BACK TO BASICS

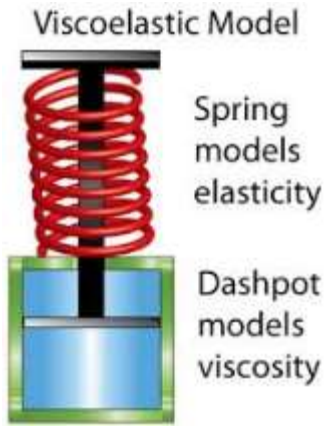
Introduction to Polymer Rheology

James P. Eickhoff Jr.
Principal Application Engineer – Rheology / Raman Technology
James.Eickhoff@Anton-Paar.com

Today's Agenda

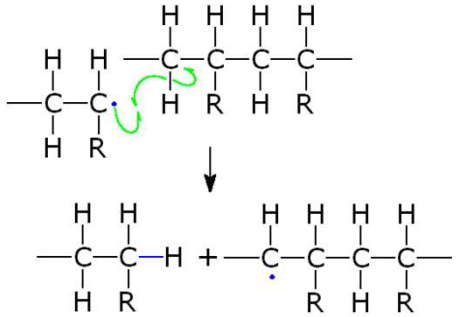
- Understand the basic theory behind rheology for polymer analysis
- Recognize the various types of testing techniques
- Select appropriate measurement(s) for material characterization needs

α ALPHA	ι IOTA	ρ RHO
β BETA	κ KAPPA	σ SIGMA
γ GAMMA	λ LAMBDA	τ TAU
δ DELTA	μ MU	υ UPSILON
ε EPSILON	ν NU	φ PHI
ζ ZETA	ξ XI	χ CHI
η ETA	ο OMICRON	ψ PSI
θ THETA	π PI	ω OMEGA



What is a Polymer?

- **Definition**
  - Any natural and synthetic compound of usually high molecular weight consisting of up to millions of repeated linked units, each a relatively light and simple molecule
- **Examples**
  - Natural polymers (biopolymers): proteins, carbohydrates
  - Synthetic polymers: plastics



Typical Classification of Polymers

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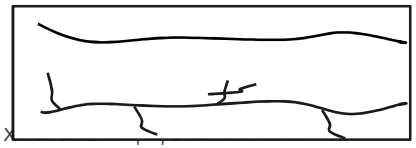
Thermoplastic polymer

- They are high molecular weight polymers whose chains associate through weak Van der Waals forces (PE)
- This type of polymer turns into a liquid when heated and freezes to a glassy state when cooled sufficiently.
- Partially crystalline or amorphous
- Low tensile strength
- Low melting points
- Easy to mold and remold
- It can be recycled

Examples

- Polyethylene
- Polypropylene
- Polycarbonate

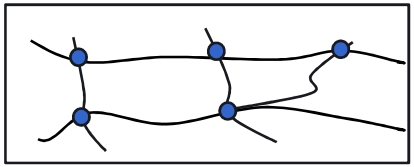


Elastomer

- Low density of chemical bonds between molecule chains (weakly cross-linked)
- These polymers when heated only soften and further chemically decompose
- Low tensile strength
- Can withstand high temperatures without losing their rigidity
- Not possible to recycle

Examples

- Vulcanized rubber

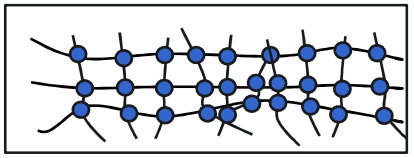


Thermosetting polymer

- High density of chemical bonds between molecule chains (densely cross-linked)
- These polymers when heated only soften and further chemically decompose
- High tensile strength
- Can withstand high temperatures without losing their rigidity
- Not possible to recycle

Examples

- Bakelite
- Epoxy resins (cured)
- Polyester resins (cured)



Importance of Rheology

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Rheology

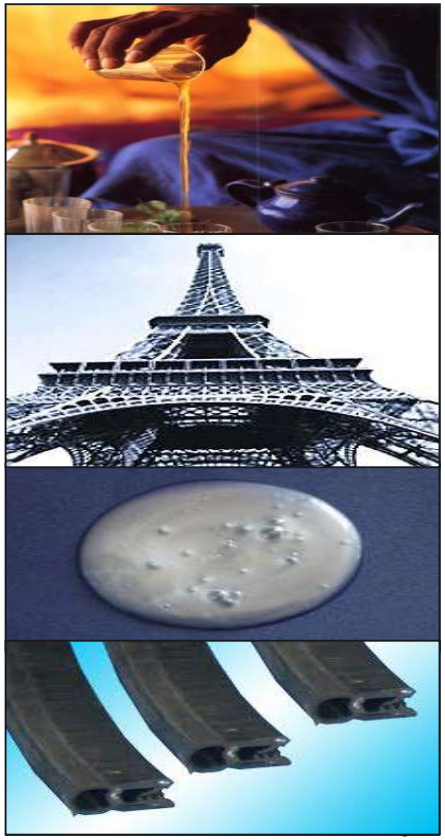
- Study of deformation and flow behavior of all kinds of materials
- From Greek ῥέω rhéō, "flow" and -λογία, -logia, "study of“
- Term coined by Prof. Bingham and Prof. Reiner in 1920
- πάντα ῥεῖ (*panta rhei*), meaning "everything flows/is in a state of flux"

Rheometry

- Experimental techniques and tools used to determine the rheological properties of materials

Differences Between Flow & Deformation

- **Flow properties** are used to characterize fluids.
  - When a force is applied to a fluid, it flows.
  - When the force is removed, the fluid does not regain its original shape. Fluids lose, or dissipate, energy as flow and heat.
- **Response to deformation** is used to characterize solids.
  - When a force is applied to a solid, it deforms.
  - When the force is removed, the solid returns to its original shape. Solids store energy and use it to recover or maintain shape.
- Most materials exhibit both **fluid (viscous)** and **solid (elastic) behavior**. They are **viscoelastic**.
- Rheology describes how **all kinds of materials** respond to an applied force.



Importance of Rheology for Polymer Processing

- Melting temperature and glass transition temperature - important information for processing and for properties of final products
- Zero-shear viscosity and low shear rate behavior can be used to predict manufacturing problems like irregularities in molded parts
- High shear viscosity correlates to processing condition: extrusion, injection molding, film blowing
- Average molar mass and absolute molar mass distribution (MMD)
- Crossover point G’ = G” relative determination -> relative MMD determination

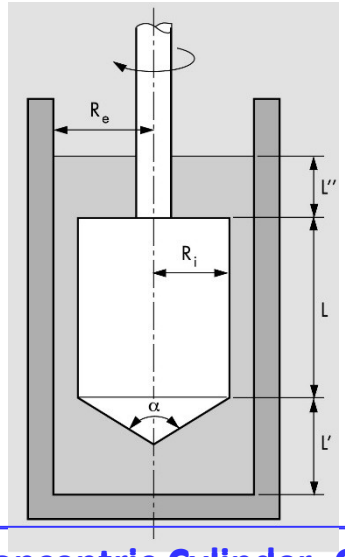
How are Rheological Measurements Made?

- Viscosity and Modulus are calculated from Shear Stress and Shear Rate (Viscosity) or Shear Stress and Strain (Modulus).
- When Measuring Viscosity:
  - Control Shear Stress → Measure Shear Rate
    - Hit the sample with a force and see how fast it moves
  - Control Shear Rate → Measure Shear Stress
    - Move the sample so fast and see how much force is required
- When Measuring Shear Modulus:
  - Control Shear Stress → Measure Strain
    - Hit the sample with a force and see how far it moves
  - Control Strain → Measure Shear Stress
    - Move the sample so far and see how much force is required
- When measuring Viscosity or Modulus, then, one rheological parameter is controlled while the other is the measured sample response.

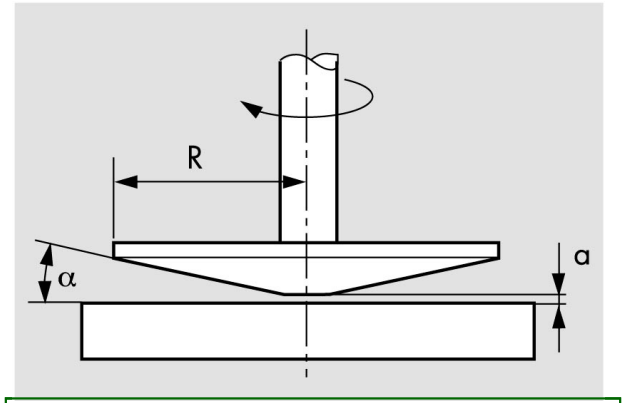
$$\text{Viscosity} = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{\tau}{\dot{\gamma}}$$

$$\text{Shear Modulus} = \frac{\text{Shear Stress}}{\text{Strain}} = \frac{\tau}{\gamma}$$

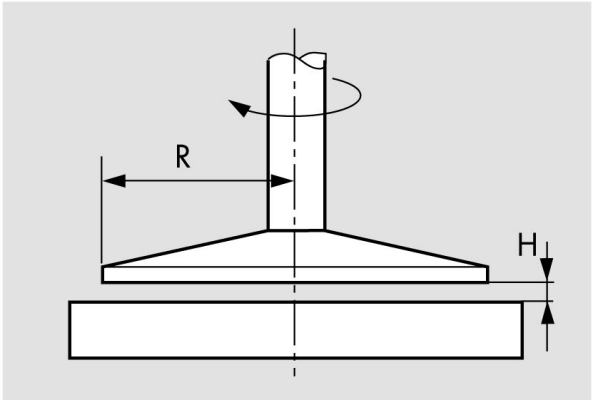
Common Measuring Geometries



Concentric Cylinder, CC
For flowable samples
Sample must be able to flow and fill the gap upon loading with no entrapped air



Cone & Plate, CP
For flowable samples (dispersions only with a limited particle size)
Cone gap a = 50 µm thus max. particle size ≤ (h/10) = 5 µm
Sample must be able to flow and fill the gap upon loading

