

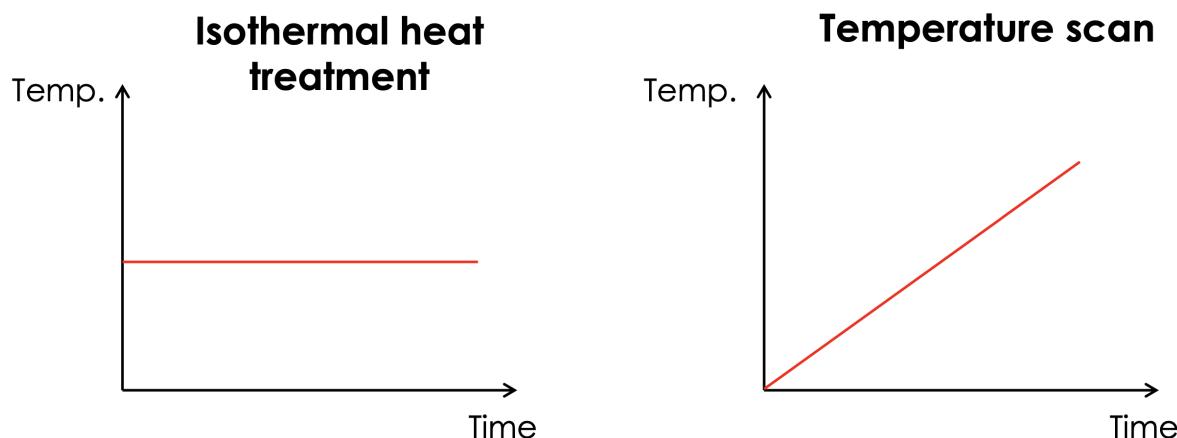
6. Thermal Analysis

Introduction to Thermal Analysis

Thermal analysis refers to a group of techniques in which a physical property is measured as a function of temperature, while the sample is subjected to a controlled temperature programme (heating, cooling or isothermal). It involves the measurement and analysis of various thermal properties of materials, including their heat capacity, thermal conductivity, expansion coefficient, phase transitions, and more.

Temperature programs are specific temperature profiles or sequences that are applied during thermal analysis experiments. These programs involve controlled heating, cooling, or isothermal treatment at different temperature stages. Two common types of temperature programs used are:

- ▶ Isothermal Heat Treatment, which involves subjecting a sample to a constant temperature for a specific period of time. This technique is used to study the changes that occur in a material under steady-state conditions at a particular temperature. For instance, phenomena such as phase transformations, aging, crystallisation, and sintering. Isothermal heat treatment is particularly useful for investigating the kinetics, transformation rates, and microstructural changes of materials at a given temperature, and for studying phenomena occurring away from equilibrium temperature.
- ▶ Temperature Scanning, also known as thermal scanning or temperature ramping, involves continuously changing the temperature of a sample at a controlled rate. This technique is employed to investigate a material's response to a wide range of temperatures, including its thermal transitions, decomposition, melting, and other temperature-dependent behaviours. This enables the identification of phase transitions, determination of transition temperatures, and characterization of thermal stability. Temperature scanning is thus particularly suitable for studying the thermodynamics of materials.



Various thermal analysis techniques have been developed and are widely used in various scientific and industrial fields. Some common techniques used in thermal analysis include:

- ▶ Differential Scanning Calorimetry (DSC) measures the heat flow into or out of a sample as it is subjected to a controlled temperature program. It is used to determine phase transitions, such as melting points, glass transition temperatures, and reaction enthalpies.

- ▶ Thermogravimetric Analysis (TGA) measures the weight changes of a sample as it is heated or cooled under controlled conditions. It helps determine the thermal stability, decomposition temperatures, and the presence of volatile components in a material.
- ▶ Dynamic Mechanical Analysis (DMA) measures the mechanical properties of a material as a function of temperature. It is particularly useful for studying the viscoelastic behaviour, glass transition, and damping properties of polymers and composites.
- ▶ Thermal Mechanical Analysis (TMA) measures the dimensional changes of a sample as a function of temperature. It provides information about the coefficient of thermal expansion, softening temperatures, and viscoelastic properties of materials.
- ▶ Differential Thermal Analysis (DTA) measures the temperature difference between a sample and an inert reference material as they both undergo the same controlled temperature program. The sample and reference are subjected to identical heating or cooling conditions, and any temperature difference observed between them is indicative of thermal events occurring in the sample. DTA is primarily used to investigate phase transitions, such as melting, crystallisation, glass transition, and other thermal effects.
- ▶ Temperature Programmed Desorption (TPD) studies the desorption of molecules from the surface of a solid material as it is heated under controlled conditions. It is commonly applied in surface science and catalysis research to understand the interaction between adsorbed species and solid surfaces. TPD provides valuable information about the desorption kinetics, desorption energies, and surface coverage of adsorbed species on a material's surface, which helps in understanding surface reactions, catalyst performance, surface characterisation, and adsorption-desorption processes.

Thermodynamics Reminder

The First Law of Thermodynamics states that the total energy of a system is conserved:

$$\Delta U = Q + W$$

where ΔU is the change in internal energy of the system, Q is the heat transferred to the system and W is the work done on the system. Joule and Calories are common units of energy, where $1 \text{ cal} = 4.184 \text{ J}$.

Enthalpy (H) is a thermodynamic property that relates to the total energy of a system, including its internal energy and the energy associated with pressure and volume changes. It is commonly used to describe the amount of heat absorbed or released in a process at constant pressure. Mathematically,

$$H = U + PV$$

where U is the internal energy of the system, P is the pressure and V is the volume. In the differential form,

$$dH = dQ + VdP = TdS + VdP$$

which is the Gibbs-Duhem equation, where T is the temperature and S is the entropy.

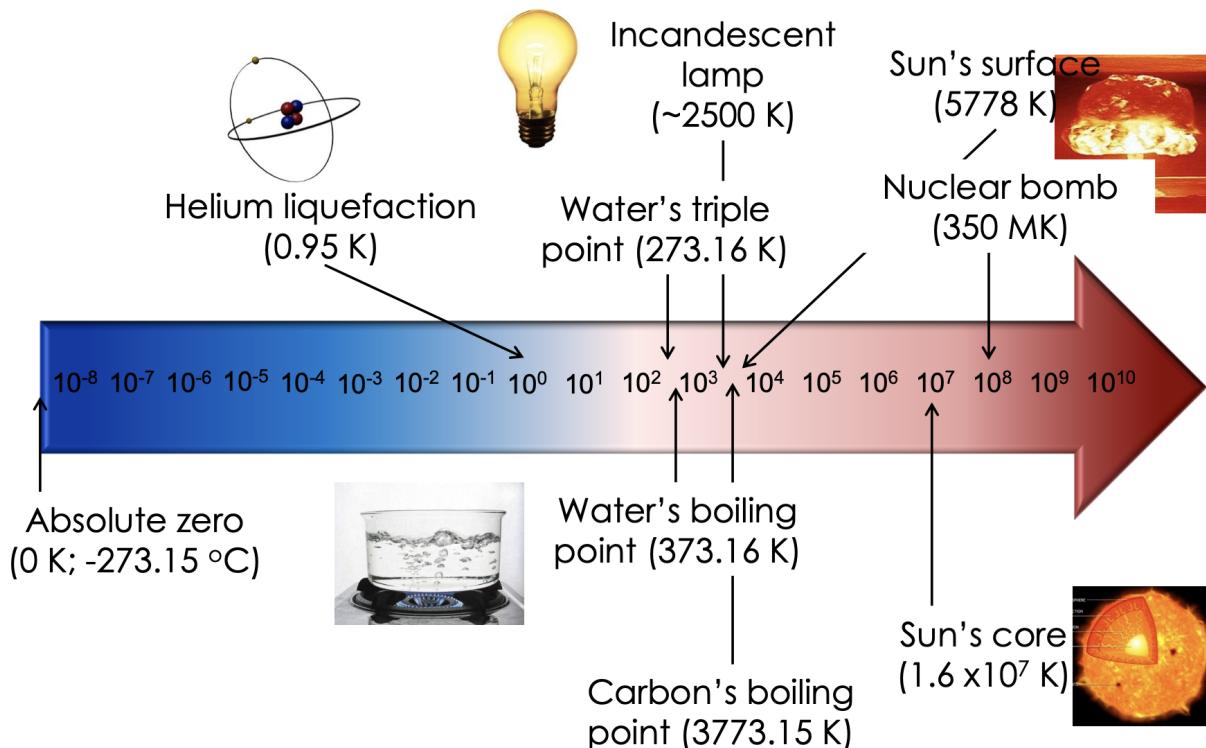
The heat capacity (C_p) is a measure of the amount of heat energy required to raise the temperature of a substance by a certain amount. It quantifies the ability of a substance to store heat energy. Mathematically,

$$C_p(T) = \frac{dQ}{dT} = \left(\frac{\partial H}{\partial T} \right)_p$$

Exothermic and endothermic processes are classifications used to describe the direction of heat flow in a system during a chemical reaction or a physical change. They refer to whether heat is released or absorbed by the system, respectively. The convention here is to consider the product analysed as the reference:

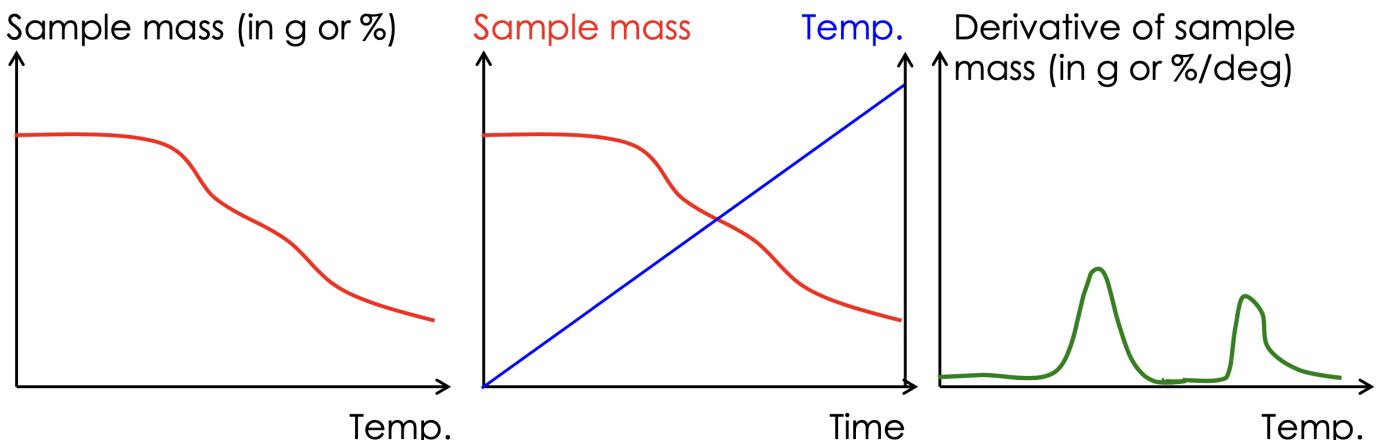
- ▶ Product absorbs heat from surrounding (endothermic): $\Delta H > 0$
- ▶ Product transfers heat to the surrounding (exothermic): $\Delta H < 0$

Finally, some important temperatures are indicated as follows:



Thermogravimetric Analysis

In TGA, the mass of a sample is continuously monitored as the temperature is increased or held constant over a period of time:



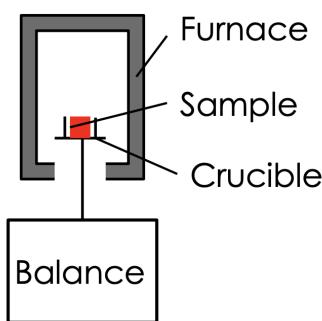
There are several potential reasons for changes in the sample's mass:

- ▶ Desorption or adsorption of gases.
- ▶ Phase transitions.
- ▶ Oxidative or thermal decomposition.
- ▶ Oxidation reactions in air or oxygen-rich atmosphere.
- ▶ Reduction reactions in hydrogen-rich atmosphere.

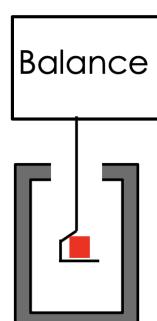
The configuration of the sample and the balance can vary depending on the specific setup used:

- ▶ Top loading: the sample is placed on a pan or crucible, which is then positioned on top of the balance. This arrangement allows for easy loading and removal of the sample from the top of the TGA instrument. It is commonly used when the sample is in a solid or powdered form.
- ▶ Hand down configuration: the sample is suspended from a vertical balance beam or arm. The sample is usually attached to a thin wire or thread, and its weight change is measured as it hangs freely. This configuration is often used when analysing gases or volatile liquids.
- ▶ Horizontal arrangement: the sample is placed horizontally within the TGA instrument. The sample is usually supported on a holder or tray, and the balance is positioned beneath it.

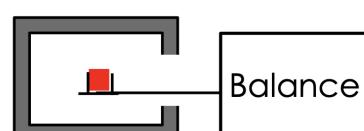
Top loading



Hang down



Horizontal arrangement



Various operational factors can influence the TGA experiment:

1. Gas density and buoyancy: as the temperature changes, the density of the surrounding gas can also change. This can create a buoyancy effect, where the sample experiences a slight downward force due to the difference in gas density. The temperature range in TGA experiments typically spans from room temperature (RT) to high temperatures, commonly reaching up to 1000 °C.
2. Sample preparation:
 - ▶ The sample should be representative of the product or material being analysed, accurately reflecting its composition and characteristics.
 - ▶ The mass of the sample should be appropriate for the specific sensitivity of the TGA instrument being used. TGA typically requires a relatively small amount of sample. In many cases, the quantity of sample used is less than 0.1 g, while sensitivities associated with different types of balances commonly used in TGA involve semimicrobalance (10 µg), microbalance (1 µg), and ultramicrobalance (0.1 µg). Therefore, insufficient or excessive sample mass can affect the accuracy of the measurements.

