Part II: Capillary Rheometry

A method to predict flow properties under processing conditions
Outline

• Range of Applications for Capillary Rheometry

• Introduction into capillary rheometry: Principle of Operation and theoretical background

• Test results on LDPE: Complete Capillary Characterisation

• Advanced Test Types: pVT, Relaxation, Thermal Degradation etc.
Capillary Rheometry: Main Applications

VISCOSITY

Resistance to Flow
Pressures in Process

SHEAR VISCOSITY

BULK
$\eta(T, \xi, t)$

INSTABILITY
$\tau$

SURFACE EFFECTS
Wall Slip $V_w(T, T)$
(see 3 below)

LUBRICATION
PHASE SEPARATION
ADDITIVES

EXTENSIONAL VISCOSITY

FREE FORM DEFORMATION
UNIAXIAL
BIAXIAL
CONVERGENT FLOW

MELT RUPTURE
$\sigma(\xi)_{max}$

CONVERGENT FLOW

$\eta(T_n, \xi_n, b_n)$
$\lambda(T_n, \xi_n, b_n)$
is the operational area for a process, or process part.

$[\frac{\Delta \eta}{\Delta T}, \frac{\Delta \lambda}{\Delta T}]$
Temperature Sensitivity of Process

$[\frac{\Delta T}{\Delta \lambda}, \frac{\Delta T}{\Delta T}]$
Time Sensitivity of Material

$[\frac{\Delta \eta}{\Delta b}, \frac{\Delta \xi}{\Delta b}]$
Process Suitability of Material

ELASTICITY

(Memory of Previous State)

DIE SWELL
LONG DIE
SHORT DIE

PVT
STRESS RELAXATION
NO FLOW STRESS
$P$
$t_{RELAX}$

$\frac{\tau_f}{P}$
$t$

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Repeat from the previous session: Basic Terms

Shear Force $F$

Displacement $u$

Normal Force $N$

Shear Force $F$

area $A = a \cdot b$

Height $d$

Initial length $L$

$\gamma = \frac{u}{d}$  \hspace{1cm} Strain [$\cdot$]

$\dot{\gamma} = \frac{d\gamma}{dt}$  \hspace{1cm} Shear Rate [1/s]

$\tau = \frac{F}{A}$  \hspace{1cm} Shear Stress [Pa]

$\varepsilon = \ln \frac{l}{L}$  \hspace{1cm} Extension [$\cdot$]

$\dot{\varepsilon} = \frac{1}{L} \frac{dl}{dt}$  \hspace{1cm} Extensional Rate [1/s]

$\sigma = \frac{F}{A}$  \hspace{1cm} Extensional Stress [Pa]
Typical Shear Rate Ranges

- Sagging, Levelling
- Extrusion, Injection Moulding
- Mixing, Blade Coating, Brushing
- Roll Coating, Spraying

Rotational-Rheometer
- Sample: Water up to solids
- Results: Shear-Viscosity, Yield Stresses, Visco-Elasticity, Relaxation...

High Pressure Capillary-Rheometer
- Sample: Water up to high viscous
- Results: Shear-Viscosity, Elongational-Viscosity, Wall Slip...
Principle of Operation

Given quantity: piston speed ⇒ wall shear rate
Measured quantity: pressure drop ⇒ wall shear stress

⇒ small ram extruder
Laminar Pipe Flow

Isothermal, stationary Flow of an incompressible fluid

Newtonian

\[ \gamma_{\text{app}} = \frac{4 \cdot Q}{\pi R^3} \]

\[ \tau_{\text{app}} = \frac{R \cdot \Delta P}{2 \cdot L} \]

\[ n = \frac{d \left( \log \tau \right)}{d \left( \log \gamma \right)} \quad \text{Non-Newtonian Index (Ostwald-de Waele)} \]
What are we doing to get flow curves?

measurement:

\[ \dot{\gamma}_{app} = \frac{4 \cdot Q}{\pi R^3} \]

\[ \tau_{app} = \frac{R \cdot \Delta P}{2 \cdot L} \]

Ramp in steps

\[ \Delta \tau = \frac{\tau_{true}}{\dot{\gamma}_{true}} \]

\[ \eta = \frac{\tau_{true}}{\dot{\gamma}_{true}} \]
Correction: Entrance zone of a capillary die

Aim of the test: to separate entrance pressure and shear pressure drop.

