Materials Characterization by Thermal Analysis (DSC & TGA), Rheology, and Dynamic Mechanical Analysis (Part 2)

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Applications Scientists & Sales Representative

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What Does TA Instruments Make?

- Differential Scanning Calorimeters
- Thermogravimetric Analyzers
- Simultaneous Differential Thermal Analyzers
- Microcalorimeters of many types
- Dilatometers and Thermomechanical Analyzers
- Thermal Diffusivity
- Thermal Conductivity
- Mechanical Testers
- **Dynamic Mechanical Analyzers**
- Rotational Rheometers
- Rubber Rheometers
Dynamic Mechanical Analyzers

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Is DMA Thermal Analysis or Rheology?

- **Thermal Analysis**
  - measurement as a *function of temperature or time*.

- **Rheology**
  - the science of *stress* and *deformation* of matter.

- **DMA** mechanically *deforms a sample* and measures the sample response. The response to the deformation can be monitored as a *function of temperature or time*. 
DMAs from TA Instruments

RSA G2
Discovery DMA 850
ARES G2 and DHR
DMA mode

Q800
Discovery DMA 850

• Direct Drive Motor
  • Non-contact motor for applying static and dynamic deformation
  • Constructed from high performance, lightweight composites for maximal stiffness and minimal inertia
  • Fastest motor control over widest continuous force range: 0.1 mN to 18 N
    ▪ 50 ms step-displacement response
    ▪ 100× improvement in stress accuracy
  • Apply any combination of static and dynamic forces up to 18 N
• **Air Bearing & Optical Encoder**
  
  • Stiff, frictionless air bearing supports rectangular drive shaft
  
  • Set of 8 porous carbon air bearings for frictionless ‘floating’ of the drive shaft
  
  • Superior displacement control, sensitivity over unsupported and spring-supported designs
  
  • Optical encoder for displacement over 25 mm travel range with 0.1 nm resolution
    
    ▪ 100× smaller displacements
    
    ▪ 5 nm oscillation displacement control
RSA G2 Schematic: Dual Head Design

- Transducer Motor
- Air Bearing
- LVDT
- Upper Geometry Mount
- Lower Geometry Mount
- Transducer
- Motor
- Air Bearing
- Drive Motor
DMA Oscillation Testing

• Viscoelastic materials (polymers, gels, composites)
• Oscillatory Deformation, controlled Frequency and Amplitude (Strain or Stress)
• Information provided:
  ▪ Storage Modulus, Loss Modulus and Tan Delta
  ▪ Glass Transition, Relaxation Time, Cure behavior
  ▪ Polymer structure- Bulk property relationships
Oscillation Testing

- An oscillatory (sinusoidal) deformation (strain) is applied to a sample.

- The material response (stress) is measured.

- The phase angle $\delta$, or phase shift, between the deformation and response is measured.
Oscillation Testing: Response for solids and liquids

Purely Elastic Response (Hookean Solid)

\[ \delta = 0° \]

Purely Viscous Response (Newtonian Liquid)

\[ \delta = 90° \]
Oscillation Testing: Viscoelastic Material

Phase angle $0^\circ < \delta < 90^\circ$
DMA Viscoelastic Parameters

The Modulus: Measure of materials overall resistance to deformation.

The Elastic (Storage) Modulus:
Measure of elasticity of material. The ability of the material to store energy.

The Viscous (Loss) Modulus:
The ability of the material to dissipate energy. Energy lost as heat.

