Company Logo

K. N. Toosi University of Technology

Faculty of Materials Science and Engineering

# Materials Characterization Methods

## Twelfth Session
## (Thermal Analysis)

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# Thermal Analysis

## Content

1. Introduction
2. Methods
   - 2.1. DSC
   - 2.2. TGA
   - 2.3. STA
   - 2.4. DTA
   - 2.5. DMA
   - 2.6. TMA

# Thermal Analysis

## 1. Introduction

# Thermal Analysis

## 1. Introduction

## Thermal Analysis (TA)

TA is a group of analytical techniques that measure properties or properties changes of materials as a function of temperature.

Techniques in which a physical (thermal) property of a substance is measured as a function of temperature while the substance is subjected to a predetermined temperature profile.

**THERMAL ANALYSIS IS f (T)**

# Thermal Analysis

## 1. Introduction

**When matter is heated:**

**1) Physical Changes:**

- ✓ Phase change such as melting Vaporization,
- ✓ Crystallization,
- ✓ Transition between crystal structures,
- ✓ Change in microstructures in metal alloys & polymers

**2) Chemical Changes:**

- ✓ Include reaction to form new products,
- ✓ Oxidation,
- ✓ Decomposition,
- ✓ Dehydration,
- ✓ Corrosion

# Thermal Analysis

## 1. Introduction

**Thermal analysis**

**Measure**

**Mass, Volume, Temperature, Heat, Pressure, …**

**without Changing in Composition**

# Thermal Analysis

## 1. Introduction

Most TA instruments use samples with masses in the **1-20 mg** range which are placed in **pans or crucibles** (typically made from metal or a ceramic) for analysis. The plot of the measured property as a function of temperature is sometimes called a '**thermogram**'.

**Atmospheric control** is often an important factor in many TA experiments and the use of **inert** (such as helium or nitrogen) or **oxidative** (air) **atmospheres** can have a significant impact on the results obtained. In addition to the reactive nature of the atmosphere, differences in thermal conductivity and density can also have an effect.

# Thermal Analysis

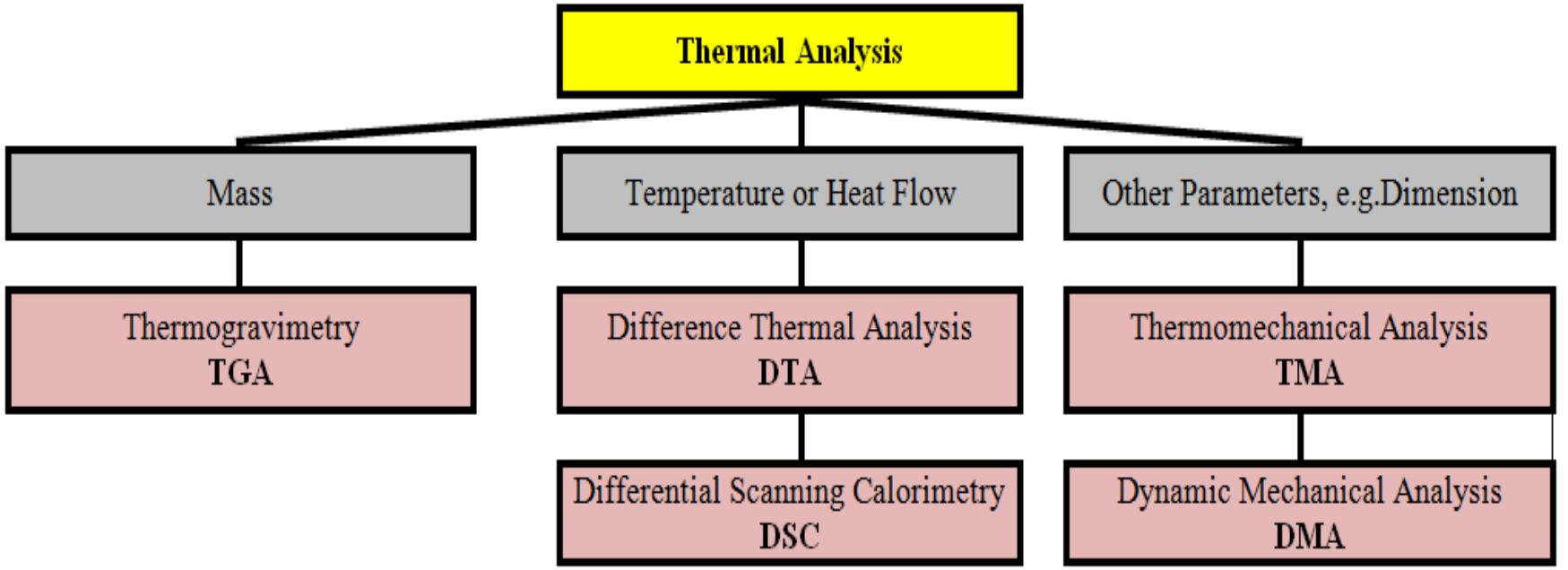
## 2. Methods

# Thermal Analysis

## 2. Methods

**Methods of Thermal Analysis**

Classification of the TA methods is based on measured physical parameters (mass, temperature or heat flux, mechanical and other parameters e.g. dimension).



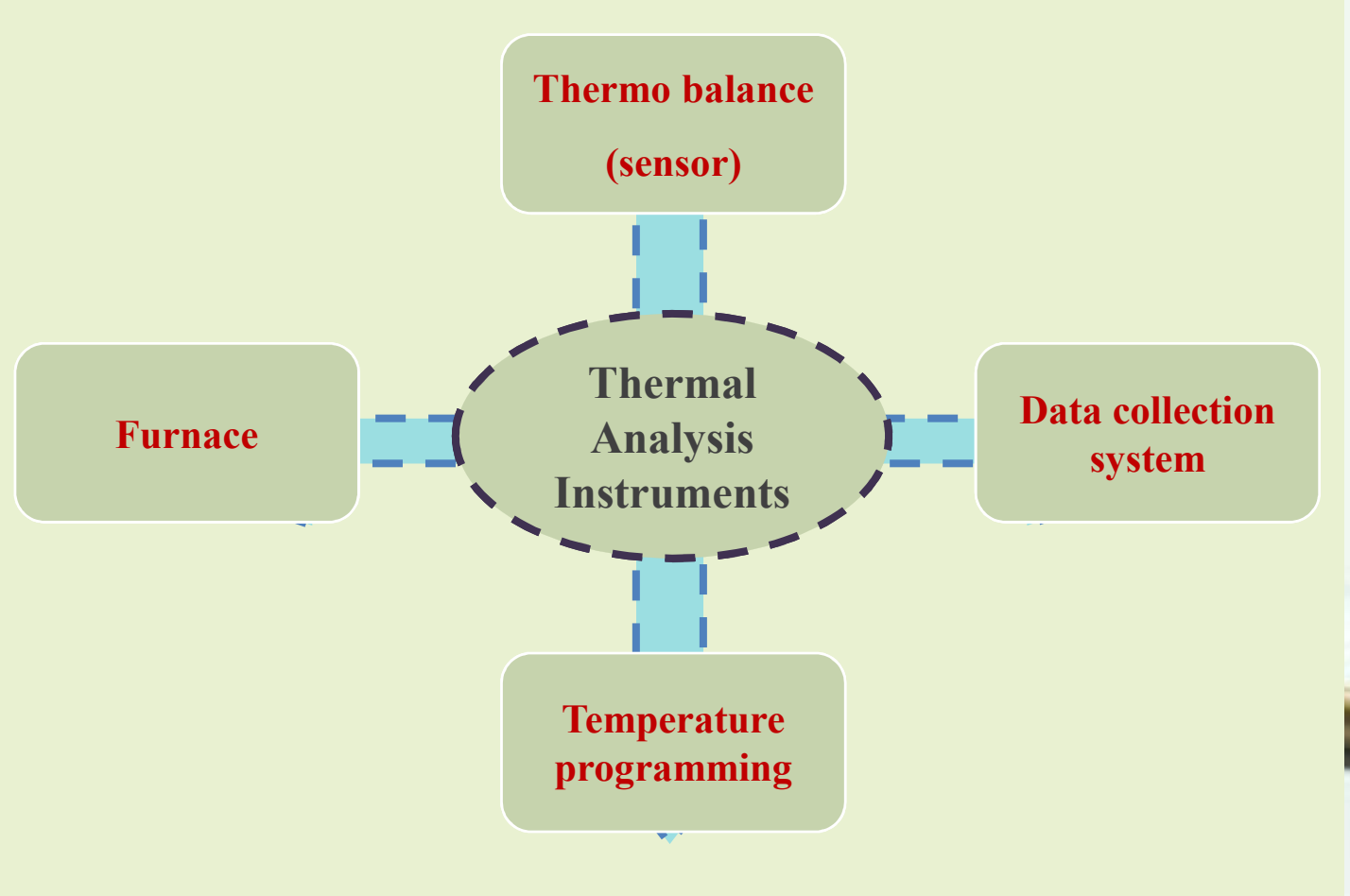
# Thermal Analysis

## 2. Methods

| Techniques | Abbreviations | Properties | Decompositions | Instruments |
|---|---|---|---|---|
| **Thermogravimetry** | TGA | Change in Weight | Oxidations | Thermo-Balance |
| **Difference Thermal Analysis** | DTA | Temperature Difference<br>Heat Absorbed or Evolved | Phase Changes, Reactions | DTA Apparatus |
| **Thermo Mechanical Analysis** | TMA | Pressure, Deformation, Volume or Length | Mechanical Changes | TMA Dilatometer |
| **Dynamic Mechanical Analysis** | DMA | Modulus/Damping<br>Dimensional Changes | Expansion Phase Changes, Glass Transition, Polymer Curve | Various Instruments |
| **Differential Scanning Calorimetry** | DSC | Temperature or Power Difference of Heat Flow Dh/Dt | Heat Capacity, Phase Changes, Reactions | DSC Apparatus |