- ▶ The sample should not be contaminated, as impurities can impact the results and introduce errors.
 - ▶ The size and morphology of the sample can also influence the rate of changes in the mass of the sample.
3. Crucibles (alumina, platinum): those are containers used to hold the sample during TGA. The choice of crucible material depends on the specific requirements of the analysis, including factors like sample compatibility, temperature range, reactivity, and thermal conductivity.
4. Atmosphere and humidity: the atmosphere surrounding the sample during TGA can have a significant impact on the analysis and must be controlled. A protective gas, such as nitrogen (N_2), helium (He), or argon (Ar), is often used to prevent sample oxidation or other undesirable reactions. Other gases like air, carbon dioxide (CO_2), oxygen (O_2), or hydrogen (H_2) in argon can be used to create specific conditions for the analysis. Also, humidity levels in the environment can affect certain samples and should be controlled.
5. Change of physical properties of the sample during measurement (e.g., volume): the physical properties of the sample may change as a result of temperature variations. For example, some samples may undergo volume changes or structural modifications, which may impact the weight measurements.
6. Motion of sample: it is important to ensure that the sample remains in a stable position and does not move or shift significantly during the analysis. Unintended movement can introduce errors and affect the accuracy of the results.
7. Heating rate: the heating rate determines how quickly the temperature increases and can influence the observed weight changes and reactions. Different heating rates can be employed to study the sample's behaviour under various conditions and to capture specific phenomena.

TGA has a wide range of applications:

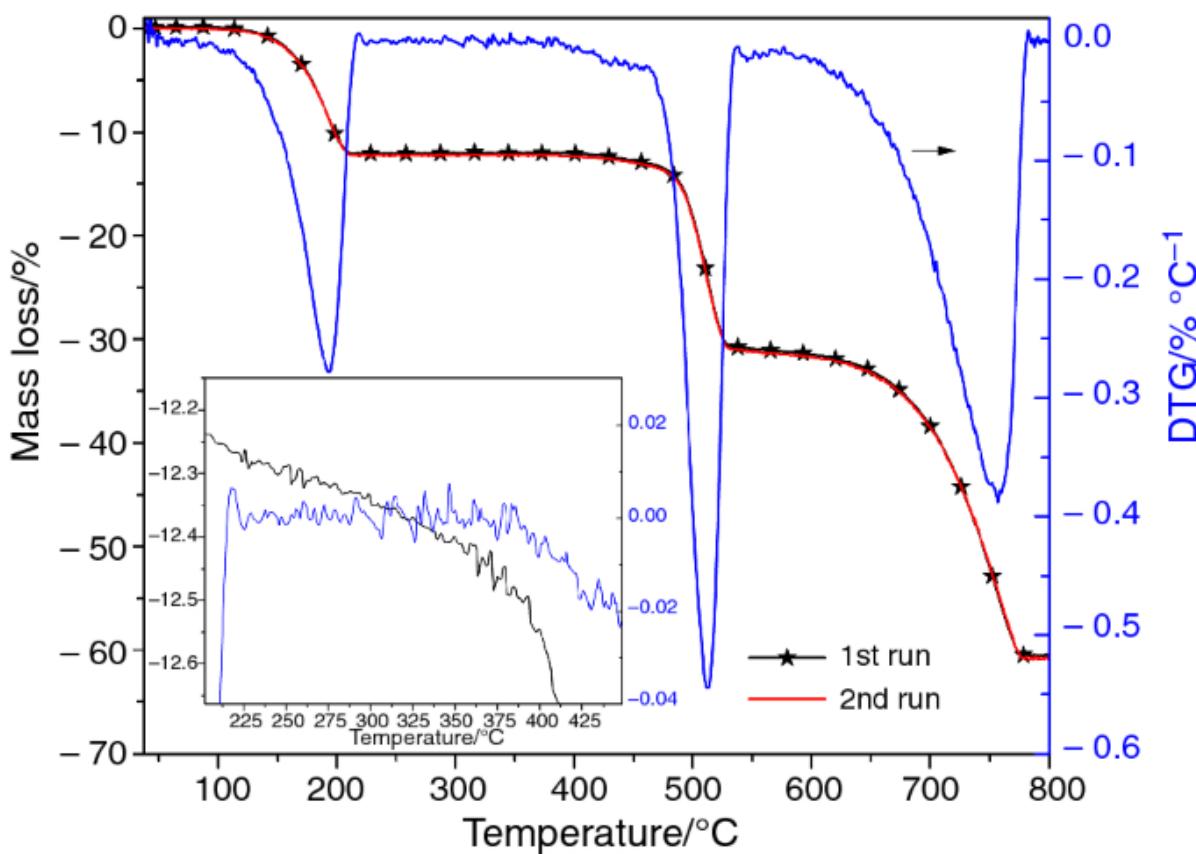
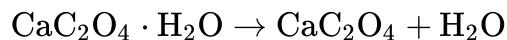
1. Product characterisation: characterise products by analysing their thermal properties and composition, including:
 - ▶ Thermal stability: the temperature at which a material starts to decompose or undergo significant changes in its structure, which provides insights into its stability.
 - ▶ Decomposition temperature: the temperature range at which a material decomposes.
 - ▶ Purity: assess the purity of a sample by measuring the weight loss associated with impurities or contaminants.
 - ▶ Composition and moisture content: determine the composition of a sample by analysing the weight changes associated with different components. It can also measure the moisture content in a material.
2. Properties examination: examine various properties of materials, including:
 - ▶ Adsorption/desorption processes: by monitoring weight changes, TGA can provide information about the adsorption capacity, surface area, and interactions with different gases or vapours.
 - ▶ Vaporisation processes of volatile components, such as solvents or volatile organic compounds: the weight loss observed during TGA can reveal the vaporisation behaviour and evaporation kinetics of the sample.
 - ▶ Reaction kinetics and stoichiometry of chemical reactions that occur during heating: by monitoring the weight changes, it is possible to determine reaction rates, activation energies, and reaction mechanisms.
 - ▶ How reactive gases, such as oxygen or hydrogen, interact with a sample.

TGA Curves

The collected data is typically presented in the form of curves:

- Thermogravimetric curves, also known as TG curves, display the change in sample weight (mass) as a function of temperature or time. TG curves provide a visual representation of the weight changes that occur during the TGA experiment. Different weight loss or gain events, such as decomposition, vaporization, or adsorption, appear as peaks, plateaus, or slopes on the TG curve.
- The derivative of the TG curve, abbreviated as DTG, is often used when the weight loss or gain steps are not well-defined or when additional information is required. The curve represents the rate of weight change (mass loss or gain) per unit temperature or time, allowing for the identification of different weight change events and their corresponding temperatures or time intervals.

For example, the decomposition of calcium oxalate monohydrate in nitrogen is often used as a calibration method in laboratory:



Each of the three plateaus represents the point at which the decomposition process is complete. Based on stoichiometry, a theoretical weight percentage loss can be calculated for each of the three different reactions, which can be compared to the measured values for calibration.

Two important parameters can be obtained from the plots. First, the onset temperature, the temperature at which the weight loss begins. This is where a noticeable deviation is present in the TG curve. Since the DTG curve represents the derivatives of TG, it is easier to find the onset temperature from the DTG plot. Another important parameter is the component content,

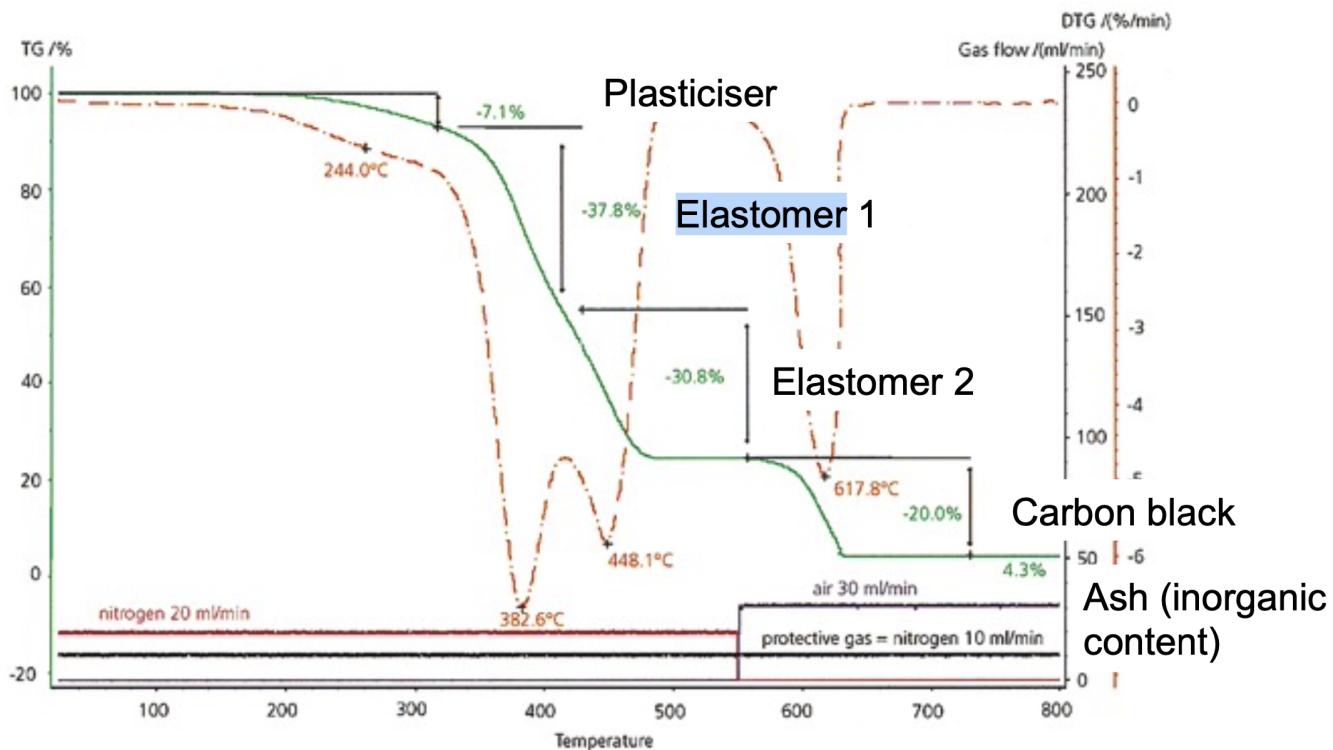
$$G_i(\%) = \frac{\Delta m}{m_0} \times 100$$

where Δm is the mass change over the temperature range considered and m_0 is the initial mass of the sample. Notice that, the y -axis of the TG curve usually expressed in terms of percentage of the initial mass. Here, the component content can be simply determined by reading the y -axis.

The table below summarises some key temperature ranges in TGA:

Temperature range (°C)	Potential phenomenon
<150	Evaporation of volatiles Removal of moisture
150 - 450	Removal of crystallization water Decomposition of organics
450-900	Carbon combustion

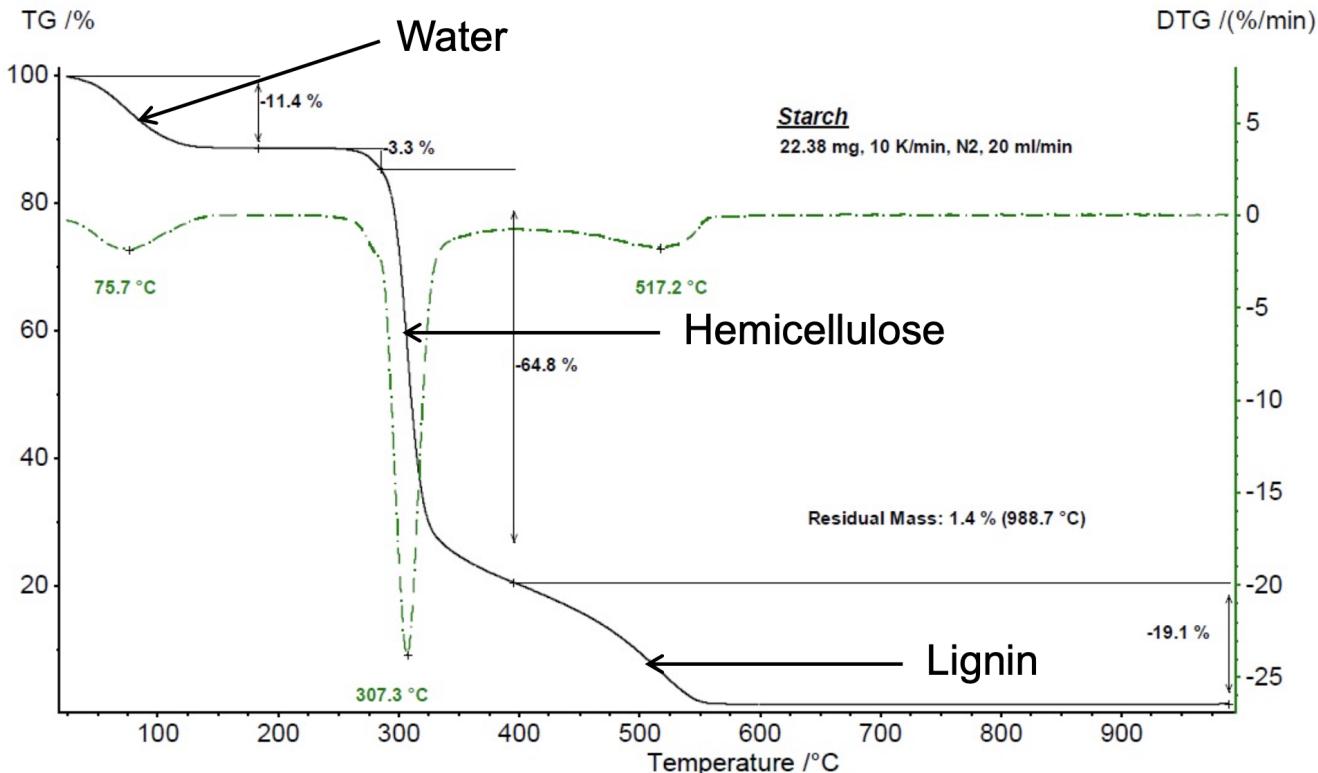
As mentioned, TGA is broadly applicable. For instance, in the composition analysis of rubber:



The plasticiser, which involves low molecular weight compounds that is incorporated into the rubber polymer matrix to increase its mobility, undergoes vaporization first. The elastomers, which are the principal components of rubber that provides its elasticity and flexibility, subsequently decomposes. The carbon black, which is a common filler to increase the rubber's strength and abrasion resistance, does not undergo significant weight loss but rather remains as a residue or ash after thermal decomposition of other