Tan Delta:
Measure of material damping - such as vibration or sound damping.

\[ E^* = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \]

\[ E' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \cos \delta \]

\[ E'' = \left( \frac{\text{Stress}^*}{\text{Strain}} \right) \sin \delta \]

\[ \tan \delta = \left( \frac{E''}{E'} \right) \]
Storage and Loss of a Viscoelastic Material
Happy & Unhappy Balls

Modulus is the same
tan δ is very different

E' (\text{dyn/cm}^2)

Freq [rad/s]

\tan_\delta (\text{}\text{)}
Stress Relaxation Happy and Unhappy Balls

Happy ball has an infinite relaxation time.
Dynamic Temperature Ramp

- Glassy Region
- Transition Region
- Rubbery Plateau Region
- Terminal Region

log $E'$ (G') and $E''$ (G'')

- Storage Modulus ($E'$ or G')
- Loss Modulus ($E''$ or G'')
Glass Transition $E'$ Onset, $E''$ Peak, and Tan $\delta$ Peak

- **Storage Modulus $E'$ Onset:**
  - Occurs at lowest temperature, relates to mechanical failure

- **Loss Modulus $E''$ Peak:**
  - Occurs at middle temperature
  - Related to the physical property changes
  - Reflects molecular processes - the temperature at the onset of segmental motion

- **Tan Delta Peak:**
  - Occurs at highest temperature; Used historically in literature
  - Measure of the "leatherlike" midpoint between the glassy and rubbery states
  - Height and shape change systematically with amorphous content.

Glass Transition of Polycarbonate

- Available from TA for Instrument verification

PC sample

p/n: 982165.903

Clamp:
- single cantilever
- Temperature: ambient to 180°C
- Heating rate: 3°C/min
- Frequency: 1 Hz
- Amplitude: 20 µm
Glass Transition is a Range, not a Temperature
Crystallinity, Molecular Weight, and Crosslinking

Increasing MW

Cross-linked

Increasing Crystallinity

3 decade drop in modulus at $T_g$

Increasing MW

Amorphous

Crystalline

Temperature

$T_m$

log Modulus
PET Film: Effect of Frequency on Tg

- PET film tested at 0.1 Hz, 1 Hz and 10 Hz
DMA Deformation Modes

- **Axial**
  - Tension
    - Thin Films
    - Fibers
  - Compression
    - Soft solids
    - Foams
    - Gels
  - Bending
    - Thermosets
    - Composites

- **Rotational**
  - Parallel Plate
    - Thermoplastic
    - Thermosets
    - Elastomers
  - Torsion
    - Thermoplastic
    - Thermosets
    - Composites
Tension DMA

• **Young’s Modulus (E)**
  - Easy to adjust clamps to accommodate different samples. Allows for thermal expansion or shrinkage.

• **Dimensions:**
  - Length can be adjusted directly, measured by instrument.
  - Thickness up to 2 mm

• **Materials:**
  - Polymer films (Mylar, Kapton)
  - Elastomers (o-rings, seals)
  - Free films of coatings (dried paint)
  - Fibers, bundled or single.
Storage Modulus of PET Fiber - Draw Ratios

Glass Transition of EPDM - DHR DMA Tension

--- Fresh Sample
----- Aged Sample
Effect of Solvent

- Automotive coating measured with and without solvent
Humidity Influence: Nylon Film
Compression DMA

- Compression Modulus (E)
- Soft materials with high elasticity.
- Must be compressible, without yielding under deformation.
- Dimensions:
  - Ideally cut to diameter of the plates. Can also accommodate smaller disks or rectangles.
  - 1-10 mm thick
- Materials:
  - Foams (mattress, packaging, anti-vibration)
  - Soft Elastomers (above Tg only!)
  - Stiff hydrogels, biological tissue
Foam Compression DMA: Temperature Ramp Rate
Effects of Humidity on Glass Transition of Foam
Bending DMA

• **Flexural Modulus (E)**
• 3 Point Bend (unclamped) and Cantilever (clamped)

• **Dimensions**
  - Fixed lengths: (i.e. 40, 25 and 10 mm 3PB)
  - Width up to 12.5 mm
  - Thickness ideally less than 1/10 length.

• **Materials**
  - Unfilled thermoplastics (Cantilever only > Tg)
  - Elastomers (Cantilever)
  - Thermosets (3PB)
  - Composites (3PB)
  - Metals (3PB)
What Causes $E'$ Increase after $T_g$?