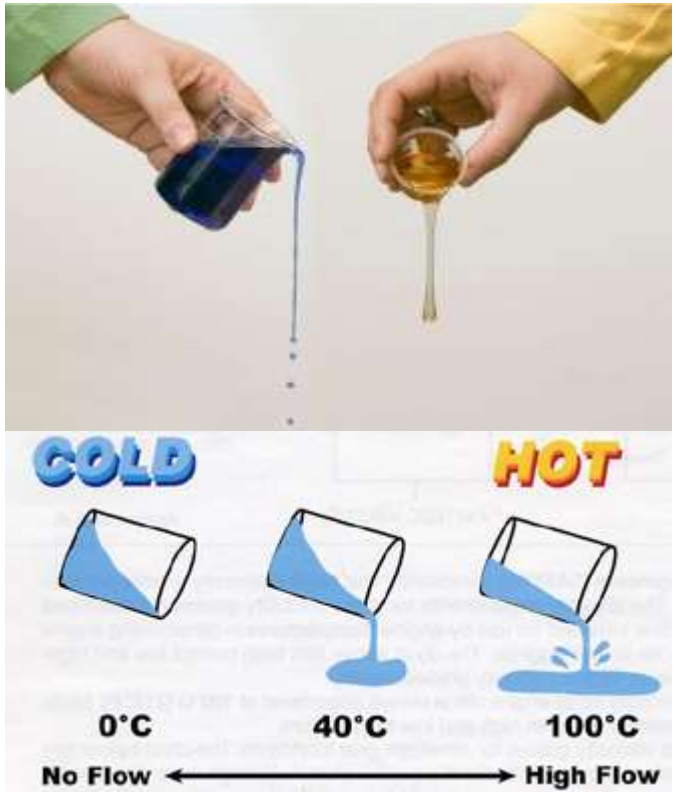


Parallel Plate, PP
For liquids, gels, pastes, soft solids, polymer melts

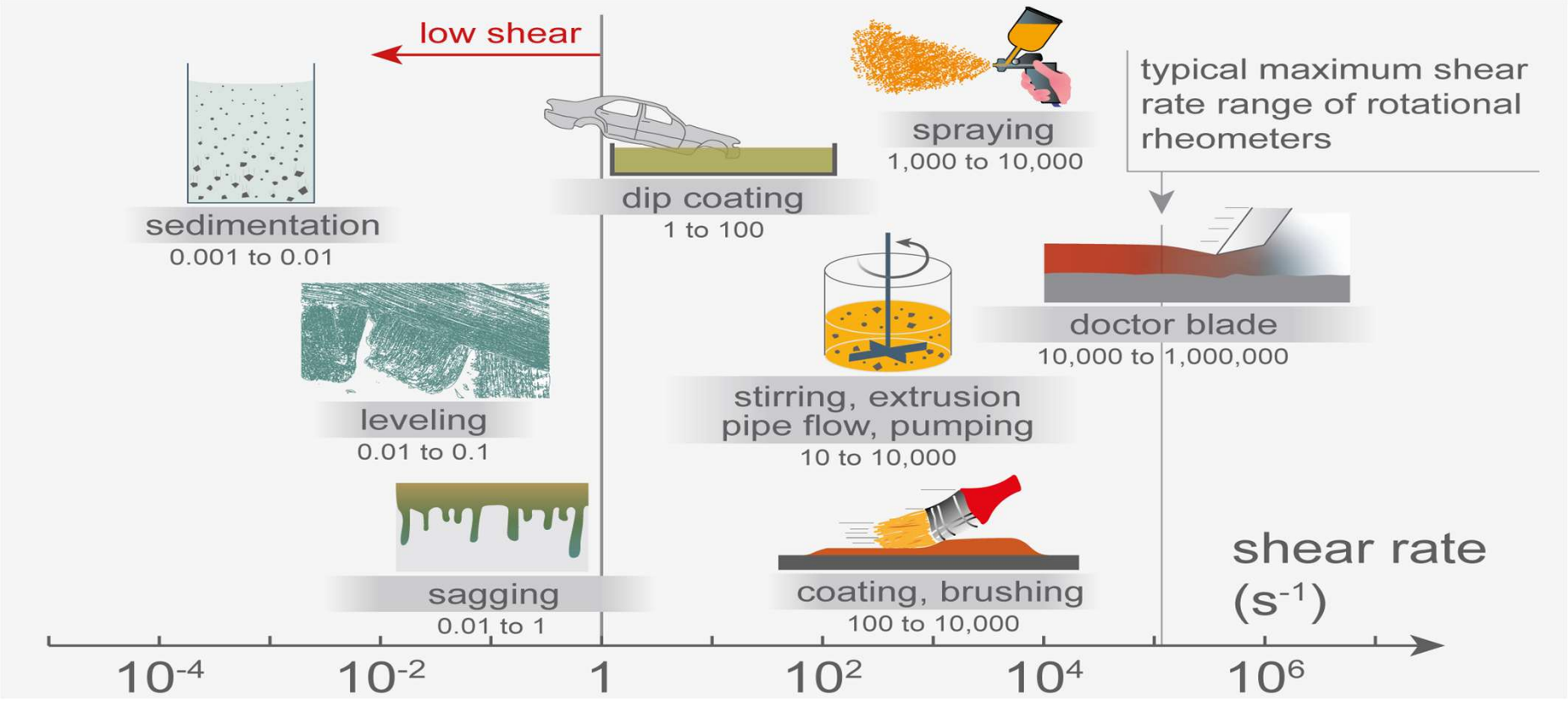
☞ **The keys to absolute measurements are a well defined sample shape (flow field) and a small gap.**

What is Viscosity?

- “Property of a fluid that tends to prevent it from flowing when subjected to an applied force”.
- Dependent on temperature.
- Requires that the material be flowing to be measured.
- Describes the flow properties of fluids and viscoelastic fluids.
- In structured material, viscosity is dependent on temperature, shear rate and shear history.
- **Unless the material is an unstructured fluid (water, pure oil), then viscosity is a <u>CURVE</u> not a <u>POINT</u>.**



Why is Shear Rate Important?



The Four Flow Behaviors

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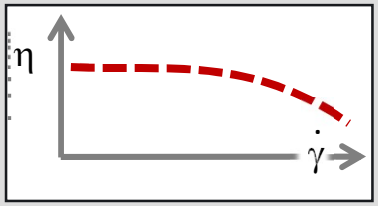
Ideal viscous

Newtonian

- viscosity is a material constant
- from water to high viscosity oil

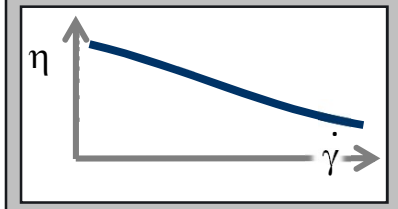
Shear thinning



Visco-elastic liquid

- constant at low shear
- shear thinning at high shear rates
- polymer solutions, melts

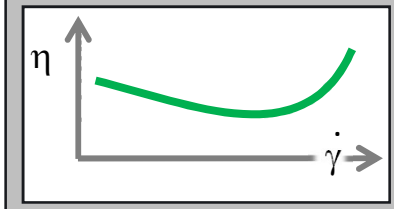
Shear thinning



Visco-elastic gel

- infinite viscosity at low shear
- shear thinning
- emulsions, suspensions, gels

Shear thickening

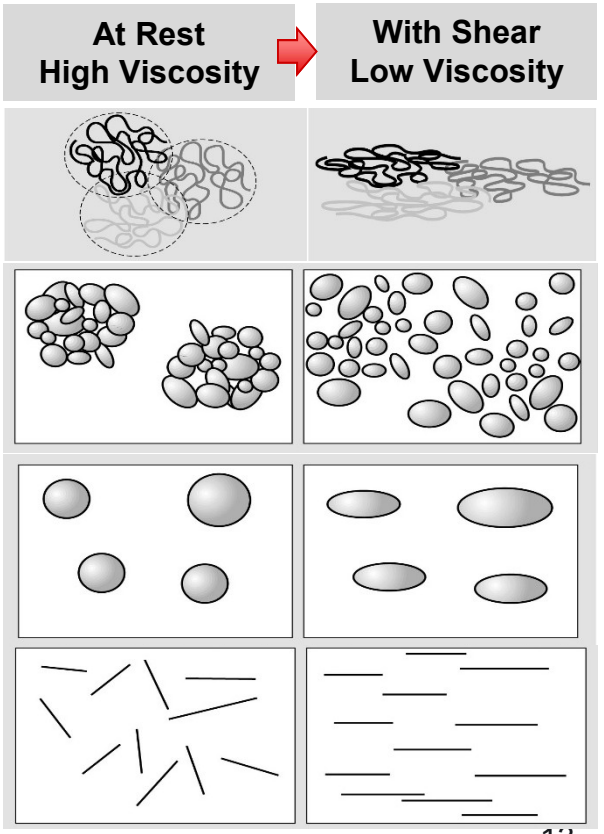


Visco-elastic paste

- shear thinning at low shear but shear thickening at high shear
- dispersions

Shear Thinning – What is the Cause?

- Shear thinning occurs in non-Newtonian fluids due to changes in particle/molecular orientations or alignment in the direction of flow.
- Polymer solutions/melts – entanglements/coils at rest unfold and align with the applied shear
- Suspensions – agglomerates at rest break up with applied shear
- Emulsions – droplets spherical at rest elongate with the applied shear
- Dispersions – solid particles randomly oriented at rest align with the applied shear
- In all cases, disorder (high viscosity) at rest to order (low viscosity) with applied shear



What Causes A Fluid to Exhibit Zero Shear?

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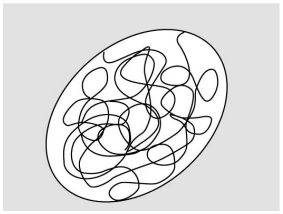
Unlinked Polymers in the low-shear range and zero-shear viscosity

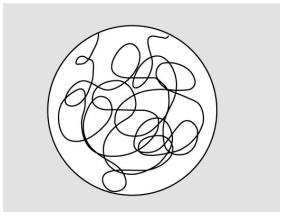


Superposition of two processes

1) Orientation of the macro – molecules under shear load

⇒ **disentanglements**

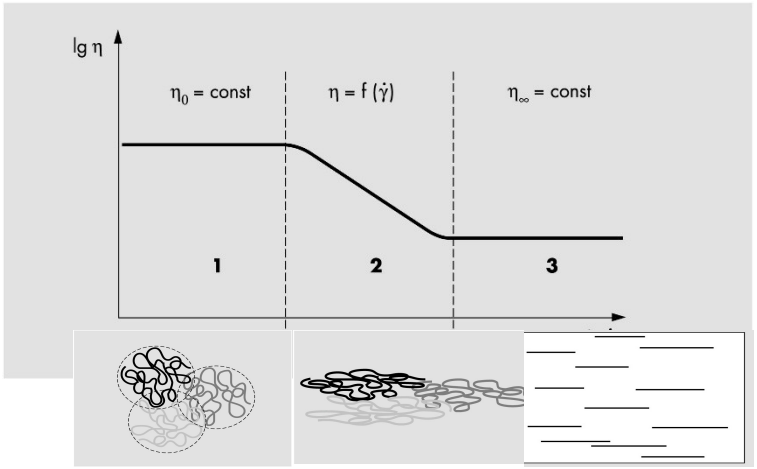
⇒ here, the viscosity decreases



2) Re - coiling due to visco - **elastic** behavior

⇒ **re - entanglements**

⇒ here, the viscosity increases

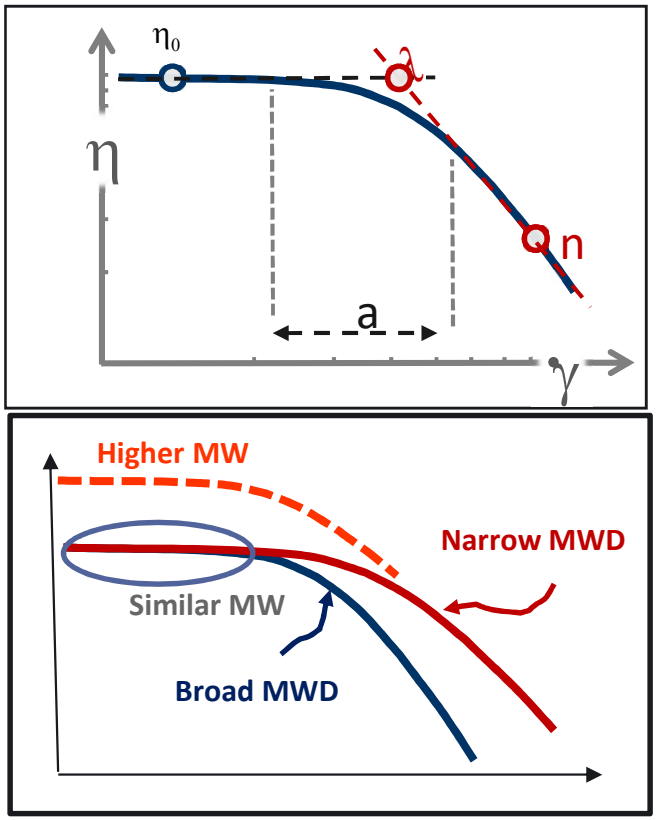


Result:

In the low-shear range there is no change in the total viscosity value, which is referred to as the η_0 **- value**. This low-shear range mostly occurs at $\dot{\gamma} < 1\ s^{-1}$