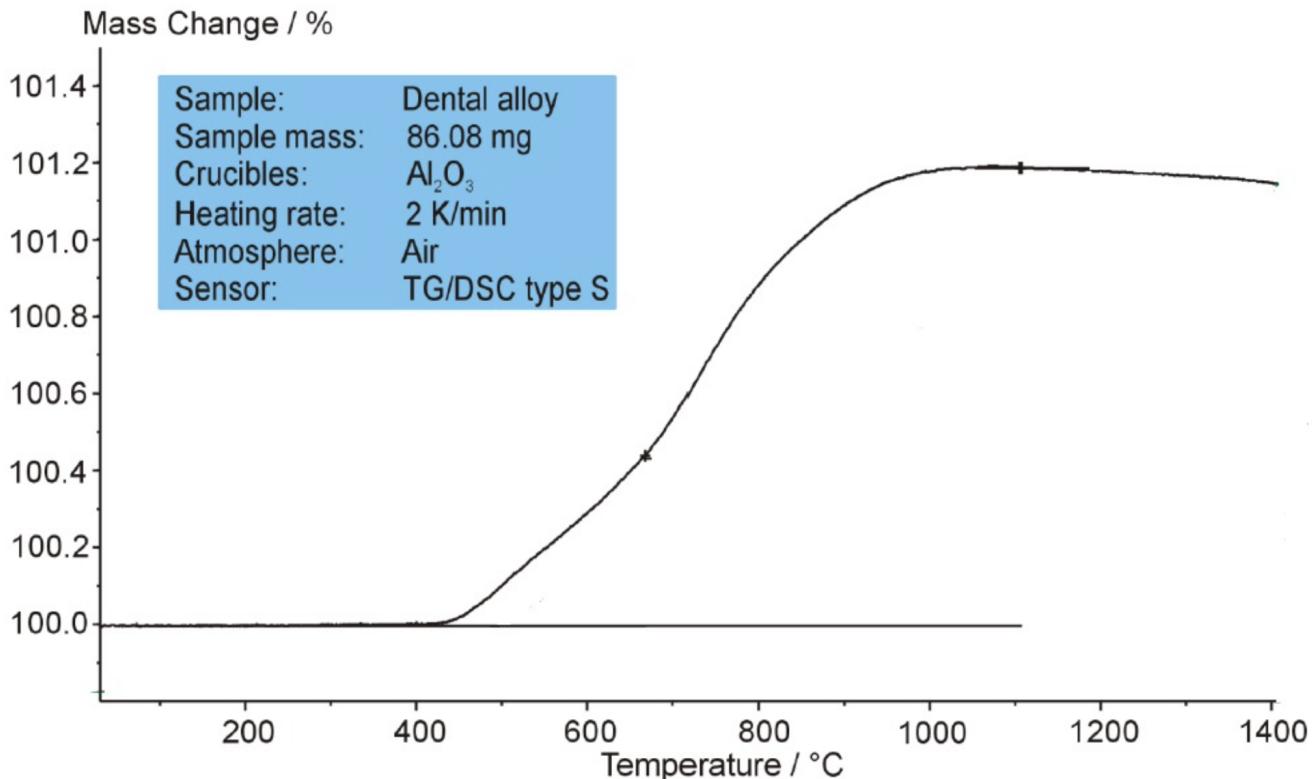
components. Finally, after complete combustion of carbon black, ash remains, which consists primarily of inorganic residues such as silica, calcium carbonate, or metal oxides, that are often added to rubber formulations, for one reason or another.

Another example where TGA is applied in the component analysis of starch in a nitrogen atmosphere:



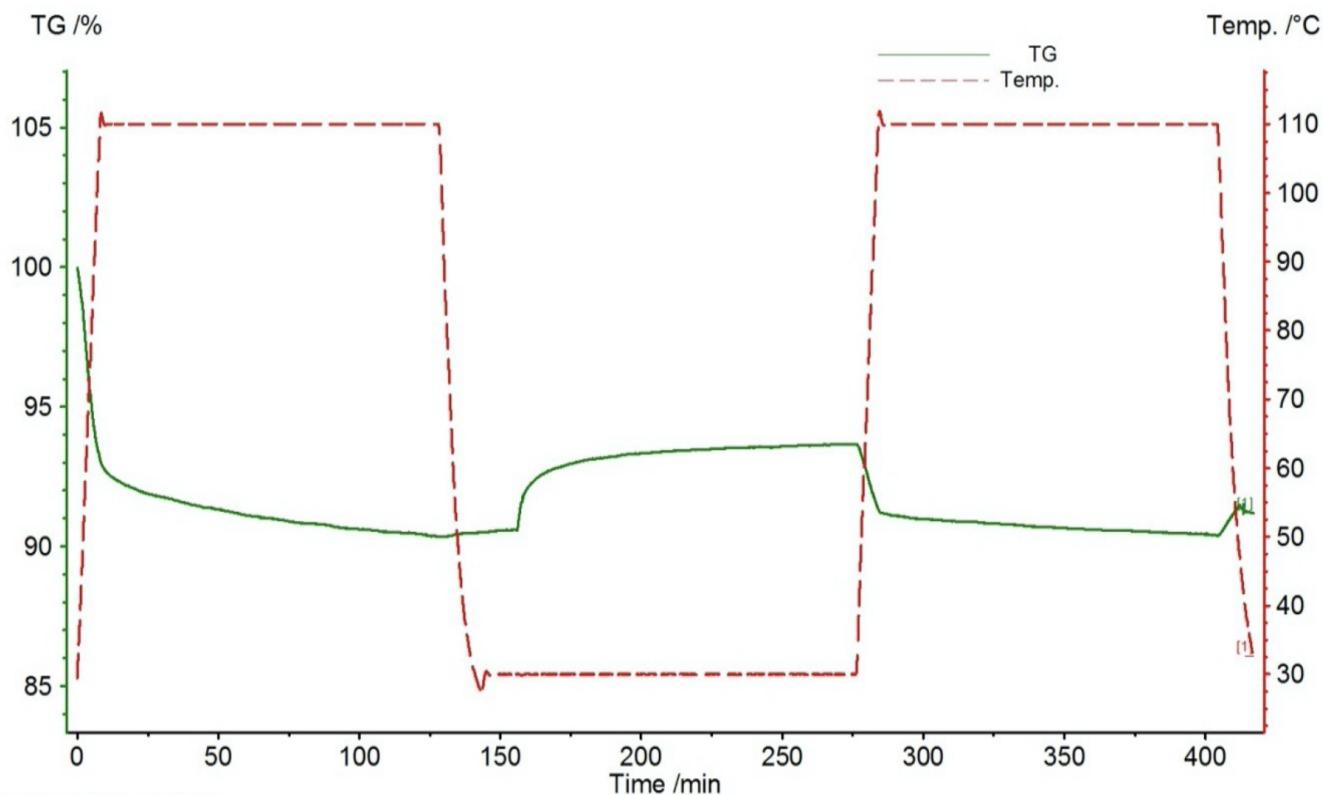
Starch typically contains a certain amount of bound water, which vaporises first. The complex carbohydrate hemicellulose, the principal component of the plant cell wall which is composed of various sugars, decomposes subsequently. Lignin, which provides structural support to plant, finally degrades.

Another example for alloy in an air atmosphere:



At elevated temperatures, oxidation reactions occur, particularly for those alloys containing metals such as iron, nickel, or aluminium.

Another example is in the study of adsorption/desorption:

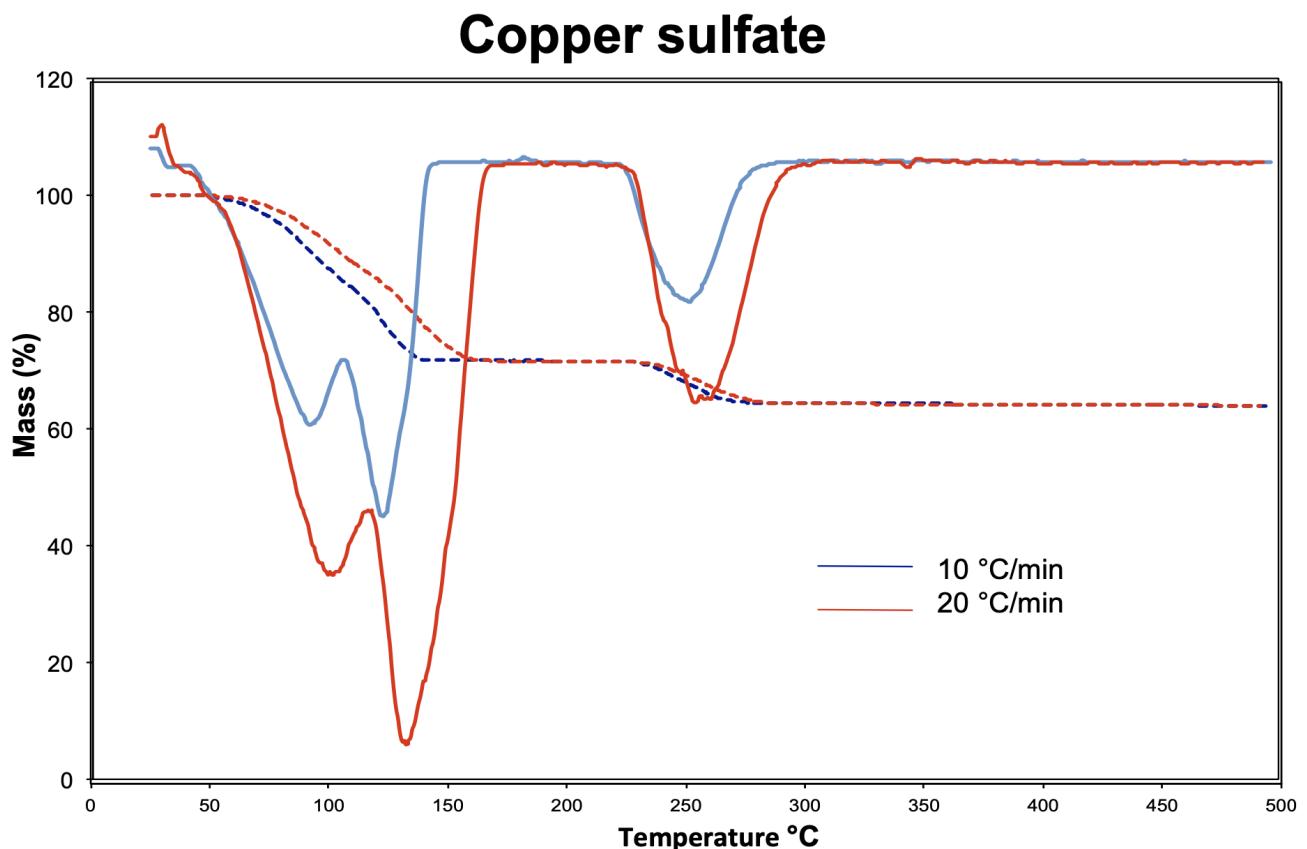


where the adsorption capacity follows the same calculation as in the case of the component content G_i .

The influences of the various operational factors as previously mentioned can also be visualised on the plots:

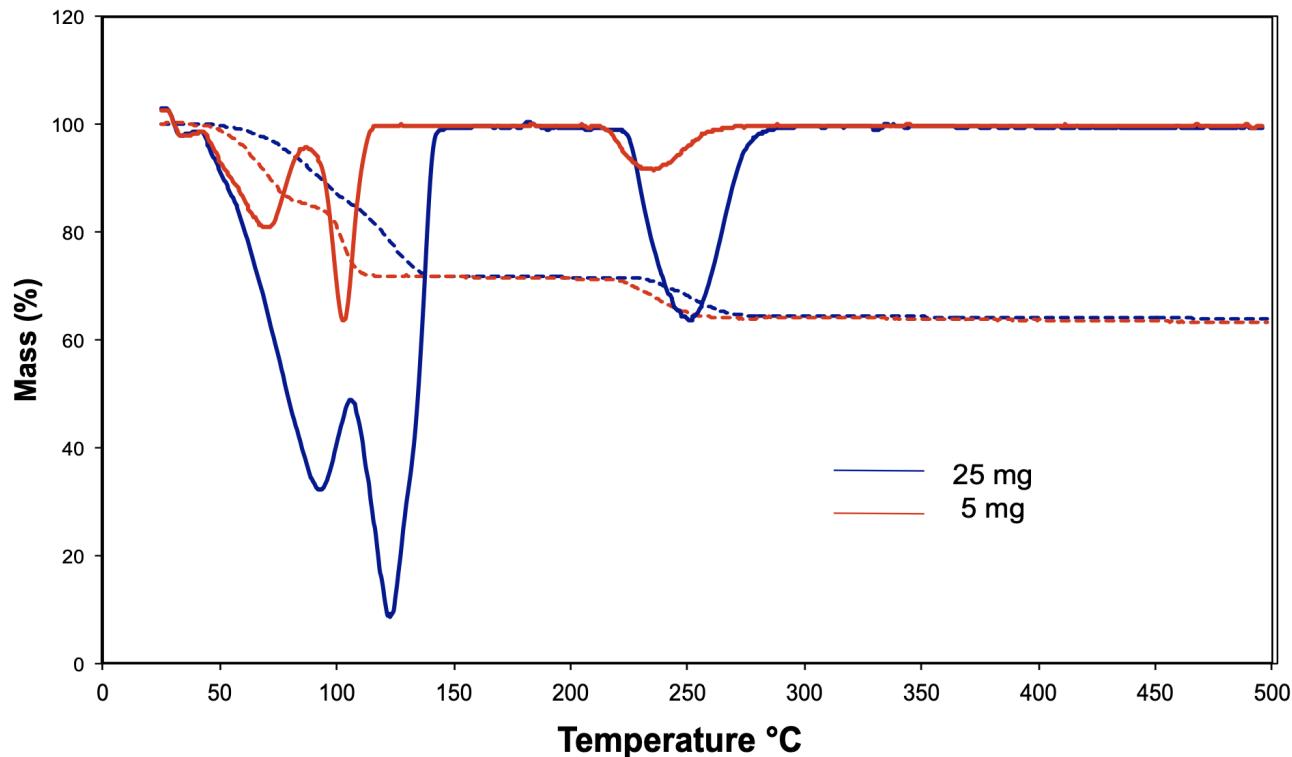
1. Heating rate:

- Higher heating rates generally result in broader, more smeared peaks in the DTG plot. This is because higher heating rates may cause overlapping reactions: when a sample undergoes decomposition, it may involve multiple simultaneous or sequential reactions. These reactions can occur at different temperature ranges and result in weight loss or gain. During rapid heating, the temperature may rise quickly, causing some reactions to take place simultaneously. The individual weight loss or gain contributions from each reaction may therefore not be clearly distinguished in the TG plot.
- Higher heating rates generally shift the peaks in the DTG plot to higher temperatures. The peak position represents the temperature at which the weight loss rate is the highest. At a higher heating rate, the sample is exposed to increasing temperatures more rapidly. This also highlights the benefits of analysing the onset temperature, as it is only dependent on sample properties such as composition and does not change with increasing heat rates.



