AMADE DAYS

Thermal analysis: application to polymer characterisation

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OUTLINE

1. The GRMT research group

2. Thermal analysis methods

2.1. Diferential thermal analysis: DTA vs DSC
2.2. Thermogravimetry TG.
2.3. Dynamic mechanical analysis DMA
2.4. Rehology
2.5. Thermomechanical analysis TMA
2.6. Dilatometry DIL

3. Numerical calculations

3.1. Kinetics
3.2. Simulating the curing of resins

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The GRMT research group

OUR RESERCH TOPICS

- Characterization and degradation of commercial ceramics.
- **Characterization of polymers.**
- Mechanical alloying.
- Development of amorphous materials and soft magnetic nanomaterials from the synthesis of precursors by rapid solidification and/or mechanical alloying

OUR EQUIPMENT

- Dynamic Mechanical Analysis (DMA): METTLER TOLEDO DMA/SDTA861e
- Thermo-Mechanical Analysis (TMA): SETARAM Setsys Evolution 16
- Differential Scanning Calorimetry (DSC): METTLER TOLEDO DSC822e, and TA INSTRUMENTS Q2000
- Thermogravimetry (TGA): METTLER TOLEDO TGA/DSC 1 and SETARAM Setsys Evolution 16
- FT-IR: spectrometer (Bruker ALPHA II)
- Rehometry: ANTON PAAR

Thermal analysis methods

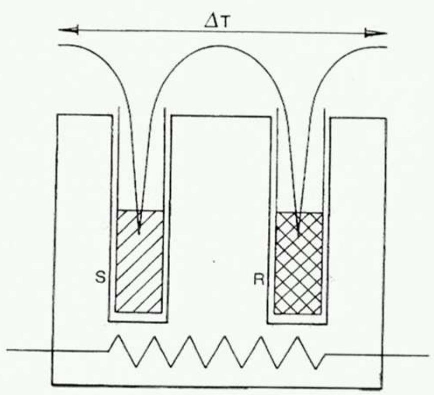
- Thermal analysis (TA): continuous observation of a thermometric property at constant temperature or with a controlled temperature change. This thermometric property can be optical, electrical, magnetic, etc.

- Thermal analysis techniques measure a signal generated in a sample as a function of temperature.

- Signal
  - Heat exchange: DSC & DTA (calorimetry).
  - Dimensional change: TMA & dilatometry.
  - Mass change: thermogravimetry (TG)
  - Evolved gases: EGA
  - Photons emision: thermofluorescence
  - Mechanical excitation: Rehology & DTMA

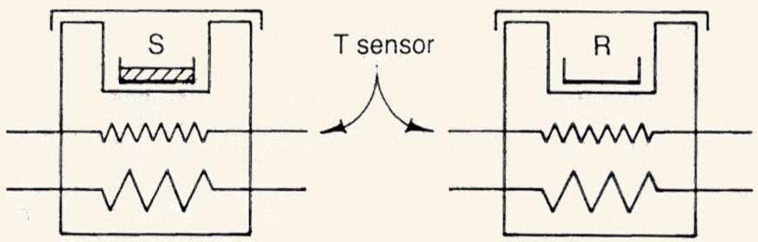
Thermal analysis methods

DTA



- Both the sample and the reference are placed symmetrically inside an furnace so as to ensure **identical heating between the sample and the reference.**
- **The DTA measures the temperature difference (ΔT)** between sample (S) and reference (R) as a function of reference temperature or time.
- **Heat transfer is** basically done by conduction along a certain path and can therefore be **evaluated from the measurement of ΔT**

DSC



- Sample and Reference are isolated in **two independent furnaces**.
- The system supplies a different power to the two independent furnaces so that **the temperature difference between sample and reference remains zero**.
- The DSC signal is the difference between the power supplied to the two furnaces.