- Sample sagging after $T_g$
- Solution: use cantilever clamp instead of 3-p bending

Instrument: RSA G2
Clamp: 3-p bending
Temperature: 50°C to 180°C
Heating rate: 3°C/min
Frequency: 1 Hz
Amplitude: 10 µm
Fiber Reinforced Polymer - 3 Point Bending

![Graph showing the storage modulus and loss modulus for Fiber Reinforced Polymer in the machined and transverse directions as a function of temperature.](image)
Torsion DMA

• **Shear Modulus (G) “Modulus of Rigidity”**
• Ideal for very high modulus materials; accommodates wide range of dimensions.

• **Dimensions:**
  - Small: 7 mm long, 3 mm wide, 0.5 mm thick
  - Large: 40 mm long, 12.5 mm wide, 4 mm thick
  - Cylinder: 1.5, 3 or 4.5 mm diameter

• **Materials:**
  - Thermoplastics and Thermosets
  - Elastomers
  - Composites
  - Metals
Fiber Reinforced Polymer - Torsion

![Graph showing Storage modulus $G'$ and Loss modulus $G''$ as functions of temperature T.](image)

- Machined Direction
- Transverse Direction

Temperature $T$ (°C)

$G'$ (Pa)

$G''$ (Pa)

Tan(delta) tan(δ)

© TA Instruments
Torsion: Metallic Glass (Amorphous Metal)
Parallel Plate DMA

- **Shear Modulus (G)**
- Full range of viscoelastic behavior (glassy, rubbery and terminal region).

- **Dimensions:**
  - 25, 8 or 4 mm parallel plates
  - 0.5 – 3 mm gap thickness

- **Materials:**
  - Thermoplastics: load above softening point, ramp temperature down.
  - Thermosets: cure in place on disposable plates.
  - Elastomers: cut disk and glue to plates.
  - Adhesives: too soft to test with linear DMA
Hot Melt Adhesive: Parallel Plates

Glass Transition

Terminal Region
Rubber DMA: Parallel Plates

Temperature $T$ ($°C$)

Storage modulus $G'$ (Pa)
Loss modulus $G''$ (Pa)

Tan(delta) tan(θ)

- SBR
- NBR
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- **Rotational Rheometers**
- Rubber Rheometers
Rotational Rheometers
What is Rheology?

Rheology: The study of stress-deformation relationships
Rheology: the study of flow and deformation

Viscosity
- Non-Newtonian Viscosity
  - Shear thinning
  - Shear thickening
  - Thixotropy
  - Yield Stress
- Viscosity under processing conditions

Modulus
- Measure viscoelastic properties
  - Storage Modulus
  - Loss Modulus
  - Tan Delta
- Changes with time, temperature

\[
\text{Stress} \div \text{Shear rate} = \text{Viscosity}
\]

\[
\text{Stress} \div \text{Strain} = \text{Modulus}
\]
Discovery Hybrid Rheometer Technology

- Patented Active Temperature Control
- Force Rebalance Transducer Control Electronics
- Patented Advanced Drag Cup Motor
- Patented Smart Swap Geometries
- Dual Reader Optical Encoder (Patent Pending)
- Patented Magnetic Bearing
- Radial Air Bearing
- New True Position Sensor (Patent Pending)
ARES G2: Separate Motor and Transducer

Torque Transducer maintains the null position as the sample is deformed.

Sample torque to be measured directly, without contributions from motor friction or inertia.

Normal Force Transducer provides highly accurate normal force measurements.

High stiffness for precise gap control.

