

M5052
CHARACTERIZATION OF MATERIALS AND NANOMATERIALS
Graduate Program in Nanotechnology

THERMAL ANALYSIS METHODS
TGA, DTA, DSC



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THERMAL ANALYSIS

A group of techniques in which a physical property of a substance (or reaction products) is measured as a function of temperature

The substance is subjected to a controlled temperature program

TGA

Thermogravimetric
Analysis

DTA

Differential Thermal
Analysis

DSC

Differential Scanning
Calorimetry

DMA

Dynamical Mechanical
Analysis

TMA

Thermo Mechanical
Analysis



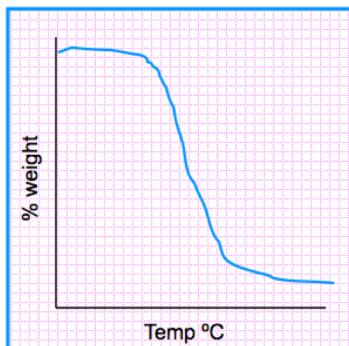
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TGA:

THERMOGRAVIMETRIC ANALYSIS

- Changes in mass of a sample measured continuously as a function of temperature and time



- The data is plotted in a thermogram
 - Graph of mass (or weight%) vs temperature
 - Weight vs. time can be plotted too
 - $\%wt v. t$ is more useful if temperature (T) ramp is not linear
- TGA is mainly quantitative
 - Can be qualitative in some cases
- Simple, yet versatile and powerful technique



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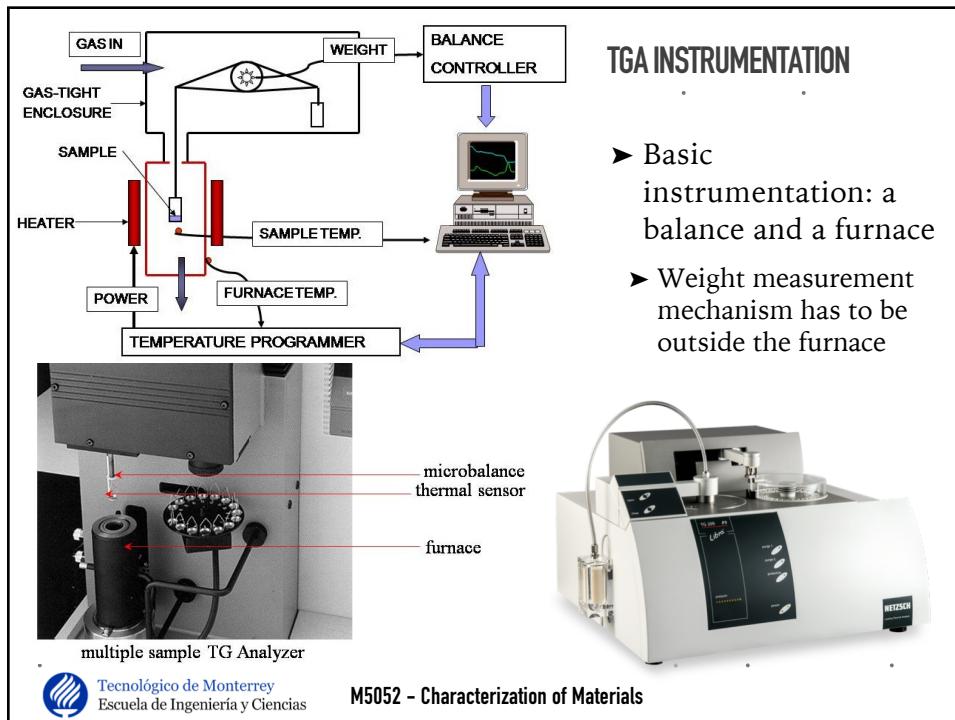
TGA: FUNDAMENTAL PRINCIPLES

- TGA was initially developed to determine the stability and temperature composition dependence of inorganic precipitates
- Currently is a widely used technique and lots of different samples can be analyzed
- Process that occur in TGA
 - Humidity loss
 - Loss of water of crystallization
 - Chemical decomposition
 - Pyrolysis in inert atmosphere
 - Oxidation
 - Loss or gain in weight
 - Other reactions (depending on the atmosphere used)



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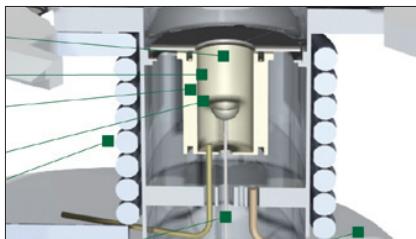


TYPICAL TGA EXPERIMENTAL PARAMETERS

- Initial sample weight: 1–100 mg
- Typical volumes of 40 μL to 500 μL
- Typical heating rate: 5–10 $^{\circ}\text{C}/\text{min}$
- Heating can also be much faster, depending on the instrument
 - Can be as high as 200 K/min, and as low as 0.1 K/min
- Heating steps can be programmed instead of linear ramp
- Combination of heating ramps and isothermal periods to study phenomena at specific temperatures (e.g. kinetics)
- Atmosphere selection
 - Air, O_2 , N_2 , Ar, He, etc.
- Control of gas flow rate
 - Typical flow rates in the order of tens of mL/min (SCCM, standard cubic centimeters per minute)
- Purge Gas can be changed during the experiment
 - E.g. to heat in inert atmosphere and then test oxidation at a certain temperature



TGA EXPERIMENT



TGA 4000.



Pyris 1 TGA.

- Sample is placed in a sample pan, which is supported by, or hangs from, a precision balance
- Balance resolution typically of $1 \mu\text{g}$
 - Can be as low as $0.1 \mu\text{g}$ in some instruments
- The pan resides in a furnace and is heated during the experiment
- Room Temp to 1700°C
 - Depends on furnace model and on sample holder used
 - Cooling of the sample by air or inert gas flow is done at the end
 - Can cool from 1000°C to 50°C in ~ 20 min to allow quick loading of another sample
 - Cooling experiments are not common in TGA



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TGA ANIMATION



- <https://www.youtube.com/watch?v=TjxWGN0s2fY>



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SAMPLE PANS



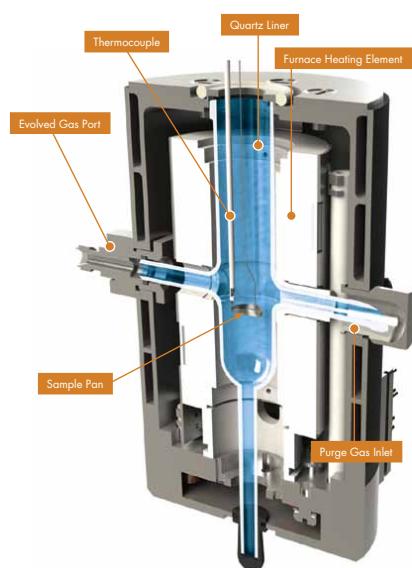
- ▶ Material must be inert to atmosphere and sample
- ▶ Most common: Pt, Al₂O₃
- ▶ Platinum:
 - ▶ T_{max} 1100 - 1200 °C
 - ▶ Inert, easy to clean
- ▶ Alumina (polycrystalline Al₂O₃):
 - ▶ T_{max} > 1500 °C
 - ▶ May react with certain oxides at high temperatures
- ▶ Sapphire (crystalline Al₂O₃)
- ▶ Quartz
- ▶ Gold



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TGA EXPERIMENT



- ▶ A purge gas controls the experiment environment.
- ▶ Gas flows over sample and exits through the exhaust
- ▶ Gas may be inert (N₂, Ar) or reactive (Air)
- ▶ Some instruments allow reduced pressure (partial vacuum)
- ▶ Volatile decomposition products may be carried for further analysis



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TGA ANALYSIS

- ▶ Furnace temperatures usually calibrated using the *Curie point* of magnetic materials
- ▶ Magnetic field pulls sample down a certain apparent weight
- ▶ At the Curie temperature the sample loses magnetization and the “magnetic mass equivalent” disappears
- ▶ Highly automated instruments are commercially available
 - ▶ Autosamplers are available which tare the sample holder, load the sample, heat and record data, cool and unload the sample
- ▶ A thermocouple is located as close as possible to sample
 - ▶ This introduces a brief delay between actual sample temperature and the recorded value
 - ▶ Reproducibility of temperature measurements usually is $\leq 2 \text{ }^{\circ}\text{C}$
 - ▶ Slower heating ramps may be useful if more precise temperature measurements are required



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EVOLVED GAS ANALYSIS IN TGA

- ▶ Analysis of gas products: 2 or more instruments are combined
 - ▶ TGA-FT-IR: used when a small set of evolved gases with characteristic IR spectra are produced: H₂O, CO₂, solvents
 - ▶ TGA-MS: Mass spectroscopy of products (volatile materials). Can detect very low levels of materials
 - ▶ TGA-GC/MS: Produced gases are separated by gas chromatography, and peaks identified by mass spectroscopy



TGA-FT-IR



TGA-MS

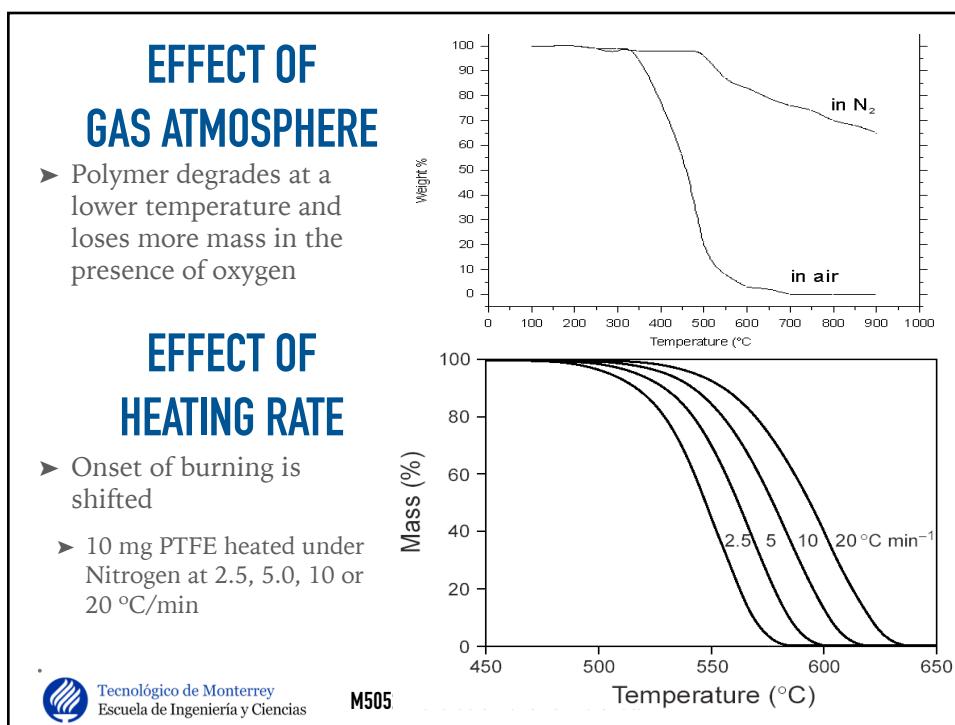
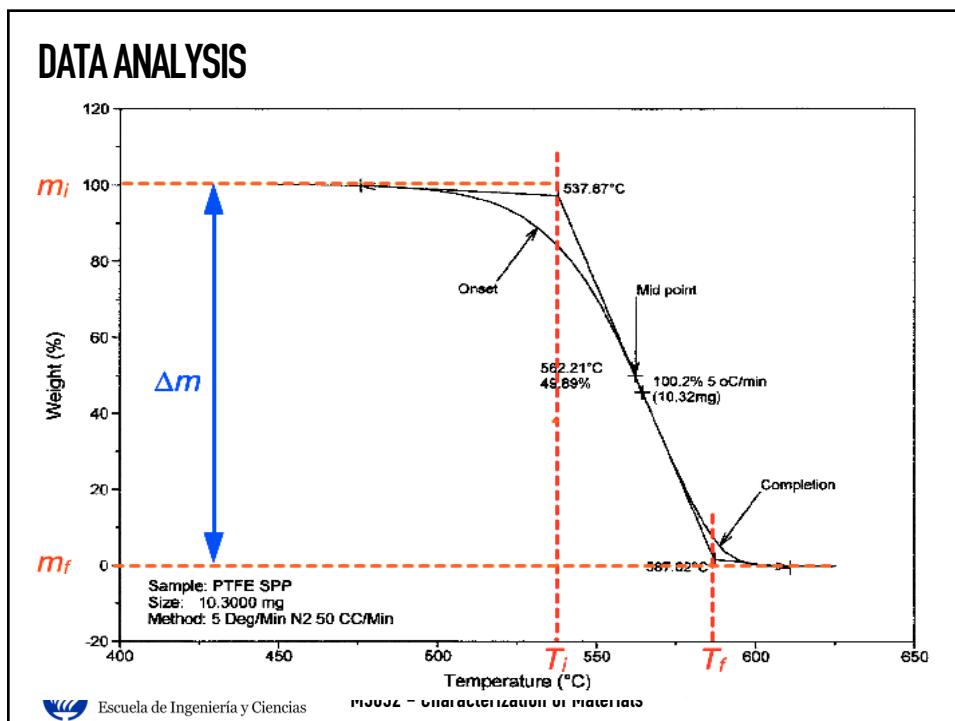


