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Ministry of Higher Education and Scientific Research
Ibn Khaldoun University. Tiaret
Faculty of Material Sciences

Educational Handout

PHYSICAL CHARACTERIZATION OF MATERIALS

LMD Level – Master 2
Organic Chemistry

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Foreword

This document is designed for master's (LMD) students specializing in organic chemistry, as part of the official curriculum. The primary objective of this course is to equip students with comprehensive knowledge of methods for the physical characterization of materials, with a particular focus on polymer materials, which have become increasingly significant in contemporary life. Through this course booklet, students will become acquainted with various characterization techniques, including thermogravimetric analysis (TGA), differential thermal analysis (DTA), thermomechanical analysis (TMA), and X-ray diffraction (XRD). The concepts acquired are reinforced through practical exercises, enabling students to interpret various thermograms and diffractograms and to extract pertinent information regarding the materials under analysis. This course booklet serves as an educational reference, created with the aim of ensuring relatively uniform and coherent instruction. It also fulfills a didactic purpose, aiming to identify essential concepts as well as the practical knowledge associated with this module.

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Chapter I

Thermogravimetric Analysis

TGA

General Overview

Thermal analysis comprises a comprehensive array of material characterization techniques predicated on examining the variation of a physical property as a function of temperature. This approach is fundamentally macroscopic, addressing material behavior through thermodynamic considerations of equilibrium states and irreversible processes, as well as kinetics associated with state changes (transition phenomena) and the relaxation phenomena that may accompany them. In the specific context of macromolecular materials, or polymers, the analysis of thermal responses facilitates the elucidation and microscopic interpretation of phenomena such as glass transition, melting/crystallization, physical and chemical aging, and phase segregation, contingent upon the specific circumstances.

Table 1. Thermal analysis techniques

Analysis Technique	**Instrument Used**	**Measured Parameter**
Thermogravimetric Analysis (TGA)	Thermo balance	Mass
Differential Thermal Analysis (DTA)	DTA Instrument	Temperature difference
Differential Scanning Calorimetry (DSC)	DSC Calorimeter	Difference in heat flow
Thermomechanical Analysis (TMA)	Dilatometer	Difference in volume or length

Abbreviations:

DEA: dynamic electrical analysis
DTA: differential thermal analysis
DMA: dynamic mechanical analysis
DEA: differential enthalpic analysis
TMA: thermomechanical analysis

1 Thermogravimetric Analysis

1.1 Definition

Thermogravimetric analysis (TGA) is a thermal analysis technique that involves measuring the change in mass of a sample over time, under a specified temperature or temperature profile. Thermogravimetry encompasses four primary components:

- The sample
- The mass,
- The time,
- The environment.

This definition was established by the International Confederation for Thermal Analysis and Calorimetry ***(ICTAC).***

Thermogravimetric Analysis (TGA) or Thermogravimetry (TG) refers to the measurement of the change in the mass of a sample when subjected to a temperature regime. TGA quantifies the variation in mass of a sample as a function of temperature, with the mass being determined from the weight reading provided by the balance (measuring device). Thermogravimetry measures the variation in mass as a function of temperature.

Reminder: A balance always measures weight, which is the resultant force of a mass. The same mass can exhibit different weights depending on:

1. Its density relative to the surrounding fluid (temperature, pressure, humidity, etc.);
2. Its relation to gravity, expressed as **p = mg**.

The balance provides a mass indication only after calibration.

1.2 Measurement and the Sensor

To accurately ascertain the variable mass of the sample, it is imperative that the measuring instrument is capable of continuously recording mass readings. A conventional balance is inadequate for this purpose; therefore, specialized instruments have been developed to address this specific application.

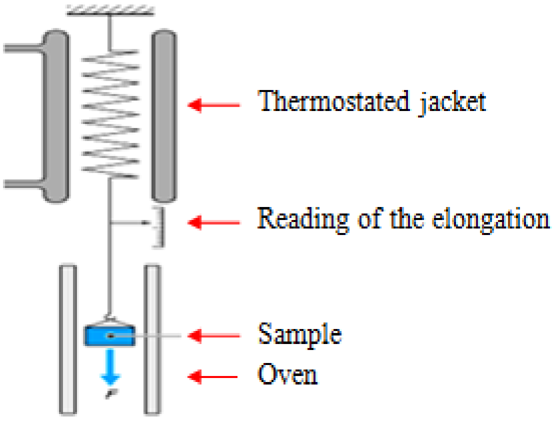


Figure 1. Peson McBain

Historically, various types of balances have been developed to address measurement challenges, notably the silica spring devices introduced by McBain and Bakr in 1926 (Figure 1). In this design, weight is directly measured by the elongation of a spring, which is affixed at its upper end to a fixed frame. The sample is suspended from the opposite end via a suspension mechanism, allowing immersion in the experimental chamber. Silica was selected for the spring due to its low thermal expansion and chemical inertness. While the initial deformation of the spring is substantial, the change in mass is minimal. Several methods have been developed to measure the position, and consequently the elongation, including optical and electromagnetic techniques.

There are several configurations for sample placement:

Vertical suspension involves suspending the sample from the beam (e.g., SETARAM, Perkin Elmer).

Vertical support entails placing the sample on an upper plate attached to the beam (e.g., Netzsch, SETARAM).

In the horizontal configuration, the sample is positioned directly at the end of the beam or the parallelogram (e.g., TA Instruments, Mettler-Toledo).

Each configuration presents distinct advantages and disadvantages concerning measurement quality, interference effects, and ergonomics.

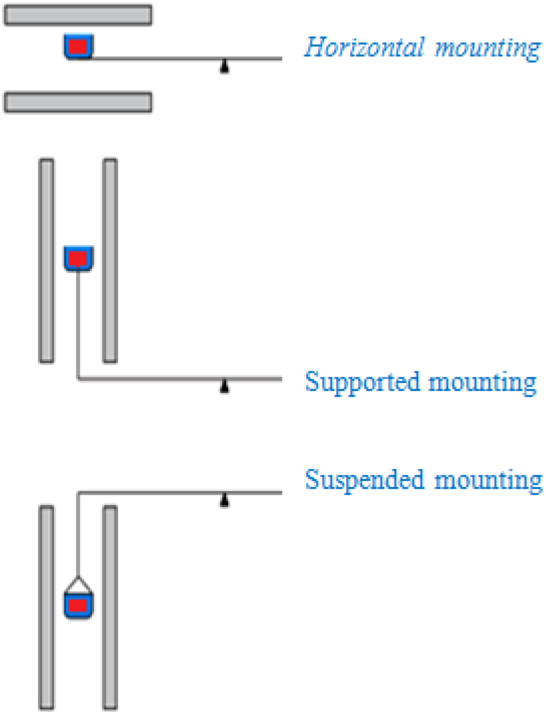


Figure 2. *Sample arrangement in the oven*

1.3 Measurement and Associated Parameters

Measurement Range: This refers to the difference between the minimum and maximum quantities detectable by the balance.

Standard Deviation/Background Noise: This denotes the level of parasitic signal that contains no informational content.

Calibration: This encompasses all operations that establish, under specified conditions, the relationship between the values indicated by a measuring device or system (or the values represented by a material measure or reference material) and the corresponding values of the quantity realized by standards.

Quantities: This pertains to the property of a phenomenon, body, or substance that can be quantitatively expressed as a number and a reference.

Measurement Accuracy: This is defined as the closeness of agreement between the measurement result and the true value of the measured quantity.

Repeatability: This is the ability of an instrument to provide very similar indications for the same load placed multiple times in practically the same manner on the load receptor under reasonably constant test conditions.

Measurement Trueness: This refers to the ability of a measuring instrument to provide indications free from systematic error.

Measurement: refers to a series of operations designed to ascertain the value of a specific quantity. It involves a process of experimentally obtaining one or more values that can be reasonably attributed to a given quantity. It is important to note that measurements are not applicable to qualitative properties.

Measurand: denotes the specific quantity to be measured, such as the vapor pressure of a water sample at 20 °C.

The detection limit: is defined as the lowest measurement of a quantity that can be quantified with precision.

Accuracy pertains: to the quality of a sensor, encompassing both the metrological properties of trueness and repeatability.

Maximum capacity: refers to the highest weighing capacity, excluding the additive tare capacity.

Repeatability: is the degree of agreement between the results of measurements of the same measurand conducted under varying conditions.

Linearity characterizes: a balance's ability to maintain a linear relationship between the actual weight of the product and the measured value, quantifying the proportionality between the sensor's indication and the quantity to be measured.

Calibration: involves actions aimed at relating the sensor's indication to absolutely known quantities of the quantity to be measured.

Sensitivity: is defined as the quotient of the observed variable variation (DL) by the measured mass variation (DM), expressed as sensitivity K = DL/DM.

The time constant: is the response time to 63% of the amplitude for a step-type input on the sensor, such as placing or removing a mass on the platform.

Stabilization time (or warm-up time): is the duration required for the measuring instrument to stabilize after being switched on following a prolonged shutdown.

1.4 Experiments

The thermogravimetric method is employed to characterize a wide array of materials, encompassing organic, inorganic, ceramic, and metallic substances. The scope of measurements is extensive, as illustrated by the following non-exhaustive list:

- Dehydration and dehydroxylation of raw materials and both inorganic and organic products.

- Pyrolysis and decomposition of polymers, inorganic, and organic materials.

- Reactions in various reducing atmospheres (e.g., hydrogen, CO).

- Oxidation and combustion.

- Studies in corrosive atmospheres.

- Studies in humid atmospheres (water vapor).

The primary values obtained from thermograms are the mass (TG) and its derivative (DTG) with respect to time or temperature. Utilizing the DTG facilitates a clearer separation of the distinct stages within a thermogram.

1.4.1 Interpretation of Different Types of Characteristic Curves

Various families of TG curves can be observed (Figure 3):

– **Curve 1**: This curve exhibits no mass variation. However, a transformation such as fusion or another structural change, which does not involve mass variation, may have occurred and could be detected using the coupled TG-DTA or TG-DSC technique.

– **Curve 2**: This curve demonstrates a rapid mass loss at low temperature, often indicative of evaporation (volatiles) or dehydration (adsorbed water).

– **Curve 3**: This curve indicates the decomposition of the sample in a single step. Consequently, the stability limit can be defined as a function of temperature, and kinetic parameters for the decomposition reaction (such as pyrolysis) can be inferred.

– **Curve 4**: This curve reveals decomposition in multiple steps. A range of stability limit temperatures can be defined for each step. The DTG derivative curve is particularly useful for distinguishing the different steps and conducting kinetic studies.

– **Curve 5**: This curve shows a mass gain associated with the reaction of the sample with the atmosphere. This example is representative of metal oxidation with the formation of an oxide layer.

– **Curve 6**: This curve depicts a series of reactions resulting in a mass gain, followed by a mass loss. This curve may correspond, for instance, to an oxidation reaction (mass gain) followed by the decomposition of the oxide at a higher temperature (mass loss).

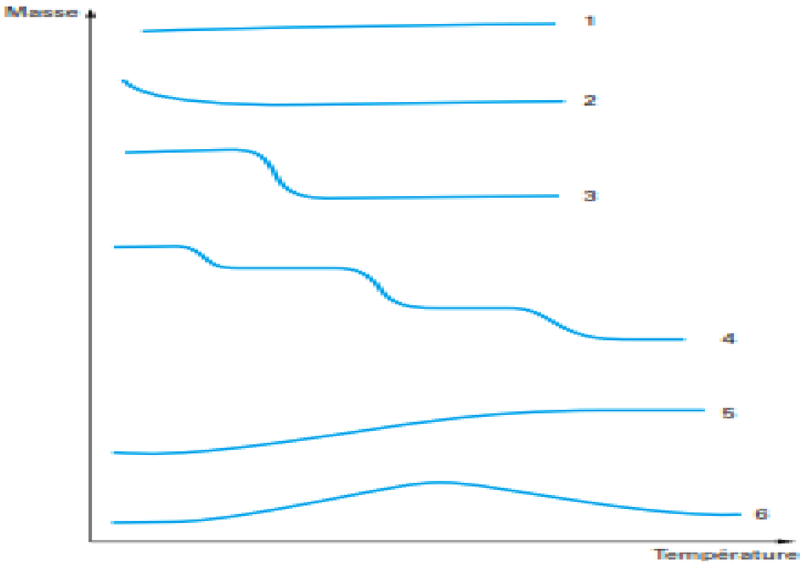


Figure 3.Different Families of TG Curves Observed in Thermogravimetry.

Samples typically range from 100 mg to 1 g and are examined over a temperature span from -100°C to +950°C, with heating rates of approximately 10 K/min. Aluminum or platinum crucibles are employed.

- 1st step: Loss of oils, water molecules (and oligomers if a polymer is present).

- 2nd step: More intense thermal degradation of chemical bonds.

- 3rd step: Combustion under oxygen, recovery of ash.

As illustrated by the following curve, thermostable materials only degrade at elevated temperatures:

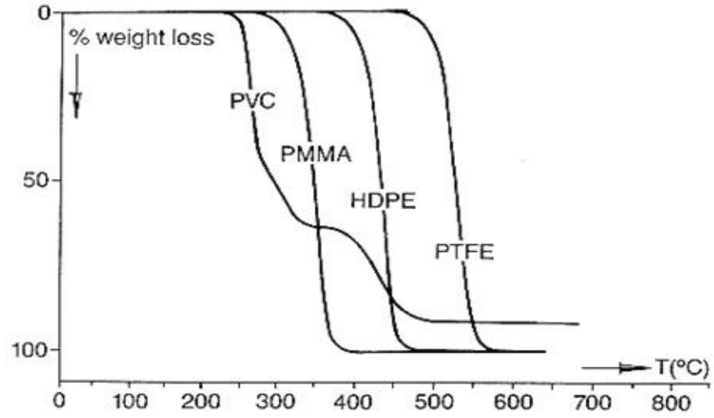


Figure 4. TG curves of some polymers

Generally, true thermostable materials exhibit minimal degradation steps. Symmetrical molecules, such as HDPE, demonstrate good thermal resistance. PVC undergoes multiple steps due to the early release of HCl molecules. Additionally, C-H bonds are weaker than C-F bonds, which accounts for the superior temperature resistance of PTFE compared to HDPE.

Utilizing the derivative of the TG curve enhances the distinction of the steps, thereby facilitating the determination of the number of components in a complex material:

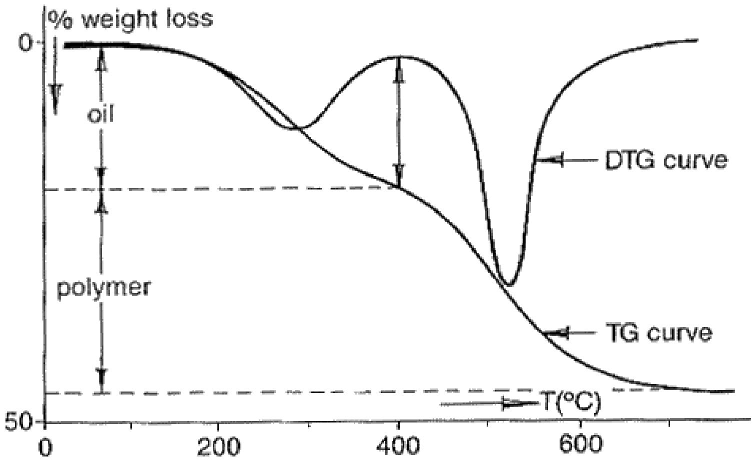


Figure 5. TGA/DTG thermogram

Exemple ;

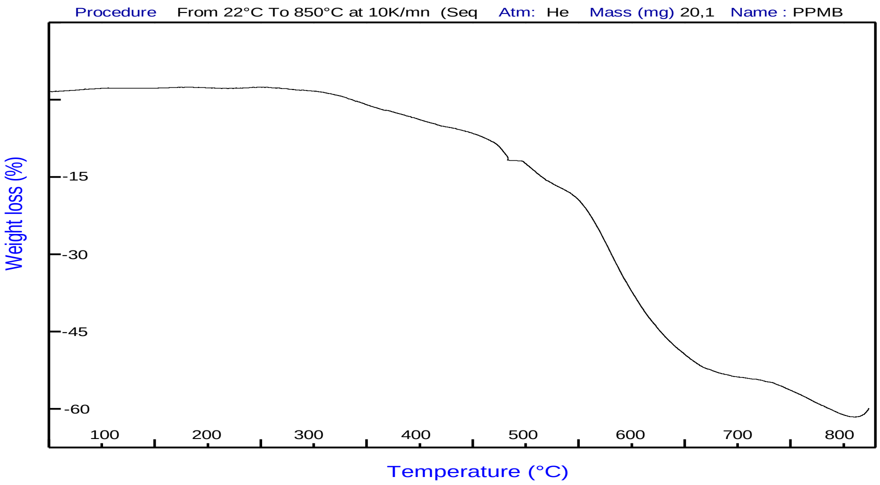


Figure 6. TGA curve of PPMB

Interpretation: This experiment is conducted under an inert atmosphere (He), with a temperature range from 60°C to 850°C and a heating rate of 10°C per minute. According to the obtained thermogram, PPMB exhibits good stability above 293°C, after which it experiences an initial mass loss.

1.5 Sample Heating

The sample heating system includes several key features:

- Regulated heating.
- Containment of the controlled atmosphere.

- Regulated cooling.

To effectively manage the atmosphere, it is essential to maintain a nearly systematic separation between the heating element and the sample chamber. This separation is achieved using a material that offers the optimal combination of chemical inertia, airtightness, and cost-effectiveness. Typically, quartz (up to 1,000/1,200°C), alumina (up to 1,800°C), or graphite (above 1,800°C) are preferred choices.

1.6 Calibration and Control Methods

In thermogravimetry, calibration focuses on the following quantities:

- Mass
- Temperature
- Time

The measurement of mass has been previously described for enhanced precision.

- Temperature measurement is generally conducted using thermocouples, and occasionally with resistive probes (platinum). Regardless of the technique and calibration method employed, the measurement largely depends on the position of the measuring device relative to the sample.

- Time measurement is the most precisely defined in metrological terms. The time bases of microcomputers are sufficiently precise, compared to other quantities, to avoid introducing significant errors.

1.7 Control of Mass Calibration of the Balance

Calibration is verified in two ways:

- **Statistically**, by measuring known masses. A series of placements and removals of a known mass is conducted. The number of placements and removals must be adequate to quantify the loss of reproducibility associated with the operation (approximately ten placements/removals suffice). This procedure can be performed with various types of masses, of differing weights.

- **Dynamically**, by using a sample with a well-defined thermal behavior, such as copper sulfate. This process allows for checking the overall functioning of the device in terms of both mass variation and temperature.

Example:

Sample: $CuSO_4$, 5 H_2O / Temperature range: from 20 to 350 °C.

Atmosphere: air / Platinum crucible Initial sample mass: 151.25 mg.

Heating rate: 3 °C/min

TG (%): absolute mass loss (g)/sample mass (g)

DTG (%/min): derivative of the TG signal with respect to time.

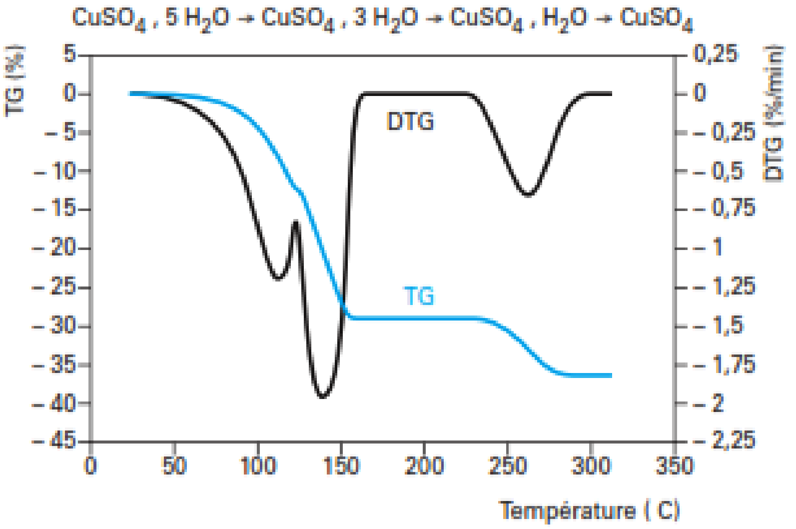


Figure 7. Dynamic monitoring of a thermobalance calibration

This figure illustrates the mass loss of copper sulfate as a function of temperature. The dehydration of hydrated copper sulfate is marked by three distinct water releases: around 70 °C (two molecules of H_2O), 120 °C (two molecules of H_2O), and 220 °C (one molecule of H_2O). By examining the TG (%) signal in this figure, it becomes evident that the magnitude of the first two mass losses (70 °C and 120 °C) is twice that of the final mass loss (220 °C).

1.8 Temperature Calibration

1.8.1 Calibration using magnetic materials

Determining the Curie point of certain materials allows for the association of a temperature with a change in apparent mass when the sample is exposed to a magnetic field. This magnetic field is generated by placing a magnet near the sample. The Curie temperature is, in fact, the point at which the material loses its magnetic properties. When subjected to a magnetic field, the material is attracted by a force, which is nullified upon reaching the Curie temperature due to the loss of the sample's magnetic properties. Consequently, the mass loss is directly linked to this transition phenomenon, with a well-defined temperature.

1.8.2 Calibration by Melting

Temperature calibration in thermogravimetric mode can be achieved by utilizing the melting of materials. This process translates melting into a mass change by exploiting the loss of mechanical integrity that occurs in the liquid state. To do this, the sample must be suspended or positioned so that its melting results in a noticeable shift in its position, thereby causing a disturbance in the mass signal of the thermogram. However, this method is somewhat imprecise due to the absence of a direct correlation between temperature, physicochemical transition, and the loss of mechanical properties. It is advisable to prioritize a calibration method using magnetic materials; this approach should be reserved as a last resort or for calibrations at very high temperatures, well above 1,131°C.

Table 1. Transition temperatures of materials.

Material	Temperature	Phenomenon
n-Octane	-56,76	Melting point
Mercury	-38,83	Melting point
n-Decane	-26,66	Melting point
phenyl ether	30	Melting point

Rubidium	39.3	Melting point
Tin	231.92	Melting point
Indium	156.95	Melting point
Cyclohexane	7	Melting point

Table 2.Table of various Curie points of reference materials.

Material	Curie temperature (°C)
Gadolinium	19.85
Nickel	353.85
Iron	769.85
Cobalt	1114.85

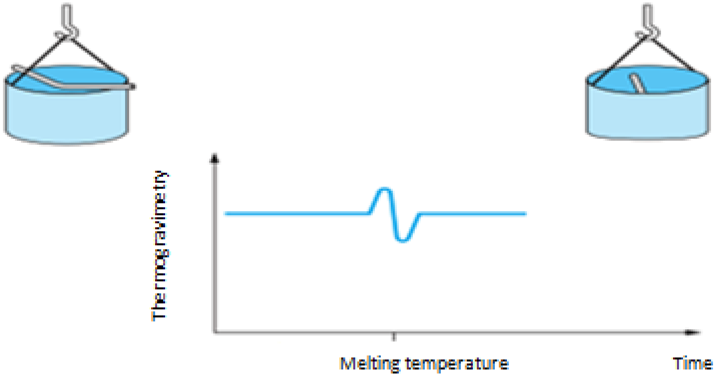


Figure 8. Calibration by melting

1.9 Applications of TG

Thermogravimetry can be applied to any sample that undergoes a mass change over time due to temperature in a specific atmosphere. Transformations such as evaporation, sublimation, and oxidation can be detected by thermogravimetry. However, transformations that do not result in a mass change, like melting or crystallization, cannot be detected by TG, necessitating the use of complementary analysis methods such as DTA or DSC, which are the most common.