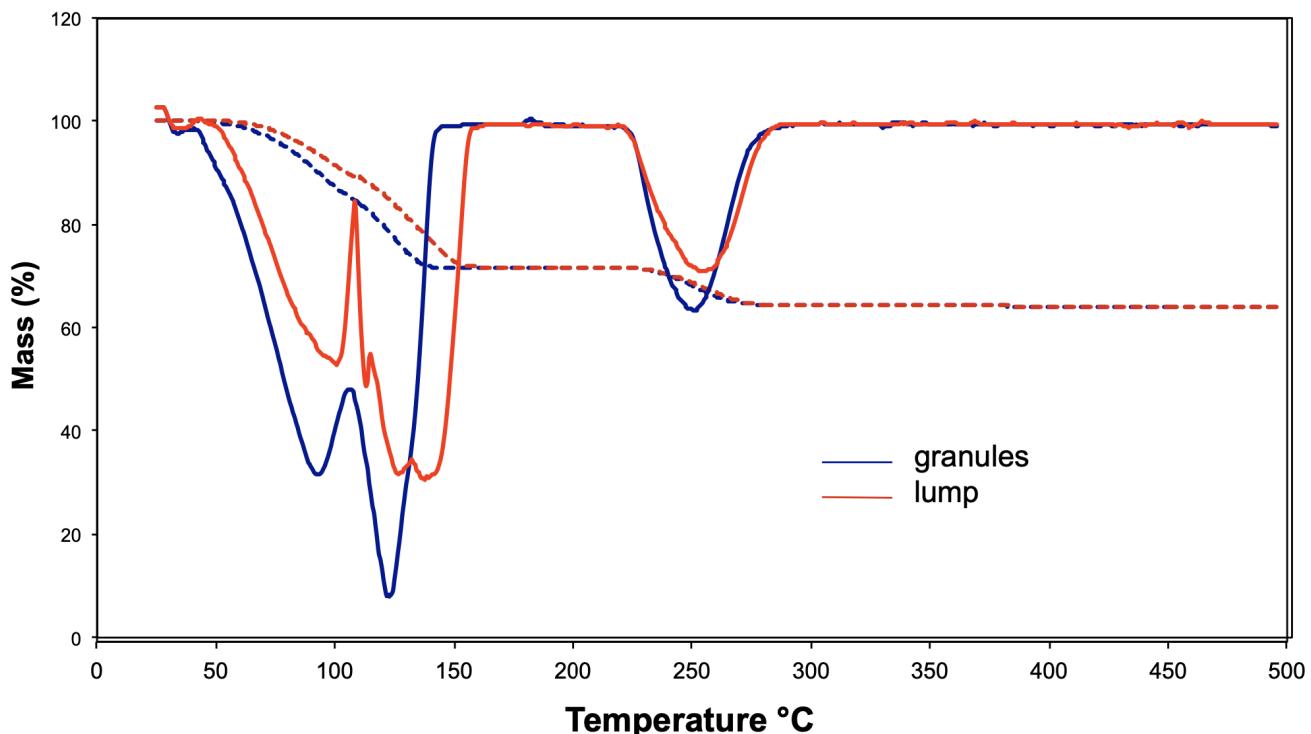
2. Sample size

- Larger sample size results in the maximum mass loss occurring at higher temperatures on the TG plot, and tend to exhibit mass loss over a broader temperature range on the DTG plot. This is because larger samples have more material to lose, and therefore, it requires more energy to break down or evaporate the constituents. Heat transfer limitations also worsen in larger samples. The larger volume of material takes longer to heat up or cool down, leading to slower reaction rates and more gradual mass loss.
- Larger sample size has fewer distinct steps on the DTG plot. This is because larger samples have more complex and overlapping thermal events occurring simultaneously or over a broader temperature range. As a result, the individual steps or peaks observed in the DTG plot for smaller samples may merge together, making it more challenging to identify specific decomposition or volatilisation processes.



3. Sample morphology

- Granular samples loses mass at a lower temperature and over a narrower temperature range. This is because the granular structure provides a larger surface area, allowing for enhanced energy interactions with the surrounding environment. The interstitial voids or spaces between individual granules allow for better heat transfer and improved access of the heating medium to the sample. As a result, the thermal energy is efficiently transmitted throughout the sample, leading to an earlier mass loss, as well as more homogeneous and uniform decomposition.



Combination of TGA With Other Techniques

To gain more comprehensive information about the sample, TGA is often coupled with other analytical techniques. For instance, evolved gas analysis (EGA) is a technique used to analyse the gases released from a sample during thermal analysis. When combined with TGA, EGA provides information about the composition and amount of gases emitted by the sample as it undergoes thermal decomposition or other reactions. This can be used, for example, in the study of the decomposition of a phenolic resin adhesive, where TGA is connected to a Fourier-transform infrared (FTIR) spectrophotometer. By subjecting the adhesive to controlled heating, TGA measures its weight loss, while the FTIR spectrophotometer analyses the evolving gases to identify the specific compounds released and the thermal decomposition pathways of the phenolic resin adhesive. Another example is in the study of polycarbonate decomposition, where gas chromatography-mass spectrometry (GCMS) is coupled with TGA. The GCMS data helps identify the decomposition products and their relative abundances, aiding in understanding the thermal degradation behaviour of polycarbonate.

Industrial Relevance

The industrial relevance of TGA lies in its ability to provide crucial information that impacts product quality, process optimisation, and material selection.

- ▶ In the pharmaceutical industry, TGA helps determine the thermal stability of active pharmaceutical ingredients (APIs), identify any potential degradation products that may affect the drug's efficacy and safety and provide insights into the moisture content and volatile impurities of pharmaceutical compounds.
- ▶ The food industry utilises TGA to evaluate the thermal characteristics of food products, such as moisture content, fat content, and protein content. TGA can help determine the quality and shelf-life of food items by assessing their thermal stability, oxidative degradation, and reaction kinetics during processing or storage, which is crucial for optimising production processes, ensuring product safety, and developing new food formulations.
- ▶ In the manufacturing industry, TGA plays a significant role in understanding the thermal behaviour of materials used in various processes. It is particularly relevant in industries dealing with ceramics, plastics, and other materials where thermal stability and reactivity are critical. TGA helps assess the weight loss, decomposition temperatures, and reaction kinetics of materials, enabling manufacturers to ensure product quality and select suitable materials for specific applications.

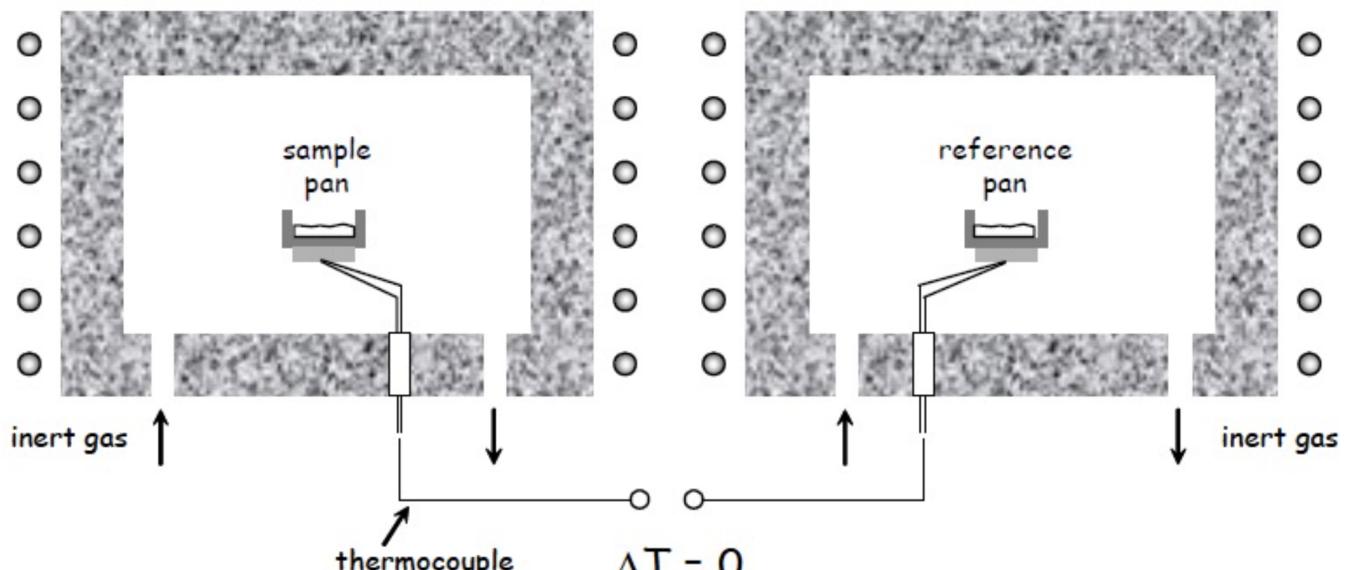
In addition to the mentioned industries, TGA finds applications in many other sectors, including polymers, chemicals, textiles, and energy. The information obtained from TGA analysis goes beyond moisture content, purity, thermal stability, and reactivity. It can also provide insights into parameters like thermal conductivity, phase transitions, crystallinity, and mechanical properties, etc.

Differential Scanning Calorimetry

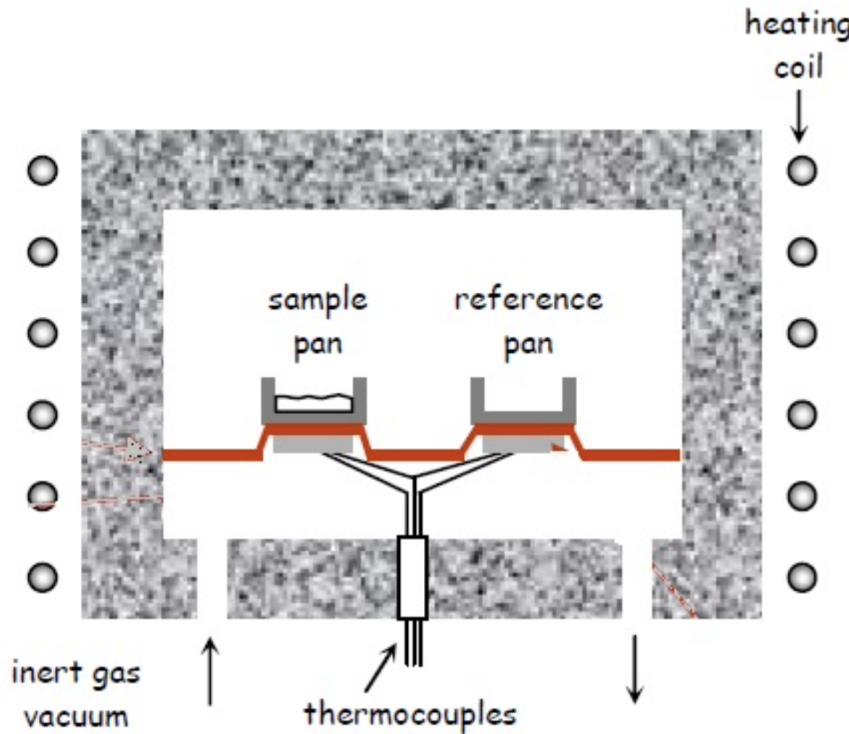
Differential Scanning Calorimetry (DSC) is a technique used to study the energy changes that occur in a sample as it is subjected to various temperature conditions. It measures the heat flow of a sample as a function of temperature. The energy changes can include processes such as phase transitions (melting, glass transition, crystallisation), ferromagnetic-diamagnetic transition, or other thermal events.

It is also worth noting that DSC requires a reference material for comparison. The reference material does not undergo the same phase transitions or thermal events as the sample but is used to establish a baseline for heat flow. Based on this, there are two common types of DCS techniques:

- ▶ Power compensated DSC: the sample and reference are placed in separate furnaces, which ensures that the sample and reference are heated or cooled independently. The objective is to maintain both the sample and reference at the same temperature, even during a thermal event in the sample. By monitoring the power needed to keep the sample and reference at the same temperature, the instrument can measure any temperature difference that occurs between the two, which provides information about the energy changes happening in the sample during the thermal event. Power compensated DSC is more commonly used in research studies that require high resolution and sensitivity. This technique allows for precise measurements of small temperature differences and is suitable for studying materials with subtle or complex thermal behaviours.



- ▶ Heat flux DSC: both the sample and reference are placed within the same furnace. The objective is to apply the same temperature profile to both sample and reference. By subjecting both the sample and reference to the same temperature conditions, heat flux DSC ensures that any observed differences in heat flow are due to the properties of the sample. The heat flows in both the sample and the reference are measured. Heat flux DSC is a more commonly used technique compared to power compensated DSC due to its simplicity.