TGA-GC/MS



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EFFECT OF HEATING RATE

- Plot of log of heating rate v. $1/T$ can give an estimate of the activation energy (related to thermal stability)

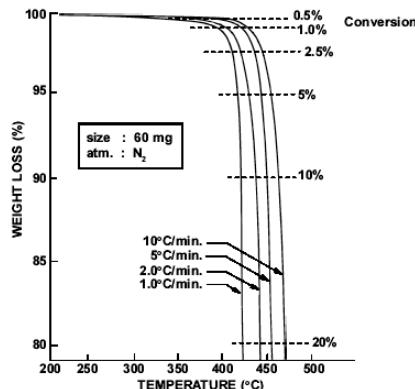


Figure 1. WIRE INSULATION THERMAL STABILITY

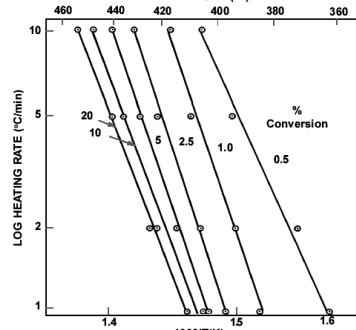


Figure 2. LOG HEATING RATE VS. TEMPERATURE OF CONSTANT CONVERSION (WIRE INSULATION)

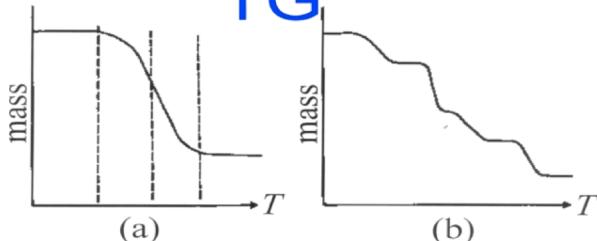


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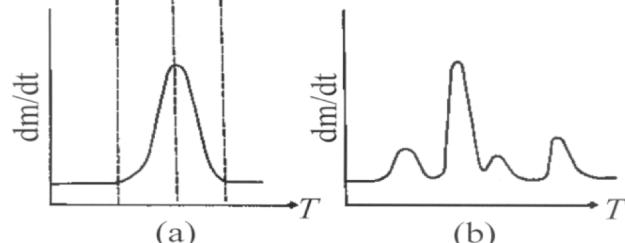
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DERIVATIVE THERMOGRAM

TG



DTG



Allows better visualization of changes in slope, giving information similar to that obtained from differential thermal analysis



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MANY APPLICATIONS IN MATERIALS AND NANOMATERIALS CHARACTERIZATION

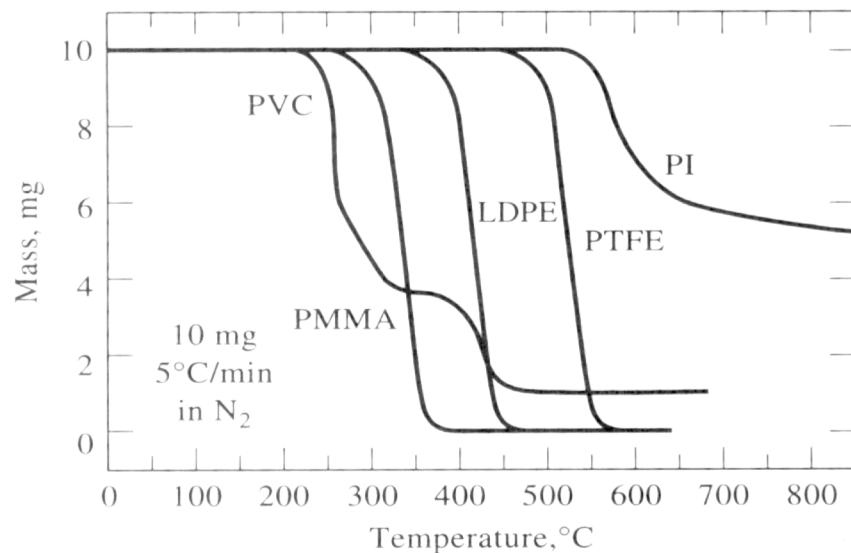
- ▶ Thermal stability (decomposition pattern)
- ▶ In specific temperatures, atmospheres, heating time, etc.
- ▶ Measuring humidity of samples
- ▶ Identification & quality control
 - ▶ Monitor repeatability of burning curve
- ▶ Degradation mechanism and kinetics
- ▶ Compositional analysis
- ▶ Additives, stabilizers, fillers, etc.
 - ▶ If components degrade at different temperatures analyses can be made without prior separation
- ▶ Impurity analysis
- ▶ Simulation of industrial processes
- ▶ Corrosion studies



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THERMAL STABILITY COMPARISON



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QUANTITATIVE ANALYSIS: RUBBER TIRE COMPOSITION

- Tire has plasticizer and oils mixed in with rubber
- First weight loss due to evaporation of oils/plasticizers (21.88 %)
- Second weight loss due to thermal degradation of rubber (43.9 %)
- Third weight loss due to burning of carbon black filler (32.3 %)
- Final residue is inert fillers and ashes (2.11 %)

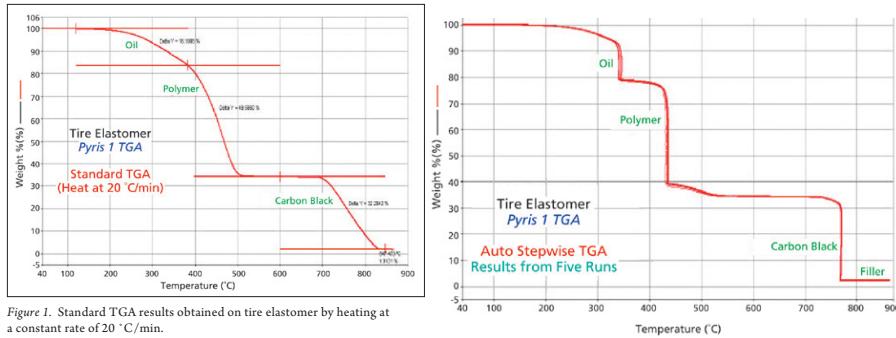


Figure 1. Standard TGA results obtained on tire elastomer by heating at a constant rate of 20 °C/min.



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QUANTITATIVE TGA ANALYSIS

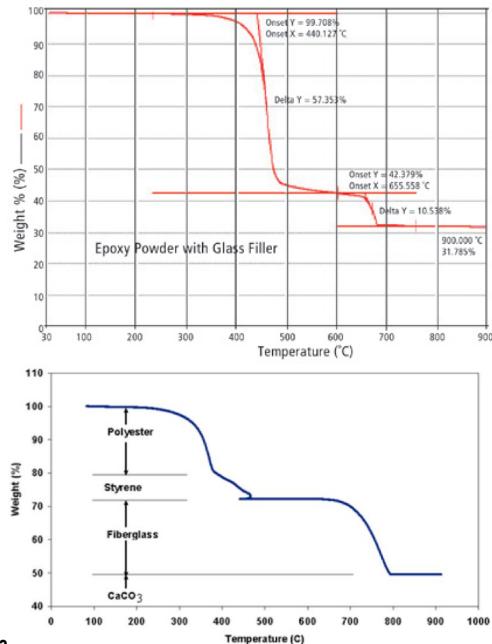
- If components degrade at different temperatures their relative amounts can be quantified

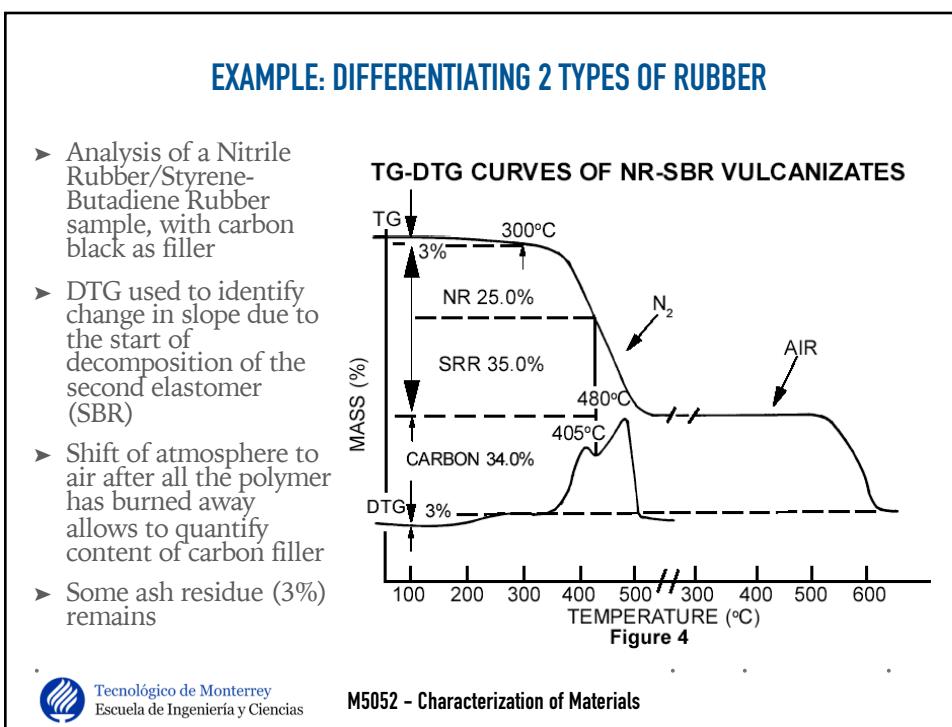
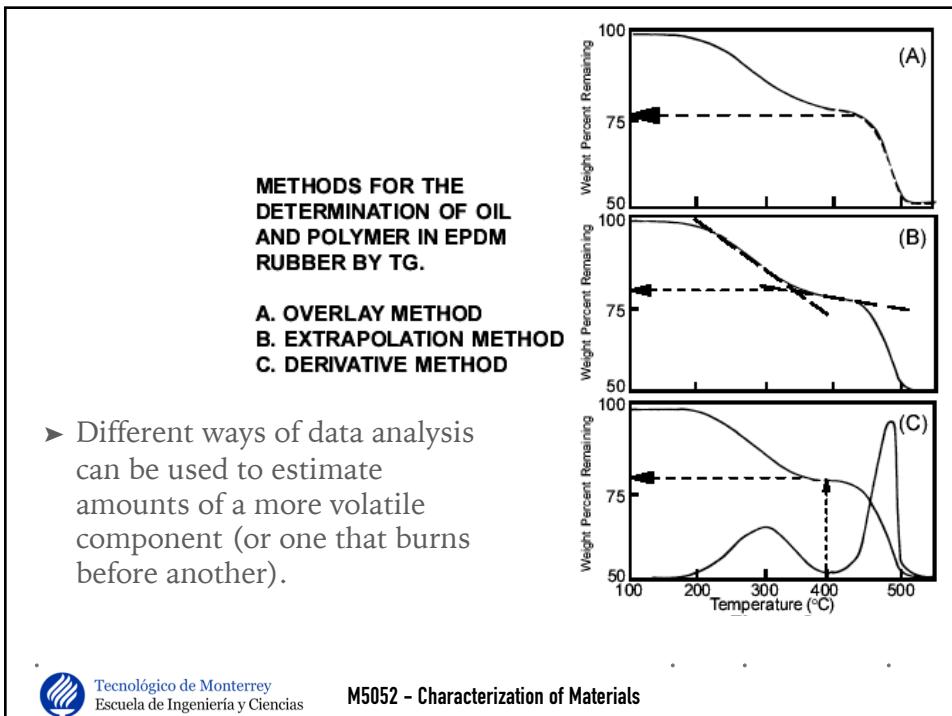
Example: Composition of a fiberglass reinforced polymer composite material

