Thermogravimetric Analysis and Calorimetry (Mexico)

Data Interpretation in TGA and DSC

Acrylamide – a low-molecular-weight polymer precursor. Related terms: Polymerization, thermal degradation. In TGA it shows a distinct mass loss around 150 °C due to volatilization. DSC may reveal an endothermic peak corresponding to the loss of bound water. Challenges include overlapping signals from moisture.

Activation Energy (E_a) – the minimum energy required for a reaction to proceed. Related terms: Arrhenius equation, kinetic analysis. Determined from TGA using methods such as Kissinger or Ozawa. Example: A polymer with $E_a \approx 180\,kJ\,mol^{-1}$ degrades at higher temperatures. Accurate baseline correction is essential.

Baseline Correction – the process of removing instrument drift and background signals. Related terms: Reference run, data preprocessing. In DSC, a flat baseline allows precise enthalpy integration. In TGA, a corrected baseline reveals true mass loss. Improper correction leads to systematic errors.

Calorimetric Sensitivity – the smallest detectable heat flow change. Related terms: Resolution, signal-to-noise ratio. High sensitivity DSC can detect glass transitions of amorphous polymers. Trade-off: Increased sensitivity may amplify noise, requiring smoothing algorithms.

Carboxyl Group – a functional group (-COOH) prone to decarboxylation. Related terms: Thermal decomposition, CO_2 evolution. In TGA, a mass loss step around 200–250 °C often corresponds to CO_2 release. DSC may show an exothermic peak if decarboxylation is coupled with oxidation.

Coefficient of Thermal Expansion (CTE) – the fractional change in dimension per degree temperature change. Related terms: Dilatometry, thermal strain. DSC can indirectly assess CTE through heat flow associated with volume change. Accurate CTE data assist in designing composite materials.

Complex Viscosity – the resistance to flow in viscoelastic materials. Related terms: Rheology, melt flow index. Though not directly measured by TGA/DSC, changes in complex viscosity manifest as shifts in glass transition temperature (Tg) observed in DSC.

Conductivity – ability of a material to transport electric charge. Related terms: Ionic conductivity, dielectric loss. DSC can detect conductivity-related transitions via changes in heat capacity. TGA may identify loss of conductive additives by mass loss.

Conversion – the fraction of reactant that has transformed into product. Related terms: Degree of cure, reaction progress. In DSC, integration of the exothermic cure peak yields conversion. In TGA, mass loss can be correlated to conversion for degradable systems.

Cooling Rate – the speed at which temperature is decreased during a DSC run. Related terms: Quench, thermal lag. Faster cooling suppresses crystallization peaks, revealing the glass transition more clearly. However, high rates may cause instrument overshoot.

Decomposition Temperature (T_d) – the temperature at which a material begins to break down chemically. Related terms: Onset temperature, thermal stability. Determined from the first derivative of the TGA curve (DTG). For a polyester, T_d ≈ 350 °C indicates suitability for high-temperature applications.

Derivative Thermogravimetry (DTG) – the first derivative of mass versus temperature. Related terms: TG, mass loss rate. Peaks in DTG correspond to distinct degradation steps. Example: A biopolymer shows two DTG peaks at 250 °C and 320 °C, indicating sequential decomposition.

Differential Scanning Calorimetry (DSC) – a technique measuring heat flow difference between sample and reference. Related terms: Heat capacity, enthalpy. Provides Tg, melting point (Tm), crystallization temperature (Tc). Accurate interpretation requires baseline matching and proper reference material.

Dynamic Mechanical Analysis (DMA) – measures mechanical response under oscillatory stress. Related terms: Storage modulus, loss modulus. While not a TGA/DSC method, DMA data complement thermal analysis by linking Tg to mechanical softening.

Enthalpy (ΔH) – heat absorbed or released during a transition. Related terms: Exothermic, endothermic. In DSC, the area under a peak equals ΔH. For a polymer melt, $\Delta H \approx 70\,J\,g^{-1}$ reflects crystallinity. Correct integration demands proper baseline subtraction.

