MULTIDRIVE: RHEO-DMA PLATFORM FOR EXTENDED POLYMER ANALYSIS

Educational Webinar

March 24th 2020

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Outline

- PART 1 ---- Introduction: DMA
- PART 2 ---- Unique Design Concept: Combined Linear-Torsional DMA
- PART 3 ---- Application: Composite industry (From Rheology to DMA on one device)

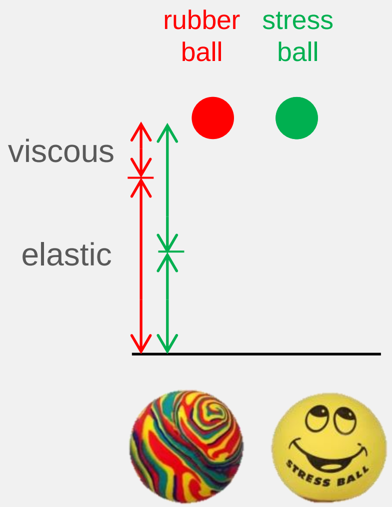
What is Dynamic Mechanical Analysis (DMA)?

Thermal analysis: study of how material properties change with temperature (thermal transitions)

DMA: measurement of viscoelastic material properties.

Changes with temperature indicate thermal transitions e.g. **glass transition temperature**.

Detailed knowledge about these properties is relevant for many practical applications



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Thermal Analysis Techniques

Increasing Sensitivity

Differential Scanning Calorimetry (DSC)

Measurement of heat flow

Thermomechanical Analysis (TMA)

Measurement of change in length

Dynamic Mechanical Analysis (DMA)

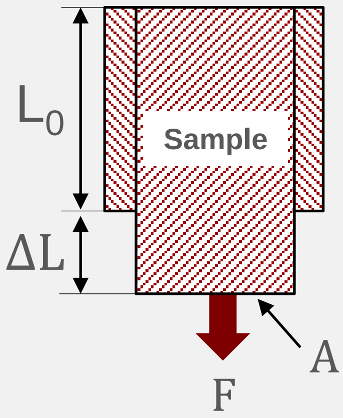
Measurement of viscoelastic properties

Advantage of DMA:

Allows measurement of weak **thermal transitions** which are *not at all or only with great difficulty* detectable using other thermal analysis techniques

Dynamic Mechanical Analysis

Principle

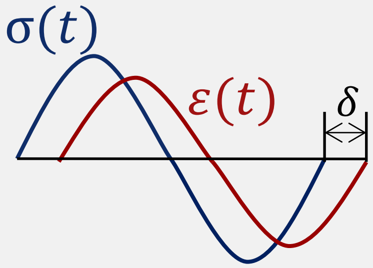


Stiffness $S = \frac{F}{\Delta L}$

Modulus $E = \frac{\sigma}{\epsilon} = \frac{F}{\Delta L}\frac{L_0}{A}$

Stress $\sigma(t) = \frac{F(t)}{A} = \hat{\sigma} * \sin(\omega t)$

Strain $\varepsilon(t) = \frac{\Delta L(t)}{L_0} = \hat{\varepsilon} * \sin(\omega t - \delta)$



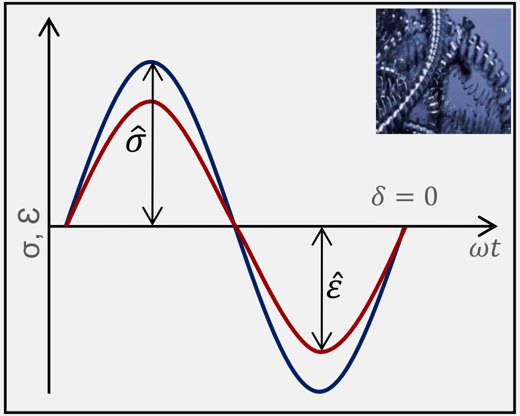
$\omega = 2\pi f$

Dynamic Mechanical Analysis

Principle

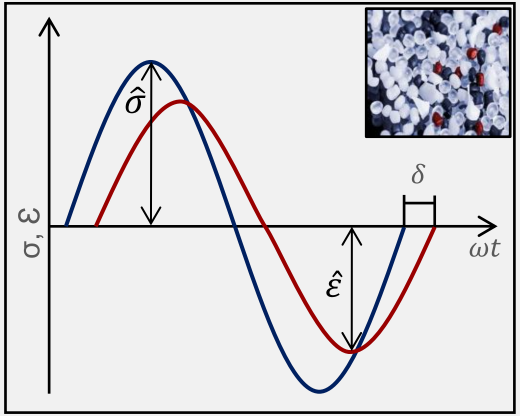
Ideally elastic behavior

Metal



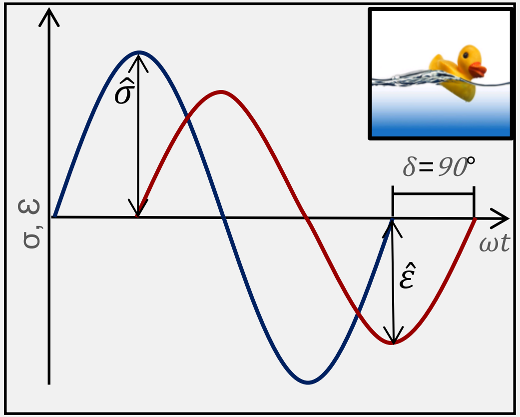
Viscoelastic behavior

Polymer



Ideally viscous behavior

Newtonian Fluids

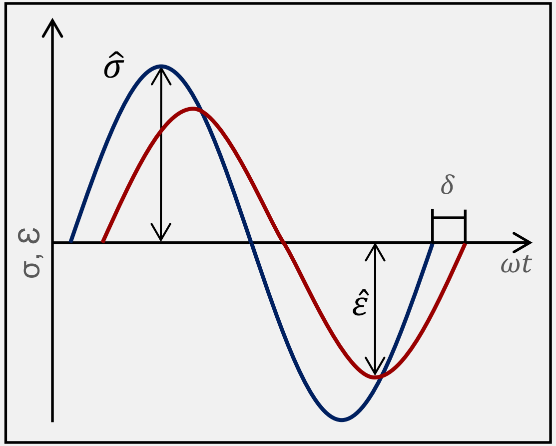


Stress $\sigma(t) = \hat{\sigma} * \sin(\omega t)$

Strain $\varepsilon(t) = \hat{\varepsilon} * \sin(\omega t - \delta)$

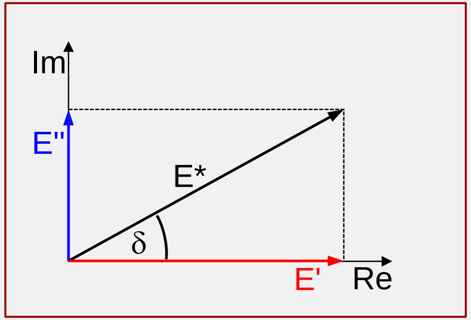
Dynamic Mechanical Analysis

Viscoelastic Moduli



stress
$\sigma(t) = \hat{\sigma} * \sin(\omega t)$

strain
$\varepsilon(t) = \hat{\varepsilon} * \sin(\omega t - \delta)$



$$E^* = E' + iE''$$

$$|E^*| = \frac{\hat{\sigma}}{\hat{\varepsilon}} = \sqrt{E'^2 + E''^2}$$

$$\tan\delta = \frac{E''}{E'}$$

Complex Modulus E* [Pa]

- “Dynamic” modulus

Storage Modulus E’ [Pa]

- **Elastic** contribution
- Stored deformation energy

Loss Modulus E’’ [Pa]

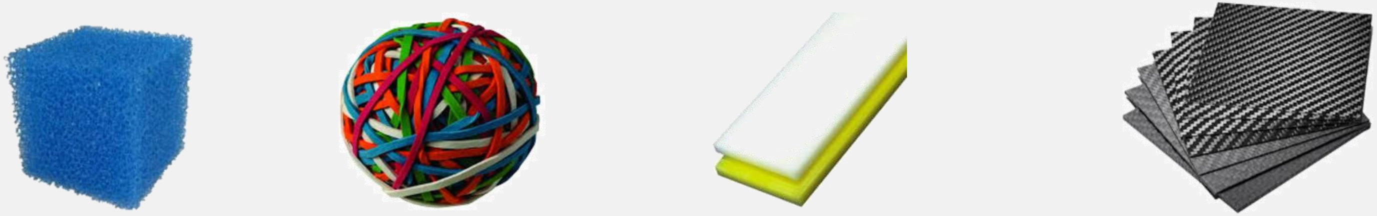
- **Viscous** contribution
- Dissipated deformation energy

