5.2 THERMAL ANALYSIS

- Thermal analysis is a form of analytical technique most commonly used in the branch of materials science where changes in the properties of materials are examined with respect to temperature.
- It is a group of techniques in which changes of physical properties or chemical properties of the sample are monitored against time or temperature, while the temperature of the sample is programmed.
- The temperature program may involve heating or cooling at a fixed rate, holding the temperature constant (isothermal), or any sequence of these.
- The sample is subjected to a predefined heating or cooling program.
- The sample is usually in the solid state and the changes that occur on heating include melting, phase transition, sublimation, and decomposition.

5.2.1 THERMAL PROPERTIES

- Thermal properties of material decide how it reacts when it is subjected to heat fluctuation (excessive heat or very low heat, for example). The major thermal properties are described in table 5.1.

Table 5.1. Thermal properties

S. No	Properties	Description
1.	Thermal conductivity	It is determining temperatures as a function of time along the length of a bar or across the surface
2.	Specific heat	It is defined as heat absorbed per unit mass per degree change in temperature
3.	Thermal expansion	Expansion due to heat is usually measured in linear fashion as the change in a unit length of a material caused by a one-degree change in temperature.

4.	Thermal stress	The stress experienced by a body due to either thermal expansion or contraction is called thermal stress.
5.	Thermo-Elastic Effect	When a solid is subjected to a load, work is done on it and it changes in volume. This will appear in the form of rise of temperature of solid when it is in stretched. Similarly, when the solid is rapidly relaxed, it will cool. This warming or cooling phenomenon is called thermo elastic effect.
6.	Thermal shock	The ability of material to withstand thermal stresses due to sudden and severe changes in the temperature at the surface of a solid body.
7.	Melting point or heat resistance	Melting point or softening point is a significant temperature level as it represents transition point between solid and liquid phases.
8.	Emissivity of Materials	The emissivity (e) of the surface of a material is its effectiveness in emitting energy as thermal radiation and varies between 0.0 and 1.0.
9.	Latent Heat of Fusion of Materials	Latent heat is the amount of heat added to or removed from a substance to produce a change in phase.

10.	Latent Heat of Vaporization Materials of	Certain amount of energy is involved in this of change of phase, When a material changes phase from solid to liquid or from liquid to gas.

5.2.2THERMAL TESTING

- Thermal Testing involves testing a product at the extremes of its intended use thermal environment for heating rate, temperature and airflow on gaseous atmosphere or vacuum with measuring case temperatures of individual components to determine the effect on product performance an long-term reliability.
- It measures based on dynamic relationships between temperature, Mas Volume and Heat of reaction.

Major methods of Thermal testing,

- Differential thermal analysis
- Dilatometer
- Differential scanning calorimetry
- Dynamic mechanical analysis
- Thermogravimetric analysis
- Thermo mechanical analysis
- Thermo optical analysis

Other common methods of thermal methods

- Dielectric thermal analysis
- Evolved gas analysis
- Laser flash analysis
- Derivatography

Table 5.2. Parameters of thermal testing

S.No	Method	Parameter testing
1.	Thermogravimetric Analysis	Mass changes
2.	Differential Thermal Analysis	Temperature Difference
3.	Differential Scanning Calorimetry	Heat Difference
4.	Evolved Gas Analysis	Gas Decomposition
5.	Thermo Mechanical Analysis	Deformation And Dimension.
6.	Dilatometer	Volume
7.	Dielectric thermal analysis	Electrical properties
8.	Thermo optical analysis	Optical properties

5.2.3THERMOGRAVIMETRIC ANALYSIS (TGA)

- The Thermogravimetric analysis (TGA) is a type of thermo analytical testing performed on materials to determine changes in weight in relation to changes in temperature,
- The TGA relies on a high degree of precision in three measurements: weight, temperature and temperature change.
- The TGA is commonly employed in research and testing to determine characteristics of materials, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues.

5.2.4 DIFFERENTIAL SCANNING CALORIMETRY

- DSC measures the energy absorbed or released from a sample as a function of time or a temperature profile.
- DSC is useful to make the measurements for melting points, heats of reaction, glass transition, and heat capacity

1. PRINCIPLE

- Differential scanning calorimetry (DSC) is based on the principle; sample and reference are maintained at the same temperature, even during a thermal event (in the sample). The energy required maintaining zero temperature different between the sample and the reference is measured.
- By calibrating the standard material (reference material), the unknown sample quantitative measurement is achievable.

