Chapter 2 EXPERIMENTAL TECHNIQUES

2.1 Introduction

Thermal Analysis is a branch of material science and it is a group of techniques in whicha physical property of a substance and/or its reaction products are measured as a function of temperature.[2.1] The thermal analysis techniques can provide wealth of information of the kinetic of phase transformations, thermal stability, thermodynamic properties, and structural relaxation and so on. It can be classified according to the type of temperature programme that the sample is subjected to and the measured output signal. Isothermal and non-isothermal (heating at constant rate) are the most commonly used temperature profiles to study the sample.

Thermal analysis technique provide a data for a wide range materials such as ceramics, metallic glasses, thin films,polymers, plastics, composites, laminates, adhesives, food, coatings,pharmaceuticals, organic materials, rubber, petroleum, chemicals, explosives, biological samplesetc. The general instrumentation for the thermal analysis primarily includes :

i. A sample holder, where the sample is kept

ii. Sensors for detecting the required properties with respect to temperature

iii. A closed chamber where the sample and sensors can be placed and the experimental parameters can be controlled according to the requirements.

iv. A computer for adjusting the experimental parameters, collecting data and performing further calculations.

Different properties are studied by different techniques. Table 2.1 reports different techniques and various properties associated with them.

Table 2.1 Different thermal analysis techniques [2.1]

Techniques	**Properties measured**
Dielectric thermal analysis (DEA)	Dielectric permittivity and loss factor
Differential thermal analysis (DTA)	Temperature difference
Dilatometry (DIL)	Volume
Differential scanning calorimetry (DSC)	Heat difference
Dynamic mechanical analysis (DMA)	Mechanical stiffness and damping
Evolved gas analysis (EGA)	Gaseous decomposition products
Laser flash analysis (LFA)	Thermal diffusivity and thermal conductivity
Thermogravimetric analysis (TGA)	Mass
Thermomechanical analysis (TMA)	Dimension
Thermo-optical analysis (TOA)	Optical properties
Derivatography	A complex method in thermal analysis

“Differential Scanning Calorimetry” (DSC) is one of the most often used thermo-analytical techniqueprimarily because of its speed, simplicity, and availability [2.2]. It is mostly used for quantitative analysis [2.3]. E.S. Watson and M.J. O'Neill developed this technique in 1962 and commercialized it in 1963 at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy [2.4]. The DSC instrument works along with a controller and associated software for acquiring the data and analysis

A differential calorimeter, measures the heat of sample relative to a reference.The temperature of sample and reference are made identical by varying the power input to the two surfaces and heats the sample with a linear temperature ramp [2.5]. Due to difference in the composition of the sample and the reference, different amount of energy will be required to raise the temperature of the cells 2, 12, 13. The energy required to do this is the enthalpy or heat capacity changes inthe sample relative to reference. Heat flows into the sample, in the endothermic reactions, whereas heat flows out of the sample in exothermic reactions. Only a few mg of material are required to run the analysis.

DSC is widely used to study thermal transitions, i.e., solid-solid transitions as well as solid-liquid and various other transitions and reactions. DSC measures the temperatures and heat flows associated with transitions in materials, in a controlled atmosphere. Some reactions need inert atmosphere, whereas others can be done in air also. Air, nitrogen, or helium atmospheres can be used in the instruments depending upon the reaction.DSC is an efficient and powerful tool for quick determination of the specific heat and enthalpy of change accompanying the primary or secondary phase transition of substance [2.6] It also provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes of materials during physical transitions that are caused by phase changes, melting, glass transitions, crystallization, oxidation, and other heat related changes [2.7].

TGA and DSC require same experimental conditions for their operation. Sometimesthey are used simultaneously. This concurrent use of two instruments is known as simultaneous thermal analysis (STA) [2.8].

