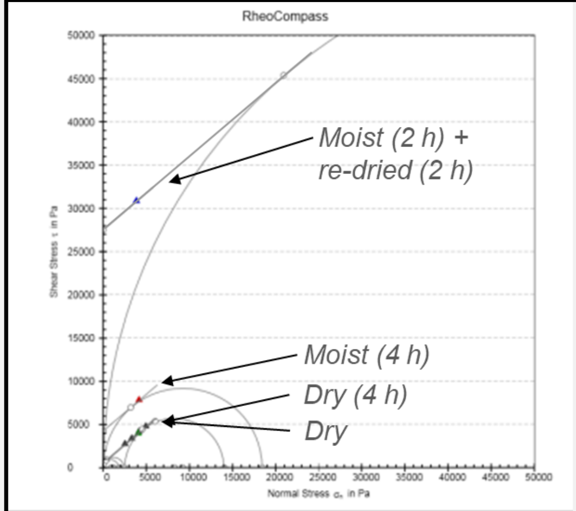




Chang, S. Y., Li, S. W., Kowsari, K., Shetty, A., Sorrells, L., Sen, K., ... & Ma, A. W. (2020).. Journal of Pharmaceutical Sciences, 109(10), 3054-3063.

CMT: Powder rheology at elevated temperatures and humidity

Shear Cell measurements at elevated temperatures



Mohr-Coulomb diagram of a pharmaceutical hot drink

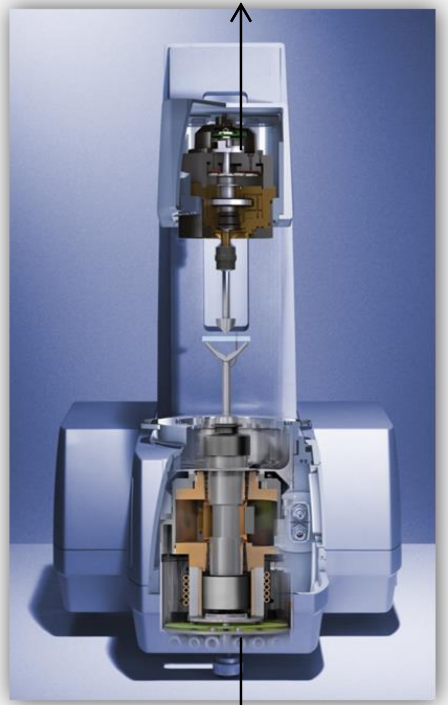
- Extrinsic factors like humidity and temperature have a huge effect on flowability of powders.
- Characterize powders -Mohr-Coulomb type analysis at elevated temperatures (-160°C to 600°C) and humidity (5 %rH to 95 %rH).
- Shear measurements:
  - Caking of a pharmaceutical hot drink
    - Dry powder (4 h at 7 %rH)
    - Moist powder (4 h at 95 %rH)
    - Moist and re-dried powder (2 h at 95 %rH, 2 h at 7 %rH)

- Influence of an increase in ambient moisture is clearly visible

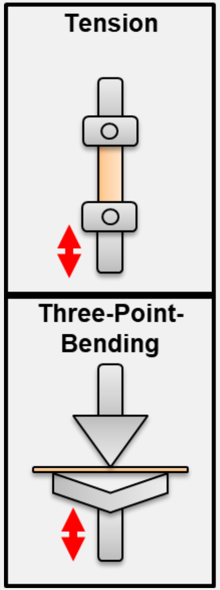
	σ_c [kPa]	σ_1 [kPa]	ffc [1]
Dry	1.9	14.1	**7.23**
Dry (4 h 7% rH)	2.4	14.1	**5.81**
Moist (4 h 95 %rH)	18.5	14.1	**0.76**
Moist + re-dried (2 h 95 %rH & 2 h 7 %rH)	119.4	14.1	**0.12**