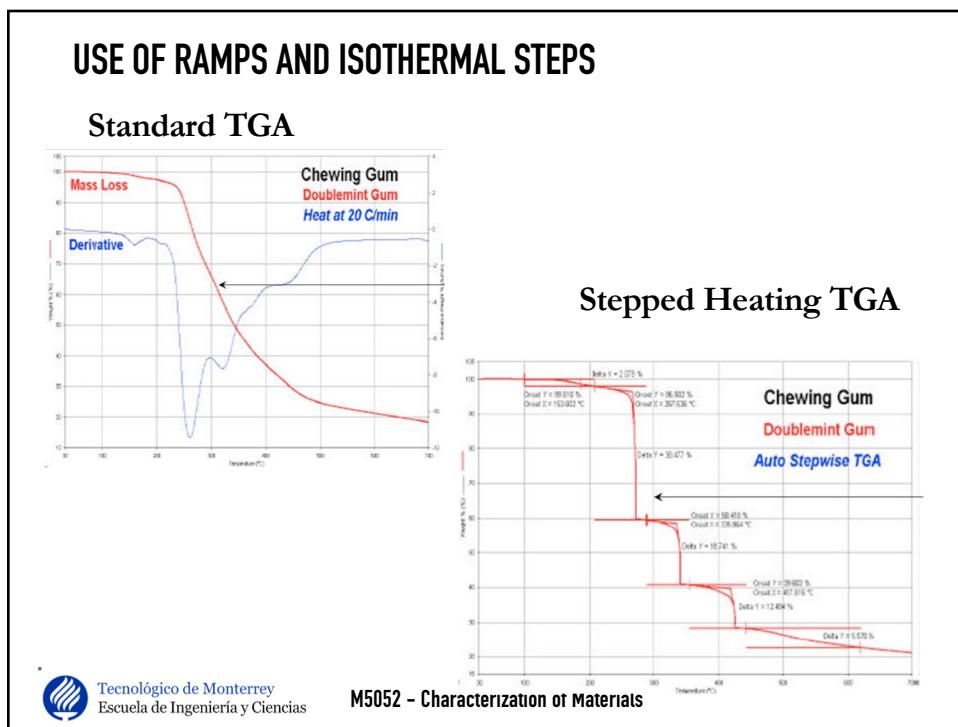
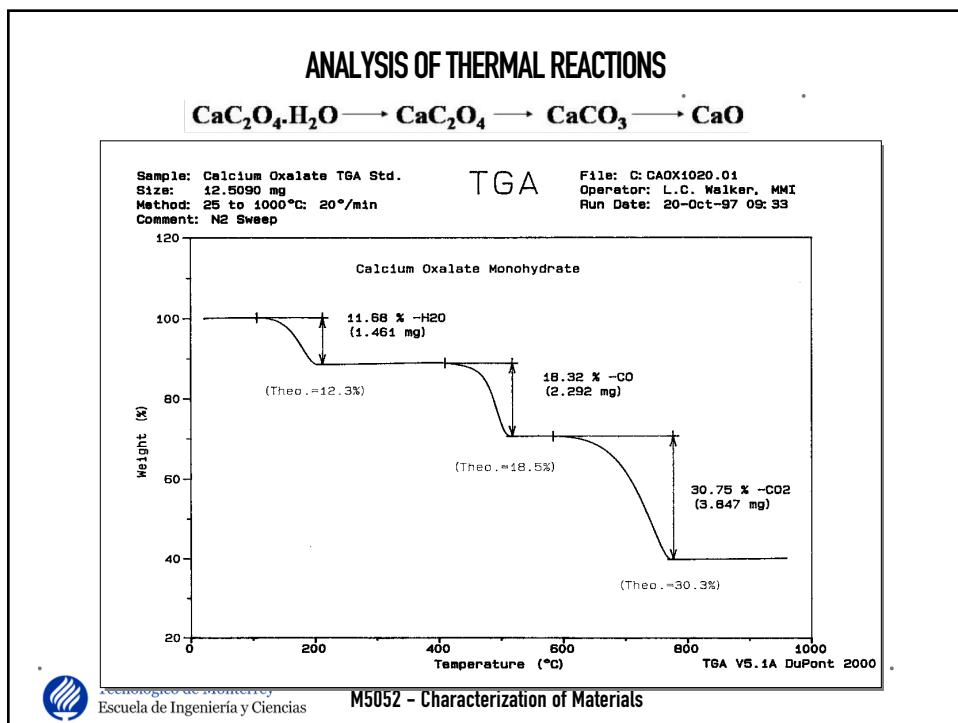


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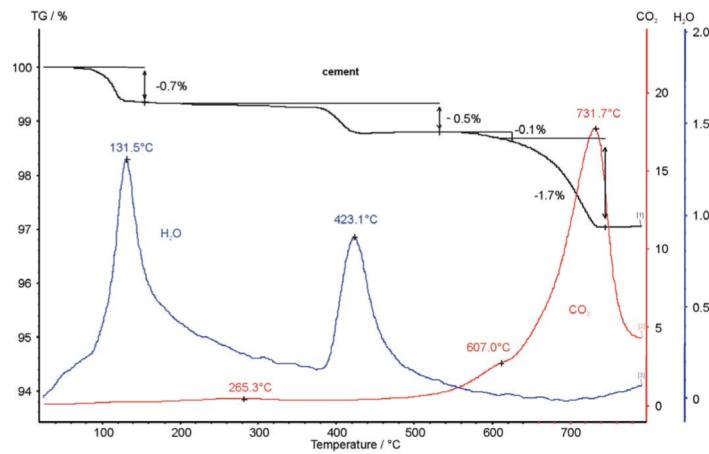






TGA-FTIR OF CEMENT

- Temperature range
- RT –800°C
- Heating rate
- 10 K/min
- Atmosphere
- Air, 40 ml/min
- Sample mass
- 43.6 mg
- Crucible
- Pt/Rh with lid



- Water lost from dehydration of calcium sulfate, and calcination of calcium hydroxide
- Magnesium carbonate decomposes before (~607 °C) calcium carbonate (~732 °C)

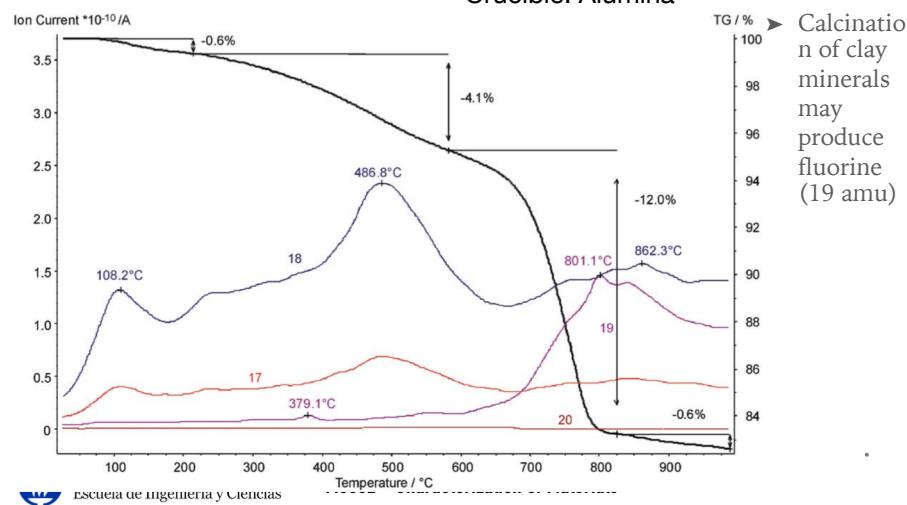


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TGA-MS OF CLAY BRICK

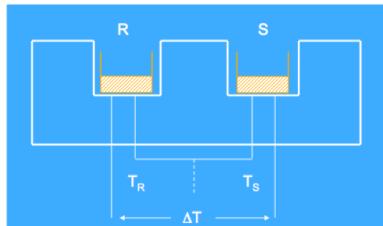
- Temperature range: RT –1000°C
- Heating rate: 10 K/min
- Atmosphere: Air, 40 ml/min
- Sample mass: 21.7 mg
- Crucible: Alumina



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DIFFERENTIAL THERMAL ANALYSIS

- Measures the temperature difference between a sample and an inert reference during heating or cooling processes
 - Empty sample pan would heat faster than an inert reference
 - Alumina, SiC, glass are commonly used
- Data plotted in function of temperature and/or time
 - Can be isothermal or at different heating rates
- Sample chamber may allow atmosphere control
 - Inert gas, or reactive gas flow, some have pressure control



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DTA CURVES

- When a characteristic thermal event occurs, a signal is recorded, indicating a difference in temperature

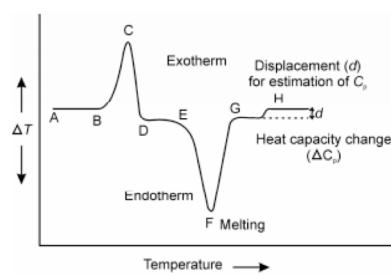
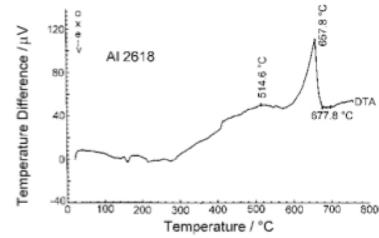


Fig. 11.3: A representation of the DAT Curve showing exotherm, endotherm and base line changes

• APPLICATIONS

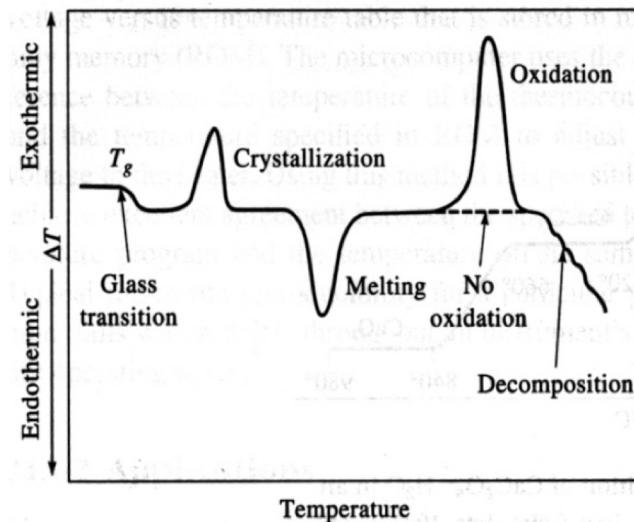
- To construct phase diagrams
- To study phase transitions
- Qualitative analyses only
 - Lack of quantification of heat flow and even of weight measurements does not allow quantification



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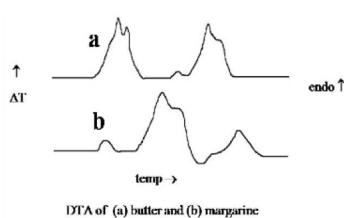
TYPICAL DTA THERMOGRAM OF A POLYMER



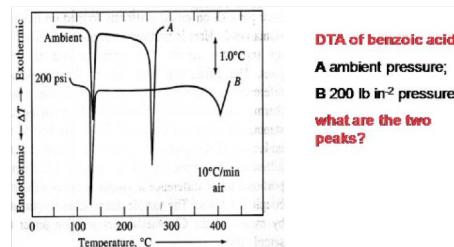
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QUALITATIVE ANALYSIS



DETERMINATION OF PHASE TRANSITIONS



CHARACTERIZATION OF INORGANIC MATERIALS

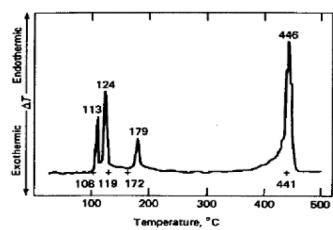


FIGURE Differential thermogram for sulfur. [Reprinted with permission from J. Chiu, Anal. Chem., 35, 933 (1963).]

- The peak at 113°C corresponds to a solid-phase change from the rhombic to the monoclinic form, while the peak at 124°C corresponds to the melting point of the element.
- Liquid sulphur is known to exist in at least three forms, and the peak at 179°C apparently involves a transition among these.
- The peak at 446°C corresponds to the boiling point of sulphur



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QUALITATIVE ANALYSIS OF POLYMER MIXTURES

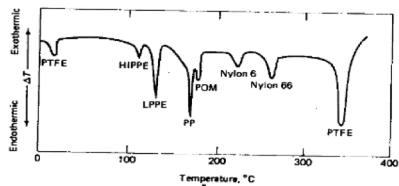
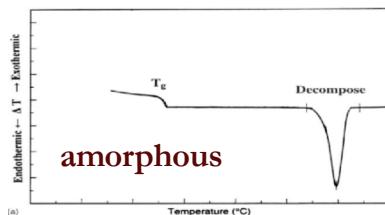


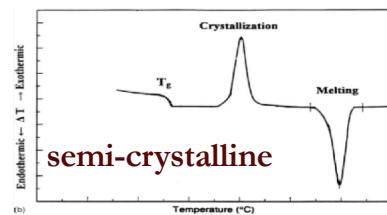
FIGURE Differential thermogram for a mixture of seven polymers. PTFE = polytetrafluoroethylene; HIPPE = high-pressure polyethylene; LPPE = low-pressure polyethylene; PP = polypropylene; POM = polyoxymethylene. [From J. Chiu, *DuPont Thermogram*, 2, (3), 9 (1965). With permission.]

