



Sveučilište u Zagrebu
Fakultet kemijskog
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University of Zagreb
Faculty of Chemical Engineering and Technology

Structure and properties of polymer materials

seminars

Zagreb, October 2021

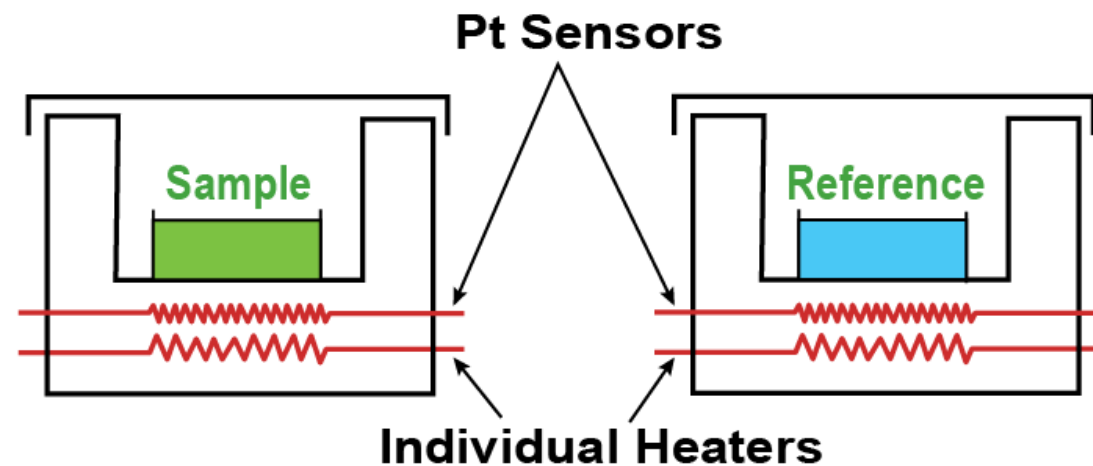
DIFFERENTIAL SCANNING CALORIMETRY (DSC)

- Measures the heat absorbed or liberated in the material during heating or cooling
- (common) calorimeter – heat flow in a sample
- differential calorimeter – heat flow in a sample vs. reference as a function of time

$$\text{mJ/s} = \text{mW}$$

Modes and principles of operation

Power-compensating DSC



Temperature differences between the sample and reference are "compensated" for by varying the heat required to keep both pans at the same temperature. The energy difference is plotted as a function of sample temperature.

- Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere
- These measurements provide quantitative and qualitative information about physical and chemical changes that involve **endothermic** or **exothermic processes**, or **changes in heat capacity**

Information obtained from DSC

- glass transition temperatures
- melting points and boiling points
- crystallization time and temperature
- percent crystallinity
- heats of fusion and reaction
- specific heat (heat capacity)
- oxidative stability
- curing kinetics (in thermosets)
- curing degree
- reaction kinetics
- purity
- thermal stability

DSC Signals

DSC measures the difference in heat flow rate ($\text{mW} = \text{mJ/s}$) between a sample and inert reference as a function of time and temperature

Heat Flow

- Endothermic: heat flows into the sample as a result of either heat capacity (in heating mode) or some endothermic process (melting, evaporation, etc.)
- Exothermic: heat flows out of the sample as a result of either heat capacity (in cooling mode) or some exothermic process (crystallization, curing, oxidation, etc.)

DSC: Terminology

- **Amorphous phase** – The portion of material whose molecules are randomly oriented in space. Thermosets and some thermoplastics
- **Crystalline phase** – The portion of material whose molecules are regularly arranged into well defined structures consisting of repeat units. Very few polymers are 100 % crystalline
- **Semi-crystalline polymers** – Polymers whose solid phases are partially amorphous and partially crystalline. Most common thermoplastics are semi-crystalline
- **Endothermic transition** – A transition which absorbs energy
- **Exothermic transition** – A transition which releases energy
- **Melting (fusion)** – The endothermic transition upon heating from a crystalline solid to the liquid state. The melt is another term for the pure polymers in liquid phase
- **Crystallization** – The exothermic transition upon cooling from liquid to crystalline solid.
- **Enthalpy of melting/crystallization** – The heat energy required for melting or released upon crystallization. This is calculated by integrating the area of the DSC peak

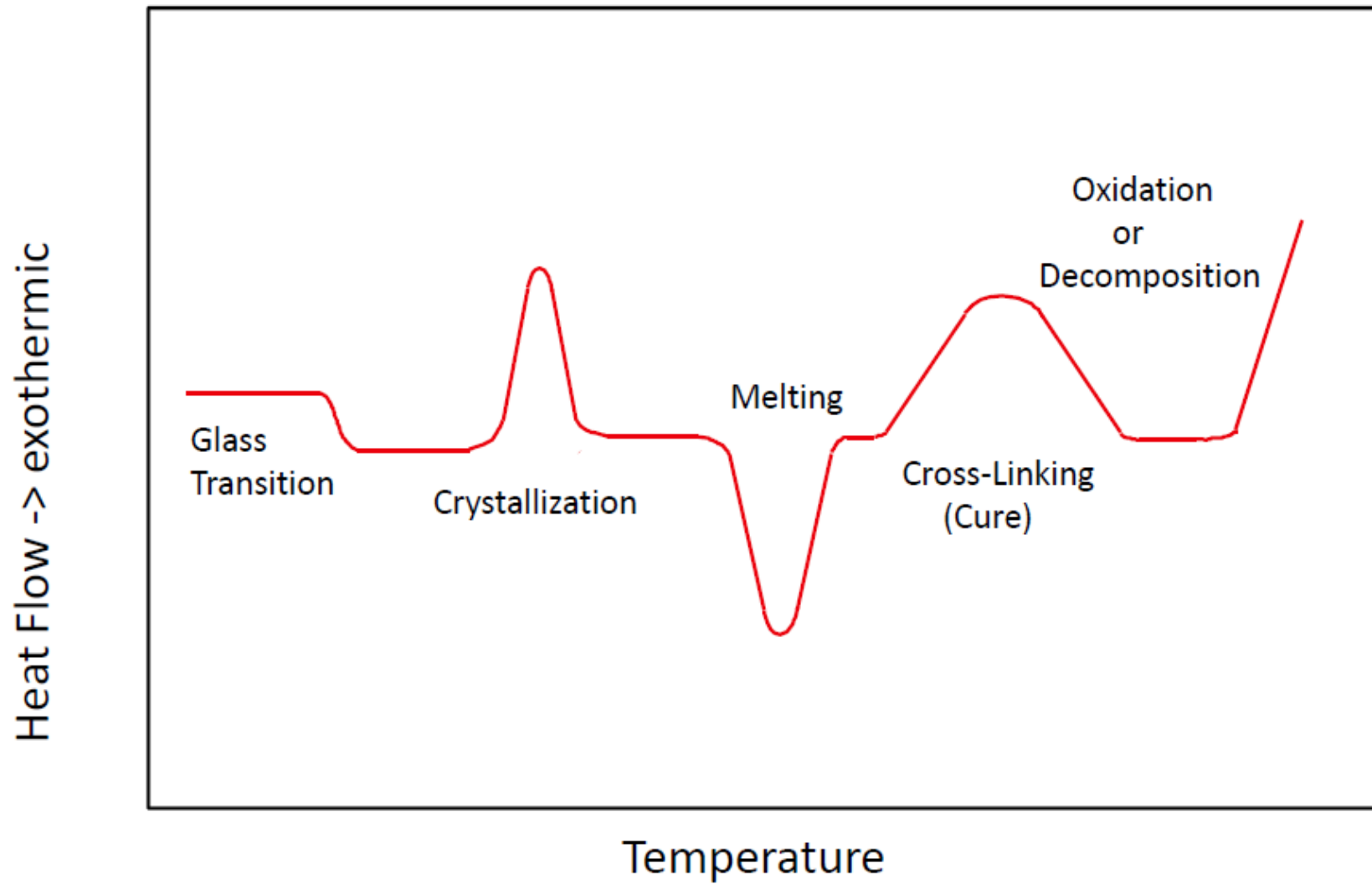
Amorphous



Semicrystalline



Typical DSC output



Glass transition, T_g

- 2nd order transition (no latent heat)
- Below $T_g \rightarrow$ glassy state, available motions of polymer chains are limited
- Above $T_g \rightarrow$ rubbery state, more modes of motion of polymer chains are accessible
- Only polymers that exist in the amorphous state exhibit glass transition

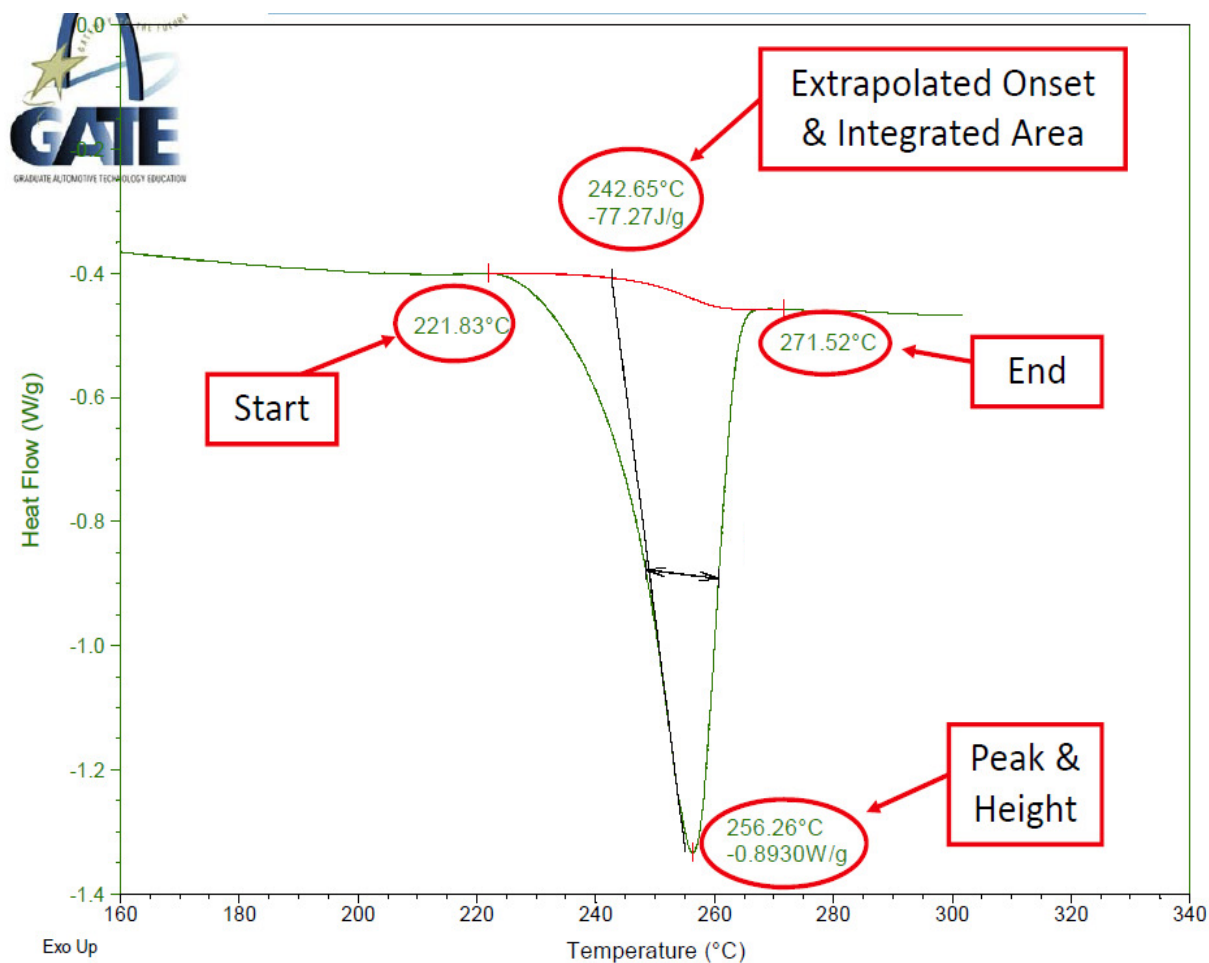
Melting, T_m (fusion, T_f)

- At the melting temperature (T_m) the chains are allowed to move around freely, they do not possess any ordered arrangements
- 1st order transition, polymers absorb heat, endothermic transition
- When the melting temperature is reached, the temperature does not rise upon heating until all the crystals have completely melted
- Melting occurs only in a crystalline polymer

Crystallization, T_c

- 1st order transition, polymers release heat, exothermic transition
- Crystallization occurs only in polymers that can form crystals
- Crystalline polymers frequently possess amorphous domains. This is the reason why a polymer can exhibit both a glass transition temperature and a melting temperature
- The amorphous portion undergoes the glass transition only, and the crystalline portion undergoes melting only

Observation of melting (fusion)