1.9.1 Oxidizing or Reducing Atmosphere

In most cases, oxidation results in a non-volatile compound, and the corresponding mass gain from the interaction between the sample and the atmosphere is studied, along with the associated kinetics (whether fast or slow) and the type of attack (deep or superficial). For the study of slow phenomena, precautions must be taken to address potential disturbances or drifts in the balance. In such experiments, it is sometimes necessary to maximize the exchange surface between the environment and the sample to facilitate the reaction. Typically, mass gains are observed (as the corrosion product remains fixed on the sample), though mass losses can occur more rarely (if the corrosion product decomposes at higher temperatures or separates from the sample by flaking, for example).

1.9.2 Lyophilization

This process involves the removal of water, present as ice in a compound, through sublimation. To replicate this operation in thermogravimetry, the sample must be cooled to a very low temperature, allowing the water trapped in the sample's pores to crystallize. Subsequently, to perform sublimation, the sample should be placed under high vacuum.

1.9.3 Dehydration

Water can exist in various forms within a sample and can be characterized using thermogravimetric analysis:

– **Adsorbed water**, free water, or surface-bound moisture: this type of water evaporates quickly upon heating the sample. To accurately measure this water content, it is crucial to correct for buoyancy, especially when humidity levels are low;

– **Bound water**, structural water, hydrates: here, the bonds are stronger, necessitating heating the sample to higher temperatures (above 100°C) for complete dehydration;

– **Water resulting from dehydroxylation**: these bonds are even stronger, requiring higher decomposition temperatures. Thus, it is possible to distinguish different types of water based on the decomposition temperatures observed on the TG curve.

1.9.4 Adsorption/desorption

The mass of a compact layer of nitrogen molecules covering a solid surface of 1 cm² is 0.03 µg. The amount of solid surface needed for an adsorption study depends on the balance's characteristics. A precision beam balance with a 100 g capacity can weigh a monomolecular layer of nitrogen over several square decimeters. The sample's shape must be suitable for this type of experiment, with a very high surface area relative to its mass. The carrier gas must uniformly "wash" the entire surface of the sample. The sample should be aligned with the flow direction and offer minimal resistance to the gas passage (as the gas always follows the path of least resistance).

1.9.5 Catalysis

Thermogravimetric analysis measures the properties of the catalyst itself, rather than the catalyzed reaction. The effectiveness of catalysts is linked to their capacity to adsorb the gas or gases involved in the reaction onto their surfaces. Thermogravimetry enables the quantification of the adsorption properties of the relevant gas or gases on the catalyst (the sample) by observing the increase in its mass. Additionally, thermogravimetry can determine the specific surface area or pore diameter of the catalyst.

1.10 Quiz .

1.

What is the primary physical property measured by a TGA instrument as a function of temperature or time?

☐ A. Mass change

☐ B. Heat flow

☐ C. Viscoelastic modulus

☐ D. Dimensional change

2.

In a typical TGA thermogram of a calcium oxalate monohydrate sample, what does the first mass loss step around 100ºC to 150ºC usually represent?

☐ A. Oxidation of the organic ligand

☐ B. Dehydration of bound water

☐ C. Sublimation of the calcium salt

☐ D. Decomposition into Calcium Carbonate

3.
Why is a constant purge gas flow (e.g., Nitrogen or Air) essential during a TGA experiment?

☐ A. To increase the weight of the sample through buoyancy
☐ B. To prevent any temperature changes in the furnace
☐ C. To calibrate the thermocouple
☐ D. To remove decomposition products and protect the balance mechanism

4.
Which of the following crucible materials is most suitable for high-temperature TGA (up to 1500ºC) involving corrosive inorganic flux?

☐ A. Alumina (Aluminium Oxide)
☐ B. Polymer (PTFE)
☐ C. Aluminum
☐ D. Silver

5.
What is the Derivative Thermogravimetry (DTG) curve used for in TGA analysis?

☐ A. To determine the absolute density of the sample
☐ B. To correct for buoyancy effects automatically
☐ C. To measure the total heat of reaction

☐ D. To identify the temperature of the maximum rate of weight loss

6.

In the kinetic analysis of TGA data, how does increasing the heating rate (β) typically affect the observed decomposition temperature?

☐ A. The total mass loss increases significantly

☐ B. The decomposition shifts to higher temperatures

☐ C. The decomposition temperature remains constant

☐ D. The decomposition shifts to lower temperatures

7.

Which atmospheric condition would you use to distinguish between the 'carbon black' content and the 'inorganic filler' content in a rubber compound?

☐ A. Maintain a high vacuum throughout the run

☐ B. Use a reducing atmosphere of Hydrogen

☐ C. Switch from Nitrogen to Air/Oxygen at high temperature

☐ D. Keep a static Argon atmosphere

8.

What is the primary advantage of using 'Modulated TGA' (MTGA) compared to standard linear TGA?

☐ A. It increases the sensitivity of the balance by 100 times

☐ B. It allows for the measurement of glass transition (Tg)

☐ C. It eliminates the need for a purge gas

☐ D. It allows for the continuous determination of activation energy (Ea)

9.

If you observe a mass 'increase' during a TGA run in an Air atmosphere, what is the most likely chemical process occurring?

☐ A. Cracking of polymer chains

☐ B. Decomposition of a carbonate

☐ C. Oxidation of a metal or lower oxide

☐ D. Evaporation of a high-boiling solvent

10.

Level 2: How does the sample mass affect the resolution of a TGA experiment?

☐ A. Smaller sample masses always produce more noise and lower resolution

☐ B. Large samples are required to see any decomposition at all

☐ C. Mass has no effect as long as the heating rate is constant

☐ D. Large sample masses can lead to thermal gradients and poor resolution

<u>Solutions(A.B.D.A.D.B.C.D.C.D)</u>

1.11 Exercises

Exercise 01. The analysis of a polymer material (PVA) by TGA yielded the thermogram shown in Figure 9. What conclusions can be drawn from these results?

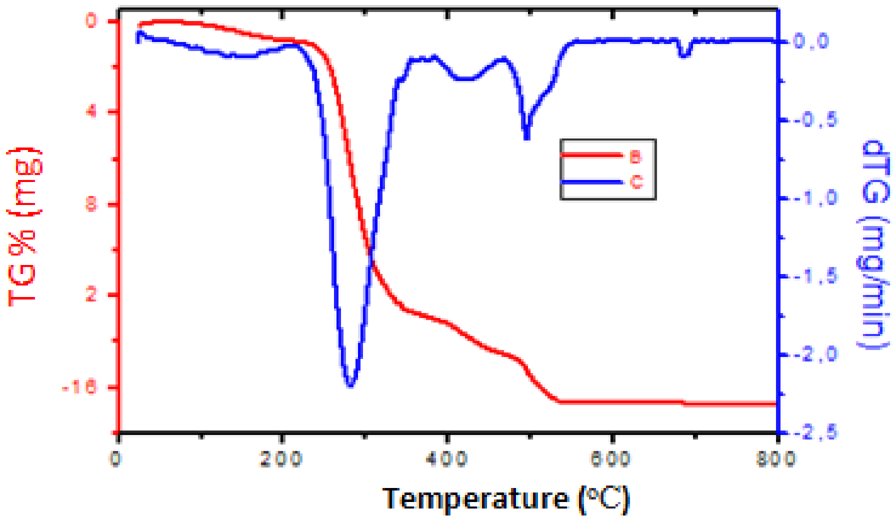


***Figure 9** : TGA curve of PVA*

Exercise 02. The thermogram below illustrates the TGA results of a nanocomposite synthesized with varying matrix/reinforcement ratios (PVA/ montmorillonite).

1. What is the aim of this analysis?

2. What is the purpose of incorporating the reinforcement?

3. Conclude this study.

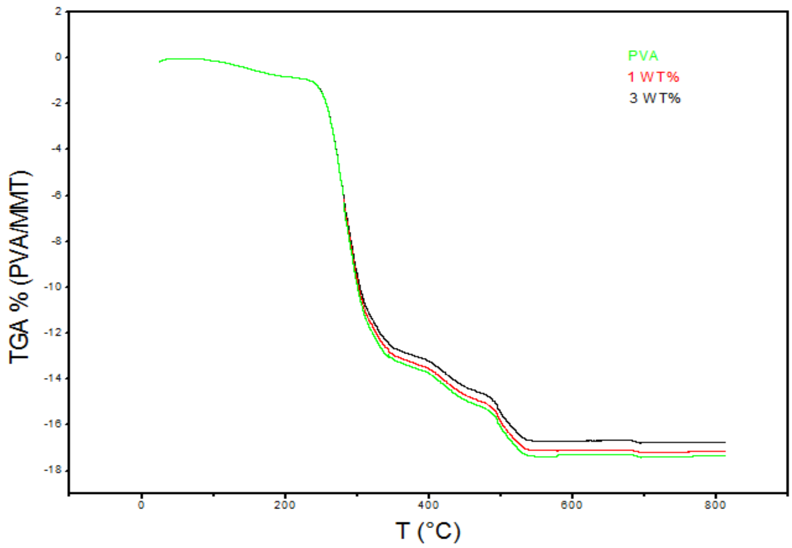


***Figure 10**. TGA curve of nanocomposites PVA/MMT*

Exercise 03. Using the DATA, plot the TGA and DTG curves,

- Indicate the temperatures at which mass losses occur.

- What is the thermal stability range of the different materials?

- How can this mass loss (M3) be characterized: as thermal decomposition or merely solvent evaporation?

Chapter II

Differential Thermal Analysis and Differential Scanning Calorimetry

DTA & DSC

2 *Differential Thermal Analysis and Differential Enthalpic Analysis*

2.1 Principle

Differential calorimetric techniques operate on the principle of measuring changes in the thermal energy supplied to the sample under analysis, compared to that supplied to an inert reference substance, to implement a controlled temperature program. In differential thermal analysis (DTA), the key parameter measured is the temperature gradient between the sample and the reference, with identical heat fluxes supplied to both. This technique is primarily used for high-temperature material studies, reaching up to 1,600°C. Conversely, the most prevalent technique for polymer characterization is differential scanning calorimetry (DSC), which facilitates quantitative analysis of energy transitions. Essentially, it measures the electrical power gradient required to maintain both the sample and the reference at the same temperature, whether under isothermal conditions or during a controlled temperature ramp. Classical applications of this technique include;

- Determining the glass transition temperature

- Measuring the degree of crystallinity

- Identifying the melting temperature

- Studying phase segregation

- Analyzing product purity (pharmacology)

- Measuring the polymerization rate of resins

-Monitoring polymer degradation.

The small sample masses needed (a few milligrams), the rapid measurement speeds (temperature change rates around 10°C/min), the widespread availability of commercial devices, and their extensive laboratory use make these techniques fundamental for studying the thermal properties of polymers and composites.

2.2 Equipment

DTA and DSC devices are designed with two identical, temperature-controlled chambers: one for the sample and the other for the reference. In DSC, power compensation systems consist of two identical furnaces, with the measured parameter being the power gradient supplied to both furnaces to maintain the same temperature. However, in most setups, the heating system for the chambers is unified, and the temperature gradient between the two chambers is measured. This measurement is the desired outcome in DTA, while in DSC, it is converted into an electrical power gradient using heat transfer equations, a process that remains transparent to the user.

A critical aspect of using these techniques is the need for rigorous equipment calibration, which ensures the accuracy of both temperature and energy measurements. This calibration is performed using reference materials with known transition temperatures and enthalpies, such as the melting of indium.

The choice of the most appropriate equipment for the applications at hand must take several other factors into account:

- The accessible temperature range: this generally varies from –160 °C (using liquid nitrogen) to 700 °C, and therefore covers the range suitable for use with polymers and composites;

- The required sample mass: for products synthesized in small quantities, but also to improve temperature accuracy, it is preferable to use a model that requires small masses (on the order of a few milligrams). On the other hand, for composites and heterogeneous materials more generally, it is important to use sufficiently large sample volumes to be representative of the product's composition.

-Temperature accuracy.

- The range of temperature variation rates.

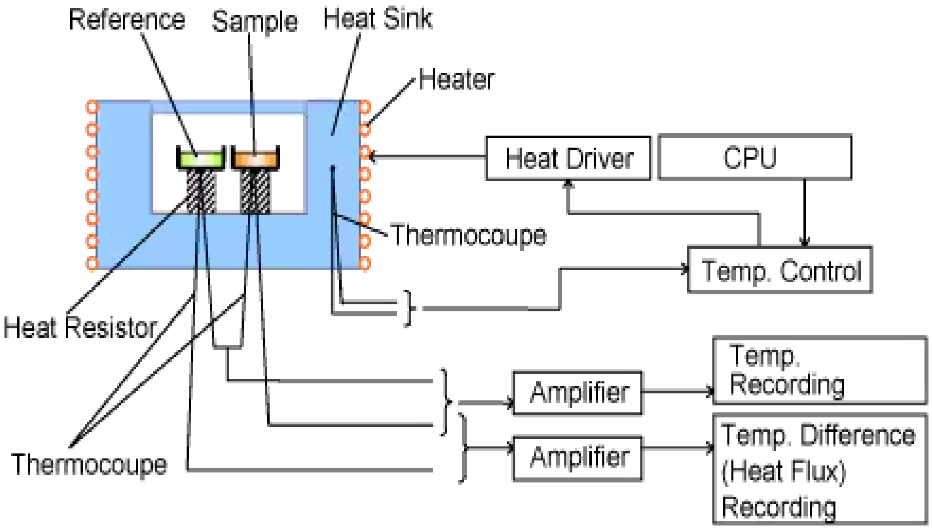


Figure 11. Assembly of a differential scanning calorimetry (DSC) analyzer

2.3 Characterization of Amorphous Polymers

The glass transition is the primary state change that occurs in amorphous polymers. It involves the transformation from a supercooled liquid state to a glassy state during cooling, specifically in the region of the glass transition temperature (Tg). Although this phenomenon does not represent a phase transition in the thermodynamic sense [2], it is marked by significant changes in dimensional, mechanical, and thermal properties.

2.3.1 Glass Transition

Various structural parameters influence the glass transition temperature of polymers, including tacticity, molar mass, and the presence of bulky side groups. In DSC, the glass transition temperature (Tg) is indicated by a sudden change in heat capacity, as illustrated in figures 2. This change in heat capacity, ΔCp, is directly derived from the change in heat flow, ΔW, recorded at the passage of Tg:

$$\Delta c_p = \frac{\Delta W}{\beta m}$$

where m : mass of the sample, B : temperature scan rate.

Tg is defined either at the point of semi-vitrification (midpoint of the cp jump) or at the temperature where a change in W (T) occurs (onset) during heating [3].

For precise measurements, it is essential to specify not only the method used to determine Tg but also the temperature scan rate and, more broadly, the thermomechanical history of the sample. For instance, Tg is sensitive to the mechanical orientation experienced by the sample, as well as the cooling rate during passage through Tg, prior to measurement. If this rate increases, the structure is locked in with lower density and higher free volume, resulting in an increased glass transition temperature measured during reheating [4].

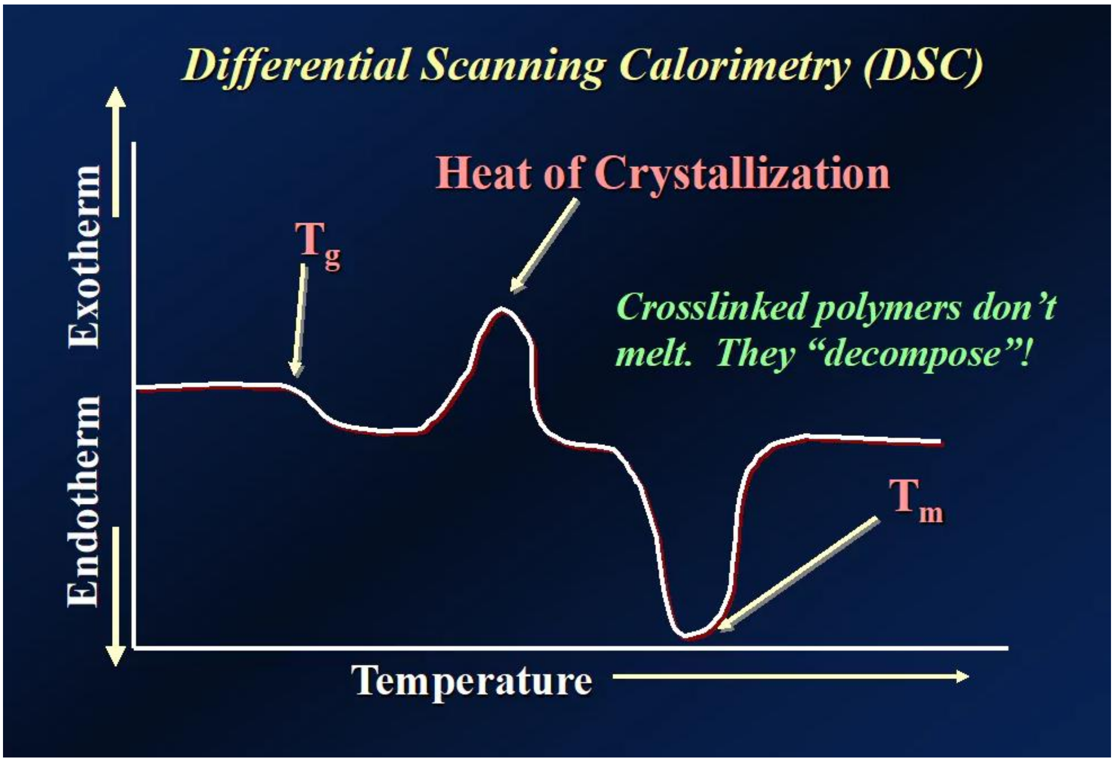


Figure 12 : *DSC curve*

2.3.2 Chemical Structure

Calorimetric techniques can offer insights into the chemical structure of polymers, as the glass transition temperature is typically sensitive to it. For instance, the glass transition temperature of polymers changes based on the stereoregularity of the chains. In the case of poly(methyl methacrylate) (PMMA), Tg can range from 50 to

130 °C as PMMA transitions from the isotactic to the atactic form [5]. Similarly, the glass transition temperature of copolymers or polymer blends varies depending on the type of copolymerization (block, alternating, statistical) and the compatibility of the blends. For compatible blends or statistical copolymers, only a single glass transition temperature is observed, which varies according to the glass transition temperatures (Tg_1 and Tg_2) of the homopolymers, following rules such as the Fox equation [6].

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}}$$

Where W_1 and W_2 represent the mass fractions of the components. While this law is validated in certain instances [7], more sophisticated models have been developed [7][8] that consider the specific interactions between components. In the case of incompatible mixtures, two distinct glass transitions are typically observed, each associated with one of the components [6]. Consequently, calorimetric studies can yield insights into the degree of compatibility of the polymers and facilitate the construction of a phase diagram.

2.3.3 Molar Mass

The initial investigations into how the glass transition temperature (Tg) varies with the molar mass of polymers were carried out by Fox and Flory. They proposed an equation of the form [6];

$$T_g = T_{g\alpha} - \frac{K}{M_w}$$

Tg: asymptotic limit at Tg (Tangent to a curve at a point at infinity)

K: constant depending on the polymer.

Mw: polymer weight-average molar mass.

2.4 Characterization of Semi-Crystalline

Polymers Differential Scanning Calorimetry (DSC) is particularly effective for assessing the degree of crystallinity in polymers. The enthalpy of fusion is derived from the area beneath the endothermic peak [refer to figure 12 for]. Calculating the degree of crystallinity, according to the formula;

$$\mathbf{X = DH_m / DH_{m0}}$$

necessitates knowledge of the enthalpy of fusion DH_{m0}, , for a crystal of the same polymer. This can be extrapolated from (DH_m, x) diagrams for polymers with a known degree of crystallinity [11]. Standard values of DH_{f0} are available for many polymers [3]. The primary uncertainty in determining x stems from estimating the baseline of the thermogram. Therefore, proper calibration of the instrument is essential. The melting temperature of a polymer (T_m) can also reveal information about its morphology, particularly regarding the thickness of crystalline lamellae. The Gibbs-Thomson equation describes the variation of Tm as a function of [11]:

$$T_f = T_{f_o}\left(1 - \frac{2\Delta H_s}{\ell \Delta H_{f_o}}\right)$$

Where Tmo: melting temperature of a crystal of infinite size,

DHs: enthalpy related to the base surface area of the crystallites.

2.4.1 Structure and Phase Segregation

Phase segregation in polymers, particularly the coexistence of different crystalline phases, can be observed through AED. This segregation is indicated by the emergence of multiple melting peaks, with their maximum temperatures depending on the crystalline structure [12].

2.5 Physical Aging

2.5.1 Amorphous Phase

Unlike chemical aging [thermooxidation, photooxidation (UV)], which causes an irreversible evolution of the material due to chain cross-linking or bond breaking, physical aging (or structural relaxation) is a reversible phenomenon affecting the amorphous phase of polymers [13]. It results in densification and increased rigidity (embrittlement) of the polymer when maintained at temperatures ranging from Tg – 60 °C to Tg. This factor is particularly significant for amorphous polymers whose service temperature is below the glass transition temperature: PET, PMMA, polystyrene (PS), or polycarbonate (PC), which have glass transition temperatures between 75 and 130 °C, are affected.

It is crucial not to confuse this phenomenon with a melting peak. The simple criterion to differentiate them is to heat the polymer beyond Tg to erase its history (aging), and then record a second thermogram, on which an aging peak does not reappear.

An example is provided in figure 13 for PET. The area of the endothermic peak reveals the excess enthalpy eliminated during isothermal aging, thereby defining the degree of progress of the process.

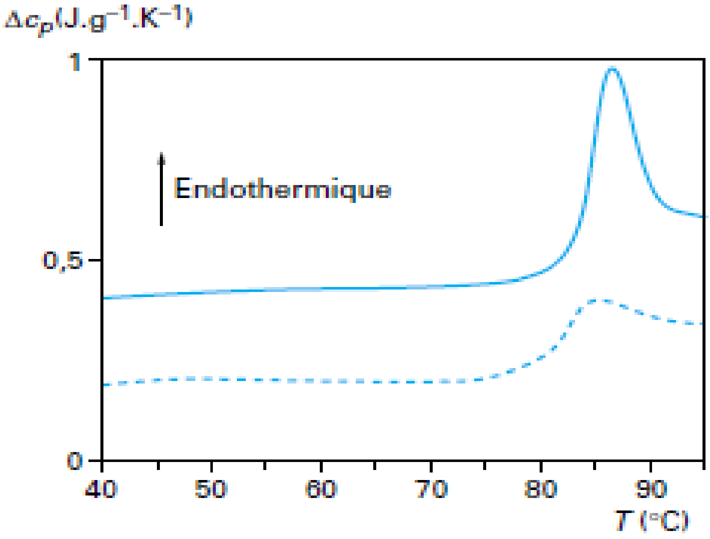


Figure 13. Thermogram of aged polyethylene terephthalate (solid line) and unaged polyethylene terephthalate (dashed line)

2.5.2 Crystalline Phase

Physical aging, as defined above, is a secondary factor for semi-crystalline polymers, primarily because it is generally less apparent [14], and secondly because the mechanical properties largely depend on the behavior of the crystalline phase. A type of aging involving another physical process is the ability of semi-crystalline polymers to recrystallize and, more broadly, the thermal instability of the crystalline phase [15]. This factor is particularly significant in polyethylenes (PE), whose crystalline phase is unstable before melting. The morphological evolution can also be tracked by analyzing the melting thermograms [16].

2.6 Additives

The primary purpose of introducing additives, particularly plasticizers, is to modify the mechanical properties of polymers. For instance, the glass transition temperature of PVC can be shifted from 70 to -20 °C by varying the formulation [17]. Calibration to adjust the dosage of the compounds can therefore be conducted based on analysis using calorimetric techniques.