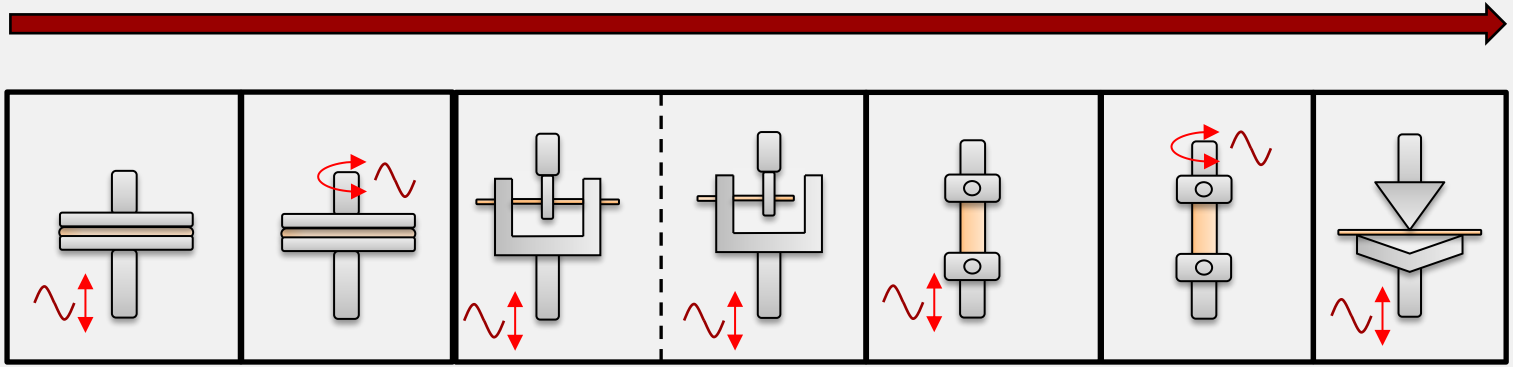
Loss Factor tan δ [-]

- Dimensionless damping factor
- ‘Index of viscoelasticity’

Selection of DMA Deformation Mode

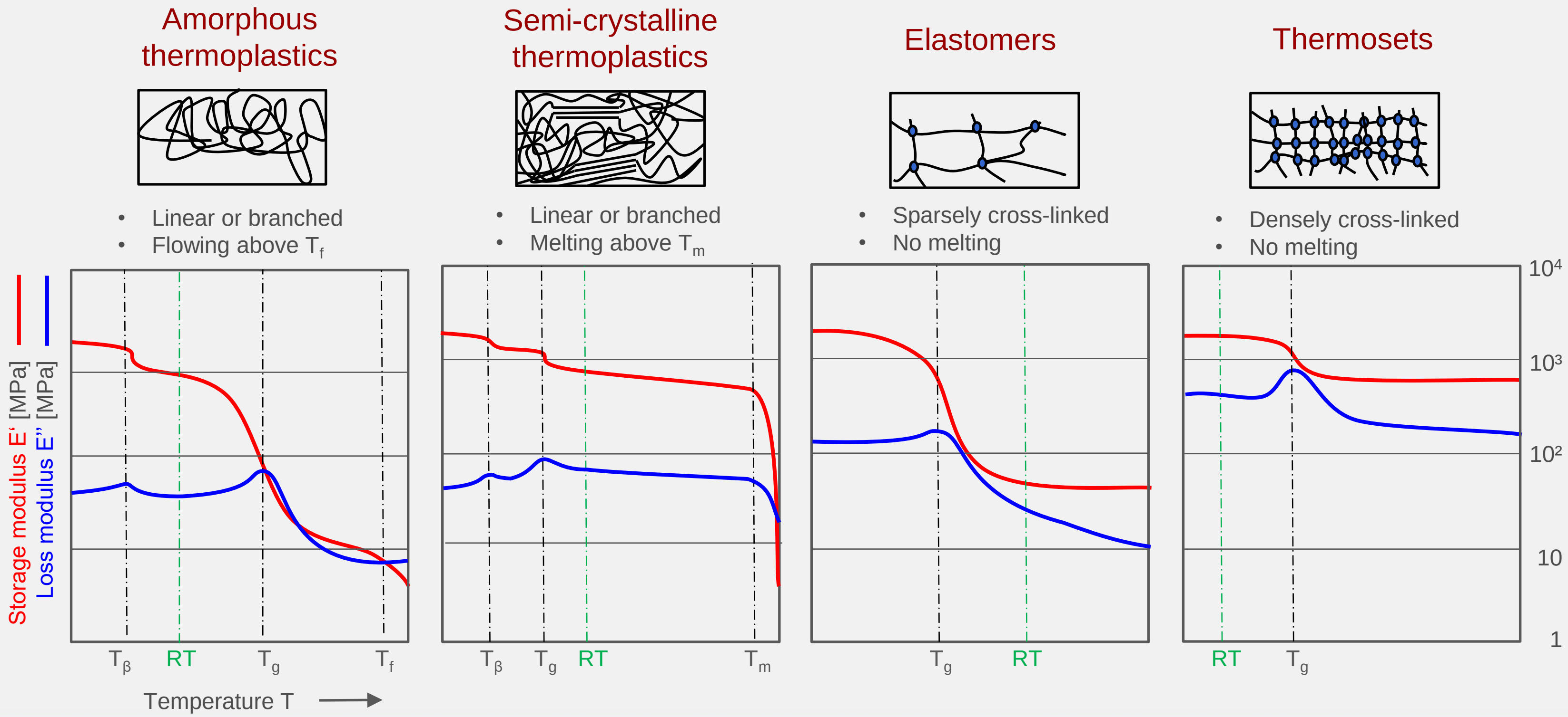
Foams Elastomers Thermoplastics Reinforced Polymers





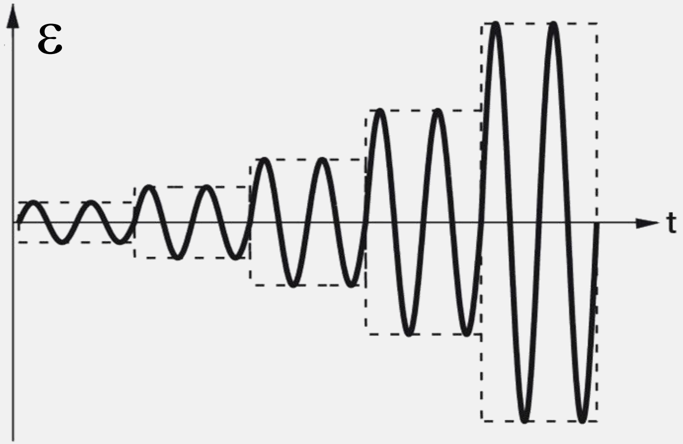
DMA Thermograms of Different Polymers

Overview of Typical Examples

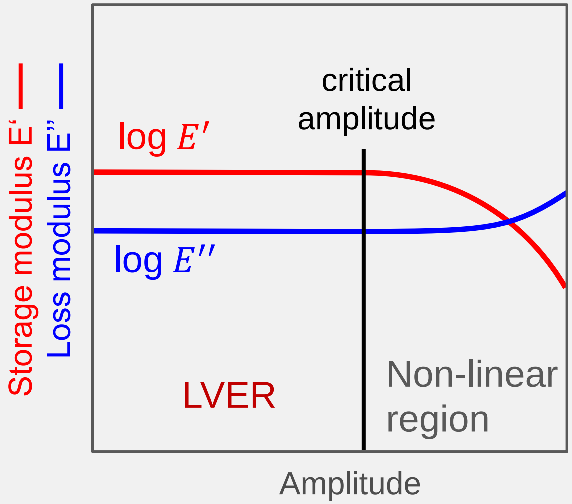


DMA Test Types

Amplitude Sweeps



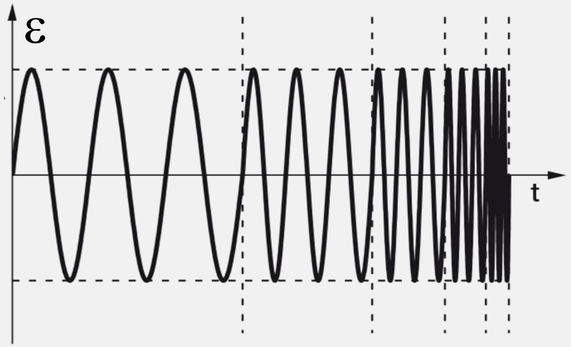
f = const
T = const
$\hat{\epsilon}\,/\,\hat{\sigma}$ = var.