There are a few operational conditions and limitations for DSC instruments:

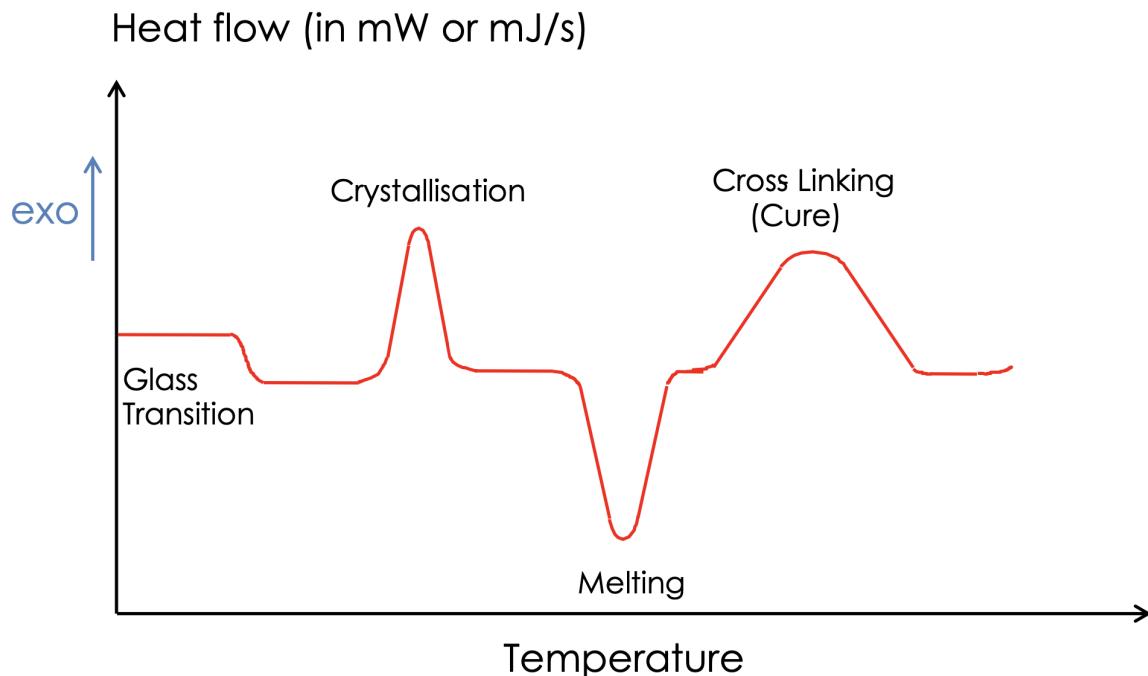
- ▶ DSC instruments often use purge gases, such as nitrogen or helium, to create a controlled atmosphere around the sample. These gases help remove any unwanted gases or vapours from the system, ensuring a clean and stable environment for the sample. Purging also prevents contamination from atmospheric gases that could interfere with the DSC measurements.
- ▶ Check thermal conductivity of purge gas: this can affect the heat transfer in the system and the accuracy of heat flow measurements.
- ▶ DSC instruments are capable of operating within a wide temperature range typically ranging from -180°C to 750°C. For experiments requiring temperatures below ambient, an intracooler can be used to achieve sub-ambient temperatures.
- ▶ Nitrogen is commonly used as a purge gas for DSC experiments conducted at room temperature and above. However, at low temperatures, nitrogen can condense, leading to potential issues. In such cases, helium is often used as the purge gas. At high temperatures above 600°C, argon is typically used as the purge gas due to its high stability and resistance to oxidation.
- ▶ The DSC technique requires a relatively small amount of sample material, typically ranging from 1 to 20 mg.
- ▶ The sample used should accurately represent the characteristics of the material under study, in terms of composition, structure, and any other relevant properties. An appropriate sample mass should be used to avoid any pressure build-up inside the instrument. The mass should be within the instrument's capacity while ensuring accurate measurements and reliable results. The sample should also be in good contact with the pan or disk used in the DSC instrument. This ensures efficient heat transfer and accurate measurements.

- ▶ No reaction can take place in a DSC. Prior to conducting any DSC experimentation it is useful to run a corresponding TGA in order to identify the exact onset point of degradation. Exceeding the degradation onset temperature in a DSC is not recommended, as this can lead to erroneous results due to the numerous exothermic and endothermic events associated with the transition. Also, condensation of the desorbed organic volatiles from the sample pan back into the DSC instrumentation can occur and can lead to contamination of the system, which will affect subsequent analysis.
- ▶ Pans: DSC experiments can be performed using either closed or unclosed pans. Closed pans are sealed, preventing any exchange of gas between the sample and the surrounding environment. Unclosed pans allow for gas exchange, which can be useful when studying volatile samples or samples undergoing reactions with the atmosphere. It is important to select a pan material that is chemically inert with respect to the sample. Aluminium pans are commonly used in DSC experiments when the temperature range is below 600 °C.
- ▶ Scan rate: the rate at which the temperature is changed during a DSC experiment. Common scan rates in DSC experiments can range from as low as 0.001 °C/min to as high as 500 °C/min, although typical scan rates are often in the range of 5-20 °C/min. The scan rate in DSC can affect the sensitivity of the measurements. Faster scan rates generally result in greater sensitivity. This is because faster scan rates increase the flow of heat in the system. As the temperature changes more rapidly, any thermal events or transitions in the sample can be detected more quickly and with higher precision. On the other hand, slower scan rates typically lead to better resolution. This is because slower scan rates allow for the establishment of more distinct thermal gradients within the sample, which facilitate the differentiation and detection of various thermal events, such as phase transitions or chemical reactions, with greater clarity and precision. Slower scan rates enable the instrument to capture more detailed information about the thermal behaviours of the sample.

DSC Curves

A typical DSC curve consists of a plot of heat flow as a function of temperature.

- ▶ The curve starts with a baseline, which represents the heat flow between the sample and the reference material under a constant temperature condition. This baseline serves as a reference for subsequent changes in heat flow.
- ▶ As the temperature is gradually increased, the DSC curve may exhibit a broad, shallow peak or a gradual slope. This region corresponds to the heat absorption or release due to changes in heat capacity, such as glass transitions, polymer chain relaxations, or solvent evaporation.
- ▶ An endothermic peak appears as a negative (downward) deflection. It represents the absorption of heat by the sample and indicates processes such as melting, vaporisation, sublimation, or other endothermic reactions. The peak position indicates the temperature at which the transition occurs.
- ▶ An exothermic peak appears as a positive (upward) deflection. It represents the release of heat from the sample and indicates processes such as crystallisation, solid-state reactions, or exothermic decomposition. The peak position indicates the temperature at which the transition occurs.
- ▶ After the occurrence of endothermic or exothermic transitions, the curve typically returns to the baseline as the system reaches thermal equilibrium. The curve extends beyond the transitions and settles into a final baseline. This baseline reflects the heat flow between the sample and reference material at higher temperatures when no further transitions are occurring.



For first-order transitions

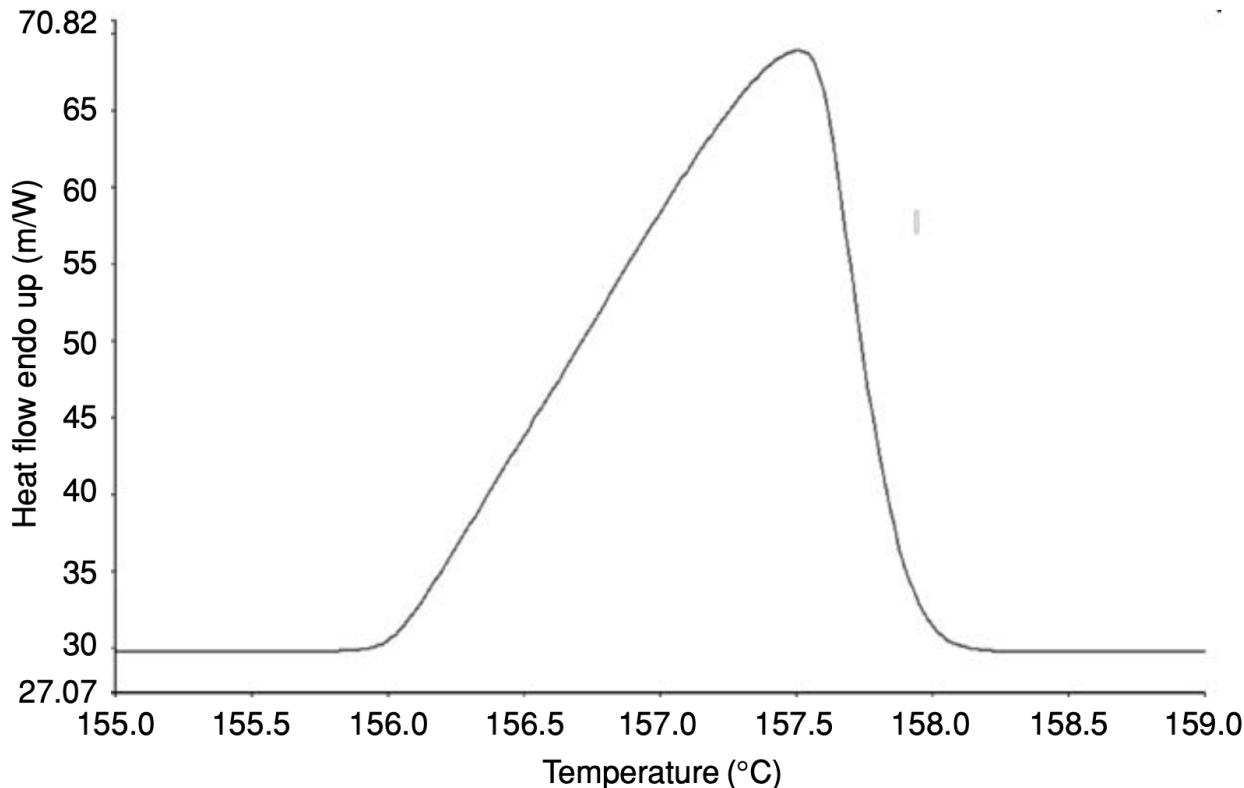
$$dG = -SdT + VdP$$

where $S = -(dG/dT)_P$ and $V = (dG/dP)_T$ discontinuities (steps) are observed in entropy, enthalpy or the volume. The first derivative of a step is a peak, so the heat flow curve, which is the first derivative of the enthalpy curve, shows a peak from a melt transition.

DSC curves are useful in analysing a variety of thermodynamic properties of a material.

Single Crystal Melt

One example is to determine the melting point and the enthalpy of melting for a single crystal like artemisinin:



Because of the nature of the measurement, during a DSC experiment, there will always be some degree of broadening of the peak associated with any phase change. In theory the melt of a pure single crystal at an infinitely slow scan rate should result in a peak that is infinitely narrow, but broadening of the peak occurs as a direct result of the thermal gradients that occur across a sample. Thermal gradients are caused by the time it takes for energy to transfer through the sample. As a result, the only accurate method of measurement of the melting point of a pure crystalline material is to quote the extrapolated onset temperature which is where melting begins. The peak maximum or half height transition point will vary as a function of particle size and sample mass, and it does not reflect the true melting point. In contrast, the onset temperature should not vary with changes in any of these parameters, nor with changes in heating rate, provided calibration has been performed correctly.

- For determination of the onset temperature, a line is extrapolated from the slope of the leading edge of the peak to the x -axis. The point at which the line bisects the x -axis is denoted the extrapolated onset temperature.

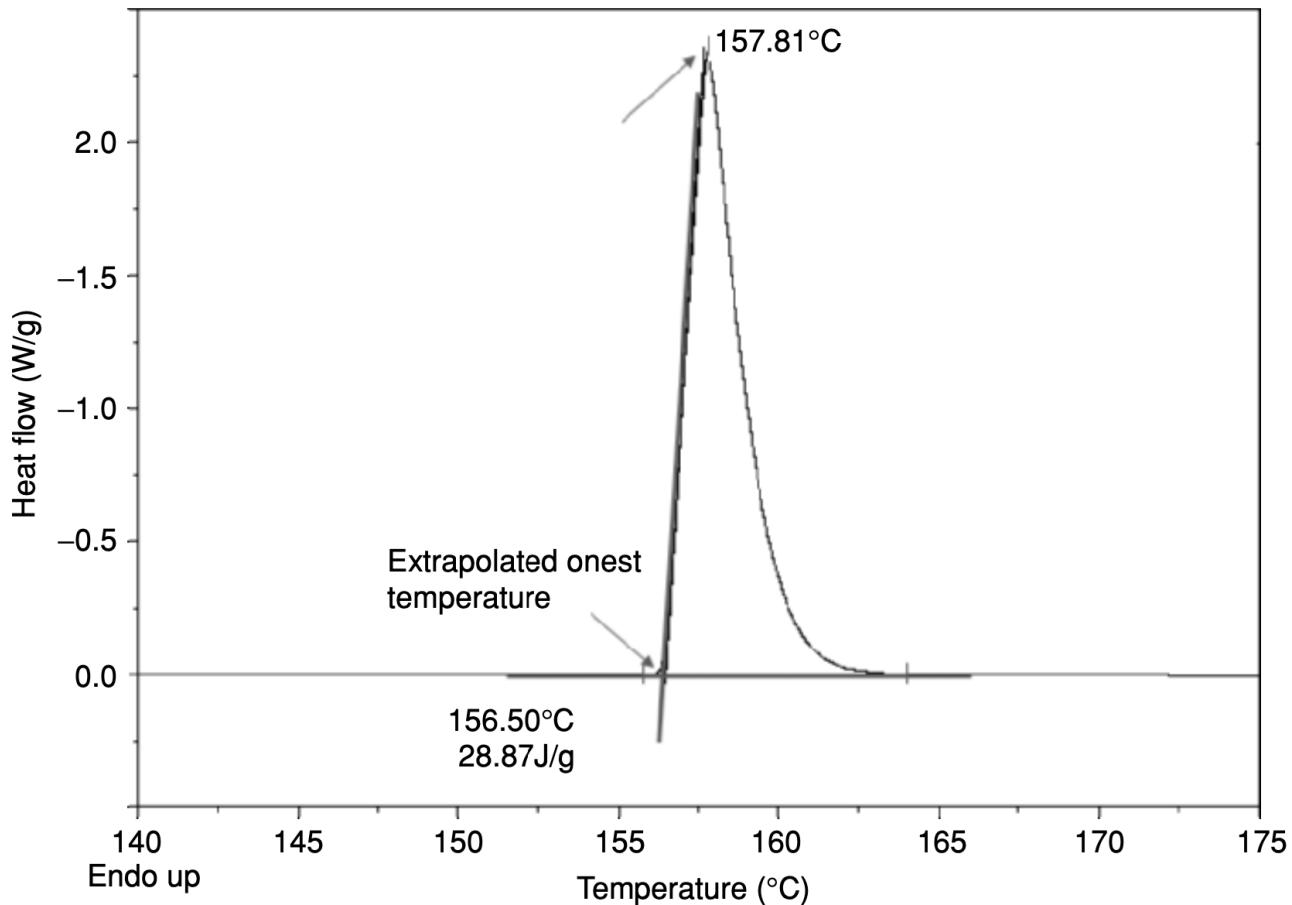
Moreover, in theory, a 100% pure material should melt with an infinitely sharp and infinitely narrow peak if there were no thermal gradients across a sample (sometimes called thermal lags). However, because it takes time for energy to flow into a sample, the peak is broadened and reduced in height. Thus:

- The slope of the leading edge of the melt profile of such a material provides a measure of the maximum possible rate of absorption of energy into a material, or put another way, it is a measure of the thermal resistance to energy absorption.

