

Effect of Glass Transition Temperature (T_g)



Smart Materials Structures and Systems
Laboratory
IIT Kanpur

Contents

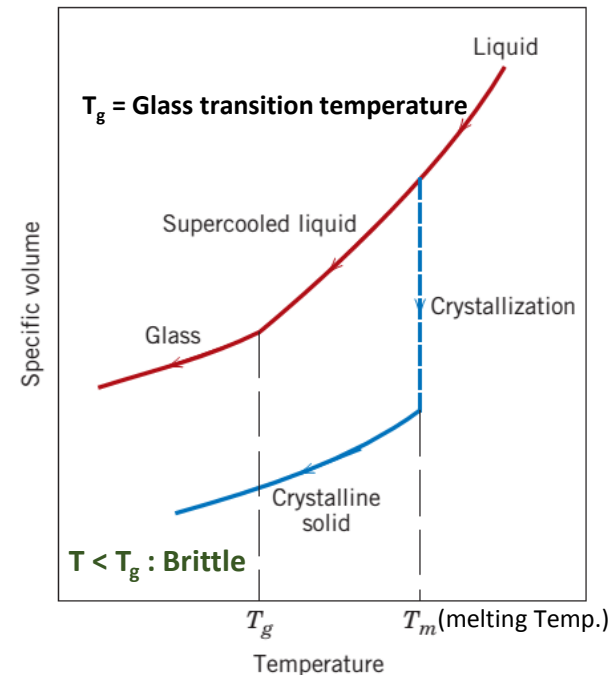
- ✓ What is Glass Transition temperature, T_g ?
- ✓ Experimental methods to determine T_g
- ✓ Factors affecting T_g



Glass Transition Temperature (T_g)

- ✓ **Definition** : The temperature at which the polymer experiences the **transition** from **rubbery to rigid states**.
- ✓ **Below T_g** , it becomes **hard and brittle** like glass, due to **reduction** in the **motion of large segments of molecular chains** with decreasing temperature.
- ✓ Different for each polymer.
- ✓ **Glass transition** happens **only** to polymers in the **amorphous state**.

<i>Material</i>	<i>Glass Transition Temperature [°C (°F)]</i>	<i>Melting Temperature [°C (°F)]</i>
Polyethylene (low density)	-110 (-165)	115 (240)
Polytetrafluoroethylene	-97 (-140)	327 (620)
Polyethylene (high density)	-90 (-130)	137 (279)
Polypropylene	-18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Poly(vinyl chloride)	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

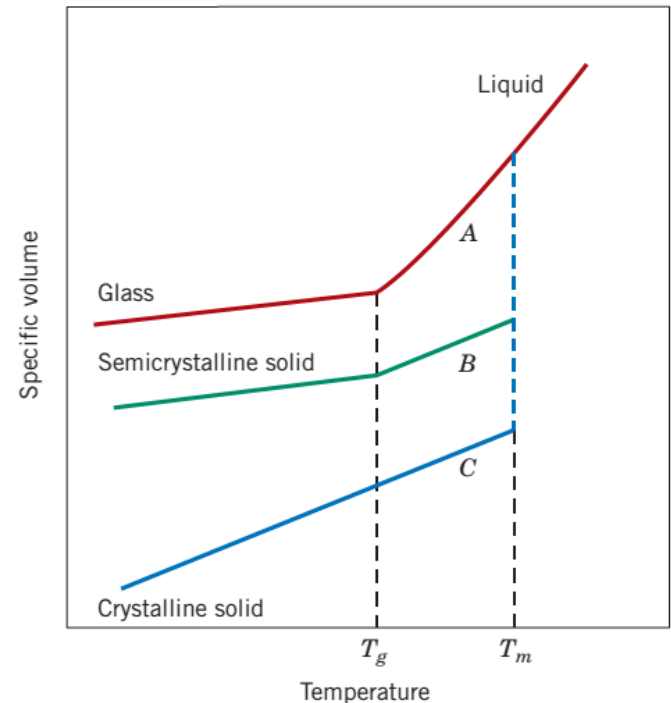


- **Hard plastics** like **polystyrene** and **poly(methyl methacrylate)**, are used **below their glass transition temperatures** (*glassy state*) as their T_g 's are well above room temperature (around 100°C).
- **Rubber elastomers** like **polyisoprene** and **polyisobutylene**, are used **above their T_g 's**, (*rubbery state*), where they are soft and flexible.