2.7 Comparison with differential thermal analysis (DTA and DSC)

Differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are often confused. However, there is a fundamental difference between these two methods. With a DSC device, one measures differences in energy, while with DTA, one measures differences in temperature.

2.8 Quiz.

1.

In a heat-flux DSC, what is the primary physical quantity measured by the instrument to determine the heat flow of the sample?

☐ A. The volume expansion of the sample pan.

☐ B. The change in mass of the sample as it is heated.

☐ C. The temperature difference (ΔT) between the sample and a reference.

☐ D. The electrical power required to keep the sample and reference at the same temperature.

2.

Which of the following thermal transitions is considered an endothermic process in a DSC heating scan?

☐ A. Thermoset curing.

☐ B. Oxidative degradation.

☐ C. Melting of a crystalline polymer.

☐ D. Crystallization from a melt.

3.

The glass transition (Tg) is observed on a DSC curve as:

☐ A. A baseline shift representing a change in heat capacity (Cp).

☐ B. A vertical drop in the baseline to zero heat flow.

☐ C. A broad endothermic peak indicating mass loss.

☐ D. A sharp, narrow exothermic peak.

4.

Why is an inert purge gas (like Nitrogen) typically used during a standard DSC experiment?

☐ A. To act as a catalyst for crystallization.

☐ B. To decrease the sensitivity of the heat flow sensor.

☐ C. To prevent sample oxidation and ensure uniform heat transfer.

☐ D. To increase the melting temperature of the polymer.

5.

If you observe a large endothermic peak at 100°C in a sample known to be a hydrogel, this most likely represents:

☐ A. The evaporation of residual water.

☐ B. The decomposition of the polymer backbone.

☐ C. The Tg of the polymer network.

☐ D. A calibration error of the instrument.

6.

What is the purpose of performing a 'Heat-Cool-Reheat' cycle in DSC analysis of polymers?

☐ A. To ensure the sample has completely decomposed.

☐ B. To check if the sample pan has leaked during the first run.

☐ C. To calibrate the furnace temperature at multiple points.

☐ D. To erase the thermal history of the sample and see its intrinsic properties in the second heat.

7.

An 'Enthalpic Recovery' peak is often seen overlapping with the glass transition (Tg). This usually occurs because:

☐ A. The sample has undergone physical aging below Tg.

☐ B. The sample started to melt prematurely.

☐ C. The heating rate was too slow for the sensor to respond.

☐ D. The reference pan was heavier than the sample pan.

8.

In a DSC thermogram of a semi-crystalline polymer, 'Cold Crystallization' is observed as an exothermic peak above Tg but below Tm. What does this indicate?

☐ A. The DSC cell is contaminated with a nucleating agent.

☐ B. The sample is 100% crystalline.

☐ C. The polymer is degrading into smaller monomers.

☐ D. The sample was rapidly quenched during processing and was initially amorphous.

9.

How does increasing the heating rate (e.g., from 10°C/min to 40°C/min) affect the DSC results?

☐ A. It increases the sensitivity (peak height) but may decrease the resolution of overlapping peaks.

☐ B. It shifts all transitions to lower temperatures.

☐ C. It has no effect on the thermogram as long as the sample is small.

☐ D. It eliminates the glass transition step-change.

10.

You observe a sharp exothermic 'spike' followed by an immediate erratic baseline during a high-temperature scan. What is the most likely experimental artifact?

☐ A. The sample has reached its equilibrium melting point.

☐ B. The purge gas flow was accidentally increased.

☐ C. The hermetic pan has burst due to internal pressure.

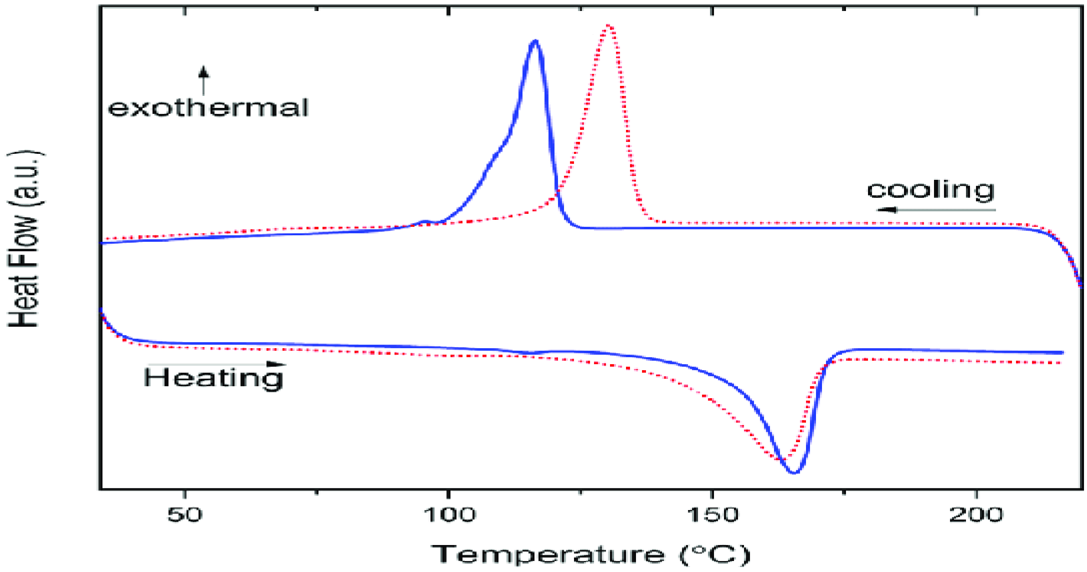
☐ D. A second-order transition has occurred.

Solutions(C.C.A.C.A.D.A.D.A.C)

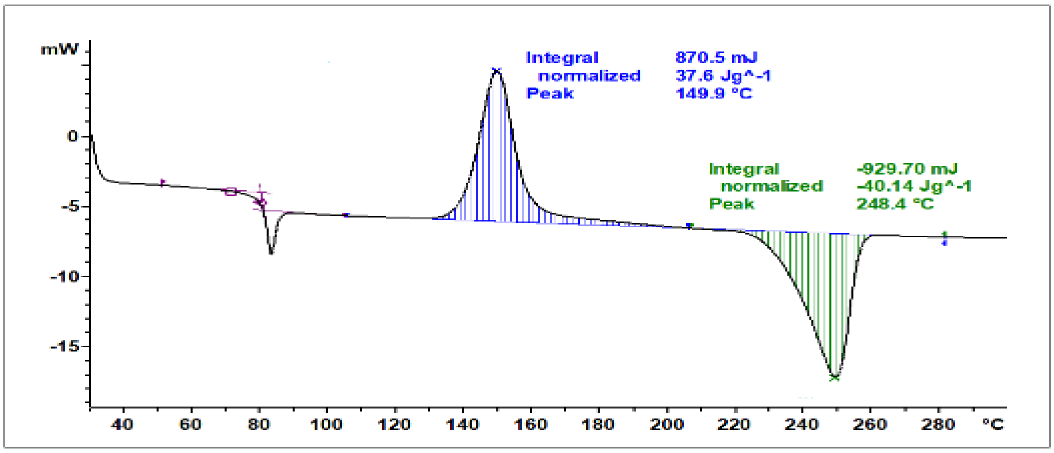
Exercise 01 A DSC analysis of the samples at a rate of 100/min yielded the following thermograms.

1- What is the microstructural nature of these polymers?
2- Are these thermograms complete? If not, discuss any missing transitions.

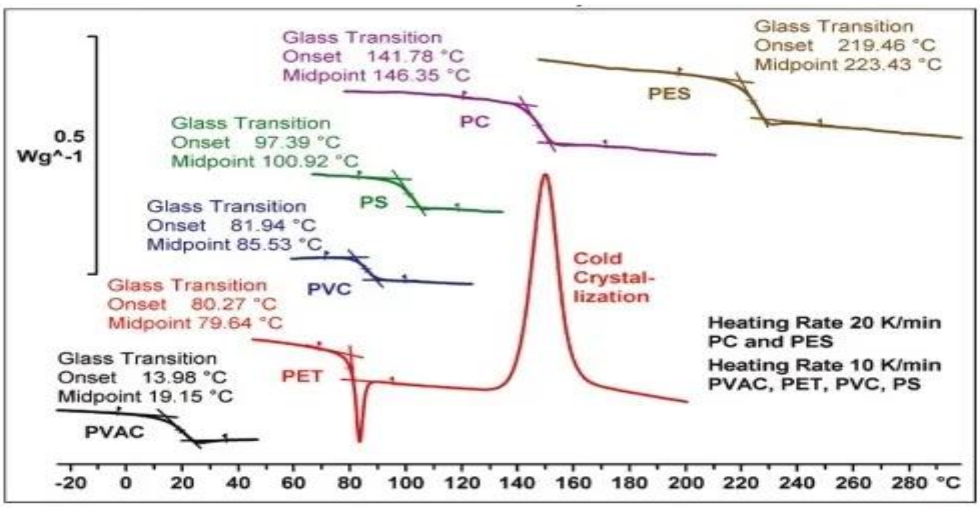
Thermogram 01



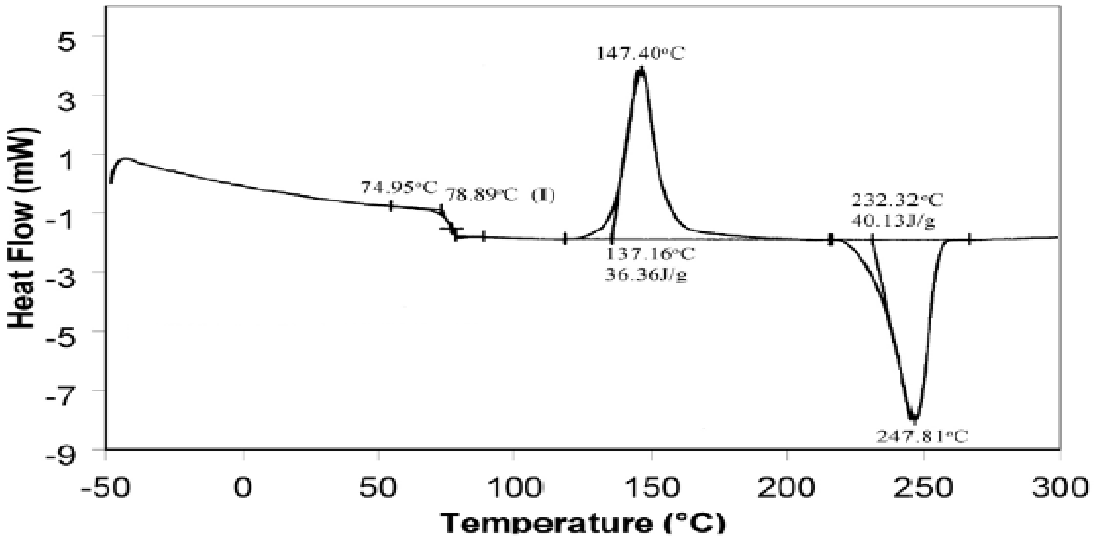
Thermogram 02



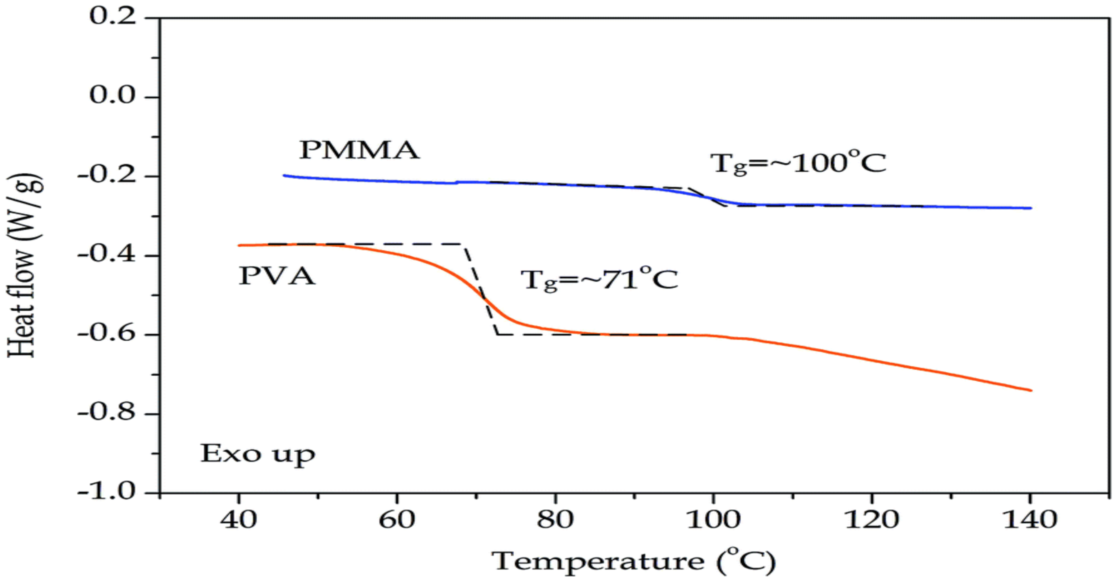
Thermogram 03



Thermogram 04



Thermogran 05



Exercise 02 Consider two polymers: a semi-crystalline polymer A and an amorphous polymer B. Illustrate the DSC thermograms of a 50/50 blend of these two polymers in the following scenarios:

1- If the two polymers are not miscible
2- If the two polymers are miscible

Chapter III

Thermomechanical Analysis

TMA

3 Thermomechanical Analysis

3.1 Introduction (recap of the mechanical behavior of polymers)

The mechanical behavior of polymers is marked by a striking diversity. Under identical conditions of use, and from a technological standpoint, polymers can exhibit rigidity and brittleness, ductility, or a rubber-like quality. Thus, within the polymer family, there exists a wide range of behavior types: viscoelastic, viscoplastic, hyperelastic, hardening, and damageable. This diversity is also evident within a single polymer when certain characteristics are altered or simply by changing its conditions of use. It may be rigid and brittle, ductile, or elastic, among others. This does not imply that a polymer's behavior is variable or uncontrolled. Instead, numerous parameters govern its behavior, and there are many possible elementary processes.

3.2 Behavior and Elementary Processes

The mechanical properties of polymers are analyzed using the tools of continuum mechanics, similar to other material classes. The fundamental postulates of continuum mechanics—that at every point occupied by the body there is a material point; each point moves continuously; two infinitely close points remain close; physical properties are continuous—somewhat obscure the physical reality, which is that the material's response involves discrete and discontinuous elementary deformation processes, as well as the disturbances of internal energy they induce. It is in these elementary processes that polymers and metallic alloys distinguish themselves, leading to very different macroscopic behaviors (equivalent continuum medium). Deforming a polymer means, at the local level, deforming and/or moving its constituent elements, namely, its chains. Macromolecules are not rigid objects. Once their configuration covalent linkages has been set by chemistry, they can adopt different conformations spatial arrangements of all atomic groups, given the degrees of freedom allowed by chemistry (torsion energy on the valence cones). External stress can facilitate the rotation of one group or another on its valence cone, thereby modifying the chain's conformation. Two levels of conformation can be distinguished:

- **Local conformation**, which defines the spatial arrangement of groups around the chain or locally along its backbone;

- **Global conformation,** which results from the arrangement of all segments of the backbone and is characterized, at first approximation, by the mean square end-to-end distance and the radius of gyration of the chain.

Deforming a polymer involves altering local conformations, which, depending on their degree of cooperativity, can lead to changes in global conformation and/or modifications in interchain arrangements. These local conformation changes are driven by energetic interactions between non-bonded atoms (such as van der Waals forces) and by torsional potentials on the valence cones of bonded atoms. Only the latter, occurring around a discrete number of positions, result in energies on the order of kT. Without delving into specifics, it is important to note that the elementary processes of chain deformation involve activation energies and transitions from one stable position to another. The fundamental movement enabling macroscopic deformation of the polymer is, therefore, thermally activated and sensitive to the rate.

The polymer's response is influenced by the chain itself (configuration) through the conformers it permits, by the organization of the chains through the conformation changes it encourages or inhibits, and by the local loading experienced by the chain, which is the external loading adjusted by all the mechanical interactions conceivable in a highly heterogeneous medium.

Indeed, a polymer is a highly heterogeneous material whose behavior is not merely the sum of the behaviors of each phase. Thus, an injection-molded semi-crystalline polymer can be viewed as (Figure 14):
- A layered core-skin structure on the millimeter or hundred-micron scale;
- A polygonal structure at the scale of the spherulites (1 to 10 µm), possibly with micrometric fillers;
- An amorphous/crystalline lamellar structure at the sub-spherulitic scale (10^{-2} µm), potentially with nanometric fillers;
- A mesh in the crystal and a statistical coil in the amorphous regions, possibly with additives.

Each of these levels contributes to the mechanical response of the polymer. Consequently, the polymer can be the site of various mechanisms and interactions. The amorphous coil reacts according to the processes described above but is constrained by the nearby crystal. The chain in the crystal must accommodate the interactions that stabilize a conformation. The crystal presents slip systems, but some are constrained by the covalent structure of the motif. The fillers modify the local loading, and so on.

Another way to express this is to say that the microstructure of an industrially processed polymer material can involve several levels of description and several elementary processes. At the macroscopic level, this results in behavior that is highly sensitive to the mode and conditions of loading, as these will activate one or another of the possible processes.

3.3 Influential Parameters

The brief description above highlights that the key parameters influencing the mechanical properties of polymers are linked not only to the polymer itself but also to processing conditions and loading factors (such as direction and speed) or environmental conditions (including temperature, pressure, and the surrounding medium). Therefore, to effectively manage polymers and their behavior, engineers must cultivate the habit of thoroughly researching the resins they use, focusing specifically on:

- ✓ The architecture of the polymer;
- ✓ The formulation of the polymer;
- ✓ The processing of the material;
- ✓ The conditions of use.

Clearly, these parameters are not entirely independent, as the nature of the chains, to some extent, dictates their organization and behavior.

3.3.1 The Architecture of the Polymer

Naturally, the nature and number of comonomers are the primary aspects to consider. Indeed, the choice of monomers determines the flexibility of the covalent bonds in the chain backbone and, in part, their cohesion, through the physicochemical interchain interactions permitted by the substituents.

Additionally, the nature of the chains must be considered, including their tacticity, linearity, the rate and length of branches, the type of monomer arrangement (random, block, alternating) in the case of copolymers, and crosslinking. Finally, the chain length dictates their capacity to develop “physical” interactions, such as entanglements, which contribute to the mechanical strength of the final material.

3.3.2 The Formulation of the Polymer

An industrial polymer is invariably formulated to stabilize it during processing, facilitate its transformation, or adjust its final properties. Therefore, it is crucial to determine as precisely as possible the nature and levels of:

- Various additives, plasticizers, fillers, fibers, etc.;

- Components of mixtures, including the nature of the constituents and the dispersion of the phases. For instance, energy absorption during impacts is often adjusted by dispersing a nodular phase whose size determines the effectiveness of reinforcement within a matrix;

- The presence of a coupling agent between phases. This agent is sometimes a third grafted polymer that more or less stabilizes the dispersion of the phases and aids in transferring stresses from one phase to another.

3.3.3 Processing

Processing can alter:

- The architecture of the material, specifically the nature of the chains by causing branching or cross-linking, and the length of the chains by degradation. Broadly speaking, the evolution of polymer properties with molar mass exhibits threshold effects. Below a certain mass, the property is not assured; above it, it evolves slowly. Due to reasons related to synthesis or processing in the fluid state, the initial molar mass is a compromise. Consequently, it often remains close to one of these thresholds. Processing can, therefore, by reducing molar mass, severely impair one or more of the polymer’s properties;

- The formulation by consuming additives;

- The organization of the chains by inducing a microstructure: molecular extension and orientation, crystallization, and crystalline texture;

- The spatial arrangement of the components: distribution and orientation of fillers and heterogeneous phases.

3.3.4 Conditions of Use Generally

A polymer’s response may depend on:

-The type of stress: tension, compression, or shear;

- The temperature, a crucial parameter that we will discuss in detail;

- The rate of applied stress, which is as important as temperature it is important to note this from the outset;

-The pressure (at least under high pressure);

- The strain rate, since deformation leads to structural changes and thus changes in properties;

- The thermomechanical history, meaning any potential degradation during processing;

- The environment. In some cases, the humidity level can alter the behavior of hydrophilic polymers. Hydrocarbons can cause the material to swell. Not all polymers are equally sensitive to each of these parameters. Therefore, they must be considered on a case-by-case basis.

3.3.5 Effect of Temperature

The behavior of polymers is significantly influenced by temperature, as they experience behavioral transitions linked to various molecular relaxations, specifically the activation of changes in local conformations. From a macroscopic viewpoint, this results in more pronounced behavioral changes within certain temperature ranges. The most crucial of these relaxations is the alpha relaxation, associated with the glass transition, which leads to a substantial change in behavior. This occurs when the amorphous polymer chain gains sufficient mobility to undergo changes in its overall conformation, due to the cooperative nature of local movements.

Notably, this results in a sharp decrease in the elastic modulus (Figure 15), which can diminish by a factor of 100 or 1000 over a span of 5 to 10°C. Indeed, the entire behavior alters considerably within this interval. This transition marks the shift from the glassy state at low temperatures to the rubbery state at intermediate temperatures, passing through what is sometimes referred to as the viscoelastic state.

The rubbery plateau concludes when the polymer flows, entering its fluid state. In reality, a polymer under low strain is always viscoelastic to varying degrees, gradually transitioning from a glassy viscoelastic solid to a viscoelastic fluid (Figure 15). The alpha transition affects only the amorphous polymer and is therefore less significant for semi-crystalline polymers, although it remains noticeable. The temperature of this transition depends on the polymer and, to a lesser extent, on its formulation.

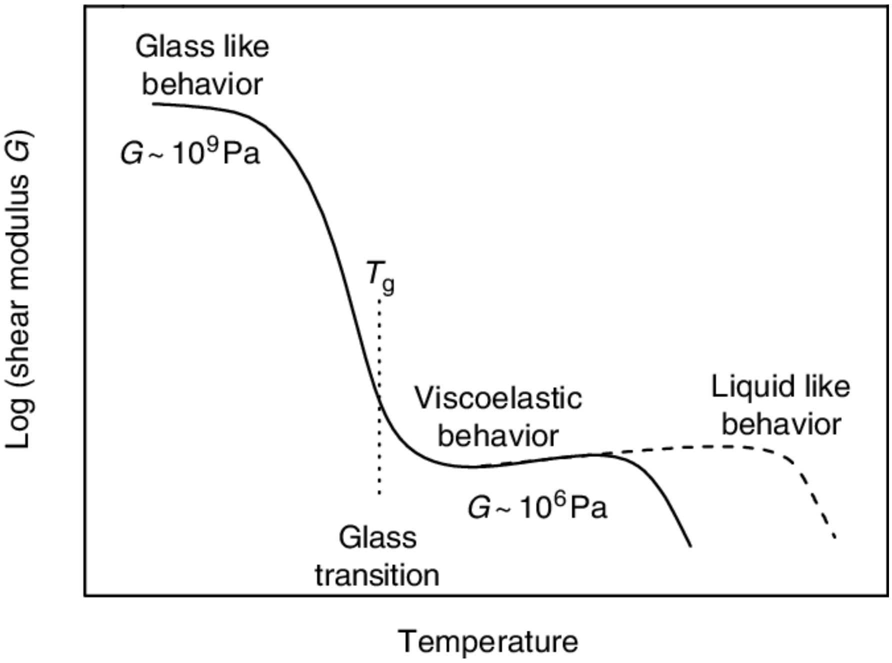


Figure 15: Schematic evolution of the elastic modulus of an amorphous polymer with temperature, transition and passage to the fluid state.