Polymers

- The peak temperature is assigned as the melting point

Pure,

low molecular weight materials

($M_w < 500$ g/mol)

(small molecules)

- The extrapolated onset is assigned as the melting point

Effect of aromaticity on melting point

Polymer	% Aromatic	Melting Range
-CH ₂ - CH ₂ -	0	105 - 135°C
PET	39	250 - 275°C
-(Ph)-O-	62	300 - 315°C
-(Ph)-S-	70	300 - 360°C

Effect of molecular weight on melting point

Olefin Formula	Mole. Wt. (g/mol)	T _m (°C)
C ₁₂ H ₂₆	170	-10
C ₂₄ H ₅₀	339	54
C ₃₀ H ₆₂	423	66
C ₃₅ H ₇₂	493	75

Effect of polymer type on melting point

Class	Structure	Melting Range
Polyolefins	-CH ₂ -CH ₂ -	85 - 174°C
Polyamides	-CH ₂ -NH-C(O)-CH ₂ -	190 - 265°C
Polyesters	-CH ₂ -O-C(O)-CH ₂ -	220 - 270°C
Polyphenylene Sulfides	-Ph-S-	300 - 360°C

Effect of hydrogen bonding on melting point

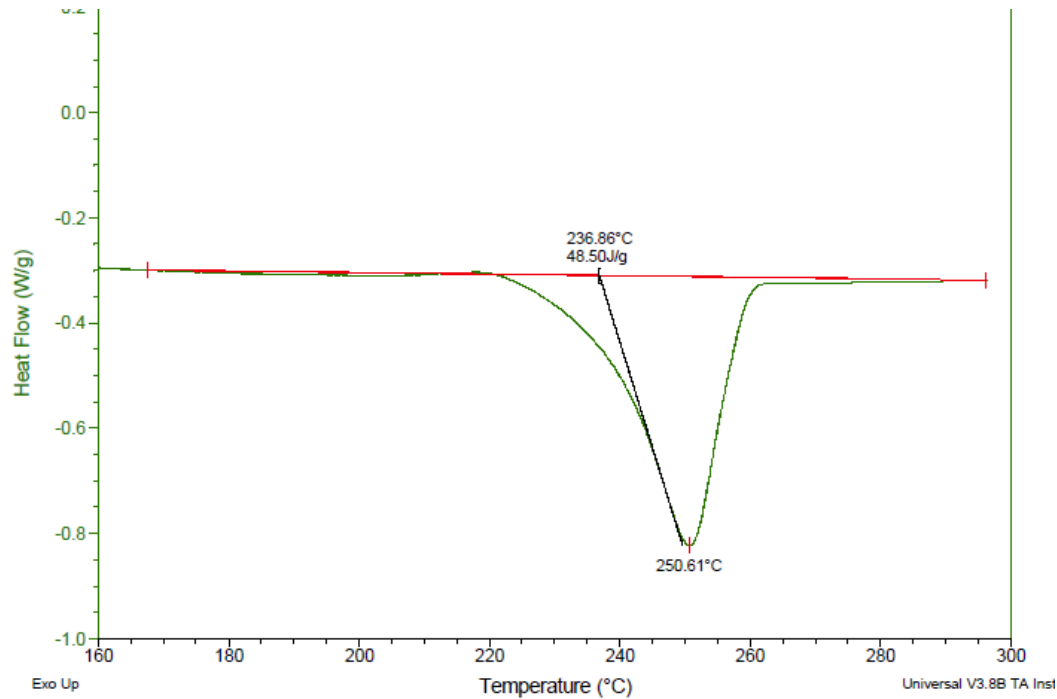
Polyamide	T _m	H Bonding
Nylon 12,2	236	Least
Nylon 10,2	242	
Nylon 8,2	279	
Nylon 6,2	326	Most

Nylon x,y where:

x = carbons in diamine section

y = carbons in diacid section

T_m and % crystallinity measurement by DSC



χ – percent of crystallinity

$$\chi = \frac{\Delta H_{exp}}{\Delta H_0} \cdot 100\%$$

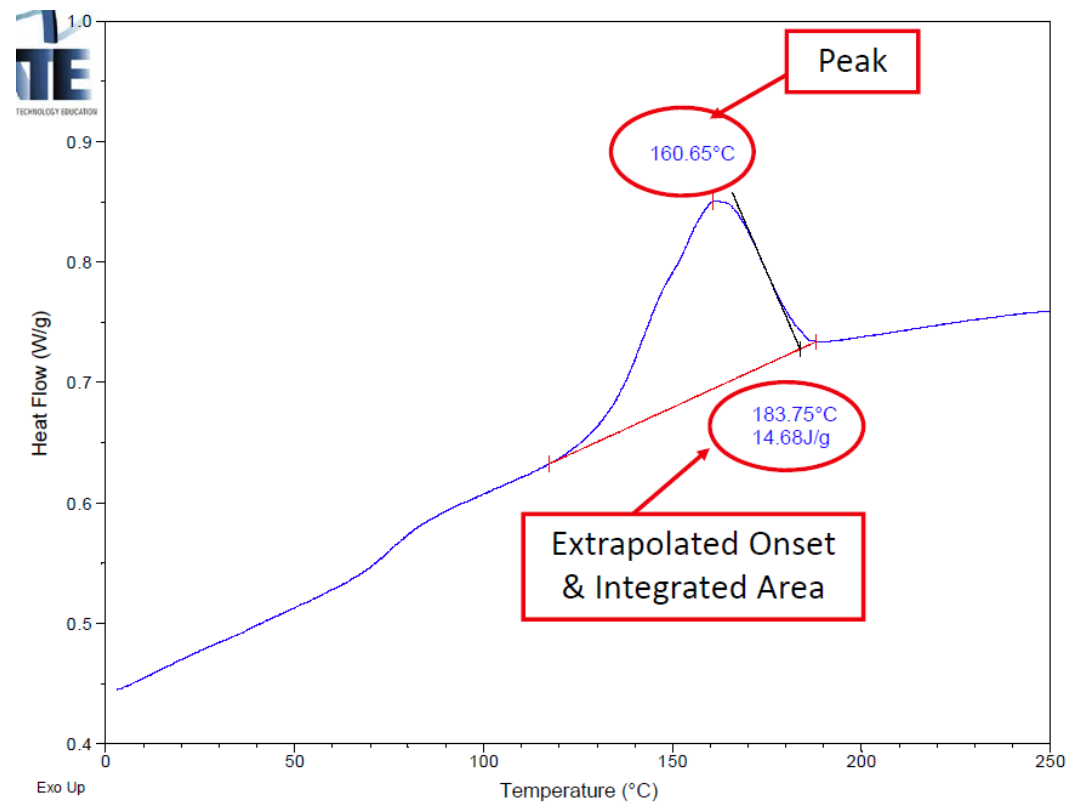
ΔH_{exp} – experimental heat of fusion (melting) for the polymer

ΔH_0 – theoretical heat of fusion (melting) for 100% crystalline polymer

Observation of crystallization

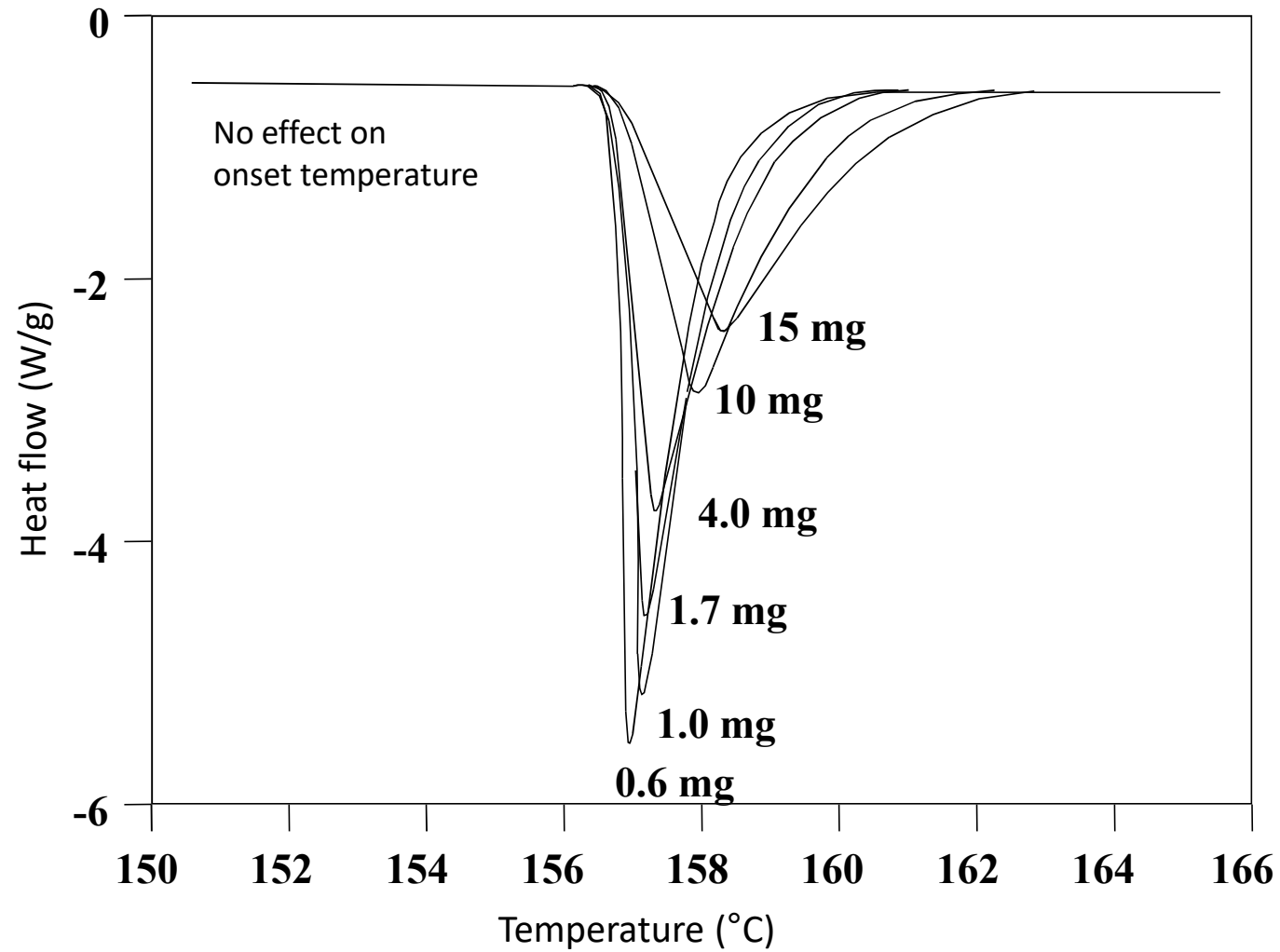
Crystallization is a two step process:

- Nucleation
- Growth
- The extrapolated onset is the nucleation temperature
- The peak maximum is the crystallization temperature