2. TYPES

There are four different types of DSC instrument

- Heat flux DSC
- Power compensated DSC
- Modulated DSC
- Hyper DSC
- Pressure DSC

The most common methods are Heat flux DSC and Power compensated DSC

3. POWER COMPENSATION DSC

- A technique in which difference of thermal energy that is applied to the sample and the reference material separately per unit of time is measured as a function of the temperature.

(a) Components

- Separate sensors and heaters are used for the sample and reference
- **Sample holder**: Al or Platinum pans
- **Sensors**: Platinum resistance thermocouples
- **Furnace**: Separate blocks for sample and reference cells
- **Temperature controller**: Differential thermal power is supplied to the heaters to maintain the temperature of the sample and reference at the program value

(b) Working

- The power needed to maintain the sample temperature equal to the reference temperature is measured.
- In power compensation DSC two independent heating units are employed.
- These heating units are quite small, allowing for rapid rates of heating, cooling and equilibration. The heating units are embedded in a large temperature-controlled heat sink.
- The sample and reference holders have platinum resistance thermometers to continuously monitor the temperature of the materials.
- The instrument records the power difference needed to maintain the sample and reference at the same temperature as a function of the programmed temperatures.
- Power compensated DSC has lower sensitivity than heat flux DSC, but in response time is more rapid. It is also capable of higher resolution the heat flux DSC.
- This makes power compensated DSC well suited for kinetics studies which fast equilibrations to new temperature settings are needed.

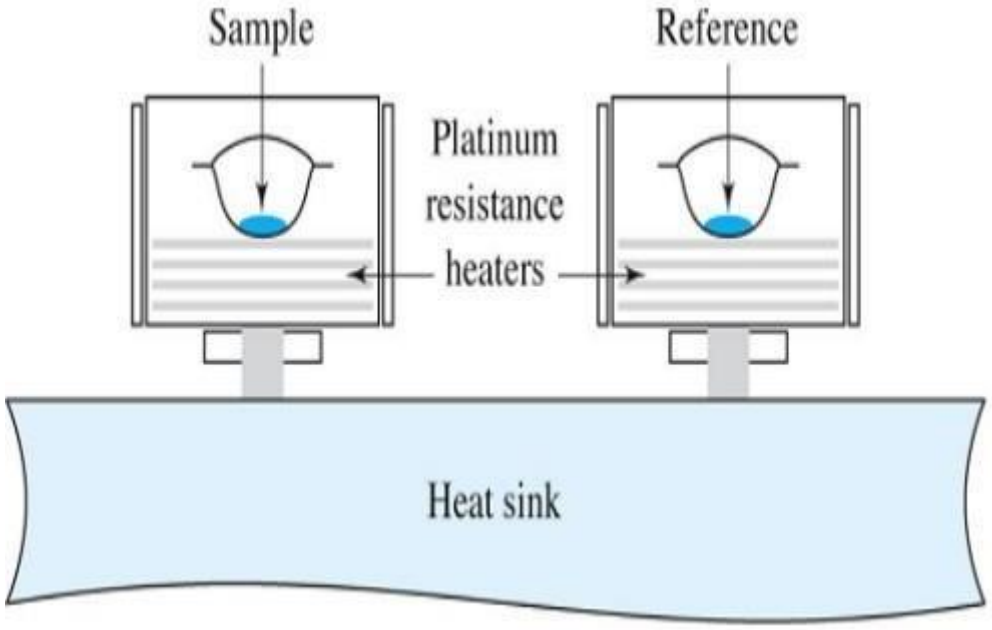


Fig. 5.1. Typical arrangement of Power compensated DSC

HEAT FLUX DSC

- In heat flux DSC, the difference in heat flow into the sample and reference is measured while the sample temperature is changed at the constant rate
- Sample and reference are connected by a low resistance heat flow path (a metal disc). The assembly is enclosed in a single furnace.

(a) Components

One blocks for both sample and reference cells

- **Sample holder:** Sample and reference are connected by a low- resistance heat flow path. Al or Platinum pans placed on constantan disc.
- **Sensors:** Chromel alumel thermocouples Furnace are used.