Curve A : Amorphous polymer

Curve B : Semi – crystalline solid

Curve C : 100% Crystalline polymers - (hypothetical case)



Five Regions of Viscoelastic behavior

Viscoelasticity = (Viscous + Elastic) behavior

Phase I : Glassy region

- ✓ Relatively high modulus
- ✓ Very hard
- ✓ High resistance to flow

Phase II : Leathery/Glass-transition region

- ✓ Sharp decrease in the elastic modulus
- ✓ Deformation not totally recoverable

Phase III : Rubbery region

- ✓ Both elastic and viscous components present
- ✓ Modulus falling rate stabilizes
- ✓ Elastic – high strain rate
- ✓ Viscous – low strain rate

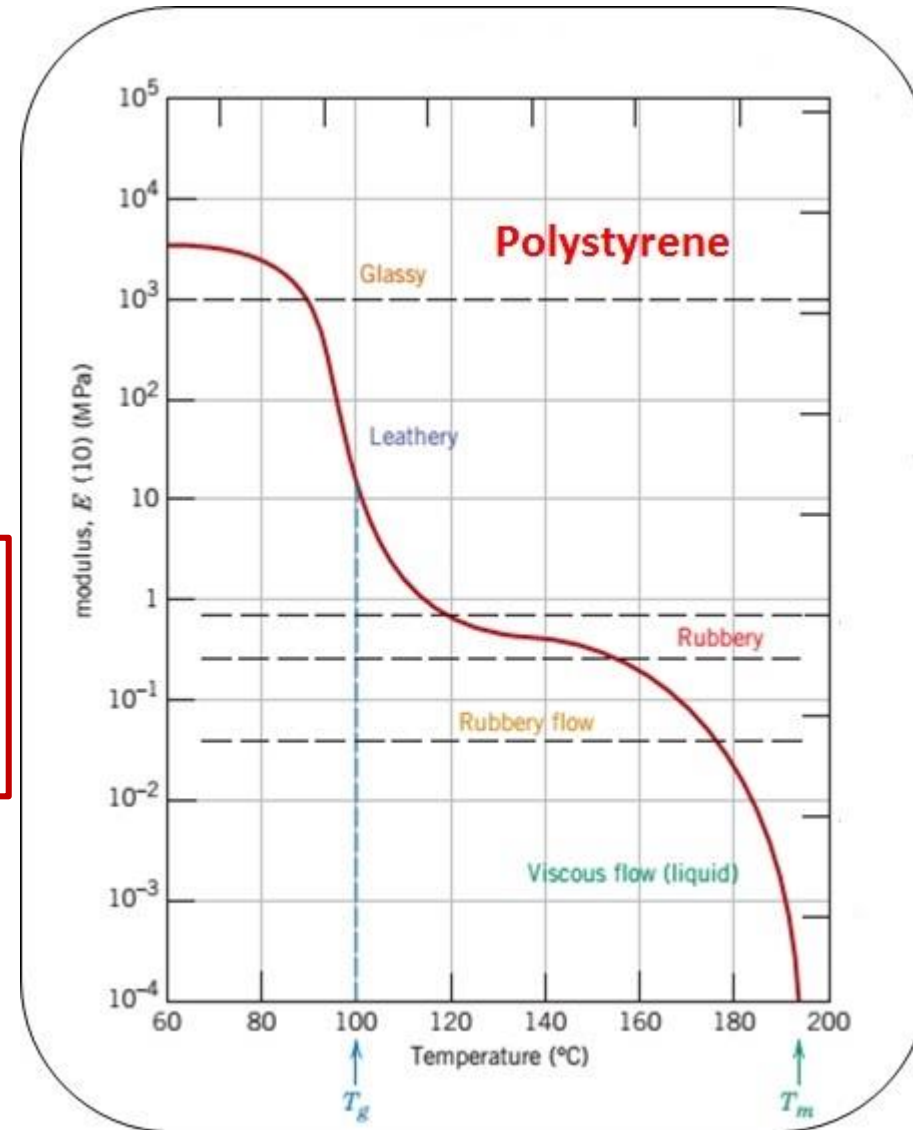
Phase IV : Rubbery flow region

- ✓ Viscosity starts dominating
- ✓ Modulus starts falling

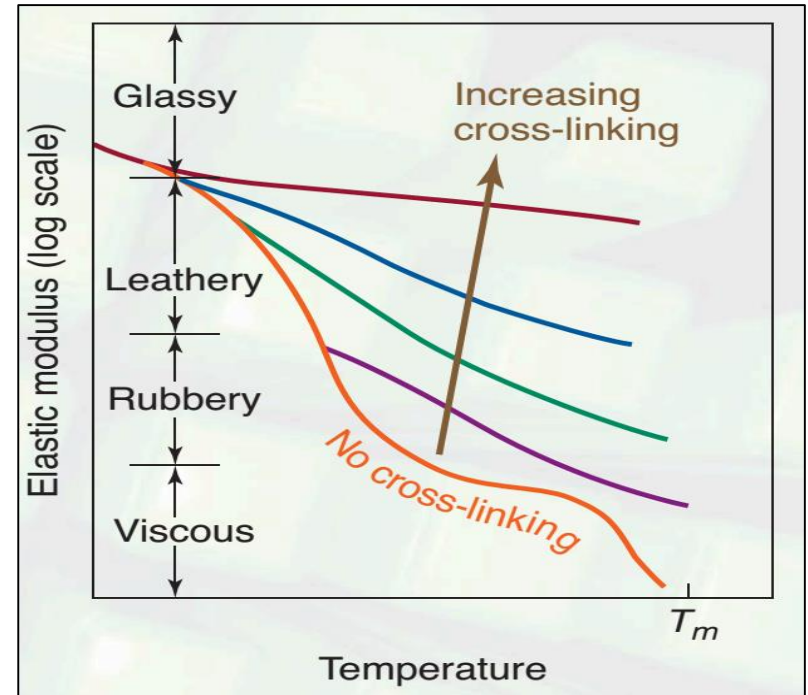
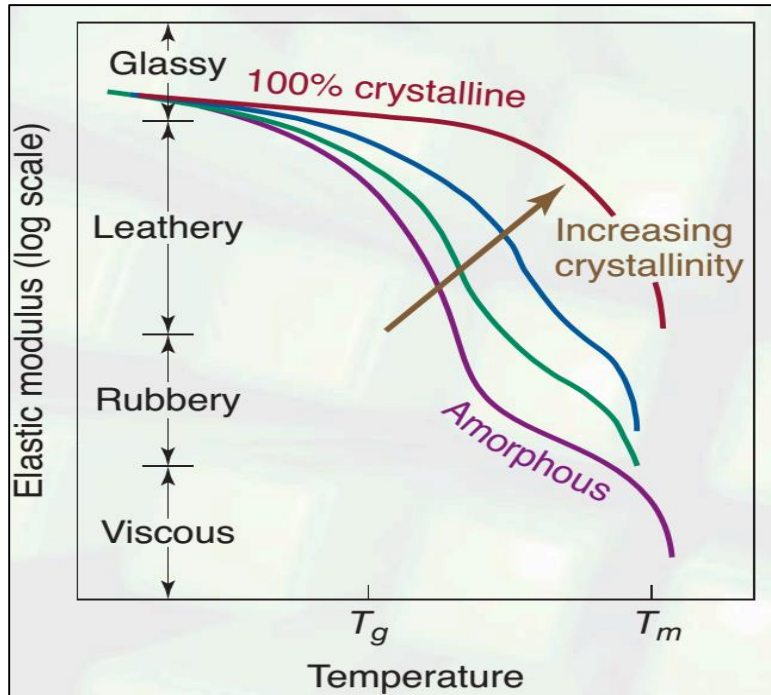
Phase V : Viscous flow region

- ✓ Modulus drops steeply

Finally - decomposition!