# 2. Methods

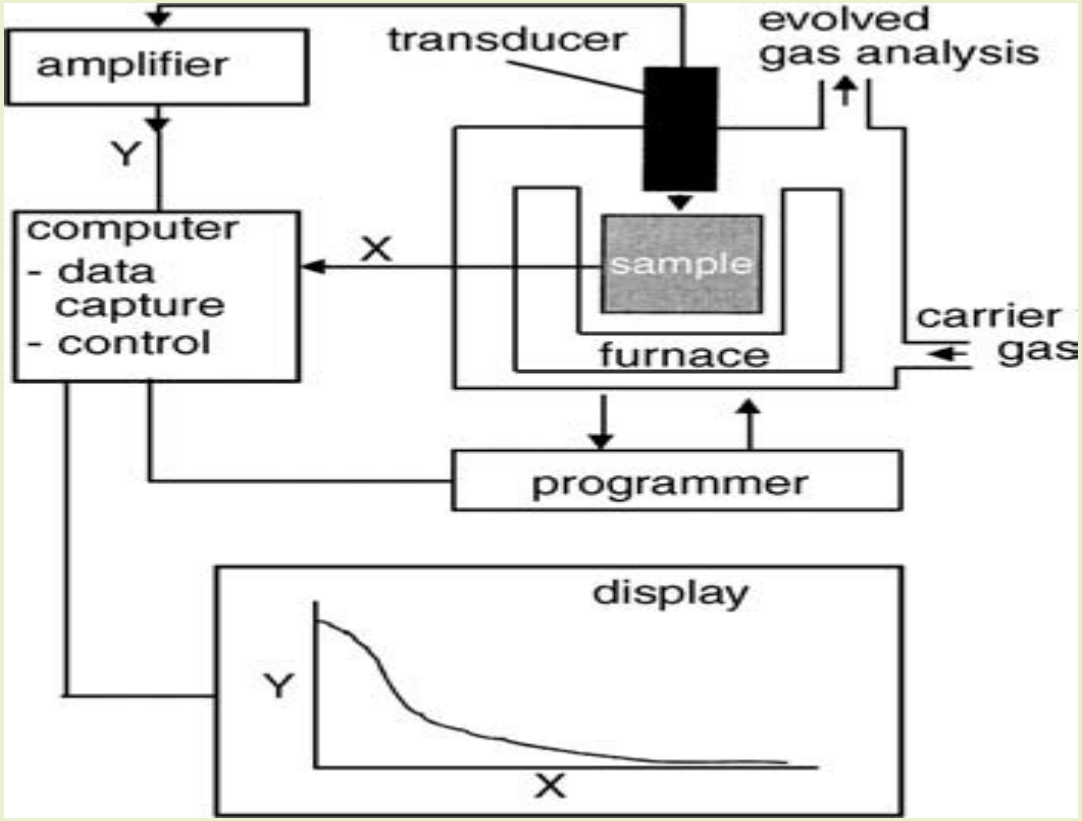
## Thermal Analysis Instruments



# Thermal Analysis

## 2. Methods

### General Instrumentation for Thermal Analysis



## 2. Methods

DSC

# Differential Scanning Calorimetry

# Thermal Analysis

## 2. Methods

### 2.1. DSC

**What is differential scanning calorimeter (DSC)?**

DSC is a thermal analysis apparatus measuring how physical properties of a sample change, along with temperature against time.

DSC instrument is designed to measure the heat flow difference between sample and reference.

DSC instruments are used both in quality control and R&D across a wide range of industries including polymers, pharmacy, electronics, chemical, academia, oil and gas, food, and metals.

Types of DSC pan (open, pin-hole, crimped an sealed) →→→

Reference material:

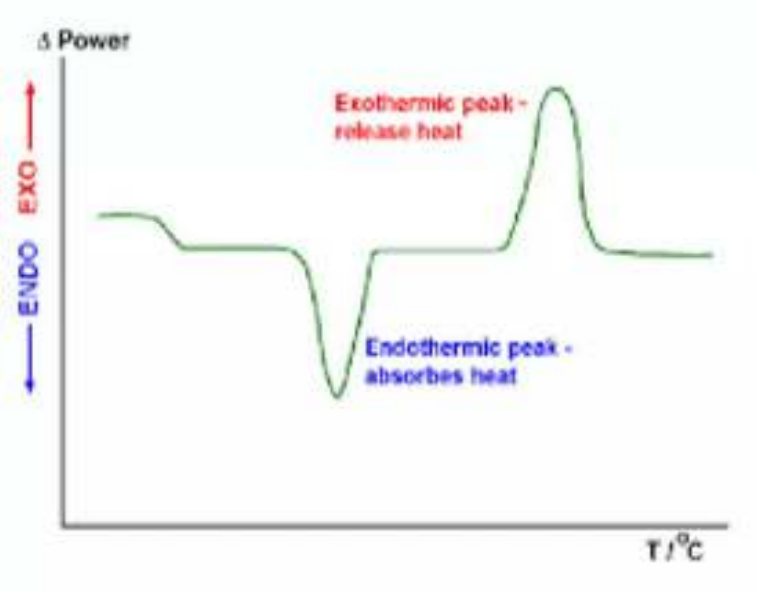
- Reference often is a piece of Indium metal are contained in small aluminum pans with crimped tops. The pans are placed on individual heaters in a furnace in a nitrogen atmosphere.
- DSC pan (commonly used as sample and reference holders) is made from aluminum.
- The pans often need to be sealed to avoid sample mass change due to evaporation.

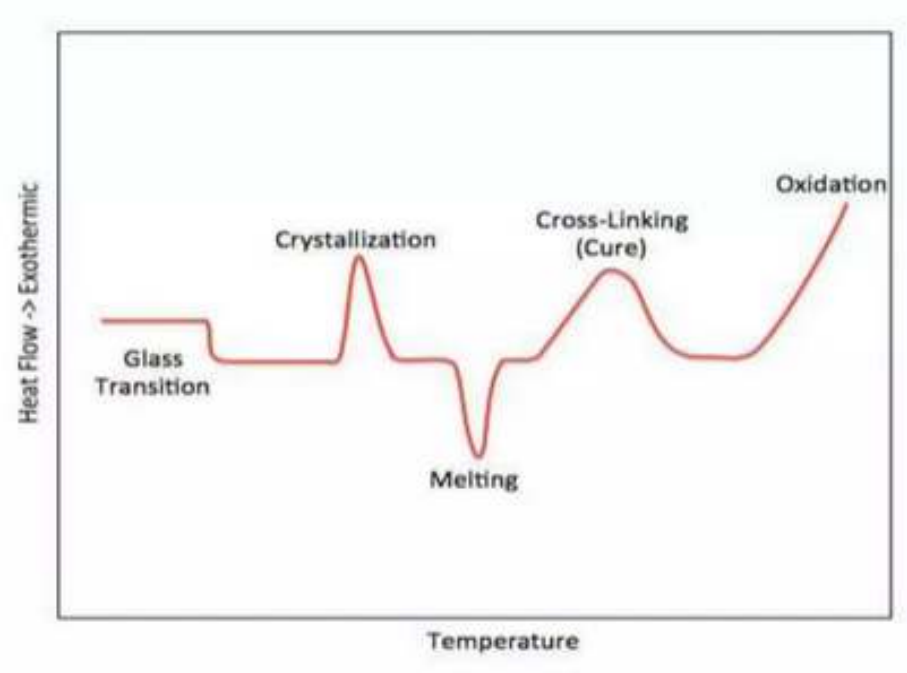
# Thermal Analysis

## 2. Methods

## 2.1. DSC

### DSC Curves



# Thermal Analysis

## 2. Methods

### 2.1. DSC

Standards for all differential scanning calorimeters (DSC) based on:

- The respective instrument,
- Application,
- Material testing specifications

**ISO 11357, ASTM E968, ASTM E793, ASTM D3895, ASTM D3417, ASTM D3418, DIN 51004, DIN 51007 and DIN 53765.**

# Thermal Analysis

## 2. Methods

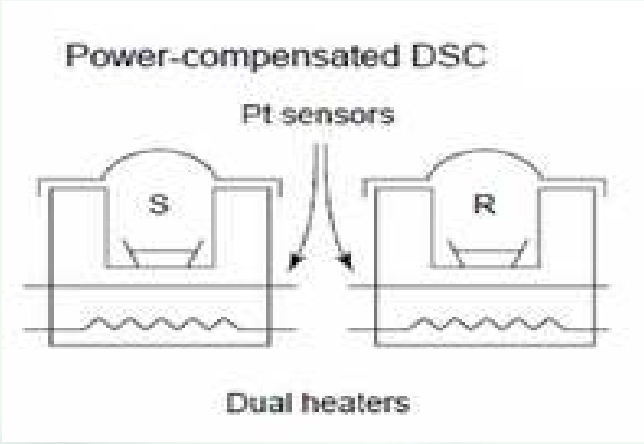
## 2.1. DSC

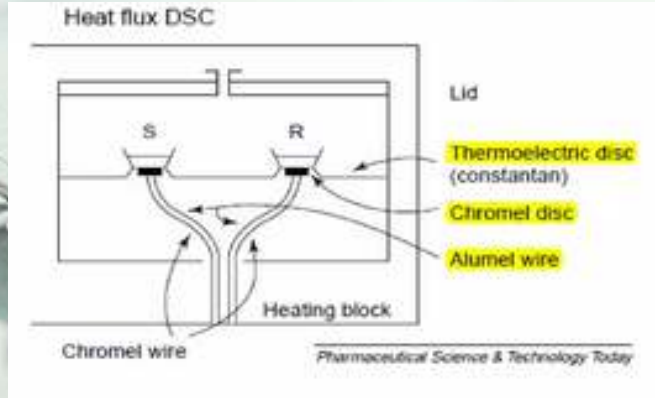
In DSC, the sample and reference are normally thermally linked through a shared thermally conductive metal plate and utilise a pair of thermocouples arranged in such a way that a differential signal (typically µV) is produced whenever there is a temperature difference between the sample and reference and the heat flow those can be monitored and converted to a measurement of power after a suitable calibration factor is determined by using melting point standards. It is also considered more sensitive at lower temperatures.

There are <u>two</u> widely used DSC systems:

- **Heat flux DSC (quantitative DTA):**
  It measures the temperature difference directly and then converts it to heat flow difference.

- **Power-compensated DSC:**
  Directly measures the enthalpy change of a sample during a thermal event. There are two separate chambers to contain the sample and reference. Each chamber has its own individual heat element to control temperature. The instrument always maintains a thermal null state (T=0). When a thermal event occurs in the sample, the power to the heating element has to change in order to maintain the sample temperature the same as that of the reference. An endothermic event causes an increase in power to heat the sample; an exothermic event causes a reduction in power to cool the sample. The amount of power change should equal the energy of heat flow to compensate for the heat release or gain of the sample. The power-compensated DSC is restricted to a maximum temperature of <500 ◦C or about 750 ◦C.