Finally,

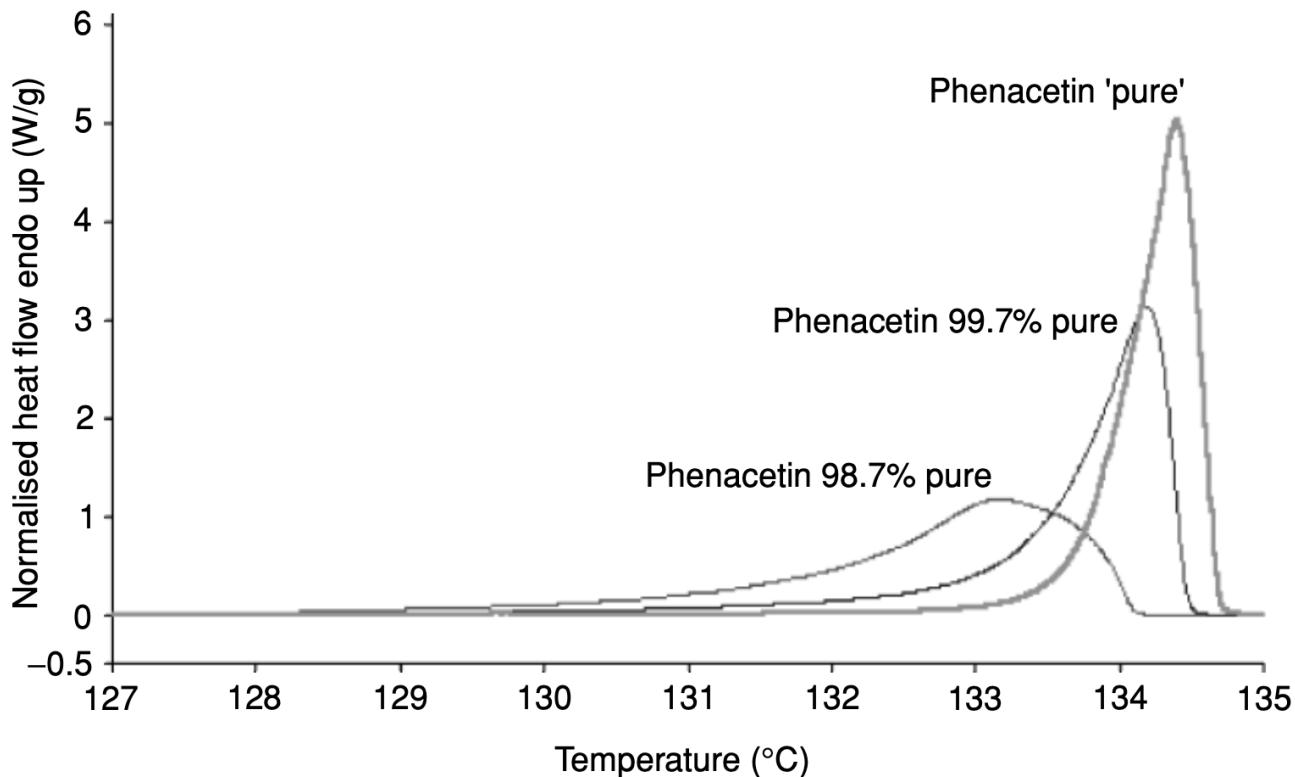
- Integrating the peak area gives the heat of fusion ΔH_f , since

$$\int \frac{dQ}{dt} \times dt = \int \frac{dH}{dt} \times dt = \Delta H$$



Effect of Impurities

In principle, when a material is slowly heated through its melting region in a DSC, the shape of the melting profile can be used to determine the purity of the substance with respect to those organic impurities which form a eutectic mix with the substance. It requires knowledge of the molecular weight of the material and can be applied to single crystalline materials of 96–98% purity and above. In practice, this is often the case for precursors and by-products which result from the manufacturing process and which may still remain in small quantities.



The basic theory behind the method is based on the observation that the presence of small degrees of impurities in an organic compound depresses the melting point; that is, the melting point is lowered with increasing amounts of impurity (which is why water freezes at a temperature below 0 °C with the addition of salt). The correlation between the melting point depression and the degree of impurity for a dilute system is defined by the van't Hoff equation:

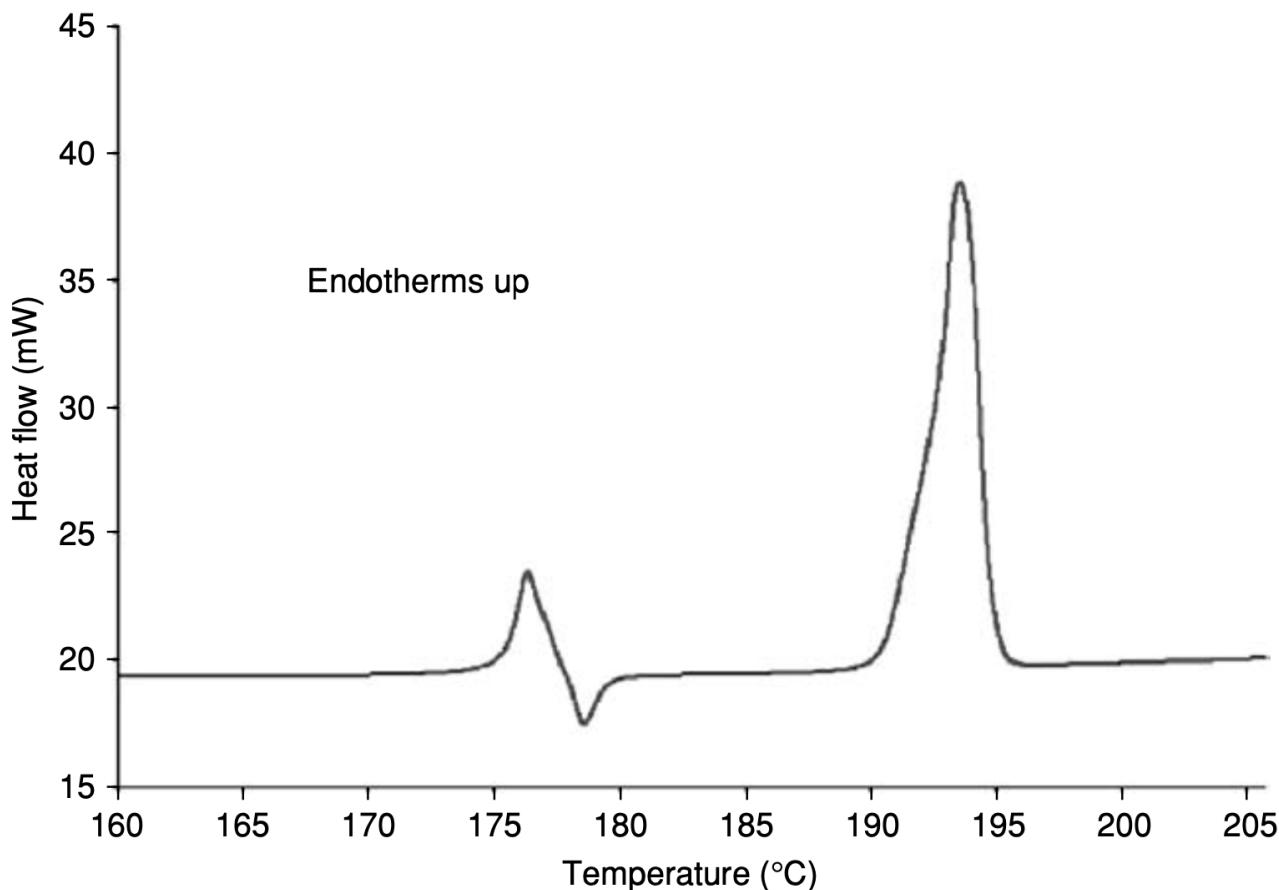
$$T_0 - T_m = \frac{RT_0^2 X_2}{\Delta H_f} \times 1/F$$

where T_0 and T_m are absolute temperatures of fusion of the pure and impure materials, ΔH_f is the molar enthalpy of fusion, F is the fraction molten corresponding to T_m and R is the gas constant.

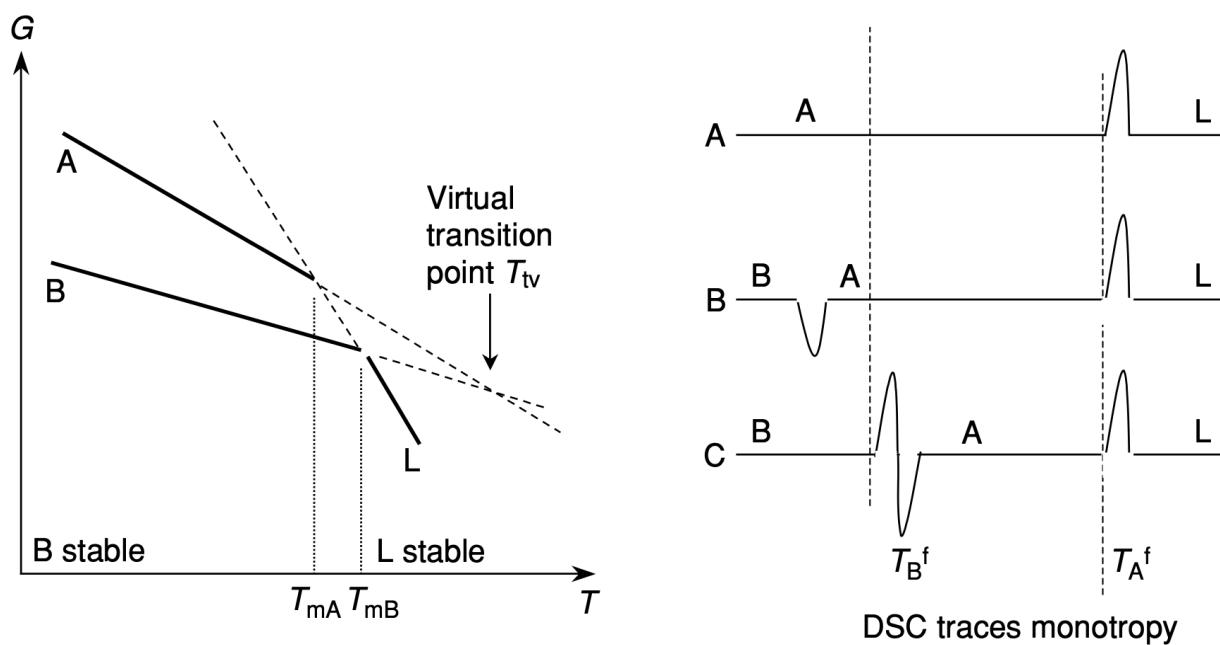
This simple and rapid method for estimating purity is therefore a potentially significant application, but it is an empirical approach and its use is restricted by interferences from other events that occur simultaneously with melting and affect the peak shape and the subsequent purity calculation. For example, these include solid–liquid interactions and polymorphic transformations. Other impurities which do not form a eutectic mix and interact in no way with the substance will not be taken account of by this calculation and need to be assessed separately, though it is possible for non-eutectic impurities to interact and affect the melting point. Provided any interactions do not affect peak shape, the purity calculation should remain unaffected, so it is possible for the individual purity of two mutually incompatible materials in a mix to be assessed from one scan. The nature of these restrictions means that great care is needed when the technique is applied to a range of unknown samples, but it can work well when applied as a quality control method to a material which is known to have no interferences.

Polymorphism

Polymorphism refers to the ability to exist in different crystalline forms. In the example of carbamazepine, it has been successfully shown that three distinct polymorphs exist:



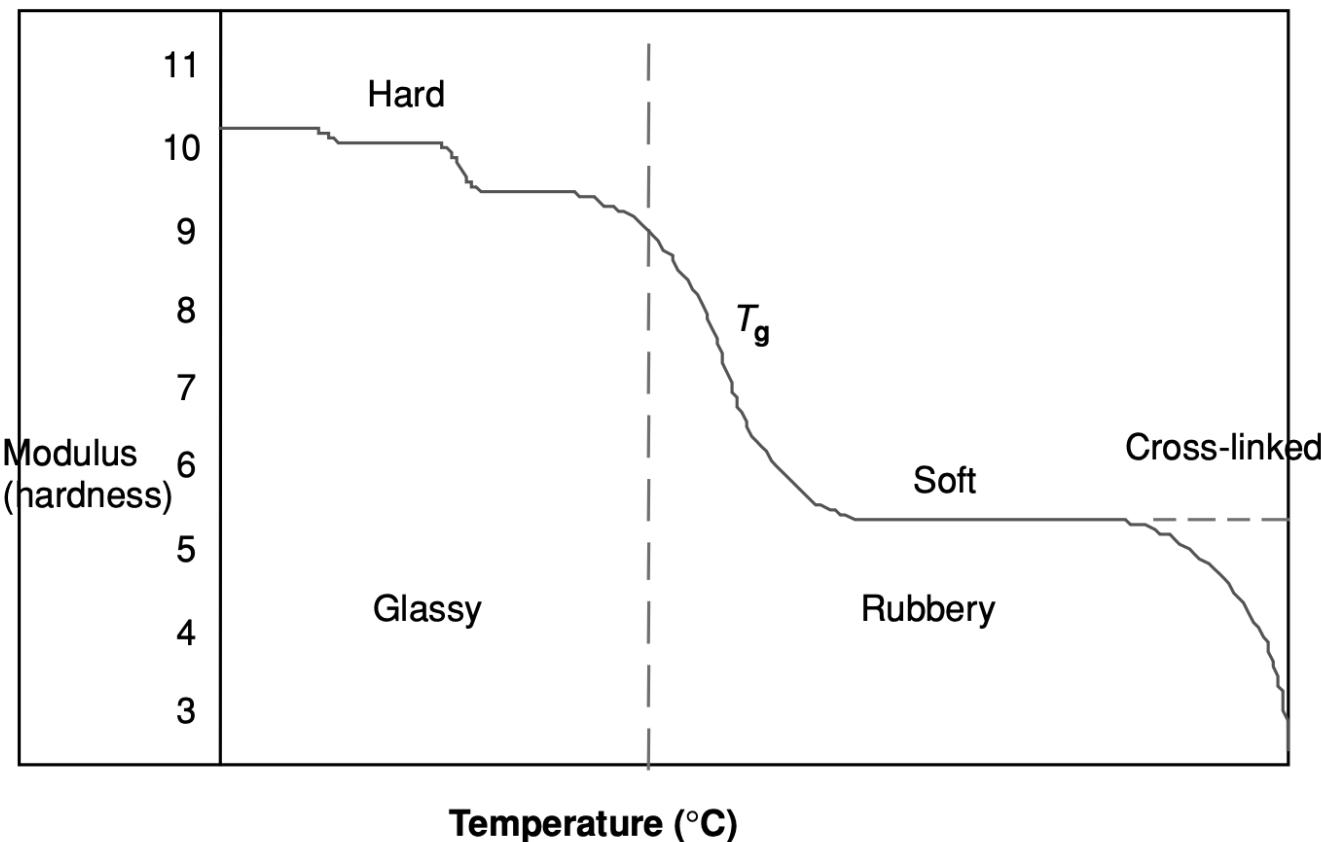
Carbamazepine form III is seen to first melt and then recrystallise. The two events occurring simultaneously and so the peaks are not separated. Neither the heat of fusion nor the heat of recrystallisation can be accurately measured in this case. This is followed by the melting of a new, more stable form. This can be explained with the thermodynamic stability relationship between the different solid phases:



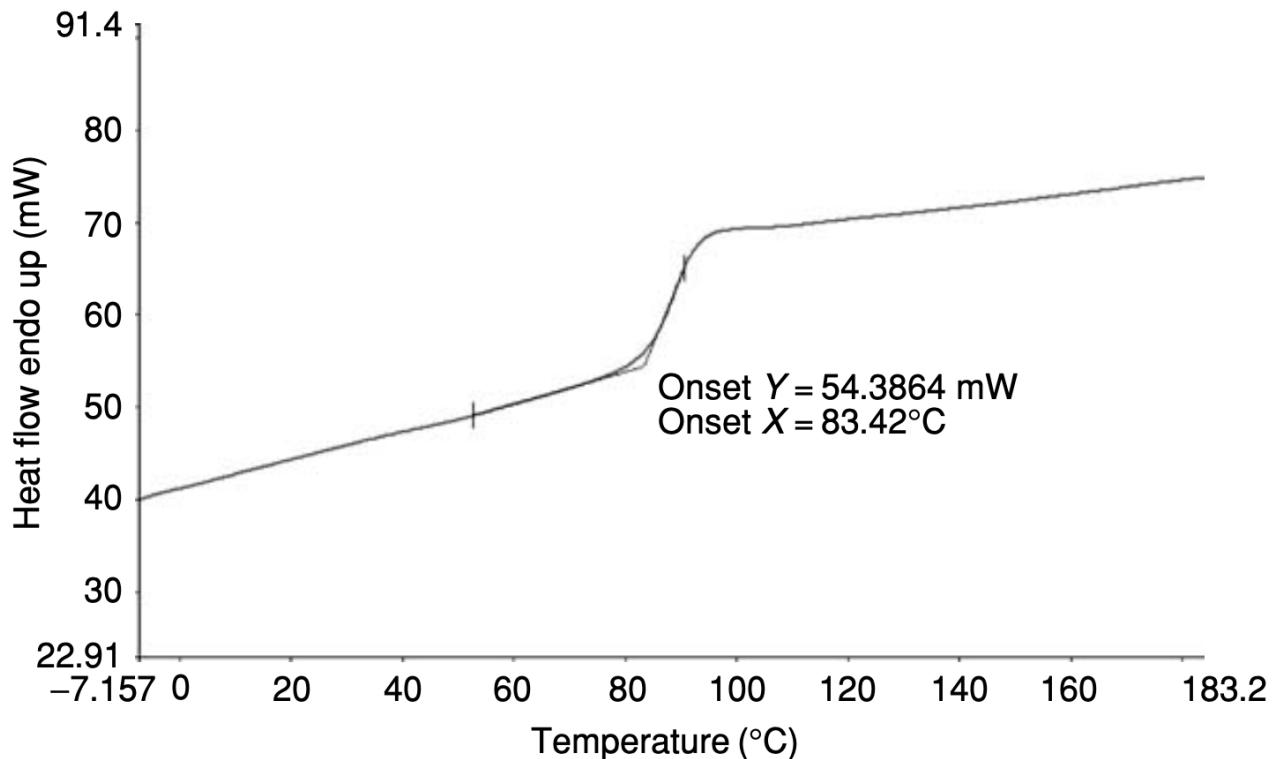
It should be noted that the more stable form is not necessarily the most thermodynamically stable form of the material. During crystallisation of a material from a chosen solvent system, depending on the extent of supersaturation and the temperature-solubility curves of each polymorph or pseudopolymorph, generally the first nucleating crystals or metastable forms are the kinetically favoured. Subsequently, as the thermodynamic equilibrium is re-established due to changes in the solubility product as the sample crystallises, the solid sample undergoes a solvent-mediated phase conversion to the more stable state. However, depending on factors such as crystal growth, temperature and solubility, this conversion may not occur and the metastable form will prevail in the solid phase. Therefore, it is possible for the thermodynamically stable B to melt and recrystallise into A, which subsequently melts as temperature is higher.

Glass Transition Temperature

Glass transition temperature (T_g) is the temperature assigned to a region above which amorphous (non-crystalline) materials are fluid or rubbery and below which they are immobile and rigid, simply frozen in a disordered, non-crystalline state. Strictly speaking, this frozen disordered state is not described as solid, a term which applies to the crystalline state, but materials in this state are hard and often brittle. However it is a frozen liquid state, where molecular movement can occur albeit over very long time periods. Material in this frozen liquid state is defined as being a glass, and when above T_g is defined as being in a fluid or rubbery state:



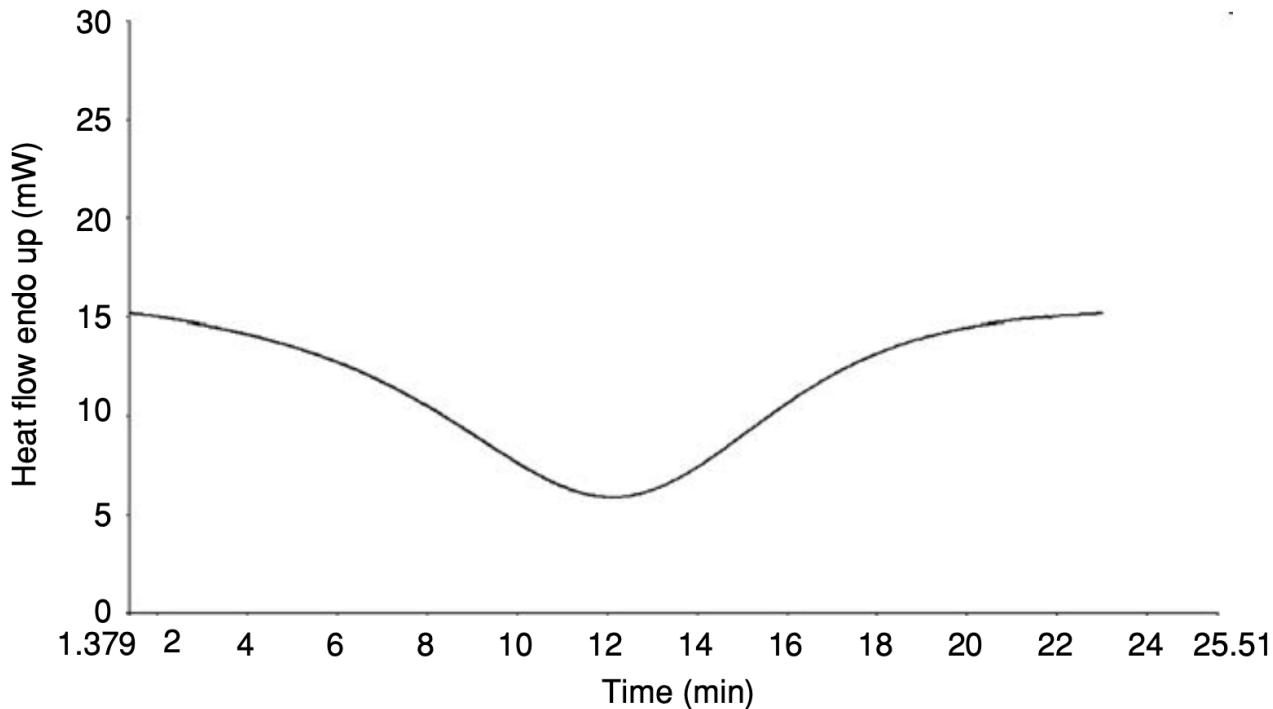
Materials in their amorphous state exhibit very substantial changes in physical properties as they pass through the glass transition. After a molecule has passed through T_g it has greater ability to move in various molecular motions, described as an increase in degrees of freedom of movement. For a given molecule these various movements may not be well defined, but they represent additional ways of absorbing energy, which means that an increase in specific heat is observed.



The glass transition temperature is influenced by many parameters including effects of additives, for example plasticisers which are added to reduce the temperature of T_g . One of the most significant plasticisers is moisture. This is well known to affect the T_g of composites, pharmaceuticals and many other materials. It can lead to loss of strength or stability at a given temperature. Cornflakes are a typical example of a material which is hard and brittle when dry at room temperature, yet with the addition of water (milk) the T_g is reduced and the cornflakes become very soft and pliable. Reactions, such as a cure reaction, which increase the molecular weight of a material will increase the temperature of T_g , since molecules need more energy and a higher temperature to move independently of one another. Another factor is the flexibility of the chemical bonds in the molecule itself. Materials with flexible bonds such as Si–O or CH₂–CH₂ have low-temperature glass transitions whereas more rigid structures have higher temperature transitions.

Cure Reactions

Curing refers to the toughening/hardening of a polymer material via cross-linking, triggered by electron beams, heat or chemical additives. The cure reactions appear as a broad exothermic peak:



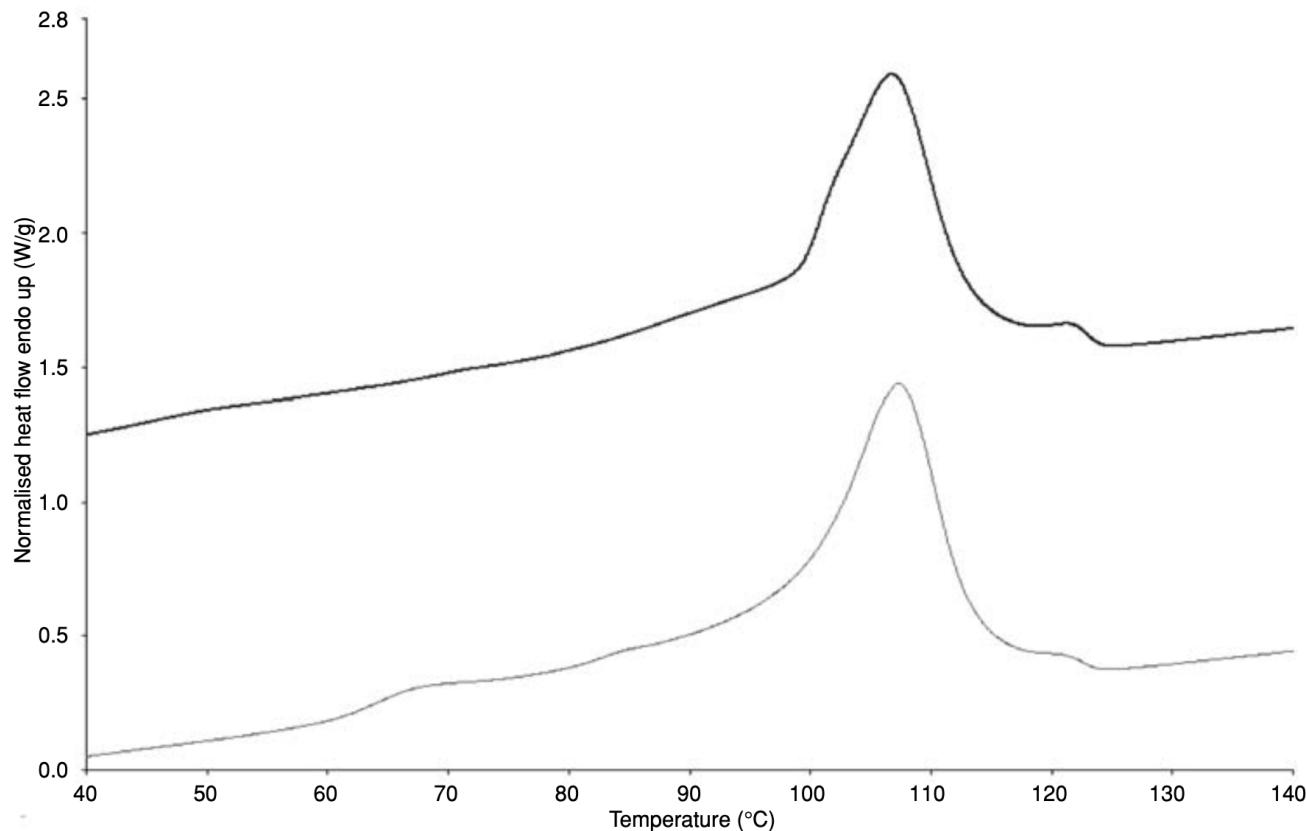
Cure reactions are normally slow events compared to typical scan times, and in order to measure them slow scan rates need be used so that the cure reaction can be measured fully before decomposition temperatures are reached. The alternative is to heat to an isothermal temperature where time can be given for the reaction to come to completion. This is also helpful when making calculations since a flat line extrapolated from the reacted portion of the sample provides an accurate baseline for peak integration.

This exotherm, the size and position (i.e. temperature range) of which is dependent on a number of factors such as the rubber type, the proportion of rubber in a sample, as well as the amount and type of cure system present, can be used for a number of purposes, for example,

- ▶ Determination of the amount of curative in a sample;
- ▶ Qualitative assessment of the type of curative or cure system present;
- ▶ Characterisation of a cure in terms of the temperature that the cure begins, or the cure time at a given temperature.