Effect of Temperature



Reference: Kalpakjian, Schmid - Manufacturing Processes for Engineering Materials, 5th ed.



Measurement of Glass Transition Temperature (T_g)



Smart Materials Structures and Systems
Laboratory
IIT Kanpur

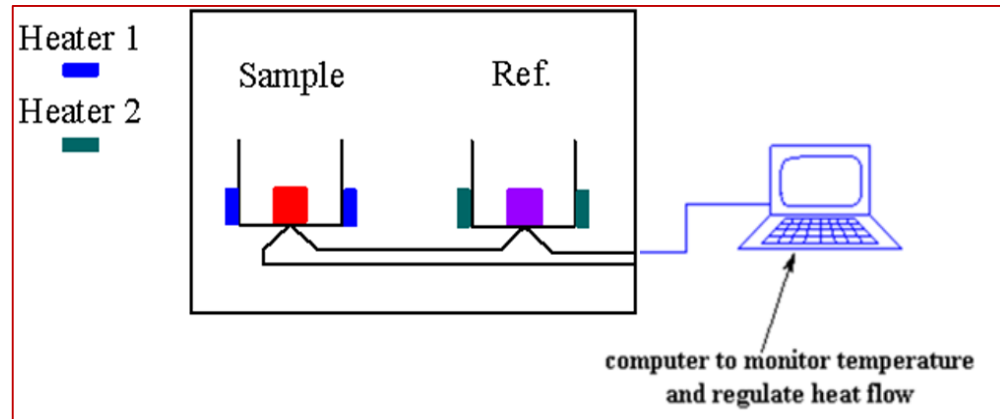
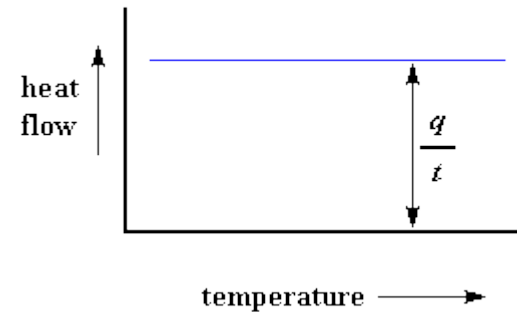
1. Measuring T_g - Differential Scanning Calorimetry (DSC)

- Two separate pans – separate heaters – same heating rate.
- The thermal properties of a sample are compared against a standard reference material which has no transition in the temperature range of interest, such as powdered alumina.

$$\frac{\text{heat}}{\text{time}} = \frac{q}{t} = \text{heat flow}$$

$$\frac{\text{temperature increase}}{\text{time}} = \frac{\Delta T}{t} = \text{heating rate}$$

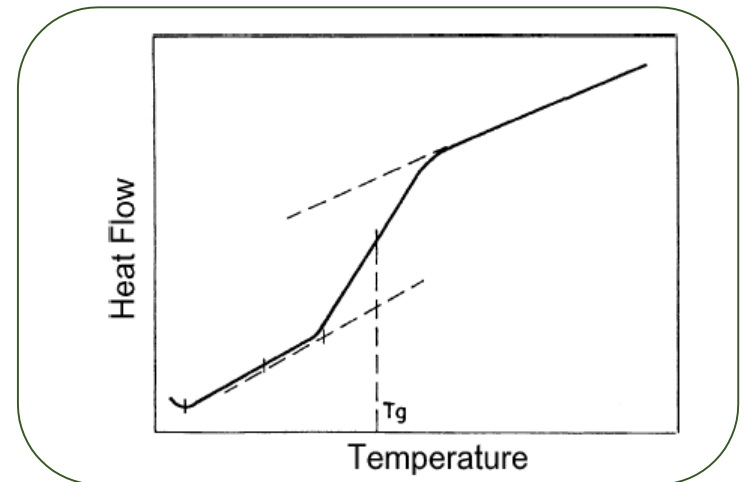
$$\frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} = C_p = \text{heat capacity}$$



- ✓ Since the **heat capacity** of a polymeric material **changes** at the T_g .
- ✓ The glass transition is detected as a **shift** in the **heat flow** versus **temperature** curve.