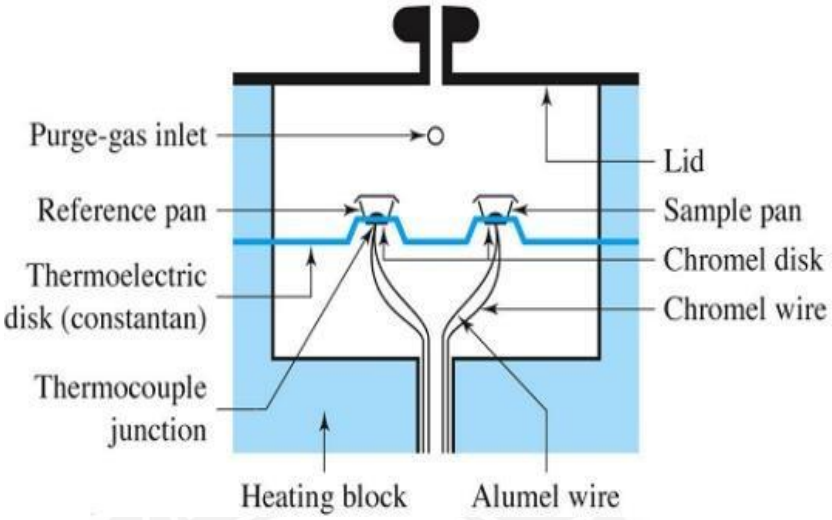


Fig. 5.2. Typical arrangement of heat flux DSC

(b) Working

- The main assembly of the DSC cell is enclosed in a cylindrical, silver heating black, which dissipates heat to the specimens via a constantan disc which is attached to the silver block.
- The disk has two raised platforms on which the sample and reference pans are placed.
- A chromel disk and connecting wire are attached to the underside of each platform, and the resulting chromel-constantan thermocouples are used to determine the differential temperatures of interest.
- Alumel wires attached to the chrome discs provide the chromel-alumel junctions for independently measuring the sample and reference temperature.

5. DSC MEASURES

- Glass transitions
- Melting and boiling points
- Crystallization time and temperature
- Percent crystallinity
- Heats of fusion and reactions
- Specific heat capacity
- Oxidative/thermal stability

- ❖ Reaction kinetics
- ❖ Purity

6. DSC Curve

- ❖ DSC Curve is plot between heat flow and temperature. It shows various peaks of measurement

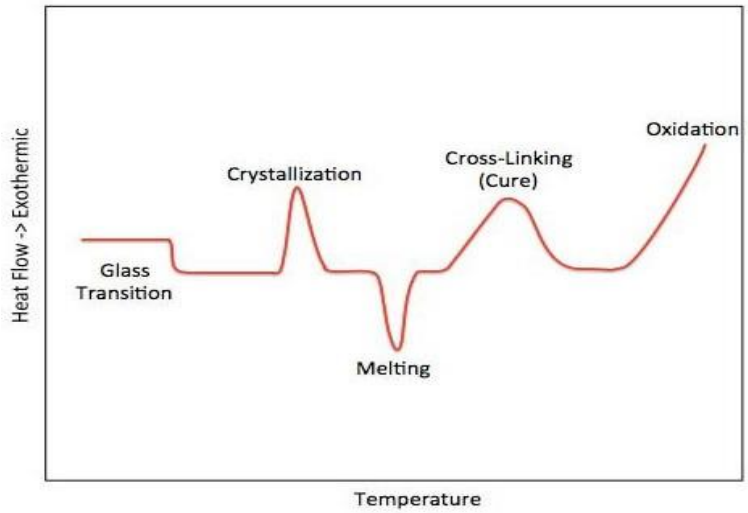


Fig. 5.3. DSC Curve

Factors Affecting DSC Curve

Table 5.3. Factors Affecting DSC Curve

Instrumental Factors	Sample Characteristic Factors
❖ Furnace heating rate ❖ Recording or chart speed ❖ Furnace atmosphere ❖ Geometry of sample holder/location of sensors ❖ Sensitivity of the recording System ❖ Composition of sample containers	❖ Amount of sample ❖ Nature of sample ❖ Sample packing ❖ Solubility of evolved gases in the sample ❖ Particle size ❖ Heat of reaction ❖ Thermal conductivity

7. APPLICATION OF DSC

- To observe fusion and crystallization events as well glass transition temperature
- To study oxidation, as well as other chemical reactions
- The transition from amorphous to crystalline is known.
- The ability to determine transition temperature and enthalpies.
- Rapid optimization of purification and manufacturing conditions

8. SOURCES OF ERRORS

- Calibration
- Contamination
- Sample preparation – how sample is loaded into a pan
- Residual solvents and moisture.
- Thermal lag
- Heating/Cooling rates
- Sample mass

9.ADVANTAGES OF DSC

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

10. LIMITATIONS OF DSC

- 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

5.2.5 DIFFERENTIAL THERMAL ANALYSIS

- Differential thermal analysis (DTA) is a thermo-analytical technique which is used for thermal analysis where thermal changes can be studied. It is used to determine the oxidation process, decomposition, and loss of water or solvent.

