- Differential scanning Calorimetry

What is a DSC?

Differential: measurement of the difference in heat flow from sample and reference side

Scanning: the common operation mode is to run temperature or time scans

Calorimeter: instrument to measure heat or heat flow.

Introduction

DSC is a technique which is part of a group of techniques called Thermal Analysis (TA). Thermal Analysis is based upon the detection of changes in the heat content (enthalpy) or the specific heat of a sample with temperature. As thermal energy is supplied to the sample its enthalpy increases and its temperature rises by an amount determined, for a given energy input, by the specific heat of the sample. The specific heat of a material changes slowly with temperature in a particular physical state, but alters discontinuously at a change of state. As well as increasing the sample temperature, the supply of thermal energy may induce physical or chemical processes in the sample, e.g. melting or decomposition, accompanied by a change in enthalpy, the latent heat of fusion, heat of reaction etc. Such enthalpy changes may be detected by thermal analysis and related to the processes occurring in the sample.

Endothermic:

When the sample absorbs energy, the enthalpy change is said to be endothermic. Processes such as melting and vaporization are endothermic.

Exothermic:

When the sample releases energy, the process is said to be exothermic. Processes such as crystallization and oxidation are exothermic.

Heat flow: a transmitted power measured in mW

Theory

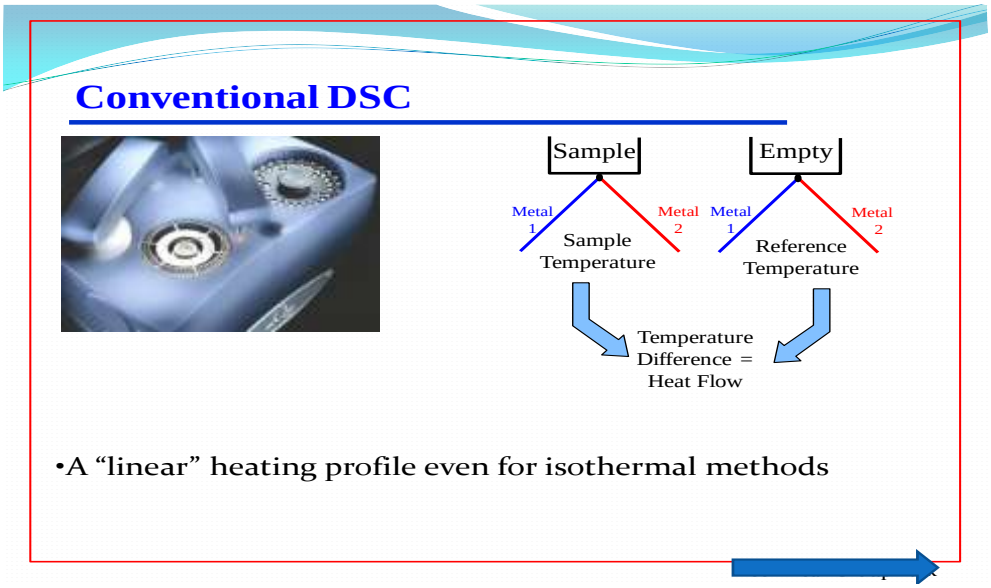
Differential scanning calorimetry or **DSC** is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity

Principle

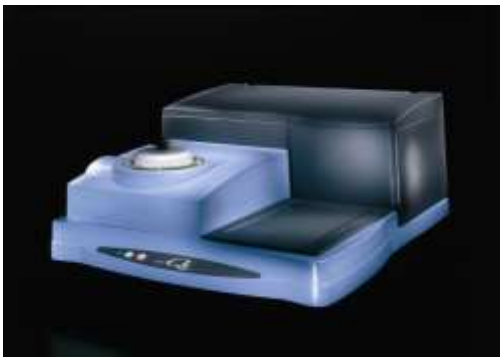
The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference.

This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions. It is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing.