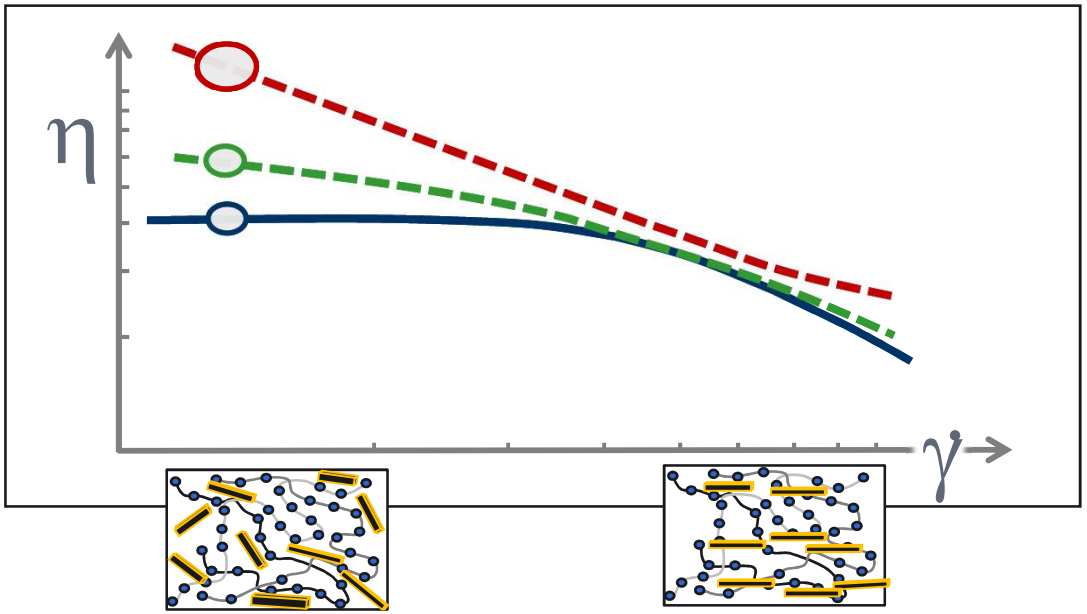
Zero Shear Viscosity Summary

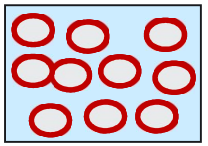
- Regression methods for zero shear viscosity fluids:
  - Carreau
  - Carreau-Gahleitner
  - Carreau-Yasuda
  - Cross
- η_0 analysis provides information on:
  - Molecular weight or concentration
    - Higher η_0 = higher MW / higher concentration
  - Molecular weight distribution (a)
    - Zero shear plateau ends sooner the broader the MWD
  - Relaxation time (λ)
    - Inverse of shear rate at end of zero shear plateau
  - Power law behavior (n)
    - Tendency towards shear thinning once η_0 is exceeded



Influence of Filler on Viscosity

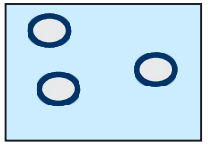
- Lower shear rates: more sensitive to interacting forces
- High shear rates: orientation of structure





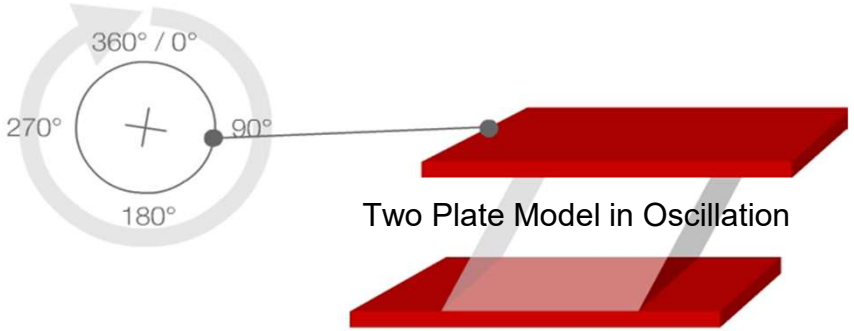
High concentration of filler

Low concentration of filler



Introduction to Oscillatory Measurements

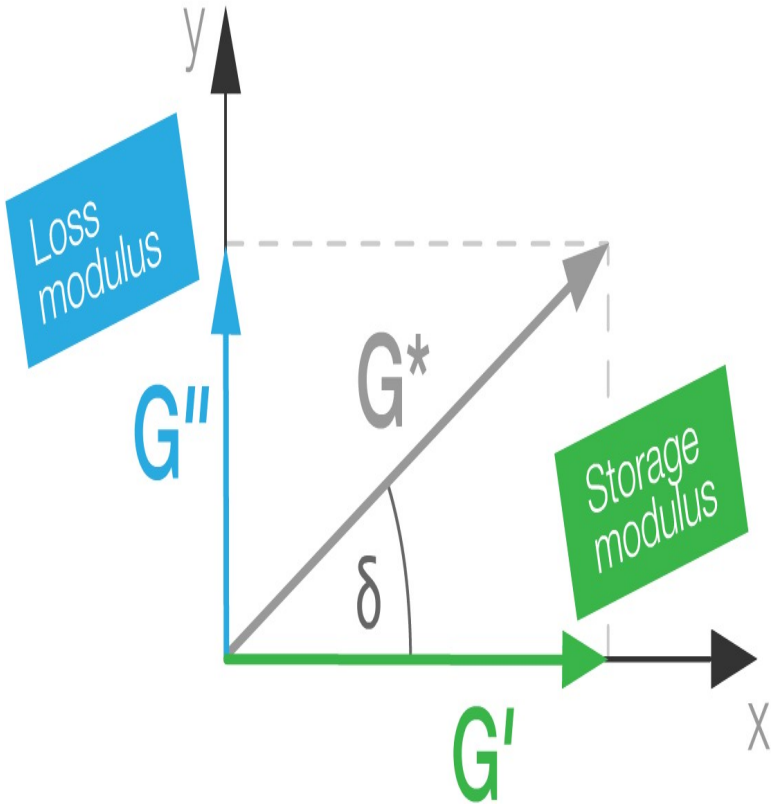
- The most effective way to measure visco-elastic properties is through oscillatory testing
- Oscillatory testing involves oscillating the sample around a fixed point (ie wiggling the sample)
- The oscillations are applied in a sinusoidal manner
- The oscillations are so small that the inherent structures in a sample are without being perturbed
- The test itself imparts no behavior in the sample



Two Plate Model in Oscillation

G*, G', G": What's Real, What's Not?

- G* is a complex number which can visualized using a complex plane or vector diagram.
- The phase angle allows separation of G* into a real part, G', and an imaginary part, G".
- A right triangle is always 90°.
- The real part, G' or G Prime, is the Storage Modulus = elastic modulus = tendency to recoil or retain shape. Its magnitude stems from the phase angle δ.
- The imaginary part, G" or G Double Prime, is the Loss Modulus = viscous modulus = tendency to flow. Its magnitude is what remains or 90° less the phase angle δ.
- G* (complex modulus) ÷ angulary frequency (rad/s) = complex viscosity η^*.



The Language of Oscillatory Measurements

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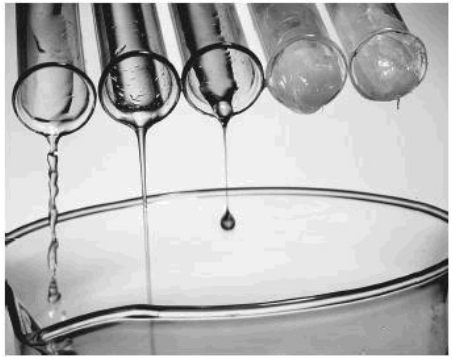
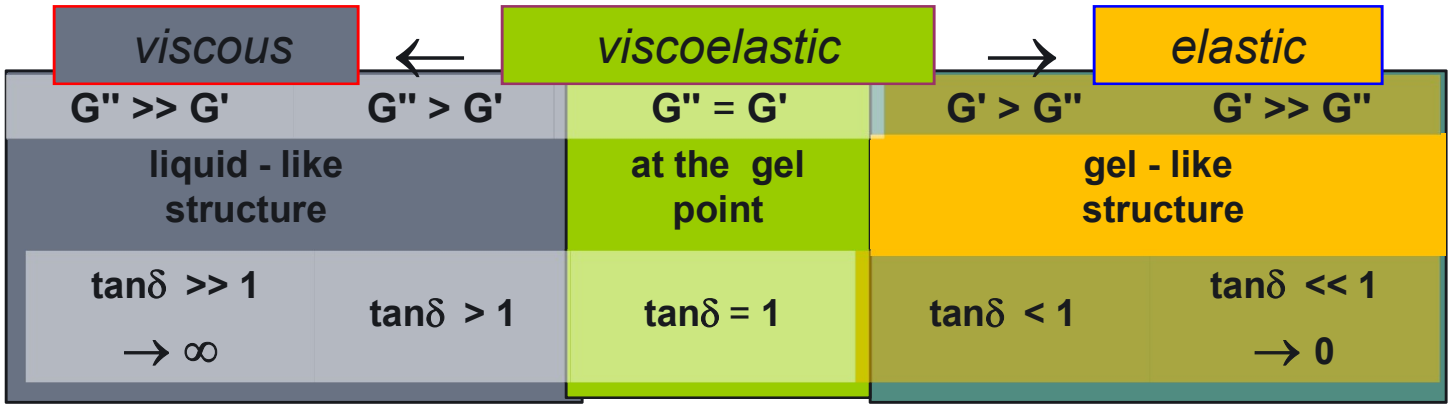
G double prime G prime Tan delta Complex viscosity		Viscous liquid Viscoelastic liquid Viscoelastic solid Elastic solid

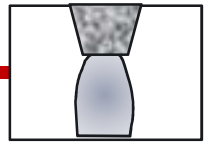
Loss Modulus G” = Viscous behavior · Storage Modulus G’ = Elastic behavior · tan d = G” / G’ = balance of viscous and elastic behavior

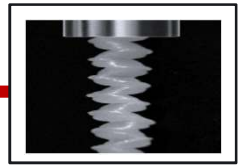


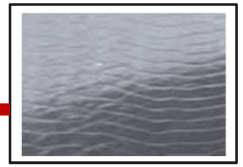
Common Processing Issues

- Too much elasticity and relaxation issues
  - Unwanted side effects due to long relaxation times and high shear processing speeds

- **Die swell**
  - after leaving the nozzle
- **Melt fracture**
  - limited processing speed
- ***Shark skin***
  - often found with LLDPE and HDPE