1. PRINCIPLE

- In DTA, the sample material and an reference material are made to undergo identical thermal cycles, (i.e., same cooling or heating programme) while recording any temperature difference between sample and reference. This differential temperature is then plotted against time, or against temperature (DTA curve, or thermogram). Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference.

2. COMPONENTS

- Furnace - This is device for heating the sample(Nickel and chromium alloy furnace)
- **Sample holder** - This is used to contain the sample as well as the reference material (Platinum alloy holder)
- **DC amplifier** - Generally a low level DC amplifier is employed.
- **Differential Temperature Detector (Thermogram)** - The function of this detector is to measure differential temperature.
- **Furnace Temperature Programme** - The main function of this is to increase the temperature of the furnace at a steady rate.
- **Recorder** - This is to record the DTA curve (automatic electronic recorder)

- **Control Equipment** - Its function is to maintain a suitable atmosphere in the furnace & sample holder.

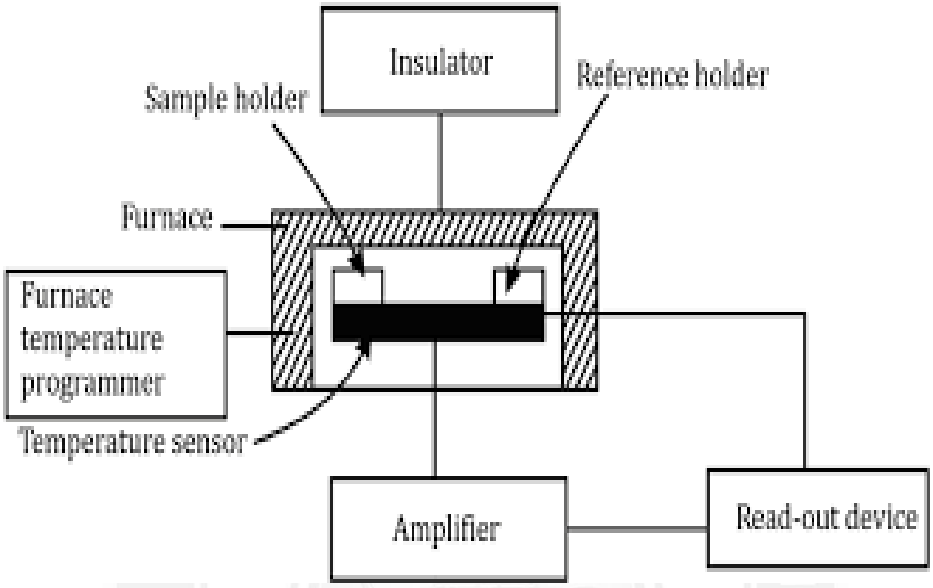


Fig. 5.4. Cross section of DTA

3. WORKING

- The sample under investigation is loaded into a container.
- This container is then placed onto the sample pan and it is marked as S (means sample). Same quantity of reference sample is placed in another container which is then placed onto the reference pan and it is marked as R (means reference).
- In order to heat the sample pan and the reference pan at an identical rate, the dimensions of these two pans should be nearly identical; moreover, the sample and the reference should have equal weights, thermally matched and should be arranged symmetrically with the furnace.
- The metal block which surrounds the pans acts as a heat sink whose temperature is increased slowly by using an internal heater.
- The sink then heats the sample and reference material simultaneously.
- Two pairs of thermocouples are used, one pair is in contact with the sample and the second pair is in contact with the reference.

- Thermocouple is attached with an amplifier which amplifies the result of differential thermocouple and sent this result to the read-out device which displays the results in the form of DTA curve or thermogram as a function of the sample temperature, reference temperature or time.
- No signal is generated if no temperature difference is observed even though the actual temperatures of both the sample and reference increasing.
- When there is a physical change in the sample then heat is absorbed or released. For example, when a metal carbonate is decomposed then carbon dioxide is released. This is an endothermic reaction where the heat is absorbed and the temperature of the sample is decreased. Now the sample is at a lower temperature than that of the reference. This temperature difference between sample and reference produces a net signal, which is then recorded.