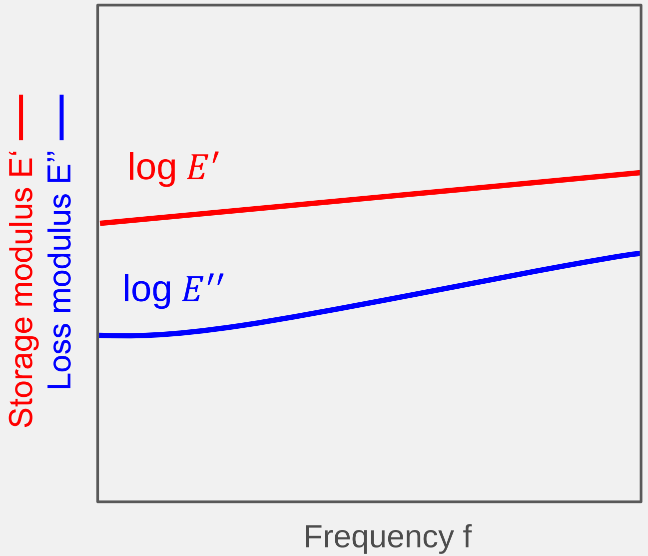
Linear-viscoelastic region (LVER)

DMA Test Types

Frequency Sweeps

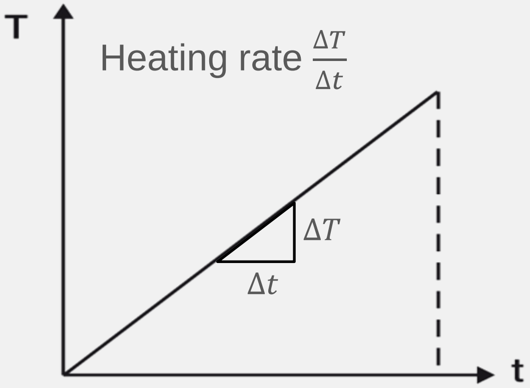


T = const.
F = var.
$\hat{\epsilon}$ = const. or $\hat{\sigma}$ = const.

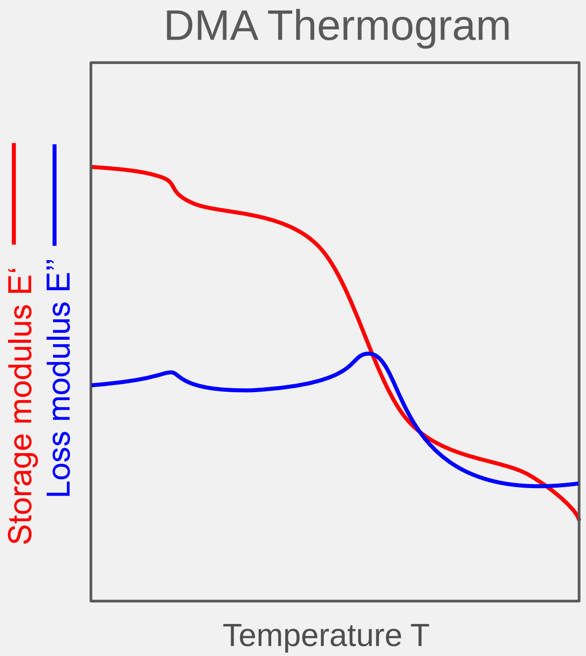


DMA Test Types

Temperature Ramps



f = const. (typical: 1 Hz)
$\hat{\epsilon}$ within LVER
T = var. (const. heating rate)



DMA Test Types

Further Possibilities

Time-Temperature Superposition

- to predict viscoelastic properties over a very wide range of frequencies

Time Sweeps

- to investigate time-dependent processes (e.g. curing, degradation)

Humidity Sweeps

- to investigate viscoelastic behavior as a function of relative humidity

Immersion Tests

- to monitor viscoelastic properties of a sample while immersed in liquid media

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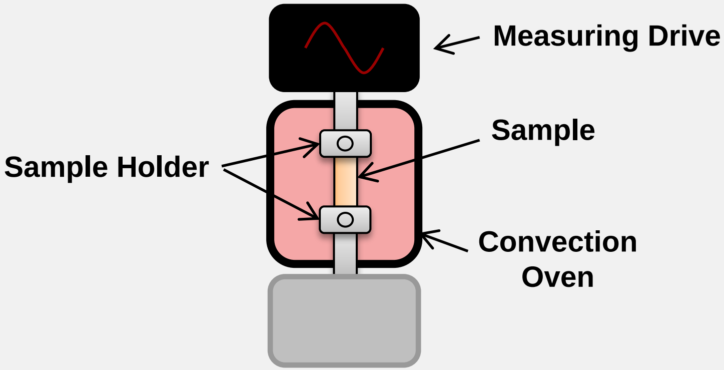
MCR 702 MultiDrive