Equilibrium Moisture Content – the moisture level a material attains under specific temperature/humidity. Related terms: Hygroscopicity, sorption isotherm. TGA can quantify moisture by a low-temperature mass loss (Eutectic Point – composition where the lowest melting temperature occurs for a mixture. Related terms: Phase diagram, solidus. DSC detects eutectic melting as a sharp peak at a temperature lower than the pure components. Interpretation helps in alloy design.

Exothermic Peak – a downward deflection in DSC indicating heat release. Related terms: Crystallization, oxidation. Example: Curing of epoxy resin produces an exothermic peak around 180 °C. Overlapping exotherms require deconvolution techniques.

Furnace Atmosphere – the gas composition surrounding the sample during TGA/DSC. Related terms: Inert gas, oxidative environment. Nitrogen prevents oxidation, while air promotes it, shifting degradation temperatures. Selecting atmosphere influences kinetic parameters.

Glass Transition Temperature (Tg) – the temperature where an amorphous material transitions from glassy to rubbery. Related terms: Heat capacity jump, amorphous phase. DSC shows Tg as a step change in heat flow. Accurate Tg determination may require modulated DSC for weak transitions.

Heat Flow – rate of thermal energy transfer per unit time. Related terms: Power, calorimetry. DSC records heat flow as $\mu W\,mg^{-1}$. Positive heat flow denotes endothermic events; negative denotes exothermic. Calibration with sapphire ensures quantitative accuracy.

Heating Rate – the speed of temperature increase during a run. Related terms: Ramp, isothermal hold. Faster rates shift TGA/DSC peaks to higher temperatures (thermal lag). Kinetic analysis often employs multiple heating rates to calculate activation energy.

Isothermal Hold – a period where temperature is held constant. Related terms: Isothermal DSC, kinetic monitoring. Useful for studying cure kinetics; the heat flow decays as the reaction progresses. In TGA, an isothermal hold can reveal steady-state mass loss rates.

Kinetic Model – mathematical description of reaction rate vs. Conversion. Related terms: Nth-order, autocatalytic. Common models include first-order degradation and Kamal-Sourour cure kinetics. Selecting an appropriate model is critical for reliable prediction.

Kissinger Method – a technique to estimate activation energy from peak temperatures at different heating rates. Related terms: Linearization, Arrhenius plot. Plotting $\ln(\beta/T_p^2)$ versus $1/T_p$ yields a straight line; slope = $-E_a/R$. Requires at least three heating rates for robustness.

Lag Time – the delay between programmed temperature and actual sample temperature. Related terms: Thermal inertia, response time. Significant lag can distort TGA/DSC peak positions, especially at high heating rates. Calibration with standard materials minimizes lag effects.

Mass Loss (%) – the percentage reduction in sample weight during TGA. Related terms: Residual mass, decomposition yield. A 5 % loss at 100 °C often indicates moisture; a 30 % loss at 400 °C may correspond to polymer chain scission. Reporting both absolute and relative loss improves comparability.

Modulated DSC (MDSC) – DSC technique superimposing a sinusoidal temperature modulation onto the linear ramp. Related terms: Reversing heat flow, non-reversing heat flow. Allows separation of overlapping thermal events, such as distinguishing Tg (reversing) from relaxation (non-reversing). Requires careful selection of modulation amplitude and period.

Oxidative Degradation – breakdown of material in the presence of oxygen. Related terms: Combustion, char formation. TGA in air shows lower onset temperatures compared to inert atmosphere. DSC may display exothermic peaks due to oxidation of degradation products. Protective atmospheres are essential for intrinsic stability assessment.

Peak Temperature (T_p) – the temperature at which a TGA or DSC peak reaches its maximum. Related terms: Onset temperature, apex. In TGA, T_p of the main degradation step often correlates with the material's thermal resistance. In DSC, T_p of melting indicates the most stable crystal form.