Direct Drive motor applies accurate and precise rotational deformation, without contributing to measured torque.
Torsion Flow in Parallel Plates

- Stress ($\sigma$): $\sigma = \frac{2}{\pi r^3} \times M$
- Strain ($\gamma$): $\gamma = \frac{r}{h} \times \theta$
- Strain rate ($\dot{\gamma}$): $\dot{\gamma} = \frac{r}{h} \times \Omega$

$r =$ plate radius
$h =$ distance between plates
$M =$ torque ($\mu$N.m)
$\theta =$ Angular motor deflection (radians)
$\Omega =$ Motor angular velocity (rad/s)
Geometry Options

- Concentric Cylinders: Very Low to Medium Viscosity
- Cone and Plate: Very Low Viscosity
- Parallel Plate: Very Low Viscosity to Soft Solids
- Torsion Rectangular: Solids

Water to Steel
Shear Rate varies across a Parallel Plate

- For a given angle of deformation, there is a greater arc of deformation at the edge of the plate than at the center.

\[ \gamma = \frac{dx}{h} \]

- \( dx \) increases further from the center,
- \( h \) stays constant

Single-point correction for the parallel plate geometry (0.76 radius)

Shear Rate is Uniform across a Cone

- The cone shape produces a smaller gap height closer to the center, so the shear on the sample is constant

\[ \gamma = \frac{dx}{h} \]

\( h \) increases proportionally to \( dx \), \( \gamma \) is uniform
Limitations of Cone and Plate

Typical Truncation Heights:
1° degree ~ 20 - 30 microns
2° degrees ~ 60 microns
4° degrees ~ 120 microns

Gap must be > or = 10 [particle size]!!
What Geometry should we use?
What Geometry should we use?
When to Use Concentric Cylinders

- Low to Medium Viscosity Liquids
- Unstable Dispersions and Slurries
- Minimize Effects of Evaporation
- Easy Sample Loading
- Weakly Structured Samples (Vane)
- Low Shear Rates

Peltier Concentric Cylinder
# Geometry Summary

<table>
<thead>
<tr>
<th></th>
<th>Parallel Plates</th>
<th>Cone and Plate</th>
<th>Concentric Cylinders</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>1-2 mL</td>
<td>50-500 µL</td>
<td>7-25 mL</td>
</tr>
<tr>
<td>Sample Types</td>
<td>Liquids, gels, soft solids, dispersions, etc.</td>
<td>Unfilled liquids, isothermal tests</td>
<td>“Pourable” liquids, low viscosities, dispersions</td>
</tr>
<tr>
<td>Benefits</td>
<td>Used for all samples. Roughened surfaces available to prevent slip.</td>
<td>Most accurate measurement of non-Newtonian Viscosity, small sample volume.</td>
<td>Least effected by sample loading technique or evaporation.</td>
</tr>
</tbody>
</table>
Polymer Rheology
Polymer Rheology: Experimental Goals

Characterization
- Average Molecular Weight
- Molecular Weight Distribution
  - Long-Chain Branching

Processability
- Shear Thinning
  - Die Swell
- Surface Roughness

Final Product Performance
- Tack and Peel
- Usable Temperature Range
- Mechanical Properties
Melt Rheology: MW Effect on Zero Shear Viscosity

- Sensitive to Molecular Weight, MW
- For Low MW (no Entanglements) \( \eta_0 \) is proportional to MW
- For MW > Critical MW\(_c\), \( \eta_0 \) is proportional to MW\(^{3.4}\)

\[ \eta_0 = K \cdot M_w \]

Viscosity vs. Shear Rate – Polymer Melts

First Newtonian Plateau

\[ \eta_0 = \text{Zero Shear Viscosity} \]

\[ \eta_0 = K \times MW^{3.4} \]

Measure in Flow Mode

Extend Range

with Time-Temperature

Superposition (TTS)

& Cox-Merz

Second Newtonian Plateau

Molecular Structure

Compression Molding

Extrusion

Blow and Injection Molding

Frequency (Hz, or rad/s)
Viscosity Measurements of LDPE at 190°C

Red and Green curves tested using rotation. Sample starts to slip at shear rates > 1 sec⁻¹.

Blue curve tested using oscillation. Can measure up to high shear rates with no slip!
Influence of Molecular Weight on Viscosity

The zero shear viscosity increases with increasing molecular weight.

The high shear rate viscosity is independent of the molecular weight.
Frequency Sweep

- The material response to increasing frequency (rate of deformation) is monitored at a constant amplitude (strain or stress) and temperature.