UNIQUE DESIGN CONCEPT AND FEATURES

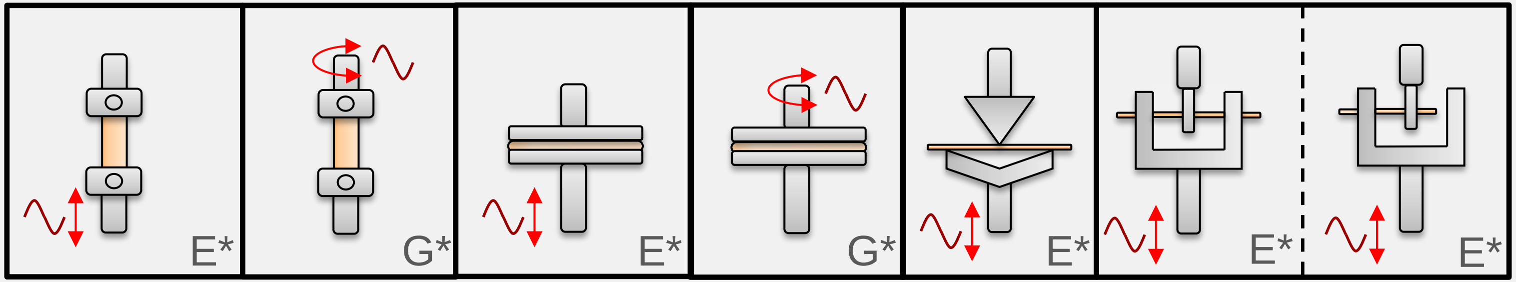
Dynamic Mechanical Analysis

Instrumentation

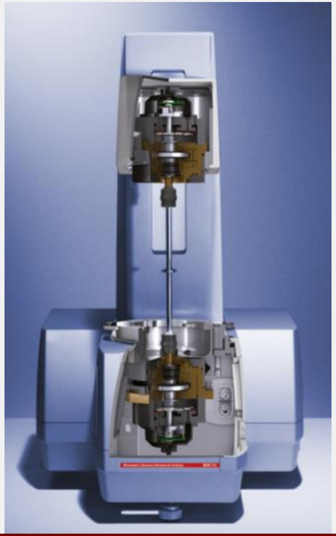


Anton Paar MCR 702 MultiDrive

DMA Deformation Modes

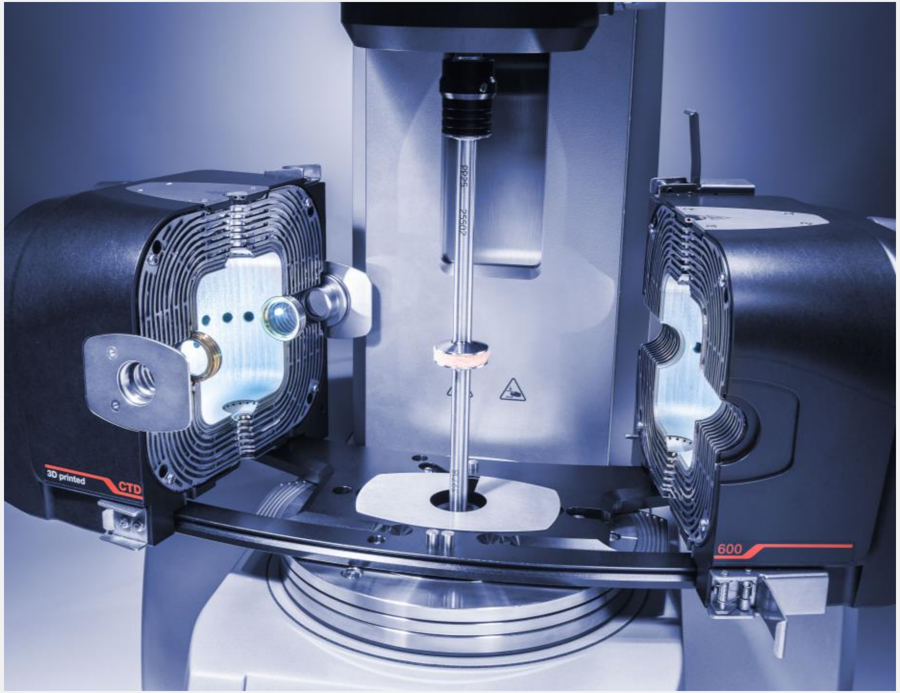


MCR 702 MultiDrive – DMA and more

TwinDrive rheometer	Single-drive rheometer	Dynamic mechanical analyzer
		

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

MCR 702 MultiDrive – CTD 600 MultiDrive Ready

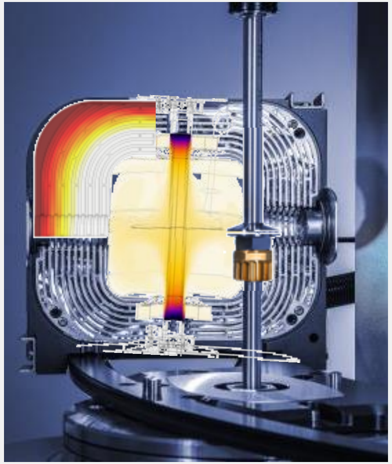


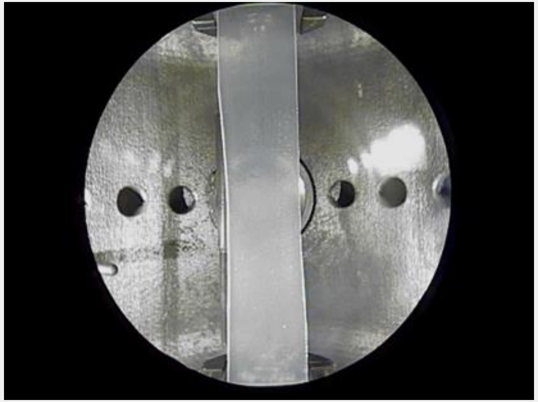
Electrically Heated Convection Oven

- State-of-the-art temperature control due to innovative 3D metal printing technology.
- Homogenous temperature distribution and stable temperature control for all measuring systems.
- Extensive temperature range -160 to 600 °C
- Low temperature options with LN_2 or gas chiller
- Integrated sample illumination
- Suitable for all measuring systems (DMA, Shear, Extensional)

MCR 702 MultiDrive – CTD 600 MultiDrive Ready

T-Gradient Minimization by CFD Simulations



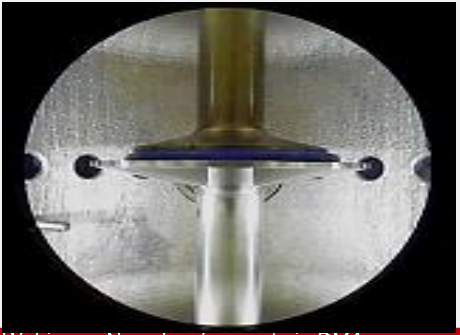


- 3D printed parts (SLM) enable perfectly guided gas flow.
- Minimization of temperature gradients in the sample.
- CFD-optimized design for lowest possible temperature gradients within the sample
- Visualization with camera possible.

CTD600 - DigiEye

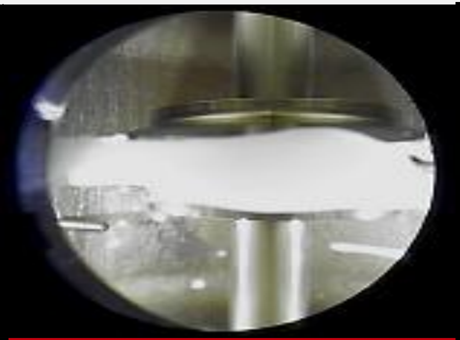
- Field of view ≈ 50 mm diameter
- Compatible with all measuring geometries
- Observation of effects like edge fracture, sagging, stringing, necking, optically visible phase transitions, degradation, gap emptying and overfilling
- Pictures and videos can be synchronized with rheological data.

Gap overfilling in a PP system

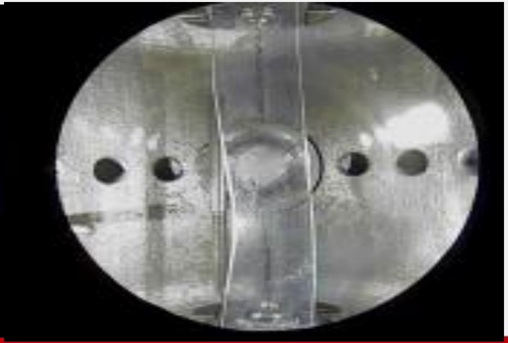


Stringing in a tack test

Gap emptying in a flow test

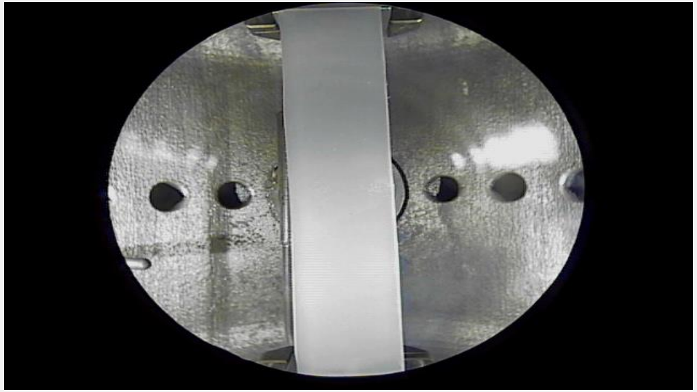


Sagging in a DMA torsion test



CTD600 - DigiEye

Heating Rate: 3.0°C/min



Semi-Crystalline Polyethylene

Opaque at low temperatures ($T < T_m$)
Transparent at high temperatures ($T > T_m$)
Temperature ramp from 70°C to 125°C

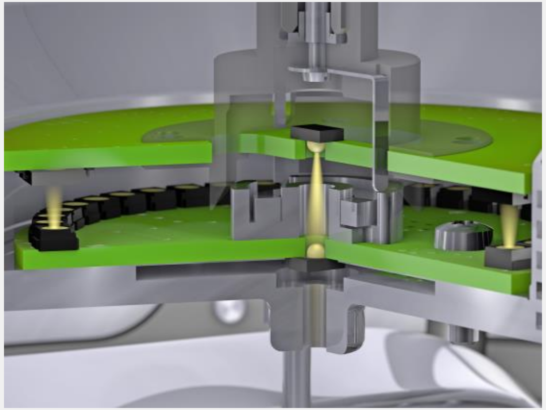
SRF measuring geometry

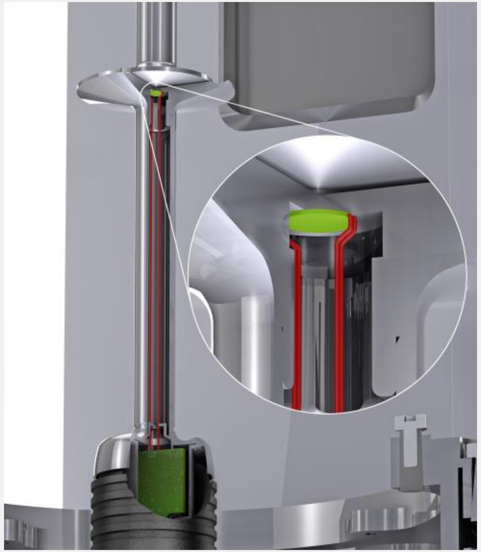
- Homogenous heating of the sample
- Homogenous temperature distribution within the sample, even at higher heating rates

MCR 702 MultiDrive – DMA Measuring Systems

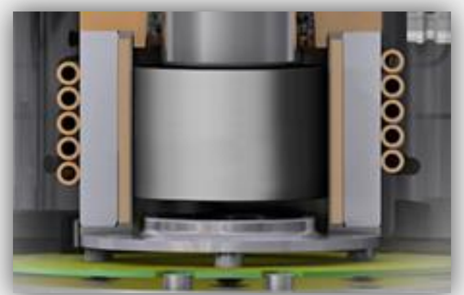
Optoelectronic technology for most precise temperature measurements

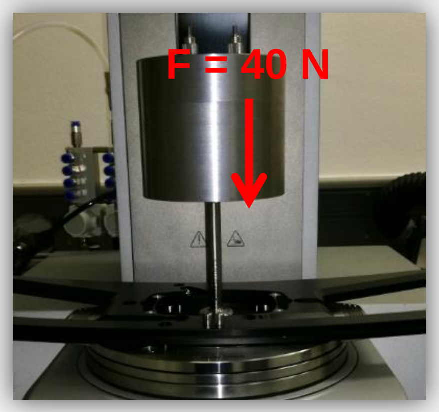
- Contact-free data and energy transfer between motor and moving measuring system.
- Based on light emission with LED and photoelectric effect using photodiodes.
- No impact on torque sensitivity in comparison to contact free transmission technologies based on induction and disturbing magnetic fields.
- Patent proposal already submitted.