Pressure transducer → Convergent Flow → Capillary die
Rosand Twin Bore Principle

\[ P_{\text{full}} = P_{\text{shear}} + P_{\text{entrance}} \]

left: capillary

right: orifice
How do we get the Extensional Viscosity?

Cogswell’s Convergent Flow Model ⇒ Extensional Viscosity

\[ \lambda = \frac{9(n+1)^2 (P_s)^2}{32 \eta \dot{\gamma}^2} \]

- Special Orifice Die according to Uni Zlin Model enables characterisation of very small extensional rates too.

\[ n = \frac{d \log \tau}{d \log \gamma} \quad \text{Non-Newtonian Index (Ostwald-de Waele)} \]

\[ \varepsilon \approx 10^{-1} - 10^{3} \text{ s}^{-1} \]

Example LDPE

LDPE at 190°C

- Low Shear Test Zero Shear Viscosity
- Low Shear 2.0mm
- Standard Shear 1mm
- Standard Shear Melt Fracture
- High Shear 0.5mm
- Low Extension 2.0mm
- Standard Extension 1mm
- Standard Extension Melt Rupture
- High Extension 0.5mm

Shear Viscosity / Extensional Viscosity (Pas)

Shear Rate / Extensional Rate (1/s)
Extensional Rheology of LDPE

⇒ Blow Moulding is mainly influenced by Extension!
Surface Instabilities LDPE

Surface shape

Cooling air
Surface Instabilities LDPE
How can the process be improved?

Dehnviskosität - Vergleichskurven zwischen Homopolymer PE und Polymerblend PE-PP

- Extensional Viscosity (Pas)
- Extensional Rate (1/s)

Sample 1
Sample 2
Sample 2
Sample 2
Sample 2
Sample 2
Sample 1
Another Example: Co-Extrusion

Similar instabilities
LDPE in Co-Extrusion Die

Figure 4  Extensional and shear viscosities for two different lots of LDPE 1, 210°C.

Figure 5  Merging area of the flat coextrusion die.

Instabilities caused by Extensional Flow Behaviour of LDPE

Further Examples: Dispersions

Capillary Rheometry can predict Die Blocking

⇒ Capillary Rheometry can predict Die Blocking
Example: Dispersion Adhesive for Spray Coating

⇒ Shear Thickening effect depends on the particle volume fraction
Wide Shear Rate Range

⇒ Rotational and Capillary Rheometry cover approx 13 decades in shear
Further Applications: Wall Slip

Wall Slip Velocity of chromium catalyzed HDPE at 190°C

- Wall slip velocity increases dramatically at just above 0.1 MPa.

Wall Slip according to Mooney Model
Critical Stress

V_{w} = 0
V_{w} ≠ 0
Equilibrium Pressure: Homogeneity

Pressure drop is important

homogeneous
inhomogeneous

⇒ For polymer blends, filled polymers, suspensions, emulsions, composites etc.
Thermal degradation / Curing

Prinzip:

$V \rightarrow t$

⇒ Gives max process time

Thermischer Abbau at 260°C

- Pressure Drop
- Shear Rate
- Extruded Volume

Pressure (MPa)

real time (sec)

Shear Rate (1/s) / Extruded Volume (cm³)
Stick-Slip

Flow Instabilities

Linear Ramp

$\text{Melt fracture}$

$\Rightarrow$ What is the max processing pressure / Shear Rate?
Melt Fracture

Unstable flow, poor product quality.

![Graph showing shear stress (Pa) vs. shear rate (1/s) and pressure (Mpa) vs. time.](image)

Shear Stress (Pa)

Shear Rate (1/s)

Pressure (Mpa)

Time
Relaxation LDPE

What happens after processing

⇒ inner stresses can lead to surface crack (automotive industry)
Compressibility

PV-Isotherm

PVT:
- Mainly needed for flow simulation
Rheometer Types

Benchtop RH2000 and Floor Standing RH7/10
Example: Test Run at RH7
Conclusion

The complete flow behaviour under processing conditions

Rosand Double Capillary System with Orifice Die:

- direct measurement of the entrance pressure drop - no extrapolation needed
- calculation of extensional viscosity according Cogswell method
- flow curve up to very high shear end extensional rates
- ability to detect wall slip by Mooney’s method
- correlation with structural changes during processing
- additional Options for detection of elastic behaviour (Die-Swell)

Thank you for your attention.