Ageing and Degradation

DSC is a useful technique for detecting the chemical and morphological changes that occur in conjunction with ageing and degradation. For example, in semi-crystalline polymers heat ageing can cause a process referred to as solid state crystallisation to occur. When such a sample is heated in the DSC, a secondary melting endotherm having a lower melting point to the principal one will be apparent. The crystals formed in this way are small and their melting point is related to their thickness, which in turn is related to the time of ageing. It is therefore possible to develop correlations between ageing time and temperature and degree of secondary crystallisation. This effect is illustrated below,



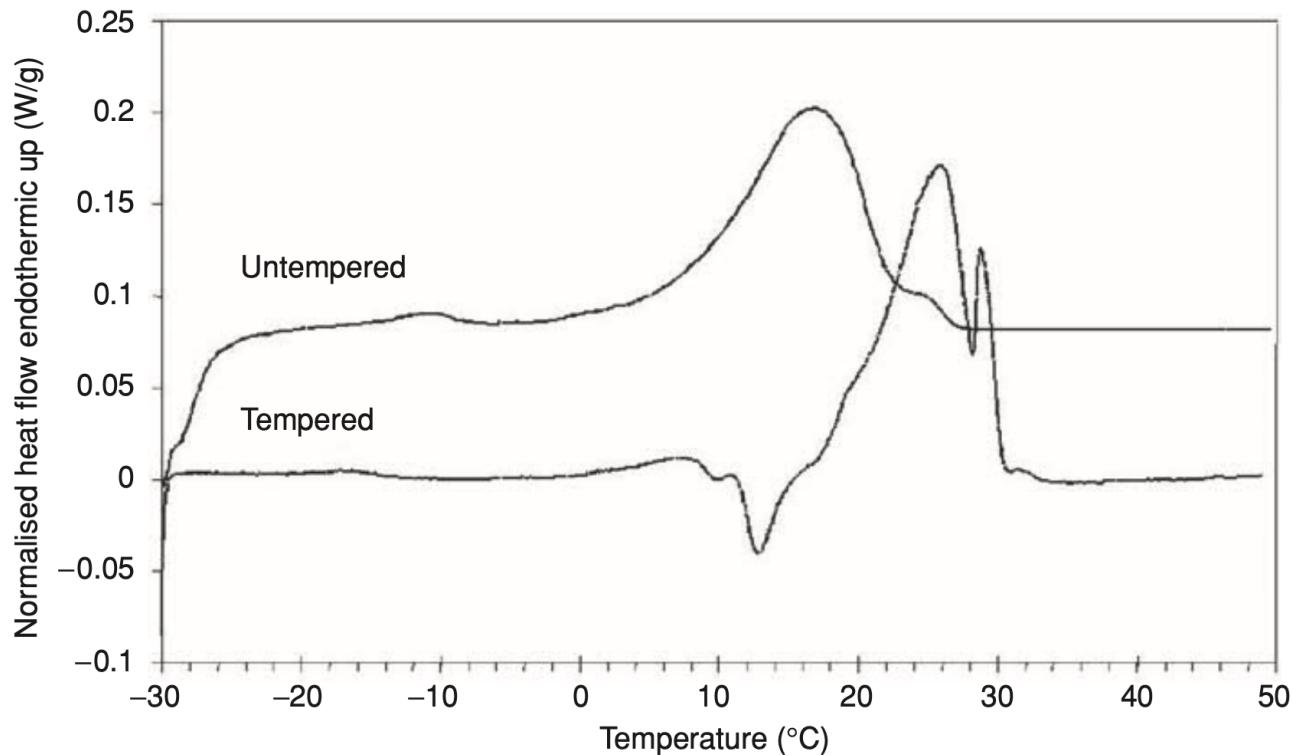
where a small endotherm at a relatively low temperature (65–70 °C) is apparent in the as-received data for sample B (bottom trace); a sample that had been heated in service and had failed as a consequence. This endotherm is absent in the as-received data for sample A (top trace), which had not been exposed to any heat in service.

Tempering: Example of Chocolate

Tempering refers to the process of heating/cooling chocolate to ensure that the cocoa butter hardens in a uniform crystal structure. A combination of temperature treatment and shearing of the material normally produces this:

Crystal	Melting T	Notes
I	17 °C	Soft, crumbly, melts too easily
II	21 °C	Soft, crumbly, melts too easily
III	26 °C	Firm, poor snap, melts too easily
IV	28 °C	Firm, good snap, melts too easily
V	34 °C	Glossy, firm, best snap, melts near body T
VI	36 °C	Hard, takes weeks to form

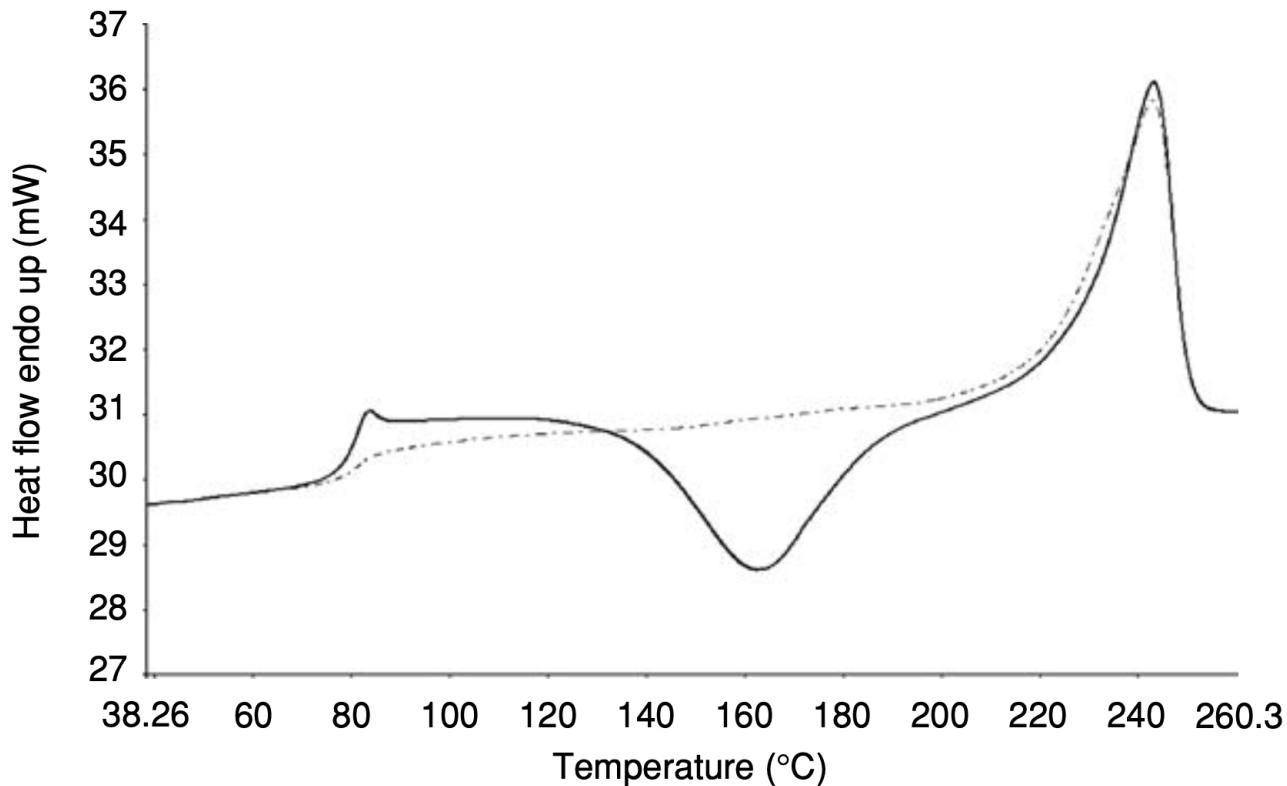
The overall aim in most chocolate manufacture is to make a stable chocolate, which will not convert to another form during storage, producing the characteristic and unacceptable white-surface bloom. This can be investigated thoroughly using DSC. The melting of different polymorphic forms in the fat component of chocolate can be clearly seen:



These observations can rationalise thermal pre-treatment of materials and can justify the success of tempering. For example, slow cooling of tempered chocolate followed by heating at 10 K/min will demonstrate the presence of stable, high-melting polymorphs (V and VI), whereas rapid cooling and the use of untempered material produce lower forms (I and II), which will subsequently melt at reduced temperatures.

Effect of Thermal History

The effect of previous heating/cooling treatments (i.e. thermal history) can impact the DSC trace of a sample. For example, fast controlled cooling pretreatment, particularly with respect to crystallinity or glassy morphology within a material. The effect of different cooling rates on morphology is easily demonstrated with PET, which shows increasing amounts of amorphous material if cooled at increasingly fast rates from the melt:

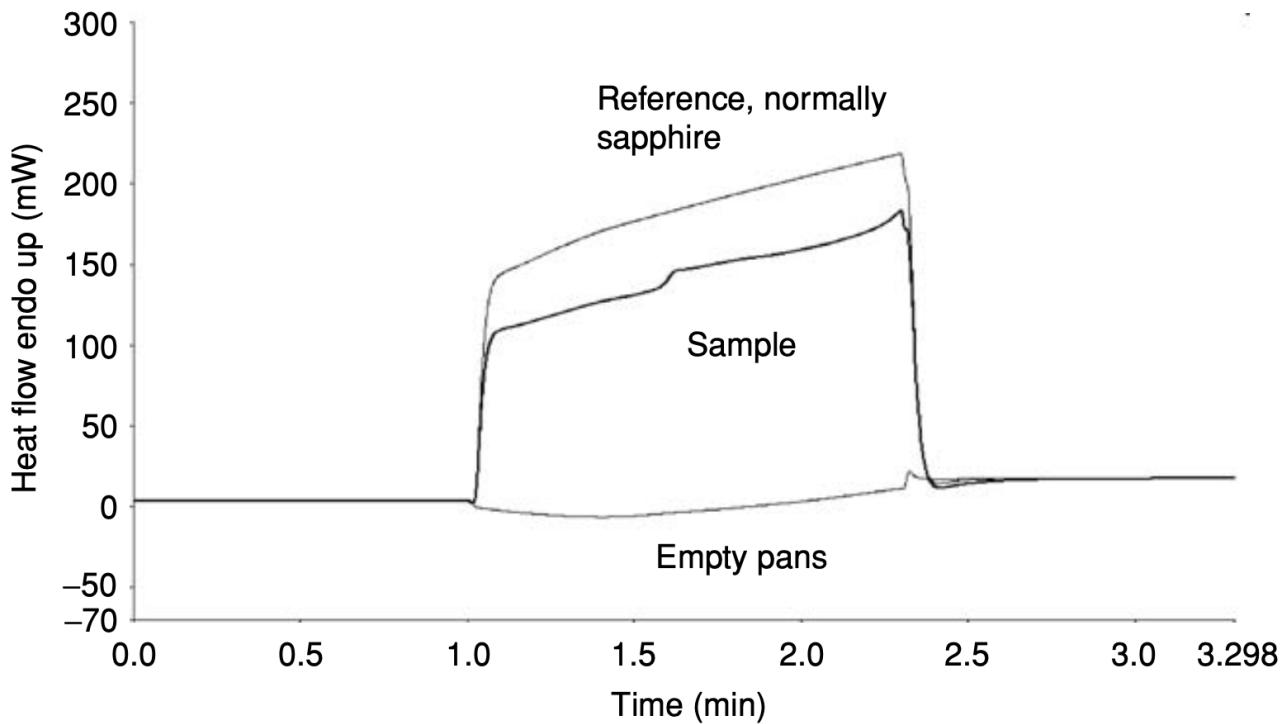


If cooled quickly (solid line), PET remains completely amorphous, and when reheated slowly it shows a large glass transition from the amorphous material, followed by crystallisation which will then occur with slow heating rates. This is termed cold crystallisation when it occurs in this way. If cooled slowly from the melt (dashed line) the PET will be partially crystalline to start with, so will not show such a significant T_g nor a cold crystallisation event.

Heat Capacity

The specific heat capacity C_p of a material can be determined quantitatively using DSC and is designated C_p since values are obtained at constant pressure. Traditionally, this is done by subtracting a baseline from the heat flow curve. The subtracted curve referenced against a standard gives a quantitative value of C_p . Experimentally, three runs are required, each consisting of an isothermal period, temperature ramp and final isotherm. This method is applied identically to the succeeding runs:

1. First run: a baseline with uncrimped empty pans placed in the furnace.
2. Second run: as above but adding a reference (typically sapphire) to the sample pan.
3. Third run: replace the reference with the sample.



By definition, C_p of sample i is:

$$C_{p,i} = \left. \frac{dH}{dT} \right)_i \cdot \frac{1}{m_i}$$

where m_i is the mass of i . By the chain rule,

$$C_{p,i} = \left. \frac{dH}{dt} \right)_i \cdot \frac{dt}{dT} \cdot \frac{1}{m_i}$$

where dG/dt is the heat flow measured for sample i and dT/dt is the heating rate. Similarly, for the reference sample:

$$C_{p,ref} = \left. \frac{dH}{dt} \right)_{ref} \cdot \frac{dt}{dT} \cdot \frac{1}{m_{ref}}$$

Combining the two equations,

$$C_{p,i} = \frac{dH/dt)_i}{dH/dt)_{ref}} \cdot \frac{m_{ref}}{m_i} \cdot C_{p,ref}$$

Summary

DSC traces can have multiple interpretations. To accurately interpret DSC traces, it is crucial to have some background knowledge about the sample being analysed. This includes information like the temperature range of interest, the type of sample (e.g., polymer, metal, or organic compound), and any expected transitions or

events that might occur during the analysis. Furthermore, when examining DSC data, several questions can be asked to aid in the interpretation:

- ▶ Endotherm or exothermic?
- ▶ Transition sharp or not?
- ▶ Is the event real? This involves considering factors like instrument artifacts, noise, or experimental anomalies that could potentially affect the data.
- ▶ Is the event same in sealed or unsealed pan? This explores whether the observed event is dependent on the sample's exposure to the surrounding environment, for example, factors like moisture or oxygen.

The table below presents a comprehensive summary of interpreting DSC trace features.

DSC trace feature	Potential explanation
Large well-defined endotherm	<ol style="list-style-type: none"> 1. Pure crystal melting 2. Solvate/hydrate loss 3. Stress relaxation
Shallow broad endotherm	<ol style="list-style-type: none"> 1. Moisture/residual solvent loss 2. Sublimation 3. Range of MWs melting
Large well-defined exotherm	<ol style="list-style-type: none"> 1. Crystallization in/from liquid state 2. Degradation of unstable material 3. Crystal structure rearrangement
Shallow broad exotherm	<ol style="list-style-type: none"> 1. Cure reaction 2. Oxidation

Industrial Relevance

Finally, DSC has significant industrial relevance across various industries:

- ▶ Pharmaceutical industry.
- ▶ Food industry.
- ▶ Manufacturing industry (ceramics, plastics, etc.).

where various aspects of the material can be derived:

- ▶ Physical state, such as whether the material exists as amorphous or crystalline forms.
- ▶ Purity: detect impurities or deviations from expected thermal behaviours.
- ▶ Polymorphism: characterise different polymorphic forms.
- ▶ Ageing and degradation: stability over time.

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