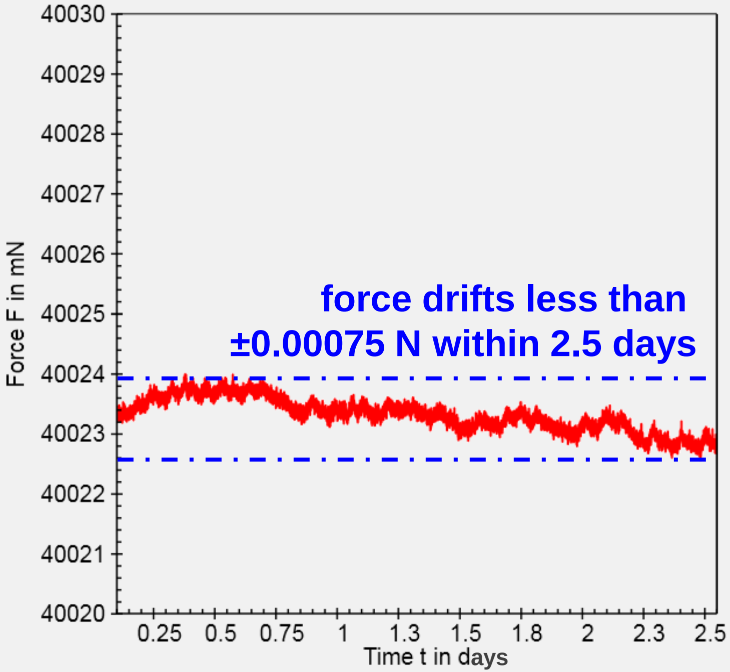




MCR 702 MultiDrive– Zero Drift in Force Measurement







Drift-free long term **creep tests possible with the Linear Drive**!

MCR 702 MultiDrive – Error Proofing

Ease of Use

Quick Connect Coupling:

- Easy Fitting of Measuring Systems.
- Ensures fast, convenient system changes without the use of a screwing mechanism (no tools required!).

ToolMaster™ :

- Transponder chips in all accessory control cables and in the measuring systems contain all relevant data (such as name, type, geometrical dimensions, factors necessary for calculations, serial number etc.,).
- No more errors due to wrong measuring system selection.

Zero Gap and Angle Setting

- Fully automatic procedure is based on high precision lift motor (stepper motor) and angular movement of the upper rotational measuring drive.
- Highest precision, perfect alignment every time.
- No zero-gap needed after removal for cleaning.

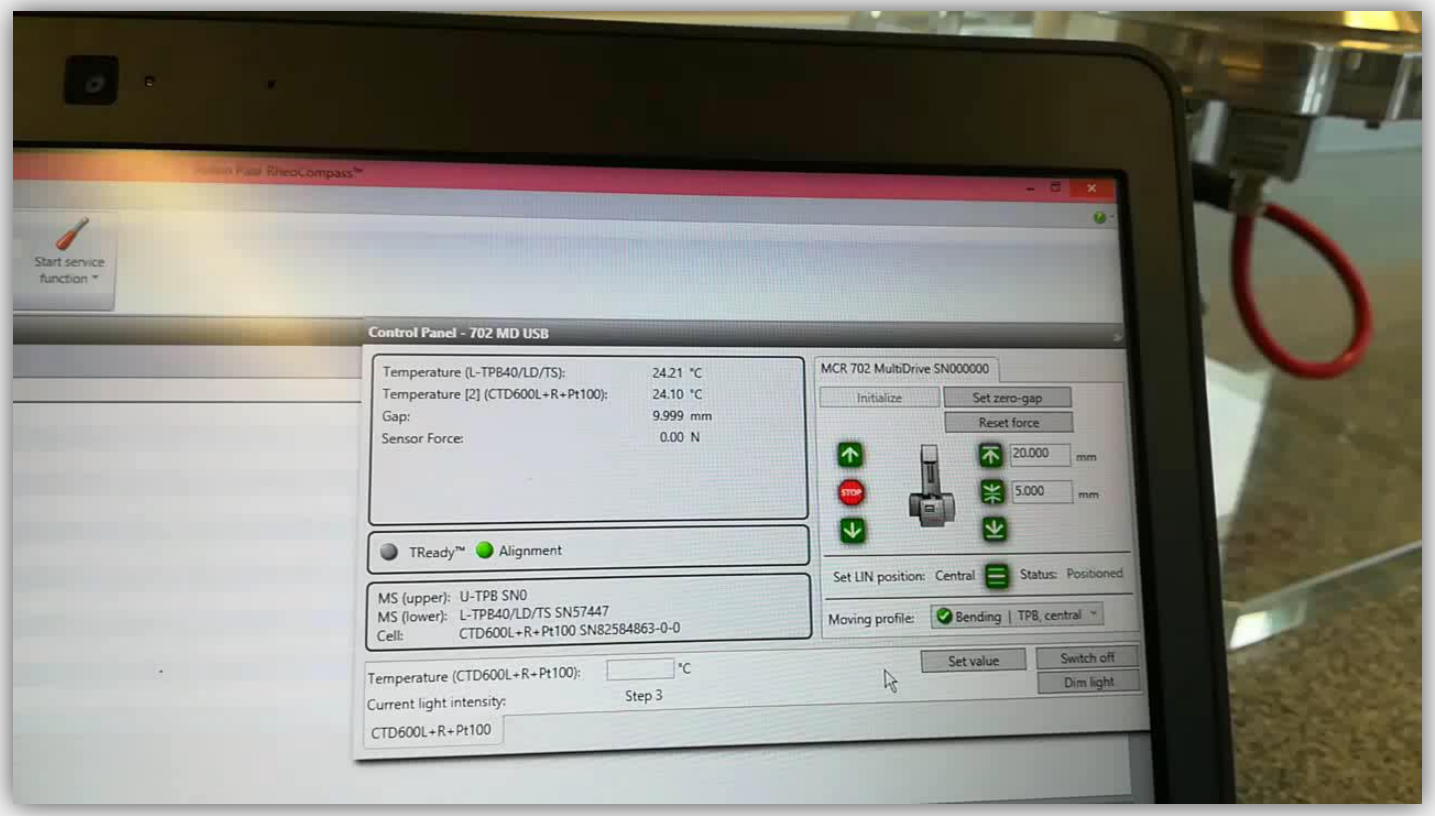
MCR 702 MultiDrive – QuickConnect Coupling

QuickConnect Coupling

Easy Fitting of Measuring Systems

- One-hand connection of measuring systems possible
- Ensures fast, convenient system changes without the use of a screwing mechanism (no tools required!)
- Integrated Toolmaster™ functionality
- Highest precision, perfect alignment every time
- No zero-gap needed after removal for cleaning
- Available for both upper and lower drive unit
- Part of the inherent MCR error proofing

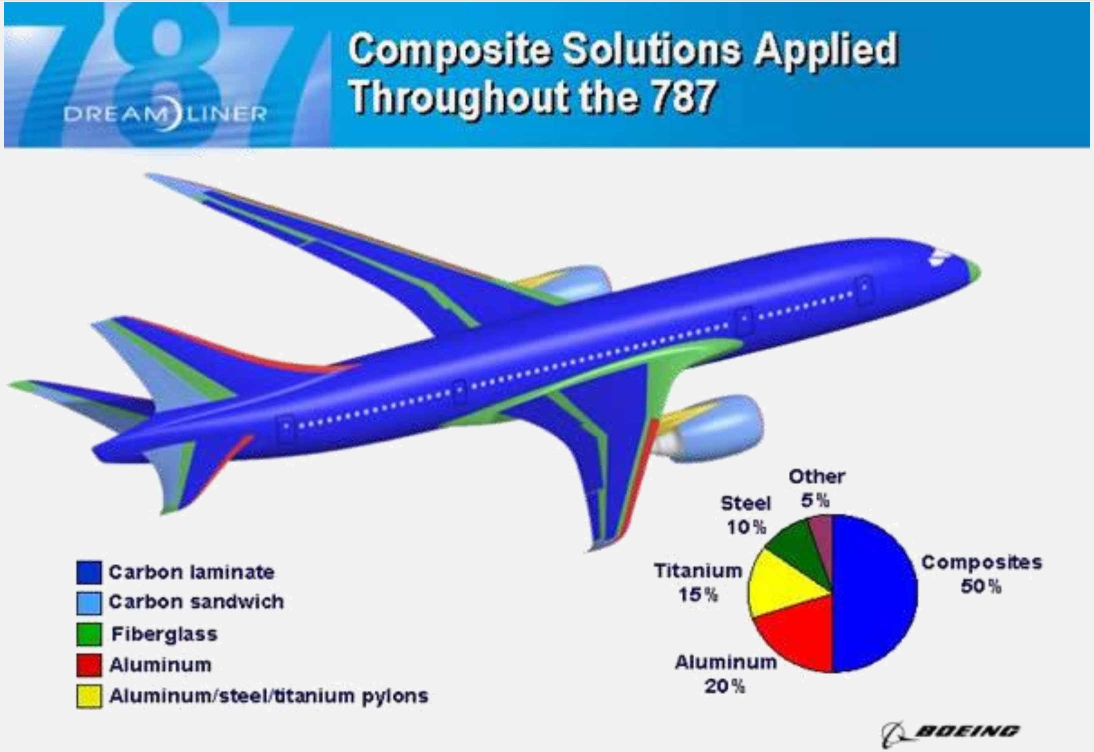
MCR 702 MultiDrive – Zero Angle Setting



MCR 702 MultiDrive in the Composite Industry

From the **Rheology** of an uncured RTM6 Epoxy Resin to **the Dynamic Mechanical Analysis** of the cured component