# Thermal Analysis

## 2. Methods

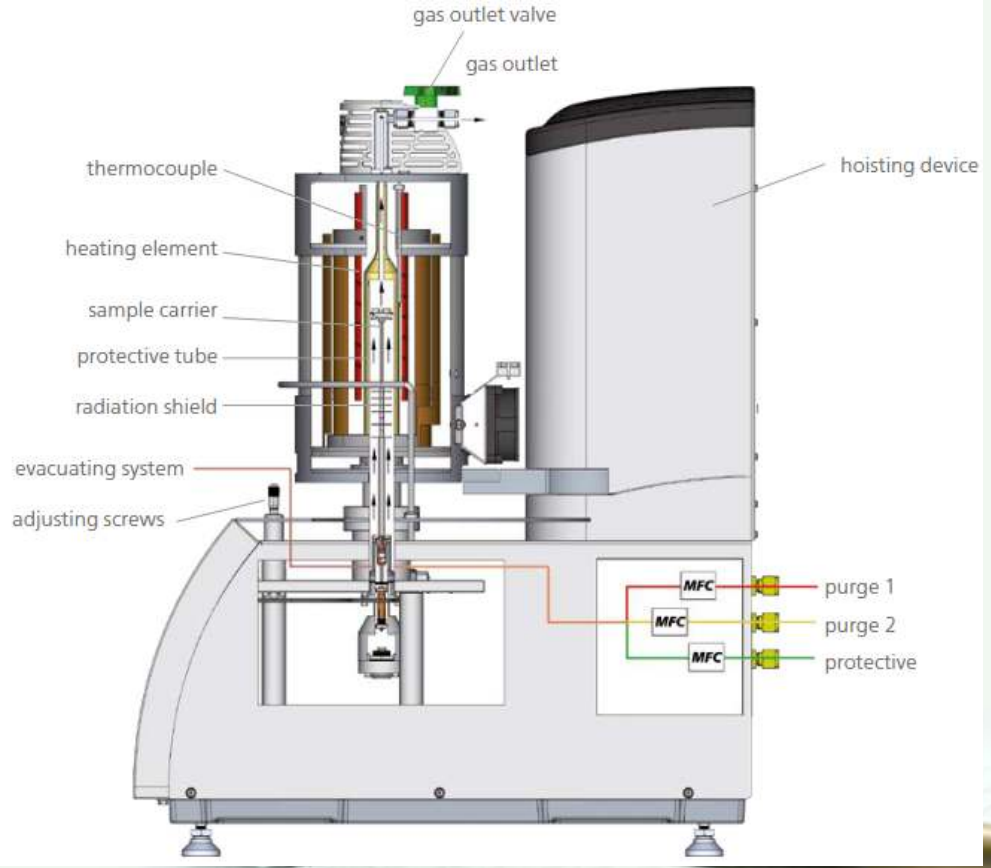
## 2.1. DSC

**DSC instrument consists of:**

1. Sample Holder
2. Furnace or Heating Device
3. Thermal Programmer
4. Amplifier & Recording System
5. Atmosphere Control

**Sample:**

- Form of Sample is dense powder or small discs
- Sample are usually 3-5 mg for analysis
- Avoid large shear forces during cutting samples because induce plastic deformation and affect DSC curves.
- Thin samples have minimum thermal gradient and are better.



# Applications

- Determination of heat capacity
- Determination of phase transformation and phase diagrams
- Physical and chemical property changes of polymers
- Glass transitions
- Melting and boiling points
- Crystallization time and temperature
- Percent crystallinity
- Heats of fusion and reactions
- Oxidative/Thermal stability
- Rate and degree of cure
- Reaction kinetics
- Purity

# Thermal Analysis

## 2. Methods

### 2.1. DSC

**Advantages:**

- Instruments are highly sensitive
- Flexibility in sample volume/form
- Characteristic transition or reaction temperatures can be determined
- High resolution obtained
- Stability of the material

**Limitation:**

- DSC generally unsuitable for two-phase mixtures
- Difficulties in test cell preparation in avoiding evaporation of volatile Solvents
- DSC is generally only used for thermal screening of isolated intermediates and products
- Does not detect gas generation
- Uncertainty of heats of fusion and transition temperatures

## 2. Methods

# TGA

# Thermo Gravimetric Analysis

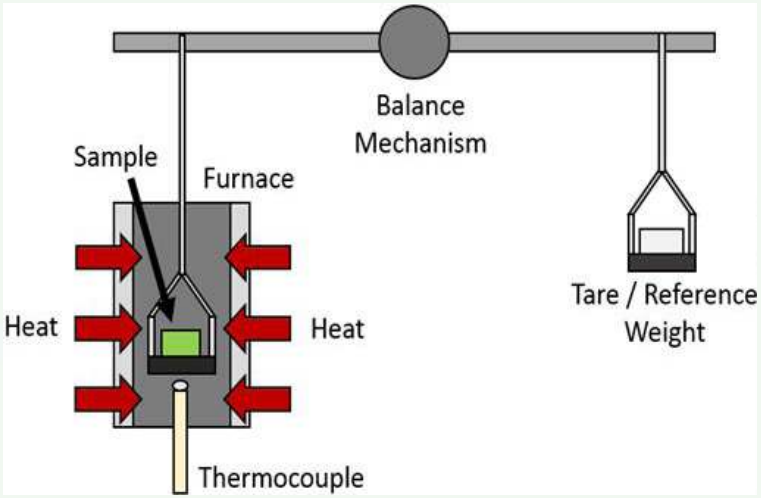
# Thermal Analysis

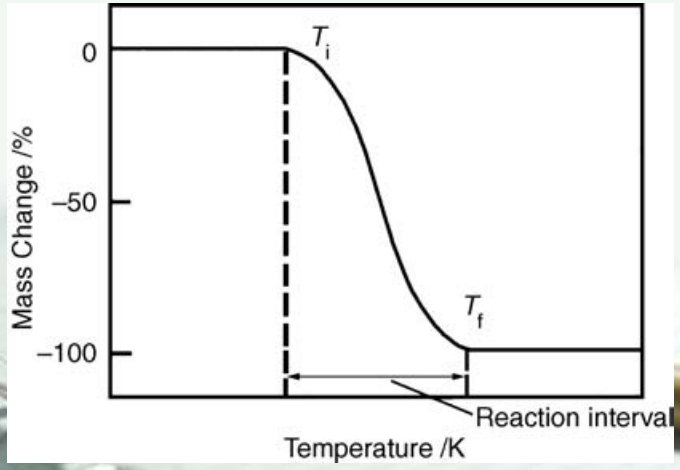
## 2. Methods

## 2.2. TGA

**What is Thermo-gravimetry Analysis (TGA)?**

TGA is a technique for measuring mass change of a sample with temperature. A sample to be measured is placed in a furnace and its mass change is monitored by a thermobalance. The main application of TG is to analyze material decomposition and thermal stability through mass change as a function of temperature in scanning mode or as a function of time in the isothermal mode. TG curves are plotted as mass change expressed in percent versus temperature or time.



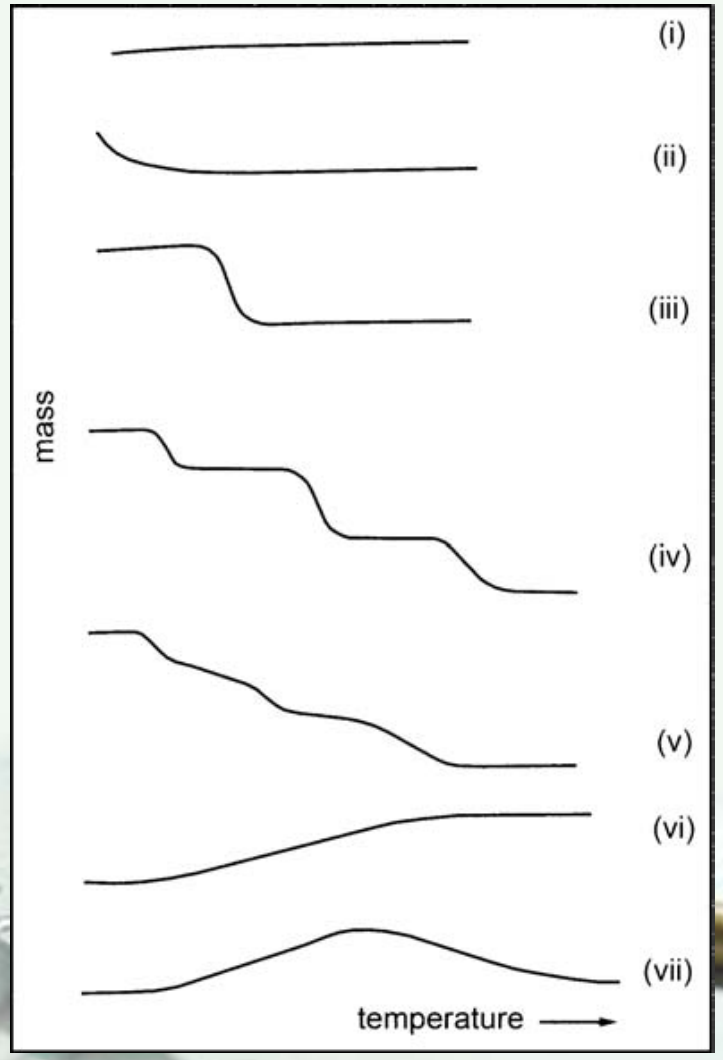
# Thermal Analysis

## 2. Methods

## 2.2. TGA

**TGA Curves Types**

(i) No decomposition with mass loss of volatile products over the temperature range.
(ii) A rapid mass loss at the initial stage of a TA curve.
(iii) One-stage decomposition curve which is typical in TG curves.
(iv) Curve of multi-stage decomposition with stable intermediates.
(v) Curve of multi-stage decomposition, but there is no stable intermediate.
(vi) Chemical reaction with mass gain has occurred in the sample (oxidation).
(vii) Mass-gain reaction occurs and then a mass loss reaction occurs at a higher temperature in the sample, which is rarely seen.