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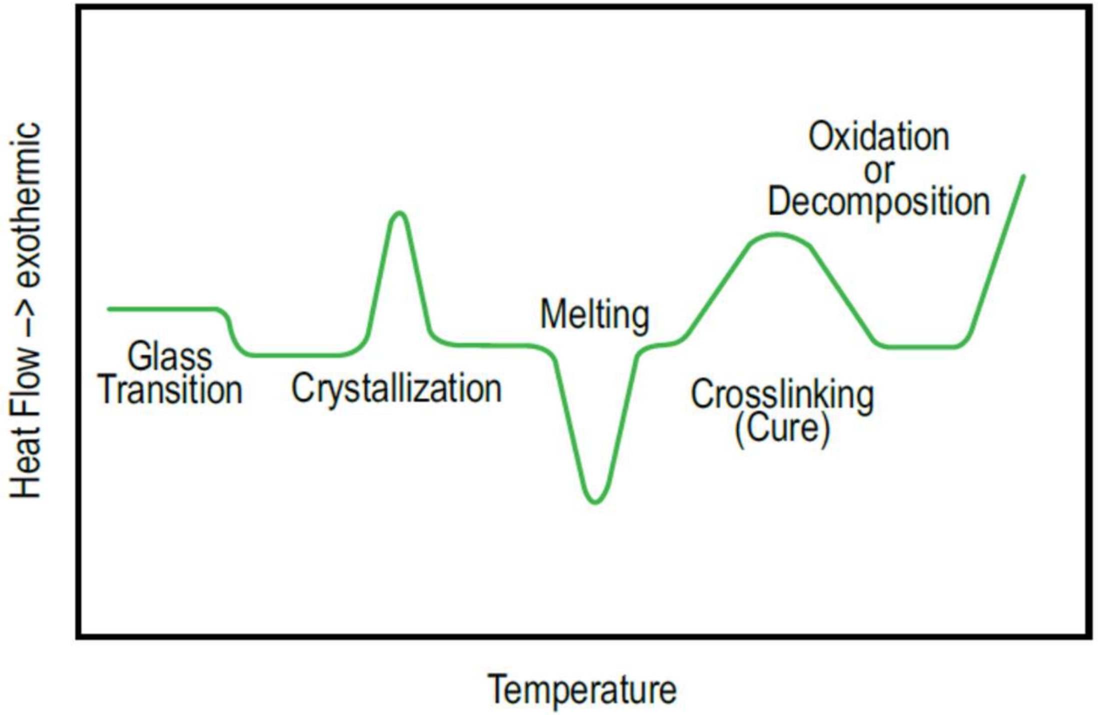
Thermal analysis methods

Differential Thermal Analysis

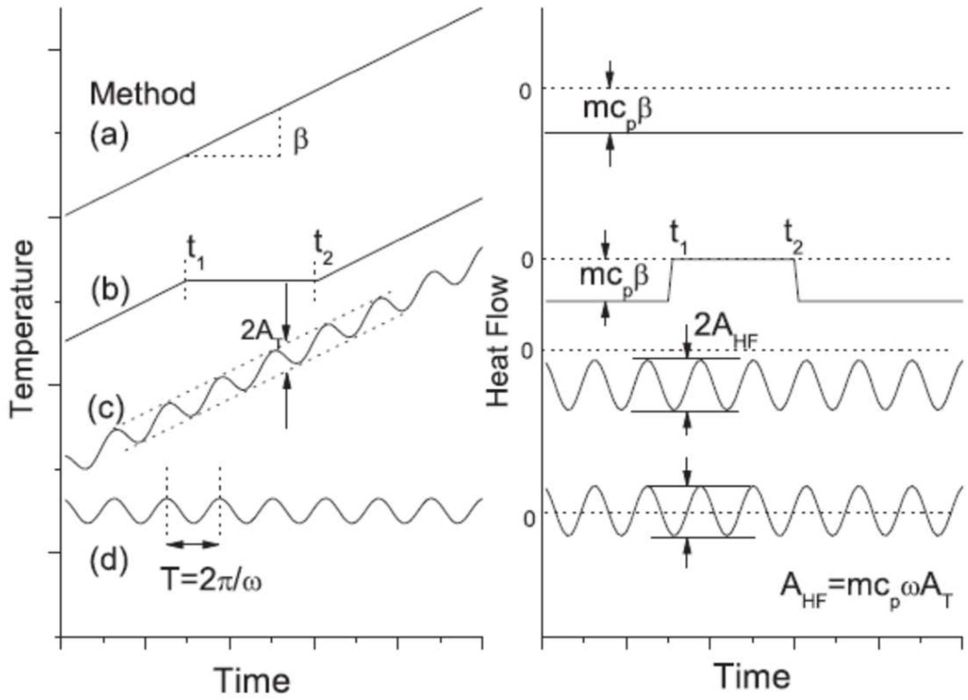


Characterization
Transition temperatures
Curing degree
Reaction enthalpies
Heat capacity
Thermal conductivity

Thermal analysis methods

Differential Thermal Analysis

$$Signal = [W] = \frac{[J]}{[s]} = mc_e\beta = \frac{[J]\cancel{[K]}\cancel{[kg]}}{\cancel{[K]}\cancel{[Kg]}[s]}$$