Each peak corresponds to the characteristic melting point of each component

STRUCTURE OF POLYMERS



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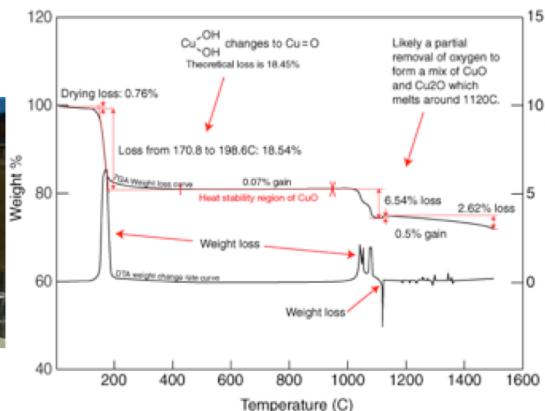


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TGA/DTA

- Additional DTA information allows better understanding of the changes in weight observed by TGA
- There are instruments that combine both techniques and data are collected simultaneously

Sampe TGA/DTA Curves for Copper Hydroxide, heated to 1500C in air
These show the weight loss of a material as it is fired



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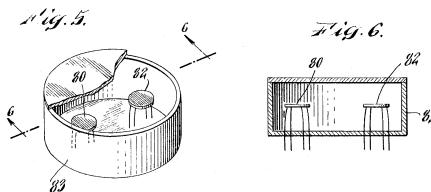
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DIFFERENTIAL SCANNING CALORIMETRY

- Measurement of temperatures and heat flow associated with transitions in materials as function of time and temperature in a controlled atmosphere
- DSC measurements provide quantitative and qualitative information about physical and chemical changes involving exothermic or endothermic processes or changes in heat capacity
- Method developed and patented in 1962, commercialized in 1963 by Perkin-Elmer

Aug. 2, 1966 E. S. WATSON ET AL. 3,263,484
DIFERENTIAL MICROCALORIMETER

Filled April 4, 1962 4 Sheets-Sheet 3

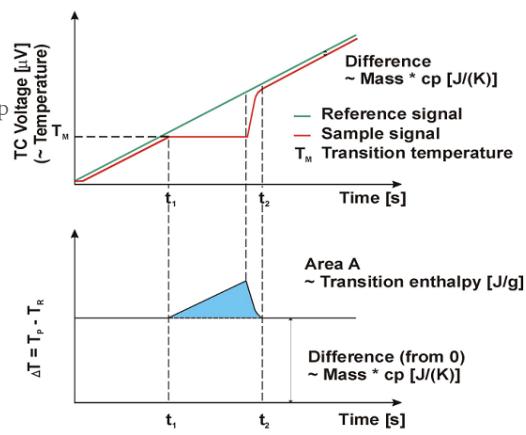


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HEAT FLUX DSC BASIC PRINCIPLES

- A sample and a reference are both heated in a furnace under a controlled environment
- Usually a linear temperature ramp
- Due to the heat capacity of the sample the reference usually heats faster
- When a transformation occurs in the sample it absorbs (or releases) thermal energy and the sample temperature stops rising linearly
- Reference temperature still rises linearly in the meantime
- Once the sample transformation ends it can reach thermal equilibrium with the furnace environment and after a short time its temperature again rises linearly together with the reference



- Heat Flux DSC measures the temperature difference between sample and reference, the area enclosed by that peak correlates (via calibration) to the heat transferred during the transition



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AT FLUX DSC

Sample and reference chamber

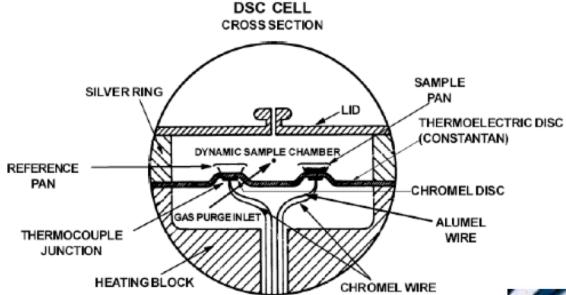
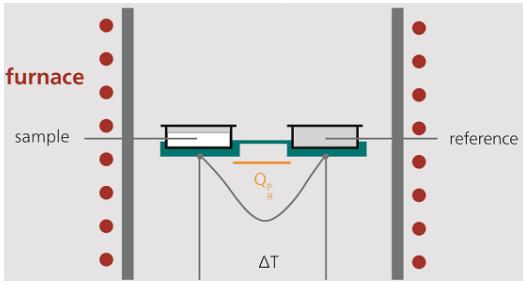


Figure 1




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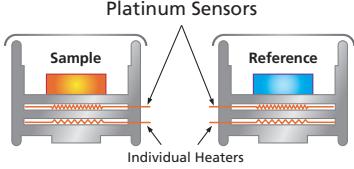
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HEAT FLOW DSC BASIC PRINCIPLES

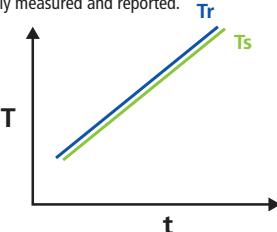
- The sample and a reference are heated in separate furnaces
- Feedback loop used to keep both furnaces at the same temperature
- Direct measurement of power necessary to keep sample at the same temperature as the reference
- Also called “power compensated DSC”

Double-furnace DSC

Two independent, small furnaces where energy change of the sample is controlled, directly measured and reported.

- Two independent small furnaces
- Measures heat flow directly
- True isothermal measurement
- Fastest heating and cooling
- Fastest response times



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HEAT FLOW V. HEAT FLUX DSC

Table 1. Heat Flow Versus Heat Flux DSC.

	Heat Flow	Heat Flux
Fast Heating (250 °C/min plus)	Yes	No
Modulated Techniques	Yes	Yes
Accuracy of Cp Values	High	Moderate
Delta H Accuracy	High	Moderate
Ease of cleaning	Very	Moderate
OIT Testing	Moderate	Easy
Isotherm Performance	Excellent	Affected by sample

- For most simple applications data from both types of DSC instruments are comparable
- Note: OIT = oxidative induction time. Sample is heated under inert gas to a temperature, then the atmosphere is changed to air and the time it takes for the material to start to burn is measured.



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DSC BASIC PRINCIPLES

- In one physical state, the specific heat of a material changes very slowly with the temperature
- During a change in physical state, the specific heat changes in a discontinuous form
- The thermal energy applied can produce chemical changes, along with changes in enthalpy, heat of reaction, heat of fusion, etc.

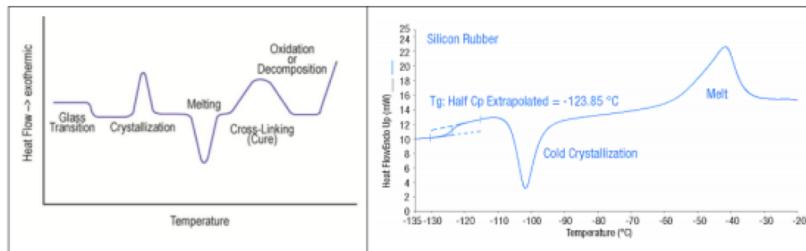


Figure 1 (left). DSC profile. In this profile, exothermic heat flow is measured versus temperature.

Courtesy: TA Instruments, Inc.

Figure 2 (right). DSC profile. Here the endothermic heat flow is measured versus temperature.

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INFORMATION OBTAINED BY DSC

- Glass transitions
- Melting and boiling points
- Crystallization time and temperature
- Percent crystallinity
- Heats of fusion and reaction
- Specific heat (heat capacity)
- Oxidative and thermal stability
- Rate and degree of cure
- Reaction kinetics
- Phase Changes
- Purity of materials

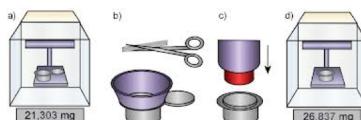


Sample Pans

Sample size: 1 - 20 mg



Standard Al pans
Usually closed by crimping



Crimped Pans



Perkin-Elmer Sample Pans	
Standard Aluminum	Aluminum Volatile
Standard Gold	Gold Volatile
Standard Copper	Large Volume (Stainless Steel)
Graphite	High Pressure Titanium
Platinum	Robotic
Alumina	Vented Aluminum

Sealed pans are used with volatile substances.
(1-3 bar pressure)
High pressure pans are an option



TYPICAL DSC CURVES

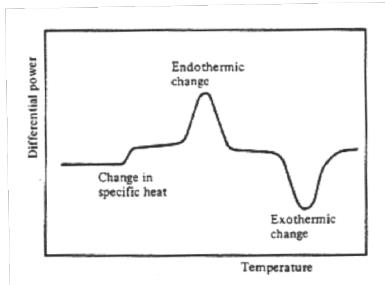


Figure 3.13: Typical DSC Curve.

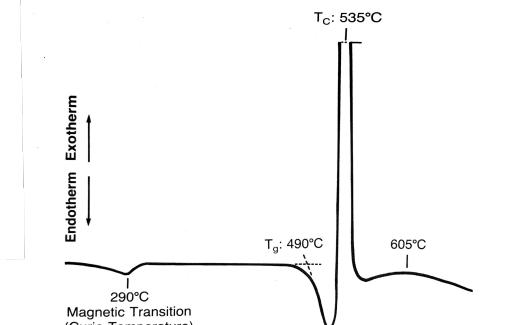
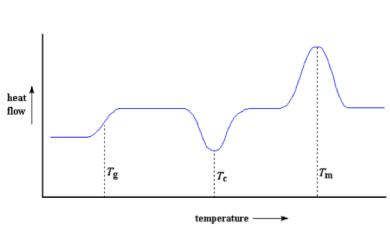


Figure 11.9. DSC of an amorphous metal alloy ribbon, in argon, at $20^\circ\text{C min}^{-1}$ heating rate.



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TYPICAL DSC CURVE (FOR A POLYMER)

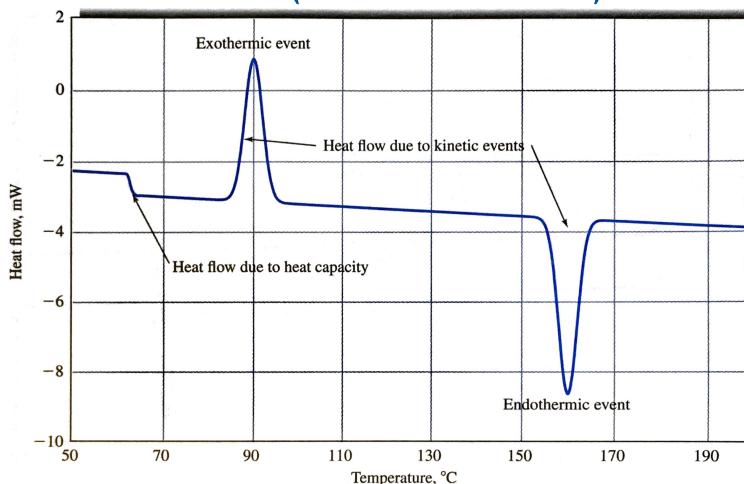


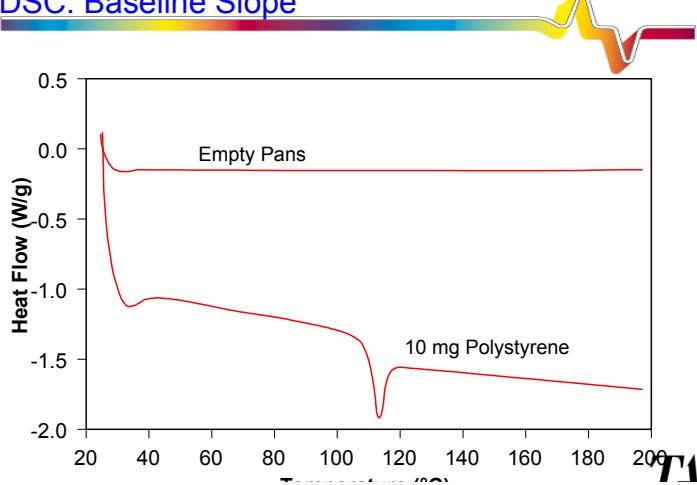
FIGURE 31-13 Typical DSC scan for a polymeric material. Note the step transition at about 63°C . There is an exothermic event at approximately 90°C and an endothermic event at 160°C . Note that the thermogram represents the sum of the heat flow due to heat capacity and kinetic processes.