- Q Series™ DSCs

Q 2000 Q 200



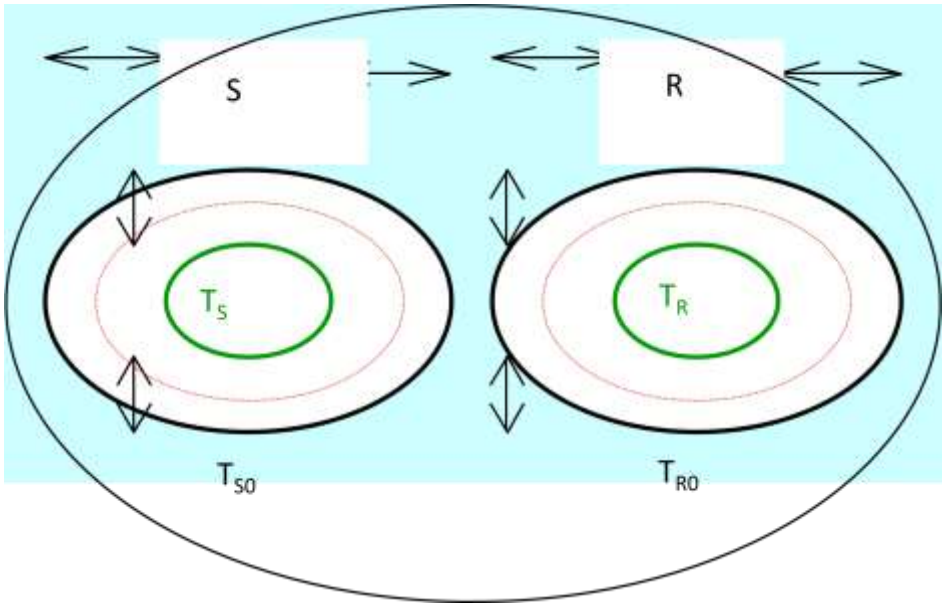
Q 20

Q 2000 is top-of-the-line, research grade with all options.

Q 200 is research grade and expandable .

Q 20 is a basic DSC

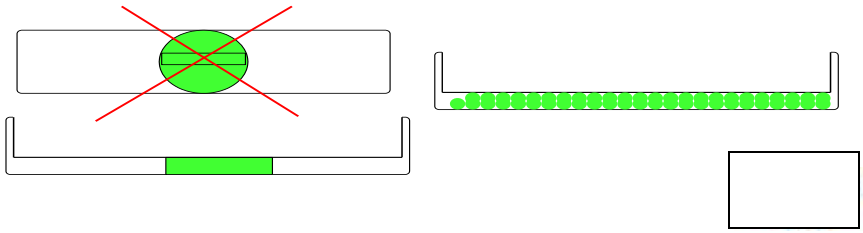
Sensor Technology



- Inner ring of thermocouples measure T_R and T_S
- Outer ring measures sensor temperatures at reference and samples sides, T_{S0} and T_{R0}
- Thermocouples act as thermal resistence, R

Sample Preparation : Shape

- Keep sample as thin as possible (to minimise thermal gradients)
- Cover as much of the pan bottom as possible
- Samples should be cut rather than crushed to obtain a thin sample (better and more uniform thermal contact with pan)