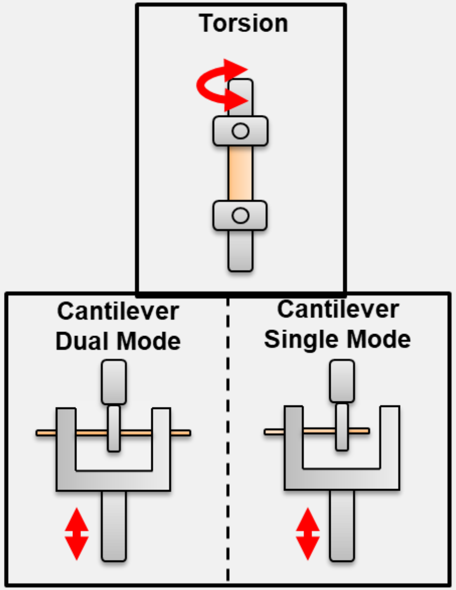
Complete DMTA analysis

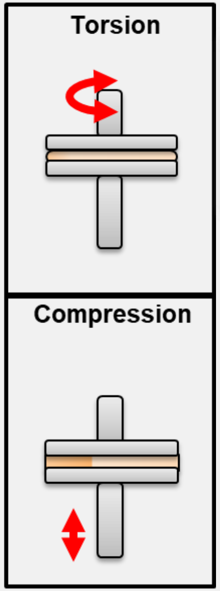
Rotational Measuring Drive

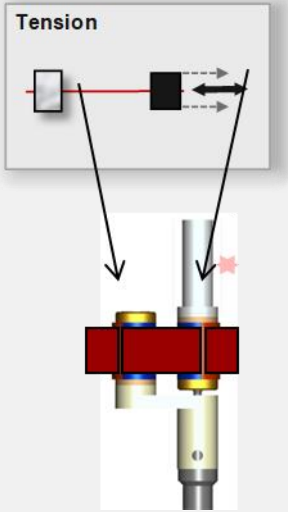


Linear Measuring Drive



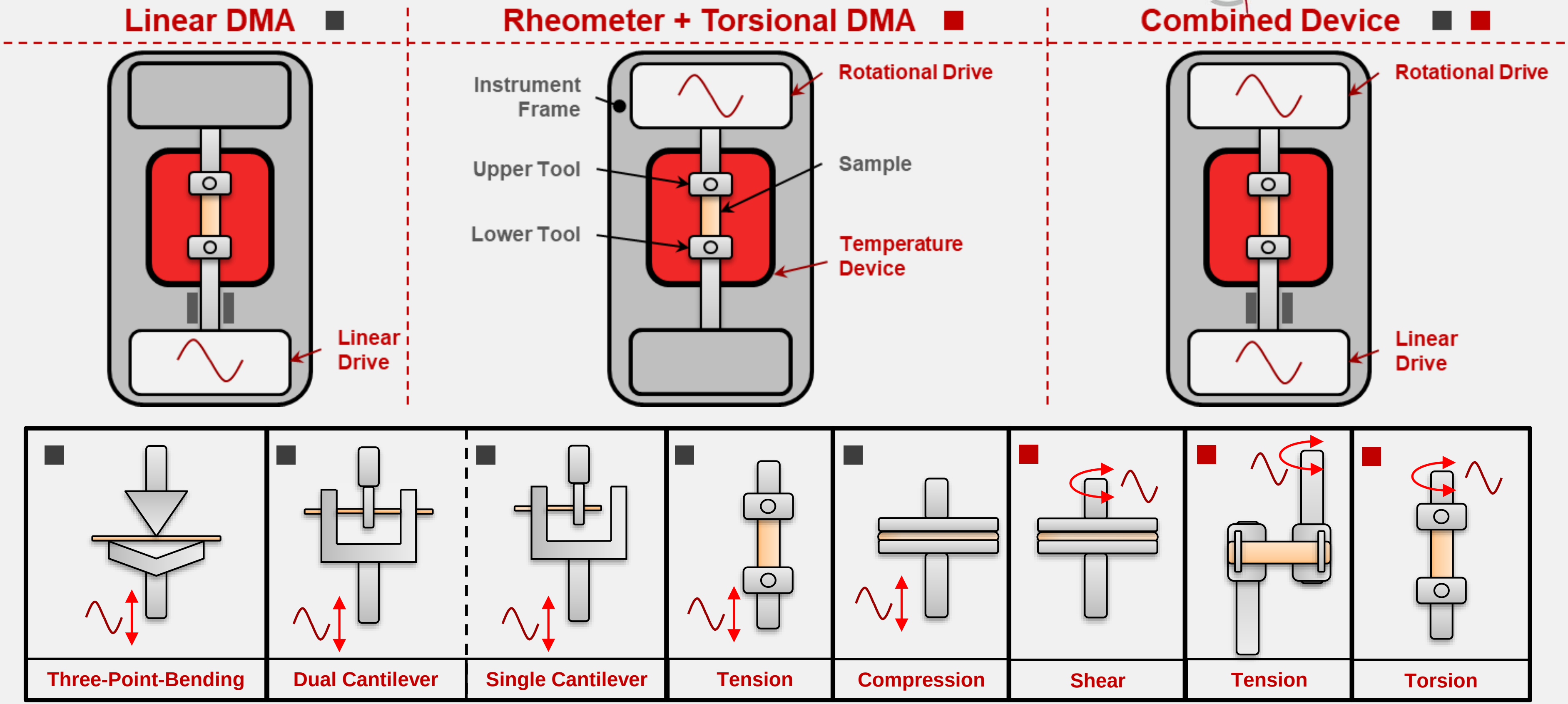






- DMTA with *rotational motor*: Solid torsion bar (SRF,SCF), parallel plate, UXF film fixture
- DMTA with *linear motor*: TPB, Cantilever (Single/Dual), SRF in Tension
- Complete DMTA possible on one device.

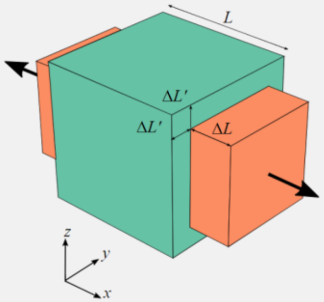
Complete DMTA analysis

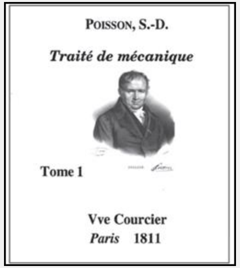


Poisson ratio determination

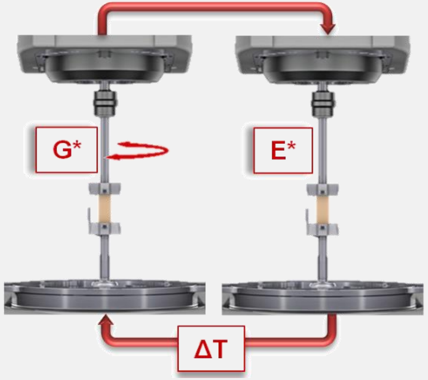