3.3.6 *Time-temperature equivalence*

The evolution of behavior with temperature mirrors what can be observed at a given temperature with the rate of loading. For amorphous polymers, a useful guideline is that cooling by –10 to –20 °C equates to an acceleration of one to two decades in loading rate (Figure 16). In rheologically simple amorphous polymers, this dual sensitivity to rate and temperature can be mitigated by employing thermally dependent shift factors.

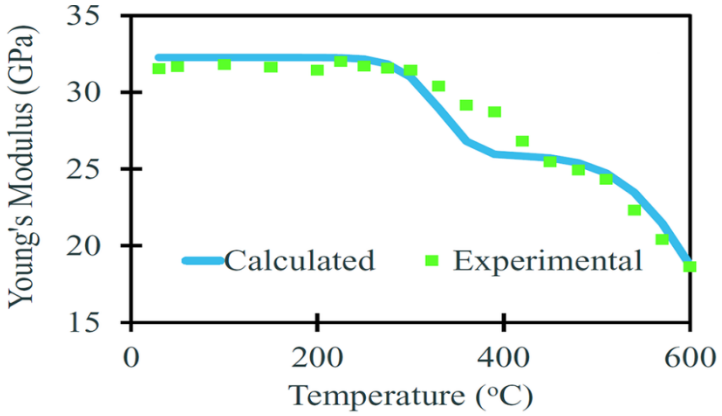


Figure 16: Elastic modulus of HIPS (shock PS) as a function of frequency and temperature (oscillatory tensile measurement)

Consequently, the different regions glassy, viscoelastic, rubbery, and fluid depicted in Figure 16 can also be identified on a scale that combines rate and temperature, precisely for elasticity modulus and qualitatively for overall behavior (Figure 17).

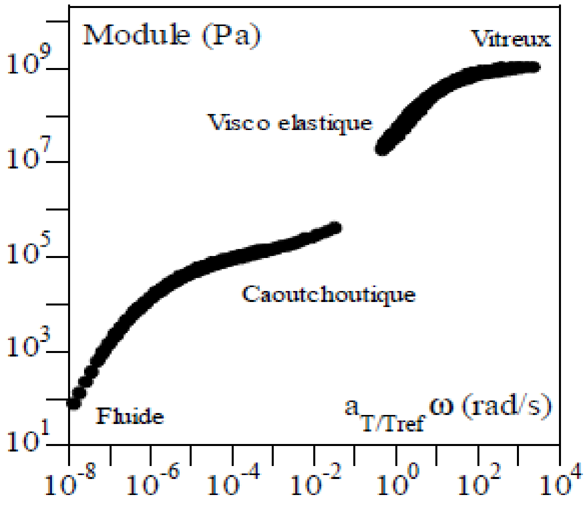


Figure 17. Master curve for a PS (Tref = 101 °C)

3.3.7 Behavior and glass transition

3.3.7.1 Glassy state

In the glassy state (characterized by low temperatures or high rates), the molecular motions accessible to the polymer are insufficient to initiate cooperative movements along the polymer chain backbone. As a result, only minor deformations are possible, and the moduli are high. Elastic deformation is governed by the enthalpic component of its internal energy, similar to metals. Even in the glassy state, the polymer is not entirely frozen. Temporal and spatial conformation fluctuations persist, controlled by temperature: the higher the temperature, the faster and more frequent they become. Thus, as the temperature rises, it becomes "easier" to deform the material. Consequently, the modulus remains temperature-dependent and decreases with increasing temperature. Similarly, the material retains its viscoelastic properties. At high stress, plastic deformation processes can be activated at moderate temperatures and rates but are ineffective at low temperatures or high rates. This leads to the existence of a ductile/brittle transition temperature (and/or rate), which is lower than the glass transition temperature. In summary, the apparent behavior of the polymer in the glassy state is viscoelastic and viscoplastic, with macroscopic ductility that varies depending on temperature and rate.

3.3.7.2 Transition Zone

The D transition zone, also known as the glass relaxation or viscoelastic zone, signifies the point at which large-scale conformational changes specifically, cooperative movements along the polymer chain backbone become feasible. Consequently, the modulus decreases rapidly, and the behavior becomes highly variable.

3.3.7.3 Rubberlike Zone

In the rubberlike zone, the temperature is sufficiently high for the chain to spontaneously explore all its possible conformations in a time much shorter than the characteristic time of the applied stress. However, the temperature remains too low to permit large-scale disentanglement of the chains. Macroscopically, the chains appear flexible, yet flow is inhibited. The material gradually becomes hyperelastic or more precisely, visco-hyperelastic if it is not crosslinked. Under large deformations, plastic processes give way to entropic elasticity. The presence of crystallinity partially offsets the loss of modulus and cohesion in the amorphous polymer. As a result, the rubbery plateau of a semicrystalline polymer is not only higher but also longer than that of an amorphous one. These factors explain why a semicrystalline polymer, such as PP or PE, can be used above its alpha transition, whereas an amorphous polymer, like PS, is restricted to its glassy plateau. To utilize an amorphous polymer beyond its glass transition, it must be crosslinked these are elastomers. Simultaneously, the crystal phase consistently exhibits enthalpic elasticity and plasticity processes. Thus, a semicrystalline polymer remains viscoplastic, with structural hardening and/or damage, on its rubbery plateau (Figure 17). It is also noteworthy in Figure 17 that PC and PP exhibit very similar macroscopic behaviors, despite involving very different processes: glassy amorphous for one, rubbery semicrystalline for the other.

3.3.7.4 Fluid Zone

The fluid zone emerges when disentanglement becomes probable. The chains appear statistically independent from one another, allowing stress to easily move them relative to each other. The behavior becomes predominantly viscous, though it retains viscoelastic characteristics.

3.3.7.5 Plasticity of Polymers

Plastic deformation, or more precisely apparent ductility, occurs through the local initiation of micro-domains in the amorphous phase, which deform and enable elementary processes such as crazing, shear bands, or more complex phenomena like cavitation, depending on the material.

-The crystalline phase behaves like any crystal, except that certain slip systems are restricted due to the presence of the molecule, which is more or less aligned with one axis of the unit cell.

-This variety of processes imparts unique characteristics to the “plasticity” of polymers, which we will summarize here:

-A strong sensitivity to temperature and loading rate, meaning the threshold increases with a higher rate or lower temperature;

-The presence of a “ductile/brittle” transition, as not all local plasticity processes result in the same apparent ductility. These transitions can be observed:

*With temperature;

*With loading rate;

*With loading modes, since not all processes are initiated by the same components of the stress tensor; thus, the polymer may appear brittle under tension and ductile under compression or shear. It is important to note that, generally, triaxial loading can make polymers more brittle.

- The dependence of yield surfaces on the hydrostatic pressure term, or in other words, the plasticity threshold's dependence on the loading mode (higher under compression than under tension, for example);

- The occurrence of volume changes during plastic deformation, which significantly impacts the modeling of polymer behavior. During its plastic deformation phase, the polymer may also undergo structural hardening, associated with molecular orientation and crystal texturing (when present), or even deformation-induced crystallization. It may also experience damage processes.

In conclusion, within the family of polymers, a multitude of different behaviors can be observed. It would be more accurate to speak not of the behavior of polymers, but rather of the behaviors of polymers. This complexity explains some of the challenges in designing polymer structures.

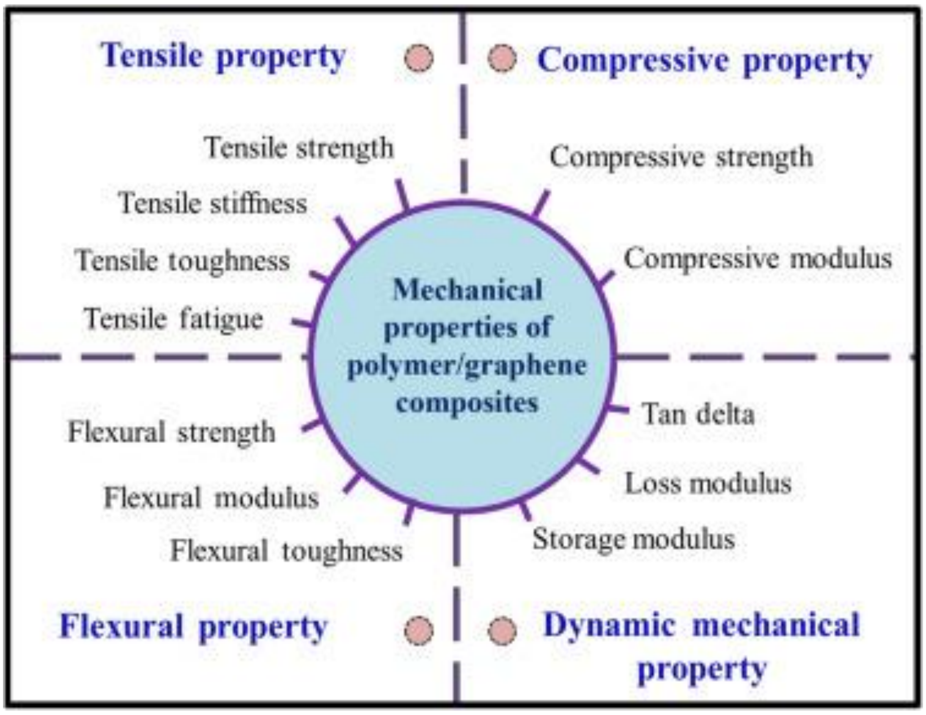


Figure 18. *Mechanical behavior of polymers*

3.4 Principle of Thermomechanical Analysis

Thermomechanical analysis (TMA) involves characterization methods that measure dimensional changes in a sample under static stress. These changes in length or volume are recorded as a function of temperature, with the corresponding stress being either elongational or hydrostatic pressure.

3.4.1 Equipment

Most commercial devices employ an LVDT (Linear Variable Differential Transformer) displacement measurement system, which detects variations in a coil's induction [18]. Elongation measurements can also be conducted using optical devices [19]. Calibration and connector elements utilize materials with a low coefficient of thermal expansion, such as quartz (a = 6 x 10^{-7} K^{-1}) or Invar (a = 10^{-7} K^{-1}) [20]. For volume measurements, the sample is placed in a liquid with a known coefficient of expansion.

Pressure adjustment and displacement detection are managed through a piston. For low stresses, the instrument can measure the linear or volumetric coefficient of expansion (dilatometry) [20].

A schematic diagram of the typical instrument is shown in Figure 19. The sample is placed in the chamber where the temperature is controlled by the thermocouple placed close to the sample. The measurements are performed in the protective atmosphere of inert gases like: nitrogen, helium or argon but also the other gases could be used i.e. air, carbon monoxide, hydrogen. Because of the relatively large mass of the sample the applied heating and cooling rates are usually slow. The rate of 5°C/ min is usually the maximum recommended value for good temperature equilibration across the specimen.

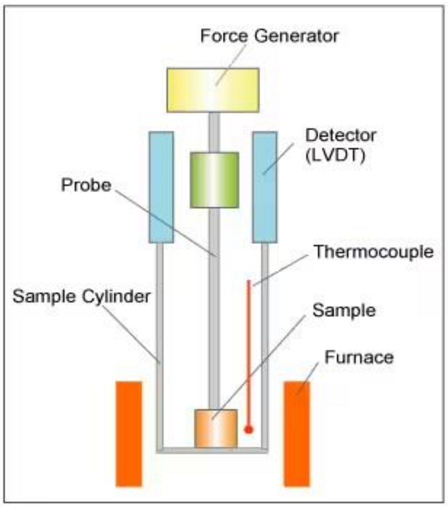


Figure 19. Schematic diagram of a thermomechanical analyzer.

The instrument comprises:

-A small-volume, regulated furnace, programmable (heating rates from 0.01 to 100 °C/min; range from -150 °C to +1,000 °C), equipped with a thermocouple positioned near the sample;

-An appropriate displacement sensor (resolution in nanometers), typically inductive (LVDT), for measuring the sample's dimensional change (measurement range of ± 5 mm; sample length up to 20 mm);

-A device to control the application of the force transmitted (range of ± 1 N or more) by the probe (or sensor) for displacement measurement to the sample; · a device for processing the resulting signal;

-A data evaluation device; a graph is produced. It is possible to work under a controlled atmosphere (inert or oxidizing) or under vacuum.

The dimensional changes of the sample relative to the holder appearing during heating or cooling are transmitted via pushrod to the highly precise inductive transducer (LVDT) sensor. The construction of the pushrod and sample holder depends on the mod of the measurements. The most commercial instruments are supplied with a variety of probes for different applications. Figure 20 presents the examples of the holding devices taken from the TMA. Every displacement of the pushrod is transformed into analog signal by the LVDT and in the next converted to digital form then recorded in the PC system and finally presented by the software as a dimensional change versus time or temperature.

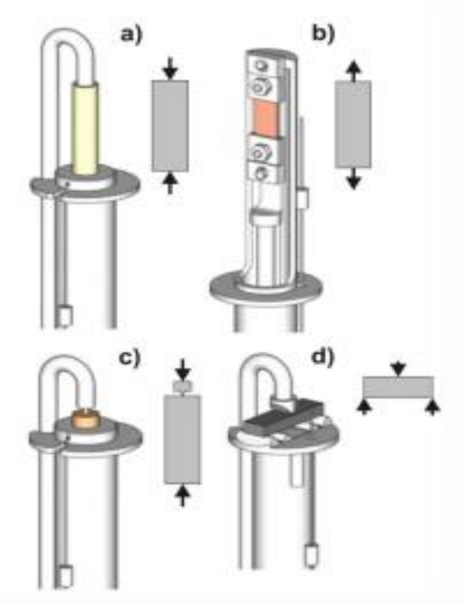


Figure 20. Holding devices for a) compression , b) tension, c) penetration, and d) 3-point bending

There are several types of the probe for TMA. The choice is dependent on the measurement purpose.

(a) 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) 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 fiber.

(c) Penetration Probe: It is used for the measurement of the softening temperature.

The materials of probes are quartz glass, alumina, and metals. The choice is dependent on the temperature range and/or the measurement purpose. In case of the TMA which enables the dynamic force control on top of the static force control, the measurement of the Stress-Strain, the Creep, the stress relaxation, and the DMA measurements can be performed.

3.4.2 Coefficient of Linear Thermal Expansion

When a material is heated the distance between individual atoms will change. For most materials the atoms get, on average, further apart (although there are some exceptions. Since the change is the same for all atoms, the total length change depends on how many atoms are in the length. This makes the length change proportional to length. Also, for small changes in temperature the length change is proportional to the temperature change. The constant of proportionality is called the coefficient of thermal expansion, denoted by the Greek letter alpha (α). This coefficient is not really constant over large temperature ranges Under the effects of increasing temperature any material will expand. This can lead to significant changes in dimensions. The Coefficient of Linear Thermal Expansion (CLTE often referred to as "α") is a material property which characterizes the ability of a plastic to expand under the effect of temperature elevation. It tells you how much the developed part will remain dimensionally stable under temperature variations. The linear coefficient 'CLTE or α' for plastic and polymer materials is calculated as:

$$\alpha = \Delta L / (L_0 . \Delta T)$$

Where: α is coefficient of linear thermal expansion per degree Celsius.

ΔL is change in length of test specimen due to heating or to cooling.

L_0 is the original length of specimen at room temperature.

ΔT is temperature change during test (°C).

Therefore, α is obtained by dividing the linear expansion per unit length by the change in temperature. When reporting the mean coefficient of thermal expansion, the temperature ranges must be specified.

The measurements are made using a thermomechanical analyzer consisting of a specimen holder and a probe that transmits changes in length to a transducer that translates movements of the probe into an electrical signal.

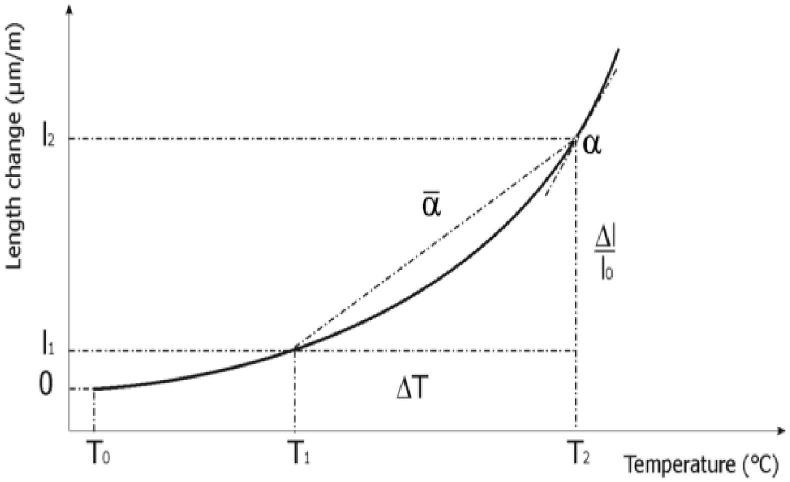


Figure 20. TMA curve

3.4.3 Characterization of Polymers

The analysis related to differential calorimetry can be applied to dilatometry. Unlike DSC, TMA provides access to length changes rather than their derivative, which corresponds to the coefficient of expansion, equivalent in thermal analysis to the heat capacity at constant pressure, cp.

The coefficient of expansion increases significantly at the glass transition temperature (by a factor of about 5 to 10 in amorphous polymers). Similarly, physical aging can be characterized by these techniques [21]. Another important application of TMA is the characterization of oriented polymers. A major shrinkage phenomenon occurs above the glass transition temperature in fibers such as PMMA, for example [22].

It is also possible to determine the static modulus in elongation as a function of temperature by knowing the deformation component linked to expansion. This type of measurement, as well as the study of isothermal creep.

3.4.4 Application

TMA is very often used to measure glass transition, based on changes in coefficient of thermal expansion which results as the free volume of the material changes at the glass transition. Figure 5 shows Tg of amorphous metal ribbons heated at 5°C/min under 2N and 0.05 force loading. Tg is defined as the onset of change in rate of the expansion (slope) at 423°C and as the shrinkage at 420°C on the second curve.

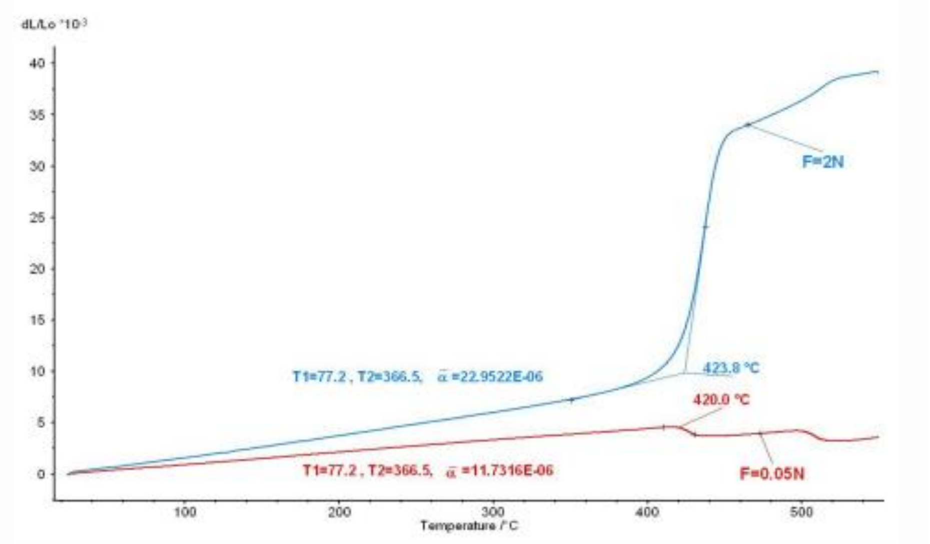


Figure 21. Plots of change in the length for two the amorphous metal ribbons under different applied loads F=2N and F=0.05N. Heating rate 5°C min^{-1} under helium (tension mode).

A fundamental property of different kinds of materials like metals or plastics is their melting point. It can be determined by DSC method but only in temperature where the heat consumption of the crystalline melting takes place. It also can be determined by the use of the thermo mechanical analyzer to identify where the sample transforms from rigid body to soft or flexible i.e. in that point where thedramatic decrease in modulus taken place and then sample deforms, even under low forces. The result of the melting temperature determination for high temperature metallic solders are present on figure 22.

Thermomechanical analysis can by also carried out in isothermal conditions for example to test polymers behavior under pressure (Figure 22). The extent to which the elastic properties of a seal remain intact after being subjected to the constant load of longer duration is very important. To test this, an elastomer seal was loaded with the force of 3 N and then relieved to 5 mN. Following a 40 hour load time, 21% compression was observed. After a 30-minute relief period, the compression had reversed by 16.2%; after 60 min, by 16.8%. The visco-elastic properties of the elastomer were such that the sample did not return to its original length even after 30 hours.

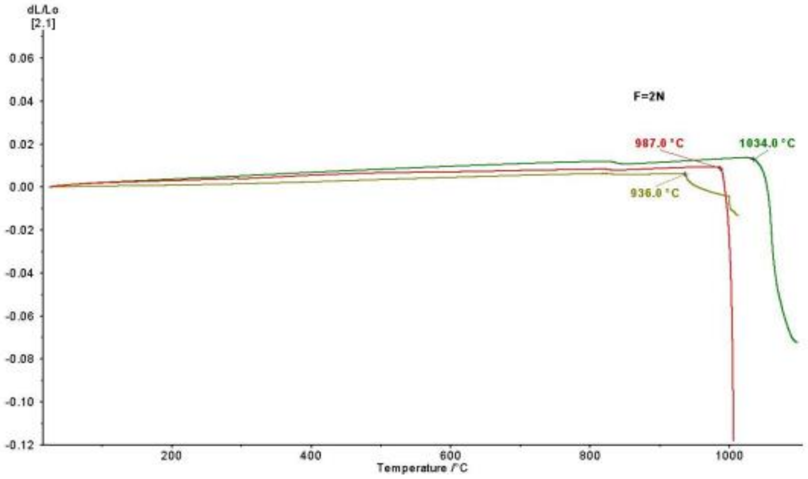


Figure 22. Softening point of a high temperature solders alloys (penetration mode).

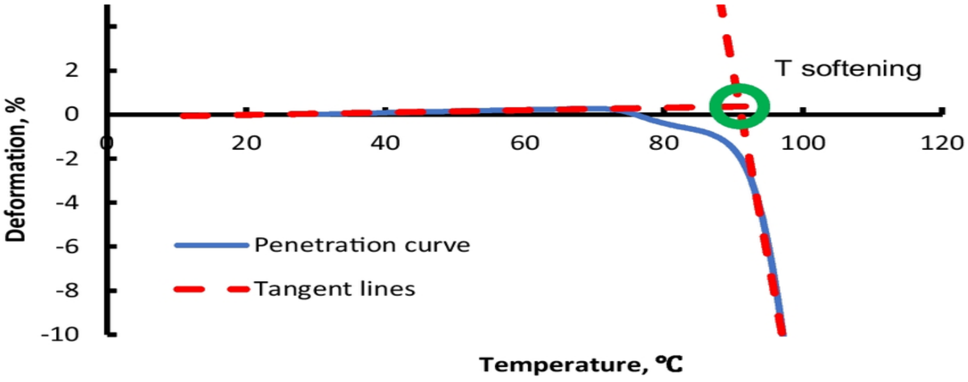


Figure 23. Determination of softening temperature TS for ABS sample by a TMA penetration test

3.5 *Interpretation of TMA curve*

TMA effects of physical transitions To investigate melting behavior, the sample is usually placed between two quartz disks and then measured with a force of 0.5 N at a heating rate of 5 K/min. The smaller the amount of sample between the quartz glass disks, the shorter the melting time. The liquid phase is consequently squeezed out earlier and more rapidly. For small samples, the onset corresponds to the melting point (Figure 24a). Flat samples, such as plastic films or surface coatings, can be measured directly with the ball-point probe. When the sample melts, the probe penetrates completely through the melt.