Applications: Composites



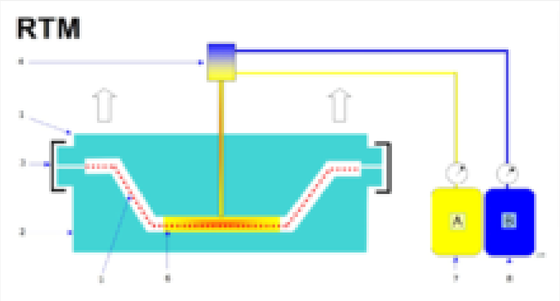
Resin Transfer Molding (RTM)

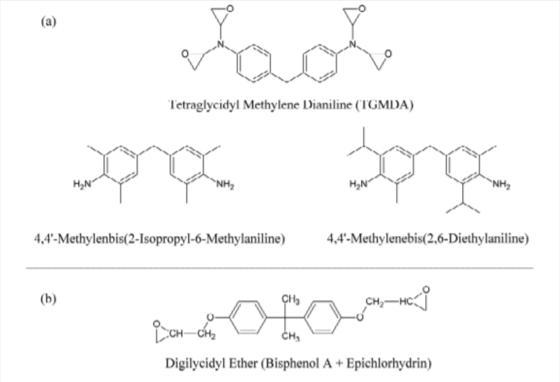
Sample: Epoxy matrix RTM 6

• RTM is based on a closed-mold process that has shown promise during last several years for manufacturing high performance composite.

•In this context, the epoxy resin **RTM6** is largely used in the manufacturing of carbon fiber-reinforced composites for aeronautic and space industries.

• Process starts from a uncured resin- goes through curing to the final cross linked product.





•A commercially available epoxy matrix RTM6

Capturing the full story of Epoxy production

Anton Paar

Rheology

-- Investigate time dependent flow properties.

-- Study macro-kinetics of the cure reaction.

-- Study the effect of the curing parameters on the cross-linking density

DMA

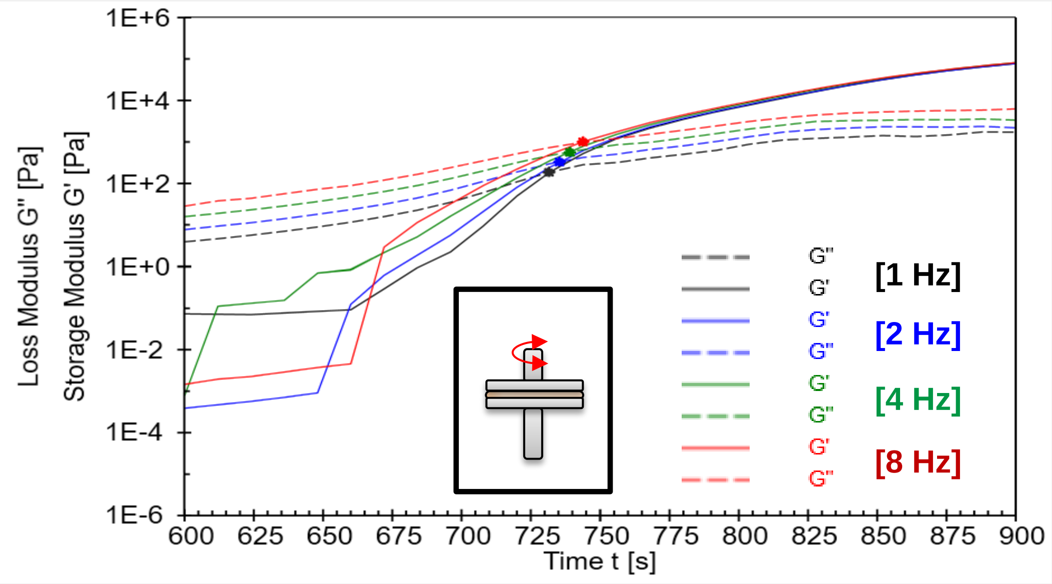
-- Effect of curing on final cured product

-- Determine Moduli (both in axial and torsional modes)

-- Determine Glass transition temperature.

Rheology: Probing RTM6 Curing

Multiwave Rheometry: Gel-point determination



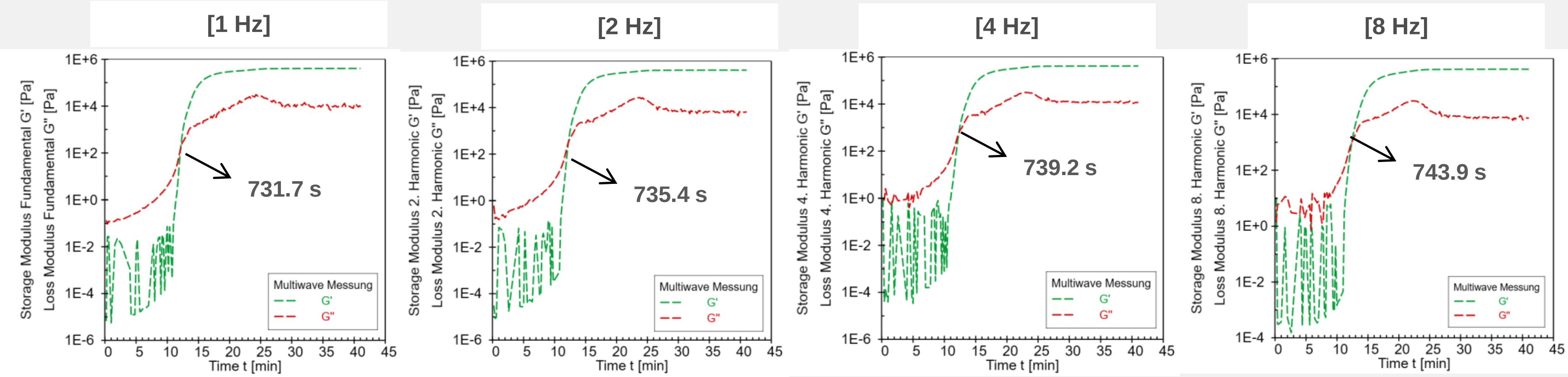
Experiment details:

- Peltier plate and hood used.
- Disposable parallel plates used.
- Temp=180 °C
- Dynamic Multiwave test used.

- The classical crossover method used to determine the gel-point is frequency and therefore **time-dependent**.
- Gel-point is strictly a material property and therefore is frequency independent.

Rheology: Probing RTM6 Curing

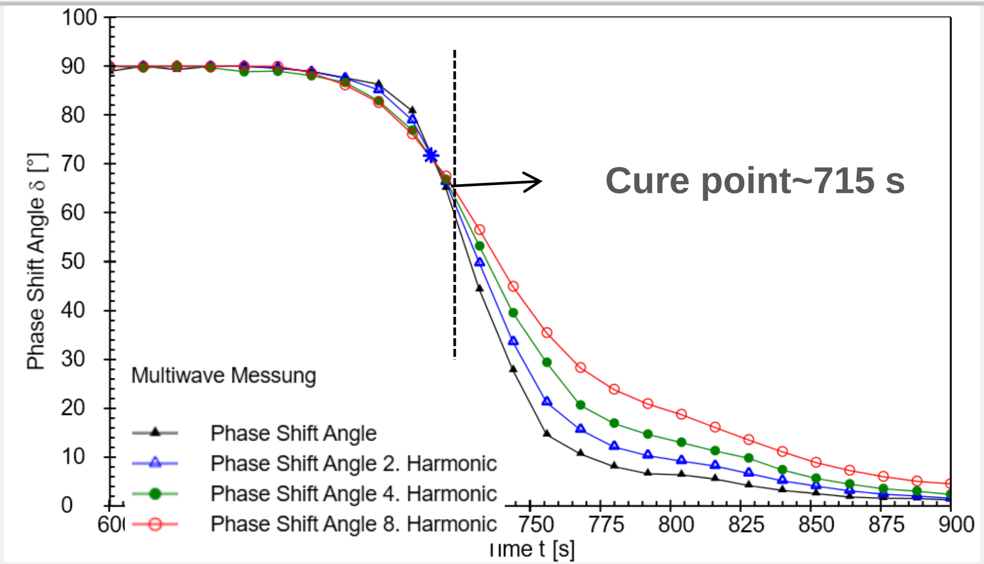
Multiwave Rheometry: Gel-point determination

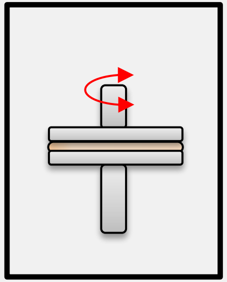


- The time of crossover slightly different for each of the frequencies studied.
- The crossover point approaches the real gel point as the frequency decreases.