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Thermal analysis methods

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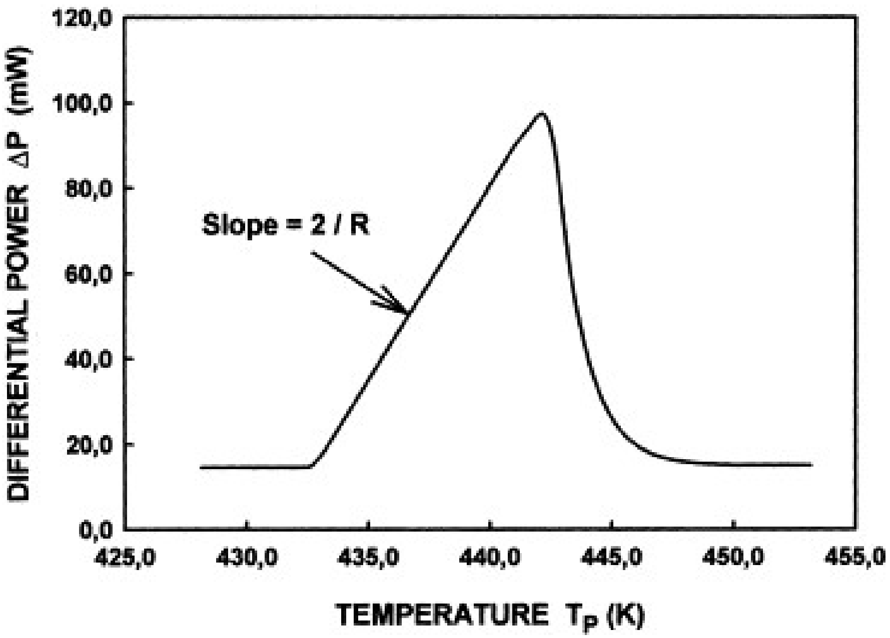
Differential Thermal Analysis