4. DTA Curve

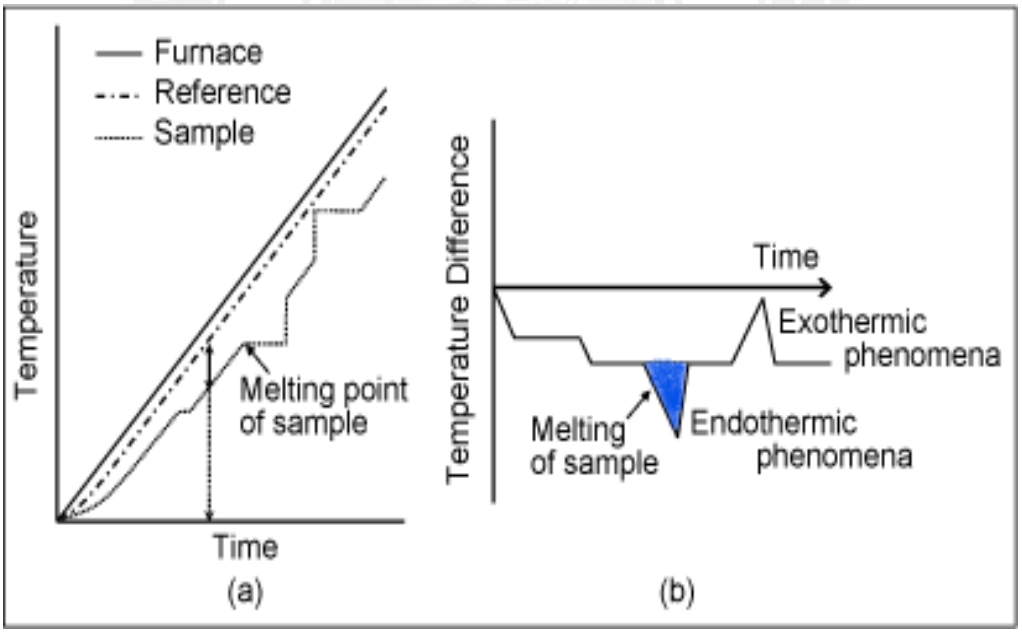


Fig. 5.5 (a) The DTA curve or thermo gram is a plot between differential temperature and time. (b) DTA curve may be endothermic (downward plot) orexothermic (upward plot)

Factors affecting DTA curve

Table 5.4. Factors affecting DTA curve

Sample factors	Instrumental factors	Physical factors
❖ Amount of the sample. ❖ Packing density. ❖ Particle size of the sample material. ❖ Degree of crystallinity. ❖ Heat capacity. ❖ Thermal conductivity. ❖ Dilutes of the diluents. ❖ Swelling of the sample. ❖ Shrinkage of the sample	❖ Size or shape of the holders. ❖ Material of the sample holder. ❖ Recording system sensitivity. ❖ Rate of heating of the sample. ❖ Atmosphere around the sample. ❖ Thermocouple location in the sample. ❖ Instrumental design.	❖ Adsorption. ❖ Change in the crystal structure. ❖ Crystallization. ❖ Desorption. ❖ Change in the crystal structure. ❖ Vaporization. ❖ Sublimation. ❖ Melting.

5. ADVANTAGES

- ❖ It can be operated at very high temperature ranges.
- ❖ Highly sensitive technique.
- ❖ Flexibility in crucible volume
- ❖ Both exothermic and endothermic reactions can be determined accurately.

6. DISADVANTAGES

- ❖ There is lot of uncertainty in transition reactions and heat of fusions upto 20-50\%
- ❖ Destructive limited range of samples time consuming usually not qualitative.

7. APPLICATIONS

- Used to identify the minerals both qualitatively and quantitatively.
- Rapid identification of the compositions of mixed clays
- Polymer's characteristics can be easily characterized.
- Degree of crystallinity can be measured.
- Degree of polymerization can be assessed.
- Many of the biological materials can be analyzed.
- DTA offers a wide spectrum of useful investigations related to reaction kinetics, polymerization, solvent retention, phase-transformations, solid phase reactions and curing or drying properties of a product
- Melting point, boiling point, and temperatures of decomposition of organic compounds can be determined.
- Have wide applications for the quality control (QC) of many substances such as soil, cement, glass, etc.
- Also used to determine the thermal stability of many inorganic compound s and complexes.