The advantages of DSC technique can be summarized as [2.9]:

i. It is a fast technique, i.e., it takes a small time to perform one run.

ii. Different kind of samples such as solid, liquid, powders, and thin films can be tested in a variety of environments (air, vacuum, inert gas, etc.)

iii. A wide range of temperature can be used to analyse the phase transitions in a material, and quantitative analysis of these transitions can be done easily using software’s.

iv. The applicability of DSC can be extended to a wide variety of materials that includes the pharmaceutical and drug industry, polymers, liquid crystals, and food science. DSC can also be used to determine the oxidative stability of a material.

2.2 Principle and Theory of DSC

Principle: When a sample goes througha physical transformation such as a phase transition, more or less heat will need to flow to the samplethan to the reference (typically an empty sample pan) for maintaining both at the same temp. The amount of heat flow to the sample depends on the processwhether it is exothermic or endothermic.For e.g. when a solid sample transforms in to liquid, increment of temperature will require. So, more heat is required to flow to the sample compare to the referencebecause phase transition from solid to liquid is the endothermic processes. So sample absorbs heat as it undergoes a phase transition. Likewise, as the sample undergoes exothermic processes (Such as crystallization) less heat is required to raise the sample temp. By observing the difference in heat flow between the sample and reference, DSC is able to measure the amount of heat absorbs or release during such transition [2.10].

Theory: Differential Scanning Calorimetry is used to measure thethermodynamic quantities which can be calculated by the following equations:

Specific heat

The sudden change in the specific heat at the glass transition temperature is the one of the characteristics of all glassy materials.[2.11-2.15]. Specific heat(C_p) of the samples is easy to evaluate from DSC data using following expression:

$C_P=[m_r\Delta_s/ m_s\Delta_r]C_r$ (1)

where, m_s and $m_r$is the mass of sample and reference materialrespectively and Δ_s and Δ_r are the shifts (in J/g) for sample and reference materialrespect to base line, respectively and C_r is the specific heat of the reference material, which can be taken from the standard literature.

Enthalpy difference from glass to crystalline state

The enthalpy released during transformation from glass to crystalline state is given by:

$$\Delta H_{gc}=\Delta H_g-\Delta H_c \qquad (2)$$

where ΔH_g and ΔH_c represents the enthalpy released per unit mass of the sample during relaxation process and crystallization process respectively.The ΔH_g can be evaluated by determining the area under the curve of the specific heat versus temperature [2.16-2.17]:

$$\Delta H_g= \int C_P dT \qquad (3)$$

whereas, the ΔH_ccan be calculated by measuring the area under the crystallization peak.

Entropy difference between metastable states in glassy region

$$\Delta S=\Delta Q/T \qquad (4)$$

where, ΔQ is the amount of thermal energy absorbed by the sample is calculated by measuring the area under the endothermic peak.

Gibbs free energy difference

$$\Delta G_{gc}=\Delta G_g-\Delta G_c \qquad (5)$$

where, ΔG_g and ΔG_c represents the Gibbs free energy change in the glassy and crystalline state respectively.The $\Delta G_g$is obtained by:

$$\Delta G_g=\Delta H_g-T\Delta S \qquad (6)$$

where, ΔH_g= the heat released per unit mass by the sample in the relaxation process and $T\Delta S=\Delta Q$, is the amount of thermal energy absorbed by the sample in the glassy region.

whereas ,the $\Delta G_c$is obtained by:

$$\Delta G_c=\Delta H_c-T\Delta S \qquad (7)$$

where, ΔH_c= the heat released by the sample in the crystallization process and $T\Delta S=\Delta Q$, is the amount of thermal energy released by the sample in the crystalline region.

Entropy difference between glassy and crystalline state

$$\Delta S_{gc}=\Delta S_g-\Delta S_c \tag{8}$$

where, ΔS_g and ΔS_c represents the entropy change in the glassy and crystalline state respectively.