Semicrystalline polymers are squeezed out rather slowly from between the quartz glass disks on melting because the melt is very viscous. With three dimensional crosslinking (e.g. cross-linked PE, PE-X), an elastomer remains that is compressed but not squeezed out (Figure. 24b). No TMA effect is observed on cooling molten samples because the melt has already been squeezed out. An exception is crosslinked PE, which crystallizes with volume contraction. Amorphous polymers with a tendency to crystallize exhibit socalled cold crystallization on warming (Figure 24c). Solid-solid transitions (polymorphism) can be detected because they are accompanied by dimensional changes (strongly anisotropic). This is best measured by placing a single crystal under the 1 mm^2 probe (Figure 24d).

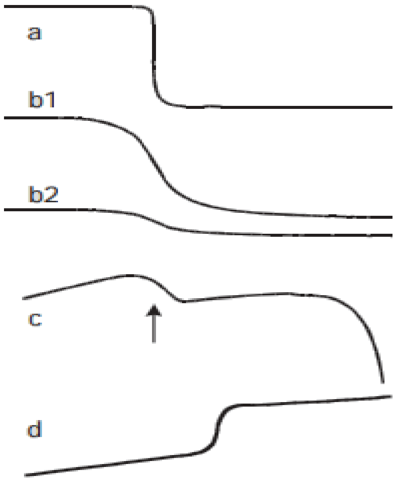


Figure 24. Typical TMA curves of transitions.

a: melting with or without decomposition,

b1: melting of semicrystalline polymers with a wide melting range

b2: the cross-linked PE-X does not melt

c: cold crystallization (arrow) can be measured because of the volume change. Afterward, the sample melts.

d: polymorphism: solid-solid transition.

3.6 Thermomechanical analysis at the glass transition

One of the TMA measurements most frequently performed is the determination of the glass transition temperature. The expansion coefficient shows a marked increase at the glass transition. This is the reason why the slope of the dilatometric curve becomes steeper at the transition (Figure 25a). The first heating curve of a new sample usually exhibits typical anomalies at the glass transition. These are caused by effects such as volume and stress relaxation, drying effects, or a foreign body (dust particle) penetrating the sample as it softens (Figure 25b, c). In penetration measurements, the ballpoint probe rests directly on the sample and penetrates more and more into the sample at the glass transition (Figure 25d). With highly filled polymers e.g. carbon fiber reinforced composites, the probe can hardly penetrate at all. These materials should be measured with the bending accessory using a load of 0.5N for example (Figure. 25e).

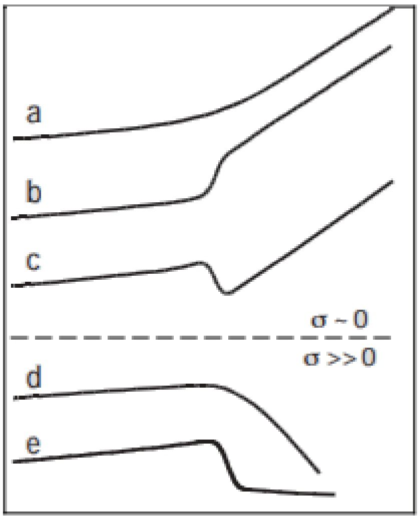


Figure 25. TMA glass transition (a, b, c dilatometric with very low compressive stress σ)

a: ideal glass transition due to the increasing expansion coefficient,

b: swelling of the sample at the glass transition,

c: contraction of the sample at the glass transition,

d: glass transition measured in penetration mode,

e: the bending accessory allows Tg to be determined even with samples of highly filled polymers that show hardly any effects with other measurement modes

Quiz.

This quiz focuses on fundamental concepts such as thermal expansion and probe types, and addresses more complex interpretations like the glass transition, kinetics, and material-specific behaviors.

1.

What is the primary physical property measured by Thermomechanical Analysis (TMA) as a function of temperature or time?

☐ A. Weight loss or gain.

☐ B. Dynamic storage modulus.

☐ C. Dimensional change (length or volume).

☐ D. Enthalpy of phase transitions.

2.

Which TMA probe geometry is most suitable for determining the Coefficient of Thermal Expansion (CTE) of a rigid, flat sample?

☐ A. Penetration probe (pointed-tipped).

☐ B. Tension film fiber accessory.

☐ C. Expansion probe (flat-tipped).

☐ D. 3-point bending probe.

4.

Why is it common practice to perform a 'second heat' or a baseline run in TMA?

☐ A. To increase the crystallinity of the polymer.

☐ B. To ensure the sample has completely evaporated.

☐ C. To calibrate the weight of the probe.

☐ D. To eliminate the influence of thermal history and residual stresses.

5.

In a TMA expansion curve, a sudden increase in the slope (rate of expansion) usually indicates which transition?

☐ A. Crystallization.
☐ B. The Glass Transition (Tg).
☐ C. Decomposition.
☐ D. Melting (Tm).

6.

When determining the Tg of a thin coating on a metal substrate, why might TMA be preferred over DSC?

☐ A. TMA allows for the sample to be liquid during the test.
☐ B. DSC cannot reach temperatures below 0°C.
☐ C. TMA can measure the color change of the coating.
☐ D. TMA is more sensitive to mechanical changes in very small mass fractions.

7.

A TMA penetration test shows a sharp downward 'dip' in the curve followed by a plateau. What does the depth of this dip represent?

☐ A. The total crystalline content.
☐ B. The thermal conductivity of the sample.
☐ C. The rate of crosslinking (curing).
☐ D. The softening point or heat deflection temperature.

8.

If a polymer sample shows 'shrinkage' (negative expansion) just before the Tg in a TMA curve, what is the likely cause?

☐ A. The sample is undergoing an exothermic reaction.
☐ B. The probe is too heavy and is crushing the sample.
☐ C. The sample has a negative Coefficient of Thermal Expansion.
☐ D. Relaxation of oriented polymer chains (Internal Stress).

9.

In 'Modulated TMA' (MTMA), the temperature is varied sinusoidally. What is the main advantage of this technique?

☐ A. It measures the chemical composition of evolved gases.
☐ B. It prevents the sample from melting.
☐ C. It allows the test to be completed in half the time.

☐ D. It can separate total dimensional change into reversible and non-reversible components.

10.

How does the crosslink density of a thermoset affect its CTE above the glass transition (Tg) in a TMA experiment?

☐ A. Higher crosslink density generally results in a lower CTE in the rubbery state.

☐ B. Higher crosslink density causes the CTE to become infinite.

☐ C. The CTE increases because the chains are closer together.

☐ D. Crosslinking has no effect on expansion, only on the Tg value.

Solution (C.C.D.B.D.D.D.D.A)

Example: Measurement of the Glass Transition

The glass transition is frequently observed in polymers and is notably accompanied by an increase in free volume, which in turn affects the coefficient of expansion. Near the glass transition temperature (Tg) of polymers, the coefficient of thermal expansion (CTE) undergoes a sudden change, allowing the determination of this transition temperature using TMA.

For a specific polymer, the coefficient α measured at temperatures above the glass transition is approximately three times greater than that measured in the glassy state. The following figure exemplifies the evolution of length as a function of temperature for polymer. Additionally, a melting zone (Tm) indicating the presence of crystalline regions can be observed.

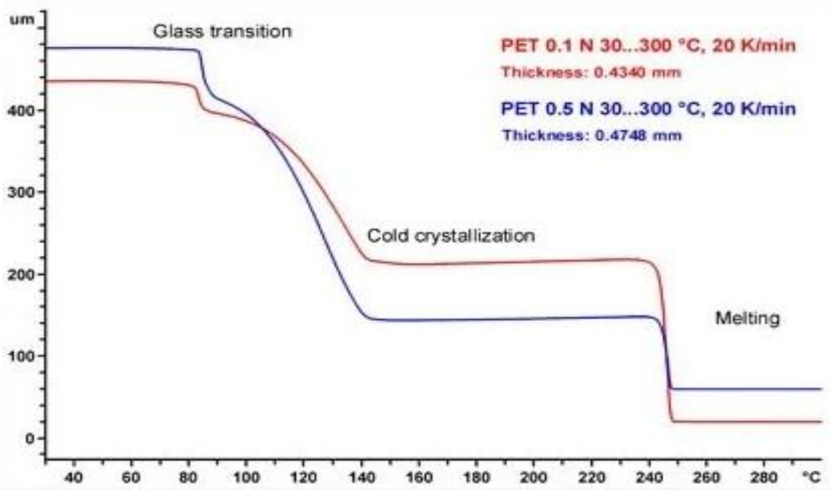


Figure 26. TMA curve for polymer

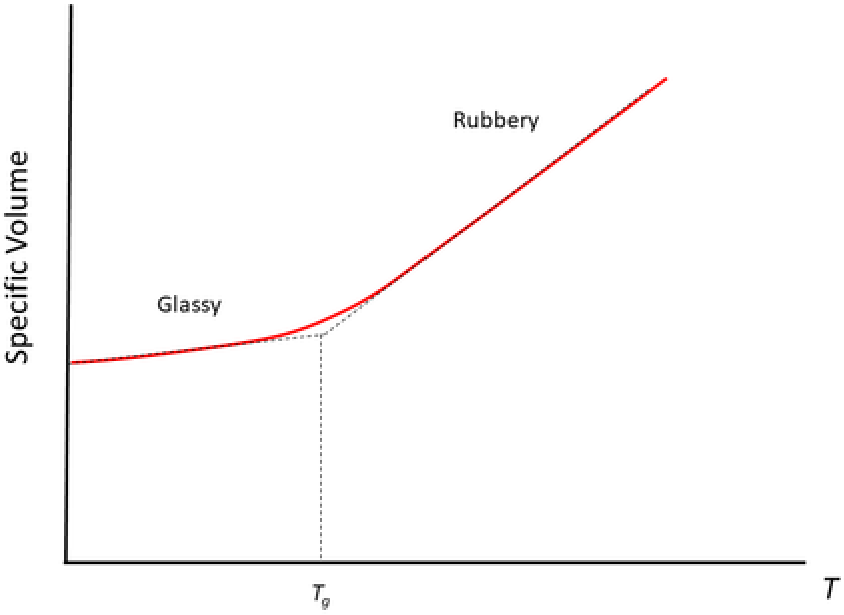


Figure 27. TMA curve of thermoset resine

Chapter VI

Dynamic Mechanical Analysis (DMA)

4 Dynamic Mechanical Analysis (DMA)

4.1 General Overview

4.1.1 Principle In DMA

dynamic stress either replaces or is superimposed on static stress. By applying a dynamic load to the sample, one can characterize relaxation phenomena associated with transitions such as the glass transition (primary relaxation) or those without thermal manifestation (secondary relaxations). The mode of loading whether three-point bending, tension, torsion, shear between parallel plates (T > Tg), or single or double cantilever depends on the temperature range, which influences the polymer's viscosity, and the sample's dimensions [26]. By recording the elastic and anelastic components of deformation respectively in phase and in quadrature with the stress as a function of temperature (at a fixed frequency) or frequency (at a fixed temperature), one can determine the storage moduli in shear (G') and elongation (E'), the corresponding loss moduli (G'', E''), and the mechanical loss angle [tan d: G''/G' (or E''/E')].

4.1.2 Equipment

Commercial DMA devices are typically equipped to perform the functions of a thermomechanical analyzer (TMA). The principle of deformation measurement is identical to that of TMA, utilizing either an optical system or an LVDT system, but it is essential to distinguish between the elastic and anelastic components. Two separate devices are employed for applying force: one manages the approach phase and the application of static stress (stepper motor, coil), while the other handles the application of dynamic stress (coil). These components are regulated by a force sensor. When selecting equipment, it is crucial to consider the device's versatility, including the range of loading modes available (longitudinal or rotational vibrator, sample holder shapes) and their compatibility with the sample type, particularly its viscosity. Key factors to consider include:

- Thermal control

- The range of accessible excitation frequencies (typically from about 10–2 to 102 Hz)

- The capability to operate at a fixed frequency with variable temperature or at a fixed temperature with variable frequency

- The ability to perform TMA functions

- The precision in stress and deformation measurements

- The minimum and maximum applicable loads

- The range of measurable module

- The geometry of the samples

- The software support for data analysis.

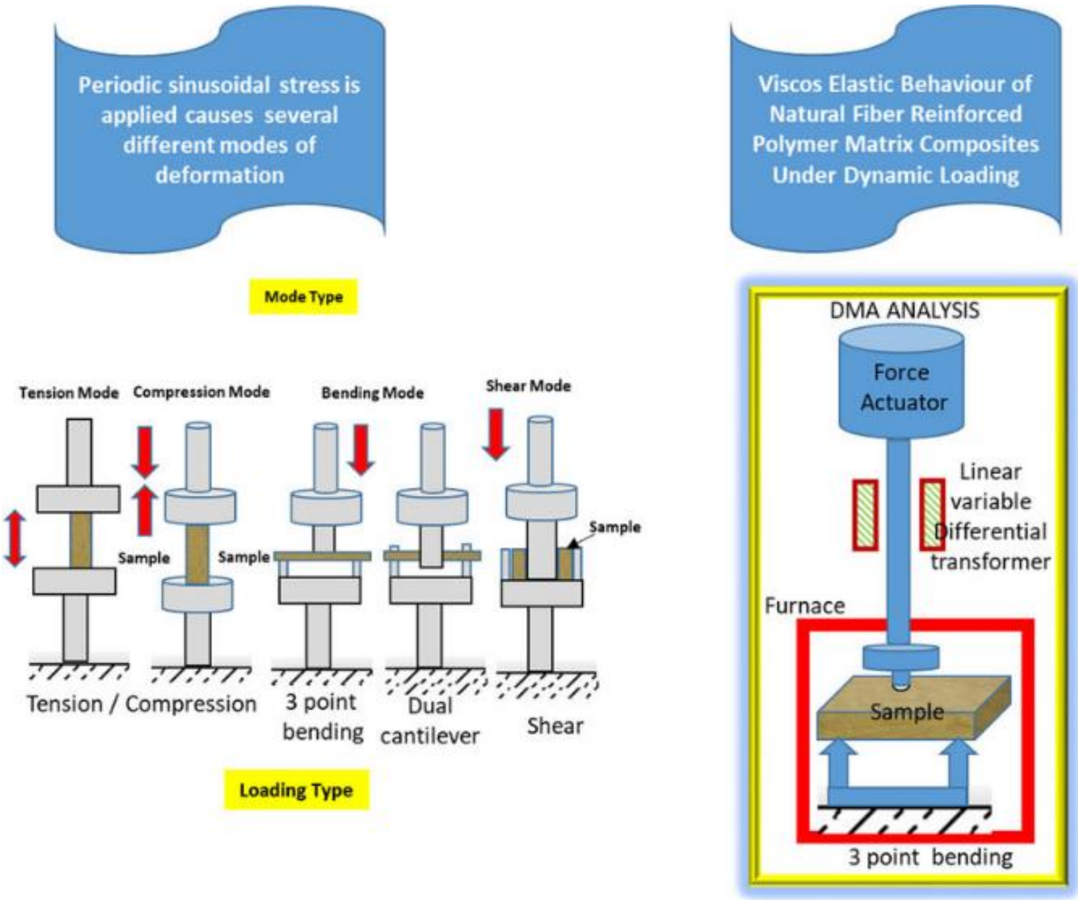


Figure 27. Types of deformation and examples of geometries,

The geometry of the sample holders dictates the testing process. The choice of deformation type is particularly influenced by the material's nature (solid, paste, or liquid) and its state (glassy, glass transition, rubbery, hardening, fluidification, melting, etc.) during the test. Generally, three scenarios may present themselves to the experimenter, depending on the modulus value:

- ✓ Materials with a high Young's modulus ($E > \sim 10$ GPa), such as certain composites or ceramics, are examined under tension-compression or bending.
- ✓ Solid materials with a lower modulus are characterized under tension-compression or shear;
- ✓ Pasty materials are typically analyzed in shear. Liquids (e.g., oils, paints, adhesives, varnishes) are exclusively tested in shear; in this case, the sample holder consists of a piston immersed in a container holding the sample, with the piston exciting the viscoelastic liquid through an annular pumping motion.

There are sample holders specifically adapted to each type of deformation or the material's unique characteristics.

4.2 Characterization of Amorphous Polymers

Mechanical relaxation modes in amorphous polymers are indicated by a peak in the loss angle at a temperature T_{max} when measured at a fixed frequency (angular frequency w_0) while varying the temperature. Figure 28 illustrates an example of DMA spectra obtained from PMMA in a three-point bending test.

The relaxation kinetics determines the evolution of T_{max} as a function of the solicitation frequency:

$$T_{max} = f\,(w_0).$$

The relaxation time is also defined as $\tau\,(T_{max}) = 1\,/\,w_0$, and its variation with Tmax characterizes the relaxation process under consideration.

In amorphous polymers, at least two relaxation modes are typically observed: the primary α mode, which corresponds to the viscoelastic manifestation of the glass transition, where the relaxation time follows a Vogel-Fulcher type equation;

$$\tau = \tau_{0v} \exp \frac{A}{T - T_0}$$

With:
t_{0v}:pre-exponentialfactor,
A : constant sometimes related to the free volume of the polymer [24],
T_0 : temperature approximately 40-50 °C below Tg.

Recent models associate A and T_0 with the fragility of a glass, indicating its sensitivity to the glass transition phenomenon [27]; and the secondary β mode, which corresponds to more localized motions in the amorphous phase [28], with a relaxation time that follows an **Arrhenius**-type equation:

$$\tau = \tau_{0a} \exp \frac{\Delta H}{kT}$$

With:
ΔH:activationenthalpy, t_{0a} : pre-exponential factor, k : Boltzmann constant.

Relaxation phenomena in polymers typically cannot be explained by a simple process with a single relaxation time. Consequently, the shape of the loss peaks is analyzed using the concept of distributed processes or coupled modes, as detailed in references [19] [29].

DMA is employed to:

- ✓ Monitor the evolution of material structure through their mechanical properties during various aging cycles;
- ✓ Characterize polymer blends, filled polymers, and composites when a specific property is under consideration;
- ✓ Determine the anisotropy of mechanical properties in oriented polymers [30].

4.3 *Characterization of semi-crystalline polymers*

In semi-crystalline polymers, the primary and secondary relaxation modes previously described are generally present, although they are attenuated, particularly the primary mode [19]. At higher temperatures, an additional mode associated with the crystalline phase is usually observed, as seen in PE [31] or PVDF [32].

The indexing of the modes is as follows:

α : crystalline relaxation;

β : primary relaxation (associated with Tg);

γ : secondary relaxation (figure 28).

It can be beneficial to monitor the evolution of mechanical properties in relation to the degree of crystallinity or as a function of the aging of the crystalline phase, such as recrystallization [33].

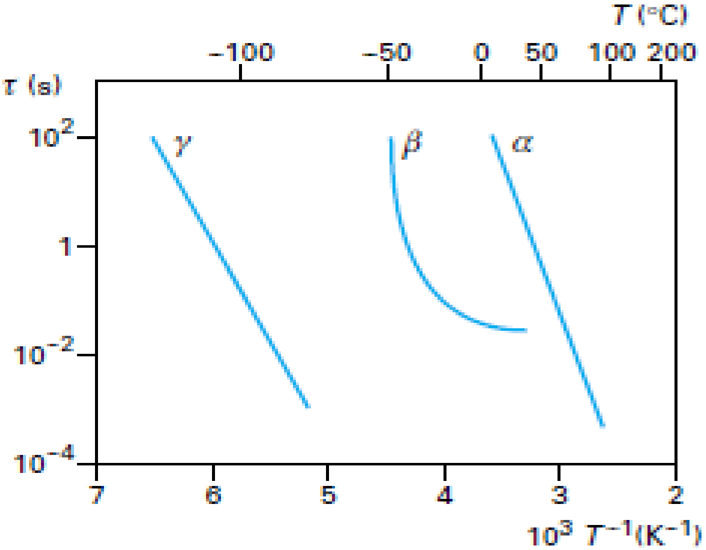


Figure 28. Kinetics of mechanical relaxations of poly(vinylidene fluoride)

4.4 Application Examples

4.4.1 Polymer Blends

A polymer blend, or mixture, is similar to metal alloys, where at least two polymers are combined to form a new material with distinct physical properties. Polymer blends can be broadly categorized as follows.

Blends are considered heterogeneous or incompatible if the components exist in separate phases, typically with the minor component dispersed within a matrix of the dominant component. The compatibility of a blend also depends on temperature; in such cases, the blend is deemed partially miscible. When blends are incompatible, mechanical energy is required to disperse the minor phase (mixing), and coalescence can occur if the blend's morphology is not stabilized. Interfacial forces, such as interfacial tension, become significant and can notably alter the blend's rheological characteristics.

Furthermore, the elastic properties of non-compatible blends rely on energy storage mechanisms at the interphase. The relaxation of the dispersed phase itself often takes much longer than the relaxation of the polymer chains of the individual components. Figure 29 illustrates the dynamic spectrum of a PMMA/PS blend with varying volume fractions of the minor phase1. The additional low-frequency contributions in G’ are attributed to the form relaxations of the large dispersed domains of the minor phase. If the average droplet size is known (from TEM, for example), the interfacial tension can be calculated from the average relaxation time of the droplet relaxation. Incompatible blends exhibit distinct glass transitions for each component, although the values may differ from those of the pure components. Homogeneous blends, on the other hand, show only one glass transition. Thus, evaluating the glass transitions provides insights into compatibility and interphase effects. Figure 30 presents the tan δ trace of a PPO/HIPS 50:50 blend, modified with MBS, a (methyl-methacrylate-butadiene-styrene) copolymer2. The modifier appears as an additional transition at -45 °C, independent of the concentration. The poor compatibility results from the specific structure of the MBS, which consists of a PMMA shell embedding a core of SB rubber.