Poisson's Ratio μ:
Rubber: 0.5
Thermoplastics: 0.35 ... 0.45
Glass: 0.18 … 0.3
Foam: 0.1 … 0.5

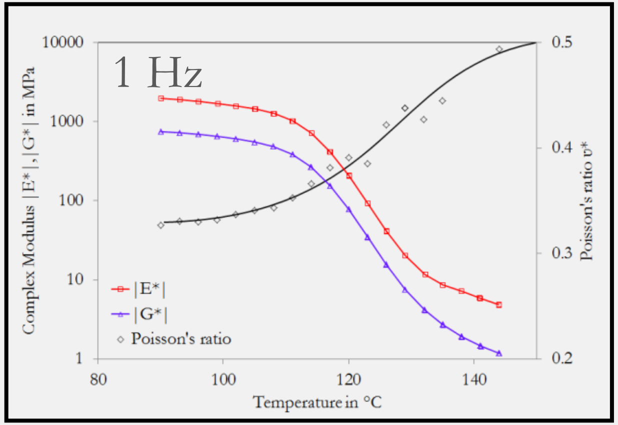
- Sequential execution of measurements in torsion and tension
- Stepwise increase in temperature and repeat above.
- Linear viscoelastic Poisson's ratio $|\nu^{*}|$ determined as a function of temperature and/or frequency in a single run, using a single specimen.
- Poisson's ratio constant in the glassy region; increases as the glass transition is approached



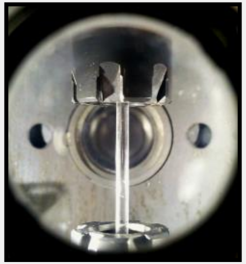


Poisson's ratio: $\mu = -\frac{\varepsilon_{trans}}{\varepsilon_{axial}} = -\frac{dL'}{dL}$