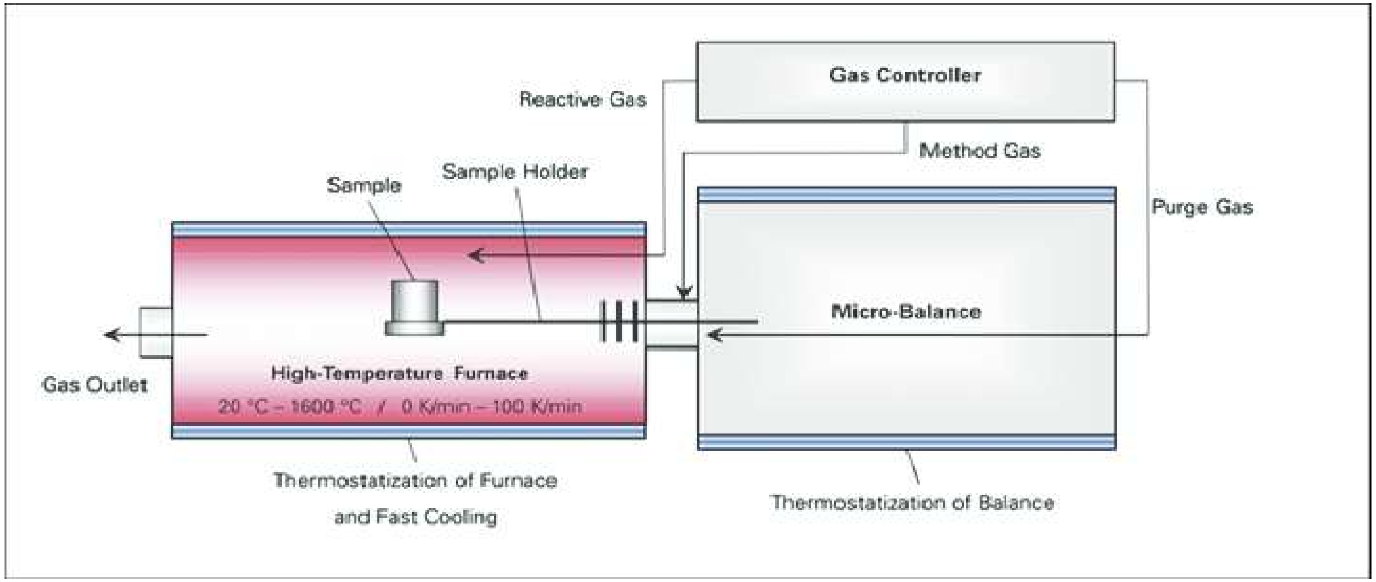
$$R = Rs + R_1 + R_2$$

$$Rs = LsAs\lambda_s$$

Thermal analysis methods

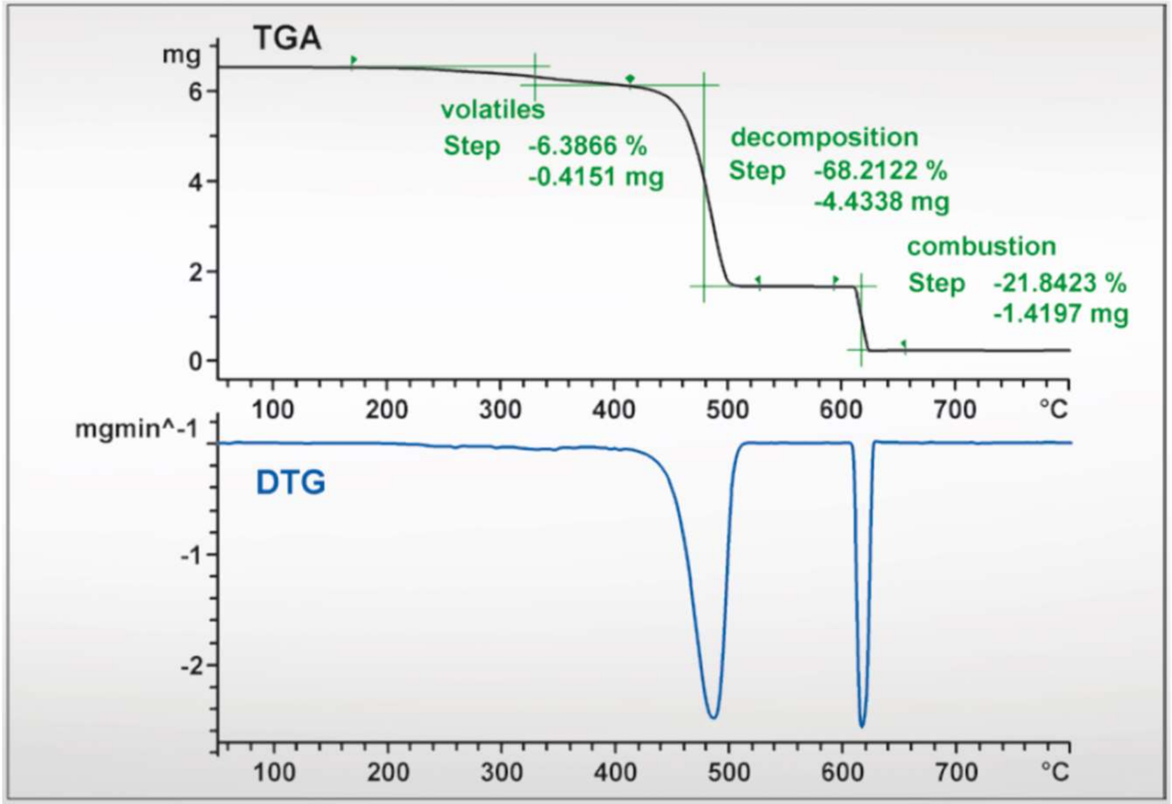
Thermogravimetry

- **<u>mass</u>** of a sample is measured **<u>over time</u>** as the temperature changes
- can be used to **<u>evaluate the thermal stability of a material</u>**