# Thermal Analysis

## 2. Methods 2.2. TGA

**TGA instrument consists of:**

1.Microbalance

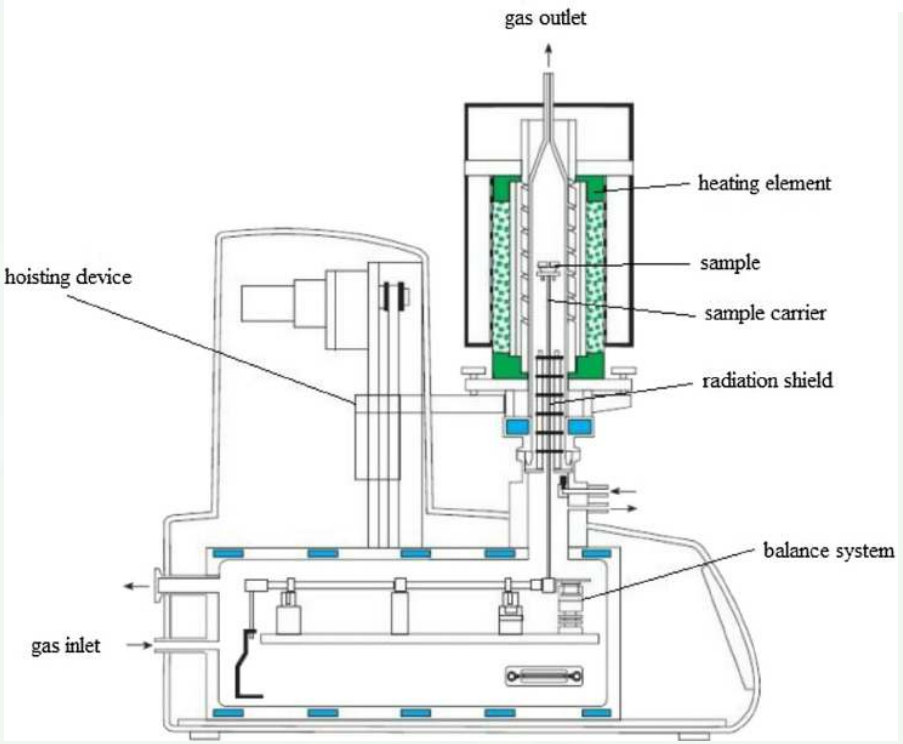
2.Furnace

3.Temperature Programmer

4.Computer

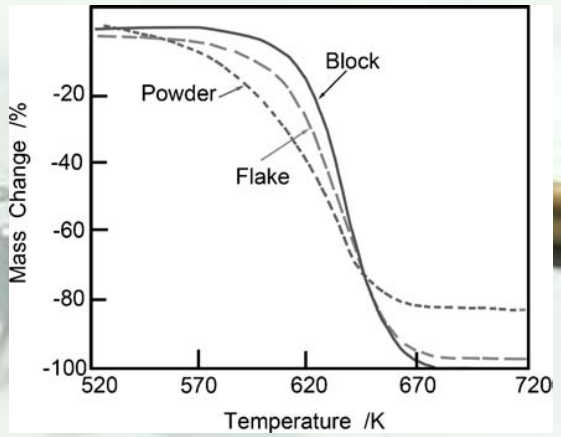
4. Sample carrier

**Purge gas system :** For prevention of oxidation, $N_2$ Ar, He, etc and for oxidation, $O_2$ or air.




**Sample**:

- Sample mass, volume and form are important for recording accurate and reproducible TGA. In general, small sample mass is better for minimizing temperature deviation and is usually about several milligrams.
- Samples can be in block, flake, fiber or powder form.
- A block sample should be ground or sliced and avoid excessive force during such mechanical processing, because mechanical deformation of the sample may also affect the TG curves.

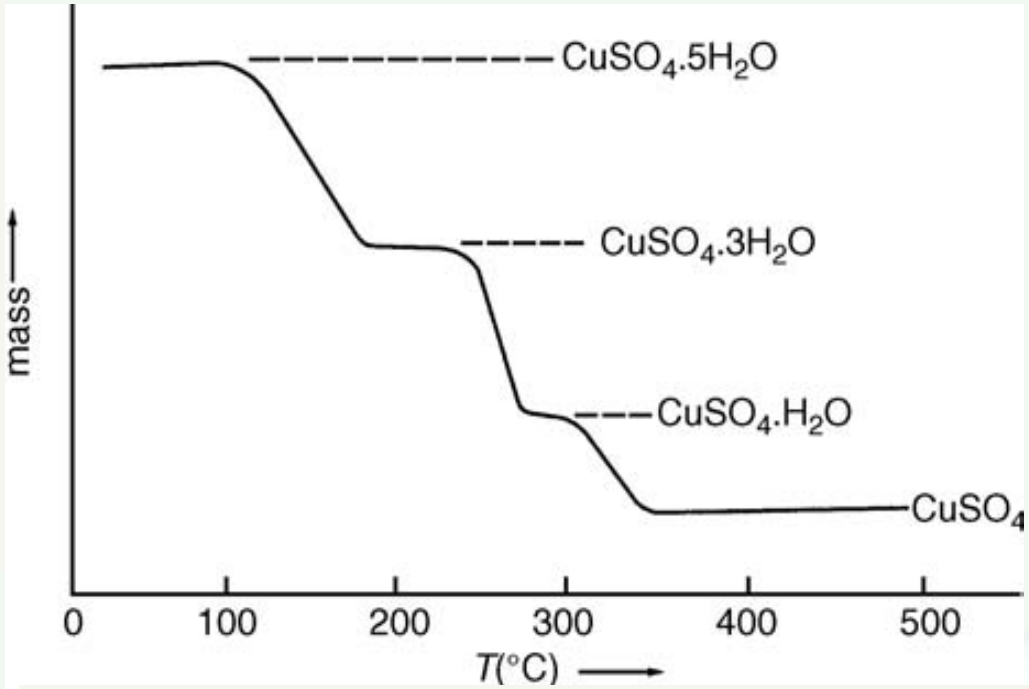


# Thermal Analysis

## 2. Methods | 2.2. TGA

## Applications

- Dehydration
- Desorption
- Decomposition
- Oxidation
- TG curves can also be used for quantifying compositions of composites containing thermally decomposable components.




An example of TGA analysis of the thermal stability of $CuSO_4.5H_2O$. Crystal water loss occurs at separated.

# Thermal Analysis

## 2. Methods

## 2.2. TGA

**Advantages of TGA:**

- Small quantity of sample (few milligrams )required
- It is possible to analyse both solid and liquid samples.
- Minimal preparation of the sample is necessary.

**Disadvantages of TGA:**

- Verification is only indirect.
- It is not able to actively verify the presence of a specific substance.
- Data interpretation is not always straight forward.
- Non-homogeneous material cannot be tested.
- Sensitive to heating rate

## 2. Methods

## STA

# Simultaneous Thermal Analysis

# Thermal Analysis

## 2. Methods

## 2.3. STA

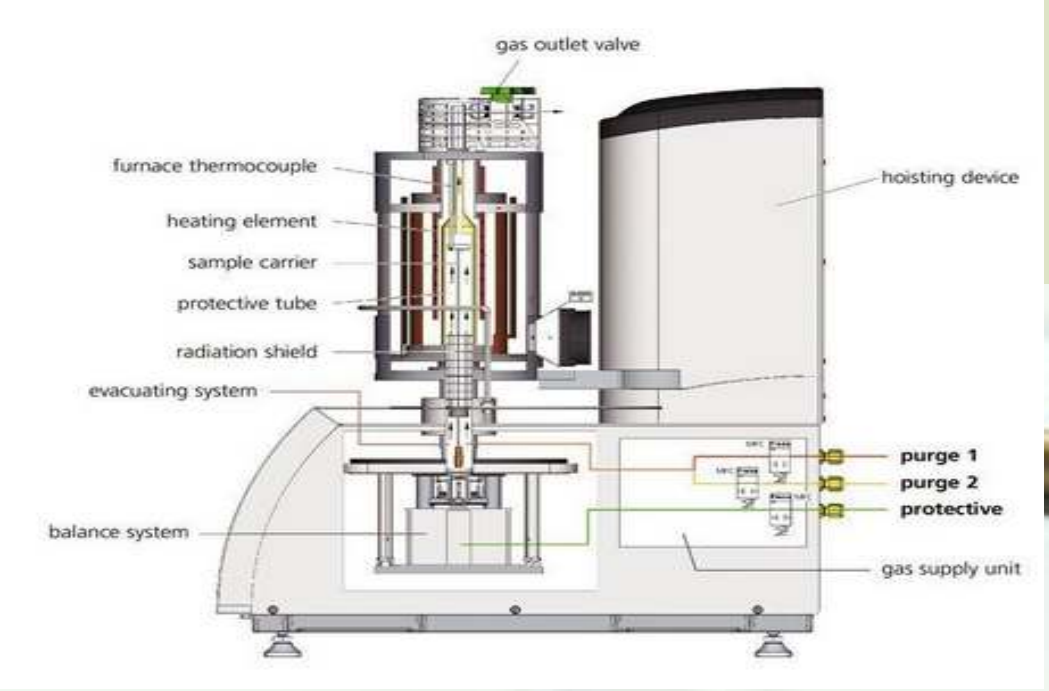
**What is Simultaneous Thermal Analysis (STA)?**

Simultaneous thermal analysis (STA) is a thermal analysis technique that most commonly combines thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) in a single instrument for simultaneous measurement. A good way to describe an STA is that it's the multitool of the thermal analysis world.

TGA measures the sample weight changes whilst DSC measures the heat flow of a sample over a temperature range

It is based on standards:

ISO 11358, ASTM E793, DIN 51004, DIN 51006, DIN 51007.



# Thermal Analysis

## 2. Methods

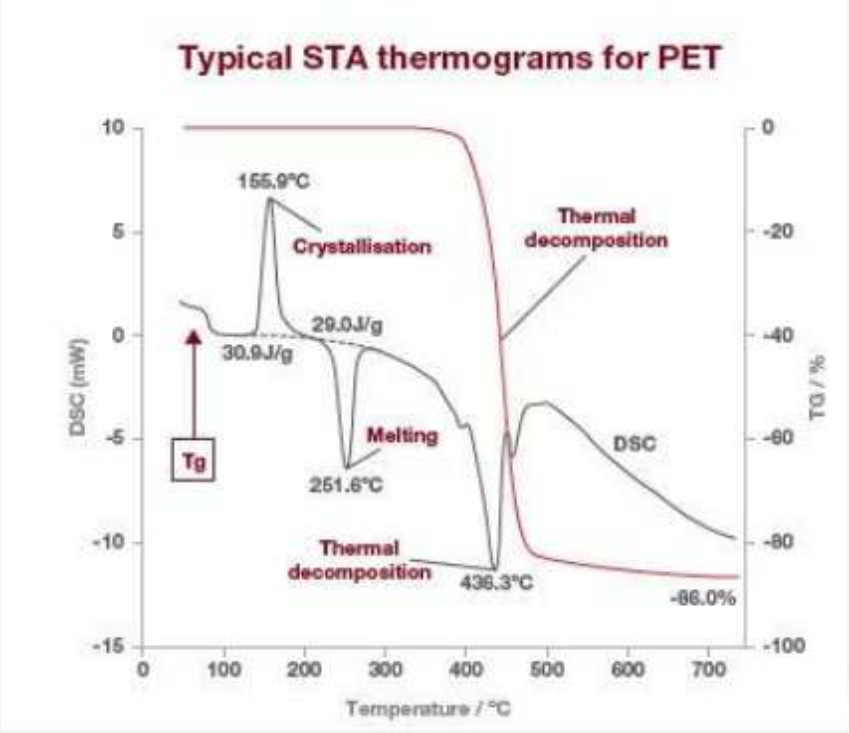
## 2.3. STA

Thermogravimetric analysis is when sample is placed in a furnace on a highly sensitive balance. The mass of the sample is monitored against time or temperature in oxidative or an inert atmosphere.