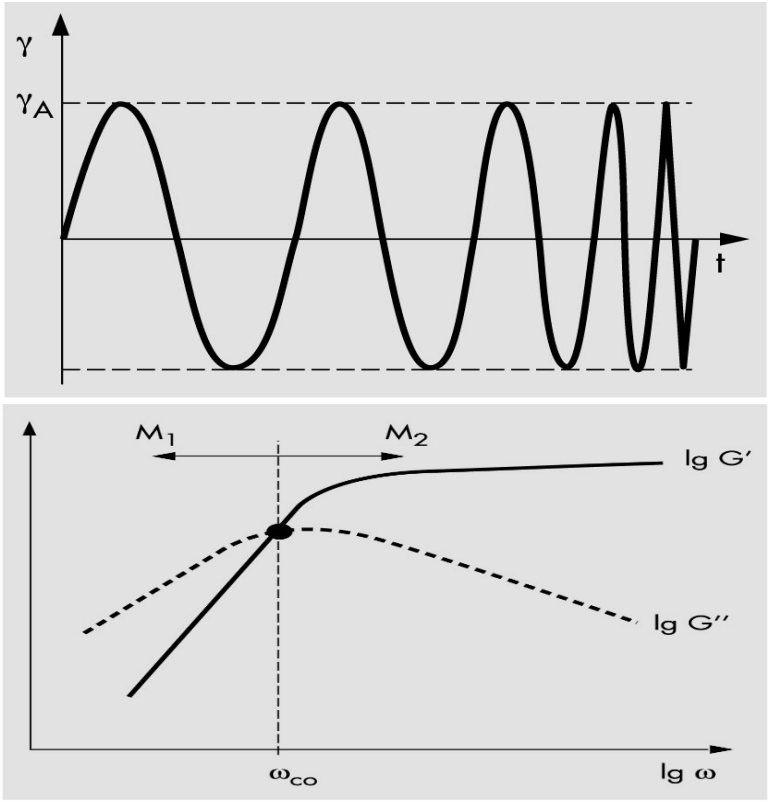


- **Use processing additives** (e.g. PPA) => reduced risk of melt fracture during extrusion
- **Modification of MMD** => lower storage modulus G' at higher frequencies (shifted cross over towards higher frequencies)
- **Deborah-Number** *De = processing shear rate (smallest diameter) * relaxation time -> If possible, increase processing temperature to decrease relaxation time, De low as possible*

$$De = \frac{Relaxation\ time}{Processing\ time} = \lambda * \dot{\gamma}$$

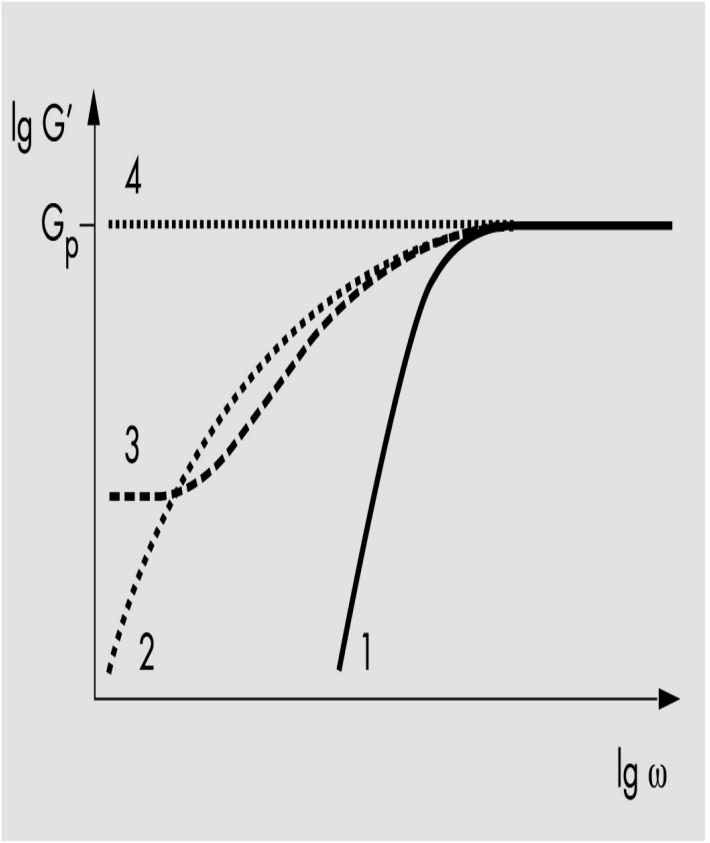
Frequency Sweep

- Frequency of oscillation is ramped with the amplitude held constant
- Short term relaxation (high frequency) and long term relaxation (low frequency) behavior
- Quantifies zero shear viscosity for viscoelastic liquids
- Shape of G' and G" curves over frequency characteristic for material type, i.e. gel, emulsion, melt, paste, dispersion
- Provides information in MW, MWD, degree of crosslinking, stability, impact resistance, etc….

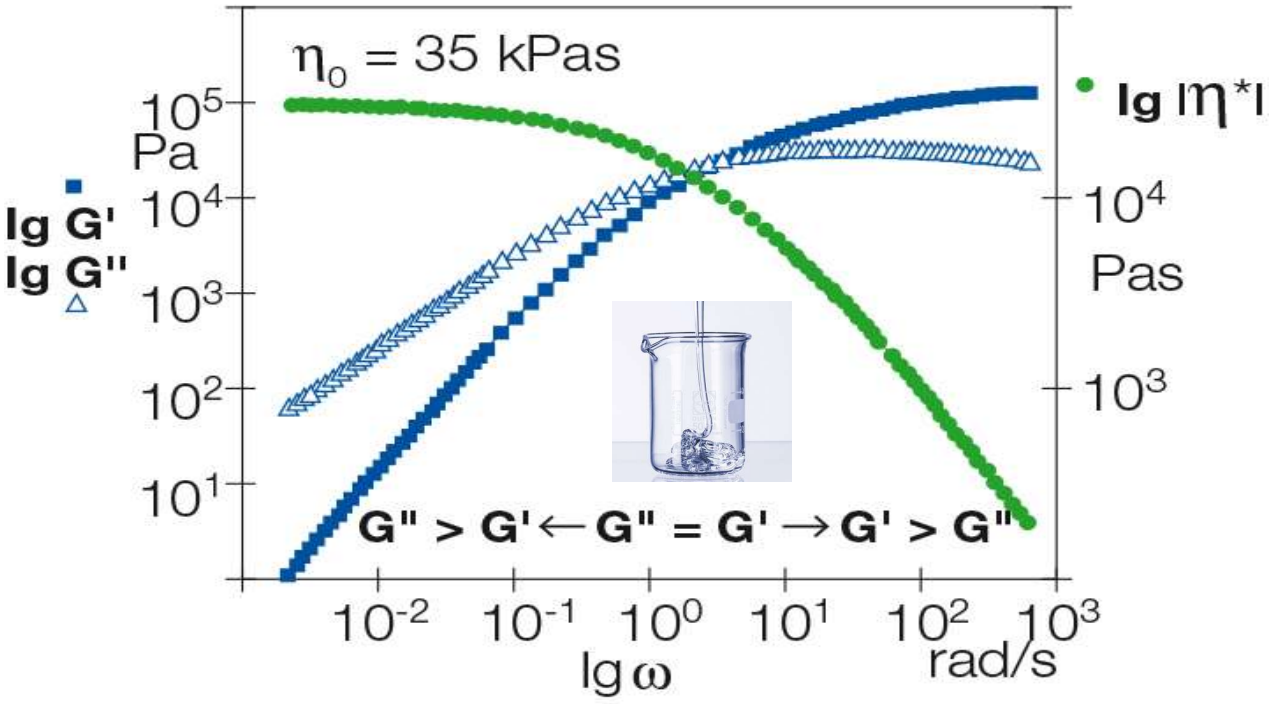


Fingerprinting from Frequency Sweeps

- (1) polymer with unlinked molecules degrees of cross-linking and a narrow MMD
- (2) polymer with unlinked molecules and a wide MMD
- (3) sparsely cross-linked polymer, flexible gel or dispersion low structural strength at rest
- (4) densely cross-linked polymer, rigid gel or dispersion with high structural strength at rest



Uncrosslinked, Amorphous Polymer Melt



PDMS
Poly-di-methyl-siloxane

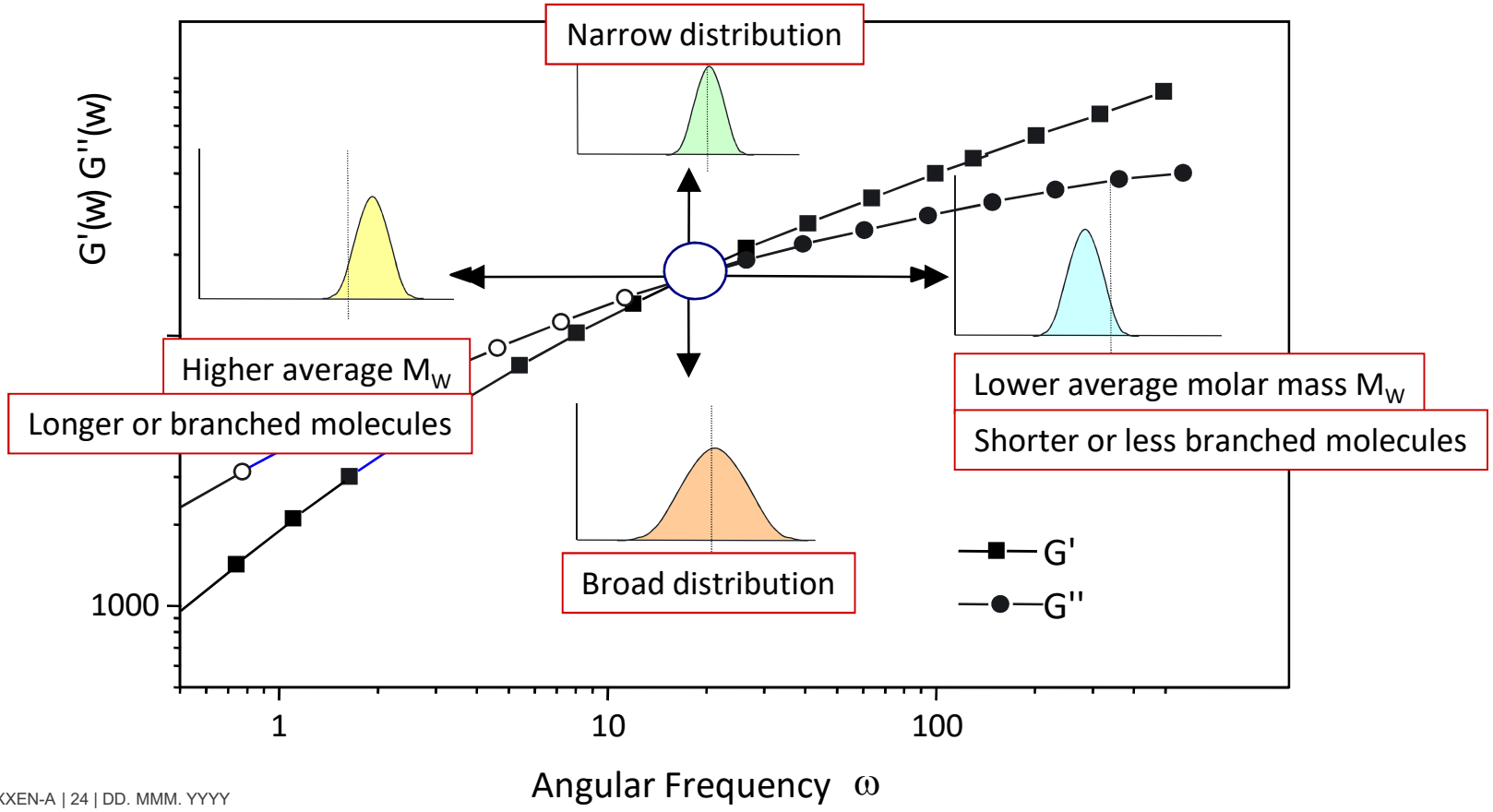
Typical behavior of

uncrosslinked polymers

with crossover point
G' = G"