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DSC: Baseline Slope



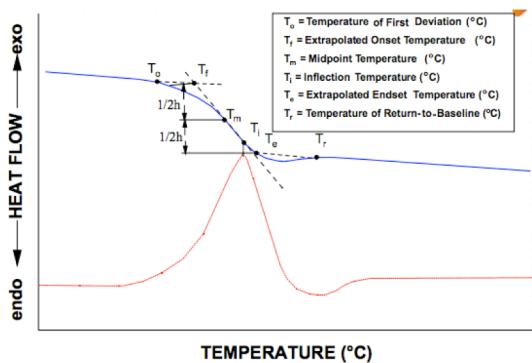
- Calibration should provide flat baseline with empty pans
- Polymers should always have an endothermic slope due to increasing heat capacity with increasing temperature



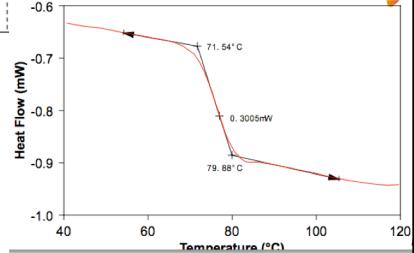
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MEASUREMENT OF GLASS TRANSITION, T_g



- Above the glass transition temperature (T_g) polymer chains have higher mobility and thus the polymer has higher heat capacity
- Mobile polymer chains have more vibrational modes and absorb more heat



T_g of PET



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DETERMINATION OF ONSET TEMPERATURES

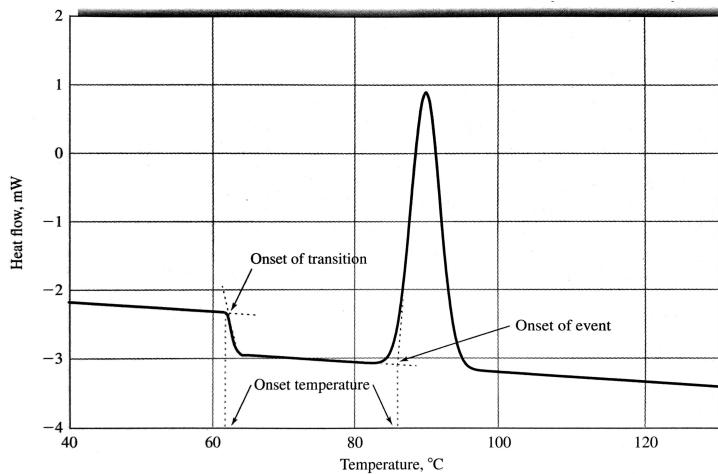


FIGURE 31-15 Determination of onset temperatures for a transition and an exothermic event (crystallization).

- The crossing point of the extrapolated tangent lines is taken as the onset



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DSC OF PET

- DSC curve of polyethylene terephthalate in nitrogen
- Power input in mW as y axis
- Glass transition (T_g) at 83.9 °C
- Onset at 79.7
- Baseline changes due to heat capacity change
- Crystallization peak at 165.7 °C
- Exothermic process, less heat flow required to increase sample temperature
- Melting peak at 250.2 °C
- Specific heat (J/g) for physicochemical processes can be quantified

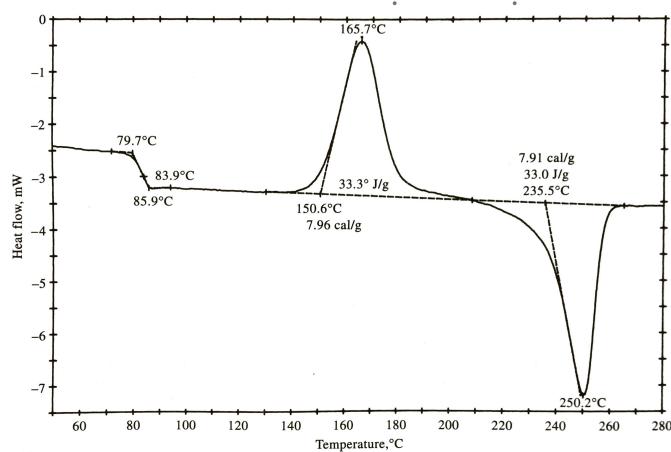


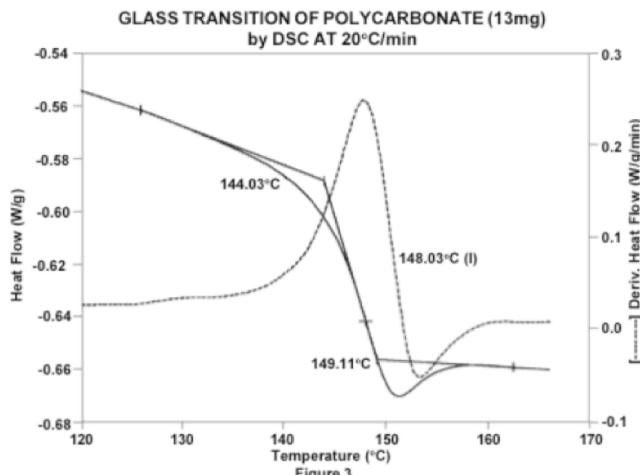
Figure 31-15 Differential scanning calorimetry output from a thermal instrument showing the thermal transition for polyethylene terephthalate. (Courtesy of DuPont Instrument Systems, Wilmington, DE.)



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GLASS TRANSITION BY DSC



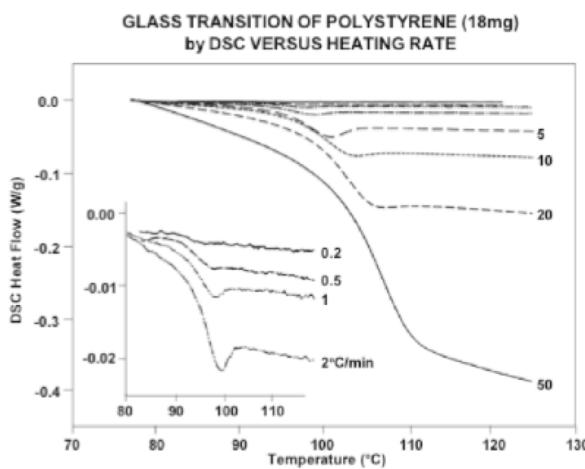
- Derivative of heat flow can be used to locate the inflection point of a transition



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HEATING RATE EFFECT ON T_g MEASUREMENTS



- Position of glass transition can shift due to heating rate
- Apparent higher T_g for higher heating rate
- Absorption of heat by the sample is not instantaneous
- A higher heating rate requires a larger heat flow, thus the step size is larger



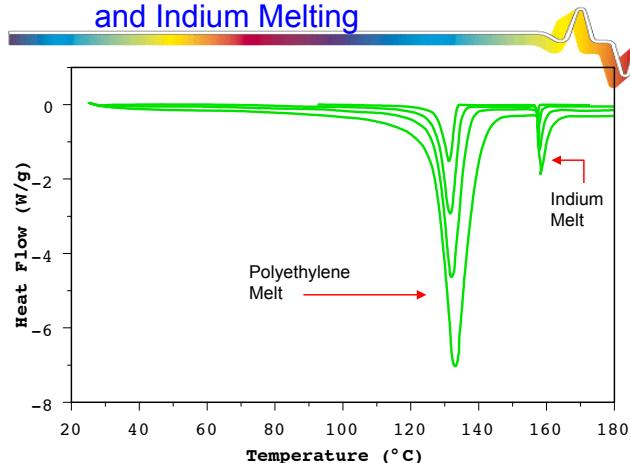
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EFFECT OF HEATING RATE IN T_M

- ▶ Position of melting peak of polymers also affected by heating rate
- ▶ For pure metal the onset of melting is almost independent of the heating rate
 - ▶ Change in peak area but heat of fusion measured (J/g) should be constant
 - ▶ Higher heating rate requires higher heat flow
- ▶ NOTE: Indium is used as standard for calibrating temperature measurements in thermal methods such as TGA and DSC

DSC: Effect of Heating Rate on HDPE and Indium Melting

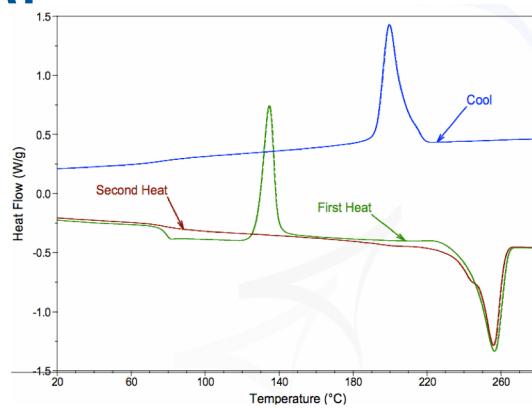


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THERMAL HISTORY

- ▶ Thermal history affects DSC results
- ▶ The cooling rate can affect:
 - ▶ Crystallinity of semi-crystalline materials
 - ▶ Enthalpic recovery at the glass transition
- ▶ For polymers and other materials it is important to run heat-cool-heat experiments to see the effect of, or to eliminate, thermal history



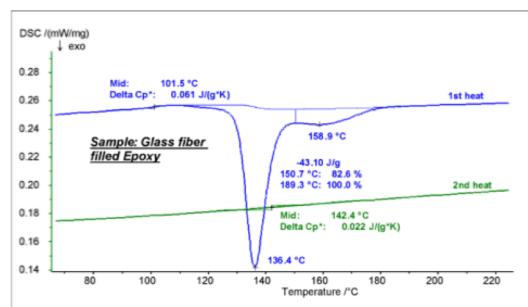
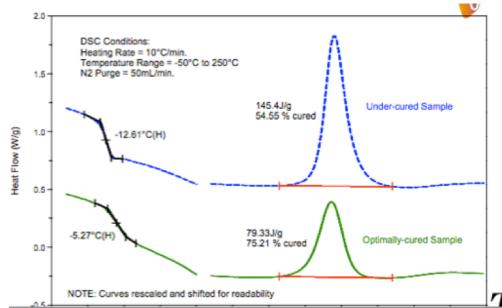
- ▶ Example, PET heating-cooling cycles:
 - ▶ Heating at 10 °C/min
 - ▶ Cooling at 10 °C/min
 - ▶ Heating at 10 °C/min



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APPLICATION EXAMPLE: DETERMINATION OF % CURE OF EPOXY



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- Heat released during cross-linking reaction (cure) is proportional to the percent of cure

DSC APPLICATION IN PHARMACEUTICAL INDUSTRY

- Method is widely used in pharmaceutical industry to determine purity
- Change in melting point due to impurities is easy to measure by DSC
- Measurements of crystallization percentage of pharmaceuticals is also important
- Polymorphism (presence of different crystalline forms) can be determined by DSC via differences in melting points of polymorphs and by observation of heat release due to recrystallization

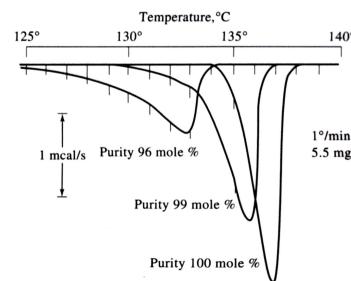


Figure 31-17 Differential scanning calorimetry study of samples of the drug phenacetin. (Reprinted with permission from H. P. Vaughan and J. P. Elder, Amer. Lab., 1974, 6(1), 58. Copyright 1974 by International Scientific Communications, Inc.)

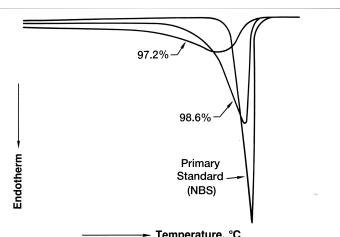


Figure 11-11. Effect of purity on the melting peak shapes (DSC) of benzoic acid. Reprinted from DSC-2 Manual, Perkin-Elmer, Feb. 1976, pp. 4-5; with permission of the Perkin-Elmer Corporation.