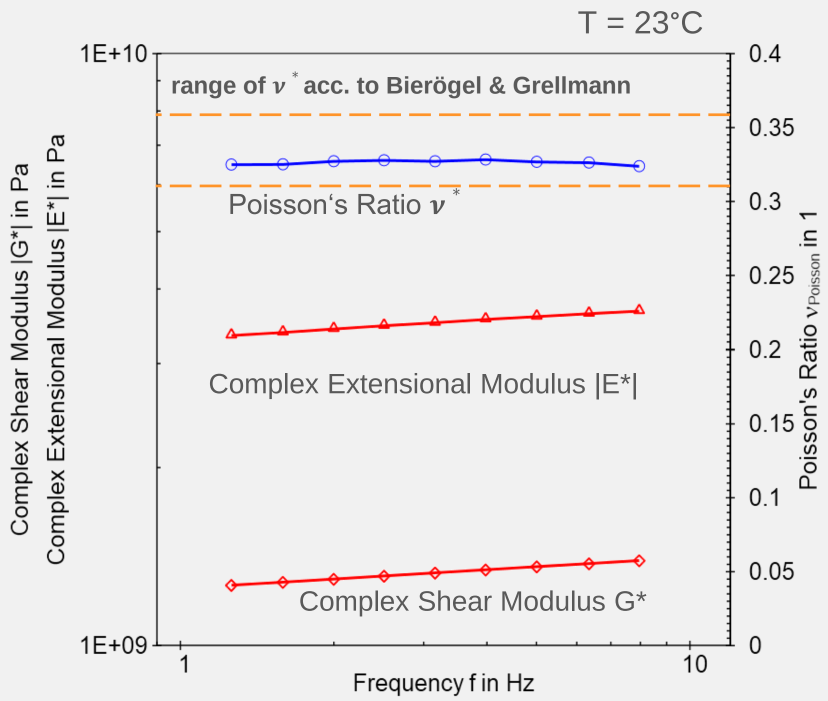


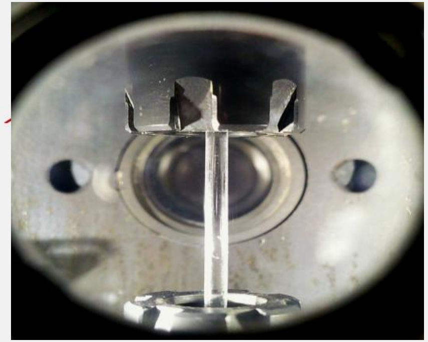
$$|\mu^{*}(t,T)| = \frac{|E^{*}(t,T)|}{2|G^{*}(t,T)|} - 1$$



Poisson ratio determination

Sample: PMMA-GS (moulded)
Cylindrical bars (D=2 mm, L=30 mm) with Solid Circular Fixture



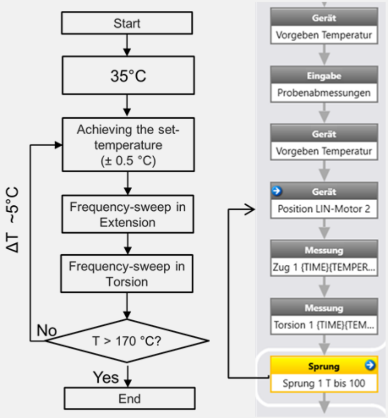


- Good agreement with literature values.
- Poisson‘s ratio is time (frequency), temperature and strain dependent.
- Reliable Poisson‘s ratio values are scarce in material databases.
- Direct measurements are time consuming and prone to errors.