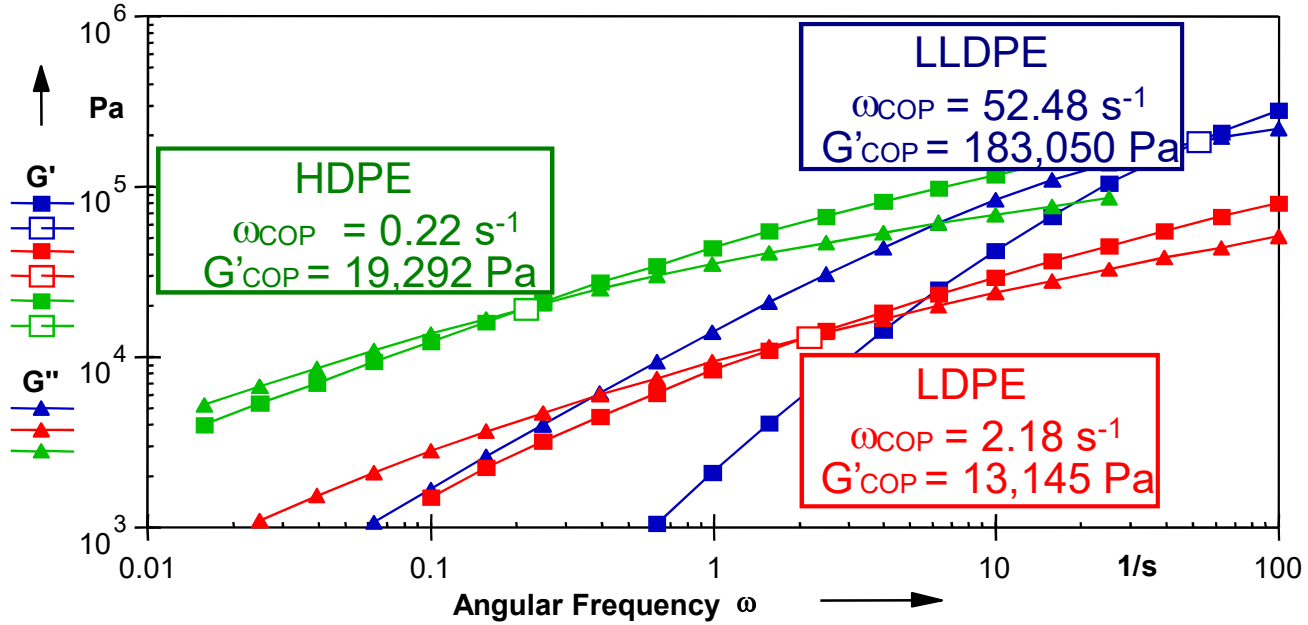
γ = 10%
T = +23°C

Frequency Sweep and Molar Mass M_w

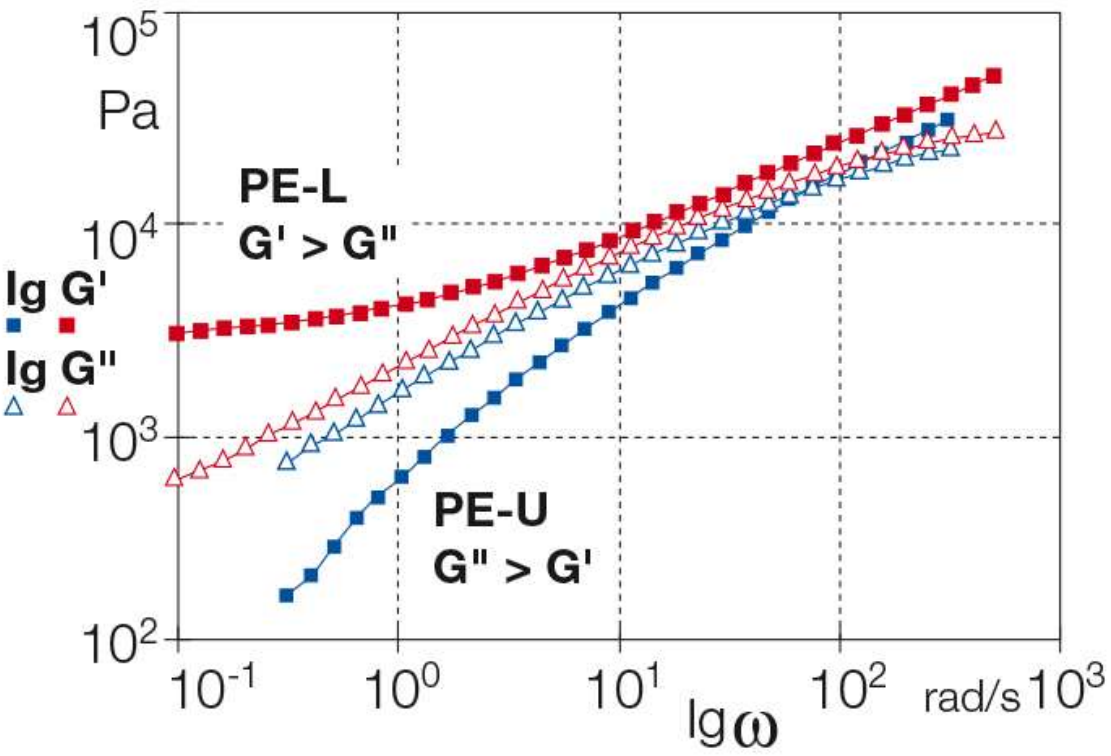


Measurements on Three Different Polyethylene Melts

- An increasing average molar mass is expressed in a COP moved to lower angular frequencies
- A vertical shift of the COP towards lower modules (G'_{COP}) indicates a wider MMD



Uncrosslinked & Crosslinked Polyethylene



Polyethylene
with functional groups

Uncrosslinked (PE-U) ■ △

Crosslinked (PE-L) ■ △

At a low frequency:
higher G'- value indicates a higher **degree of crosslinking**

γ = 1%
T = +170°C

Master Curve Background

Anton Paar

Time Temperature Superposition

- Due to increasing T the relaxation times are getting shorter
- Shift factor $a_T=\lambda(T)/\lambda(T_{ref})$ or based on viscosity $a_T=\eta(T)/\eta(T_{ref})$
- Frequency sweeps (FS) measured at various T can be shifted horizontally
- Only applicable for unlinked and unfilled polymers
- Each FS measured at T can be shifted by a_T to the so called reference temperature T_0
- High temperatures correspond to short relaxation time behaviors (wams samples are softer and thus molecules find it easier to relax while low temperatures correspond to long relaxation time behaviors (cold samples are stiffer and thus molecules find it hard to relax)

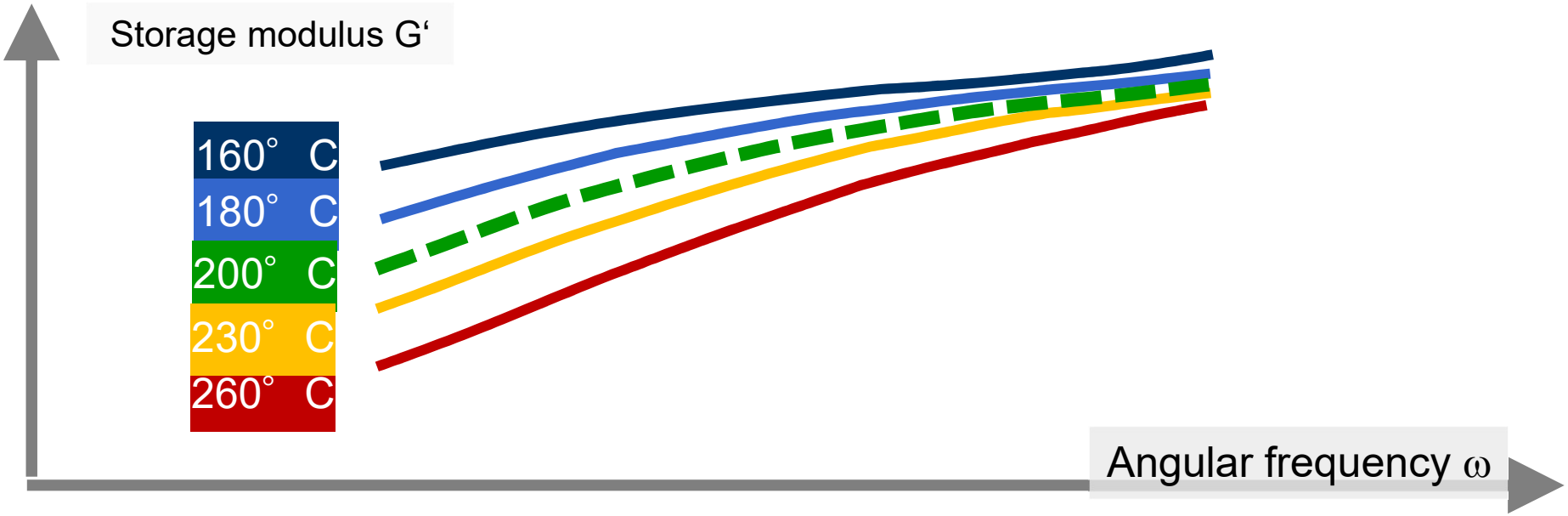
(+) Enlarged frequency range beyond what can practically be measured
(+) Information about practically relevant shear rates up to 100,000s^{-1}
(+) Determination of the zero shear viscosity