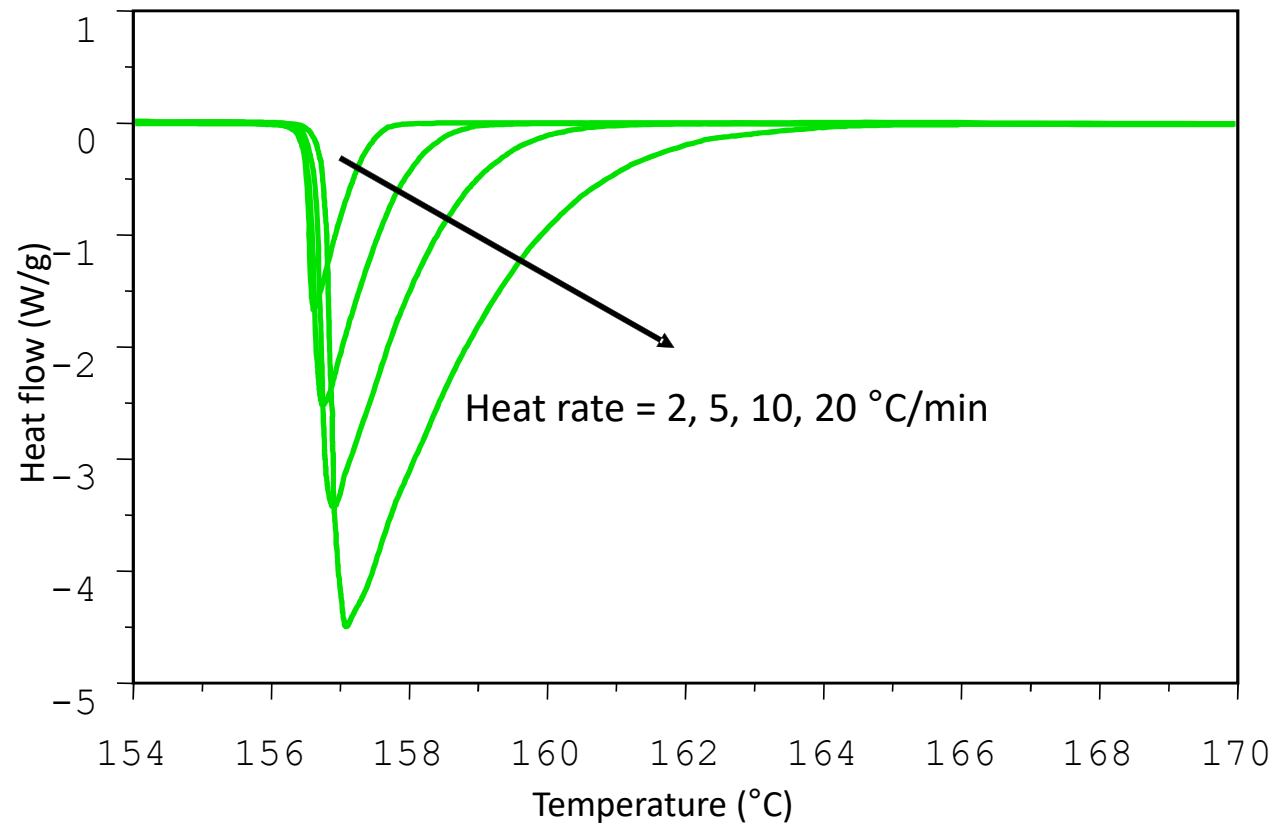


Parameters affecting T_m , T_c

Sample mass



Cooling/heating rate

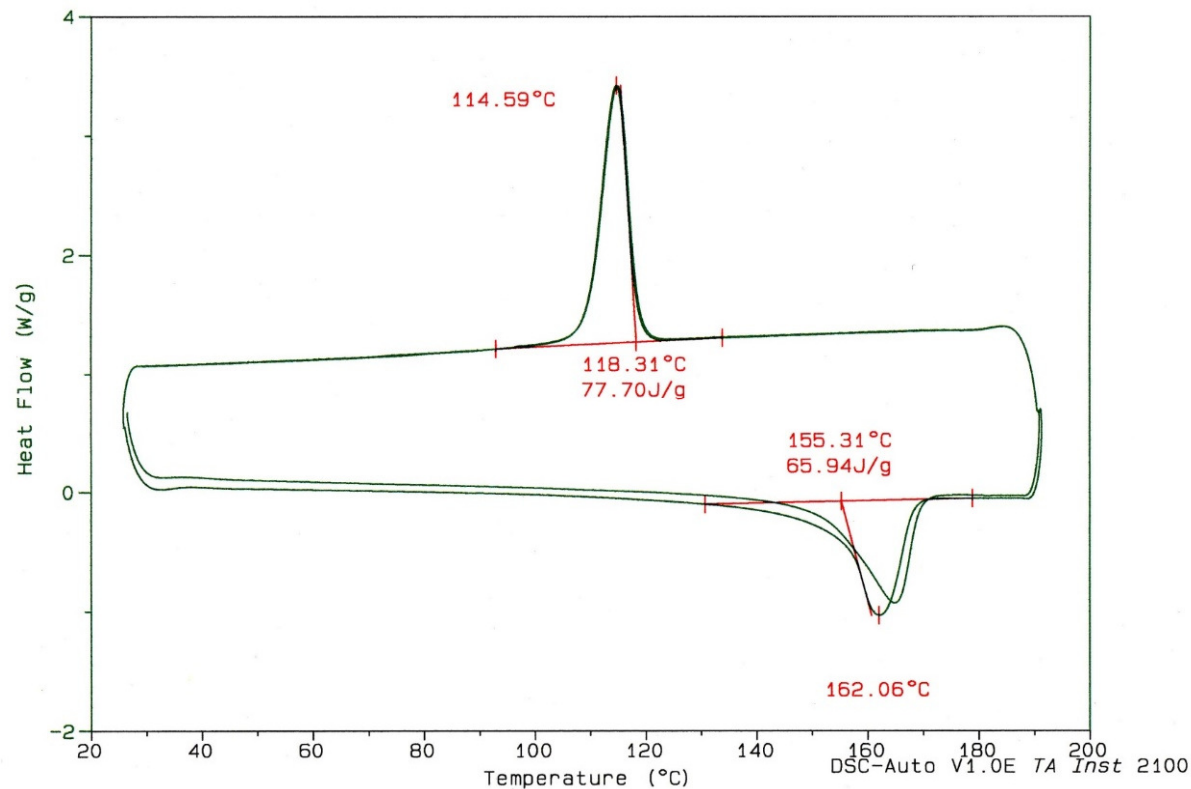


T_m – shifted to higher temperatures

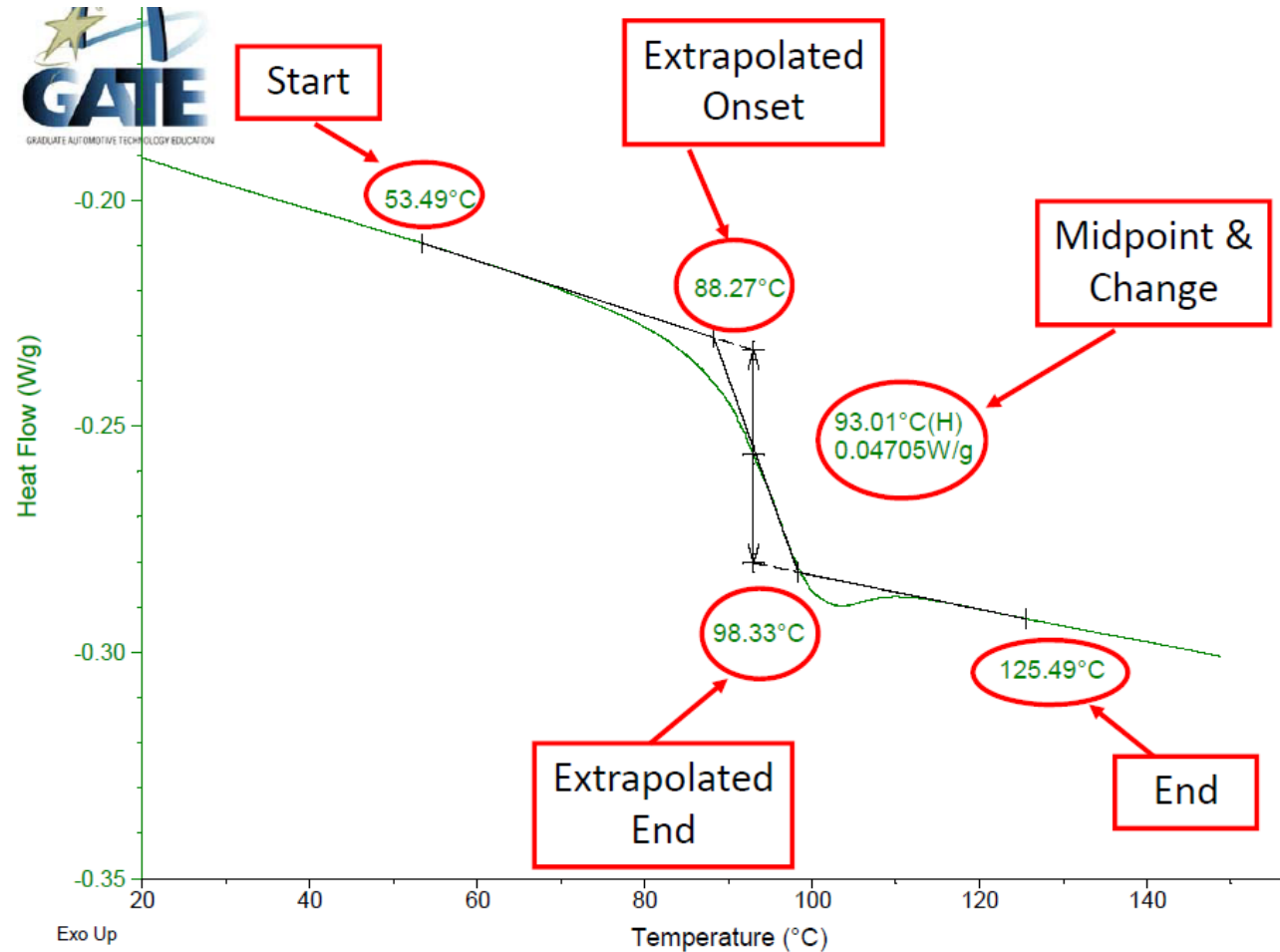
T_c – shifted to lower temperatures

Thermal history

- The thermal history of a sample will affect the results. Internal structure of thermoplastics is strongly affected by the thermal history imparted during processing
- The rate of cooling from the melt can result in either a crystalline (ordered) or amorphous (random) internal structure
- Running heat-cool-heat experiments to eliminate thermal history



Measurement of T_g



- The transition does not occur suddenly, but usually takes place over a temperature range
- To overcome this problem the temperature in the midpoint of the inclined part of the graph is by definition the T_g .

T_g is affected by:

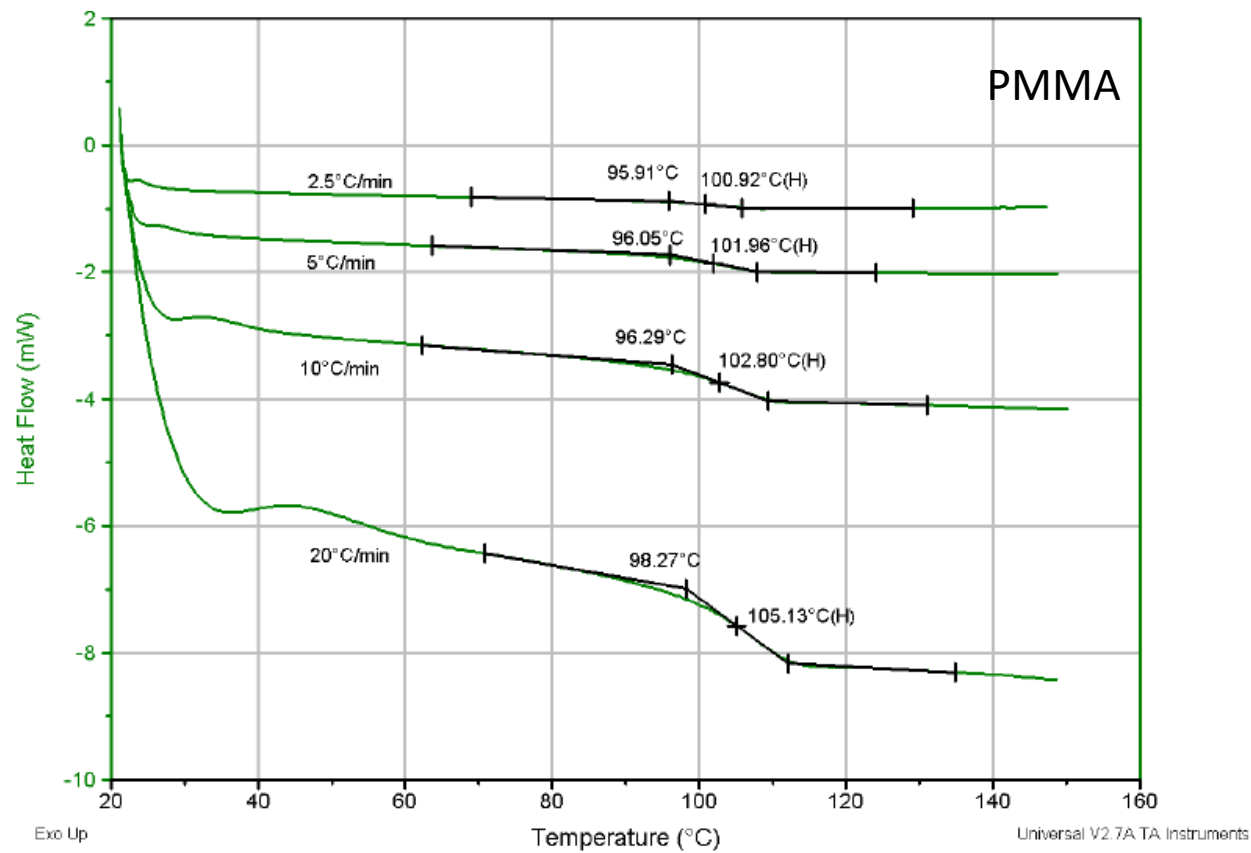
- Heating rate
- Molecular weight
- Chemical structure
- Crystallinity
- Crosslinking
- Amount of plasticizer
- Physical aging
- Blending / copolymerization
- Amount of fillers (in composites)

Anything that effects the mobility of the molecules, affects the heat capacity, which in turn affects the T_g