The change in mass of the sample is plotted against time or temperature. The percentage reduction in mass at given temperatures can be seen in the TGA thermogram.

TGA alone can give you information on moisture content, residual solvents, and the amount of desorbed or decomposed components emitted at given temperatures or over a certain period of time.

**With STA you get more complete thermal information about your sample, including exothermic and endothermic events.**

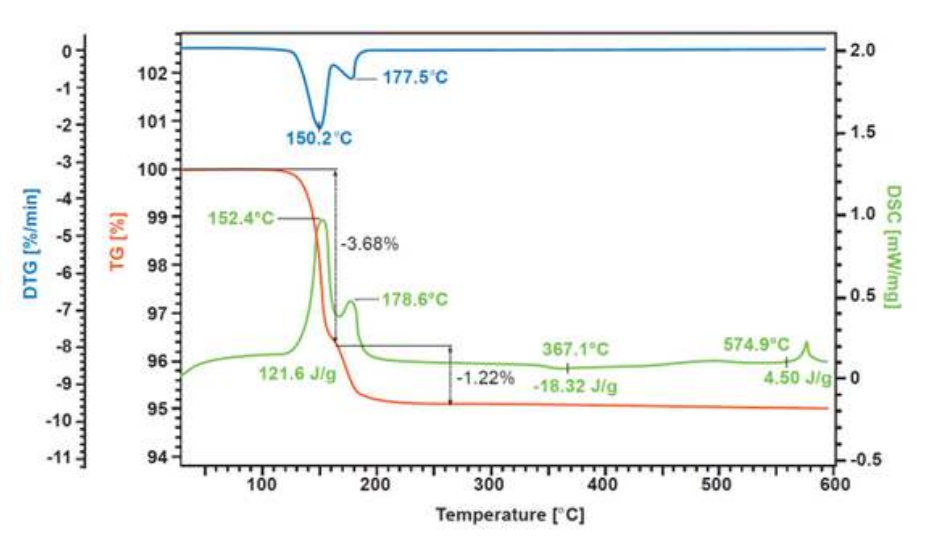


# Thermal Analysis

## 2. Methods

## 2.3. STA

The test conditions are perfectly identical for the TG and DSC signals (same atmosphere, flow rate, vapor pressure on the sample, heating rate, thermal contact to the sample crucible and sensor, radiation effect, etc.).




The application example gives an impression about the information obtained by a STA (TGA-DSC) measurement. The result provides information about the exact composition of the cement sample as you can determine the amount of humidity, the quality and amount of the contained quartz as well as the temperature stability of the material.

# Thermal Analysis

## 2. Methods | 2.3. STA

# Applications

| | |
|---|---|
| ➢ Compositional analysis | ➢Compositional analysis |
| ➢ Decomposition temperatures | ➢enthalpy |
| ➢ Engine oil volatility | ➢Endo- / Exothermic reactions |
| ➢ Flammability studies | ➢phase transformation |
| ➢ Lifetime predictions | ➢Melting point |
| ➢ Measurement of volatiles | ➢Glass point |
| ➢ Oxidative and thermal stabilities | ➢Crystallinity |
| ➢ Catalyst and coking studies | ➢Thermal stability |
| ➢ Hyphenation to identify out-gassing products | ➢oxidation stability |
| ➢Mass change as % and mg | ➢Purity |
| ➢Rate controlled mass loss | ➢Solidus / Liquidus relationship |
| ➢Evaluation of mass loss | ➢Product identification |
| ➢Residual mass evaluation | |

# Thermal Analysis

## 2. Methods | 2.3. STA

**Advantages of STA:**

- Using STA means you get two experiments in one with identical parameters for both data sets to eliminate uncertainty that could come from sample preparation and differing instruments.
- Both data sets are also collected on the same sample in the same furnace with same gas flow to give better correlation of time/heat flow and time/mass change phenomena in time-sensitive operations.
- STA instruments are suited for research and routine applications in polymers, food, pharmaceuticals, nano-materials, metals and oil as it combines analysis techniques within one instrument.

**Disadvantages of STA:**

- Complicated instrument
- The instrument has more sensors.

# Thermal Analysis

## 2. Methods

**DTA**

**D**ifferential

**T**hermal

**A**nalysis

# Thermal Analysis

## 2. Methods

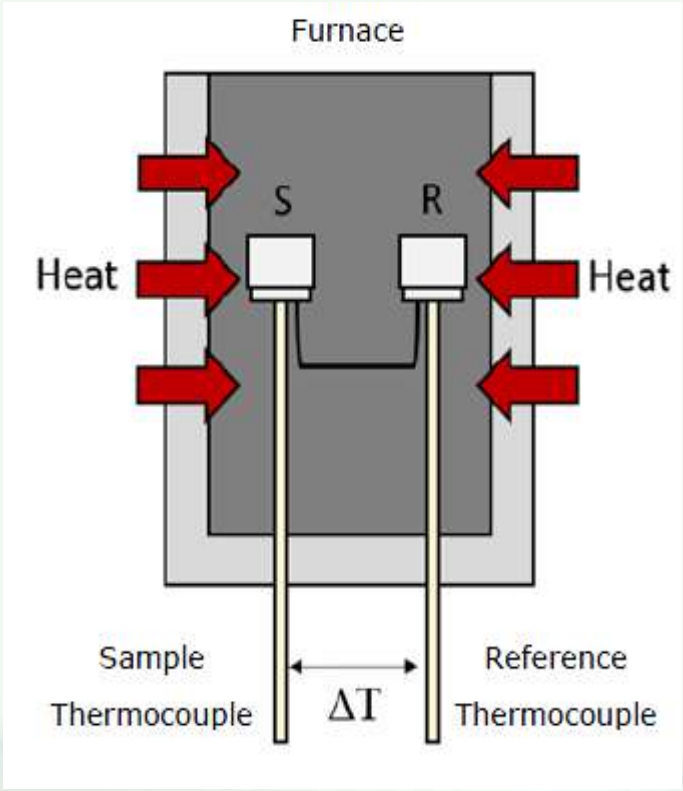
## 2.4. DTA

**What is Differential Thermal Analysis (DTA)?**

A DTA instrument is designed to measures **temperature differences between sample and reference.**

A sample and reference are symmetrically placed in a furnace. In 1899 **Robert Austen** improved this technique by introducing two thermocouples and the temperature difference between the sample and reference are measured by these two thermocouples:

- One is in contact with the underside of the sample holder (also called the crucible).
- The other is in contact with the underside of the reference holder.




## Reference material conditions:

- It does not undergo thermal events over the operation temperature range,
- It does not react with any component in the instrument,
- It has similar thermal conductivity and heat capacity to the sample being examined.

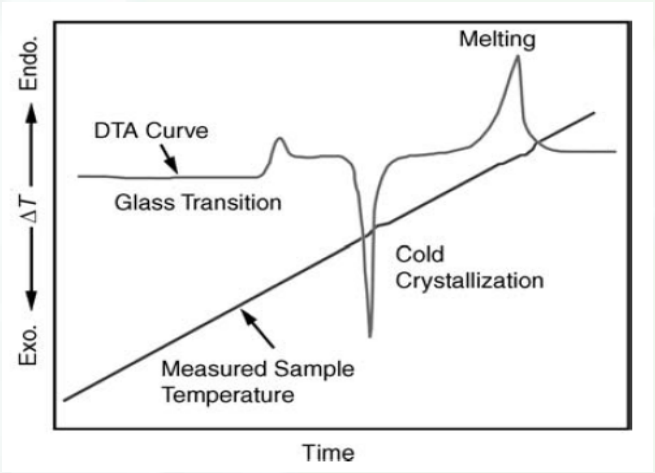
# Thermal Analysis

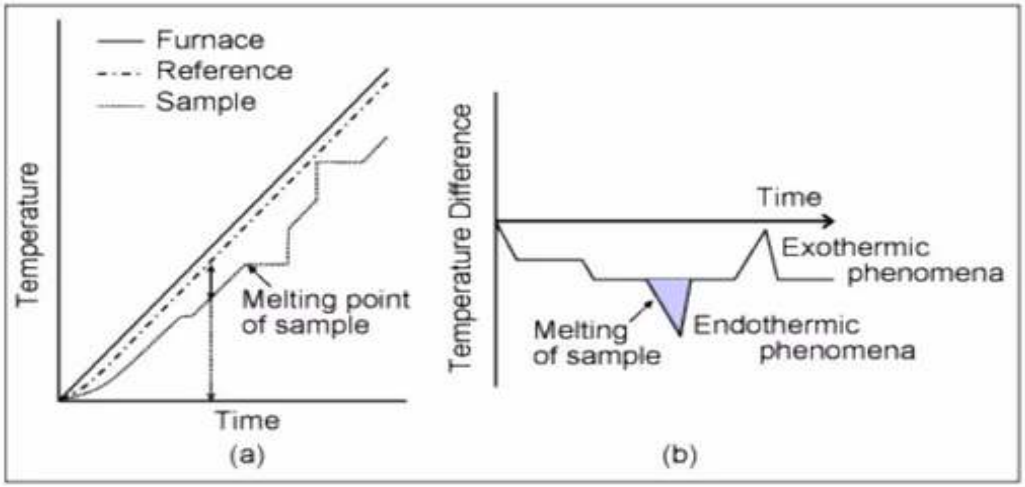
## 2. Methods

## 2.4. DTA

### Characteristics of DTA Curves

**The DTA curve is a plot of T versus reference temperature or heating time when heating rate is constant.**




ΔT= Temperature difference between sample and reference

ΔT= 0 When no thermal event occurs in the sample.
(Because of similar thermal conductivity and heat capacity between sample and reference)

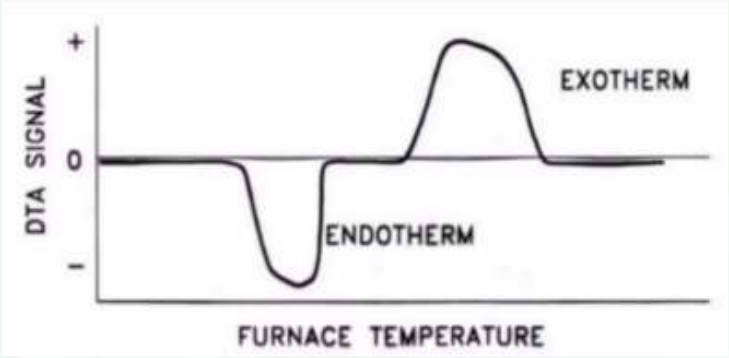
ΔT<0 When the thermal event is endothermic (absorbing heat).
(An endothermic event makes the sample temperature lower than the reference temperature)