Master Curve in Action

Anton Paar

Horizontal shift towards the reference temperature T0

- TTS example: horizontal shift of storage modulus G‘

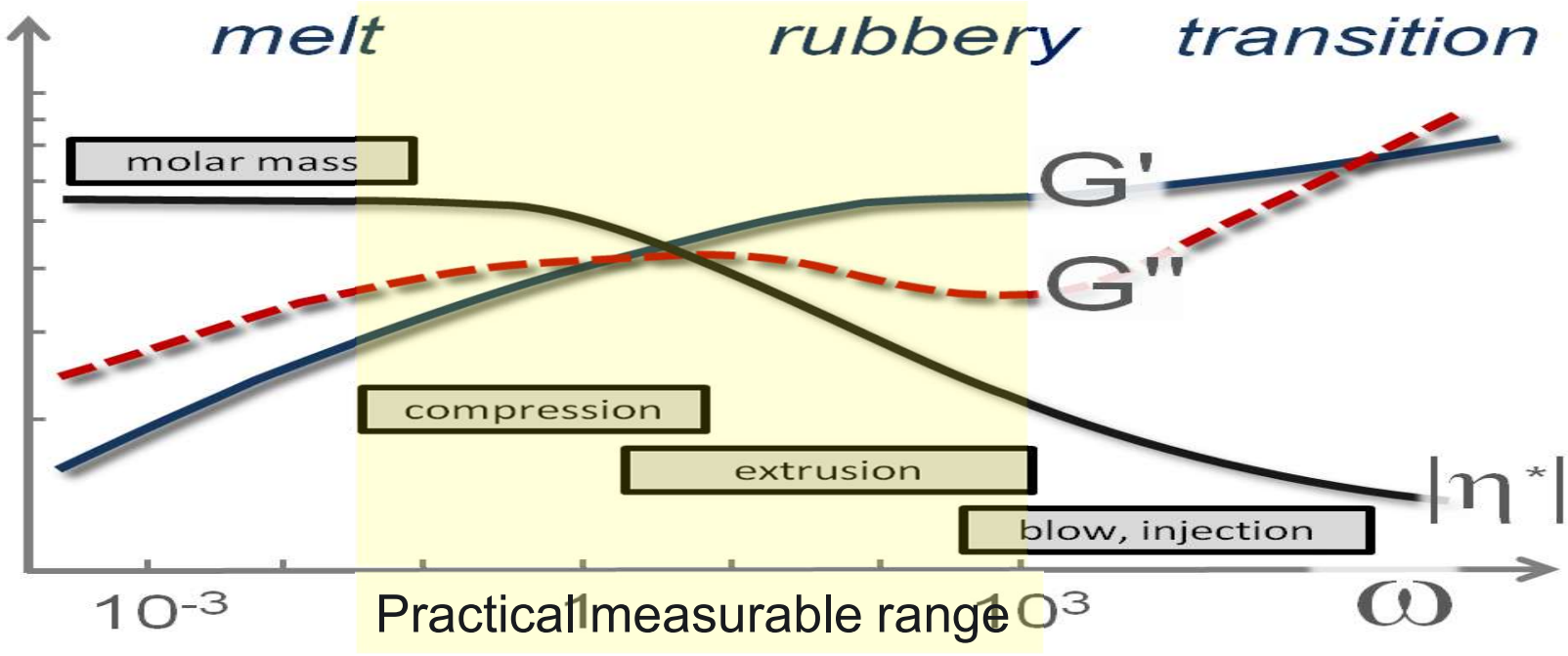


Master Curve Provides More Information

Anton Paar

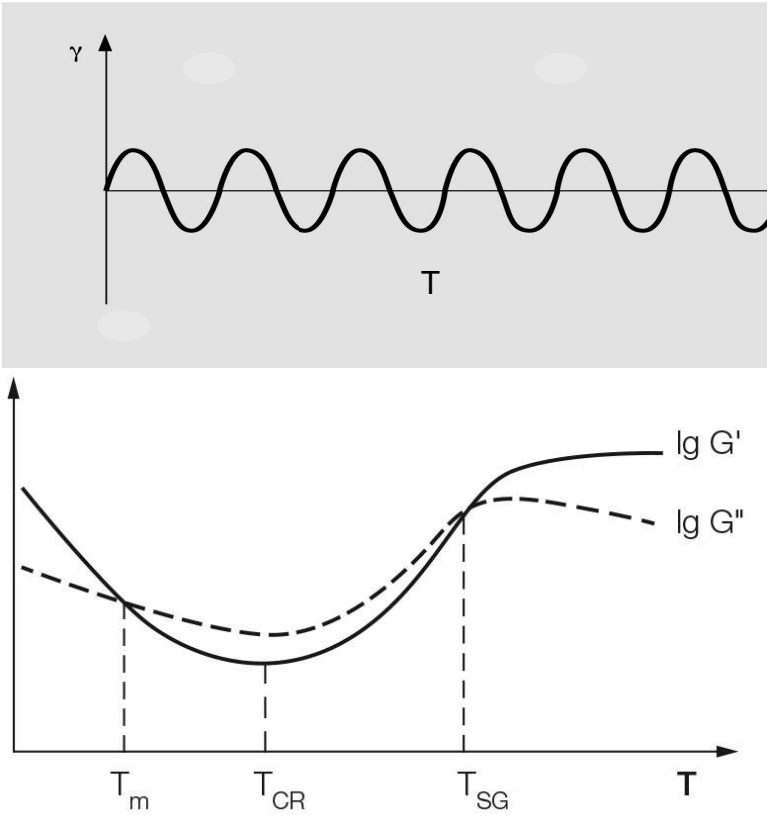
Horizontal shift towards the reference temperature T0

- TTS example: shift of storage modulus G‘
- The range above the transition region is called glassy region

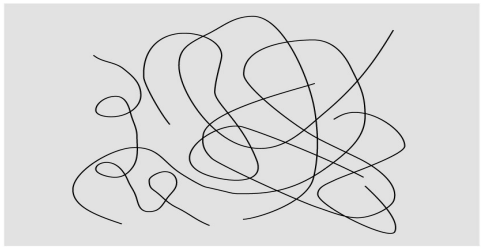


Why test with temperature?

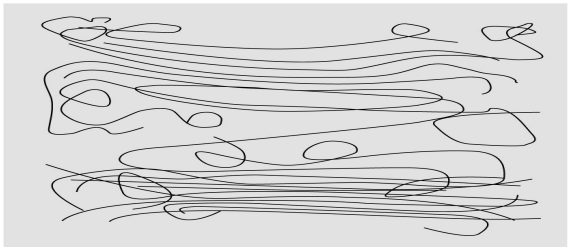
- Tracks changes in **viscoelastic behavior** as temperature ramps up and/or down
- Run at **appropriate amplitude and frequency,** staying within the LVER when applicable (may require pre-testing at defined temperatures)
- Reveals key thermal behaviors:
  - Gelation, curing, degradation
  - Crystallization, melting, glass transition
  - Freeze-thaw stability and other phase changes
- Ideal for studying **processing windows**, **reaction kinetics** and **thermal stability**



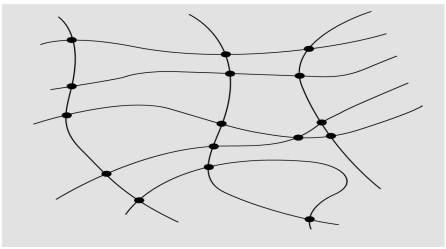
Typical Temperature Sweeps for Polymers



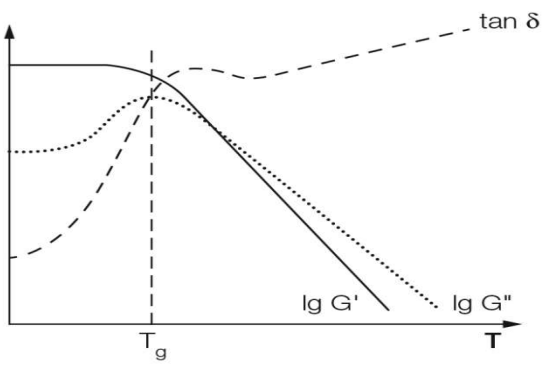
Amorphous
Unlinked, Without Any Order

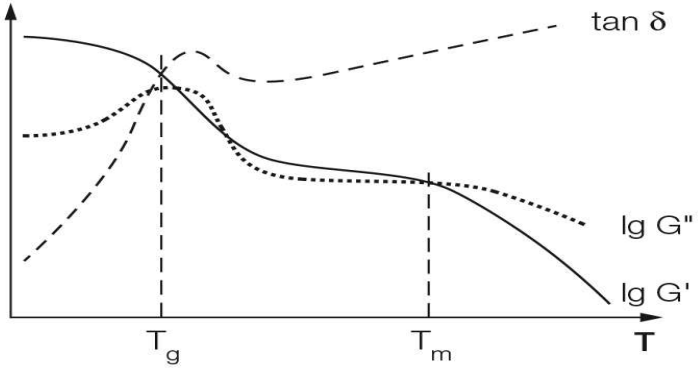


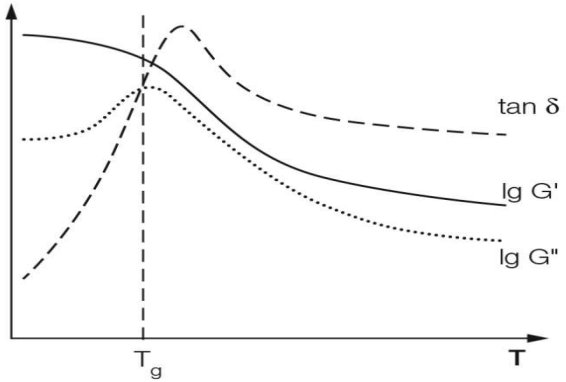
Partially Crystalline
Unlinked, Partially Crystalline Order



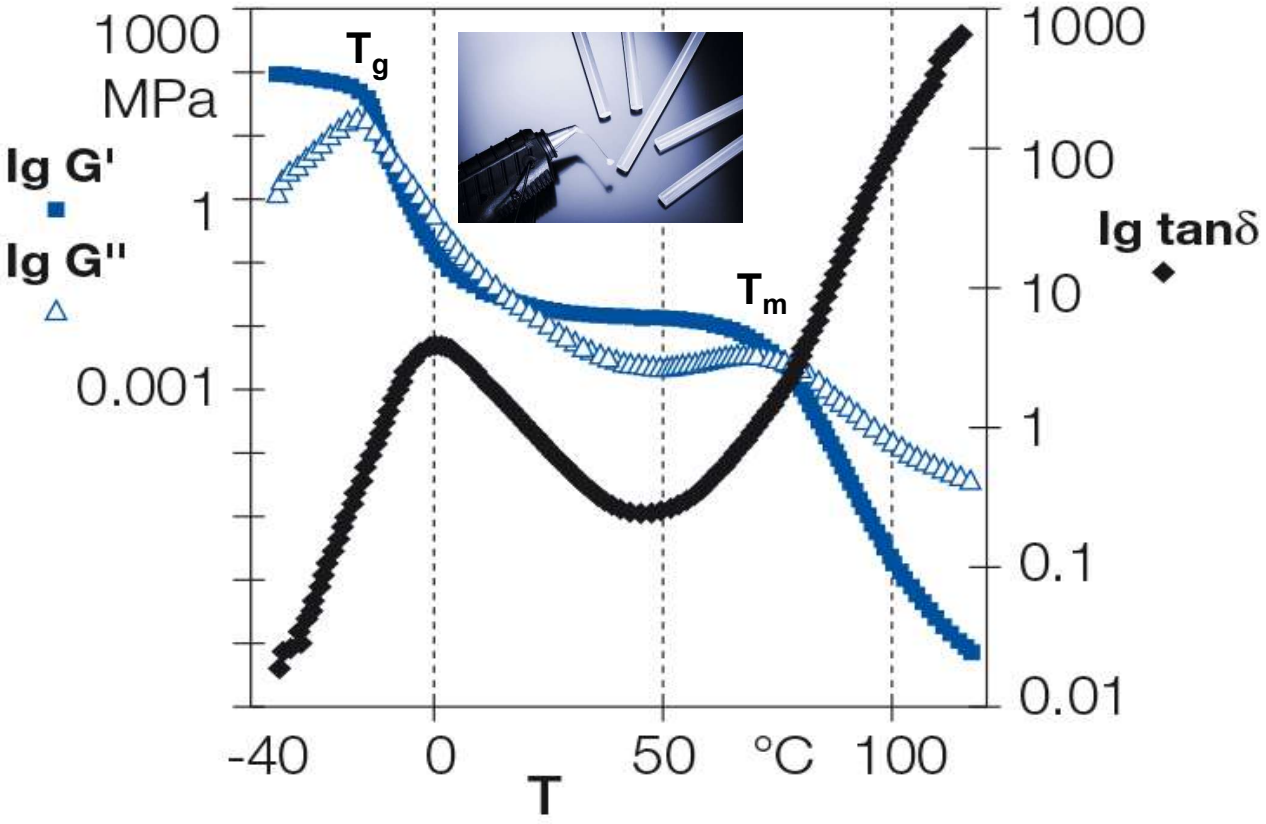
Chemically Cross-linked
Covalent Primary Bonds