The amount of heat required to raise the temperature of one gram of the polymer one degree Celsius is called the **heat capacity**.

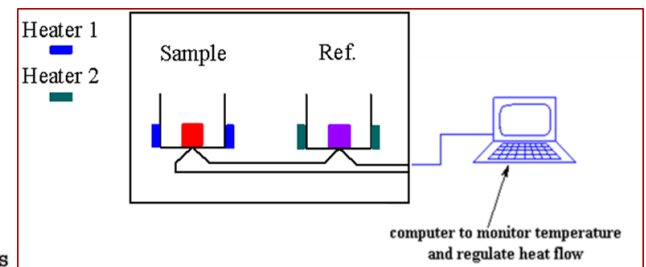
- Change doesn't occur suddenly, but takes place over a temperature range.
- We usually just take the middle of the incline to be the T_g .
- Graph shows polymers have a higher heat capacity above the glass transition temperature



Higher the T_g – Higher is the cross-linking density & vice versa

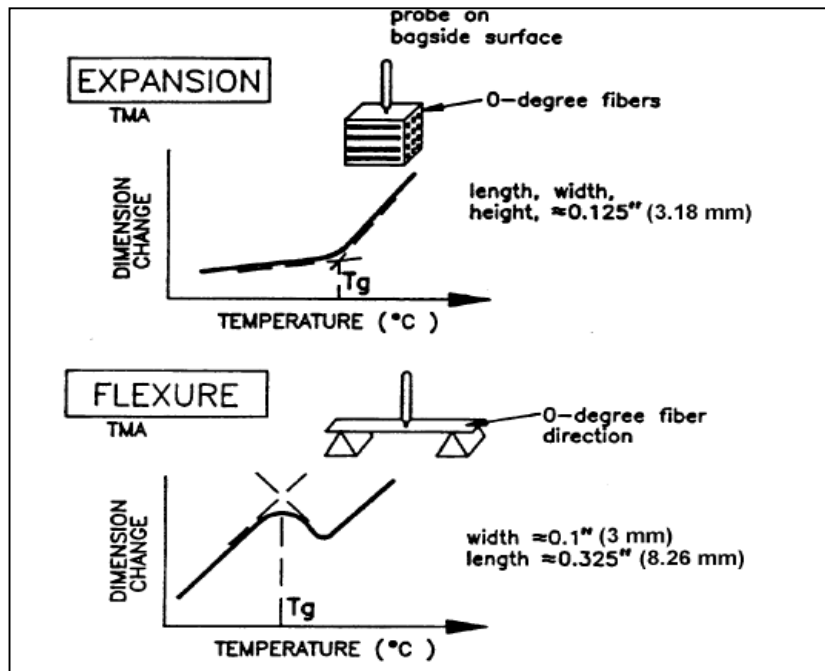


Smart Materials Structures and Systems
Laboratory
IIT Kanpur

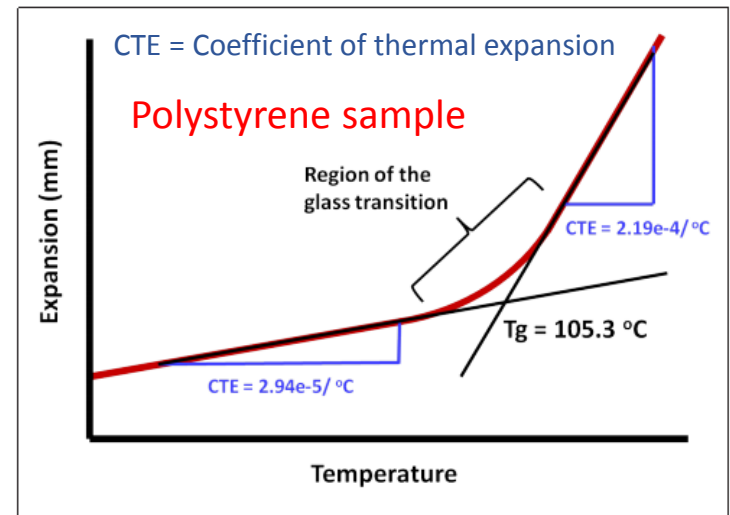


2. Measuring T_g – Thermomechanical Analysis

- Thermomechanical analysis techniques such as expansion, flexure, or penetration may also be used to determine the T_g .
- In expansion TMA, the coefficient of **thermal expansion** is measured as a **function of temperature**.
- The T_g in a polymer corresponds to the point in the expansion curve where the free volume begins to allow for **greater chain mobility**.
- As the temperature rises **past the T_g** , the adhesive will begin to **soften**, **loses** some **tensile strength** and also experiences a **rise in its CTE** (Coefficient of thermal expansion)



Reference: Engineering Materials : Ashby & Jones, 4th Ed.



Reference: Menard K. et al., Basics of thermomechanical analysis

Reference: <http://pslc.ws/macrog/dsc.htm>