5.2.6 THERMO-MECHANICAL ANALYSIS

- A technique in which a deformation of the sample under non-oscillating stress is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. Thermo mechanical analysis (TMA) easily and rapidly measures sample displacement (growth, shrinkage, movement, etc.) as a function of temperature, time and applied force.

1. PRINCIPLE

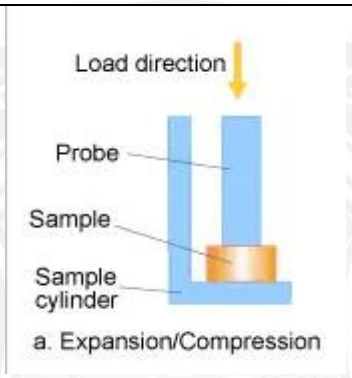
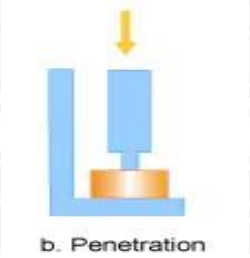
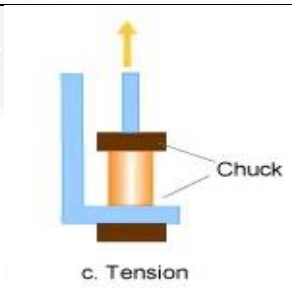
- Thermo mechanical analysis (TMA) is used to measure the dimensional changes of a material as a function of temperature by applying stress. The stress may be compression, tension, flexure or torsion.

2. COMPONENTS

- Transducer (Linear Variable Displacement Transducer (LVDT), laser optoelectronic etc.,

- ❖ Probe (made up of quartz glass) Thermocouple Furnace
- ❖ Force generator

3. PROBES ON DIFFERENT LOADING CONDITION

Loading Condition	Load Application	Purpose
(a) Expansion/ Compression Probe		It is used for the measurement of the deformation by the thermal expansion and the transition of the sample under the compressed force is applied
(b) Penetration Probe		It is used for the measurement softening temperature.
(c) Tension Probe		It is used for the measurement of the thermal expansion and the thermal shrinkage of the sample such as the film and the fibre.

4. CONSTRUCTION AND WORKING

- 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 construction of the pushrod and sample holder depends on the mode of the measurements.

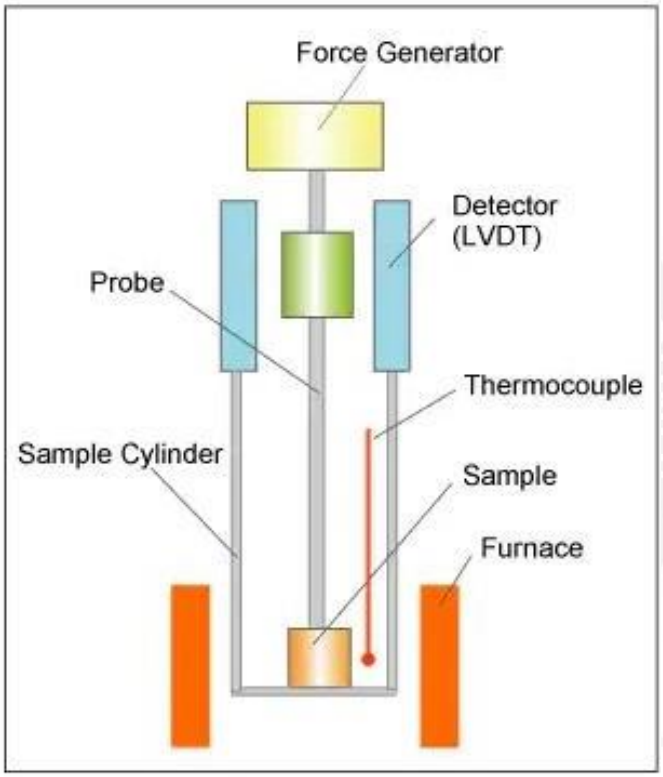


Fig. 5.6. Working of Thermo mechanical analyser

- The thermocouple for temperature measurement is located near the sample. The rate of 5 degrees C/min is usually the maximum recommended value for good temperature equilibration across the specimen
- 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.

- Every displacement of the pushrod is trans-formed into an analog signal by the LVDT, converted to digital form and then recorded in the computer system, and finally presented by the software as a dimensional change versus time or temperature.