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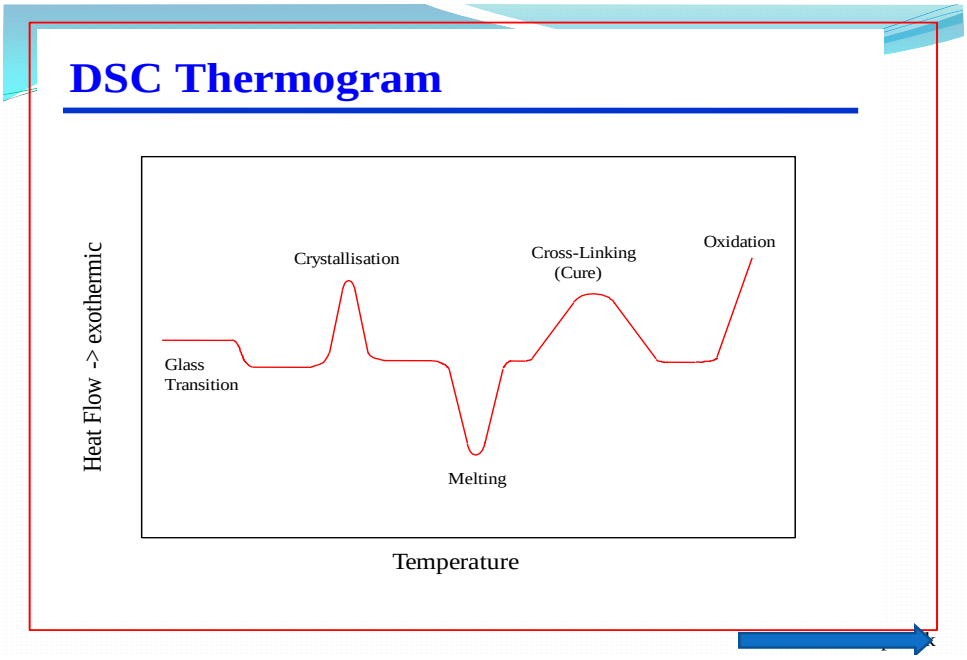
DSC THERMOGRAM

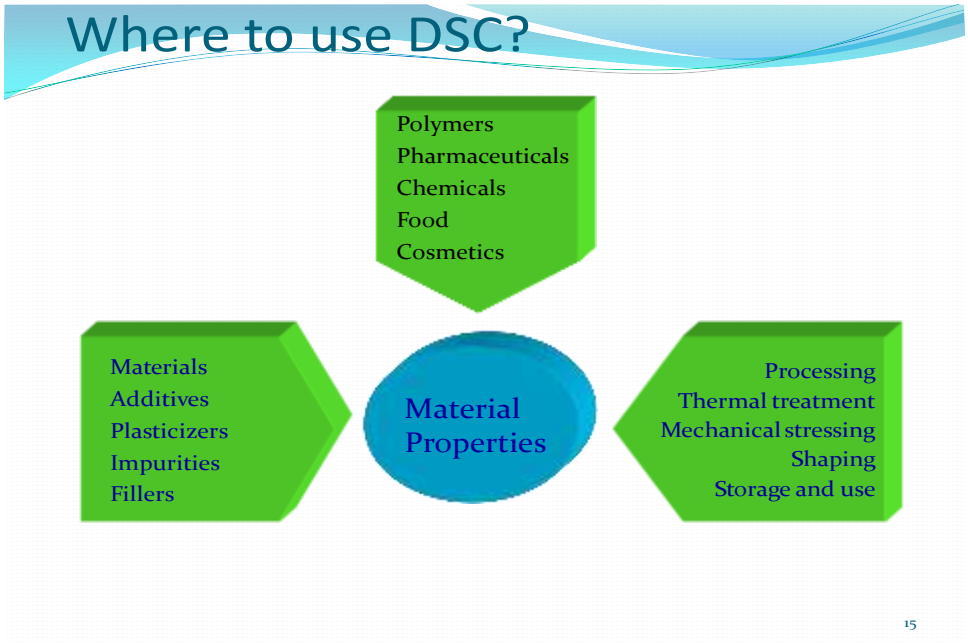


DSC: Main Sources of Errors

- Calibration
- Contamination
- Sample preparation – how sample is loaded into a pan

- Residual solvents and moisture.
- Thermal lag
    - Heating/Cooling rates
    - Sample mass
- Processing errors

Where to use DSC?