ΔT>0 When the thermal even is an exothermic (releasing heat).
(An exothermic event makes the sample temperature higher than the reference temperature)

# Thermal Analysis

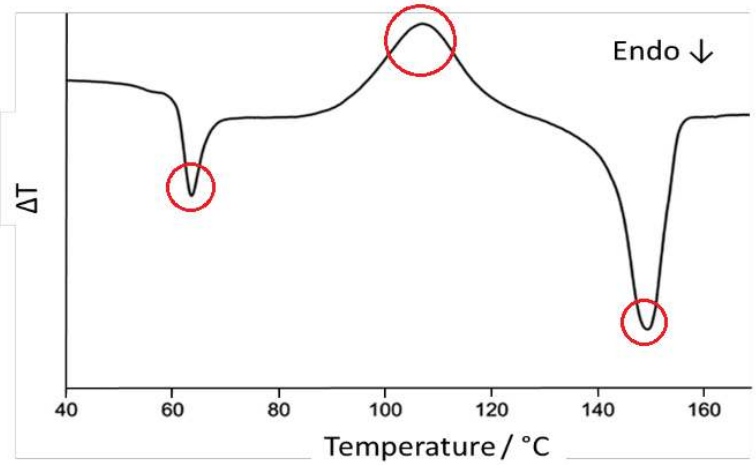
## 2. Methods

## 2.4. DTA




- ✓ Sharp Endothermic- changes in crystallanity or fusion Broad
- ✓ Exothermic- dehydration reaction
- ✓ Physical changes usually result in endothermic curves
- ✓ Chemical reactions are exothermic

- ✓ Around 60 °C: Endothermic, glass transition (Tg) of the polymer
- ✓ 90-120 °C: Exothermic, cold crystallisation between Tg and the melting point
- ✓ Around 140 °C: Endothermic, melting



# Thermal Analysis

## 2. Methods

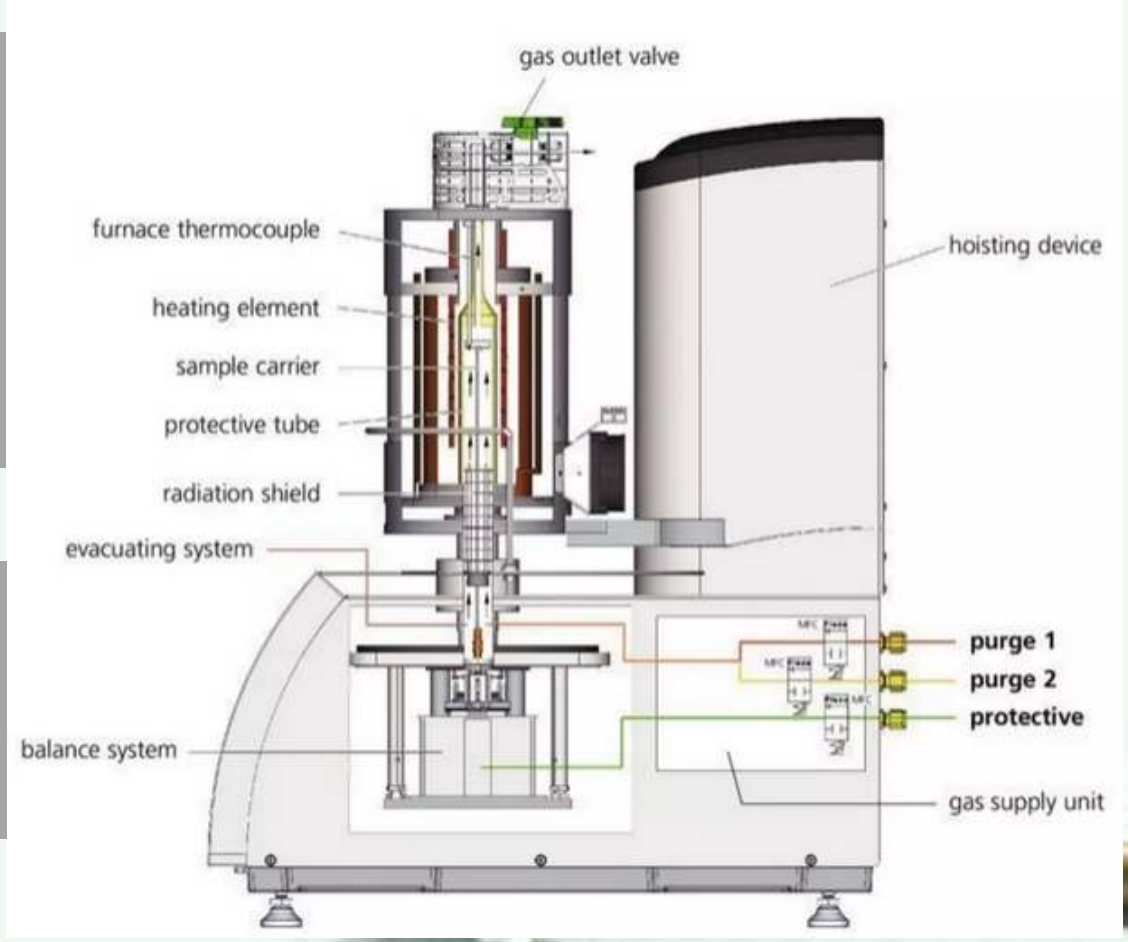
## 2.4. DTA

**DTA instrument consists of:**

1. Sample Holder
2. Furnace or Heating Device
3. Thermal Programmer
4. Amplifier & Recording System
5. Atmosphere Control

**Sample Holder** called crucible and are made up of metallic (Aluminum, Platinum) & ceramic (silica).

Sample are usually **1-10 mg** for analysis.



# Applications

- DTA curves for two substances are not identical. Hence they serve as finger prints for various substances.
- This technique is used for testing the purity of the drug sample and also to test the quality control of many substances like cement, soil, glass.
- Used to study the characteristic study of polymeric materials.
- Used for the determination of heat of reaction, specific heat and energy change occurring during melting.
- DTA offers a wide spectrum of investigations related to reaction kinetics, solvent retention, Phase-transformations, solid-phase reactions and drying properties of product.
- Analysis of Biological samples: DTA curves are used to date Bone remains or to study archaeological materials.
- Measurement of Crystalline: measurement of the mass fraction of crystalline material in semi-crystalline polymers.
- Moisture content in the sample can be determined.
- DTA method also provides a simple and accurate way of determining the melting, Boiling, and decomposition points of organic compounds. Generally data appears to be more consistent and reproducible than those obtained with hot stage or a capillary tube.

# Thermal Analysis

## 2. Methods

### 2.4. DTA

**Advantages of DTA:**

- Instrument can be used at high temperature.
- Instrument is highly sensitive.
- Flexibility in crucible volume/form.
- Characteristic transition or reaction can be accurately determined.

**Disadvantages of DTA:**

- Uncertainty in heat of fusions.
- Reaction or transition estimation is only 20%to50% in DTA.
- Need calibration over the entire temperature for DTA.

## 2. Methods

**DMA**

# Dynamic Mechanical Analysis

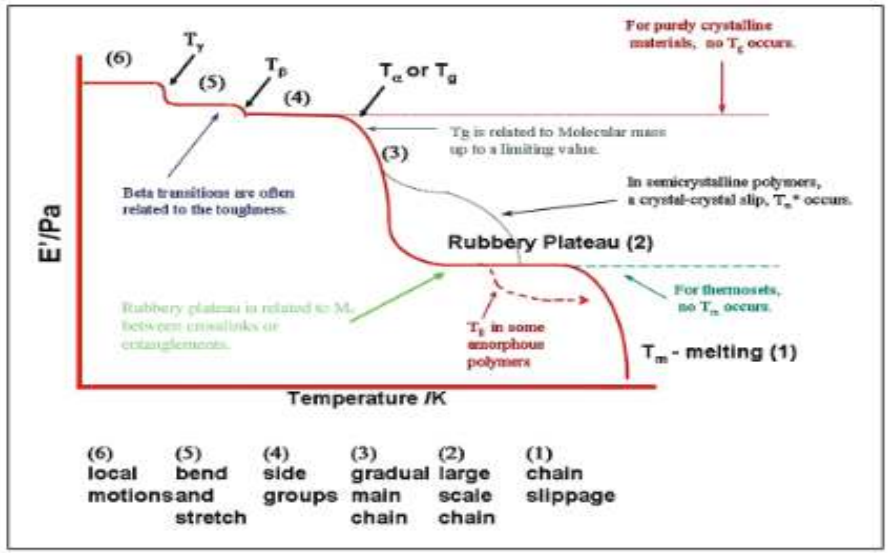
# Thermal Analysis

## 2. Methods

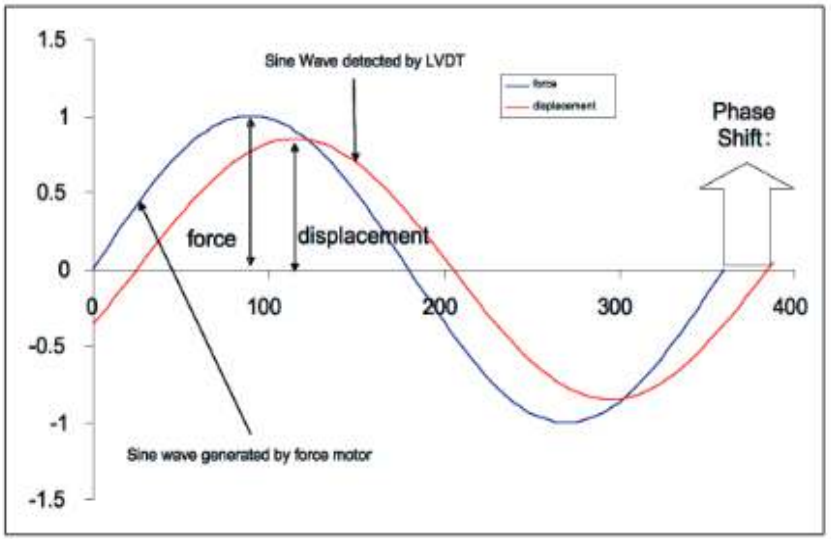
## 2.5. DMA

### What is Dynamic Mechanical Analyzer (DMA)?

DMA, is a technique such that a small deformation is applied to a sample in a cyclic manner. This allows the material's response to stress, temperature, frequency and other parameters to be studied and the mechanical properties of polymers are evaluated. Typically, these experiments involve heating to evaluate how the polymers' mechanical properties vary with temperature.