- Strain should be in LVR
- Sample should be stable
- Remember – Frequency is 1/time so low frequencies will take a long time to collect data – i.e. 0.001Hz is 1000 sec (over 16 min)
Time-Dependent Viscoelastic Behavior

- **T is short (< 1s)**
- **T is long [24 hours]**
Time-Dependent Viscoelastic Behavior

- Silly Putties have different characteristic relaxation times
- Dynamic (oscillatory) testing can measure time-dependent viscoelastic properties more efficiently by varying frequency (deformation time)
Frequency Sweep - Time Dependent Viscoelastic Properties

Frequency of modulus crossover correlates with Relaxation Time
Influence of Molecular Weight on $G'$ and $G''$

The intersection of $G'$ and $G''$ shifts to lower frequency as MW increases.

![Graph showing the influence of molecular weight on $G'$ and $G''$.]
Influence of MWD on $G'$ and $G''$

Increasing MWD (polydispersity)

Higher crossover frequency: lower $M_w$
Higher crossover Modulus: narrower MWD

SBR polymer melt
- $G'$ 310 000 broad
- $G''$ 310 000 broad
- $G'$ 320 000 narrow
- $G''$ 320 000 narrow

Modulus $G'$, $G''$ [Pa]

Frequency $\omega a_T$ [rad/s]
High MW Contributions

400,000 g/mol PS
+ 1% 12,000,000 g/mol

400,000 g/mol PS
+ 4% 12,000,000 g/mol

Macosko, TA Instruments Users’ Meeting, 2015
Example: Surface Defects during Pipe Extrusion

HDPE pipe surface defects

Surface roughness correlates with $G'$ at low frequency $\rightarrow$ broader MWD or small amount of a high MW component

- $G'$ rough surface
- $G'$ smooth surface
- $\eta^*$ rough surface
- $\eta^*$ smooth surface
Tack and Peel of Adhesives

- Bond strength is obtained from peel (fast) and tack (slow) tests.
- Tack and Peel are a function of viscoelastic properties at different frequencies.

![Graph showing Tack and Peel performance of a PSA](image)
Extensional Viscosity

- Application to processing:
  - many processing conditions are elongation flows
  - testing as close as possible to processing conditions (spinning, blow-molding)

- Relation to material structure:
  - non linear elongation flow is more sensitive to polymer structure than shear flows (branching, polymer architecture)
LLDPE (Low branching)

LLDPE, $T = 130 \, ^\circ C$

- $0.01 \, s^{-1}$
- $0.1 \, s^{-1}$
- $1 \, s^{-1}$
- $3 \, s^{-1}$
- $10 \, s^{-1}$

[Steady Shear Viscosity * 3]

$\eta_e (\text{Pa-s})$

time $\varepsilon [s]$
LDPE (High branching)

\[ \eta_e(t) \quad [\text{Pa-s}] \]

**Warning:** Overlay units don't match, Frequency

LDPE, \( T = 150 \, ^{\circ}\text{C} \)
- 0.003 s\(^{-1}\)
- 0.01 s\(^{-1}\)
- 0.03 s\(^{-1}\)
- 0.1 s\(^{-1}\)
- 0.3 s\(^{-1}\)
- 1 s\(^{-1}\)
- 3 s\(^{-1}\)
- 10 s\(^{-1}\)
- 30 s\(^{-1}\)

[Steady Shear Viscosity * 3]
Thermosets and Gels
Thermosets and Gels

• What is a Gel?
  ▪ A soft solid that contains a polymeric network and a substantial fraction of solvent
  ▪ Latin: *gelatus* (frozen; immobile)

• “A substantially dilute crosslinked system that exhibits no flow in the steady state.”

• Chemical Gel: Network of covalent interactions.