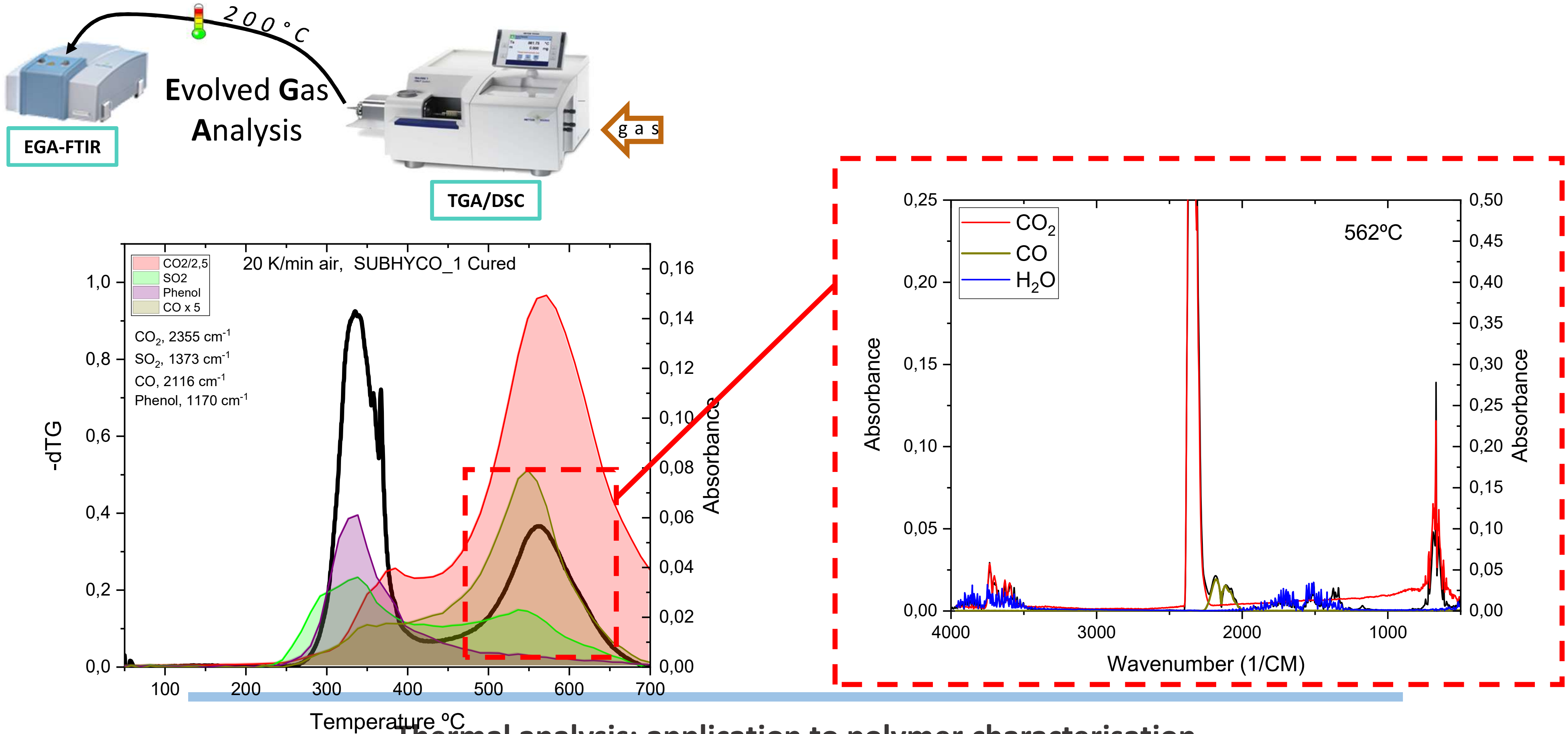


Thermal analysis methods

Thermogravimetry



Thermal analysis methods



Thermal analysis: application to polymer characterisation

Thermal analysis methods

Dynamic Mechanical Analyzer (DMA)

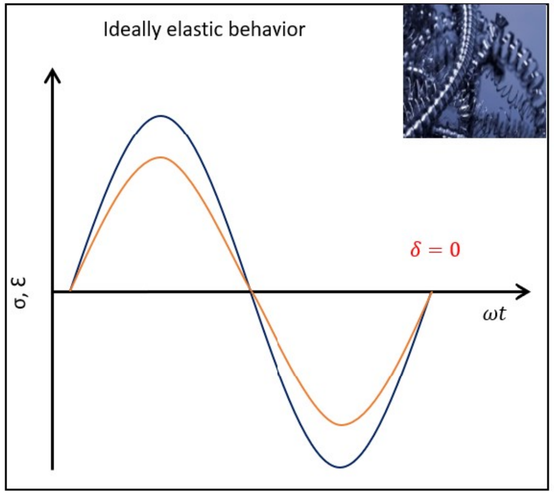
- **Evaluation of complex modulus**: it is important to unravel the viscoelastic properties of a solid

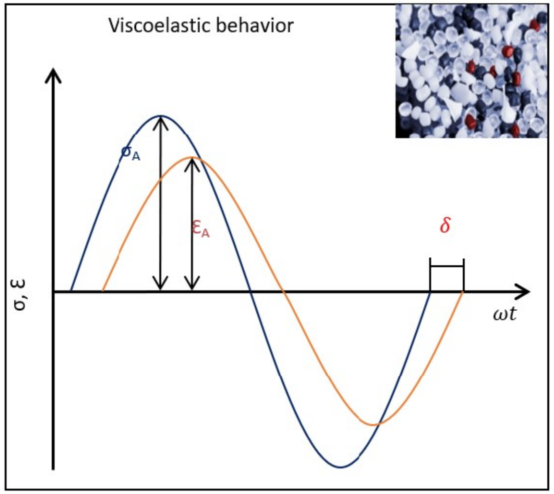
- It can give information about the major and minor (secondary and tertiary) **phase transitions in materials such as polymers**.