Polymorphic Transition – change between different crystal structures of the same compound. Related terms: Polymorph, solid-state transformation. DSC detects such transitions as subtle endothermic or exothermic peaks. Recognizing polymorphism is vital for pharmaceuticals where bioavailability depends on crystal form.

Reference Material – a standard sample used for calibration. Related terms: Sapphire, indium. Sapphire provides a reliable heat capacity standard for DSC calibration. Calibration ensures that measured enthalpies are traceable to SI units.

Residual Mass – the amount of sample remaining after a TGA run, expressed as % of initial mass. Related terms: Char yield, ash content. High residual mass may indicate inorganic fillers or formation of stable carbonaceous char. Interpreting residual mass helps identify filler content.

Rheology – study of flow and deformation. Related terms: Viscosity, shear rate. Though not directly measured by TGA/DSC, rheological data complement thermal analysis by linking Tg to melt viscosity, informing processing windows.

Sample Preparation – steps taken to ready material for analysis. Related terms: Grinding, pan selection. For TGA, a typical sample mass is 5–10 mg in an alumina pan; for DSC, 2–10 mg in a hermetic pan. Inconsistent preparation introduces reproducibility issues.

Scanning Rate – synonymous with heating rate in DSC/TGA. Related terms: Ramp speed, temperature program. Selecting an appropriate scanning rate balances resolution (low rates) against experimental time (high rates). Kinetic parameters derived from multiple scanning rates improve reliability.

Second-Order Kinetics – reaction rate proportional to the square of the concentration of one reactant or product of two reactants. Related terms: Autocatalytic, reaction order. In TGA, many polymer degradations follow second-order kinetics, reflected in the curvature of the DTG plot. Accurate modeling may require numerical integration.

Signal-to-Noise Ratio (SNR) – measure of signal strength relative to background fluctuations. Related terms: Noise floor, data quality. High SNR in DSC enables detection of weak transitions like subtle glass transitions. Signal averaging and proper shielding improve SNR.

Specific Heat Capacity (Cp) – amount of heat required to raise temperature of unit mass by one degree. Related terms: Calorimetry, thermodynamic property. DSC directly measures Cp changes; a step in Cp indicates Tg. Quantitative Cp values aid in thermodynamic modeling of processes.

Standard Deviation (σ) – statistical measure of data spread. Related terms: Reproducibility, error analysis. Reporting σ of replicate TGA/DSC measurements conveys method precision. Large σ may signal instrument drift or inconsistent sample handling.

Thermal Gravimetric Analyzer (TGA) – instrument that records mass change as temperature varies. Related terms: Thermogravimetry, mass loss. Provides degradation onset, decomposition steps, and residual mass. Coupling with FTIR or MS enables evolved gas analysis for mechanistic insight.

Thermal Lag – delay between furnace temperature and actual sample temperature. Related terms: Response time, heat transfer. Causes apparent shift of TGA/DSC peaks to higher temperatures, especially at high heating rates. Compensation algorithms or low-rate scans mitigate lag.

Thermal Stability – resistance of a material to chemical change at elevated temperatures. Related terms: Degradation temperature, lifetime. Assessed by TGA onset temperature and DSC exotherm absence. Materials with $T_d > 500\,°C$ are considered highly stable for aerospace use.

Thermogravimetric Curve (TG) – plot of mass versus temperature or time. Related terms: DTG, mass loss profile. Interpretation involves identifying plateaus (stable regions) and slopes (degradation zones). Multi-step TG curves suggest complex composition.

Thermodynamic Equilibrium – state where macroscopic properties remain constant over time. Related

terms: Gibbs free energy, reversible process. DSC can approach equilibrium by using very low heating rates or modulated techniques, producing sharper transitions.