Smart Materials Structures and Systems
Laboratory
IIT Kanpur

3. Measuring T_g – Dynamic Mechanical Analysis (DMA)

- Most useful for studying the viscoelastic behavior of polymers.
- A **sinusoidal stress** is applied and the **strain** in the material is measured to determine the **modulus**.
- The **temperature** of the sample or the **frequency of the stress** are often varied, leading to variations in the modulus.
- This approach can be used to locate the glass transition temperature of the material
- Because **sinusoidal stress** is applied, complex elastic modulus can be expressed as $E^* = E' + jE''$;
 - ✓ **Storage modulus (E')** - Measure of **elastic response** & the stored energy.
 - ✓ **Loss modulus (E'')** - Measure of **viscous response** & the energy dissipated as heat.

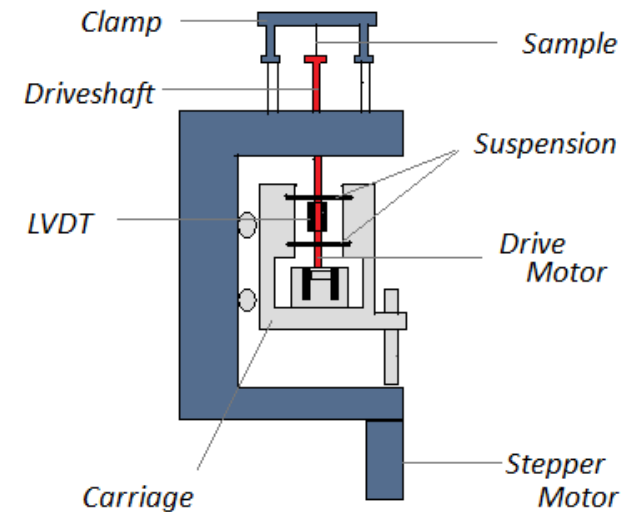
Stress, $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$

Strain, $\epsilon(t) = \epsilon_0 \sin \omega t$

- **Pure elastic case**, stress is proportional to strain, we have

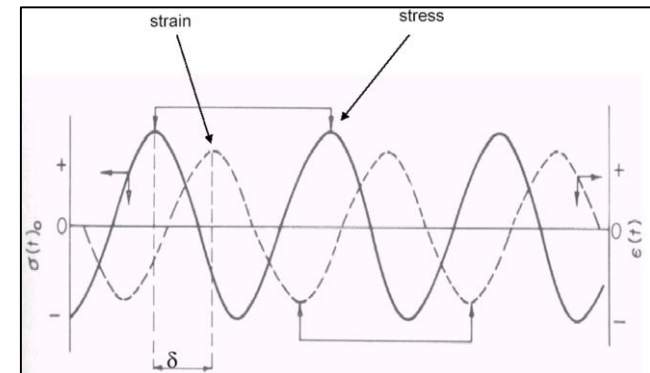
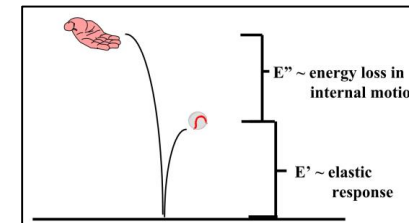
$$\sigma(t) = E \epsilon(t)$$
 Therefore, $\sigma_0 \sin(\omega t + \delta) = E \epsilon_0 \sin \omega t$
 Hence, $\delta = 0$
- **Pure Viscous case**, stress is proportional to strain rate, we have

$$\sigma(t) = E \frac{d\epsilon}{dt} \implies \sigma_0 \sin(\omega t + \delta) = E \epsilon_0 \cos \omega t \implies \delta = \pi/2$$