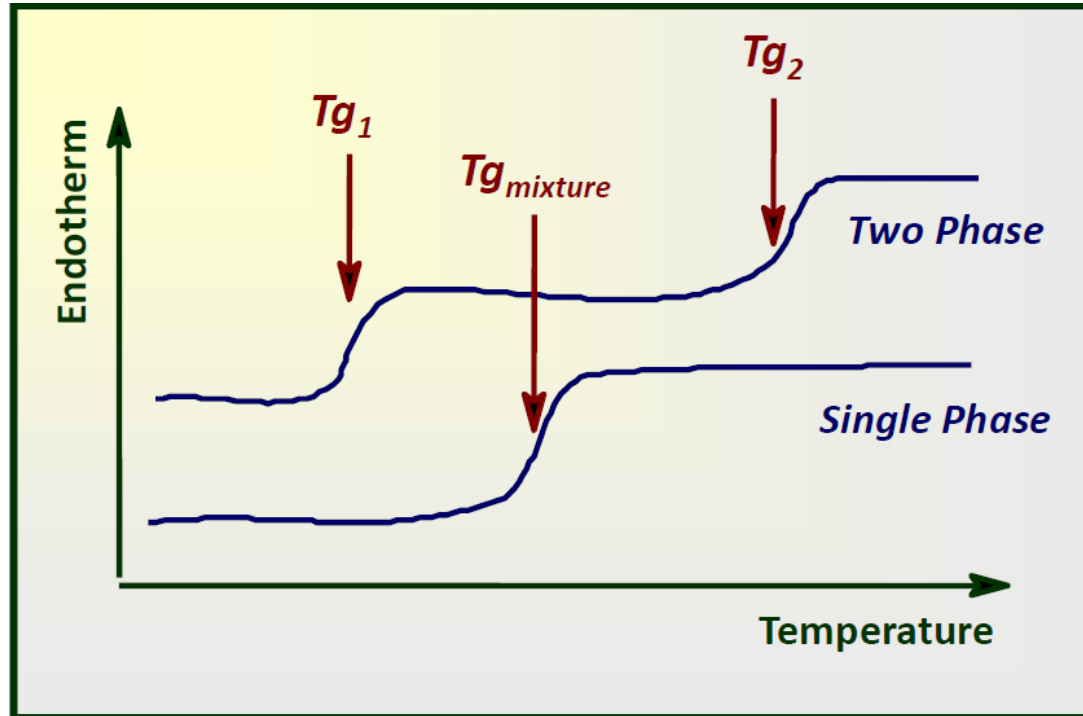
DSC: Effect of heating rate

Faster heating rates increase sensitivity but decrease resolution

- Good starting point is 10 °C/min



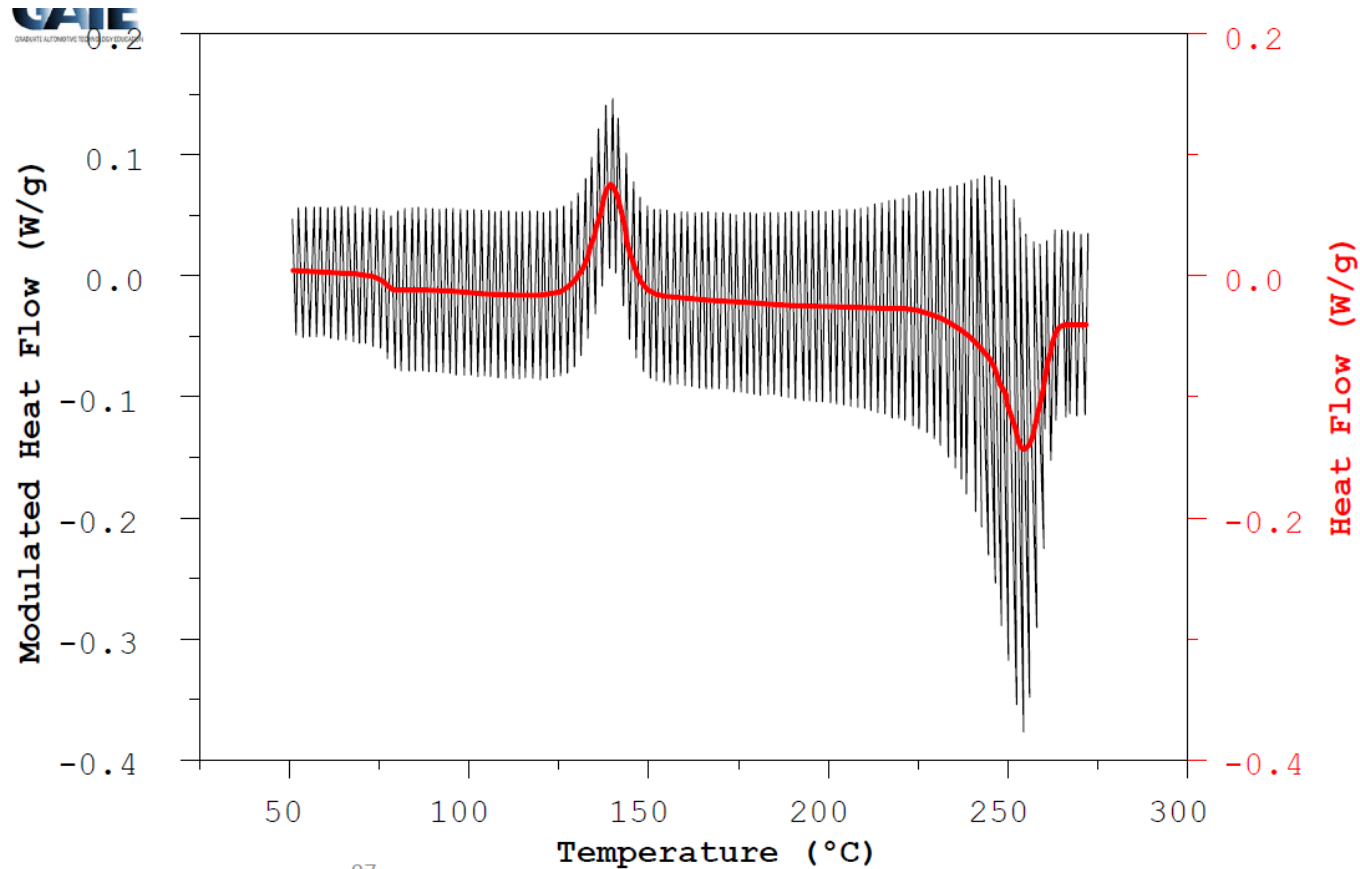
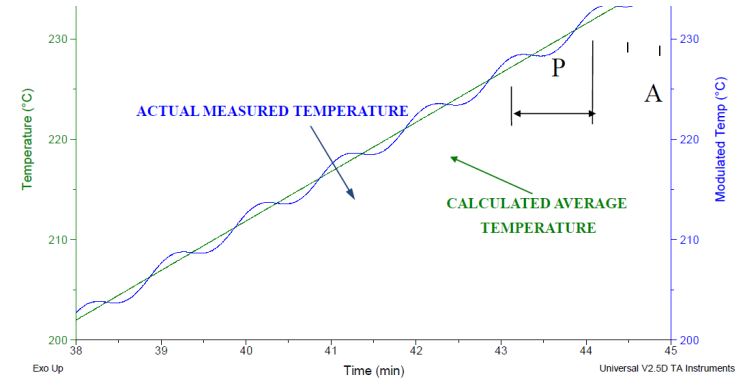
Effect of miscible and immiscible blends on T_g



Modulated DSC

Sinusoidal heating rate \rightarrow Amplitude of heat flow

http://www.tainstruments.com/pdf/literature/TP_006_MDS_C_num_1_MDSC.pdf



Modulated DSC

Increased sensitivity upon transitions

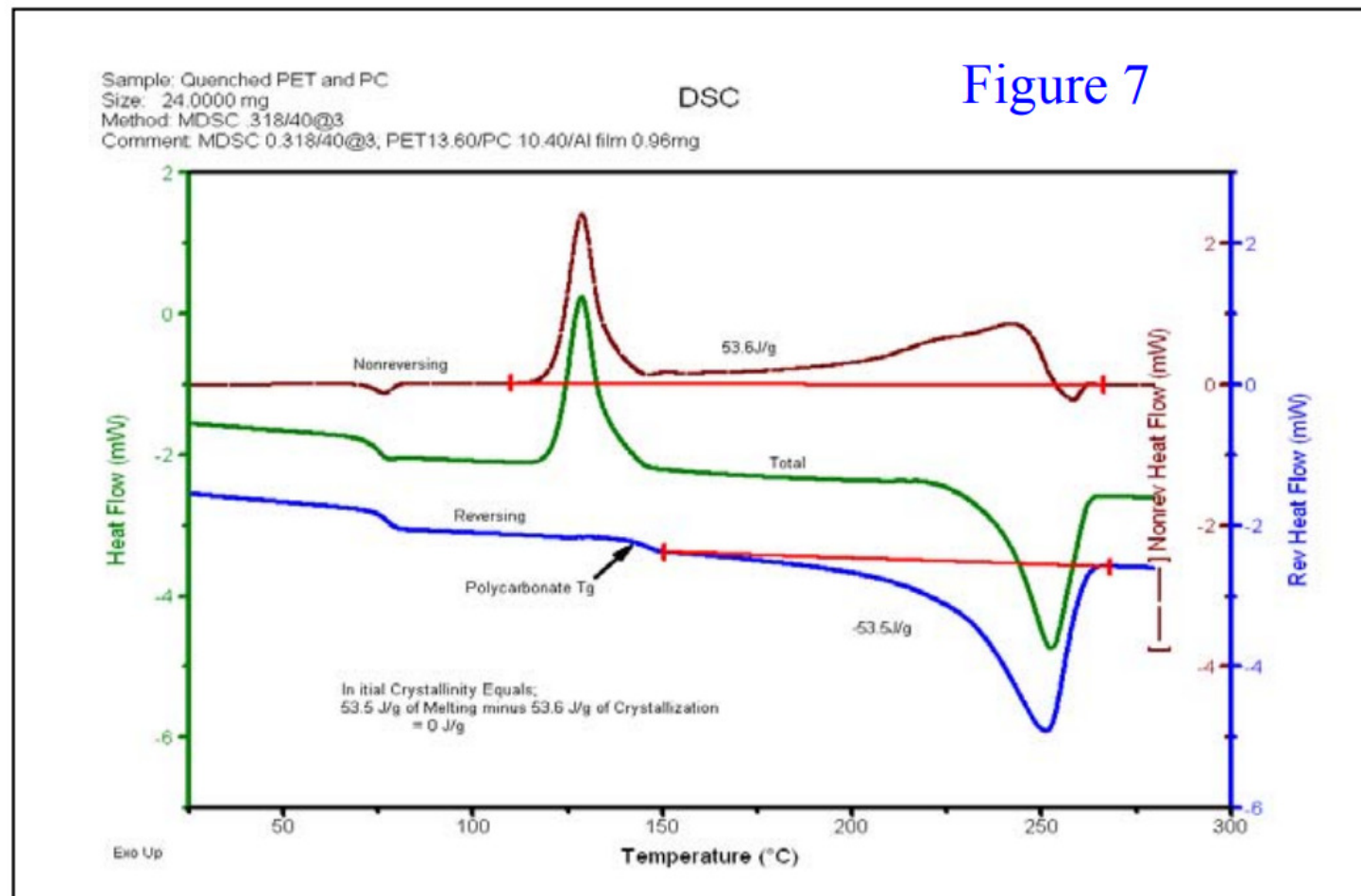
Typically, T_g measurements in highly filled, reinforced, or highly crystalline polymers are difficult by conventional DSC. This is because these measurements by DSC are based on detection of a heat capacity change, and the addition of fillers and reinforcers or increased crystallinity dilutes the change being measured. The **high sensitivity of modulated DSC** permits the detection of weak or subtle glass transitions.

Modulated DSC

Separation of complex transitions

Modulated DSC deconvolutes total heat flow into two constituents: heat capacity related (reversing) heat flow and kinetic (nonreversing) heat flow. This deconvolution allows for the separation of complex and overlapping transitions.

$$\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)$$



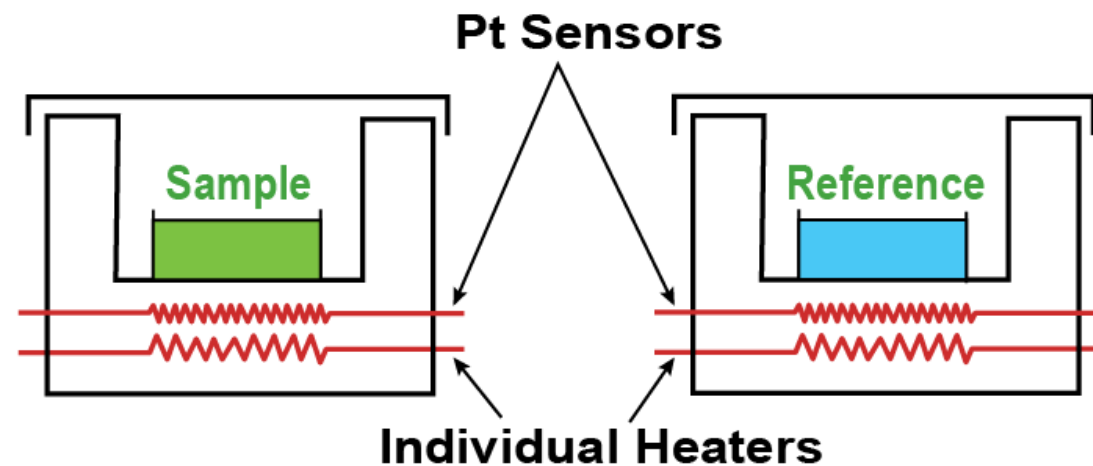
Modulated DSC

Quantifying Polymer Blend Composition

Properties of polymer blends can be significantly affected by small changes in blend composition. DSC has proven to be an effective technique for characterizing and quantifying polymer blends based on the presence of multiple glass transitions or melts. Overlapping transitions of one component can sometimes interfere with the ability to detect the glass transition of another, necessitating multiple experiments and decreased sample throughput. MDSC is able to resolve such overlapping transitions.