The $\Delta S_g$is obtained by:

$$\Delta S_g=S_{conf.}+\int_0^T[Cp/T]\,dT \tag{9}$$

whereS$_{\text{conf, is the}}$ configurational entropy and is defined as:

S_{conf}=-klnWhere, W denotes the total number of different ways in which atoms can arrange themselves in a particular fashion and is given by: W=N!/{(A_aN) !(B_bN) !(C_cN) !}where, N is the total number of the atoms present in system.A_a is the fraction of the A atom, B_b is the fraction of the B atom, C_c is the fraction of the C atom.Whereas, configurational entropy are taken to zero for the calculations of $\Delta S_{c.}$ This is because there is only one way to arrange the atoms in the correct ordered array (W=1) [2.18]. Therefore, the entropy of crystalline state can be written as[2.19]:

$$S_c=\int_0^T[Cp/T]\,dT \tag{10}$$

The area of C_p/T versus T curve gives the entropy of the crystalline region of the system.

2.3 Basics of DSCInstrument

There are four different types of DSC instrument

1. Heat flux DSC
    - i) The Disk Type Measuring System– Heat Flux DSC
    - ii) The Cylinder measuring system – Heat Flux DSC
    - iii) The turret-type measuring system – HF DSC
    - iv)Micro differential DSC–modified HF DSC
2. Power compensated DSC
3. Modulated DSC
4. Hyper DSC

5. Pressure DSC

1. 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 [2.20]. The sample and reference are connected by a low–resistance heat–flow path using metal disc. Both of them are enclosed in the same furnace. The resulting heat flow is small because sample and reference are in good thermal contact. This system is a modification of differential thermal analysis (DTA), differing only by the fact that the sample and reference crucibles are linked by good heat–flow path.

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. A separate thermocouple embedded in the silver block serves a temperature controller for the programmed heating cycle. And inert gas is passed through the cell at a constant flow rate of about 40ml/min [2.21]. The thermal resistances of the system vary with temperature. Under such situation instruments can be operated in the ‘calibrated’ mode, during which the amplification is automatically varied with temperature to give a nearly constant calorimetric sensitivity [2.22].

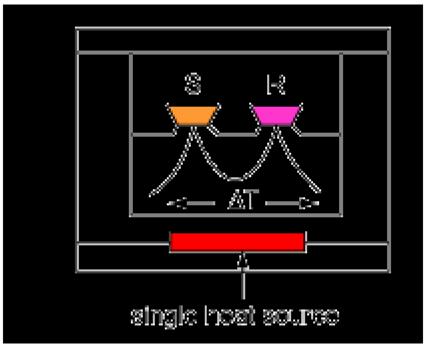

Fig.2.1 Schematic diagram of heat flux DSC
(Source: http://www.mtarr.co.uk)

Fig.2.2 A picture of DSC (Shimadzu, Model DSC-50)

i)The Disk Type Measuring System– Heat Flux DSC

The heat exchange in this type, takes place trough a disk which is solid sample support with a medium thermal conductivity. Its features are high sensitivity and small sample volume [2.23].

ii) The Cylinder measuring system – Heat flux DSC

The heat exchange takes place between the(big) cylindrical sample cavities and the furnace with a low thermal conductivity (thermopile). It is using a cylinder type measuring system by two sintered alumina cylinders set parallel and symmetrical in the heating furnace. This is appropriate for large samples.

iii)The turret-type measuring system – HF DSC

In turret type, the heat exchange takes place via small hollow cylinders which also serve as sample support. This is ideal for determining the purity of metals.

iv) Micro differential DSC–modified HF DSC

This method is a combination of an isothermal calorimeter and a HF-DSC mode device. In an isothermal calorimeter, the heat generated by the sample flows through the thermal resistance into a water jacket. The temperature difference across the thermal resistance is measured. [2.24] the temperature range is very narrow (–20 °C to ≈120°C).

2. Power compensation DSC

There are two independent heating units employed for the sample and reference which are quite small. The heating units are embedded in a large temperature- controlled heat sink.

In power compensation DSC, the temperatures of the sample and reference are kept equal to each other while both temperatures are increased or decreased linearly. The instrument records the power difference needed to maintain the sample and reference at the same temperature as a function of the programmed temperatures. The sample and reference holders have platinum resistance thermometers to continuously monitor the temperature of the materials.