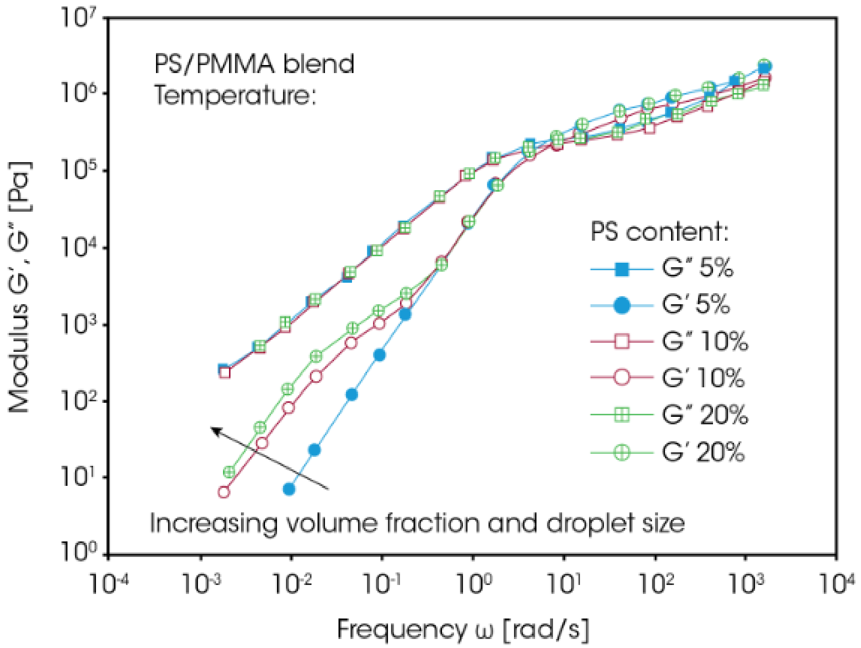


Figure 29. the increase contributions of G' at low frequency can be used to calculate the interfacial tension of non-compatible blends1

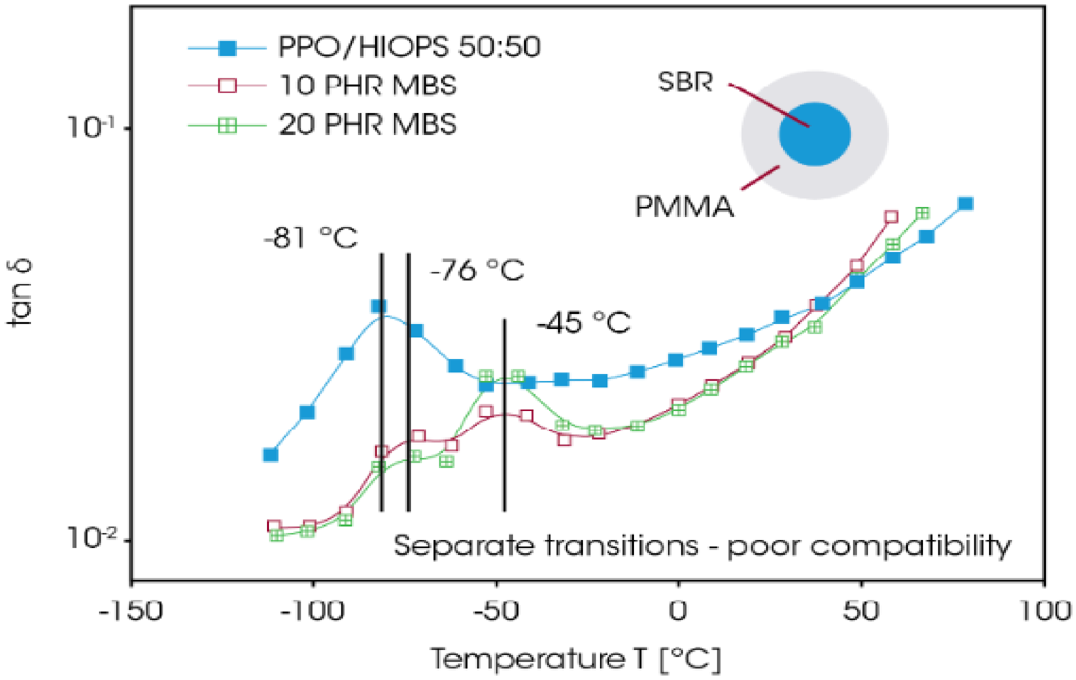


Figure 30. PPO/HIPS blend modified with MBS. The additional transition at -45 °C independent of concentration proves poor compatibility2.

4.5 *Enhancing the Impact Behavior of Polystyrene Juice Cans*

Orange juice cans molded from rubber-modified high impact polystyrene (HIPS) resins show variations in impact resistance. High impact phenomena are associated with mechanical deformations occurring within milliseconds. Due to the equivalence of time and temperature, rapid mechanical processes at ambient temperature correspond to low-speed testing at low temperatures. Consequently, energy absorption, indicated by the magnitude of tan δ at the ß peak and measured at frequencies of 1Hz, correlates with toughness and impact resistance (Figure 31). The shift in the glass transition temperature Tg and the ß peak results from compounding effects, either due to the compatibilization of the rubber and polymer phases. In this context, differences in tan δ arise from variations in the quantity and type of rubber impact modifier used.

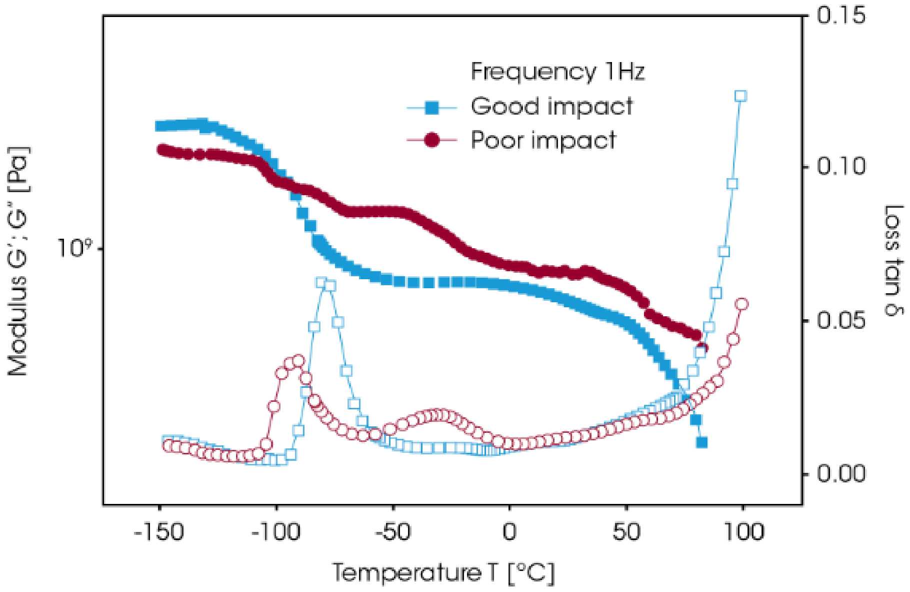


Figure 31. DMA trace of HIPS. The good impact performance results from the compatibility of the rubber and styrene phase, showing as one ß transition instead of two in the compound with poor impact properties.

4.5.1 *Toughness and flexibility of adhesives*

For most applications, hot melt adhesives must exhibit both toughness and flexibility at their operating temperature. In bookbinding, the compounds used should not become brittle within the expected temperature range. Figure 32 illustrates the dynamic modulus and loss behavior of a typical hot melt (block copolymer). Variations in storage modulus highlight a significant performance difference at the operating temperature. The level of the loss modulus is indicative of the adhesive's flexibility, while toughness can be quantitatively linked to the transition represented by tan δ.

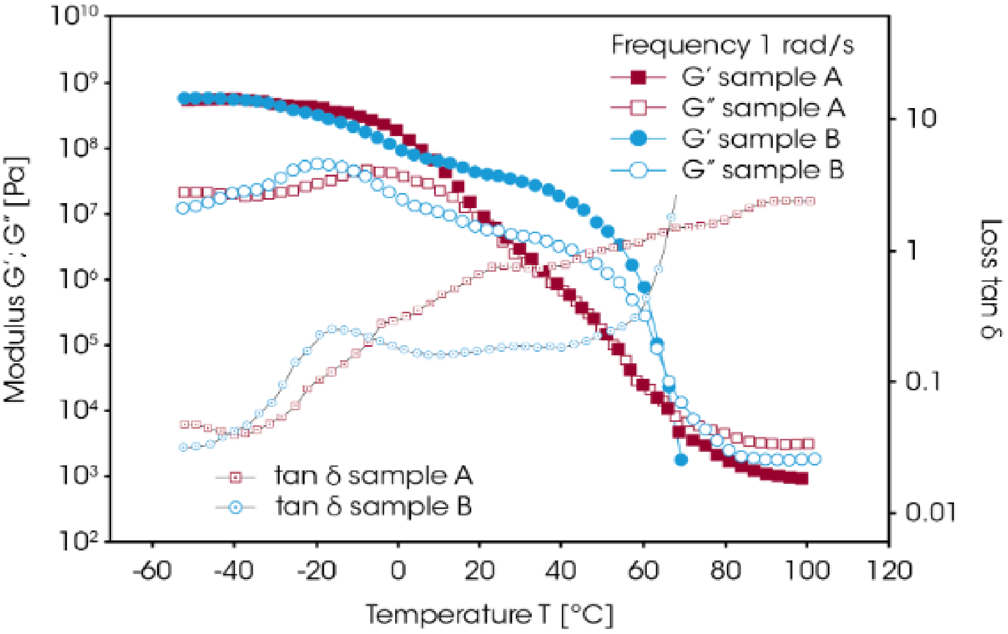


Figure 32. Flexibility correlates with the loss modulus, toughness relates to the tan δ peaks

4.5.2 Conclusion

Dynamic Mechanical Analysis (DMA) is an extremely powerful technique to characterize the thermal and mechanical properties of solid samples. DMA allows users to characterize the viscoelastic properties of the material such as storage modulus, loss modulus and tan δ. These properties help understand the final performance properties of the solid products and tie it to the material chemistry. It is also one of the most sensitive techniques to measure the glass transition temperature of a material which can be used for quality control, development, informing processing conditions, and troubleshooting failed products. A representative chart of the application of DMA at different stages of manufacturing is shown below.

Quiz

1.

In a DMA scan of an amorphous thermoplastic, what molecular event is associated with the sudden, multi-decade drop in the storage modulus (E') and the primary peak in tan δ?.

☐ A. The onset of long-range cooperative segmental motion.

☐ B. The transition from a liquid melt to a rubbery state.

☐ C. The alignment of polymer chains into crystalline lamellae.

☐ D. The breaking of covalent bonds in the polymer backbone.

2.

How does the presence of crystalline regions in a semi-crystalline polymer affect the storage modulus (E') curve compared to a purely amorphous polymer above Tg?

☐ A. It eliminates the tanδ peak entirely.

☐ B. It causes the Tg to disappear from the DMA thermogram.

☐ C. It creates a rubbery plateau because crystals act as physical crosslinks.

☐ D. It causes the modulus to drop to zero immediately after Tg.

3.

According to the kinetic theory of rubber elasticity, how does increasing the crosslink density affect the storage modulus (E') in the rubbery plateau region?

☐ A. The modulus remains constant regardless of crosslinking.

☐ B. The modulus increases linearly with the concentration of crosslinks.

☐ C. The modulus decreases because crosslinks disrupt chain packing.

☐ D. The modulus becomes frequency-independent only at very low crosslink densities.

4.

You are analyzing a blend of two polymers and observe two distinct peaks in the tanδ curve. What does this indicate about the blend?

☐ A. The blend is perfectly miscible at the molecular level.

☐ B. The two polymers are immiscible and form a phase-separated blend.

☐ C. One of the polymers has completely degraded during processing.

☐ D. The two polymers have reacted chemically to form a new copolymer.

5.

What is the physical significance of a sub-ambient β-transition peak in a DMA tanδ scan for a polymer like Polycarbonate?

☐ A. It represents localized rotations of side groups or small chain segments.

☐ B. It indicates the start of oxidative degradation.

☐ C. It shows the temperature at which the polymer becomes brittle.

☐ D. It marks the point where the polymer melts.

6.

If a plasticizer is added to a PVC sample, how will the tanδ peak change in a DMA experiment?

☐ A. The peak will become much sharper and move to 0°C.

☐ B. The peak height will decrease until it is no longer detectable.

☐ C. The peak will shift to a higher temperature due to increased volume.

☐ D. The peak will shift to a lower temperature and likely broaden.

7.

Which DMA parameter represents the 'damped' or dissipated energy as heat during a deformation cycle?

☐ A. Complex Modulus ($E*$)

☐ B. Loss Modulus (E'')

☐ C. Storage Modulus (E')

☐ D. Poisson's Ratio

8.

In the context of DMA, what does a tanδ value greater than 1.0 signify about the material state?

☐ A. The material has reached its ultimate tensile strength.

☐ B. The polymer chains have become completely immobilized.

☐ C. The material is in its perfectly glassy state.

☐ D. The material is behaving more like a viscous liquid than an elastic solid.

9.

Why does increasing the oscillating frequency in a DMA test typically shift the observed Tg to a higher temperature?

☐ A. Higher frequencies cause the polymer to melt faster.

☐ B. The polymer absorbs more moisture at higher frequencies.

☐ C. The storage modulus decreases as frequency increases.

☐ D. Chain segments have less time to rearrange, requiring more thermal energy to keep up with the stress.

10.

For a thermosetting resin, what happens to the area under the $\tan\delta$ peak as the degree of cure (crosslinking) increases?

☐ A. The area remains constant but the peak moves to 0 Kelvin.

☐ B. The area decreases because the number of mobile segments decreases.

☐ C. The area stays the same because the chemical composition is identical.

☐ D. The area increases because more energy is needed to break the crosslinks.

Chapter V

X-ray Diffraction

5 Principle

X-ray diffraction analysis (XRD) employs X-rays to investigate and ascertain the crystalline structure of materials by measuring the diffraction of X-rays by the atomic planes within the material. This technique is sensitive to the relative positions and types of atoms, as well as the scale over which crystalline order is maintained. Consequently, it is well-suited for identifying and quantifying the crystalline fraction in a material (including the quantification of mixtures), determining the spacing between lattice planes and the extent of their persistence, and analyzing preferential order and the epitaxial growth of crystallites. Essentially, it examines length scales ranging from a few tenths of an angstrom to several nanometers and responds to order over tens of nanometers. Different disciplines refer to this technique using various terms:

- ✓ For materials science: X-ray diffraction (XRD)
- ✓ For chemistry: powder X-ray diffraction (PXRD)
- ✓ Physics: wide-angle X-ray scattering (WAXS)

X-ray diffraction is typically conducted on samples in the form of finely divided powders; however, it is also possible to obtain diffraction from surfaces and solid samples. This technique finds applications in the following fields:

Pharmaceutical Industry

X-ray diffraction is a highly effective tool for analyzing solid-state drugs, playing a crucial role at every stage of drug development, testing, and manufacturing. Many pharmaceutical products possess a crystalline structure, and this technique is essential for their precise characterization. For instance, once an active drug compound is isolated, an indexed powder X-ray diffraction pattern is recorded to ascertain the crystalline structure of the product, file a patent, and safeguard the company’s investments.

Forensic Science

X-ray diffraction is pivotal in the analysis of trace evidence, which may include fragments of glass, paint chips, hairs, stains, and powdered substances. Identifying and comparing small quantities of material can be instrumental in either incriminating or exonerating a person suspected of a crime.

Geology

In mineral exploration, X-ray diffraction is a frequently employed technique. Mineralogists were among the pioneers in the field of X-ray crystallography following the discovery of this method. The introduction of X-ray diffraction has so profoundly transformed geological sciences that its absence is unimaginable. Each mineral type has a unique crystalline structure that produces a distinctive diffractogram, enabling the swift and straightforward identification of minerals in a sample. XRD data can be quantified to determine the proportion of different minerals present.

Materials Science

In materials science, X-ray Diffraction (XRD) is widely used to analyze and characterize crystalline structures, including crystal size, preferred crystallographic orientation, microstrain measurement, dislocation density establishment, and determining the relative volume of phases present in a sample, whether ceramics, polymers, or other innovative materials.

5.1 Properties of X-rays

X-rays were discovered in 1895 by the German physicist Roentgen. The typical wavelength of X-rays is $1\text{x}10^{-10}$ m (or 1 angstrom), whereas the wavelength of visible light is generally $1\text{x}10^{-6}$ m (1μ).

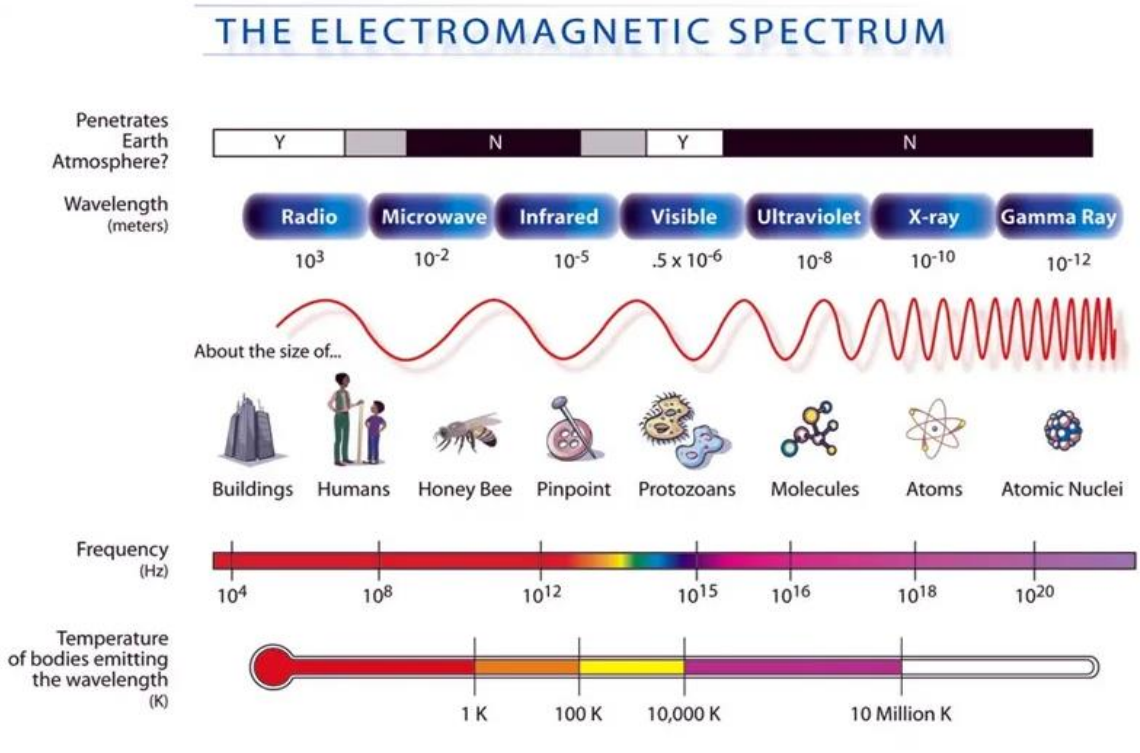


Figure 33. The electromagnetic spectrum

5.2 X-ray Production

X-rays are generated when charged particles, typically electrons, are decelerated. This occurs when high energy electrons strike a target material. As the electrons slow down upon impact, they produce a continuous spectrum of energies known as "bremsstrahlung," a German term meaning "braking radiation," due to their gradual deceleration. If the incident electrons possess sufficient kinetic energy, they can dislodge an electron from its shell, placing the atom in a high-energy state. An electron from an outer shell then promptly fills the now-vacant, lower-energy shell. This transition from a higher to a lower energy level results in the emission of a photon with a specific energy corresponding to the electron shell, producing what is known as the "characteristic spectrum" of the target material.

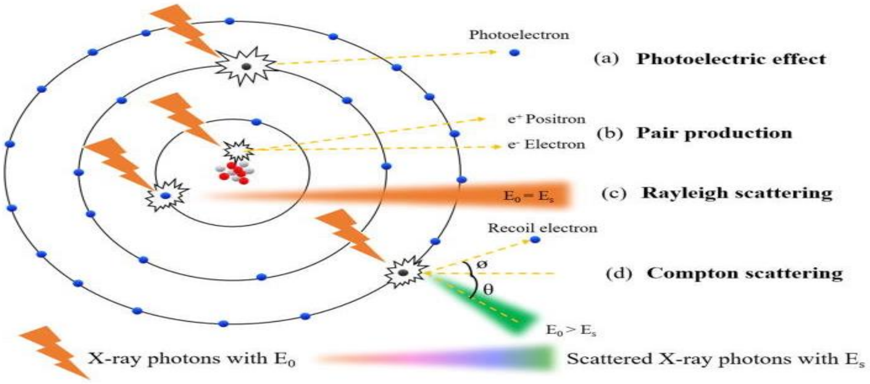


Figure 34. Interaction of an incident beam with an atom to produce X-rays.

In X-ray diffraction (XRD), the K alpha peak, depicted below, is typically utilized. Due to the quantum mechanics governing electron energies and their arrangement in shells, a characteristic peak shape is observed, with the most intense peak being K alpha 1, accompanied by a smaller K alpha 2 peak with an intensity about half that of K alpha 1.

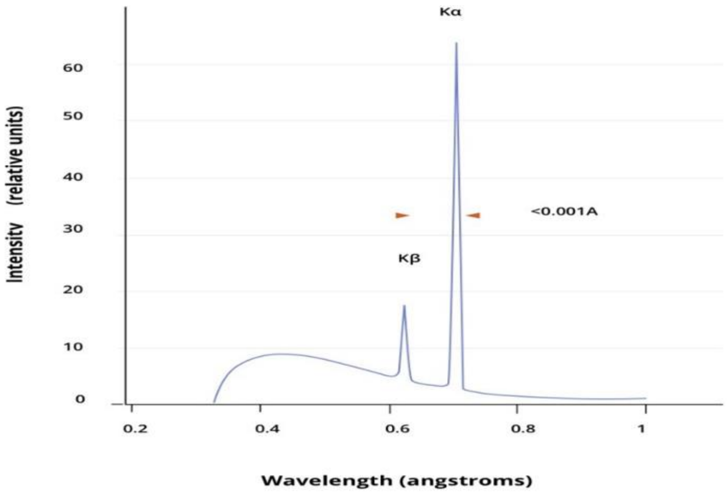


Figure 35. X-ray emission spectrum showing the characteristic peaks.

5.3 *The **Geometric** Structure of Crystals*

5.3.1 *Crystal Structure*

A crystal is a solid material composed of atoms arranged in a periodic pattern. Amorphous materials are solids that lack any order, such as certain polymers and glass. Many polymers and composites are a mixture of crystalline and amorphous phases.

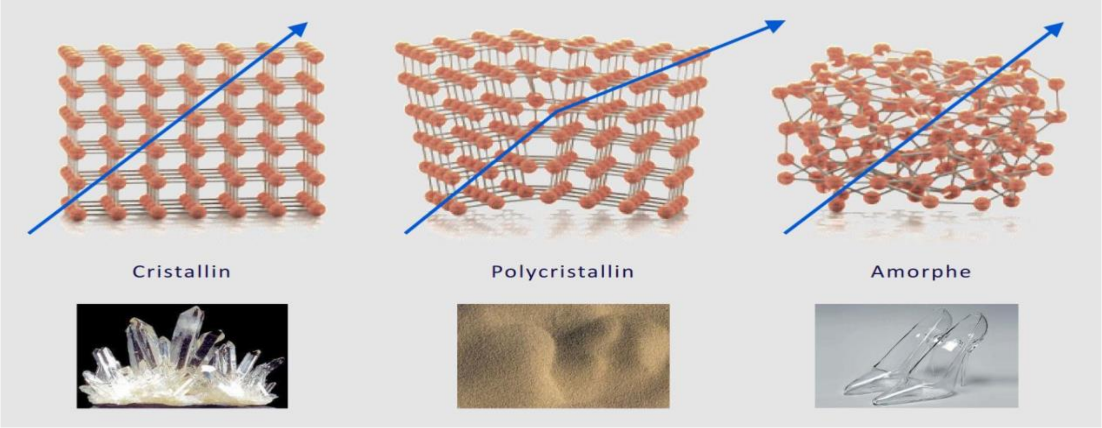


Figure 36. The different crystalline structures of materials

It is easier to describe and illustrate crystals as a set of abstract points known as a lattice. There are only a limited number of possible different point lattice structures, and these are generally referred to as the seven crystal systems. Within these seven systems, there are additional positions for atom placement, which gives rise to the 14 Bravais lattices.

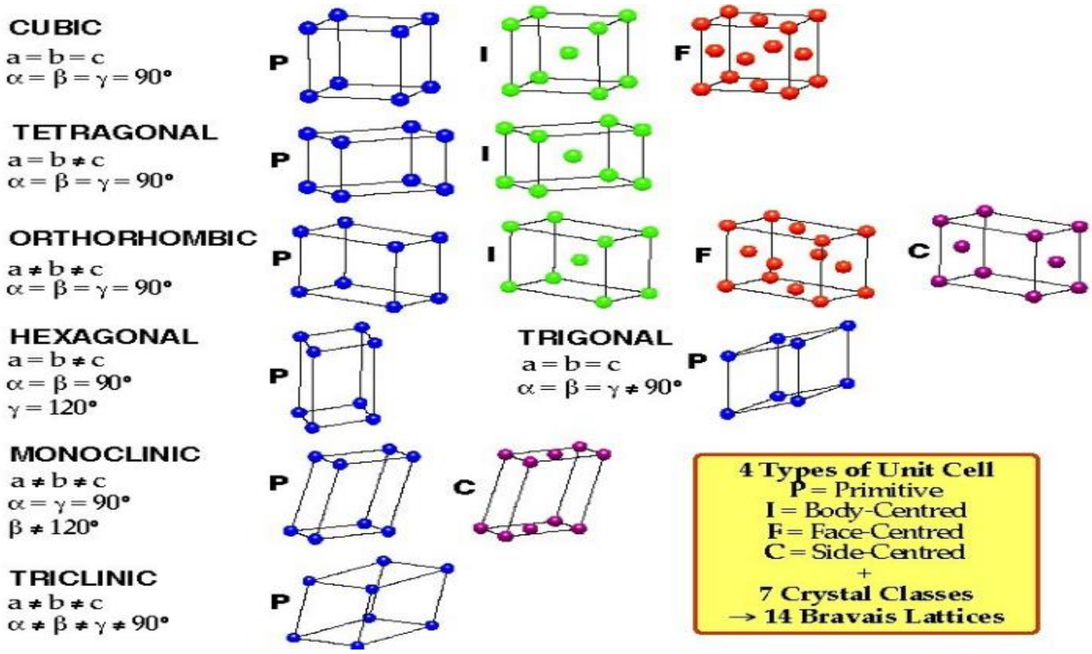


Figure 37. The 14 networks of Bravais.