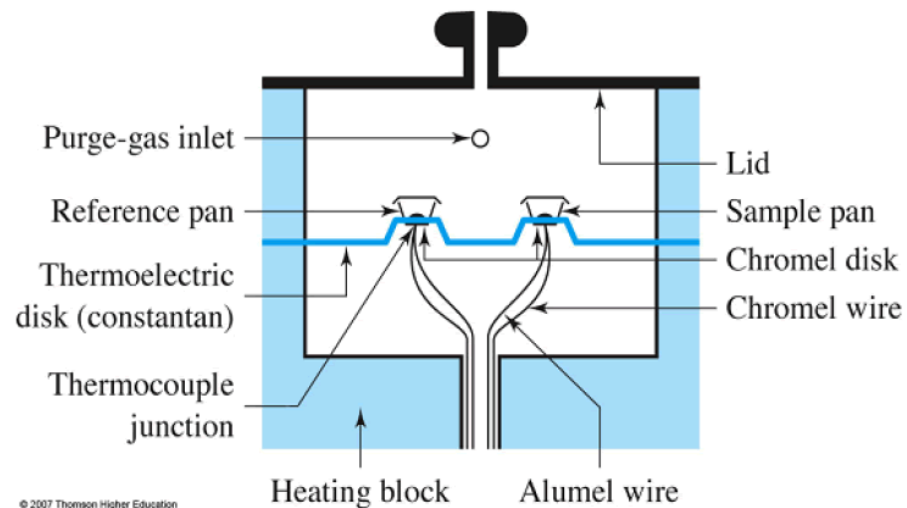
Modes and principles of operation

Power-compensating DSC

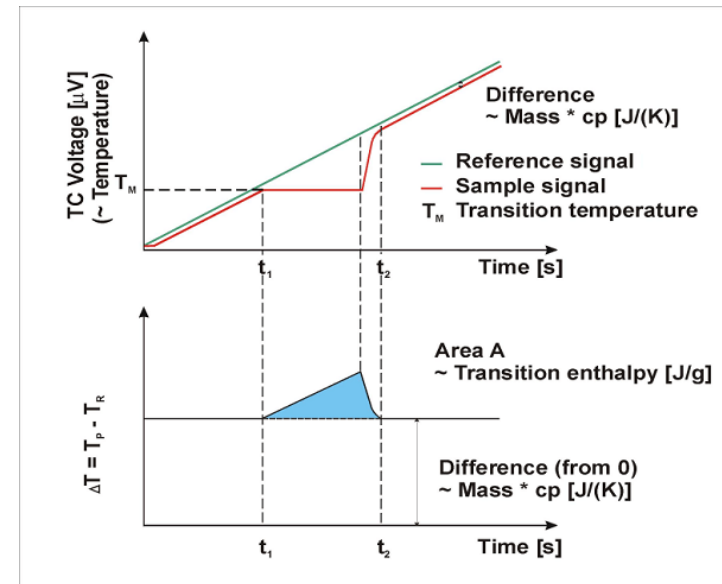


Temperature differences between the sample and reference are "compensated" for by varying the heat required to keep both pans at the same temperature. The energy difference is plotted as a function of sample temperature.

Heat-flux DSC



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Heat flux DSC utilizes a single furnace. Heat flows both into the sample and reference material via an electrically heated constantan (Cu/Ni alloy) thermoelectric disk.

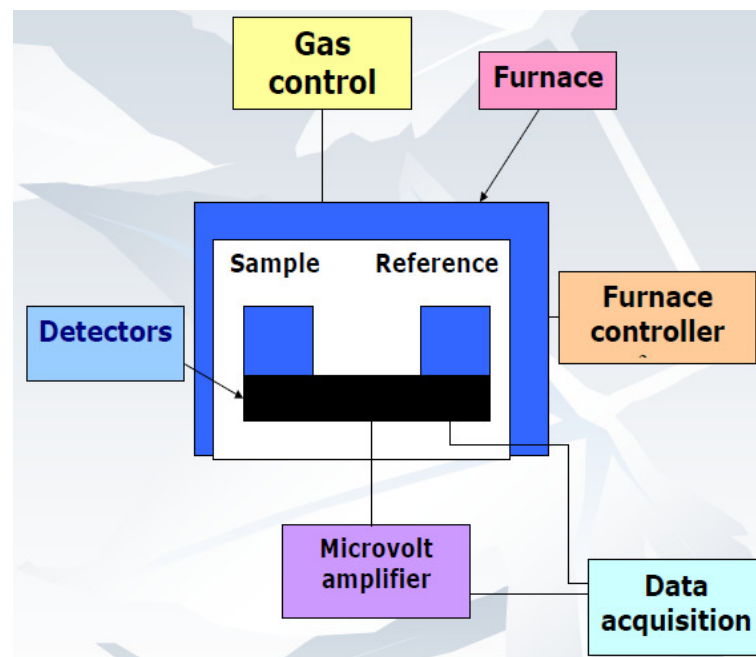
The temperature difference is measured (the difference in output of the two thermocouple junctions) that can be converted into the transition enthalpy

Diagram of a DSC apparatus

A DSC apparatus is built around a differential detector

It contains

- a signal amplifier
- a furnace
- a temperature controller
- a gas control device
- a data acquisition device



Sample shape

- Keep sample thin
- Cover as much as the bottom of pan as possible



- Cut sample to make thin, don't crush
- If pellet, cut cross section



- If powder, spread evenly over the bottom pan



or make a pellet!

Sample pans:

- always covered and clamped
- sometimes tightly sealed
- handled with care, using tweezers



Sample size

Sample size depends on what you are measuring

- If running an extremely reactive sample (like an explosive) run very small samples (< 1 mg)
- Pure organic materials, pharmaceuticals (1 – 5 mg)
- Polymers – ~10 mg
- Composites – 15 – 20 mg

Purge gas

Purge gas should always be used during DSC experiments

- Provides dry, inert atmosphere
- Ensures uniform heating
- Helps sweep away any off gases that might be released

Nitrogen – most common, increases the sensitivity

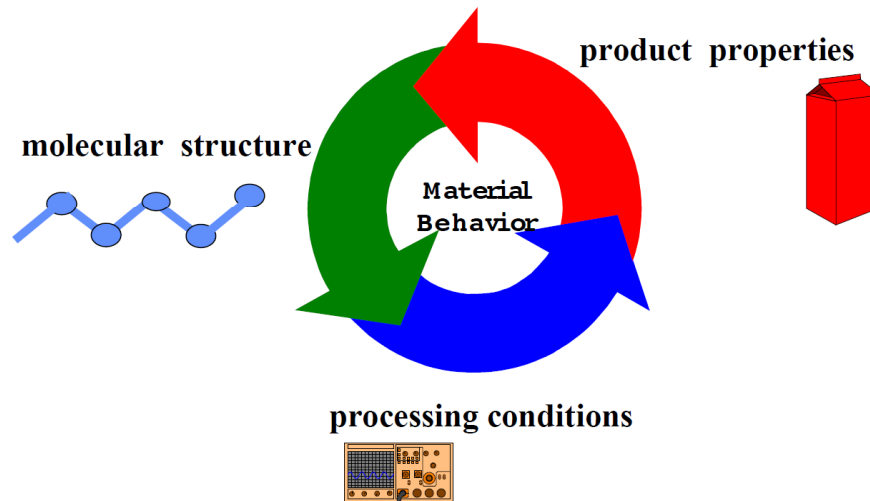
Helium – increases the resolution

Air or oxygen – used for the observation of oxidative effects

DYNAMIC MECHANICAL ANALYSIS (DMA)

- Dynamic Mechanical Analysis is a technique where a small deformation is applied to a sample in a cyclic manner. This allows the materials response to stress, temperature and frequency to be studied
- DMA is also called DMTA for Dynamic Mechanical Thermal Analysis.

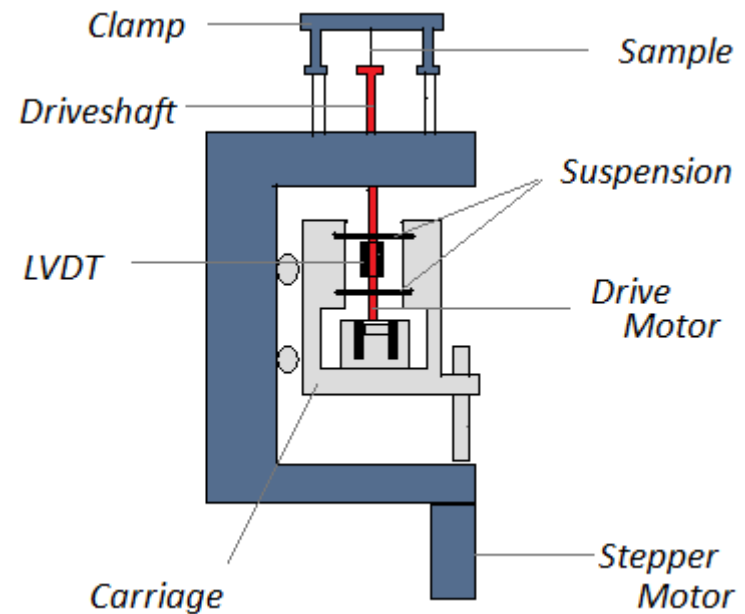
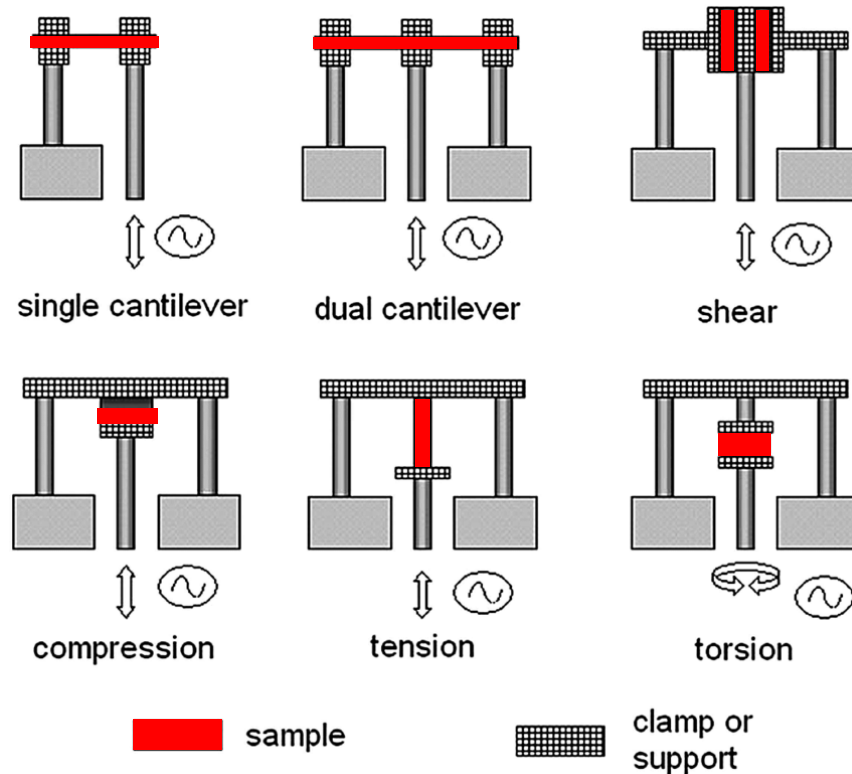
The DMA lets you relate:



DMA instrument

- motor and driveshaft are used to apply torsional stress
- linear variable differential transformer (LVDT) is used to measure linear displacement
- carriage contains the sample and is typically enveloped by a **furnace** and **heat sink**