Experiment set-up

Image: Wikipedia



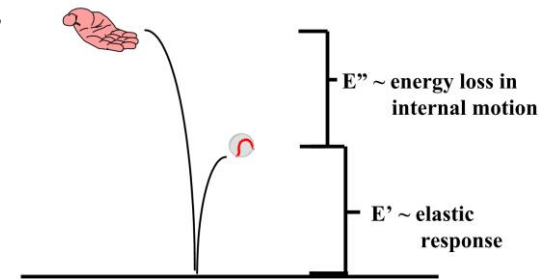
$$\tan \delta = \frac{E''}{E'}$$

where, E'' = Loss modulus (measure of heat dissipated, viscous behavior)
 E' = Storage modulus (measure of stored energy, elastic behavior)

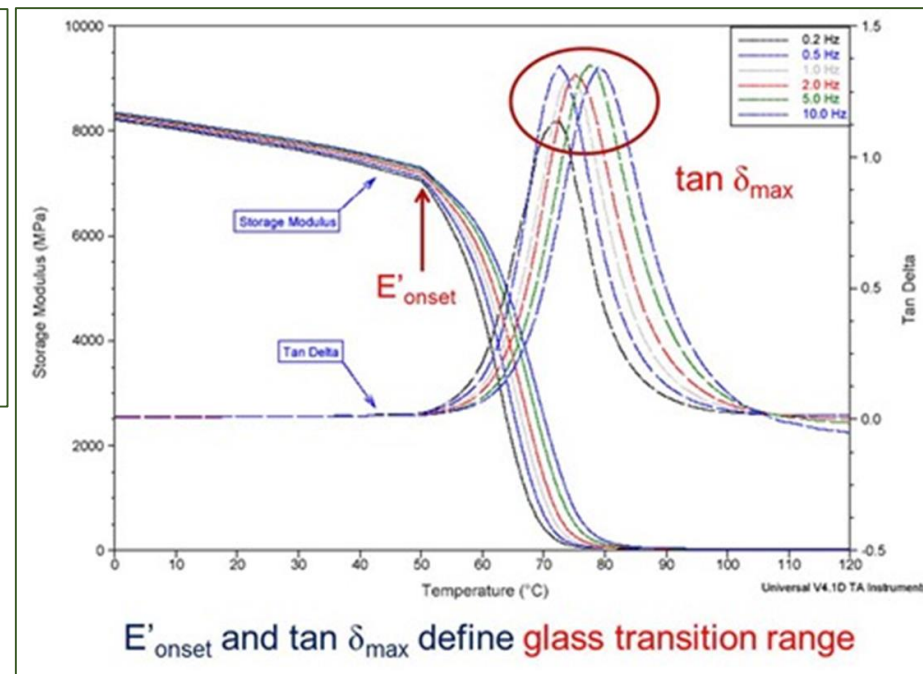
$\tan \delta$ signifies how good a material will be at absorbing energy.

$$\text{Loss modulus, } E'' = \frac{\sigma_o}{\epsilon_o} \sin \delta$$

$$\text{Storage modulus, } E' = \frac{\sigma_o}{\epsilon_o} \cos \delta$$



- δ ranges between 0° - 90° .
- As δ approaches 0° (Purely elastic behavior).
- As δ approaches 90° (Purely viscous behavior).
- At the glass transition, the **storage modulus decreases** dramatically and the **loss modulus reaches a maximum**.