Time-Temperature Superposition (TTS) – principle allowing prediction of material behavior over a wide time scale from short-term data. Related terms: Master curve, shift factor. DSC Tg data at various heating rates feed into TTS to estimate long-term stability.

Transition Enthalpy (ΔH_tr) – heat absorbed during a phase change such as melting. Related terms: Latent heat, fusion enthalpy. Measured by integrating the DSC melting peak; ΔH_tr correlates with crystallinity for semi-crystalline polymers.

Ultra-High-Resolution TGA – instrument capable of detecting sub-nanogram mass changes. Related terms: Microbalance, nanogram sensitivity. Enables study of low-loading additives or surface adsorbates. Requires vibration isolation and temperature stability.

Volatile Organic Compounds (VOCs) – low-molecular-weight species that evaporate at moderate temperatures. Related terms: Outgassing, off-gassing. TGA detects VOC release as early mass loss; DSC may show a small endothermic peak. Quantifying VOCs is critical for indoor-air quality assessments.

Weight Percent (wt %) – proportion of a component expressed as mass fraction of the total. Related terms: Composition, concentration. In TGA, wt % loss provides quantitative degradation data. For a filler-polymer composite, a 20 wt % filler leads to a residual mass of ~20 % after polymer burnout.

Zero-Shift Calibration – aligning instrument temperature readout to a known reference point. Related terms: Temperature offset, standard. Performed using a melting point standard (e.G., Indium). Accurate zero-shift reduces systematic temperature errors across the entire run.

Zero-Order Kinetics – reaction rate independent of reactant concentration. Related terms: Constant rate, linear mass loss. In TGA, a linear mass loss segment suggests zero-order degradation, often observed in uniform polymer chain scission under constant heating.

Absorption Peak – a feature in DSC where heat flow increases due to endothermic transition. Related terms: Peak area, enthalpy. The melting of a crystalline polymer appears as an absorption peak. Deconvolution of overlapping peaks can separate polymorphic contributions.

Adiabatic DSC – DSC mode where heat generated or absorbed is not exchanged with the environment. Related terms: Self-heating, runaway reaction. Useful for studying highly exothermic polymerizations; the temperature rise provides kinetic insight. Requires careful safety assessment.

Atmospheric Pressure – pressure of surrounding gas, typically 1 atm. Related terms: Vacuum, pressure-controlled TGA. Lowering pressure in TGA reduces oxygen availability, shifting oxidative degradation to higher temperatures. Pressure variations can also affect volatile evaporation rates.

Back-calculation – method of estimating kinetic parameters from experimental data. Related terms: Model fitting, regression analysis. In TGA, back-calculating activation energy from DTG curves yields values comparable to Kissinger method. Accuracy depends on data quality and model choice.

Carbonaceous Char – residual solid carbon formed during pyrolysis. Related terms: Char yield, pyrolysis. In TGA, a high residual mass (>30 wt %) often indicates char formation, beneficial for flame-retardant applications. DSC may show an exothermic char-formation peak.

Crystallinity – fraction of material that is crystalline. Related terms: X-ray diffraction, melting enthalpy. Determined from DSC by comparing ΔH_tr to the enthalpy of a 100 % crystalline reference. For polyethylene, $\Delta H_{tr} \approx 290\ J\ g^{-1}$ corresponds to 100 % crystallinity.

Deconvolution – mathematical separation of overlapping thermal events. Related terms: Peak fitting, Gaussian/Lorentzian. Applied to DSC curves with multiple melting peaks to quantify individual polymorph contributions. Requires software and appropriate baseline selection.

Desorption – removal of adsorbed species from a surface. Related terms: Outgassing, surface cleaning. TGA detects desorption as a low-temperature mass loss, often below 150 °C. Distinguishing desorption from moisture loss may involve pre-drying or inert atmosphere runs.

Dynamic Heating – continuous temperature increase during a run. Related terms: Ramp, non-isothermal. Most TGA/DSC experiments use dynamic heating to identify transition temperatures quickly. However, dynamic conditions can mask slow processes that require isothermal holds.