Sample geometry



- Technique where sample is subjected to cyclic stress and response (deformation) is measured
- Deformation can be function of temperature or time
- Deformation and stress are changed sinusoidally with time
- Deformation rate is defined by the frequency ω (number of cycles per minute)
- Insight into rheological behavior of solid polymer materials
- Response of elastic and viscous (polymers are viscoelastic materials) component under cyclic deformation

$$\varepsilon = f\left(\sigma, \frac{dF}{dt}, T, t\right)$$

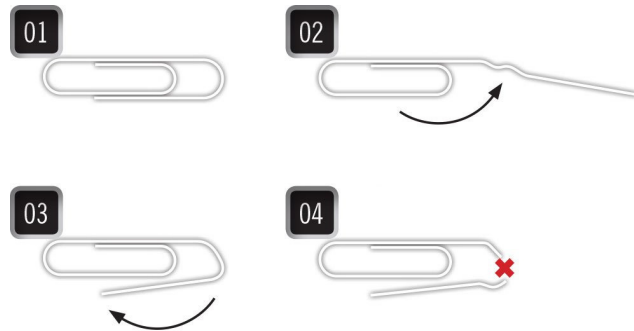
$$\sigma = \frac{F}{A_0}$$

stress

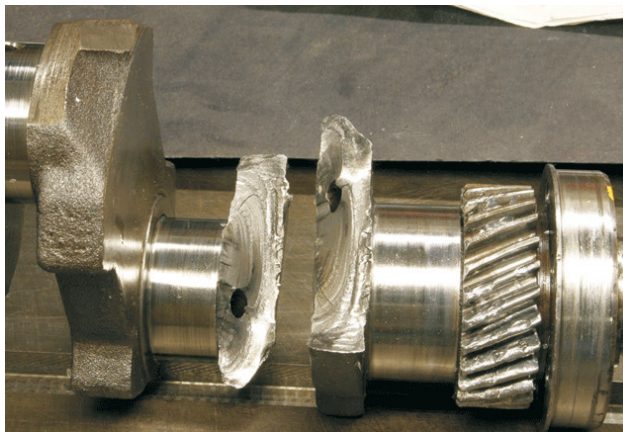
$$\varepsilon = \frac{L - L_0}{L_0} = \frac{\Delta L}{L_0}$$

deformation
(strain)

Why cyclic stress?

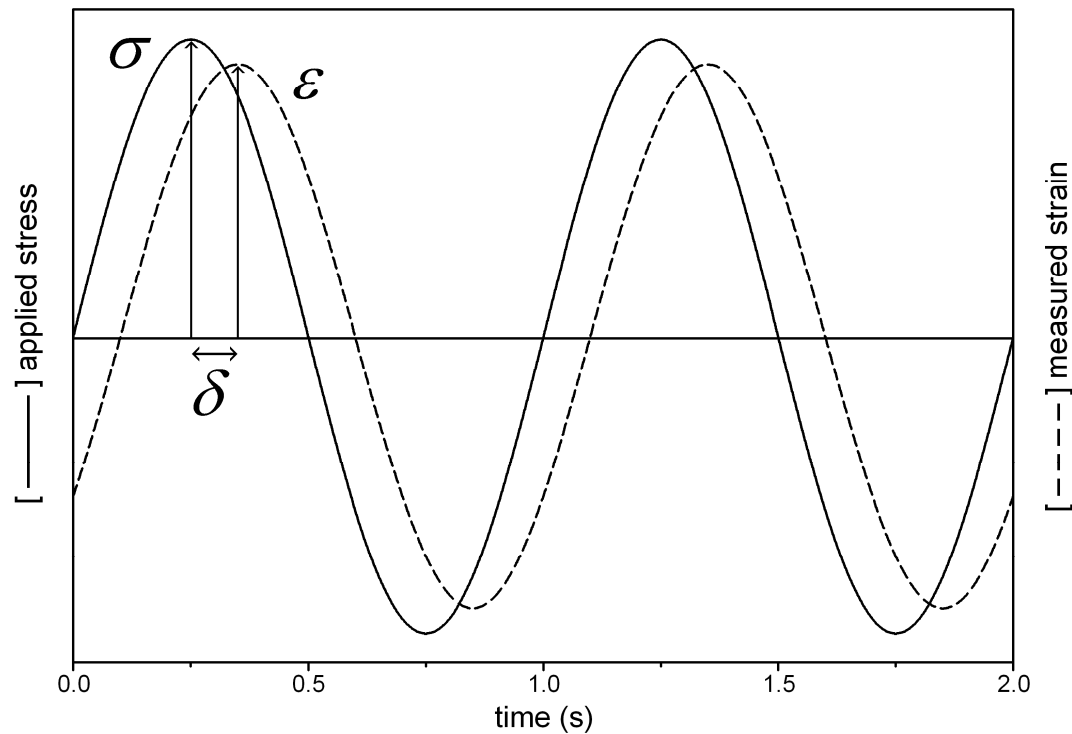


Versailles train disaster
due to broken locomotive axle



fatigue

Cyclic stress of material



σ – stress amplitude

ε – strain amplitude

Ideally elastic solids: σ and ε are in phase (Hooke's law), $\delta = 0^\circ$

Polymers $0 < \delta < 90^\circ$

Ideally viscous fluids: ε lags to σ for angle, $\delta = 90^\circ$

$$\sigma = \varepsilon E$$

Phase lag is consequence of relaxation processes in material,
part of energy of deformation is stored in material,
part is dissipated as heat

Cyclic stress of material

Primary viscoelastic functions

E' - storage modulus

- stress component in phase with deformation
- related to elastic component
- storage of energy, represents stiffness

E'' - loss modulus

- stress component related to viscous component
- proportional to lost mechanical energy which under deformation due to internal friction is transformed into heat
- loss of energy

$\tan \delta$ – phase angle (damping factor)

- ratio of loss modulus to storage modulus
- measure of the energy dissipation of a material
- indicator of viscoelasticity of material

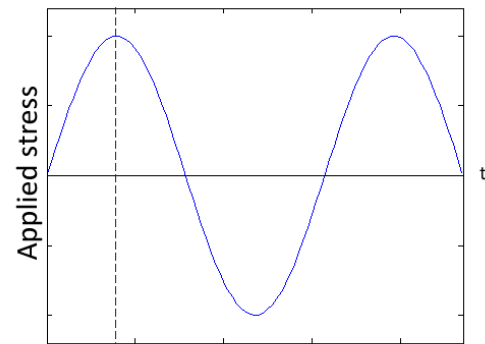
$$\tan \delta = \frac{E''}{E'}$$

E^* - Complex modulus

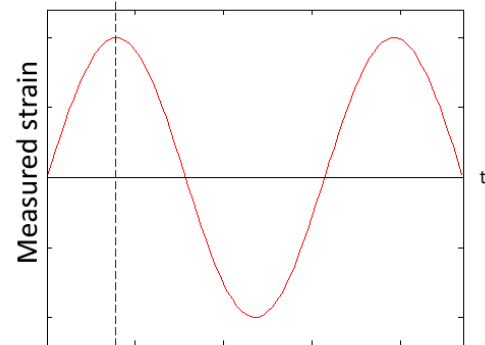
- Overall modulus representing stiffness of material; combined elastic and viscous components

$$E^* = E' + iE''$$

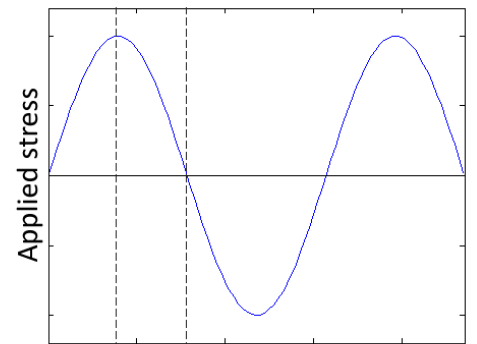
A. Ideal elastic material



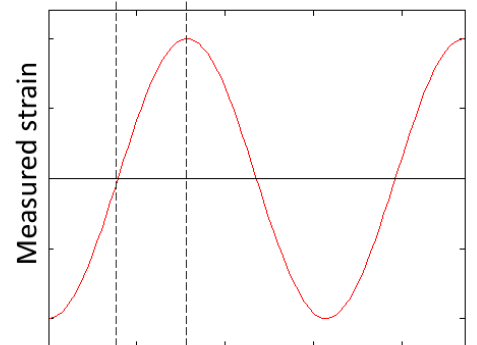
Phase lag = 0°



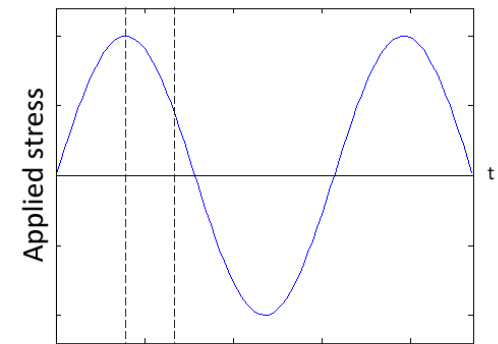
B. Viscous material



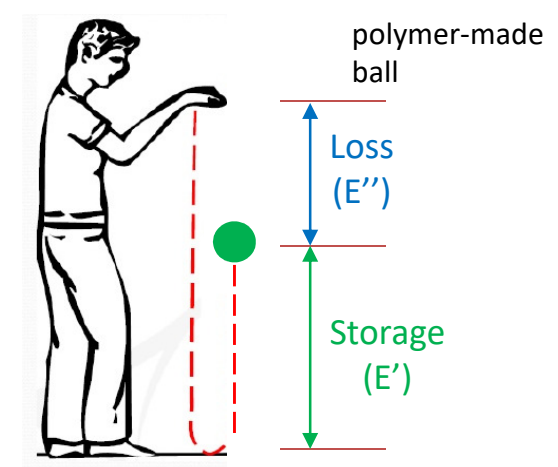
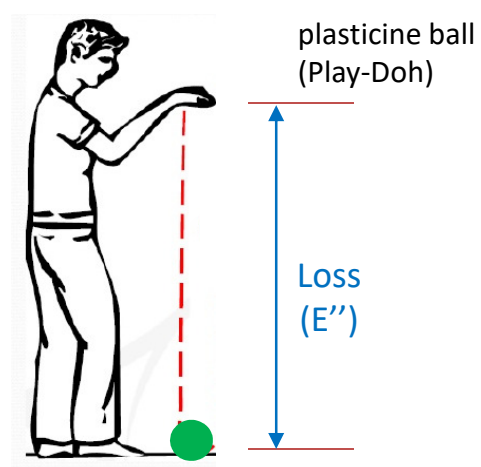
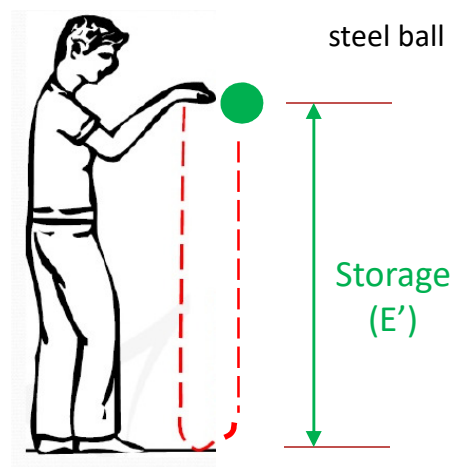
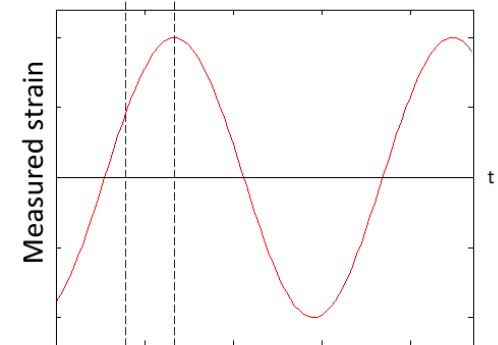
Phase lag = 90°