Power compensated DSC has lower sensitivity than heat flux DSC, but its response time is more rapid.

So, it is well suited for kinetics studies in which fast equilibrations to new temperature settings are needed. It is also capable of higher resolution then heat flux DSC [2.25].

All PC DSC are in basic principles the same. But, one of the special PC DSC is photo DSC, where direct measurementsof radiation flow occurunder a light source.

3. Modulated DSC

it is a new technique introduced in 1993 [2.26]. It separates the overlapping events of the DSC scans. In MDSC the normally linear heating ramp is overlaid with the sinusoidal function (MDSC) defined by a frequency and amplitude to produce a sine wave shape temperature versus time function.

4. Hyper DSC

Fast scan DSC has the ability to perform valid heat flow measurements with fast linear controlled rates (up to 500 K/min). The benefits of such devices are increased sensitivity at higher rates and provides the best results in medications

5. Pressure DSC

In pressure DSC, the sample can be submitted to different pressures, which allows the characterization of substances at the pressures of processes or to distinguish between overlapping peaks [2.27].Applications of this technique includes studies of pressure sensitive reactions, evaluation of catalysts, and resolution of overlapping transitions [2.28].

2.4 Calibration

Temperature Calibration

The measured temperature values are related to the emf generated at the thermocouples located under the sample. The emf is converted to temperature units using standard calibration charts. It is therefore recommended to calibrate the temperature axis using substances with precisely known melting points. One must also consider the thermal shift (DTL). Very low heating rates should be avoided during the calibration measurement.

Enthalpy Calibration

In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. An empty aluminium pan or alumina is used as the reference. At a constant rate, the temperature of both the sample and reference are increased. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes [2.29]:

$$(dq/dt)_p = dH/dt \qquad (1)$$

The heat flow difference between the sample and the reference is:

$$\Delta\ dH/dt=(dH/dt)_{sample} - (\ dH/dt)_{reference} \qquad (2)$$

and can be either positive or negative. *ΔdH/dt*is positive if the process endothermic and in most phase transitions, heat will be absorbed, therefore heat flow to the sample will be higher than that to the reference. While in exothermic process, such as crystallization, the opposite is true and *ΔdH/dt* is negative.

2.5 applications

Determination of Heat Capacity : Heat capacity (*Cp*) is defined as the amount of heat required to raise the temperature of a material by 10C. DSC plot can be used to determine Heat Capacity.When we start heating two pans, the computer will plot the difference in heat output of the two heaters against temperature that is plot of heat absorbed by the sample against temperature: The heat flow is heat (q) supplied per unit time (t), whereas, The heating rate is temperature increase (ΔT) per unit time (t),

Heat flow= heat/ time = q/t

Heating rate = temperature increase / time = ΔT / t

By dividing heat flow (*q/t)* by the heating rate(Δ*T/t)*. It ends up with heat supplied divided by the temperature increase, which is called heat capacity.

$(q/t) / (\Delta T / t) = q/ \Delta T= Cp$ =heat capacity

Thus, the slope of heat supplied versus increase in temperature gives the value of heat capacity of that sample.

The Glass Transition Temperature

On further heating the glassy sample to a certain temperature, plot will shift downward suddenly. There is an increase in the heat capacity of the sample at the temperature, which is The Glass Transition Temperature.

Crystallization Temperature

After glass transition, when sample falls into these crystalline arrangements, it gives off heat. This drop in the heat flow is shown as a big peak in the plot. The temperature at the highest point in the peak is usually considered as crystallization temperature, or Tc .Also, the area of the peak can be measured, which tells us the latent energy of crystallization of the sample.

Melting Temperature

If sample is heated past its Tc, eventually crystals begin to fall apart, that is they melt. When the sample crystals melt, they must absorb heat in order to do so. Melting is a first order transition so the sample's temperature won't rise until all the crystals have melted. The heater under the sample pan has to put a lot of heat into the sample. This extra heat flow during melting shows up as a big dip on DSC plot.