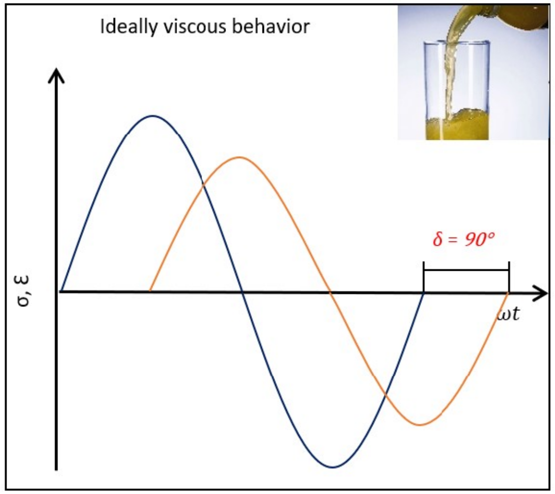
- Those minor transitions are quite difficult to probe with other methods such as differential scanning calorimetry (DSC). mechanical changes are more pronounced than changes in the heat capacity

Basic working principle

A sinusoidal oscillatory force is applied to the material and the resulting deformation or strain is measured in response to the applied stress in the linear viscoelastic region of the material.







$$\varepsilon(t) = \varepsilon_0 \sin(\omega t)$$
$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$

Rehometer

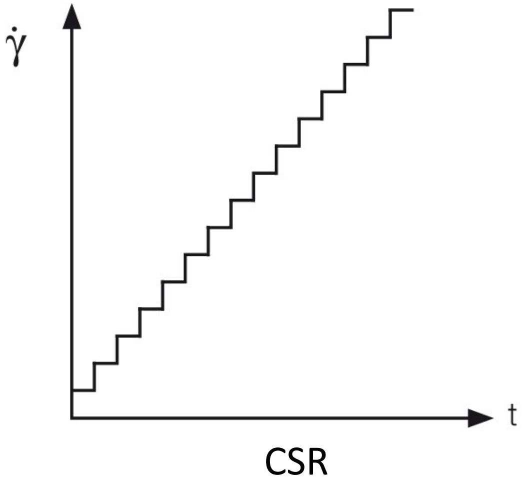
Rheology is used to describe and assess the deformation and flow behavior of materials

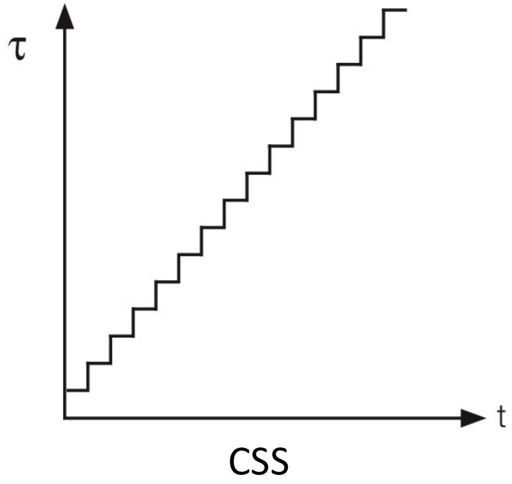
Rotational tests

- controlled shear rate (CSR): Simulates processes that are dependent on flow velocity or volume flow rate
- controlled shear stress (CSS): Simulate force-dependent applications.

$$\eta = \frac{\tau}{\dot{\gamma}}$$

$$\dot{\gamma} = \frac{v}{h}$$





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Thermal analysis methods

Thermomechanical analysis (TMA)