Bierögel & Grellmann, 2014, Quasi-static tensile test – Poisson ratio of thermoplastic materials – data in Polymers, Polymer Solids and Polymer Melts, Mechanical and Thermomechanical Properties of Polymers

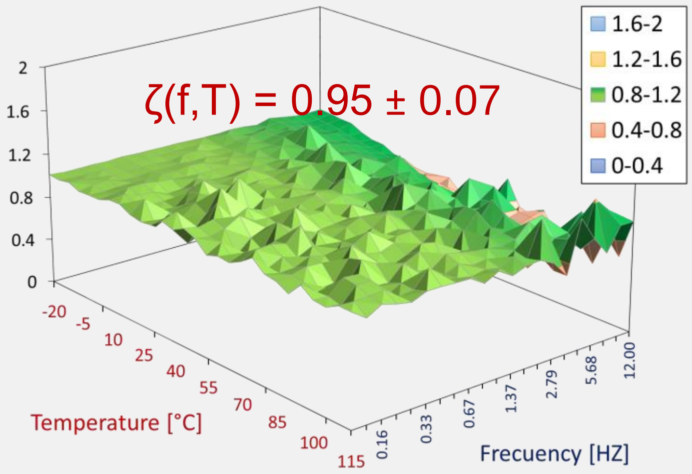
Outlook: Possibility of new experimentational metrics

Multi-Task DMA Experiment

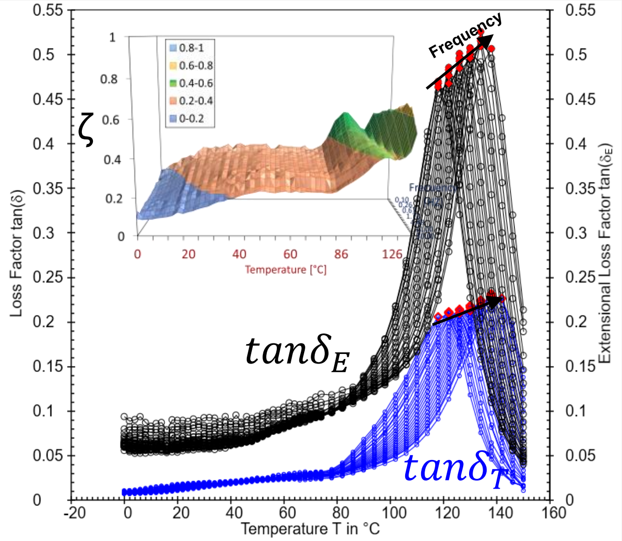


Easily programmable in the Software

Thermoplastic Polyurethane (TPU)

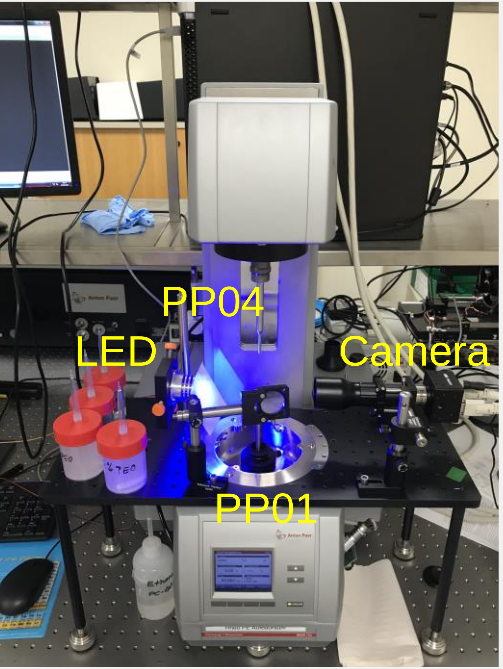


Glass fiber reinforced plastic (GFRP) :



- Dimensionless parameter ζ = $tan\delta_T / tan\delta_E$ that may provide direct information about anisotropy of the material.
- ζ(f,T) approaching 1→ isotropic material.
- ζ(f,T) differs significantly from 1→ anisotropic material.
- Can this ζ(f,T) be used as a unique dynamic fingerprint?