Factors affecting T_g

- Chain Length
- Chain stiffness
- Plasticizers
- Crosslinking
- Co-polymers



Effect of Chain Length

- **As molecular weight increases, T_g also increases.**
 - ✓ High density of branches – reduces chain mobility.
 - ✓ Crosslinking - restricts the molecular motion.
- **As molecular weight decreases, T_g also decreases**
 - ✓ Easier movement of molecules.
 - ✓ More inherent free volume in the polymer.

$$T_g = T_{g\infty} - \frac{C}{M_w}$$

$T_{g\infty}$: Glass transition temp. at infinite chain length

C : Polymeric constant

Average molecular weight, $M_w = \frac{\sum M_i N_i}{\sum N_i}$

Material	$T_{g\infty}$	C
PVC	351	81000
PMMA	387	210000
PS	373	120000

Where, M_i = molecular weight of i_{th} polymer chain;
 N_i = number of chains of that molecular weight.

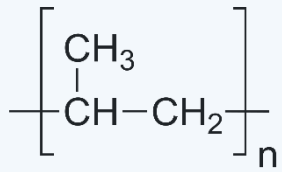


Effect of Chain stiffness

Chain stiffness - Controlled by the **ease of rotation** about the **chemical bonds** along the chain.

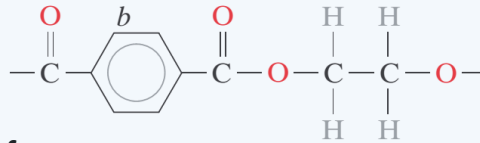
- ✓ Presence of double bonds and aromatic groups lowers chain flexibility and thus increases T_g .
- ✓ Bulky or large side groups restricts chain rotational freedom and flexibility and thus increases T_g .

Example



Polypropylene

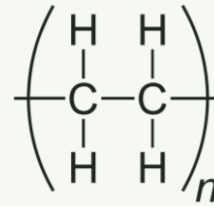
$$\begin{array}{l} T_g = -18^\circ\text{C} \\ T_m = 175^\circ\text{C} \end{array}$$



Polyester

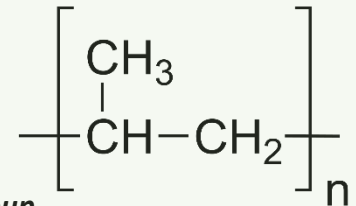
$$\begin{array}{l} T_g = 69^\circ\text{C} \\ T_m = 265^\circ\text{C} \end{array}$$

Presence of
double bond
&
aromatic ring



Polyethylene

$$\begin{array}{l} T_g = -110^\circ\text{C} \\ T_m = 115^\circ\text{C} \end{array}$$



Polypropylene

$$\begin{array}{l} T_g = -18^\circ\text{C} \\ T_m = 175^\circ\text{C} \end{array}$$

Methyl side group
heavier than
H-atom



Effect of Plasticizers

- Plasticizers are the additives that increase the plasticity or fluidity of a material and reduces the hardness and stiffness.
- Example: Phthalate esters in PVC applications imparting improved flexibility and durability.
- Thus, addition of **plasticizers reduces T_g**



Effect of Crosslinking

- Cross-linking **reduces chain mobility**, so T_g will be **increased**.



T_g for Co-polymers

- Made from two different monomers.
- T_g will be some kind of average between the two monomeric materials.
 - ✓ Assuming they were converted into polymer.
 - ✓ Will be based roughly on the weight fraction (%) of each material present in the copolymer.

$$\frac{1}{T_g} = \frac{W_{f1}}{T_{g1}} + \frac{W_{f2}}{T_{g2}}$$

T_g = Glass transition temperature of copolymer

W_{f1} & T_{g1} = Weight fraction & T_g of first monomer

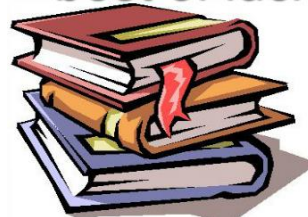
W_{f2} & T_{g2} = Weight fraction & T_g of second monomer



In the **next lecture**, we will learn about

- ✓ Polymer mechanical properties
- ✓ Factors affecting these properties

best of luck



Smart Materials Structures and Systems
Laboratory
IIT Kanpur