Temperature Sweep - Hotmelt Adhesives



Hotmelt Adhesive

Unlinked Partially Crystalline Polymer

Shows a pronounced rubber - elastic region

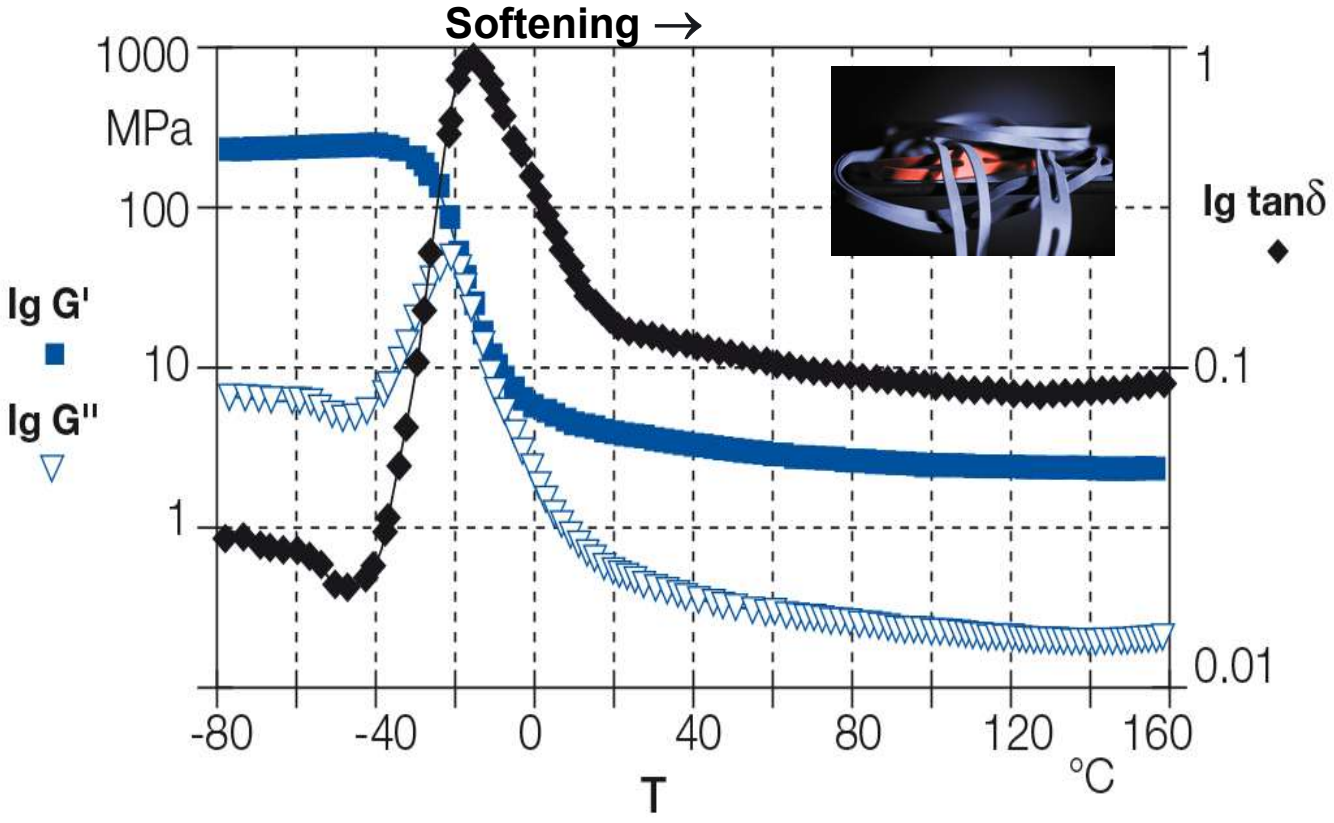
T_g = -18°C (G" max)
T_g = 0°C (tanδ max)

Melts at 78°C

G" > G' for T > T_m

tanδ = G" / G'

Temperature Sweep - Rubber



Rubber
Cross - linked Polymer

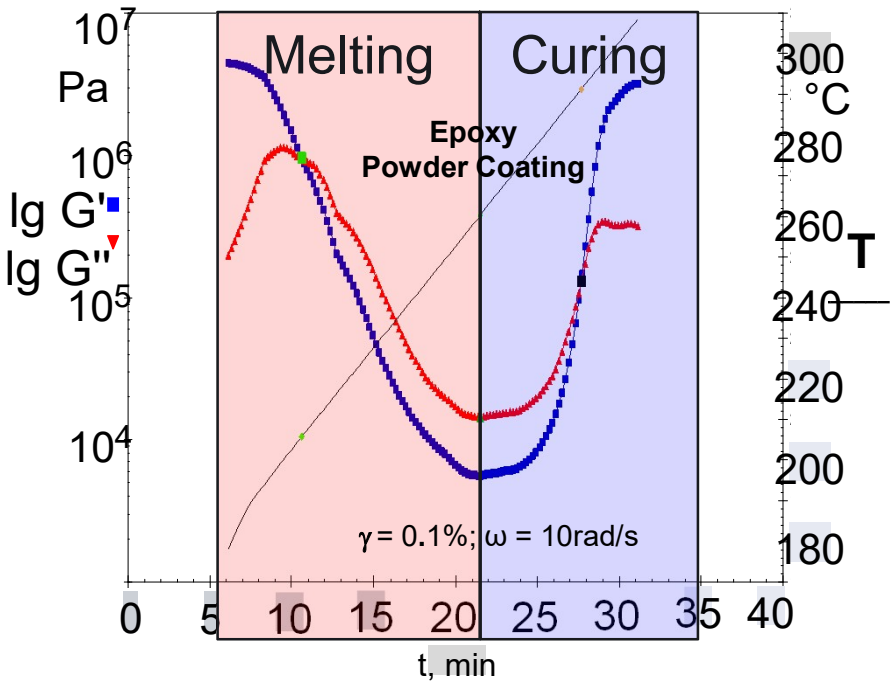
T_g = -22°C (G" max),
T_g = -16°C (tanδ max)

No melting

G' > G" also
at high temperatures

γ = 0.25 %
ω = 10 rad/s
tanδ = G" / G'

Thermal Curing Behavior



- For **thermosets**, **adhesives**, **coatings**, **inks**, and **resins**
- **Curing is a temperature-triggered reaction** involving crosslinking
- Run under **constant amplitude and frequency**
- Key transitions tracked via **G' and G" changes**
  - **T_m**= Melting Point (G'=G" as structure softens)
  - **T_{CR}**= onset of chemical reaction (aka softening point)
  - **T_{SG}**= sol-gel transition (second G'=G")
- G' increase and G" separation indicate **structure formation and final cure**

Melting Temperature
(when G' = G")
T_m = 206°C, t = 10.6 min

Onset of Curing
T_{CR} = 260°C, t = 21.5 min
viscosity minimum
η_{min}= 2470 Pas (minimum melt viscosity)

Sol-Gel Transition
(2nd time G' = G")
T_{SG} = 291°C, t = 27.7 min

DMTA of Solids with Tensile Tests

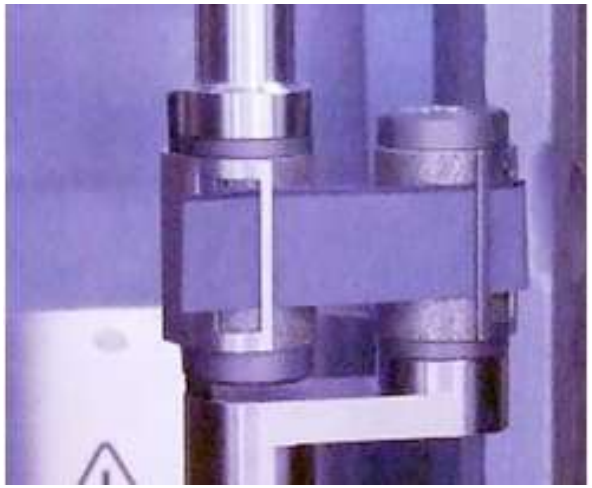
UXF Universal Extensional Fixture

Rotation:

Preset: **extensional rate** (in s^{-1})

Result: **extensional viscosity** η_E (in Pas)

SER Sentmanat Extensional Fixture



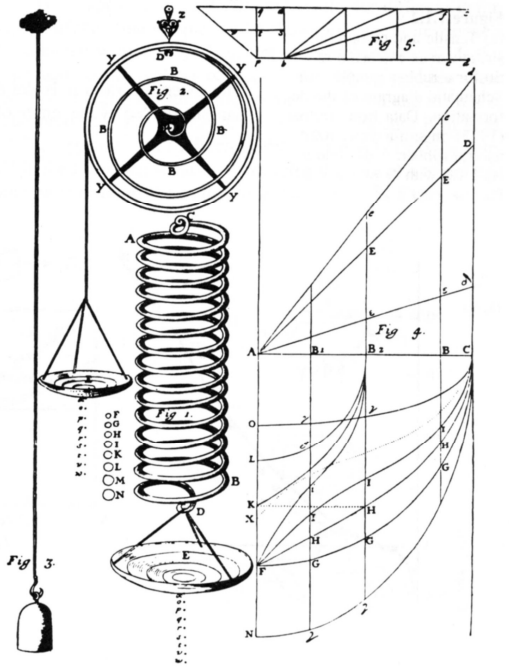
UXF Universal Extensional Fixture

Oscillation (DMA, DMTA...UXF only):

Preset: **extension (strain, deformation)**, ε (in %) and angular frequency (in ra^{-1})

Result: **storage modulus E‘ and loss modulus E“** (in Pa)

Tensile (Extensional) Tests – Young's Modulus, E



Tensile Tests

Elasticity law

E - modulus, or Young's modulus (in Pa)

s (sigma), **tensile stress** (in Pa)

ε (epsilon), **elongation** (in 1 = 100%)

$E = 2 \cdot G (1 + \mu)$ with Poisson's ratio, μ

For all kinds of materials hold that:

E, Young's modulus = (2 to 3) · G, shear modulus

Factor 3 (or $\mu = 0.5$) for stiff and brittle materials,

Factor 2 (or $\mu = 0$) for fluid materials

$$\mu = \frac{\Delta d \cdot l_0}{d_0 \cdot \Delta l}$$

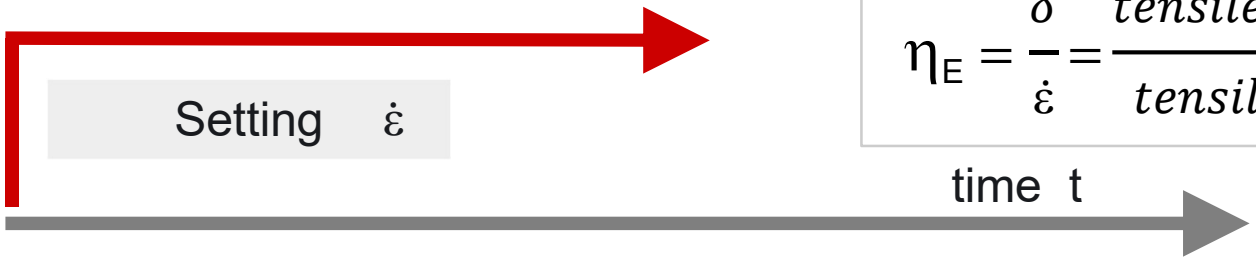
l = length, d = thickness of the specimen,