Evolved Gas Analysis (EGA) – technique coupling TGA with spectroscopic detection of gases. Related terms: FTIR, mass spectrometry. Provides chemical identity of volatiles released at each mass loss step. For a polymer, EGA may reveal CO_2, H_2O, and aromatic fragments, aiding mechanistic interpretation.

Exothermic Reaction – process that releases heat to the surroundings. Related terms: Heat release, combustion. In DSC, exotherms appear as downward deflections. Polymer curing and oxidative degradation are common exothermic processes observed in thermal analysis.

Filler Content – proportion of inorganic or organic particles added to a polymer matrix. Related terms: Reinforcement, composite. TGA quantifies filler by residual mass after polymer burnout; DSC may show reduced heat capacity due to filler dilution. Accurate filler quantification informs mechanical property predictions.

Glass Transition Step – the incremental change in heat flow at Tg. Related terms: Cp step, baseline shift. In DSC, the step height (ΔCp) correlates with polymer chain mobility. Small ΔCp may indicate partial crystallinity or cross-linking constraints.

Inert Gas – non-reactive atmosphere such as nitrogen or argon. Related terms: Purge, nitrogen flow. Prevents oxidation during TGA, allowing assessment of intrinsic thermal stability. Choice of inert gas can influence heat transfer and baseline stability.

Isoconversional Method – kinetic analysis technique that does not assume a reaction model. Related terms: Flynn-Wall–Ozawa, Kissinger-Akahira-Sunose. Calculates activation energy as a function of conversion from TGA data at multiple heating rates. Provides insight into changing mechanisms during degradation.

Lag Correction – adjustment applied to account for thermal lag. Related terms: Temperature offset,

response factor. Implemented in software by aligning known standard peaks with measured peaks. Essential for high-rate TGA/DSC to obtain true transition temperatures.

Mass Spectrometry (MS) – analytical technique detecting ionized fragments of gases. Related terms: EGA, ion detector. Coupled with TGA, MS identifies molecular weight of evolved species, clarifying degradation pathways. For a nylon sample, MS may reveal caprolactam fragments.

Modulation Frequency – rate at which temperature oscillates in MDSC. Related terms: Period, amplitude. Higher frequencies improve resolution of reversing heat flow but may suppress slow non-reversing processes. Optimization balances sensitivity and separation capability.

Multiple-Heating-Rate (MHR) Analysis – approach using several heating rates to extract kinetic parameters. Related terms: Isoconversional, linear regression. Provides robust activation energy values and validates reaction models. Requires consistent sample mass and atmosphere across runs.

Peak Deconvolution – process of fitting multiple mathematical functions to a composite DSC peak. Related terms: Gaussian fitting, baseline subtraction. Enables quantification of overlapping melting or crystallization events, essential for polymorphic systems such as poly(ethylene terephthalate).

Polymerization Degree (DP) – number of repeat units in a polymer chain. Related terms: Molecular weight, chain length. Higher DP often shifts TGA degradation to higher temperatures and raises DSC Tg. Monitoring DP via thermal analysis aids in quality control.

Pre-Exponential Factor (A) – frequency factor in Arrhenius equation. Related terms: Kinetic parameters, rate constant. Obtained from linearized kinetic plots; large A values indicate frequent successful collisions. Complementary to activation energy for complete kinetic description.

Reversible Heat Flow – portion of DSC signal that follows the temperature modulation. Related terms: MDSC, heat capacity. Represents equilibrated processes like Tg; integration yields ΔCp. Non-reversible heat flow corresponds to kinetic events such as crystallization.

Residual Stress – internal stresses locked in a material after processing. Related terms: Annealing, relaxation. DSC can detect stress release as an exothermic shoulder near Tg. Understanding residual stress helps prevent cracking during thermal cycling.