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MODULATED DSC

- A sinusoidal function is superimposed over the temperature ramp
- Micro-heating and cooling cycles occur as the overall temperature increases (or decreases) steadily
- The signal is deconvoluted in two parts with Fourier transform methods
- This separates the signal into a *reversing heat flow* (associated with heat capacity) and a *nonreversing heat flow signal* (associated with kinetic processes)
 - The reversing heat flow shows step transitions such as glass transition
 - Exothermic and endothermic events may appear in either or both
- There is also a pressure-modulated DSC, where an oscillating pressure variation (e.g. a sawtooth curve) is superimposed over a standard DSC temperature program
 - This allows simultaneous determination of heat capacity and expansibility



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MODULATED DSC EXAMPLE

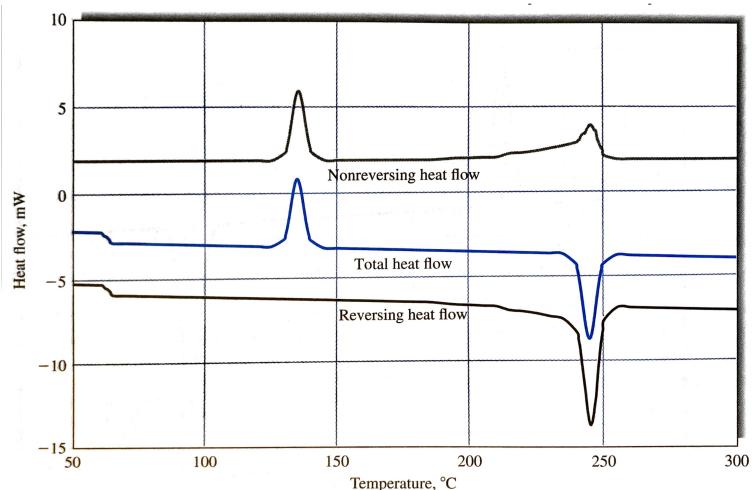


FIGURE 31-14 Deconvoluted thermogram from an MDSC apparatus showing nonreversing and reversing heat flow components. (Courtesy of TA Instruments, New Castle, DE.)



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MICROTHERMAL ANALYSIS

- ▶ AFM tip replaced with a thermally sensitive probe (e.g. thermocouple or thermistor)
- ▶ Resistive probe based on a Wollaston wire ($\text{Pt}@\text{Ag}$) is most common, electrical resistance is proportional to temperature
- ▶ Probe can be used as heater, or external heating is used
- ▶ Wollaston wire is most resistive at the tip, which will heat up when current is applied



FIGURE 31-16 A microthermal analysis probe. (Reprinted from P. G. Royall, D. Q. M. Craig, and D. B. Grandy, *Thermochim. Acta*, 2001, 380 (2), 165–173, DOI: 10.1016/S0040-6031(01)00667-0, with permission from Elsevier.)

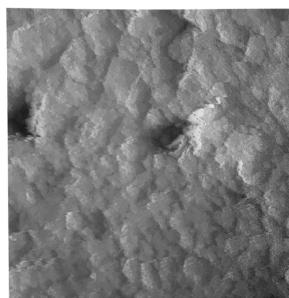


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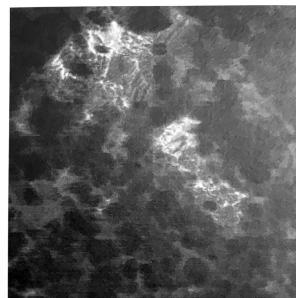
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MICROTHERMAL ANALYSIS

- ▶ Probe can operate in constant temperature mode
- ▶ Most common, simpler
- ▶ Register changes in electrical power needed to keep tip isothermal
 - ▶ More or less heat will flow away from tip depending on thermal conductivity (higher or lower) of surface below
- ▶ Probe can also operate in constant-current mode
- ▶ Changes in temperature modulation can be used to monitor thermal conductivity at different depths



(a)



(b)

FIGURE 31-18 Comparison of conventional atomic force microscopy topographic image (a) with thermal image (b) of a paracetamol pharmaceutical tablet. (Reprinted from H. M. Pollock and A. Hammiche, *J. Phys. D: Appl. Phys.*, 2001, 34, R23. With permission.)



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SCHEMATIC OF A MICROTHERMAL ANALYSIS APPARATUS

FIGURE 31-17 Microthermal analysis apparatus.

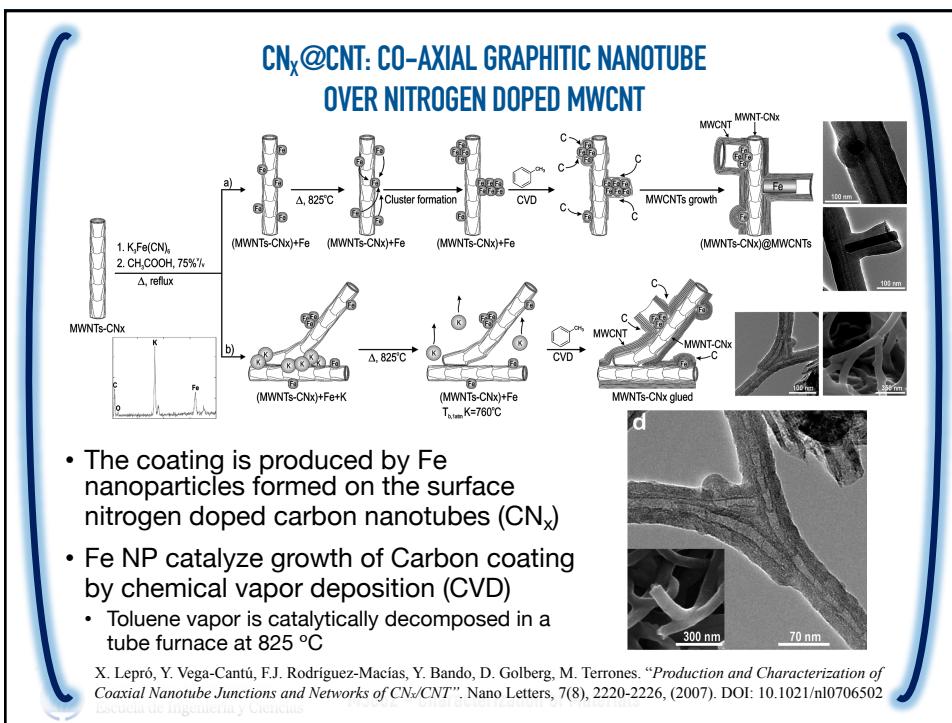
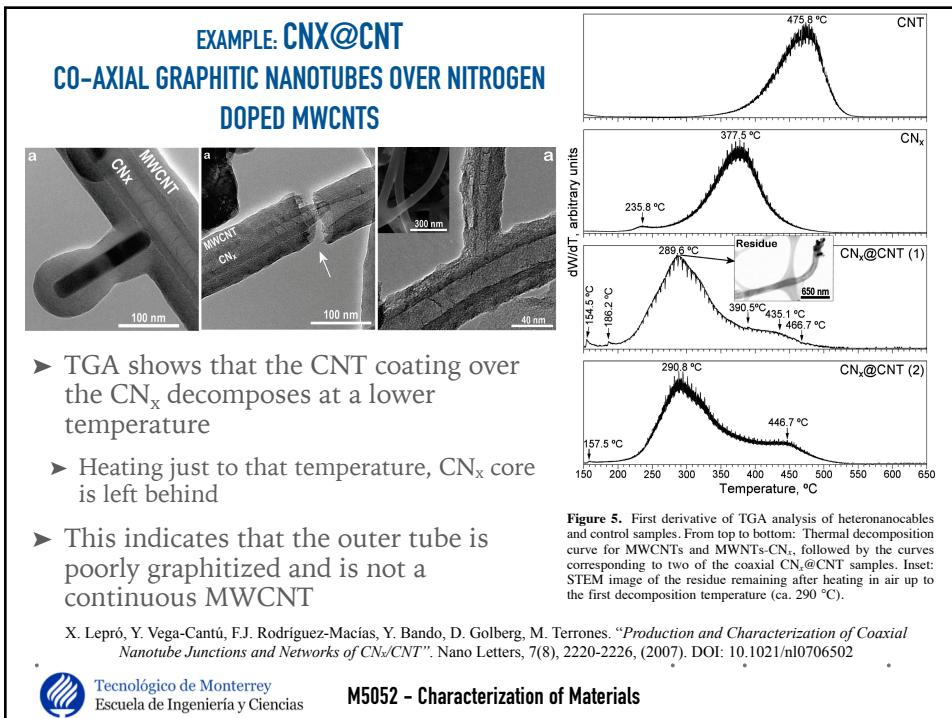
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EXAMPLE: CNT-PS COMPOSITE

- C.G. Espinosa-González, F.J. Rodríguez-Macías, A.G. Cano-Márquez, J. Kaur, M.L. Shofner, Y.I. Vega-Cantú. "Polystyrene Composites with Very High Carbon Nanotube Loadings by *in situ* Grafting Polymerization". Journal of Materials Research, 28(8), 1087-1096 (2013).
- DOI: 10.1557/jmr.2013.38
- Pyrolysis in inert atmosphere was used to determine CNT loading in composites
 - Polystyrene pyrolyzes into volatile compounds leaving the MWCNT behind
- Carbon nanotubes increase the degradation temperature of polymer in the composite
 - First derivative peak was used to compare degradation temperature (maximum decomposition rate)

FIG. 5. (a) TGA wt% versus T curves for PS-g-MWCNTs nanocomposites under nitrogen flow (10 °C/min heating). Curve *a* shows pure MWCNT with negligible weight loss up to 650 °C. PS starts to degrade at 390 °C, and pyrolyzes completely (curve *g*) leaving a residue corresponding to the concentration of MWCNT in the composites *b*: 80 wt%, *c*: 75 wt%, *d*: 67 wt%, *e*: 42 wt%, and *f*: 22 wt%. (b) shows first derivatives of wt% versus time and how MWCNT loading affects the degradation temperature, *b*: 80 wt%, $T_d = 390$ °C; *c*: 75 wt%, $T_d = 405$ °C; *d*: 67 wt%, $T_d = 418$ °C; *e*: 42 wt%, $T_d = 423$ °C; *f*: 22 wt%, $T_d = 432$ °C; and *g*: pure PS, $T_d = 417$ °C.

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ADDITIONAL THERMAL ANALYSIS METHODS

Thermomechanical Analysis and Dynamic Mechanical Analysis are important techniques in the analysis of materials (including polymers, and composites with nanomaterials)

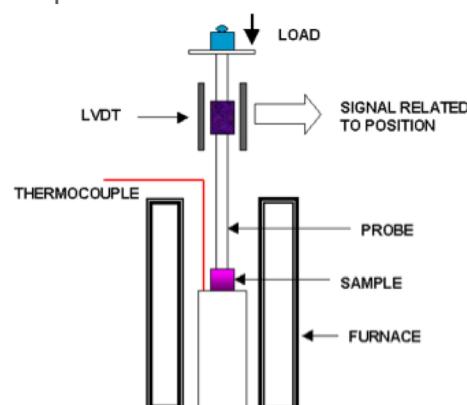
(TMA and DMA are not standard techniques in chemistry and nanomaterials characterization, while TGA, DTA and DSC are very common)



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TMA: Thermomechanical Analysis

- Used to measure dimensional changes (length, volume) as a function of temperature and/or time while applying a defined mechanical force through a probe
- Controlled atmosphere may also be important
- Sample can be a solid, a paste, or liquid
- Change in dimensions of sample produces linear displacement of the probe

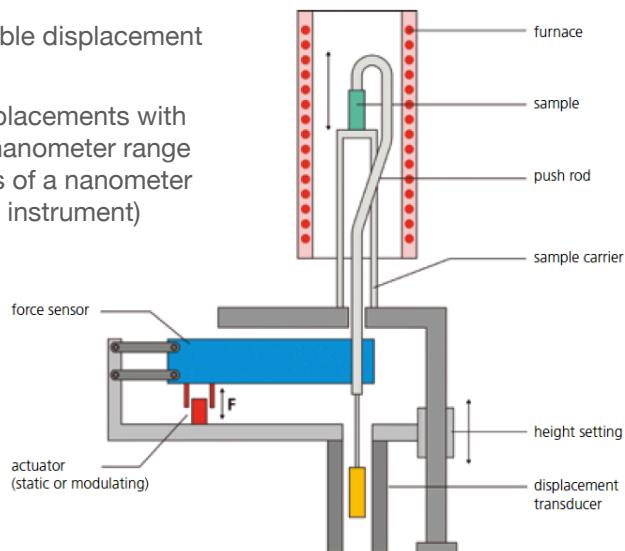


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TMA: DISPLACEMENT SENSOR

- ▶ LVDT: linear variable displacement transducer.
- ▶ Can measure displacements with resolution in the nanometer range (down to fractions of a nanometer depending on the instrument)