5. APPLICATION

- Measurement of Dimensional Change
- Coefficient of Linear Thermal Expansion
- Determination of Material Anisotropy
- Softening Temperature and Glass Transition
- Linear Thermal Expansion

6. ADVANTAGES

- Compactness and lightness
- Low operation voltage
- Measures large deformation
- Large actuation force
- Measures measure relaxation effects

7. LIMITATION

- used only for solid samples.
- Creep occurring concurrently with normal dimensional changes.
- Usage of proper probe.
- Low operational speed

5.2.7 THERMO MECHANICAL DYNAMIC ANALYSIS

- Thermo mechanical dynamic analysis, otherwise known as Dynamic Mechanical Analysis (DMA), is a technique where a small deformation is applied to a sample in a cyclic manner. This allows the materials response to

stress, temperature, frequency and other values to be studied. The term is also used to refer to the analuzers that performs the test.

- Dynamic mechanical analysis (DMA) is an important technique used to measure the mechanical and viscoelastic properties of materials such as thermoplastics, thermosets, elastomers, ceramics and metals.

1. PRINCIPLE

- A sinusoidal stress is applied and the strain in the material is measured, allowing one to determine the complex modulus. The temperature of the sample or the frequency of the stress are often varied, leading to variations in the complex modulus; this approach can be used to locate the temperature of the material, as well as to identify transitions corresponding to other molecular motions.

2. TYPES OF THERMO MECHANICAL DYNAMIC ANALYZER

- Forced resonance analyzers - Analyzers force the sample to oscillate at a certain frequency and are reliable for performing a temperature sweep.
- Free resonance analyzers- Free resonance analyzers measure the free oscillations of damping of the sample being tested by suspending and swinging the sample

3. MODE OF ANALYZER

- Stress (force) control - The structure of the sample is less likely to be destroyed and longer relaxation times/longer creep studies can be done.
- Strain (displacement) control-The better short time response for materials of low viscosity and experiments of stress relaxation are done with relative ease

4. COMPONENTS

- **Transducer Sensor (Linear Variable Displacement Transducer (LVDT)-** It is which measures a change in voltage.

- **Drive shaft or probe** - It is a support and guidance system to act as a guide for the force from the motor to the sample.
- **Drive motor** - A linear motor for probe loading which provides load for the applied force.
- **Stepper motor** - It controls the specimen dimension and measurement.

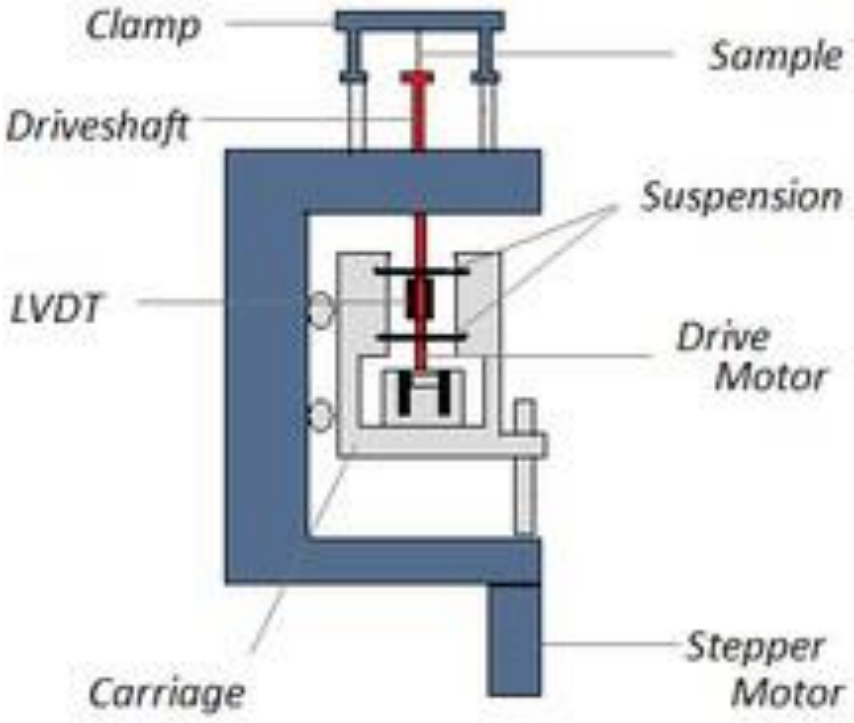
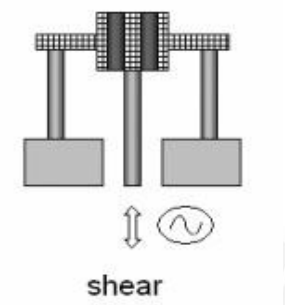
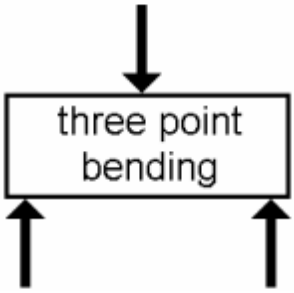
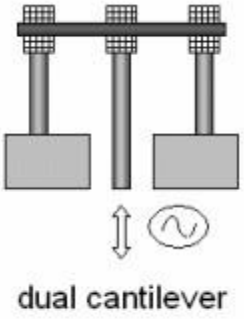