- Is the term applied to dilatometry carried out **under tension or load**

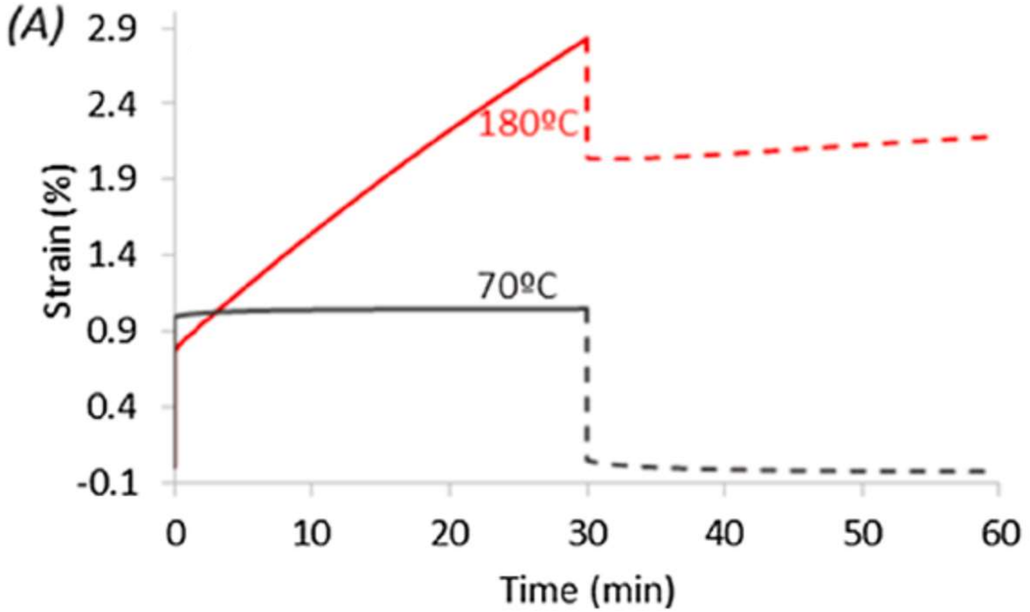
Dilatometry (DIL)

- Dilatometry is **often referred to as zero force TMA**

- When a material is exposed to temperature changes it shows a **variation in its dimension**:

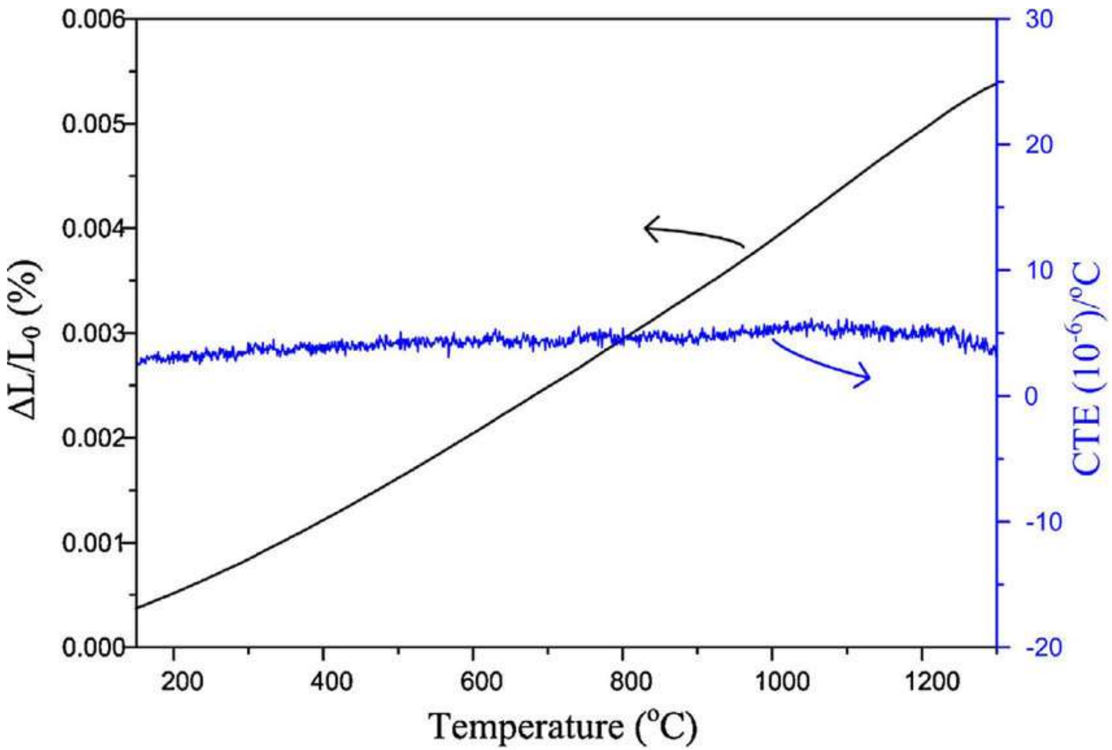
    - thermal expansion
    - phase transition
    - sintering
    - curing

Creep describes a time and temperature dependent plastic deformation under a constant force.