Runaway Reaction – uncontrolled exothermic process leading to rapid temperature rise. Related terms: Adiabatic DSC, safety. Detected in DSC as a sharp, large exotherm with a steep temperature increase. Proper instrument safeguards and low sample mass mitigate risk.

Sample Pan – container holding the material during analysis. Related terms: Crucible, sealed pan. Choice of pan material (aluminum, platinum) influences heat transfer and reactivity. Sealed pans prevent loss of volatile components, improving mass balance in TGA.

Scanning Calorimetry – generic term for DSC measurement. Related terms: Heat flow, temperature program. Provides thermal transitions with high sensitivity. Distinguishes between endothermic and exothermic events, essential for polymer characterization.

Secondary Decomposition – degradation occurring after the primary mass loss. Related terms: Char oxidation, post-cure. In TGA, appears as a second DTG peak at higher temperature. DSC may show a weak exotherm due to oxidation of char residues.

Thermal Conductivity – ability of a material to conduct heat. Related terms: Diffusivity, Fourier's law. Influences temperature uniformity within the sample pan; low conductivity can cause internal temperature gradients, affecting DSC peak shape.

Thermal Lag Compensation – algorithmic correction for temperature delays. Related terms: Lag correction, software. Adjusts recorded temperature to reflect true sample temperature, improving accuracy of kinetic parameters derived from TGA/DSC.

Thermal Runaway – uncontrolled temperature increase due to exothermic reaction surpassing heat removal capacity. Related terms: Safety, adiabatic DSC. In polymer curing, DSC can predict onset of runaway by monitoring heat flow acceleration. Proper experimental design limits this risk.

Time Constant – characteristic time for system to respond to a temperature change. Related terms: Response time, thermal inertia. Short time constants yield sharper peaks but may increase noise. Instrument manufacturers specify time constants for optimal operation.

Temperature Calibration – process of aligning instrument temperature readout with known standards. Related terms: Melting point standards, calibration curve. Regular calibration with indium (156.6 °C) and zinc (419.5 °C) ensures reliable TGA/DSC data across the measurement range.

Thermal Decomposition Pathway – sequence of chemical reactions leading to mass loss. Related terms: Mechanism, intermediate species. Combined TGA-EGA-MS studies map pathways, revealing steps such as depolymerization, cross-link scission, and char formation. Knowledge guides material design for improved stability.

Thermal Event – any observable change in heat flow or mass during analysis. Related terms: Transition, reaction. Includes melting, crystallization, glass transition, cure, oxidation, and volatilization. Precise identification requires correlation of DSC and TGA data.

Thermal Stability Index (TSI) – numerical rating derived from degradation temperature. Related terms: T_d, performance rating. Calculated as T_d – 10 °C for a given heating rate; higher TSI indicates better high-temperature performance. Used for material selection in aerospace and automotive sectors.

Thermogravimetric Differential Scanning Calorimetry (TG-DSC) – simultaneous measurement of mass change and heat flow. Related terms: Coupled analysis, hybrid instrument. Enables correlation of exothermic events with corresponding mass loss, providing comprehensive degradation insight. For a composite, TG-DSC can separate filler loss from polymer curing heat.

Transition Temperature – temperature at which a material undergoes a phase change. Related terms: Tg, Tm, Tc. Determined from DSC as the peak maximum (melting) or step midpoint (glass transition). Accurate identification aids in processing temperature selection.

Vapor Pressure – pressure exerted by a volatile component at a given temperature. Related terms: Evaporation, TGA loss. High vapor pressure compounds disappear early in TGA, producing a low-temperature mass loss. DSC may show a corresponding endothermic peak if vaporization is endothermic.

Zero-Offset – constant temperature deviation between instrument reading and actual temperature. Related terms: Calibration, temperature error. Corrected by measuring a known melting point and adjusting the temperature scale. Uncorrected zero-offset leads to systematic shift of all transition temperatures.