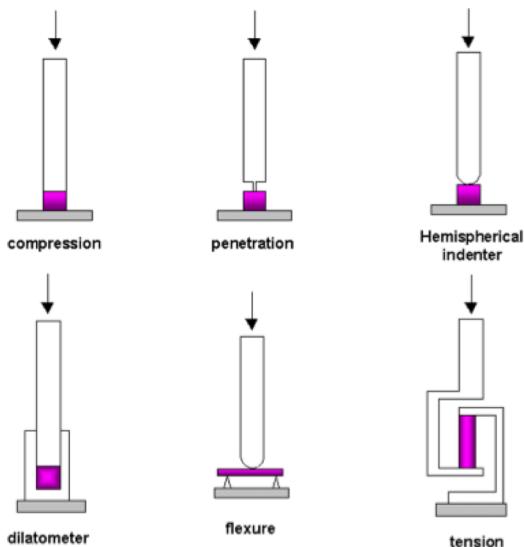


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TMA MEASUREMENT MODES

- Interchangeable probes can be used to measure different types of dimensional changes
- Expansion
- Compression
- Penetration
- Tension
- Bending
- Dilatometry



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TMA: SAMPLE HOLDERS



- Sample holders can be changed depending on type of deformation used for the analysis
- Made of silica or alumina



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TMA: DEFORMATION MODES

- Expansion
 - Flat tipped probe over sample
 - Larger probe may be used for irregular samples, powders, softer materials, films
 - Temperature ramp applied
 - Force can also be applied
 - Measures: Coefficient of Thermal Expansion, Glass transition, Compression Modulus
- Penetration
 - Extended tip or hemispherical probe
 - Hemispherical probe used to measure softening point in solids
 - Precise measurement of T_g , softening point, melting behavior

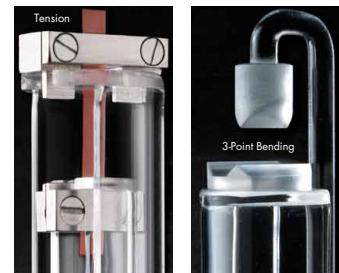


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TMA: DEFORMATION MODES

- Tension
- Measure stress/strain properties of films or fibers
- Fixed force applied while stress/strain and modulus are measured
- Measurement of T_g , shrinkage forces, curing, cross-linking density
- Dynamic mode (DTMA, MTMA) to measure viscoelastic parameters
- 3-point Bending (Flexure)
 - Used for bending properties of stiff materials (e.g. composites) and for measuring distortion temperature
 - Probe eliminates clamping effects
- Compression
 - Sample heating with a defined temperature program



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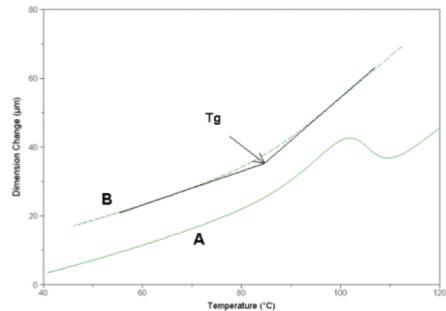
SOME TMA INSTRUMENTS



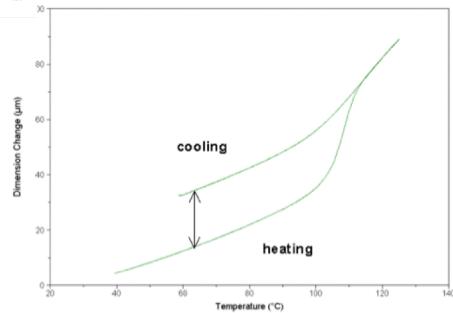
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EXAMPLES



TMA of a resin:
A) with filler
B) no filler

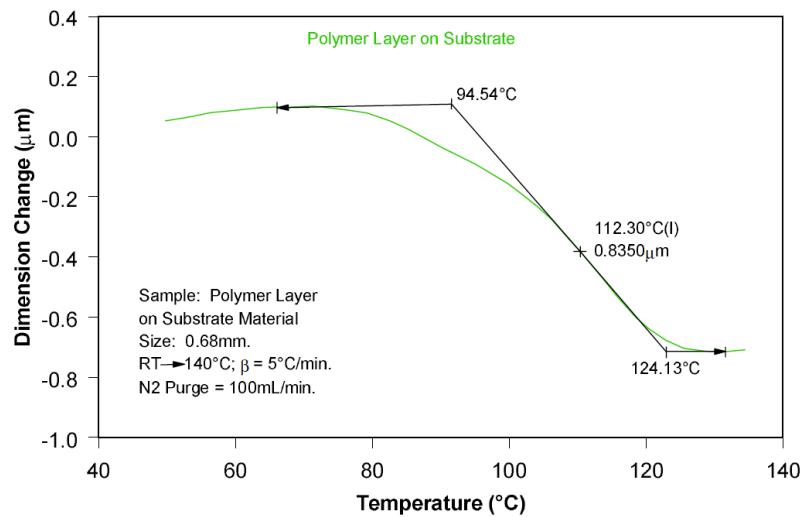


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EXAMPLE: TMA OF POLYMER FILM

TMA Penetration of Polymer Layer on Substrate Material



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TMA APPLICATIONS: GLASS TRANSITION

- ▶ Sample: rapidly cooled polymer
- ▶ Heating scan:
 - ▶ Expansion probe penetrates sample near T_g
- ▶ Second heating scan:
 - ▶ Material is more crystalline no penetration
 - ▶ Only change in coefficient of thermal expansion above and below glass transition is seen
- ▶ Difference in glass transition temperature is due to the effect of crystallinity on T_g

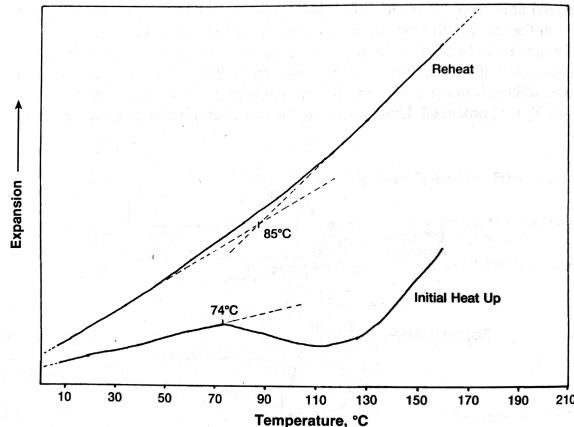


Figure 11.15. TMA of poly(chlorotrifluoroethylene) in the expansion mode.



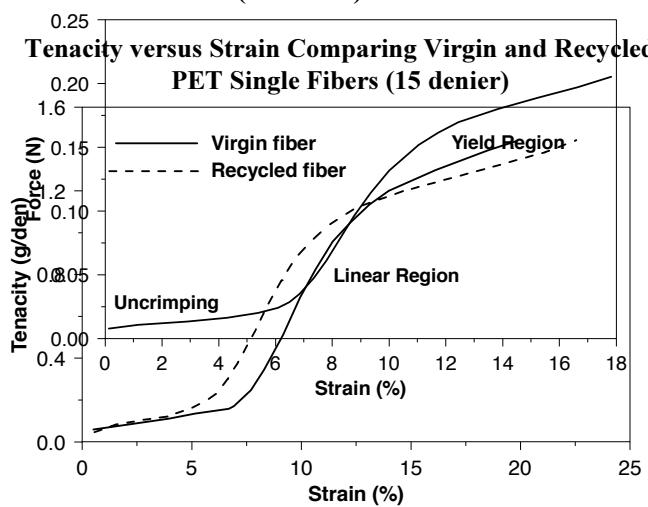
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STRESS-STRAIN EVALUATION OF PET FIBER BY TMA

- ▶ Applied initial force: 3 mN for uncrimping
- ▶ Force ramp of 0.2 N/min
- ▶ Crimp: measure of difference in length between straightened and unstraightened fibers due to undulation and bends in the fiber
- ▶ Denier: measure of fineness of fibers, weight in grams of 9000 meters of yarn or fiber. Linear density
- ▶ “Tenacity” (textile strength): force (stress) divided by linear density (denier)

Force Versus Dimension Change for Virgin PET Single (15 denier) Fiber



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APPLICATIONS AND LIMITATIONS OF TMA

- Thermomechanical analyses allow studying:
 - Thermal Expansion Coefficient
 - Anisotropic Behavior
 - Phase Transitions
 - Density changes
 - Sintering
 - Shrinkage Steps
 - Degree of cure in thermosets
 - Glass Transition
 - Softening Point
 - Penetration behavior
 - Creep Behavior
- Useful for all kinds of materials
 - Metals, polymers, ceramics, composites

➤ Limitations

- Usually limited to solids
 - Above T_m or at temperatures much higher than T_g data is unreliable
- Material creep may occur in addition to dimensional changes
- Data Interpretation requires information from other techniques
 - DSC, TGA, XRD, microscopy, etc.



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DMA: DYNAMICAL MECHANICAL ANALYSIS

- An oscillatory stress is applied on a sample as a function of temperature and time
- Frequency (0,01 - 200 Hz) and % strain are kept constant
- Delay in deformation of material is measured
 - Phase angle δ
- Study of viscoelastic properties

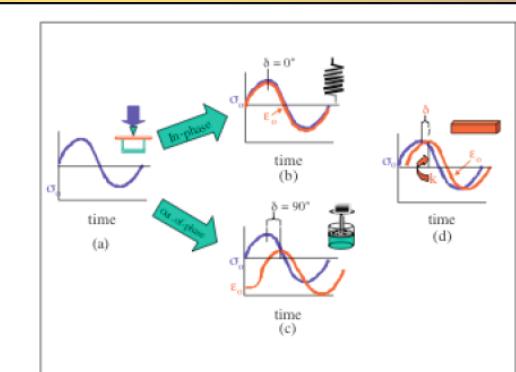
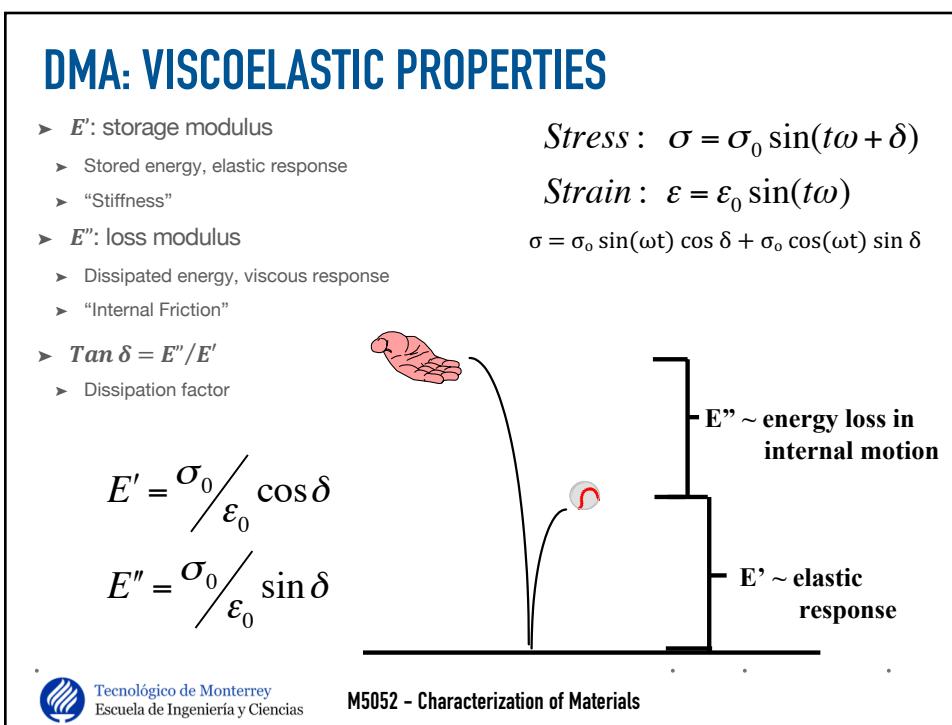
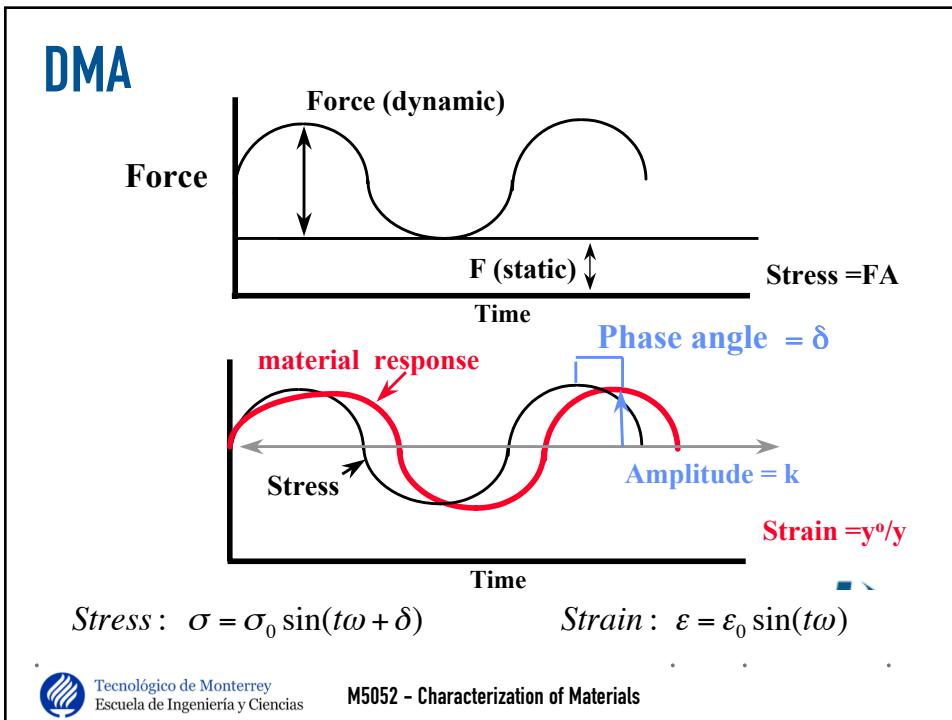


Figure 2 (a) When a sample is subjected to a sinusoidal oscillating stress, it responds in a similar strain wave provided the material stays within its elastic limits. When the material responds to the applied wave perfectly elastically, an in-phase, storage, or elastic response is seen (b), while a viscous response gives an out of phase, loss, or viscous response (c). Viscoelastic materials fall in between these two extremes as shown in (d). For the real sample in (d), the phase angle, δ , and the amplitude at peak, k , are the values used for the calculation of modulus, viscosity, damping, and other properties.