Modulus values change with temperature and transitions in materials can be seen as changes in the E' or tan delta curves



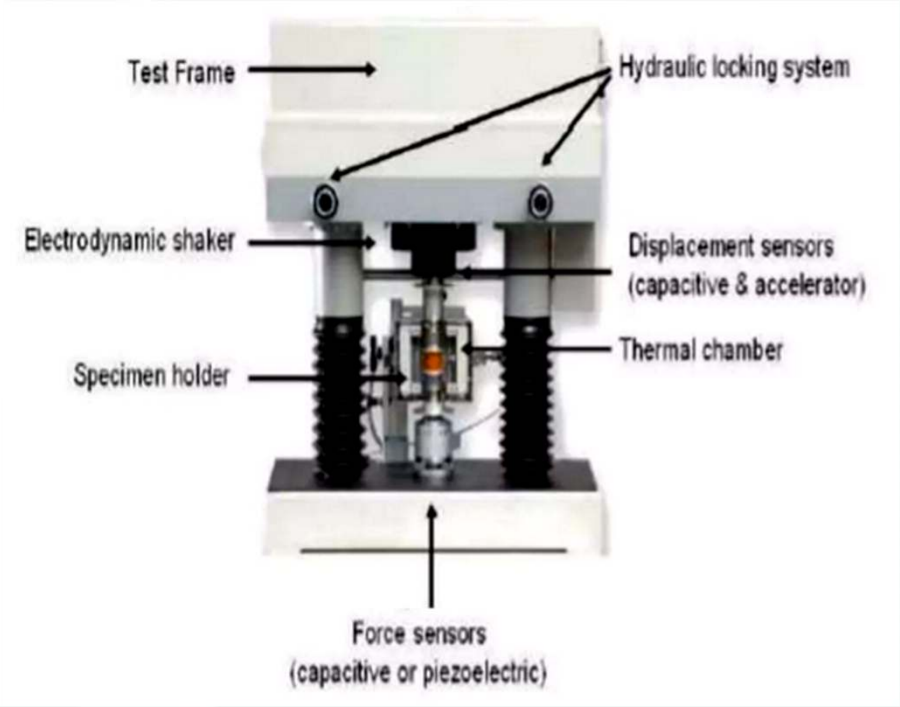

The relationship of the applied sinusoidal stress to strain is shown,with the resultant phase lag and deformation.

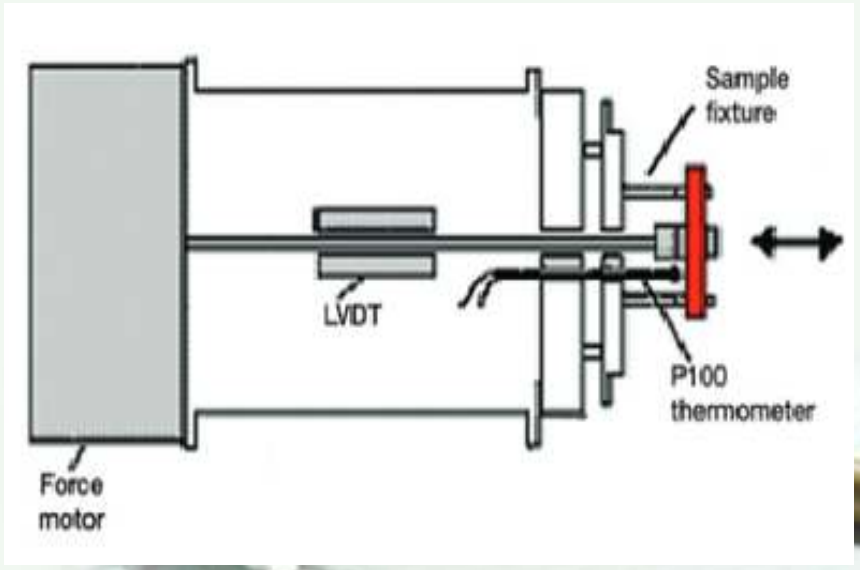
# Thermal Analysis

## 2. Methods

## 2.5. DMA

DMA works by applying a sinusoidal deformation to a sample of known geometry. The sample can be subjected by a controlled stress or a controlled strain. For a known stress, the sample will then deform a certain amount. In DMA this is done sinusoidally. How much it deforms is related to its stiffness. A force motor is used to generate the sinusoidal wave and this is transmitted to the sample via a drive shaft. One concern has always been the compliance of this drive shaft and the affect of any stabilizing bearing to hold it in position.




https://resources.perkinelmer.com/corporate/cmsresources/images/44-74546gde_introductiontodma.pdf

# Thermal Analysis

## 2. Methods

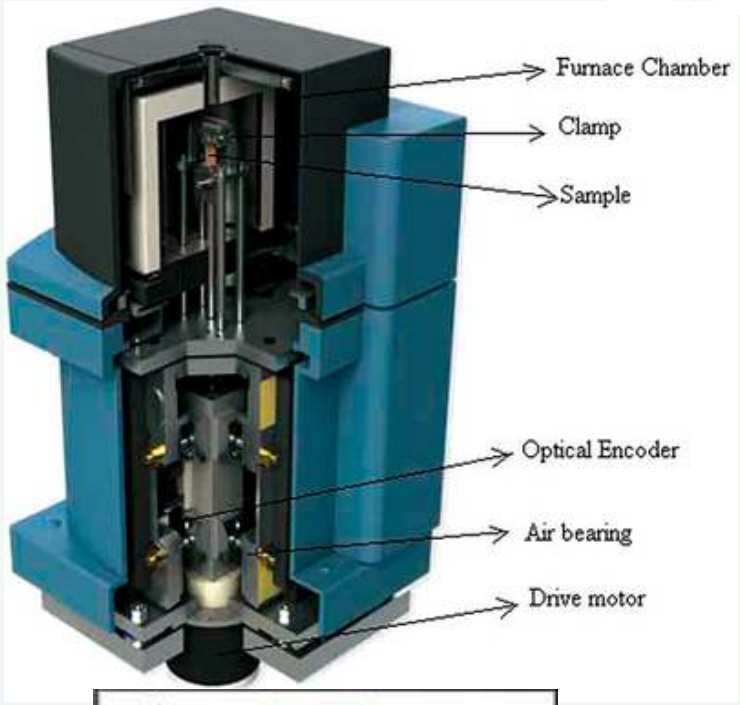
## 2.5. DMA

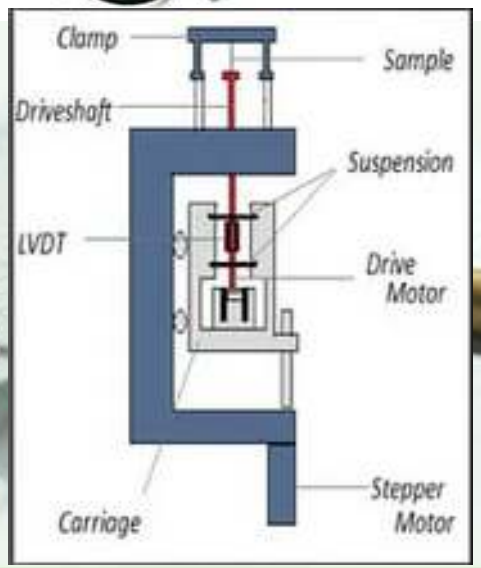
**DMA instrument consists of:**

1. Sample Holder
2. Furnace or Heating Device
3. Motor or drive shaft
4. LVDT

**Sample:**

- Preparation of sample by cutting and molding
- Samples are usually a few millimeter to few centimeter



# Applications

- Polymers
- Elastomers
- Composites
- Metals and alloys
- Ceramics
- Glass
- Adhesives
- Paint and varnish
- Cosmetics
- Oils
- Biomaterials
- Leather

**TEST MODE**

Sheer & torsion, 3-Point bending, Tension & Compression

# Thermal Analysis

## 2. Methods

## 2.5. DMA

**Advantages:**

- Determination of characterization of printed circuit board material
- Research and development for material life time predictions
- Fast analysis time(30 minutes)
- Easy sample preparation
- Calculate modulus for a range of temperatures

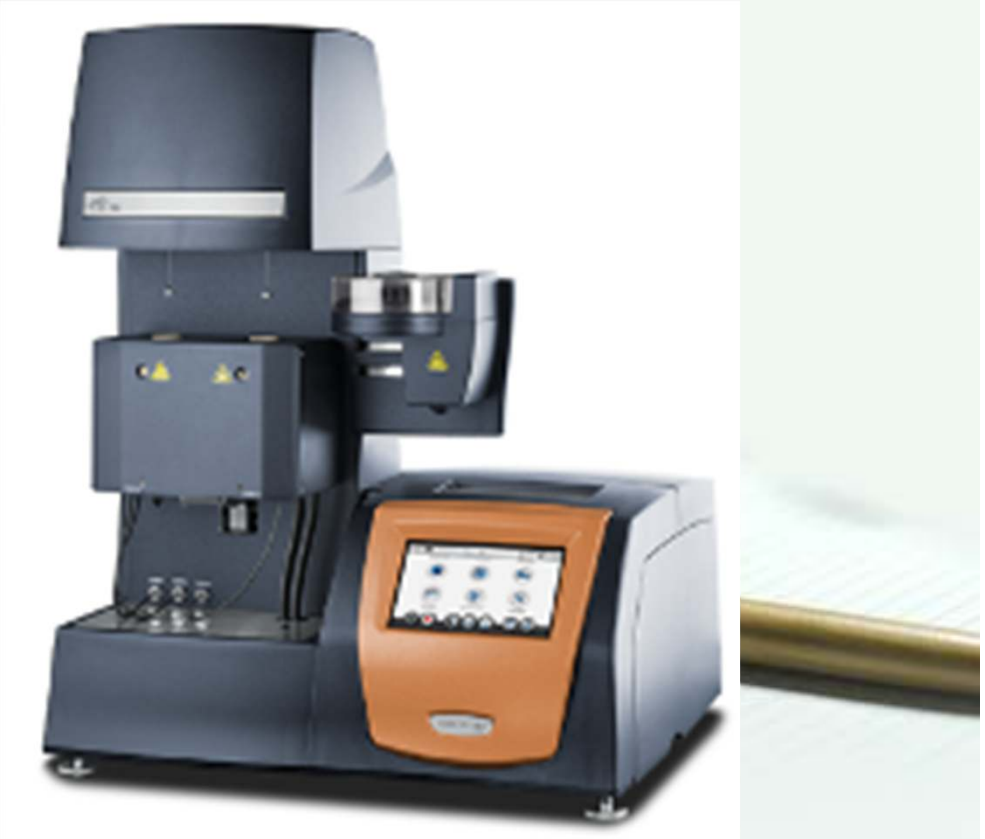
**Limitation:**

- The modulus value is very dependent on sample dimensions and measurement of sample dimensions
- Increase sample temperature due to oscillating stress