1. Paints (Tg,WL,MP)
2. Pipe Coatings(Tg,WL)
3. Powder Coatings(WL)
4. Shielding(,,)
5. PE/PP Manufacturer(MP)

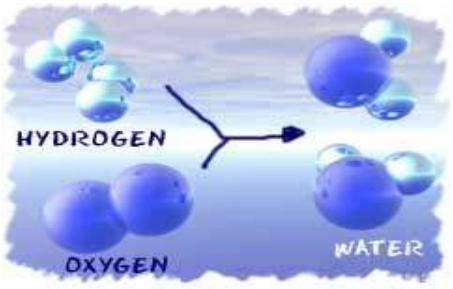
- Tg: Glass Transition
- MP: Melting Point
- WL: Weight Loss

DSC - What can it measure?

- Glass Transitions
- Melting Points
- Crystallization Times and Temperatures
- % Crystallinity
- Heats of Fusion and Reactions
- Specific Heat
- Oxidative Stability
- Rate of Cure
- Reaction Kinetics
- Purity
- Thermal Stability

Chemical reaction

A chemical reaction is a process that one or more substances (reactants) are converted to one or more new chemical substances (products) with different properties. e.g. oxidation, decomposition, polymerization etc.



Chemical reactions always involve a change in energy. Depending on whether the energy is absorbed or released during the process, they can be endothermic or exothermic

Examples

The technique is widely used across a range of applications, both as a routine quality test and as a research tool. The equipment is easy to calibrate, using low melting indium for example, and is a rapid and reliable method of thermal analysis.

Liquid crystals

DSC is used in the study of liquid crystals. As some forms of matter go from solid to liquid they go through a third state, which displays properties of both phases. This anisotropic liquid is known as a liquid crystalline or mesomorphous state. Using DSC, it is possible to observe the small energy changes that occur as matter transitions from a solid to a liquid crystal and from a liquid crystal to an isotropic liquid.

Oxidative stability

Using differential scanning calorimetry to study the stability to oxidation of samples generally requires an airtight sample chamber. Usually, such tests are done isothermally (at constant temperature) by changing the atmosphere of the sample. First, the sample is brought to the desired test temperature 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. Such analysis can be used to determine the stability and optimum storage conditions for a material or compound

Safety Screening

DSC makes a reasonable initial safety screening tool. In this mode the sample will be housed in a non-reactive crucible (often gold, or gold plated steel), and which will be able to withstand pressure (typically up to 100 bar). The presence of an exothermic event can then be used to assess the stability of a substance to heat.

However, due to a combination of relatively poor sensitivity, slower than normal scan rates (typically 2-3 °/min – due to much heavier crucible) and unknown activation energy, it is necessary to deduct about 75-100 °C from the initial start of the observed exotherm to **suggest** a maximum temperature for the material. A much more accurate data set can be obtained from an adiabatic calorimeter, but such a test may take 2–3 days from ambient at a rate of a 3 °C increment per half hour.

Drug analysis

DSC is widely used in the pharmaceutical and polymer industries. For the polymer chemist, DSC is a handy tool for studying curing processes, which allows the fine tuning of polymer properties. The cross-linking of polymer molecules that occurs in the curing process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition.

In the pharmaceutical industry it is necessary to have well-characterized drug compounds in order to define processing parameters. For instance, if it is necessary to deliver a drug in the amorphous form, it is desirable to process the drug at temperatures below those at which crystallization can occur.

General chemical analysis

Freezing-point depression can be used as a **purity analysis** tool when analysed by Differential scanning calorimetry. This is possible because the temperature range over which a mixture of compounds melts is dependent on their relative amounts. Consequently, less pure compounds will exhibit a broadened melting peak that begins at lower temperature than a pure compound.

Food science

In food science research, DSC is used in conjunction with other thermal analytical techniques to determine water dynamics. Changes in water distribution may be correlated with changes in texture. Similar to material science studies, the effects of curing on confectionery products can also be analyzed.

Polymers

DSC is used widely for examining polymers to check their composition. Melting points and glass transition temperatures for most polymers are available from standard compilations, and the method can show up possible polymer degradation by the lowering of the expected melting point, T_m, for example. T_m depends on the molecular weight of the polymer, so lower grades will have lower melting points than expected.