5.3.2 Miller Indices

Crystals are described using a notation known as “Miller indices.” Before the development of this mathematical system by William H. Miller (1801–1880) to represent any crystal face or group of similar faces (forms), there was much confusion due to the diversity of existing descriptive systems. Miller used fairly simple mathematical calculations to address this problem, and his notation has become the common language throughout crystallography. The figure below illustrates the Miller indices for a cubic structure, showing that these planes are determined by three integer numbers, with no allowance for fractions. To identify the Miller indices of a plane, we begin by observing the points at which the plane intersects each axis. We then take the reciprocal of each and convert them into integers. Negative indices are indicated by a bar over the integer, while planes are defined by three integers enclosed in parentheses. Families of planes such as (100), (001), and (010) can be collectively described using another type of brackets, namely 100.

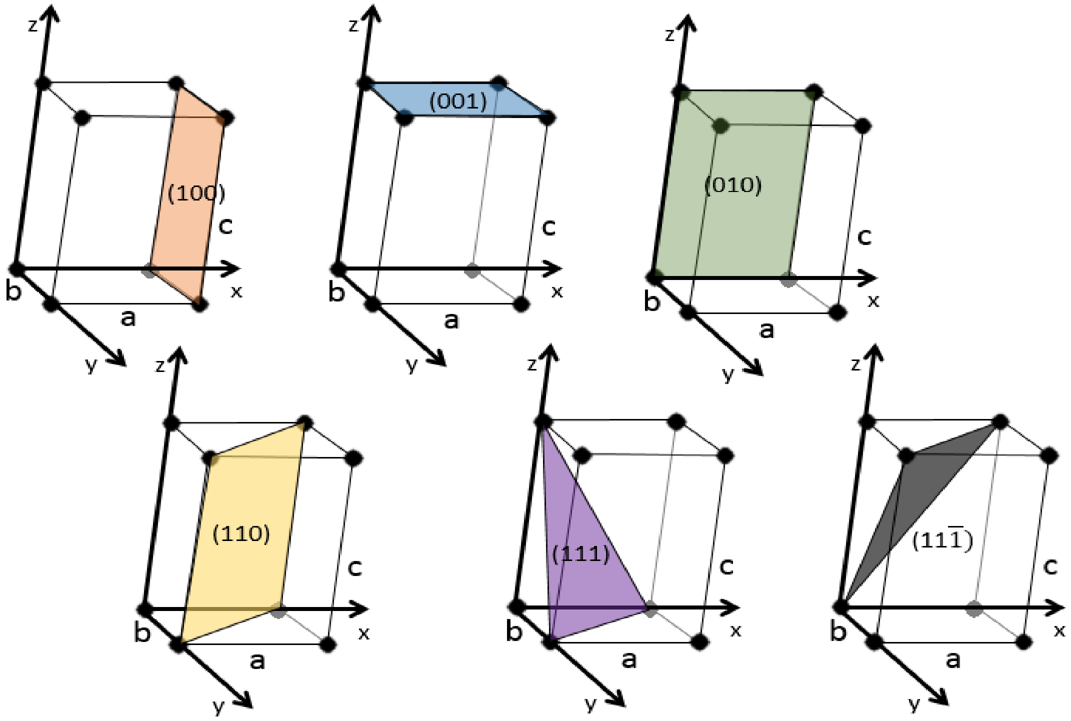


Figure 38. Different orientations in a cubic lattice.

5.4 Principle of Diffraction

5.4.1 Wave Structure

Diffraction originates from both constructive and destructive interference of waves. Two waves are said to be "in phase" if their crests and troughs are aligned at the same position. If two waves are not in phase, they can merge to form a single wave with a lower amplitude. This is called destructive interference. If the waves are in phase, they will combine to produce a wave of greater amplitude, a phenomenon known as constructive interference.

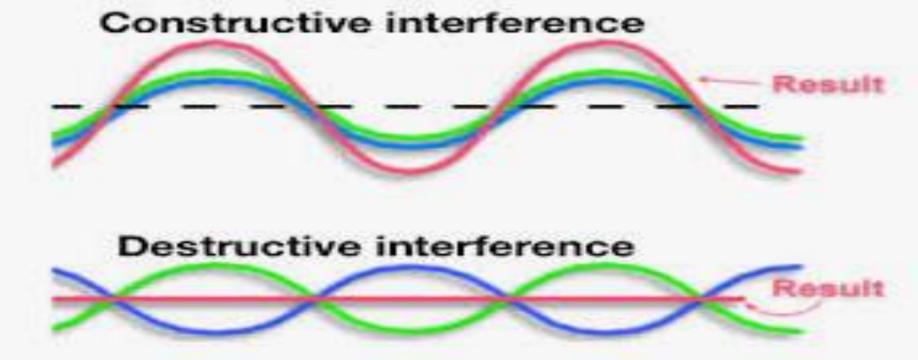


Figure 39. Constructive and destructive interference in the case of the superposition of two waves.

5.5 Interaction of X-rays with Matter

Just like electrons, when an X-ray hit a sample, various interactions can occur. For constructive diffraction to take place during an X-ray diffraction experiment, the wavelengths of the incident beam and the diffracted beam must be identical. Thus, only elastic interactions, which preserve energy, are responsible for the diffracted signal that we use in X-ray diffraction (XRD). However, there are many other interactions between the X-ray beam and the samples. Phenomena such as fluorescence and Compton scattering, which are the opposite of diffraction, can be detected by X-ray detectors. In this way, they contribute to the background noise observed in all laboratory diffraction measurements. X-ray emission occurs from the electron cloud, and scattering takes place in all directions.

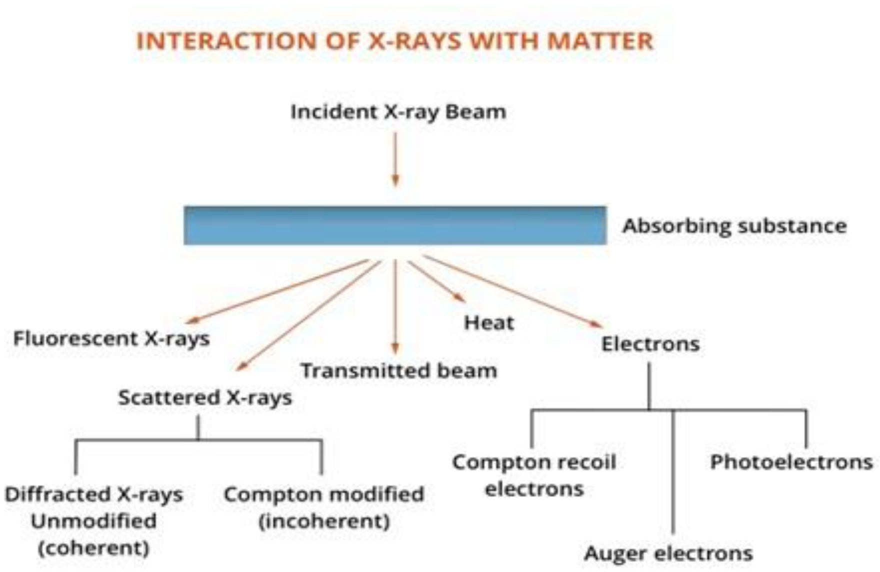


Figure 40: Interactions of X-rays with matter

5.6 X-ray Diffraction by a Crystal

X-ray diffraction involves directing radiation with a wavelength characteristic of X-rays ($0.1 < \lambda < 10$ nm) onto a crystal, regardless of its orientation. The radiation penetrates the crystal [18], leading to partial energy absorption and atomic excitation. This process results in the emission of radiation in all directions. A coherent beam can be detected due to the radiation produced by atomic planes that are in phase. The condition for this in-phase radiation is described by Bragg’s law.

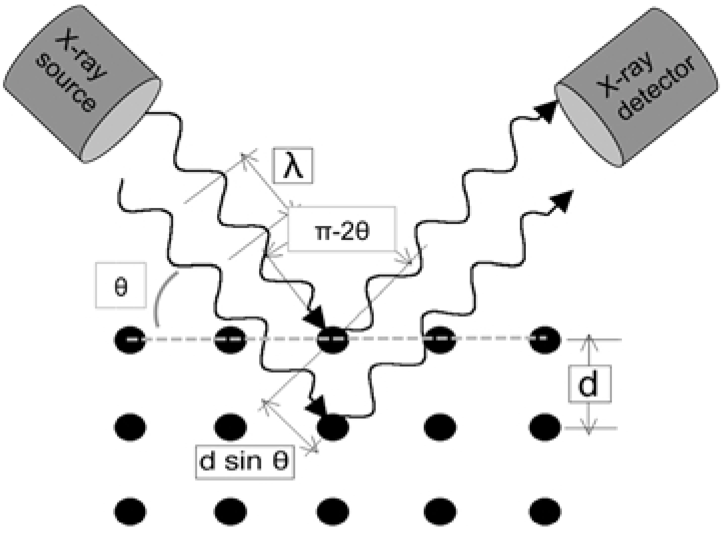


Figure 41: Concept of X-ray diffraction by a crystal and demonstration of Bragg's law

At specific angles relative to a crystal plane, X-rays will constructively interfere (diffract), producing a diffracted beam with significantly higher intensity than at other angles. This phenomenon is explained by Bragg’s Law:

$$2d \sin \theta = n \lambda$$

Here, **d** represents half the deviation, **n** is the order of diffraction, **λ** is the wavelength of the X-rays, and **θ** is the diffraction angle in degrees. [19]

X-ray diffraction data (XRD) are typically represented as a curve with X-ray intensity on the y-axis and the angle on the x-axis. Typical X-ray diffraction spectra are presented below.

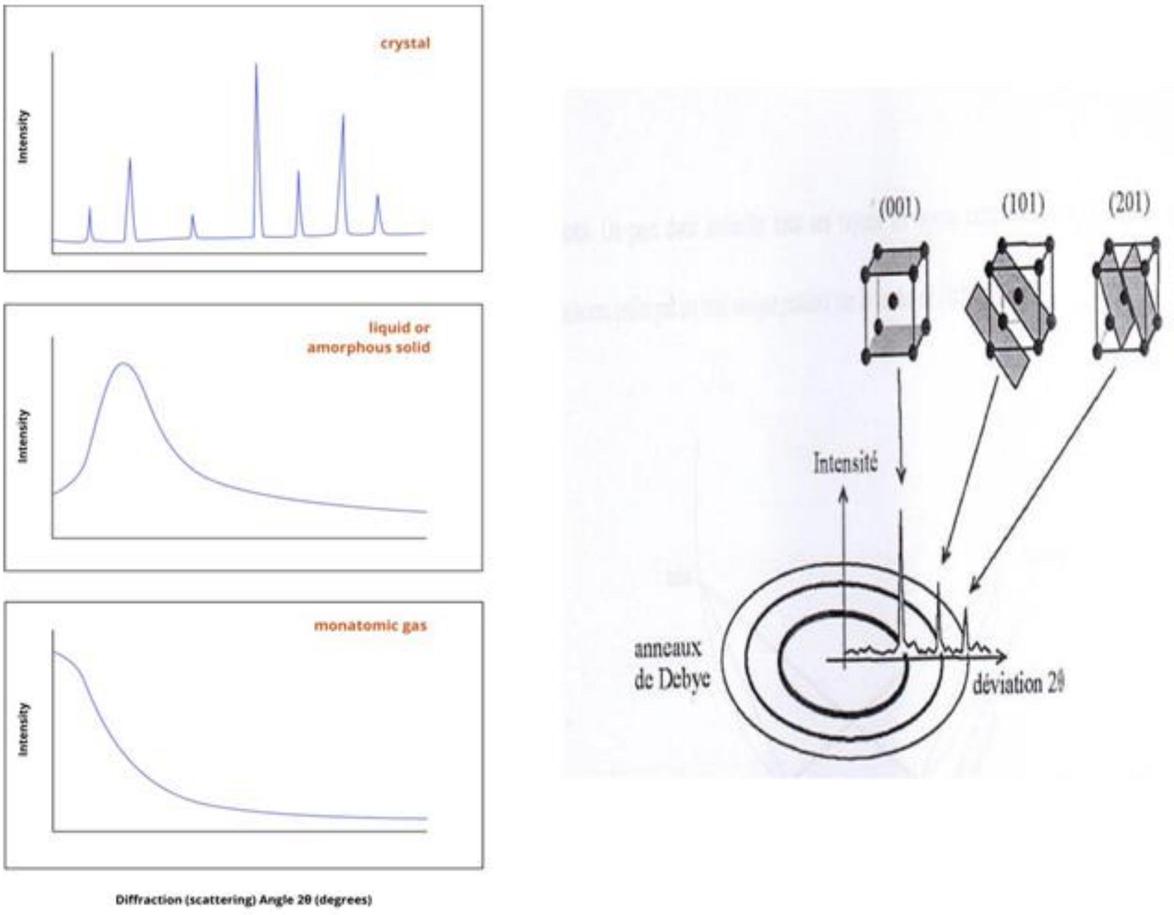


Figure 42: X-ray diffraction pattern

5.7 Bragg-Brentano Diffractometer

Most diffractometers in materials science are based on a reflection geometry in which the X-ray detector and the X-ray source are located on the same side of the sample; the X-rays emitted by the source are reflected by the material sample and directed towards the detector. This is known as reflection geometry, but it is important to remember that these X-rays are diffracted from the surface they are not reflected and do not bounce back. This is called the Bragg-Brentano type geometry, and it is the most common setup found in most laboratories. It requires fairly complex movement of the source and the detector or of the sample and the detector. A powder diffractometer in Bragg-Brentano geometry operates with a divergent beam, which widens until it reaches the sample. From there, it is focused on the receiving slit, which is then followed by the detector or secondary monochromators. The beam is again focused onto the detector in the case of secondary monochromators.

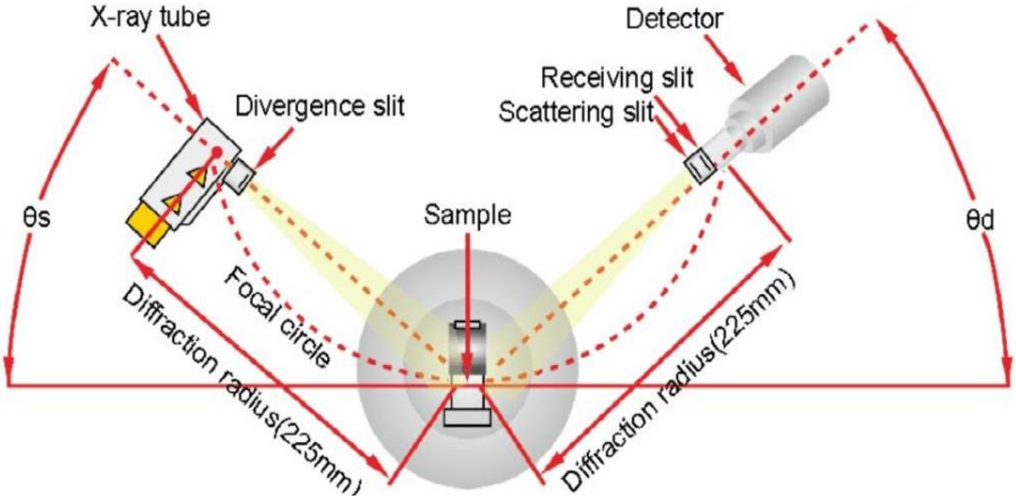


Figure 43: X-ray diffractometer in Bragg-Brentano geome

There are several models of instruments. In the first θ–θ geometry, the X-ray source, the primary optics, as well as the secondary optics and the detector all move around θ while the position of the sample remains fixed. In the second θ–2θ geometry, the primary optics and X-ray source are fixed, while the secondary optics and the detector rotate around 2θ, and the sample holder rotates around θ. The essential characteristics of both geometries remain the same regardless of which components are fixed and which rotate: the relationship between θ (the angle between the incident X-ray beam and the surface of the sample) and 2θ (the angle between the incident X-ray beam and the receiving slit-detector) is maintained throughout the analysis, and the distance between the sample and the detector and between the X-ray source and the sample is fixed and equal, defining the diffractometer circle in which the sample is always at the center.[20][21].

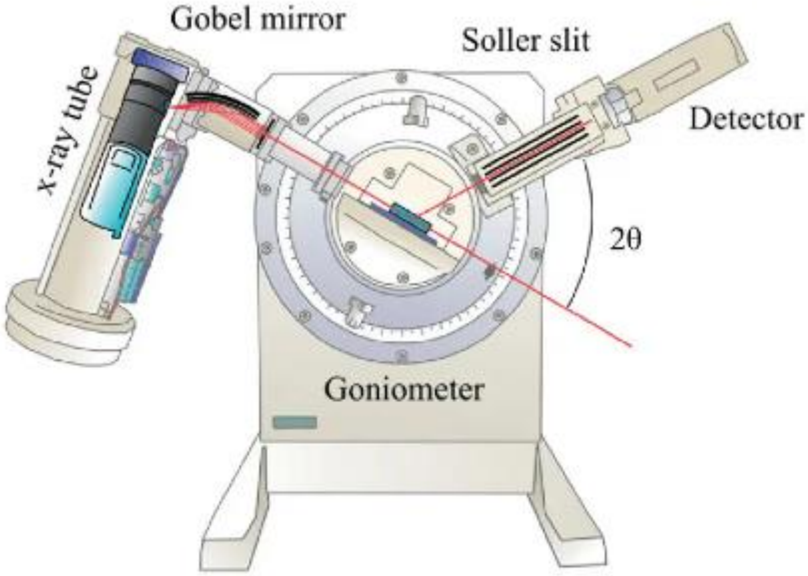


Figure 44: X-ray diffraction device.

5.8 Sample Preparation

5.8.1 Different Types of Samples

In quantitative and qualitative analyses by X-ray diffraction, counting statistics are important. Since only the crystal planes parallel to the diffraction plane will be detected, it is imperative to ensure that you obtain diffraction from several thousand grains during the measurement. Diffraction from an ideal powder yields an intense diffracted signal from all planes, and the diffracted intensity is uniform around the diffraction ring. [22]

Figure 45: Diffraction of an ideal powder (uniform intensity around the diffracted rings)

In the case of a small number of larger grains, if we take a measurement from this sample, we will obtain diffraction at certain spots around the ring. This leads to a situation where some peaks may go completely unnoticed. It then becomes impossible to identify, index, or quantify your spectrum.

Figure 46: Diffraction from a reduced number of crystallites (spottiness effect)

In the case of many solid samples, the orientation of the crystals or grains will not be uniform. However, most solids adopt a preferential orientation of the crystals within the microstructure. As a result, the diffraction ring shows non-uniform intensity. The more common orientations produce a stronger diffracted signal.[23]

Figure 47: Diffraction from textured samples (the degree of orientation can be extracted)

5.9 The Importance of Sample Height

For powder X-ray diffraction (linear beam), it is important that the sample is within a few hundred microns of the correct height. This is only about the thickness of a human hair. Failing to sufficiently fill the sample holder cavity or piling the powder above the correct height will result in extremely significant errors in the measured angle of the diffracted peak. At an incorrect height, the angles can deviate by more than 0.5 degrees and the intensities are reduced by half. [24]

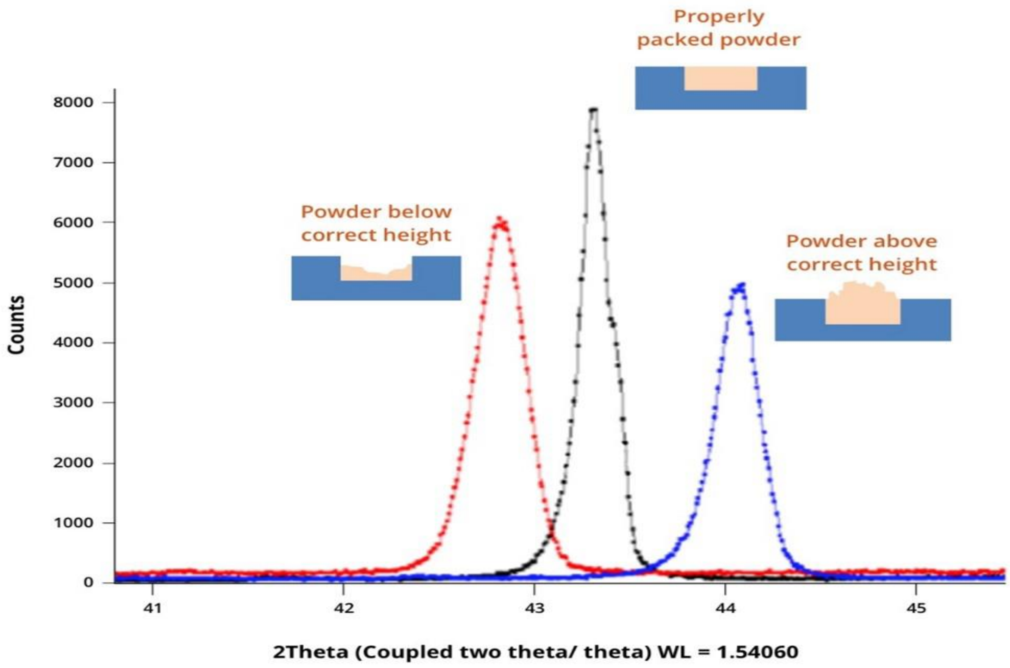


Figure 48: Effect of powder sample height on measurement accuracy.

5.10 Data Analysis

5.10.1 Identification of Sample Phases

Phase identification is the name we give to the process of determining the phases present in your material by analyzing the X-ray diffraction spectrum. This is sometimes called qualitative analysis because you are only determining what is present in your sample, but not in what quantity. Phase identification uses the position of the peaks, and their intensity, to determine what is present. This is done by comparing the peak positions with a known library of spectra. Most researchers are familiar with their materials and probably know the possible phases that may be present. However, if you have an unknown material or do not find what you are expecting, you must then search a database to try to find a match (ICDD, COD) [25]. To compare your experimental measurement, there are three main sources of diffraction spectra that you can use:

1. Commercial databases ICDD. International Centre for Diffraction Data.
2. Free online databases COD. Crystallography Open Database (crystallography.net /cod.).
3. Literature.

In many cases, materials that have been developed very recently do not exist in these databases; the best solution to identify these spectra is to use the original publication. Most publications provide the full XRD spectrum, which allows you to critically examine whether your results are in agreement with the authors' conclusions before proceeding.

5.10.2 Quantitative Analysis

Quantitative analysis refers to the use of the XRD DATA spectrum to extract quantitative data such as the grain size of the sample, the volume fraction of the phases present, or the parameters of the crystal lattice.