Rheology: Probing RTM6 Curing

Multiwave Rheometry: Gel-point determination using the Winter-Chambon Criterion

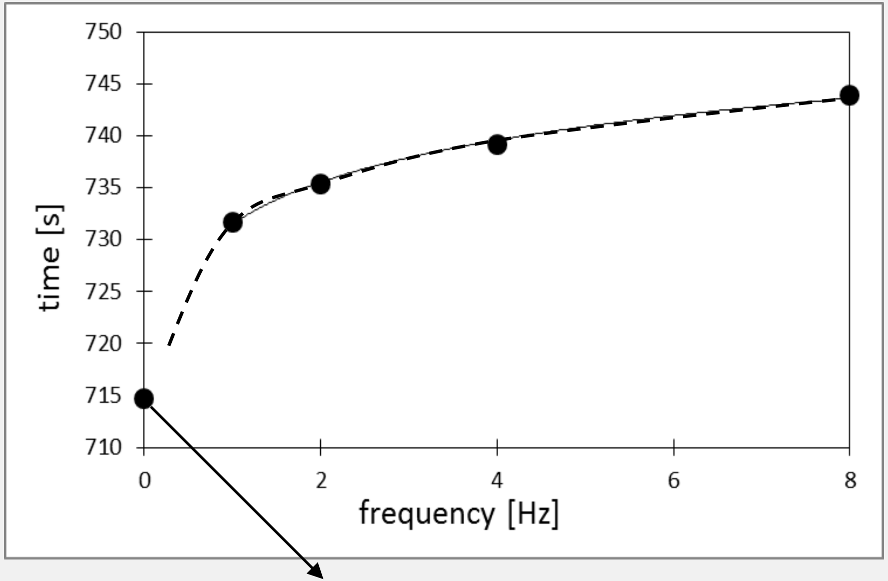




- Winter-Chambon criterion: $G'(\omega) \sim \omega^n$ and $G''(\omega) \sim \omega^n$
- The ratio of $G''(\omega) / G'(\omega)$ should be independent of frequency.
- Using the Winter Chambon criterion the cure point was determined.

Rheology: behavior during the cure reaction

Multiwave Rheometry: Gel-point determination using the Winter-Chambon Criterion

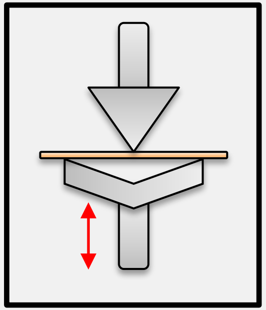


715 s as obtained by Winter-Chambon criterion

- Extrapolation of the crossover point in the limit f → 0 provides a good approximation of the real gel point obtained by Winter-Chambon criterion.
- Multiwave tests are very advantageous for curing tests.

Dynamic Mechanical Analysis

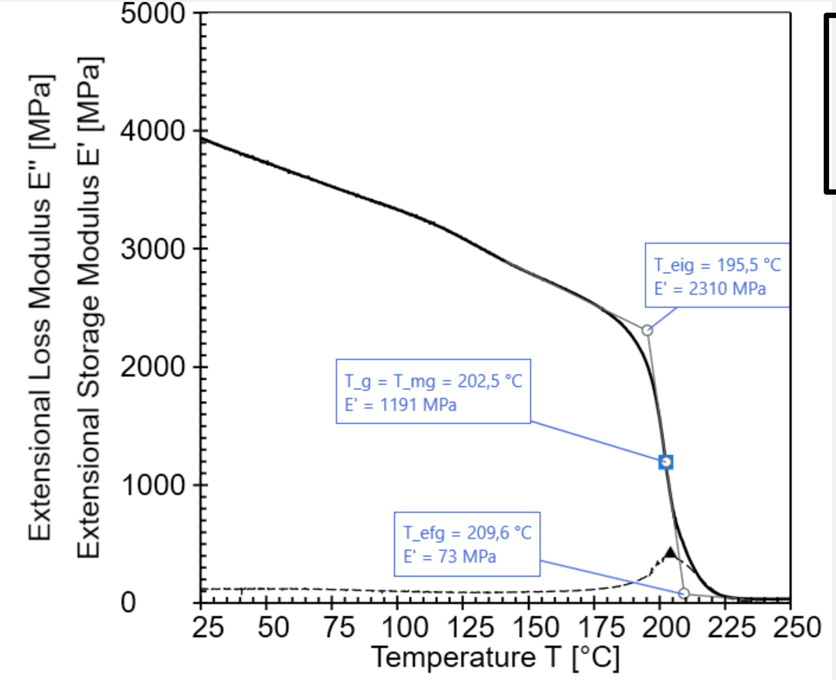
Measurements in three point bending mode

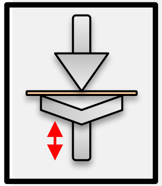


- Test conditions used:
  - Three point bend geomtery: L-TPB40 (free lenght: 40 mm)
  - Sample size: 50 x 10 x 2 mm
  - Static force= 0.5 N
  - Dynamic force = 0.3 N
  - Frequency= 1 Hz
  - Temp 25°C to 250°C
  - Heating rate: 2 °C/min

Dynamic Mechanical Analysis

Measurements in three point bending mode

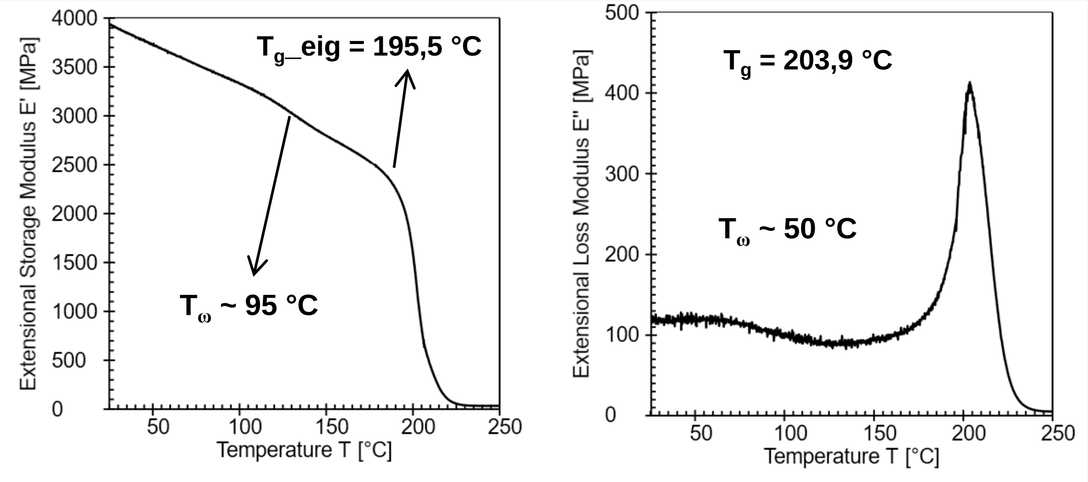




- The glass transition temperature Tg can be evaluated from the temperature-dependent functions of E’ and E” according to different standard norms
- According to the ISO 11357 E' step method, for instance, Tg onset, mid and end temperatures were found to be 195.5 °C, **202.5 °C** and 206.9 °C, respectively
- According to ASTM D4065, D4092, Tg is calculated as the maximum in the loss moduli. Accordingly, Tg = max(E’’) = **203.9 °C**

Dynamic Mechanical Analysis

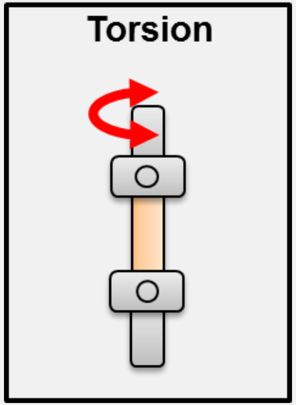
Measurements in three point bending mode



- Sub-glass transition (**T_ω ~95 °C**) can be identified from a small distinct drop.
- E'' thermograph shows a wide dissipation peak at a temperature between 50 and 100 °C.
- Sub-glass transition relaxation has been attributed to molecular arrangements resulting from moisture absorption or motions of the p-phenylene groups in the sample.
- DMA much more sensitive than TMA or DSC.