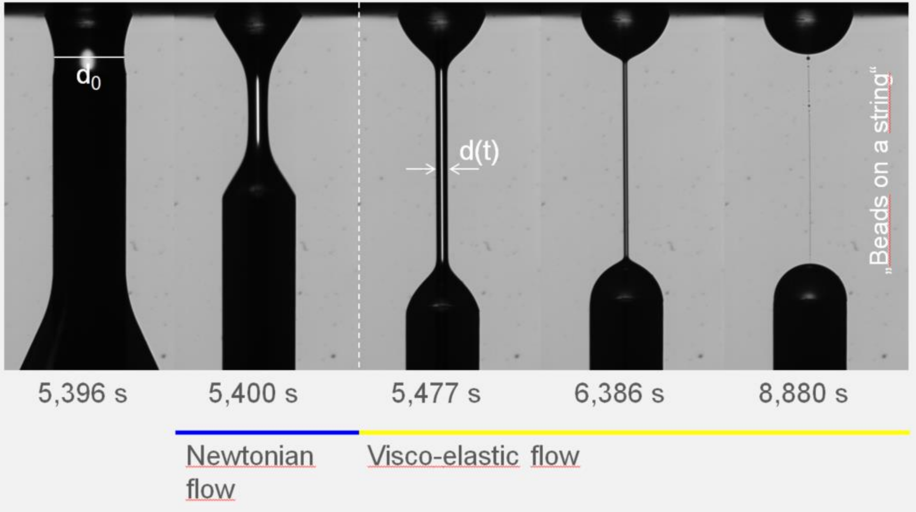
Outlook: Capillary Breakup

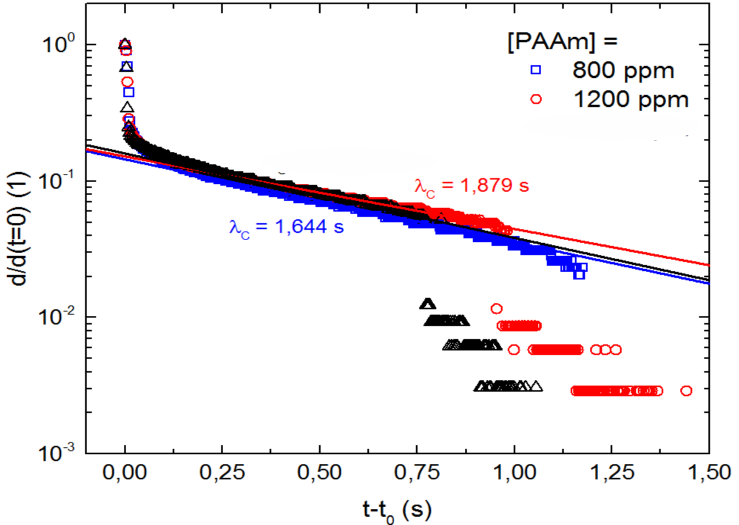


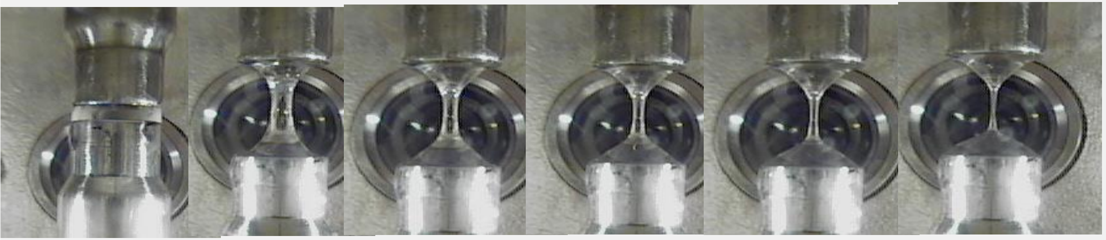
- PAAm (polyacrylamide)
- High speed (1000fps) camera
- PP04/PP01
- Fastest step time: 30 ms
- Up to 9 mm stroke
- About 10% overshoot (not optimized yet)

$$\ln \frac{d(t)}{d_0} = -\frac{t}{\lambda_C}$$

Relaxation time







Summary

A MultiDrive instrument as a universal platform for mechanical testing:

- Use as a single motor rotational rheometer (CMT):
  - All tests and all options a standard rheometer can do and have. Things like powder rheology also possible.
- Two rotational motors:
  - SMT rheometer for special applications: CPP, weakly structured fluids
  - Counter-Rotation for microscopy, flow instabilities, rheo-confocal etc.
- Use as a single linear device
  - DMA instrument: tensions, cantilever, 3 point bending, etc.
  - Extensional rheometry: Capillary break up (In progress)
- One rotational and one linear drive
  - DMA in torsion and tension on the same sample: Poisson' ratio

Anton Paar

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