5.11 Factors Affecting the Intensity of XRD Peaks

In X-ray diffraction, the intensity of the peaks refers to the area under the peak, not the peak height. The intensity of a diffracted peak is determined by the following factors:

- ✓ The structure factor
- ✓ The multiplicity of the crystal plane
- ✓ The Lorentz and polarization factors
- ✓ The temperature factor

5.11.1 Structure Factor

The structure factor contains information about the locations of atoms within the crystal and determines whether their collective interference will generate a peak for each of the different crystal planes or not. [26]

If we take the case of body-centered cubic structures, the structure factor will be a positive integer for planes where the sum of the Miller indices is an even number but will be zero when h+k+l is odd. This means that for the BCC (body-centered cubic) phase, there are systematic absences in the diffraction pattern, and this is the usual distinguishing feature by which we identify BCC systems.

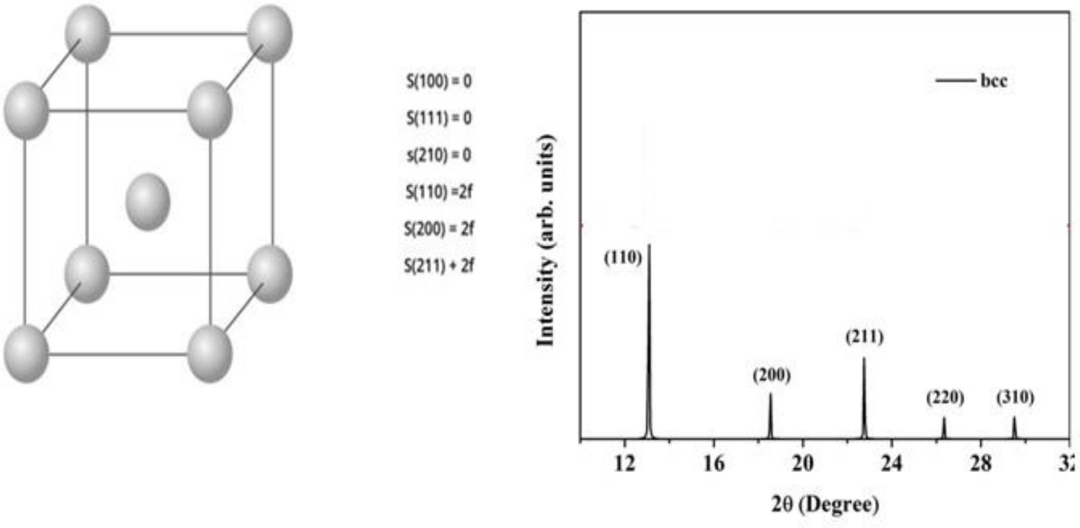


Figure 49: X-ray diffraction patterns for the body-centered cubic (BCC) structure

5.11.2 Multiplicity Factor

For many crystalline structures, particularly those with simple unit cells, there are several planes in the system sharing the same crystallography (in other words, if you observe the crystal from another angle, it will appear the same). An example of this was presented in the crystallography section. For instance, in a simple cubic system, there are six similar planes in the 100 family, just as there are six faces on a cube. In crystallographic notation, these equivalent planes have the Miller indices (100), (010), (001), (100), (010), and (001). In the cubic system, the 100 family of planes will have a multiplicity factor of 6. [27] In crystals with low symmetry, such as hexagonal and trigonal crystals, the multiplicities are generally lower. It is important to note that, for example, (100) is not simultaneously equivalent to (010) or (001) from a crystallographic point of view.

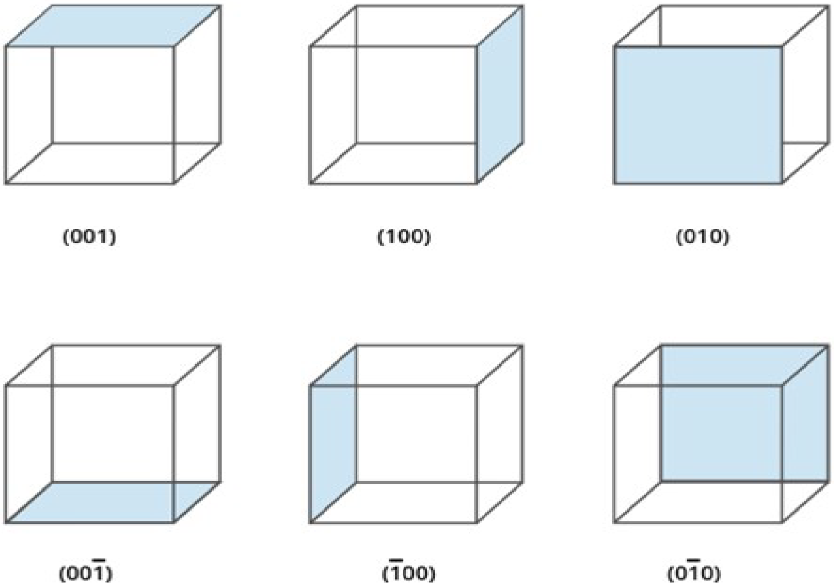


Figure 50: For the (100) family in the cubic system, there are 12 planes that are equivalent from a crystallographic point of view, so the multiplicity factor will be 12

5.11.3 Lorentz and Polarization Factors

The Lorentz and polarization factors relate to the various reasons why the diffracted intensity of a set of planes varies as a function of the 2θ angle. This includes geometric considerations, such as the fact that the number of crystals oriented to satisfy Bragg's law is greatest at small angles, and that the fraction of the diffraction cone that can intersect the detector is also largest at low angles. Polarization refers to the directional dependence of the scattered intensity. Typically, it is most significant in the orientation of the incident beam. The Lorentz and polarization factors are generally combined into the Lorentz factor. Polarization:

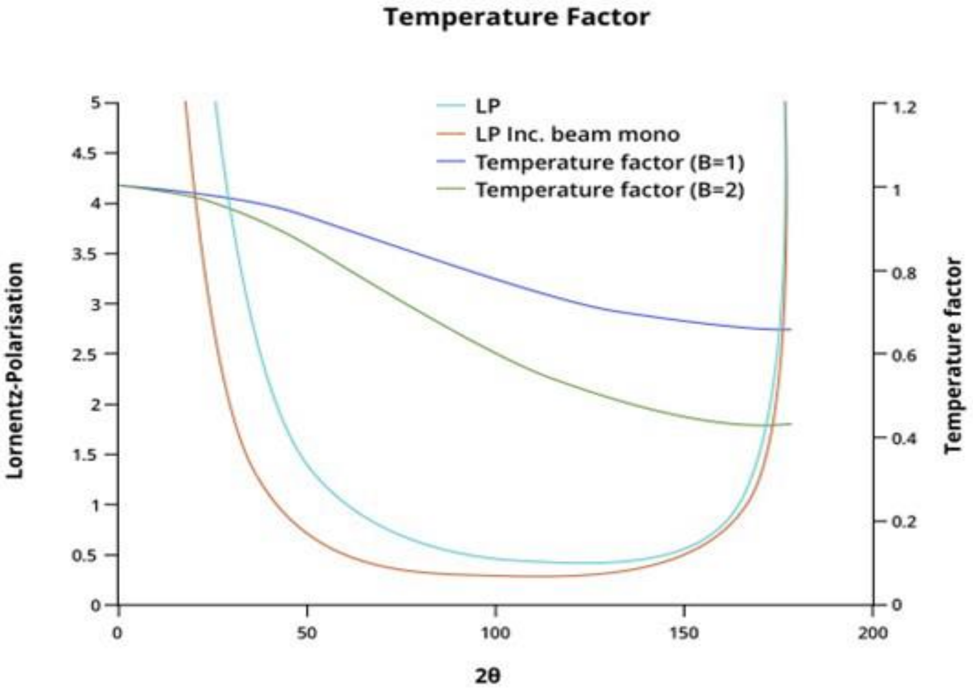


Figure 51: Influence of Lorentz and polarization factors on the diffracted intensity as a function of the 2θ angle.

5.11.4 Temperature factor

The diffracted intensity is affected (reduced) by atomic vibrations because the atoms within each plane are no longer in their "perfect" positions. The temperature factor is generally not the only contributor to variations in peak intensity; nevertheless, pattern fitting software often takes it into account. In the following equation, B represents the temperature factor and is generally between 0.5 and 1.5. It is also clear that temperature has the greatest effect at high 2θ angles and at short wavelengths. [28]

$$TF(\theta) = exp\ \{B(\sin\theta/\lambda)^2\}$$

5.11.5 Factors affecting peak width

Three factors contribute to peak broadening in the XRD instrument:

- Instrumental broadening
- Broadening due to grain size
- Broadening due to micro-strain (in proportion to dislocation density).

Instrumental broadening can be easily measured and simply subtracted from the measured peak width. However, if broadening is due to both strain and crystal size, it can be difficult to separate these effects. There are methods used to separate these effects; however, they are not always effective.

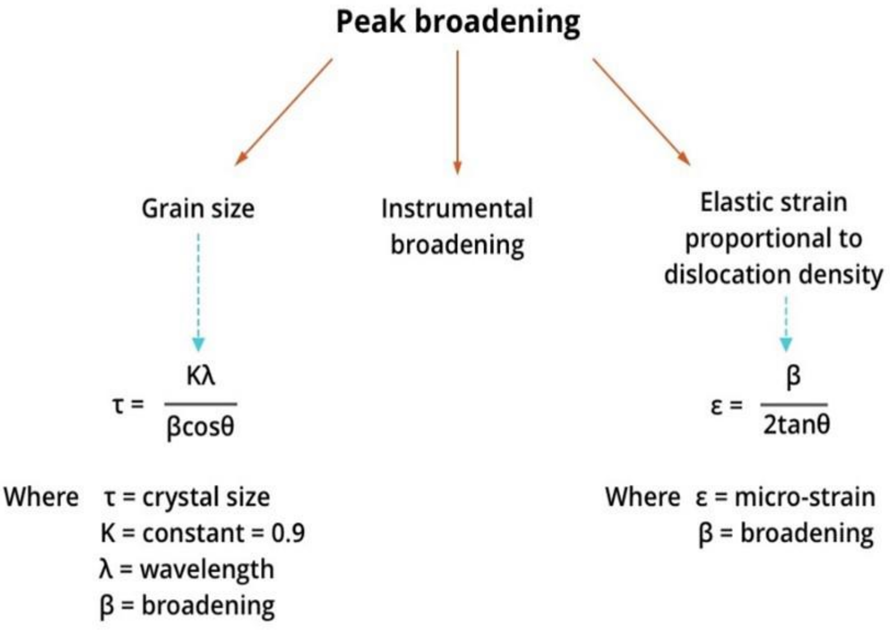


Figure 52: The different factors that influence peak width

5.12 Summary of Analysis Indices

5.12.1 The positions of the peaks indicate:

- The nature of the crystal system
- Symmetry of the space group
- Qualitative information regarding the phases

- Translational symmetry
- Unit cell dimensions

5.12.2 The shapes and widths of the peaks reveal:

- Crystallite size
- Extended defects (stacking faults, antiphase boundaries, etc.)
- Non-uniform microstrain

5.12.3 Limitations of powder diffraction:

- Single crystal-based methods use mathematical algorithms and specific peak intensities to determine structures.
- The 3D collection of points and intensities from a single crystal experiment is reduced to a one-dimensional (1D) pattern. This results in superposition and overlap of the peaks and complicates the precise determination of their intensities.

- Mixtures of multiple phases make the situation more complex.
- Crystal symmetry is not directly observable from the pattern
- Preferred orientation leads to inaccurate peak intensities.
- It should be emphasized that, to obtain satisfactory results in powder diffraction, the sample preparation must be carried out meticulously and accurately.

Quiz 1. This section focuses on Bragg's Law, the reciprocal lattice, and basic instrumentation.

1\.

According to Bragg's Law, $n\lambda=2d\sin\theta$, what does the variable 'd' specifically represent?

☐ A. The total thickness of the crystalline sample.
☐ B. The diameter of the individual atoms in the lattice.
☐ C. The distance between the X-ray source and the detector.
☐ D. The perpendicular distance between adjacent parallel planes of atoms.

2\.

Which transition in the Copper target is most commonly used to produce Kα radiation for laboratory XRD?

☐ A. An electron falling from the L-shell to the K-shell.

☐ B. Thermal vibration of the Copper nucleus.

☐ C. An electron falling from the M-shell to the K-shell.

☐ D. The ejection of an Auger electron from the valence band.

3.

What is the primary purpose of a 'filter' (such as Nickel for a Copper source) in a standard XRD experiment?

☐ A. To increase the intensity of the Kα signal.

☐ B. To remove Kβ radiation and produce a more monochromatic beam.

☐ C. To focus the X-ray beam onto a single point on the sample.

☐ D. To protect the operator from ionizing radiation.

4.

In the reciprocal lattice, what is the relationship between a real space vector a and the reciprocal vector a∗ ?

☐ A. They are always parallel and have the same magnitude.

☐ B. They are related by the square root of the unit cell volume.

☐ C. The reciprocal vector represents the time-domain equivalent of the lattice.

☐ D. The reciprocal vector is perpendicular to the plane formed by the other two real-space vectors.

5.

Which of the following describes a 'Unit Cell'?

☐ A. The external shape of a macroscopically grown crystal.

☐ B. The distance between the X-ray source and the sample.

☐ C. The smallest repeating volume that contains the full symmetry of the crystal.

☐ D. The individual atom located at the origin of the coordinate system.

6.

For a cubic crystal, if the Miller indices (hkl) increase, what happens to the interplanar spacing dhkl?

☐ A. The d-spacing decreases.

☐ B. The d-spacing increases linearly.

☐ C. The d-spacing becomes imaginary.

☐ D. The d-spacing remains constant.

7.

What does the Ewald Sphere construction help determine in crystallography?

☐ A. The exact chemical composition of the crystal.

☐ B. The melting point of the crystalline material.

☐ C. Which reciprocal lattice points satisfy the Bragg condition for a given orientation.

☐ D. The rate of crystal growth in a solvent.

8.

Which crystal system is characterized by $a \neq b \neq c$ and $\alpha=\gamma=90\neq \beta$?

☐ A. Orthorhombic

☐ B. Tetragonal

☐ C. Monoclinic

☐ D. Triclinic

9.

What is the result of 'Constructive Interference' in the context of XRD?

☐ A. A high-intensity diffraction peak.

☐ B. The complete cancellation of the X-ray signal.

☐ C. The transmutation of the sample into a different element.

☐ D. A change in the wavelength of the X-ray.

10.

The 'Atomic Scattering Factor' (ʃ) depends on which of the following?

☐ A. The pressure inside the X-ray tube.

☐ B. The number of electrons in the atom and the scattering angle.

☐ C. The magnetic field strength of the laboratory.

☐ D. The color of the crystal under visible light.

Solution(D.A.B.D.C.A.C.C.A.B)

Quiz 2. This section explores the Structure Factor, temperature factors, and factors affecting peak shape.

1.

The Structure Factor F_{hkl} is the summation of the scattering contributions from all atoms in the unit cell. What does $|F_{hkl}|^2$ represent?

☐ A. The total volume of the unit cell.

☐ B. The number of atoms in the crystal lattice.

☐ C. The intensity of the diffraction peak (ignoring Lorentz-Polarization factors).

☐ D. The phase angle of the diffracted wave.

2.

What effect does increasing the 'Temperature Factor' (or Displacement Parameter, B) have on the XRD pattern?

☐ A. It results in the appearance of 'forbidden' reflections.
☐ B. It increases the resolution of the diffraction pattern.
☐ C. It causes the peaks to shift to lower 2θ positions without changing intensity.
☐ D. It causes peak intensities to decrease, especially at higher 2θ angles.

3.

In a Body-Centered Cubic (BCC) lattice, which of the following reflections would be systematically absent (forbidden)?

☐ A. (110)
☐ B. (222)
☐ C. (200)
☐ D. (100)

4.

What is 'Anomalous Dispersion' in crystallography?

☐ A. The loss of signal due to sample fluorescence.
☐ B. The bending of X-rays as they pass through a glass lens.
☐ C. The random orientation of crystallites in a powder.
☐ D. The change in scattering factor when the X-ray energy is near an absorption edge of an atom.

5.

Why is the 'Phase Problem' the central challenge in structure determination by XRD?

☐ A. The phase of an X-ray changes to zero once it hits the crystal.
☐ B. Phases vary randomly for every atom in the cell.
☐ C. X-rays move too fast for the phase to be recorded.
☐ D. Detectors only measure intensity, losing information about the wave's phase.

6.

In Rietveld refinement, what is the 'Background' typically modeled by?

☐ A. Polynomial functions or Chebyshev series.
☐ B. The Bragg equation.
☐ C. A straight line set at zero intensity.
☐ D. The number of atoms in the unit cell.

Solution(C.D.D.D.D.A)

Quiz 3. This methodology section focuses on systematic absences, point groups, and Friedel's Law.

1.

Which of the following is the first step in determining a space group from diffraction data?

☐ A. Assigning the chemical formula to each atom.

☐ B. Measuring the melting point of the crystal.

☐ C. Indexing the reflections to determine the unit cell and Bravais lattice.

☐ D. Solving the phase problem using direct methods.

2.

What do 'Systematic Absences' in 0kl reflections (e.g., k must be even) typically indicate?

☐ A. The presence of a Center of Inversion.

☐ B. The presence of a Glide Plane.

☐ C. The crystal is a liquid crystal.

☐ D. The X-ray source is too weak.

4.

A systematic absence in the h00 reflections (where h must be 2n) indicates which symmetry element along the a-axis?

☐ A. A Mirror Plane.

☐ B. A C-centered Bravais lattice.

☐ C. An inversion center at (0,0,0).

☐ D. A 21 Screw Axis.

5.

If a crystal belongs to the 'Orthorhombic' system and its reflections show the condition h+k=2n for all (hkl), what is the Bravais lattice?

☐ A. C-centered (C)

☐ B. Primitive (P)

☐ C. Face-centered (F)

☐ D. Body-centered (I)

6.

The 'Laue Class' of a crystal is determined by which of the following?

☐ A. The color of the spots on the detector.

☐ B. The symmetry of the diffraction intensities (point group plus an inversion center).

☐ C. The number of molecules in the unit cell (Z).

☐ D. The speed at which the crystal rotates during data collection.

7.

How many 3D Space Groups exist in total?

☐ A. 230

☐ B. 7

☐ C. 32

☐ D. 14

8.

When two space groups have the same systematic absences but different point group symmetries, they are called:

☐ A. Bravais twins.

☐ B. Enantiomorphous pairs (sometimes) or non-distinguishable by absences alone.

☐ C. Isomers.

☐ D. Polymorphs.

9.

Which tool is most commonly used by crystallographers to look up space group symmetry and systematic absences?

☐ A. The Periodic Table of Elements.

☐ B. The Dictionary of Organic Compounds.

☐ C. International Tables for Crystallography, Volume A.

☐ D. The Merck Index.

Solution(C.B.D.A.B.A.B.C)

6 Bibliographical references

[1] EYRAUD (C.) et ACCARY (A.). – Analyses thermique et calorimétrique différentielles. Traité Analyse et caractérisation, P 1 295, 7-1992. Techniques de l'Ingénieur.

[2] DONTH (E.J.). – Relaxations and thermodynamics in polymers **-** Glass transition. Akademie Verlag GbmH, Berlin 1992.

[3] WUNDERLICH (B.). – Thermal analysis. Acad. Press Inc., Londres 1990.

[4] KOVACS (A.J.). – A multiparameter approach for structural recovery of glasses and its implication for their physical properties. Ann. N.Y. Acad. Sci. 371, p. 38, 1981.

[5] BIROS (J.), LARINA (T.), TREKOVAL (J.) et POUCHY (J.). – Dependence of the glass transition temperature of poly(methylmethacrylates) on their tacticity. Coll & Polym. Sci. 260, p. 27, 1982.

[6] MacKNIGHT (W.J.), KARASZ (F.E.) et FRIED (J.R.). – Solid state transition behavior of blends, dans Polymer Blends, chap. 5, vol. I. Éd. D.R. Paul, S. Newman, Acad. Press Inc., N.Y. 1978.

[7] SCHNEIDER (H.A.) et Di MARZIO (E.A.). – The glass transition temperature of polymer blends : comparison of both the free volume and the entropy predictions with data. Polymer 33, p. 3 453, 1992.

[8] COUCHMAN (P.R.). – Thermodynamics of the compositional variation of glass transition temperatures. Macromolecules 20, p. 1 712, 1987.

[9] Di BENEDETTO (A.T.) et DILANDRO (L.). – Correlation of glass transition temperature and molecular weight : A model based on the principle
of corresponding states. J. Polym. Sci.; Phys. Ed. 27, p. 1 405, 1989.

[10] ELIAS (H.S.). – Macromolecules. vol. I, chap. 9, Plenum Press, N.Y. 1977.

[11] WUNDERLICH (B.). – Macromolecular physics. Crystal melting. vol. III, Acad. Press, N.Y.1980.

[12] CHOI (C.H.). – Contribution à l'étude de la cristallisation et des transitions du poly(fluorure de vinylidène) et de quelques copolymères. Thèse, université Lyon I, 1989.

[13] TANAKA (H.), YUKAWA (H.) et NISHI (T.). – Effect of crystallization conditions on the ferroelectric phase transition in vinylidene fluoride / trifluoroethylene copolymers. Macromolecules 21, p. 2 469, 1988.

[14] HODGE (I.M.). – Enthalpy relaxation recovery in amorphous polymers. J. Non Cryst. Solids 169, p. 211-266, 1994.

[15] WUNDERLICH (B.) and GREBOWICZ (J.). – Thermotropic mesophases and mesophase transitions of linear, flexible, macromolecules. Adv. Polym. Sci. 60/61, p. 1-59, 1984.

[16] TEYSSÈDRE (G.), GRIMAU (M.), BERNES (A.), MARTINEZ (J.J.) et LACABANNE (C.). – a-relaxation / retardation mode in semicrystalline polymers with flexible chains. Polymer 35, p. 4 397, 1994.

[17] HAMMER (C.F.). – Polymeric plasticizers. Dans Polymer Blends, chap. 17, vol. II, 1978. Éd. D.

[18] Cullity, B. D., & Stock, S. R. (2001). Elements of X-ray Diffraction (3e. ed.). Addison-Wesley.

[19] Wilson, A. J. C. (Ed.). (1987). International Tables for Crystallography, Volume C : Mathematical, Physical and Chemical Tables. Kluwer Academic Publishers.

[20] Pecharsky, V. K., & Zavalij, P. Y. (2009). Fundamentals of Powder Diffraction and Structural Characterization of Materials (2 ed.). Springer.

[21] Powder Diffraction File (PDF) Database. (2023). International Centre for Diffraction Data (ICDD).

[22] International Union of Crystallography (IUCr). (2023). IUCr Journals : Acta Crystallographica. Disponible sur : https ://journals.iucr.org/

[23] International Union of Crystallography (IUCr). (2023). IUCr Journals : Acta Crystallographica. Disponible sur : https ://journals.iucr.org/

[24] Shi, X., & Kablitz, C. (2017). Advances in X-ray Diffraction for Nanomaterials Characterization. Journal of Nanomaterials Research, 12(4), 89–98.

[25] Harrison,W. A. (1989). Electronic Structure and the Properties of Solids : The Physics of the Chemical Bond. Dover Publications.

[26] Balzar, D. (1999). Voigt-function model in diffraction line-broadening analysis. Dans Defect and Microstructure Analysis by Diffraction (pp. 94–126). Oxford University Press.

[27] Reimers, J. N. (2000). Practical X-ray Powder Diffraction. Materials Characterization, 45(1), 11–26.

[28] Chien, C. L. (2007). The Physics of Magnetic Thin Films. Dans Shenoy, G. K., & Krishnan, K. M. (Eds.), Frontiers in Magnetic Materials (pp. 289–301). Springer.