• Physical Gel: Network of non-covalent interactions.
Gelation

Gel point
Hyaluronic Acid Gels:

- Hyaluronic acid gels are used as lubricating agent during abdominal surgeries to prevent adhesion and also for joint lubrication, wound healing etc.
- Rheology can monitor HA gelation and evaluate the gel strength
Gelation During Cooling

- Storage Modulus [Pa]
  - 1°C/min Cooling
  - 2°C/min Cooling

- Loss Modulus [Pa]
  - 1°C/min Heating
  - 2°C/min Heating

Temperature T [°C]

© TA Instruments
Powder Coating: Cure Test
Cure Testing - Dimensional Change

Storage modulus $G'$ (Pa)
Loss modulus $G''$ (Pa)

Change: 9.96 μm
Change: 16.56 μm

Gap (μm)

Step time $t_s$ (min)
Change in Mechanical Properties During Drying

- Relative Humidity and Temperature Controlled Chamber
- **Quantitative** measurement of modulus during drying of the bulk material.
- Characterize time of drying
  - Time needed to “set” (Crossover point)
- Determine conditions needed to achieve drying
- Test Method: constant temperature and humidity
Moisture-Cured System - Humidity Control

50°C, 50% RH
50°C, 80% RH
Flow Testing
Newtonian and Non-Newtonian Fluids

- **Newtonian Fluids** - Viscosity does not change with changes in shear rate or time.
  
  *(examples: water, oil, honey)*

- **Non-Newtonian Fluids** - Viscosity is time or shear rate dependent
  
  *(examples: mayonnaise, paint, polymer, asphalt)*
  
  - Shear – Thinning: viscosity decreases as shear rate increases
  - Shear – Thickening: viscosity increases as shear rate increases.

\[
\text{Stress} \quad \frac{\text{Shear rate}}{\text{Shear rate}} = \text{Viscosity}
\]
Flow Behaviors

- Bingham (Newtonian w/ yield)
- Bingham Plastic (shear thinning w/ yield)
- Pseudo-plastic (shear thinning)
- Newtonian
- Dilatant (shear thickening)
Viscosity of Water

Decreasing cone angle decreases contributions from surface tension at low shear rate, and secondary flow at high shear rate.

Cup and Bob (Concentric Cylinder) is ideal for low shear rates, but has significant error at high shear rate for low viscosity liquids.
Viscosity is curve, not a single value!

- Low Shear Rate
- Medium Shear Rate
- High Shear Rate

Viscosity [Pas] vs. shear rate [1/s]
Viscosity Flow Curve

What shear rate?

1) Sedimentation
2) Leveling, Sagging
3) Draining under gravity
4) Chewing, swallowing
5) Dip coating
6) Mixing, stirring
7) Pipe flow
8) Spraying and brushing
9) Rubbing
10) Milling pigments
11) High Speed coating

Log Viscosity $\eta$

shear rate (1/s)
Viscosity vs. Shear Rate - Shampoo

- Pouring out of Bottle
- Spreading

Graph showing the variation of Viscosity (η) with Shear Rate (\( \dot{\gamma} \)) for white rain shampoo and hotel shampoo.
Viscosity vs. Shear Rate - Shampoo

- White rain shampoo
- Hotel shampoo

Zero-rate viscosity: 13.29 Pa.s
Zero-rate viscosity: 1.952 Pa.s
What is Yield Stress?

- Some Structured Fluids behave like “solids” at rest.
- A critical stress must be applied for these materials to flow.
- What does Yield Stress do?
  - Stabilize against sedimentation of separation
  - Improve ease of use
  - Prevent dispensing of product
Yield Stress - Ketchup

The graph shows the stress ($\sigma$) as a function of the shear rate ($\dot{\gamma}$) for two different conditions:

- **Ketchup Flow Ramp - Sandblasted Plates**: The stress increases sharply at lower shear rates and stabilizes at a higher value.
- **Ketchup Flow Ramp - Smooth Plates**: The stress increases gradually at lower shear rates and stabilizes at a lower value.