Liquid crystals: Using DSC, observe the small energy changes that occur as matter transitions from a solid to a liquid crystal and from a liquid crystal or mesomorphous state (which displays properties of both the phases) to anisotropic liquid

Oxidative stability: It requires an airtight sample chamber at constant temperature (isothermally). First, it is done under an inert atmosphere, usually nitrogen. Then, oxygen is added to the system. Any oxidation that occurs is observed as a deviation in the baseline.

General chemical analysis: Melting-point depression can be used as a purity analysis tool. Consequently, less pure compounds will exhibit a broadened melting dip that begins at lower temperature than a pure compound.

Polymers: DSC is used widely for examining polymers to check their composition. The method can show up possible polymer degradation by the lowering of the expected melting point, which depends on the molecular weight of the polymer. So, lower grades will have lower melting points than the expected. Impurities in polymers can be determined by examining thermogram for anomalous peaks, and plasticizers can be detected at their characteristic boiling points.

References:

[2.1]R. C Mackenzie. *Thermochim Acta*., 1;(1979):28.

[2.2] https://en.wikipedia.org/wiki/Thermal_analysis

[2. 3] Thermal Methods. In: Skoog DA, Holler FJ, Crouch SR. Instrumental Analysis. India edition: Cengage Learning, 2011.p. 982,983,984

[2. 4] Thermal Analysis. In:Willard HH, Merritt LL, Dean JA, Settle FA. Instrumental Methods of Analysis. Seventh edition: CBS publishers,2012.p. 761.

[2. 5] U.S. Patent 3,263,484

[2. 6] https://en.wikipedia.org.

[2.7] http://www.dartmouth.edu/~pchem/75/pdfs/DSC.pdf.

[2.8] http://111.93.135.171/Volumes/14/08/0807-0817.pdf .

[2.9] https://en.wikipedia.org/wiki/Thermal_analysis

[2.10]http://www.tainstruments.com/pdf/literature/TP_006_MDSC_num_1_MDSC.pdf

[2.11] http://www.photometrics.net/DSC.html

[2. 12] H.S.Chen, D.Turnbull, J. Chem.Phys 48(1968)2560

[2.13] K.N.Lad, A.Pratap, K.G.Rawal, J.Mater.Sci.Lett.21(2002)1419

[2. 14] C.T.Moynihan, P.K.Gupta, J.Non-Cryst.Solids 29(1978)143

[2. 15] J.Jackle, Philos. Mag.B. 56(1987)113

[2. 16] Thermal Methods. In: Skoog DA, Holler FJ, Crouch SR. Instrumental Analysis. India edition: Cengage Learning, 2011.p. 982,983,984

[2.17]http://www.uzaktanegitimplatformu.com/UEP/uep_ylisans/ey2/ey2_download/DSC%2520Thermal2.pdf&sa=U&EI=8YxXU6Xsl9TTsAS8qoHIBA&ved=OCA0QFjAB&usg=AFQjCNEen7ydZppWT17EAOJVyCO2ouomZw

[2. 18] http://www.msm.cam.ac.uk/phase-trans/2002/Thermal2.pdf.

[2. 19] Grega Klancnik, Jozef Medved, Primoz Mrvar. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) as a method of material investigation. RMZ – Materials and Geoenvironment. 2010; 1(57):127–142.

[2. 20] http://personal.cityu.edu.hk/~bhtan/PerkinElmerThermal.ppt

[2. 21] Thermal Methods. In: Skoog DA, Holler FJ, Crouch SR. Instrumental Analysis. India edition: Cengage Learning, 2011.p. 982,983,984

[2. 22] AlexanderKS, Riga AT,Haines PJ. Thermoanalytical Instrumentation and Application. In: Ewing’s Analytical Instrumentation Handbook. Third edition: Marcel Dekker, 2009. p.462.

[2.23] Thermal Analysis. In:Willard HH, Merritt LL, Dean JA, Settle FA. Instrumental Methods of Analysis. Seventh edition: CBS publishers,2012. p. 761.

[2.24] http://www.colby.edu/chemistry/PChem/lab/DiffScanningCal.pdf.