Dynamic Mechanical Analysis

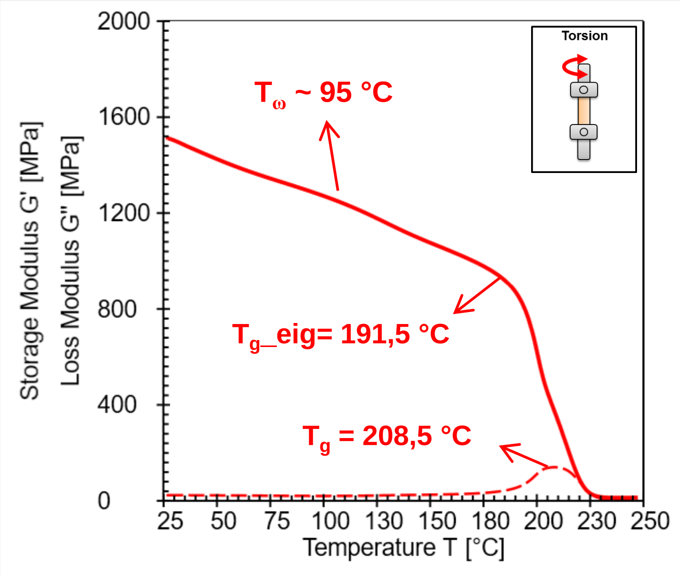
Measurements in Torsion Mode

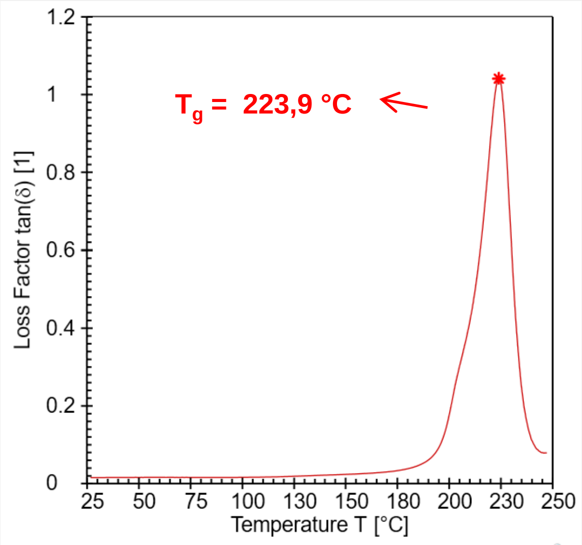


- Test conditions used:
  - SRF 5 (solid rectangular fixture)
  - Sample: 40 x 10 x 1 mm
  - Strain - Deformation = 0.01 %
  - Frequency = 1 Hz
  - Normal force = -0,2 N
  - Temp 25°C to 250°C
  - Heating rate: 2 °C/min

Dynamic Mechanical Analysis

Measurements in Torsion Mode

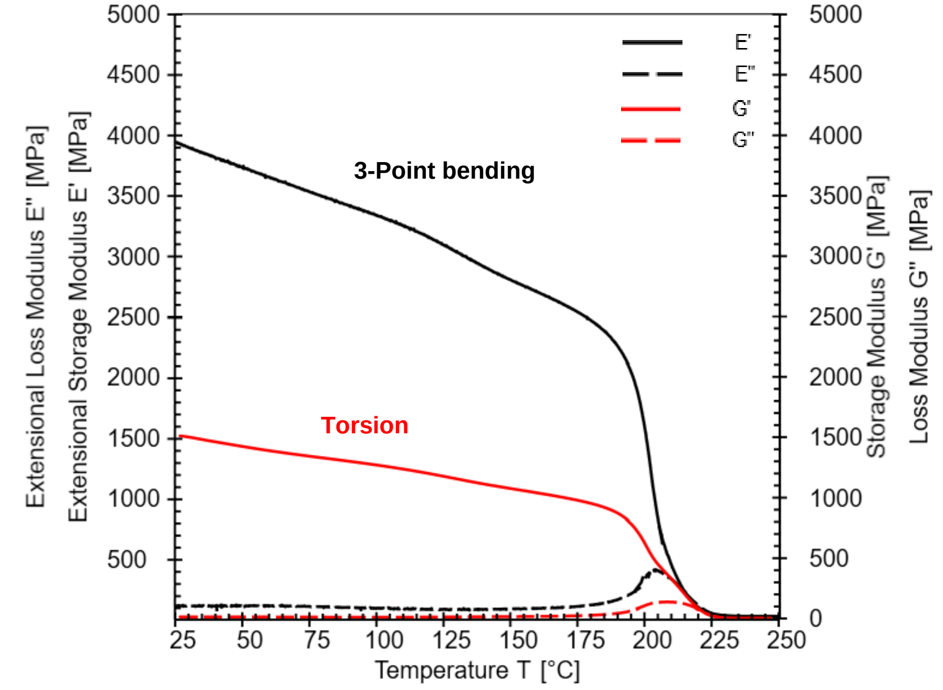


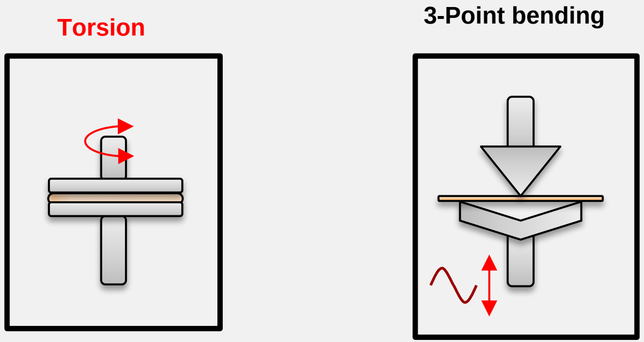


- Glass transition temperature T_g was evaluated according to different criteria.
  - T_g onset according to ISO 11357 = **191.5 °C**
  - T_g according to ASTM D4056 = **208.5 °C**
  - T_g according to ASTM E1640 = **223.9 °C**
- The measurements for the storage modulus are in very good agreement with the Literature.

Dynamic Mechanical Analysis

Comparison between **Torsional** and **Bending** measurements

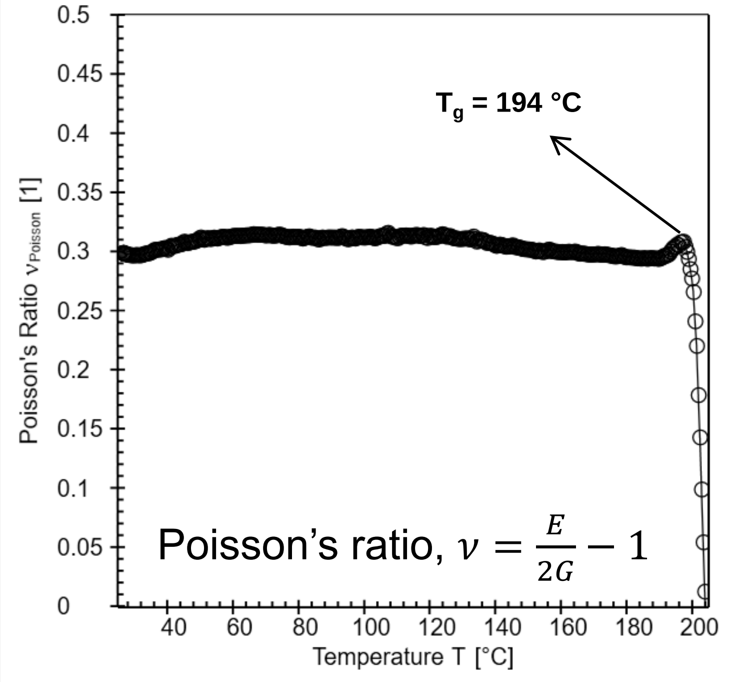




Possibility of conducting DMA measurements in **extension** and in **torsion** within one single device.

Dynamic Mechanical Analysis

Poisson ratio determination from Torsional and Bending measurements



- **Poisson's ratio (ν),** can be defined for an isotropic material as

  $$\nu = \frac{E}{2G} - 1$$

- The abrupt decrease in the Poisson's ratio coincides fairly well with the temperature glass transition (T_g = 194°C)
- The experimentally measured Poisson's ratio for the RTM 6 sample is in very good agreement with other data from literature.
- A simple way to obtain insights about Poisson ratio from two temperature sweeps in torsion and bending modes.
- Generally two devices are needed to do this.

Summary

- Viability of a MCR 702 Multidrive device with different peripherals and unique features to perform rheology and DMA on one device has been shown.
- Capturing the fully “story” of an **epoxy resin RTM6** starting from the evolution of its uncured state (Rheology) up to the DMA of the cured resin was demonstrated.
- The **rheological** study including the polymerization of the uncured resin was studied using a **Multiwave** approach according to Winter-Chambon criteria in order to characterize the gel-point.
- The **DMA** of the cured product was performed with an additional lower linear drive coupled to the MCR 702 Multidrive.
- The linear drive in combination with the EC-Motor permitted us to measured the **Poisson’s ratio** as a function of temperature for the cured epoxy resin.

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