The x-axis represents the shear rate ($\dot{\gamma}$) in 1/s, while the y-axis represents the stress ($\sigma$) in Pa (Pascal).
Wall Slip

**No slip condition**
Ideal, Assumed Velocity Profile

**Wall Slip**
Incorrect Velocity Profile

Yield Stress Measurements on Toothpaste

© TA Instruments
Controlled-Rate Measurement of Yield Stress

- Indirect Yield Stress Measurement
  - Extrapolate Stress at Shear Rate = $0.0 \, \frac{1}{sec}$
  - Assumes Newtonian viscosity after yield
  - Sample has already yielded.

- Steady-State Viscosity at low Shear Rates
  - Shear rate is decreased to very low rates.
  - Stress plateaus and approaches Yield Stress.
  - Herschel-Bulkley model
Viscosity of Protein Solutions

The graph shows the relationship between shear rate (\( \dot{\gamma} \)) and viscosity (\( \eta \)) for different protein solutions, with yield stress values indicated for each curve.

- Yield stress: 4.6e-3 Pa
- Yield stress: 1.8e-3 Pa
- Yield stress: 2.9e-4 Pa

The x-axis represents shear rate (\( \dot{\gamma} \) in 1/s), and the y-axis represents stress (\( \sigma \) in Pa).
Protein Solutions: Low Torque Sensitivity

![Graph showing shear rate vs. torque for three different torques: 261 nanoN.m, 106 nanoN.m, and 19 nanoN.m. The graph illustrates how shear rate increases with increasing torque.](image-url)
Understanding Torque

• What is a **N.m**?
  - An apple (about 150 g) on the end of a meter stick
  - **1.5 N.m**

• What is a **µN.m**?
  - A grain of salt (about 0.5 mg) on the end of a meter stick
  - **5 µN.m**

• And a **nanoN.m**?
  - A speck of dust (1 µg) on the end of a meter stick
  - **10 nanoN.m**
Thixotropy

The thixotropy characterizes the time dependence of reversible structure changes in complex fluids. The control of thixotropy is important to control:

- process conditions; for example, to avoid structure build up in pipes during rest periods
- sagging and leveling; gloss of paints and coatings
Thixotropy of Paint

Stress is ramped up, then ramped down. The hysteresis indicates the time dependence of the viscosity change, or Thixotropy.
Specialized Accessories

- Wide range of accessories for different testing needs
- Environmental controls (Temperature, humidity, pressure, etc.)
- Rheo + other technique (optical, dielectric, etc.)
- Rheology response to stimulus (UV, electric, magneto, etc.)
DHR Humidity Accessory

- Temperature Range: 5 °C – 120 °C
- Temperature Accuracy: ±0.5 °C
- Heating/Cooling Rate: ±1 °C/min maximum
- Humidity Range: 5-95%
- Humidity Accuracy: 5-90%RH: ±3% RH, >90%RH: ±5% RH
- Humidity Ramp Rate: ±2% RH/min, increasing or decreasing

- Surface Diffusion
- Bulk Diffusion
- Film/fiber Tension
Example: Glue Drying under Different Humidity

Elmers Glue Curing Under Humidity Control @ 50°C

<table>
<thead>
<tr>
<th>Relative Humidity (%)</th>
<th>Time to Modulus Crossover</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% RH</td>
<td>4 minutes</td>
</tr>
<tr>
<td>30% RH</td>
<td>6 minutes</td>
</tr>
<tr>
<td>60% RH</td>
<td>23 minutes</td>
</tr>
</tbody>
</table>
Modular Microscope Accessory (DHR)

- Connecting Rheology with structure under flow conditions (counter rotation option also available). Modular video camera, light source, and interchangeable optical objectives.
Small Angle Light Scattering (DHR)

- Simultaneous rheology and structure information
- Laser light creates interference pattern
- Pattern reflects size, shape, orientation and arrangements of objects that scatter
MagnetoRheology Accessory (DHR)

- The MR Accessory enables characterization of magneto-rheological fluids under the influence of a controlled field.
- Applied fields up to 1 T with temperature range of -10 °C to 170 °C (standard and extended temperature options).
- The system accommodates an optional Hall probe for real-time measurement and closed-loop control of the sample field.
Magneto Rheology Accessory (DHR)

- Lord MR Fluid MRF-140CG (081610) – 300µm gap at 20°C
Peltier Plate Tribo-rheometry Geometries

- Ball on three Plates
- Three Balls on Plate
- Ring on Plate
- Ball on three Balls

Also available for ETC
Coefficient of Friction Measurement

PVC on Steel with 2.0 Pa.s oil as lubricant
Geometry: 3 Balls on Plate
Temperature: 25°C, Procedure: Flow ramp

- Boundary Lubrication
- Mixed Lubrication
- Hydrodynamic Lubrication
What Does TA Instruments Make?