## 2. Methods

TMA

# Thermo Mechanical Analysis



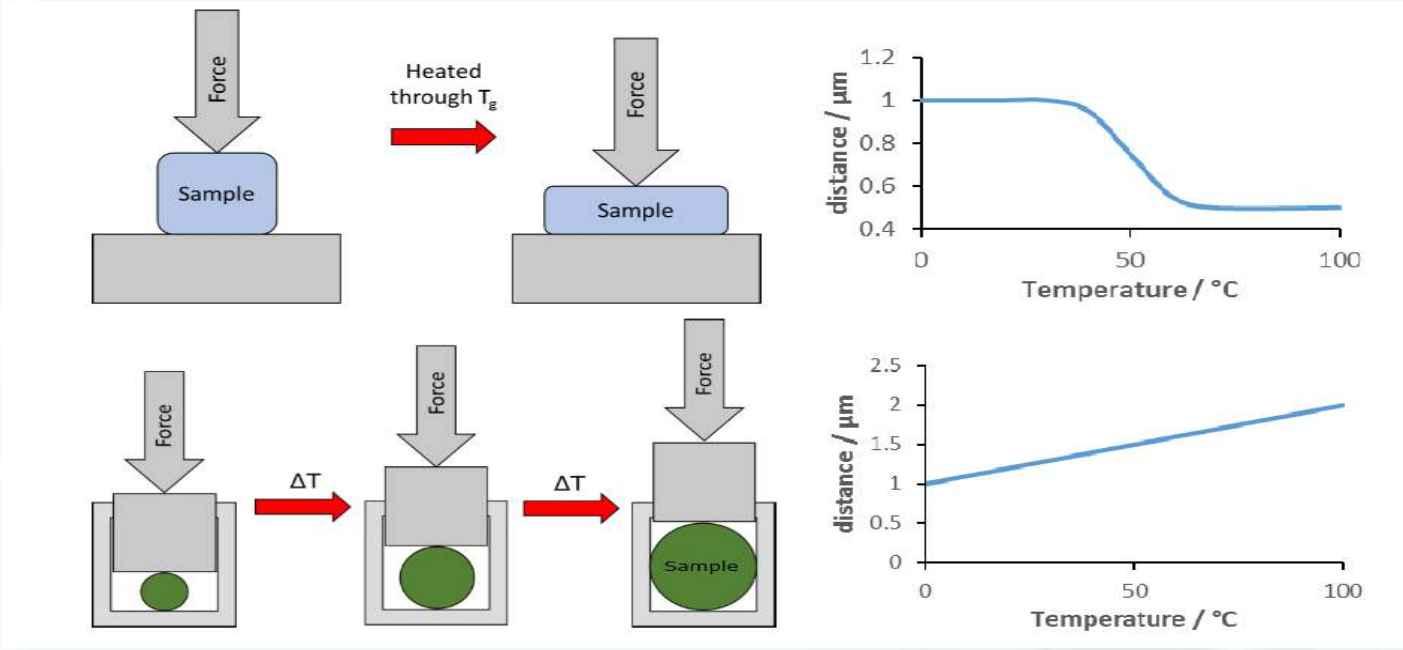
# Thermal Analysis

## 2. Methods

## 2.6. TMA

### What is Thermo-mechanical Analysis (TMA)?

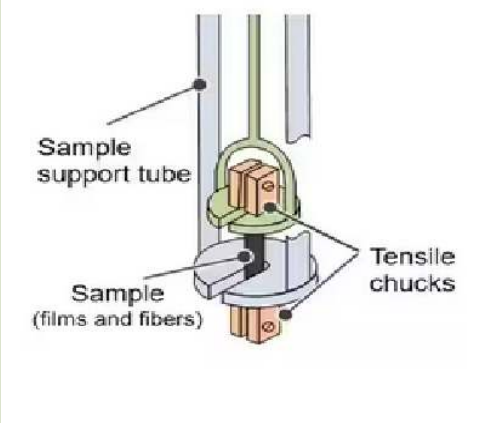
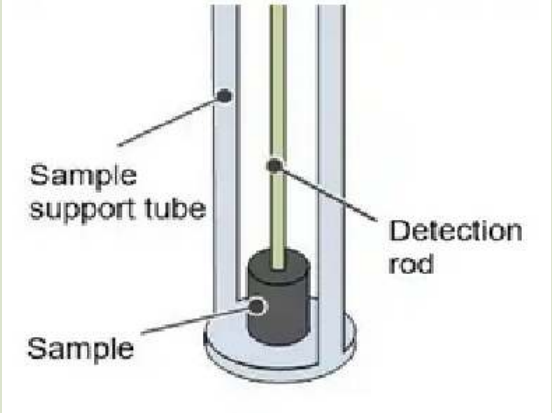
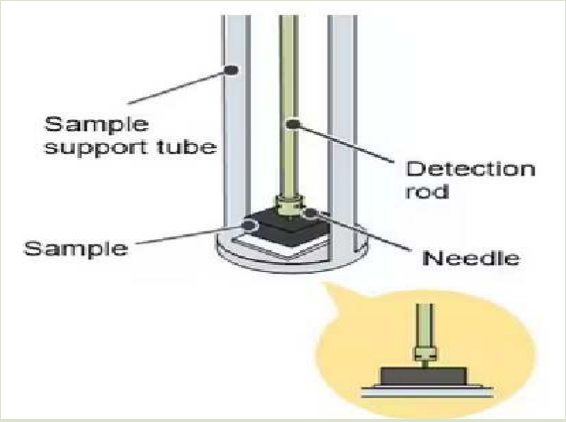
TMA is the study of the dimensional changes of a material as a function of temperature and is widely applied to the study of deformations or relaxations of materials that will be subjected to environmental temperature changes. TMA works by applying stress, usually compressive or tensional, to a material as it is heated. It is ideally suited to studying the softening of a material during a glass transition (Tg) or measuring the extent of expansion of a material during a heating or cooling.



# Thermal Analysis

## 2. Methods 2.6. TMA

### Measurement Modes

| Tension Measurement | Expansion Measurement | Penetration Measurement |
|---|---|---|
|  |  |  |
| In this method, a load is applied in the tensile direction to the film or fiber sample fixed at top and bottom by the chucks. The sample displacement, such as contraction or elongation, is then measured. | In this method, a load is applied to the sample to the extent that no deformation occurs, and the displacement resulting from thermal expansion of the sample is measured. | In this method, a probe with a needle-shaped tip is used to measure the displacement resulting from softening of the sample when a compressive load is applied. |

# Thermal Analysis

## 2. Methods

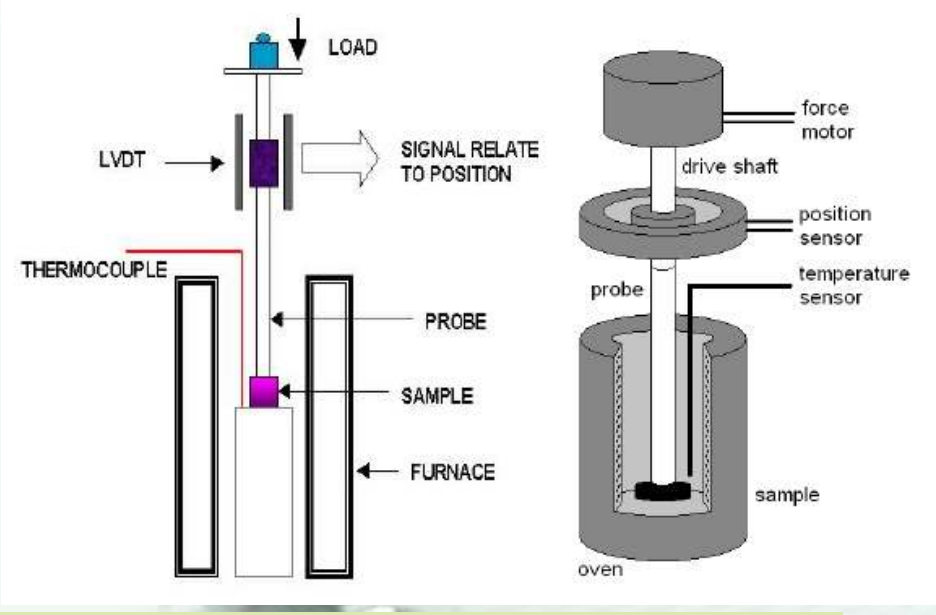
## 2.6. TMA

The sample is inserted into the furnace and is touched by the probe which is connected with the length detector and the force generator. The thermocouple for temperature measurement is located near the sample.

The sample temperature is changed in the furnace by applying the force onto the sample from the force generator via probe. The sample deformation such as thermal expansion and softening with changing temperature is measured as the probe displacement by the length detector. linear variable differential transformer (LVDT) is used for length detection sensor.

**Sample**:

- specimens shall be between 2 and 10 mm in length and have flat and parallel ends to within ±25 μm.
- Lateral dimensions shall not exceed 10 mm.




Standard of Thermalmechanical Analysis (TMA) Testing, ASTM E831

# Applications

- Measuring glass transition temperature (Tg) of polymers
- Coefficient of thermal expansion (CTE) of polymers, composites and inorganics
- Differences in CTE below and above Tg
- Differences in softening temperature before and after processing or physical aging
- Effect of post-curing on the glass transition temperature
- Dimensional stability of parts at operating temperature and loading
- Differences in thermo-mechanical behavior of films or layered composites as a function of loading direction: “machine” and “transverse” or “in-plane” and “out-of-plane”
- Shrinkage of oriented films
- TMA is mainly used for measuring elastomers, adhesives and coatings, films and fibers, rubbers and plastics, but can also measure thermal expansion in metals and ceramics.

# Thermal Analysis

## 2. Methods | 2.6. TMA

**Advantages of TMA:**

- TMA is quick and easy to carry out.
- It provides valuable information about the behavior of the material as a function of temperature change.
- Small sample size
- Low force range
- Force alteration: linear and stepwise
- Programmable temperature: (1) sequential heating and cooling cycles, (2) isothermal

**Disadvantages of TMA:**

- The sample is destroyed during the test.
- It is difficult to get accurate results for irregularly shaped objects.