C. Viscoelastic material



$0^\circ < \text{Phase lag} < 90^\circ$

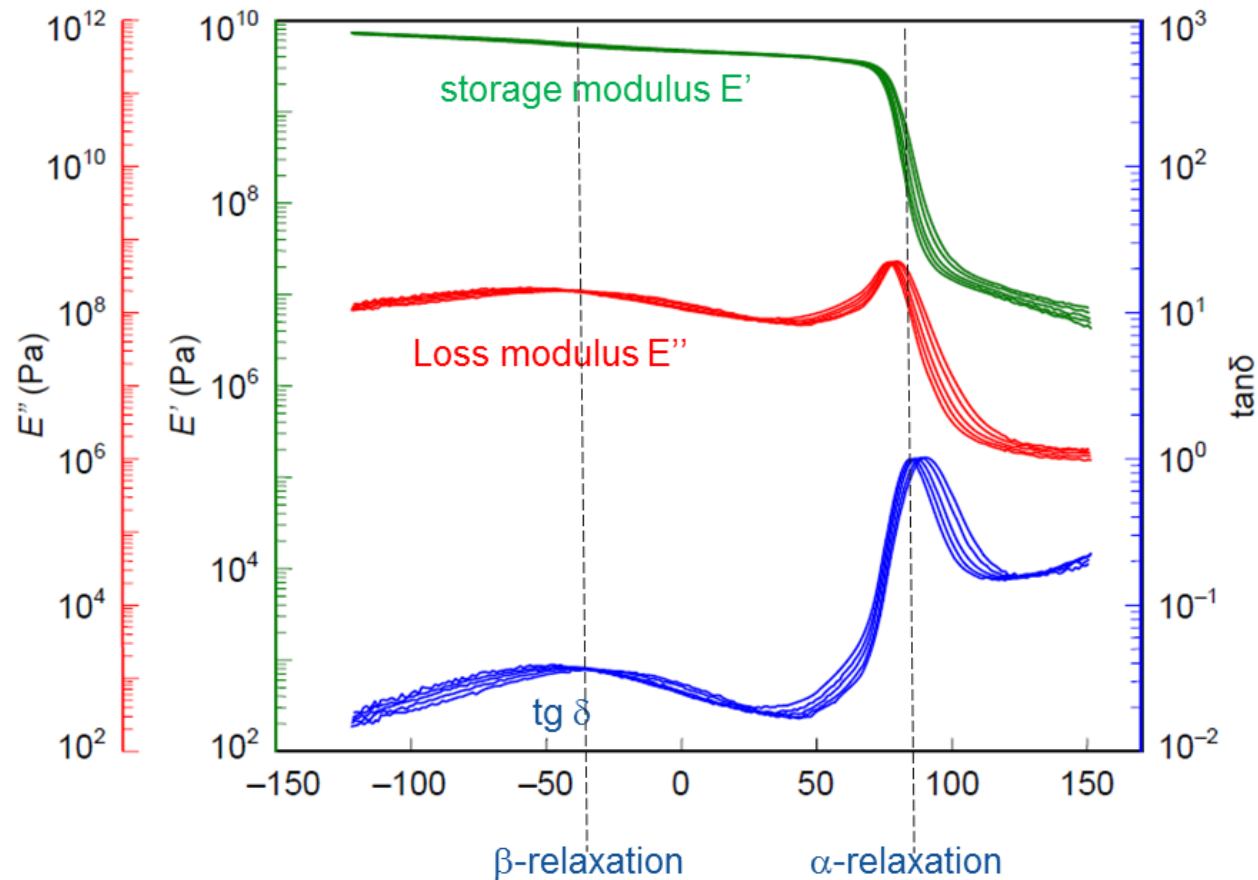


Assume that you apply a load to a polymer, some part of the applied load is dissipated by the energy dissipation mechanisms (such as segmental motions) in the bulk of polymer, and other part of the load is stored in the material and will be released upon removal of the load (such as the elastic response of a spring!).

- Increasing $\tan \delta$ indicates that your material has more energy dissipation potential so the greater the $\tan \delta$, the more dissipative your material is.
- Decreasing $\tan \delta$ means that your material acts more elastic now and by applying a load, it has more potential to store the load rather than dissipating it!

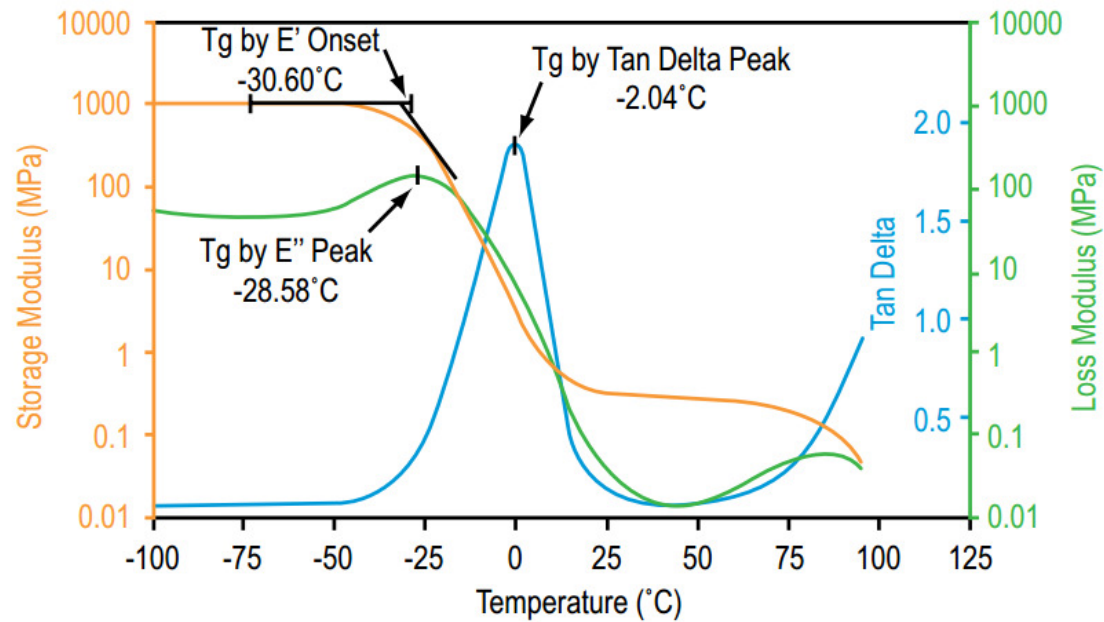
For example, in case of nano-composites (and filled polymers), increasing the nano-particle content diminishes the value of $\tan \delta$ as nano-particles impose restrictions against molecular motion of polymer chains (due to the adsorption of polymer chain on the surface of the particles) resulting in more elastic response of the material.

A typical DMA curve



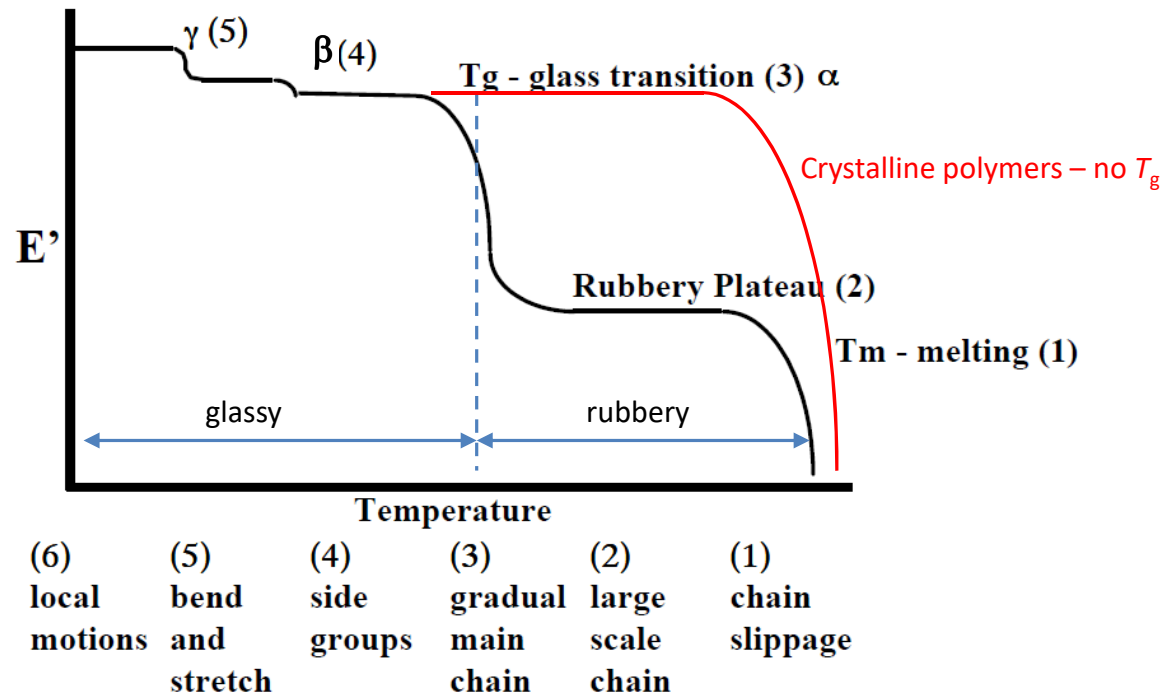
- The first transition (the largest one) is called alpha-transition. This usually corresponds to the glass transition in case of amorphous polymers or the melting in case of crystalline polymers.
- The second transition is situated to the left and is called beta-transition. This transition is usually attributed to the first occurrence of chain segment rotation in case of amorphous polymers.
- Which is the name for the third transition?

Determination of glass transition temperature (T_g)



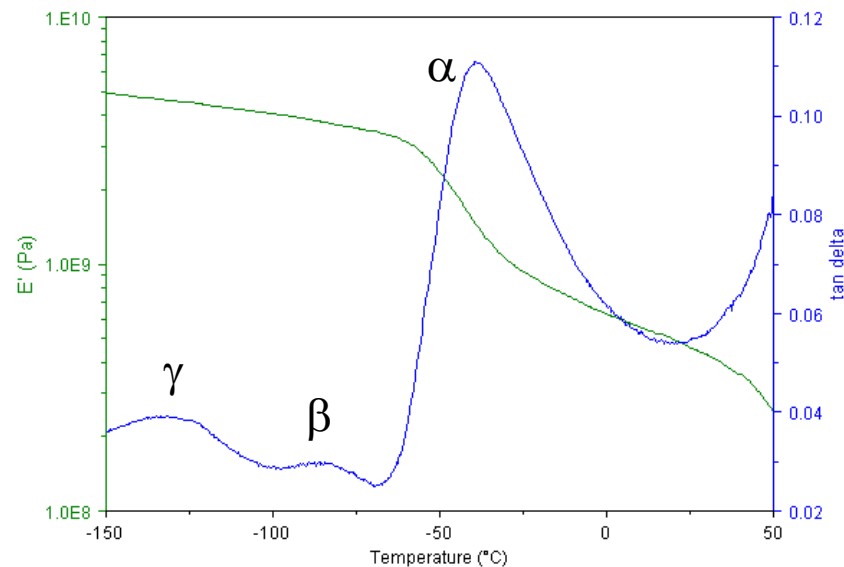
- when using the storage modulus, the temperature at which E' begins to decline is used as the T_g . Tan δ and loss modulus E'' show peaks at the glass transition
- the method of calculation should be noted

Idealized multi-event DMA scan



	(5)	(4)	(3)	(2)	(1)
Molecular motion	Bend and stretch	Side groups	Gradual main chain	Large scale chain	Chain slippage
Deformation	Hookean Behavior	Second Transition	Primary Transition	Highly Viscoelastic	Flow (melt)

Example: DMA spectra of polycaprolactone, PCL

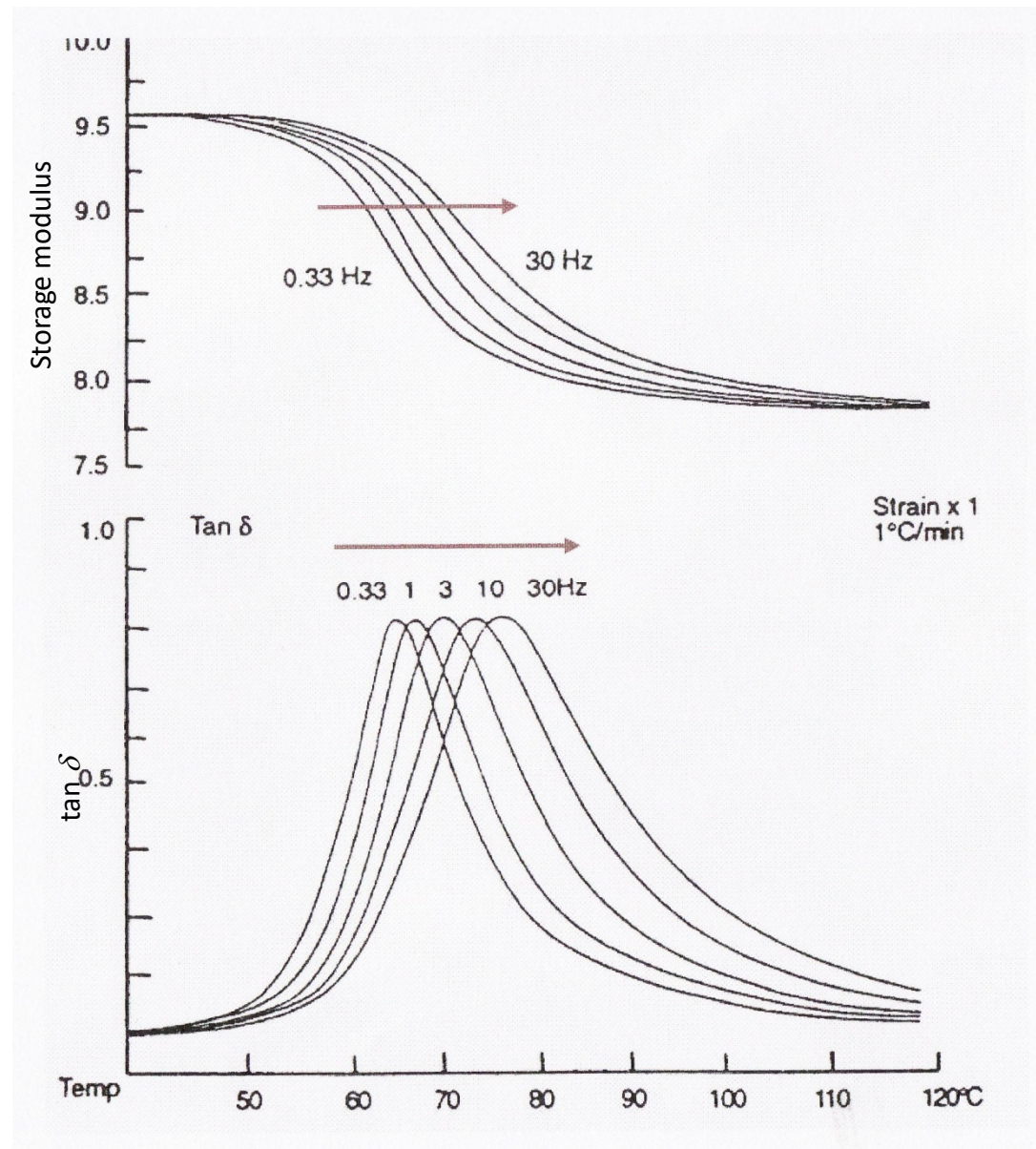


The drop in storage modulus (E') and peak in damping factor ($\tan \delta$) between -60 and -30 °C is due to the glass transition (T_g) of the amorphous polymer in this **semi-crystalline** material.