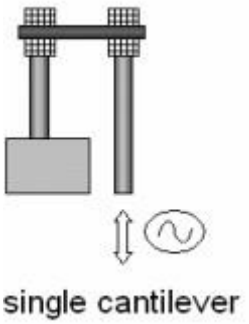
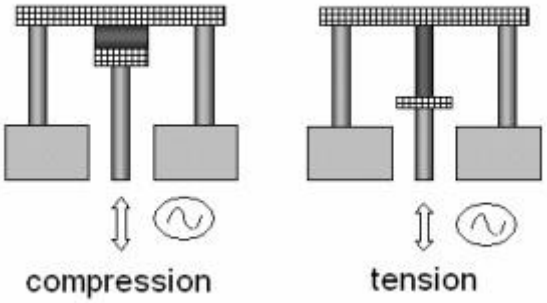
Fig. 5.7. Cross section of Thermo mechanical dynamic analyser

5. WORKING

- The sample is clamped in the measurement head of the DMA instrument. During measurement, sinusoidal force is applied to the sample via the probe or driving shaft.
- Deformation caused by the sinusoidal force is detected and the relation between the deformation and the applied force is measured.
- Properties such as elasticity and viscosity are calculated from the applied stress and strain plotted as a function of temperature or time.

Table 5.5. different loading condition

Modes	Stress application	Purpose
Shear mode		Used for evaluation of thin fibers or films or bundle of single fiber
3-point bending mode		Best for medium to high modulus materials.
Dual cantilever mode		Highly damped materials can be measured.

Single cantilever mode		Suited best for thermoplastics
Tension or compression mode		Used for low to medium modulus materials

6. DIFFERENT LOADING MODES

- The most suitable type should be selected depending on the sample shapes, modulus and measurement purpose.

7. ADVANTAGES

- It is an essential analytical technique to determining the viscoelastic properties of polymers.
- Very soft and hard samples are measured.
- Allows accurate temperature measurement.
- It can provide major and minor transitions of materials
- It is also more sensitive.

- ❖ It is able to quickly scan and calculate the modulus for a range of temperatures.
- ❖ It is the only technique that can determine the basic structure of a polymer system
- ❖ This analytical method is able to accurately predict the performance of materials in use.

8. LIMITATIONS

- ❖ It leads to calculation inaccuracies.
- ❖ The large inaccuracies are introduced if dimensional measurements of samples are slightly inaccurate.
- ❖ The oscillating stress converts mechanical energy to heat and changes the temperature of the sample.
- ❖ The maintaining an exact temperature is important in temperature scans, this also introduces inaccuracies.
- ❖ The final source of measurement uncertainty comes from computer error.

9. DMA MEASURES

- ❖ Displacement and force
- ❖ Wide range of force 1 mN to 40N
- ❖ Wide range of frequency 0.001 to 1000Hz.
- ❖ Wide stiffness range.
- ❖ Coefficient of Thermal Expansion (CTE)
- ❖ Glass Transition Temperature
- ❖ Compression Modulus of Polymeric Materials
- ❖ Viscoelastic properties such as:
  - Storage modulus (purely elastic component)
  - Loss modulus (purely viscous component)
  - Loss tangent

10. APPLICATION

- ❖ Measurement of the glass transition temperature of polymers

- Varying the composition of monomers
- Effectively evaluate the miscibility of polymers
- To characterize the glass transition temperature of a material.
- Mechanical properties in the relevant frequency range
- +Modulus information
- Measurement of different relaxations
- Molecular interaction
- Nonlinear properties
- Damping behaviour