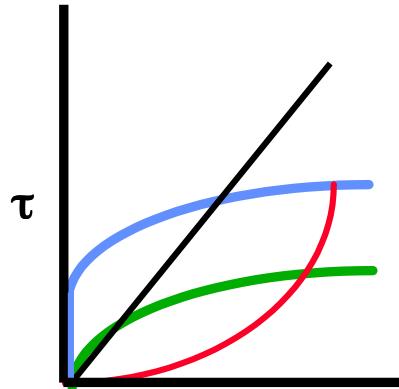
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VISCOSITY V. STRESS

- **Newtonian** behavior is linear and the viscosity is independent of rate.
- **Pseudoplastic Fluids** get thinner as shear increases.
- **Dilatant Fluids** increase their viscosity as shear rates increase.
- **Plastic Fluids** have a yield point with pseudoplastic behavior.
- **Thixotropic and Rheopectic** fluids show viscosity-time nonlinear behavior.
- For example, the former shear thin and then reform its gel structure.



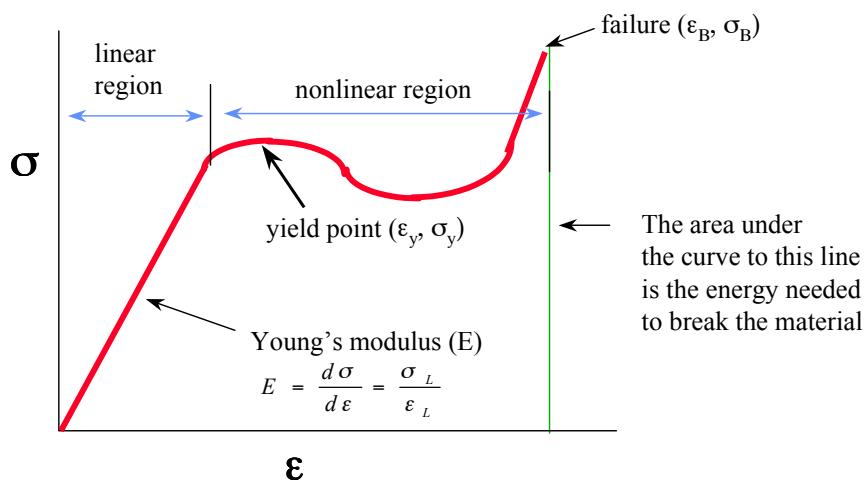
**Polymers are
Non-Newtonian Fluids**



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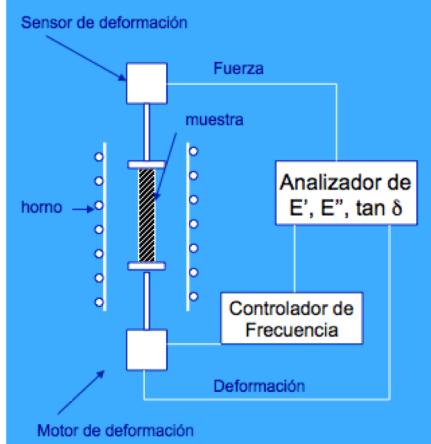
STRESS-STRAIN CURVES



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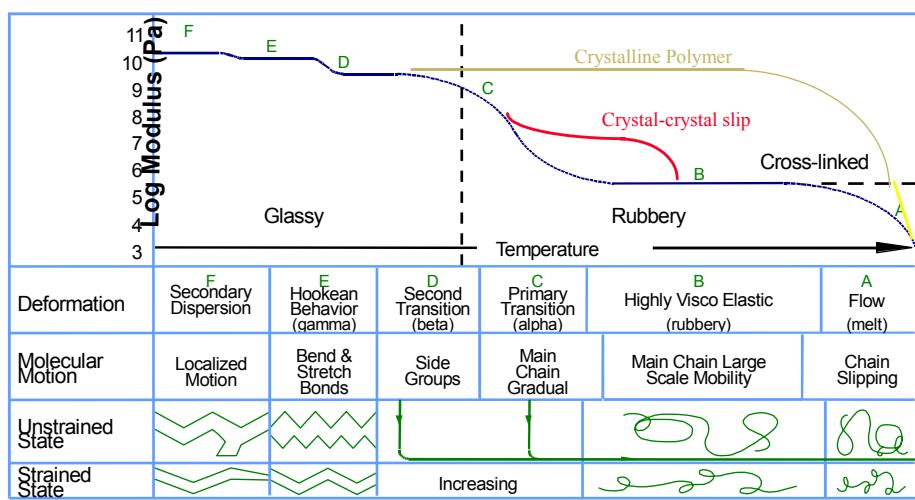
DMA INSTRUMENTATION



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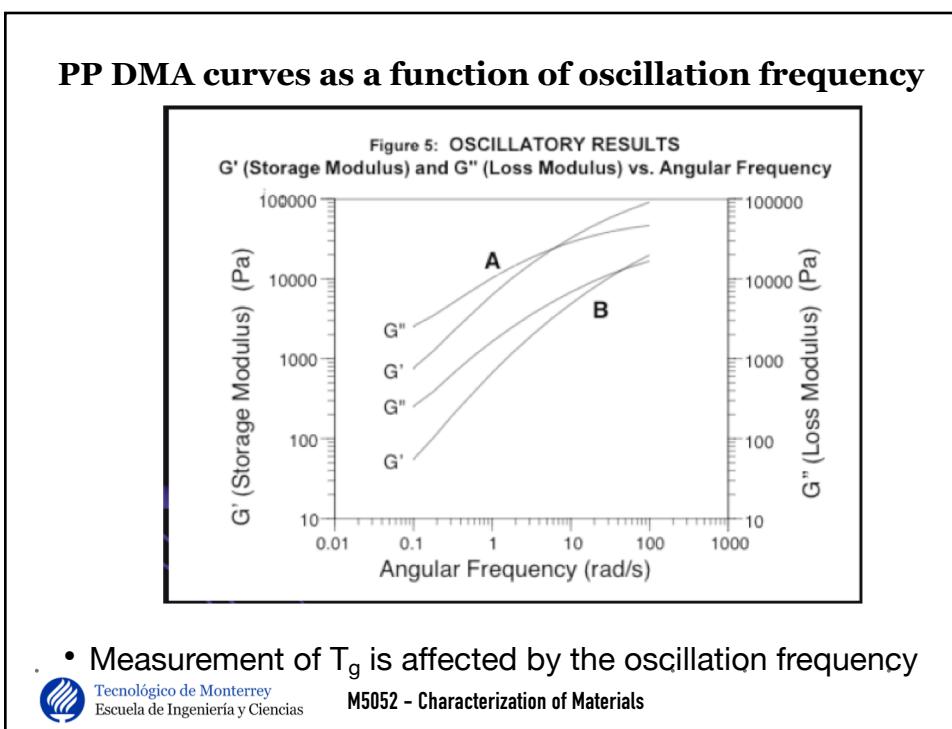
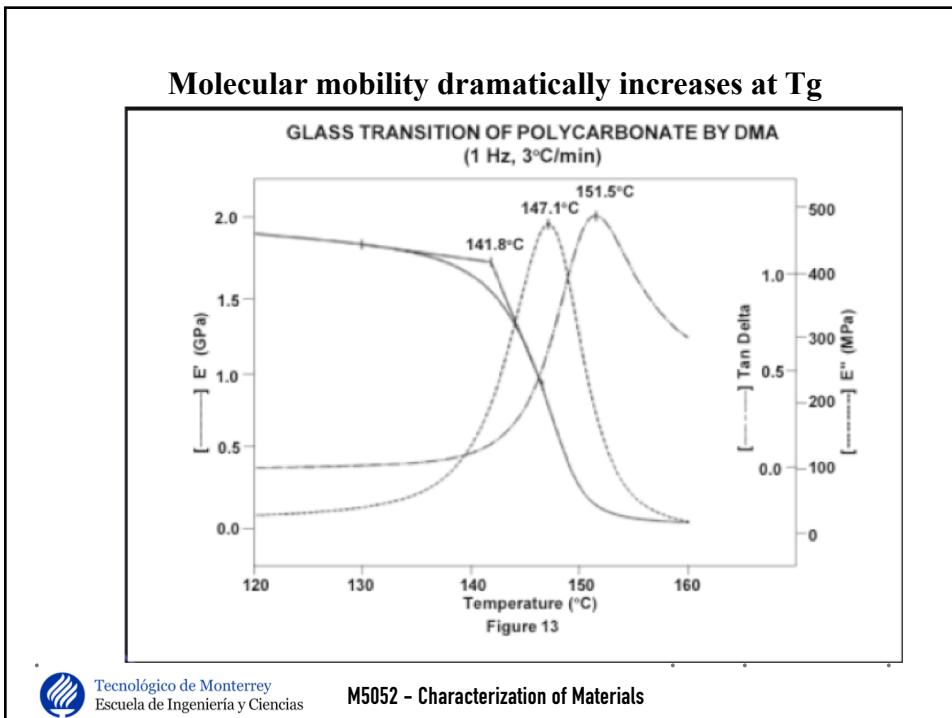
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IDEALIZED SCHEME OF MOLECULAR MOTIONS AND TRANSITIONS OBSERVED BY DMA, WITH INCREASING TEMPERATURE



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SOME APPLICATIONS OF DMA

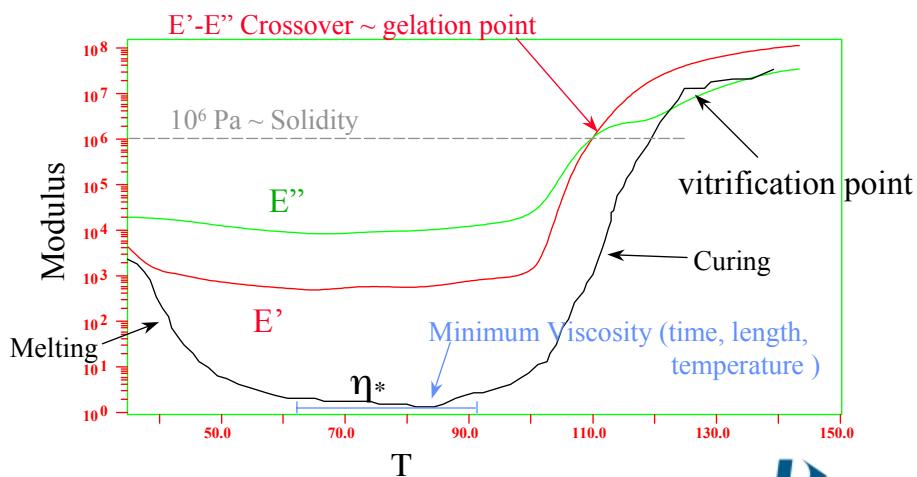
- ▶ DMA allows to relate molecular structure and processing conditions with the product properties
- ▶ Many applications in Polymer Science and Technology
- ▶ Determine upper use temperature for composites
- ▶ Selection of materials for specialized applications
 - ▶ Acoustics, automotive, aerospace
- ▶ Effect of composition on thermomechanical properties of products
- ▶ Study of phase homogeneity of copolymers and blends
- ▶ Quality Control
 - ▶ Shape of DMA curve will vary if material has different specifications
- ▶ Analysis of processing conditions



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M5052 - Characterization of Materials

ANALYSIS OF CURING OF TERMOSET POLYMERS



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