Thermal analysis methods

Coefficient of thermal expansion (CTE) and thermal expansion rate (L/L0) with temperature from dilatometric measurements



Numerical calculations

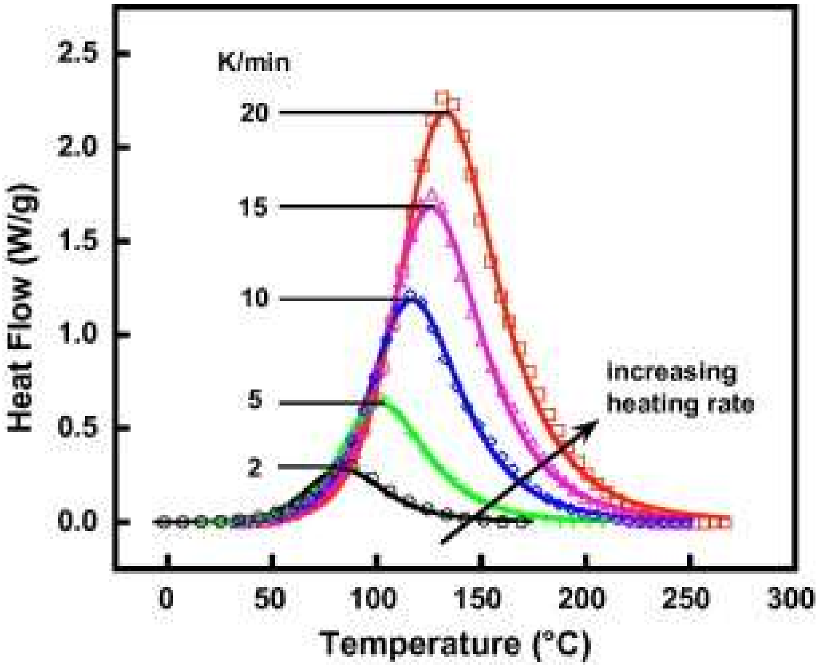
Kinetic parameters

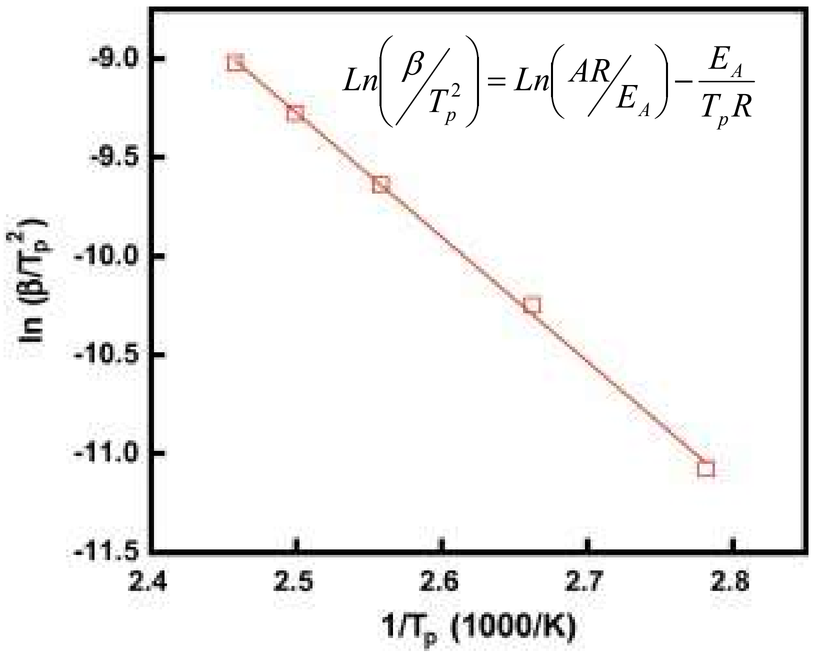
Many processes such as resin curing or its decomposition are **thermally activated**

The reaction rate dα/dt depends on the temperature k(T), which usually follows an **Arrhenius dependecy**.

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

$$k(T) = Ae^{-\frac{E_A}{k_B T}}$$





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Numerical calculations

$$\rho c \frac{\partial T}{\partial t} = \lambda \Delta T - \rho q \frac{\partial \alpha}{\partial t}$$

$$\frac{\partial \alpha}{\partial t} = A e^{-E_A/RT}(1-\alpha)$$