$\Delta l = l - l_0$ = change in length,

$\Delta d = d_0 - d$ = change in thickness

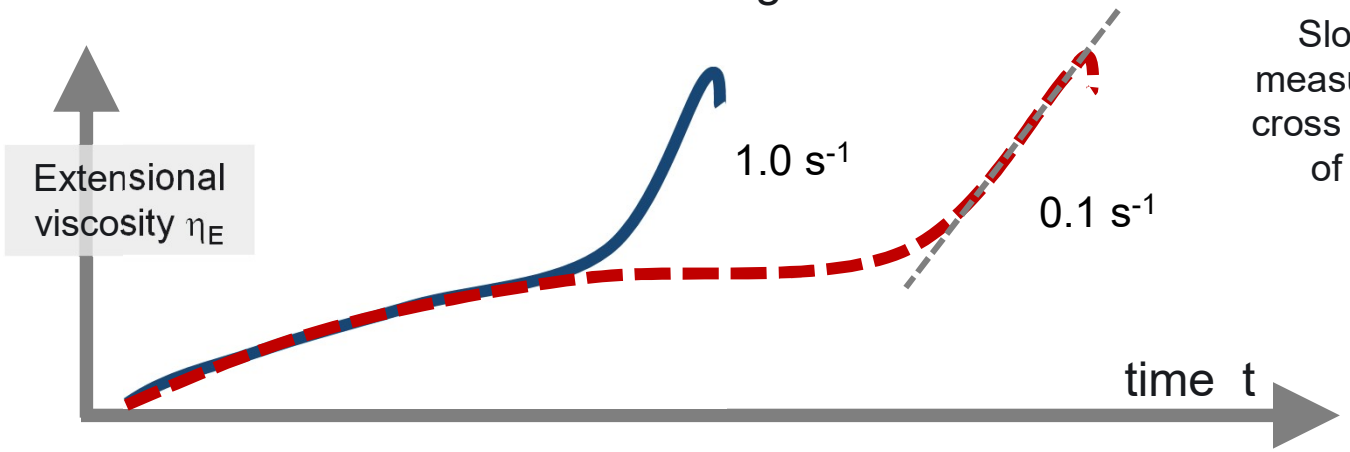
Transient Extensional Measurements

Setting: constant tensile rate



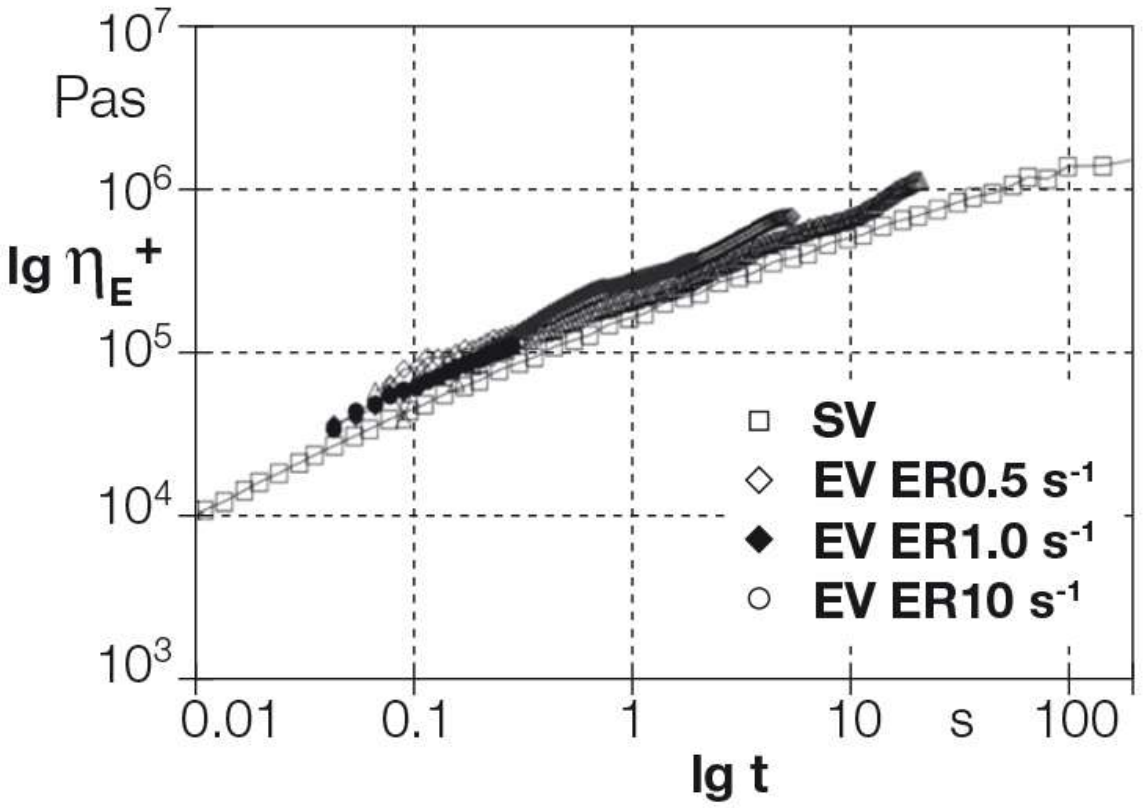
$$\eta_E = \frac{\delta}{\dot{\varepsilon}} = \frac{tensile\ stress}{tensile\ rate}\ [Pas]$$

Measurement until strain hardening or melt fracture



Slope is a qualitative measure for the degree of cross linkage or branching of polymer melts or elastomers

Tensile (Extensional) Test - Linear Polymer



Extensional viscosity η_E (in Pas), rotational test

Linear HDPE

T = 130°C,
Highly viscous polymer melt

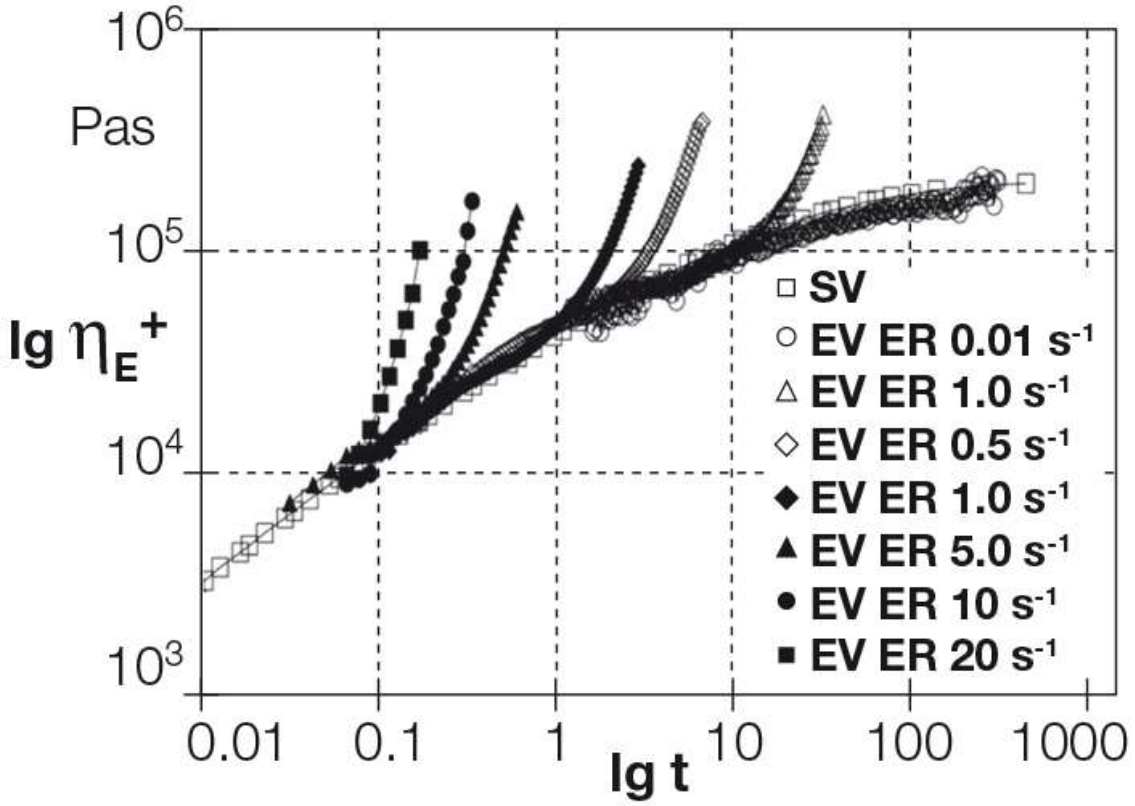
Extensional tests (SER) at various extensional strain rates (Hencky strain rates)

The curves of extensional viscosity (EV) and shear viscosity (SV) are overlapping.

Growth curve of SV, measured with cone plate.
It applies: $\eta_E^+ = 3 \cdot \eta^+$

until the break of each sample, here in the form of **strain softening.**

Tensile (Extensional) Test - Branched Polymer



Extensional viscosity η_E (in Pas), rotational test

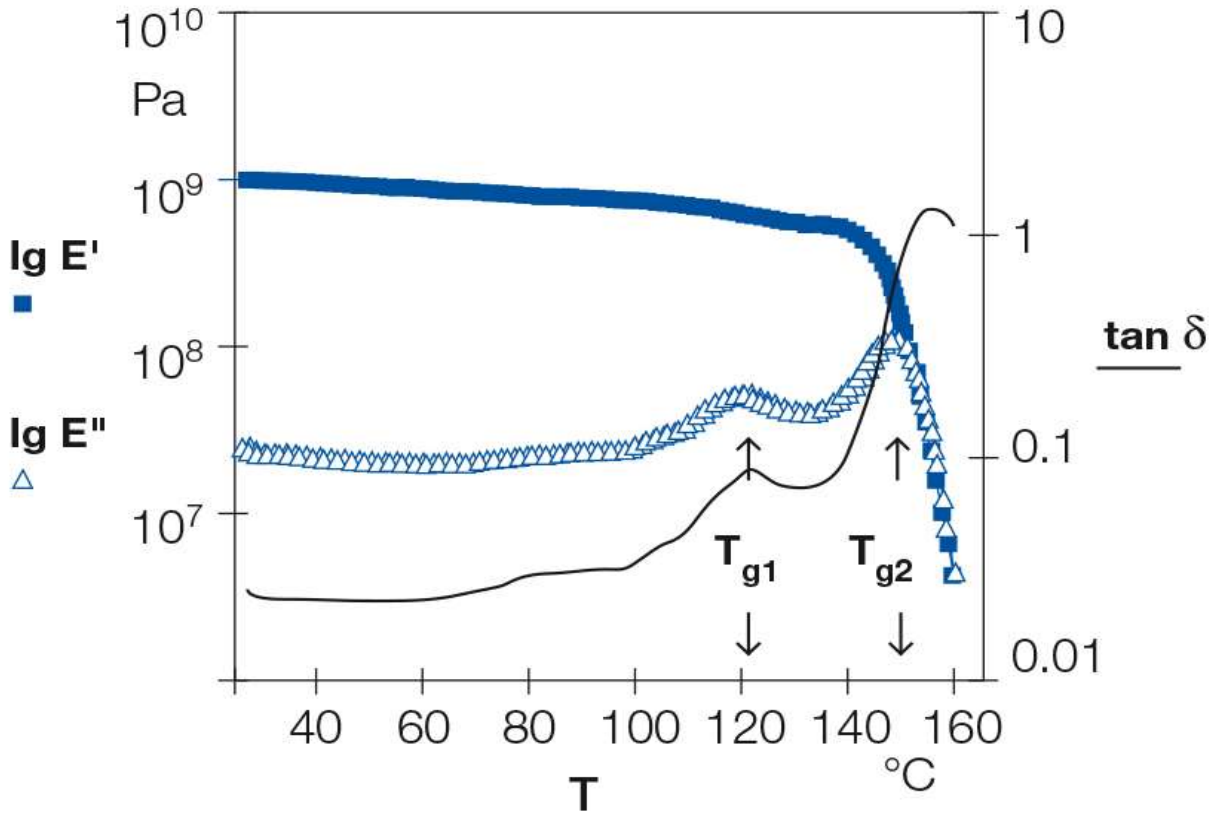
Branched LDPE

T = 150°C,
Highly viscous polymer melt

Extensional tests (SER)
at various extensional strain rates
(Hencky strain rates)
Initially, the curves of extensional viscosity (EV) and shear viscosity (SV) are overlapping.

Growth curve of SV, measured with cone plate.
It applies: $\eta_E^+ = 3 \cdot \eta^+$
until the final change in the behavior of each sample, here in the form of
strain hardening.

Tensile Test of Coextrudate Foil



Coextrudate Foil
PMMA - Polycarbonate

35µm thickness,
multilayer foil,
compound material

Analysis of T_g via the two E" maxima:

PMMA T_g = 120°C
PC T_g = 150°C

Summary

- Rheology provides a means to characterize the viscoelastic properties of wide range of polymers ranging from thermoplastics to thermosets.
- A series of rheological techniques can be employed in order to fully understand a material's behavior over a range of conditions
- A rheometer also provides a means to characterize other mechanical properties such as tack, tribology, tensile properties, optical monitoring via microscopy, and powder flow characteristics.

Your Questions