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- Simultaneous Differential Thermal Analyzers
- Microcalorimeters of many types
- Dilatometers and Thermomechanical Analyzers
- Thermal Diffusivity
- Thermal Conductivity
- Mechanical Testers
- Dynamic Mechanical Analyzers
- Rotational Rheometers
- Rubber Rheometers
Rubber Rheometers
Rubber Rheology

- Mooney Viscometer
  - Widely used in the rubber industry.

- MDR: Moving Die Rheometer
  - Rotorless cure meter (improvement on ODR), used to measure vulcanization of rubber compounds.

- RPA: Rubber Process Analyzer
  - Fully capable rheometer for characterizing elastomers and rubber compounds.
  - Capabilities beyond MDR
    - Frequency Sweeps
    - Strain Sweeps
    - Temperature Ramps
    - Stress Relaxation

- Automated Hardness and Density testers, Autoloader for MDR and RPA
**RPA (Rubber Process Analyzer)**

**Information Provided:** Storage Modulus $G'$, Loss Modulus $G''$, Tan Delta and Relaxation Modulus $G(t)$ as a function of strain, frequency, time and temperature.

**RPA Elite**

**Measured Torque**
High Stiffness transducer, not affected by compliance.

**Applied Deformation**
Direct, precise control of angle and frequency.

**Diagram**
- Transducer
- Upper heater
- Upper seal plate
- Upper die
- Sample
- Lower seal plate
- Lower oscillating die
- Lower heater
- Direct Drive Motor
Rubber Production: Where does a Rheometer fit?
RPA LAOS - Linear and Branched Polymer

• Large Amplitude Oscillatory Shear (LAOS) measures outside of the Linear Viscoelastic Region
• LAOS testing is sensitive to differences in polymer architecture not detected in Linear Viscoelastic measurements
RPA Strain Sweep- Dispersion of Filler

- The modulus of filled compounds depends on how the compound is processed.
- Longer milling time produces a better dispersion and breaks down agglomerates of carbon black.
- Testing mechanical properties helps to determine best milling time.
Curing of Rubber
What Does TA Instruments Make?

• Differential Scanning Calorimeters
• Thermogravimetric Analyzers
• Simultaneous Differential Thermal Analyzers
• Microcalorimeters of many types
• Dilatometers and Thermomechanical Analyzers
• Thermal Diffusivity
• Thermal Conductivity
• **Mechanical Testers**
• Dynamic Mechanical Analyzers
• Rotational Rheometers
• Rubber Rheometers
ESG Mechanical Testers
Load Frame Instruments
Fatigue Testing
TestBench Instruments
Linear Motor Technology

- Direct Drive Electromagnetics
  - Highest Accelerations
  - Precise
  - Clean & Quiet
  - Unmatched Durability
Materials Application Examples

**Plastics**
- TPE Fatigue
- TPU Fatigue

**Composites**
- Carbon Composite Fatigue
- E-glass Composite Fatigue

**Elastomers-Rubber**
- Tire Rubber DMA
- Tire Rubber Heat Build Up
- Tire Rubber Fatigue
- Shoe Foam Fatigue
- Molded Silicon Characterization

**Fibers-Textiles**
- Smart Textile Characterization
- Spider Silk Pull-to-Failure

**Metals**
- Hardened Steel Fatigue
- Stent Wire Fatigue
- Nuclear Fuel Rod Fatigue
- Solder Pull-to-Failure
Thank You

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