Above 50 °C the sample begins to melt and flow, thus losing all mechanical integrity. Below the T_g small peaks are evident in the $\tan \delta$ curve at -80 and -130 °C. These are the beta and gamma transitions in this polymer (glass transition is the alpha transition) and are caused by local motion of the polymer chains as opposed to large scale co-operative motion that accompanies the glass transition.

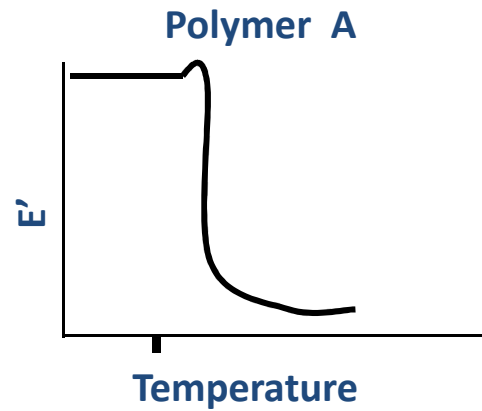
These small transitions are very difficult to observe by DSC but are often very important in determining the impact resistance of the polymer.

Effect of frequency on primary viscoelastic functions

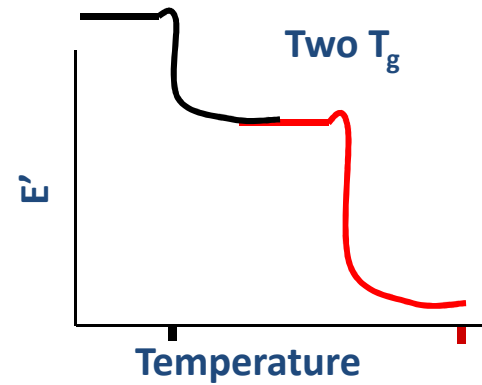
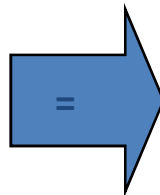
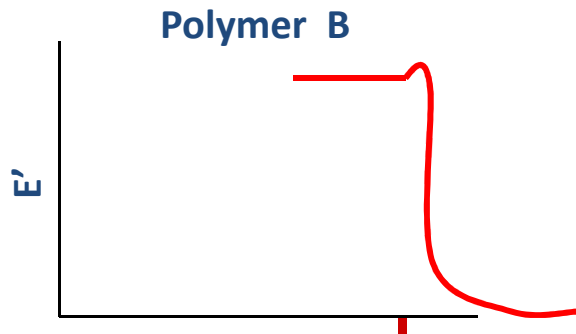


The increase in frequency produces an increase of storage modulus increases and a shift of glass transition to higher temperatures

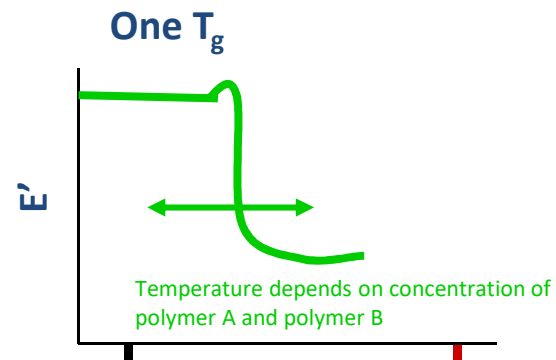
Polymer blends and copolymers



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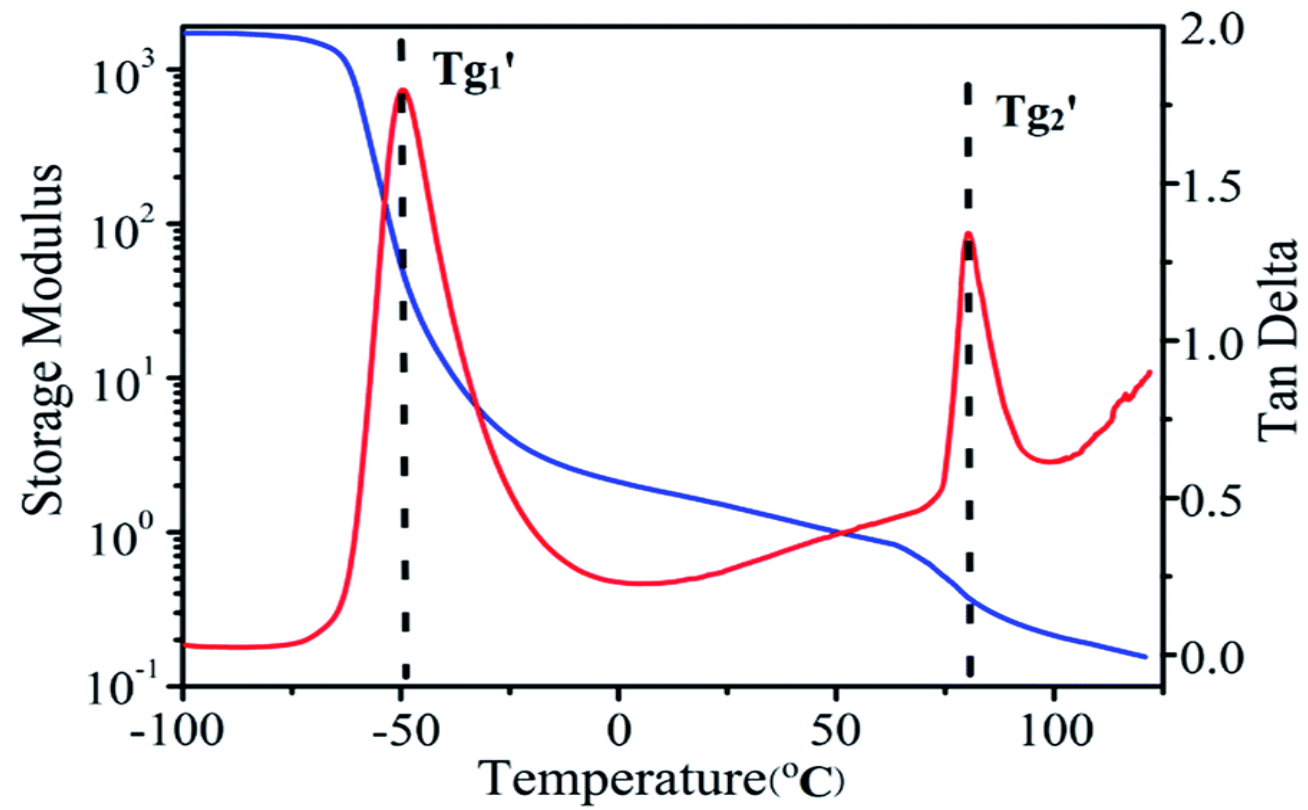


Block copolymers
Graft copolymers
Immiscible polymers



Miscible polymers
Random copolymers?

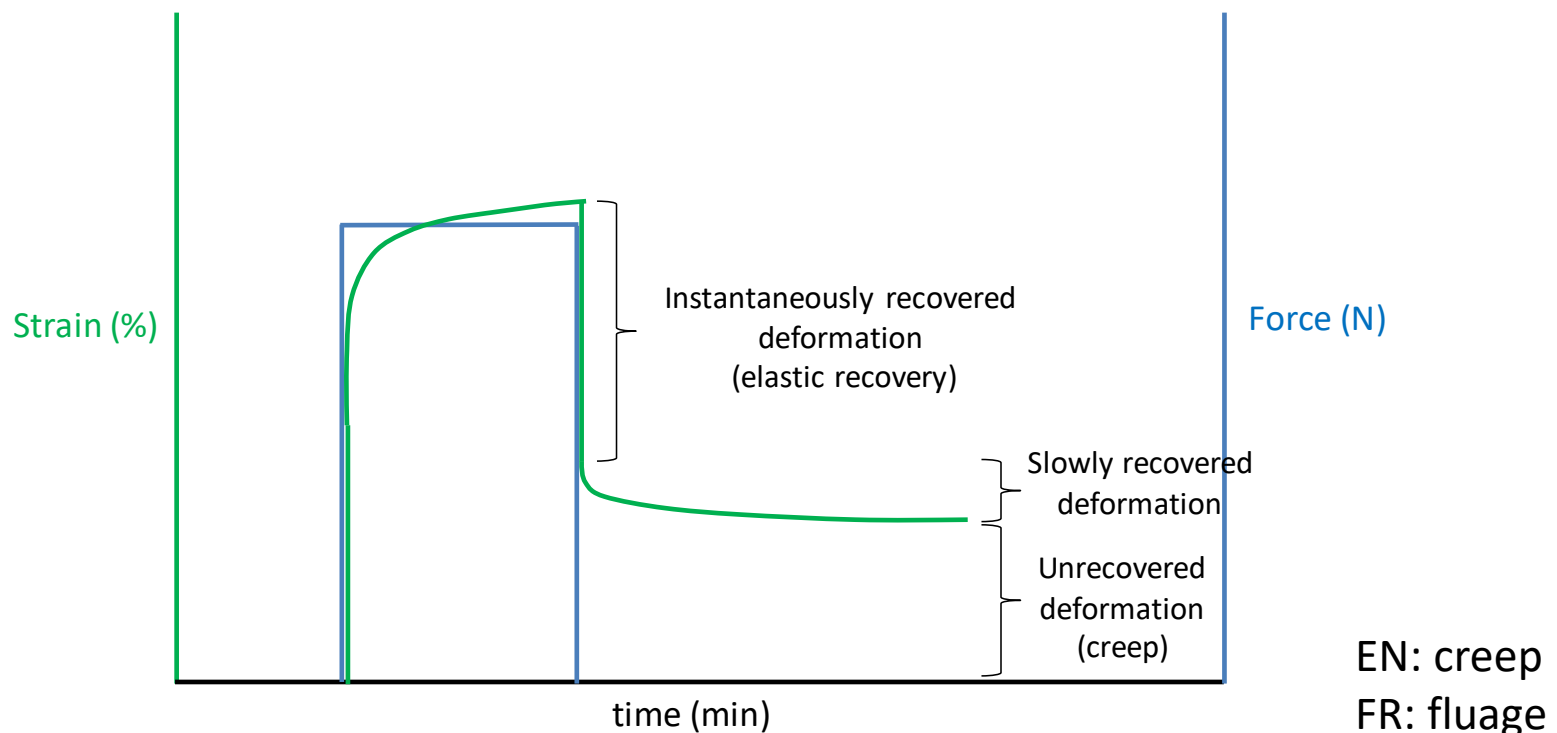
Styrene butadiene block copolymer



Secondary viscoelastic functions – creep

creep (sometimes called cold flow) is the tendency of a solid material to move slowly or deform permanently under the influence of mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material

allows one to see the distortion under constant load and also how well the material recovers from it



Why is creep important?



Genoa, Italy, August 2018

„owing to an incorrect initial assessment of the effects of concrete creep”

DMA instrument

- motor and driveshaft are used to apply torsional stress
- linear variable differential transformer (LVDT) is used to measure linear displacement
- carriage contains the sample and is typically enveloped by a **furnace** and **heat sink**

Sample geometry

