Nature and Properties of Materials

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Lecture 18

Effect and Glass Transition Temperature

In the last talk, we have discussed so much about the crystallinity and the amorphous nature of a polymer. The interesting thing is that, with respect to temperature, the polymer can actually change its physical property in a very drastic manner, not unlike many of the other solids and that important temperature is also known as the glass transition temperature of a polymer.

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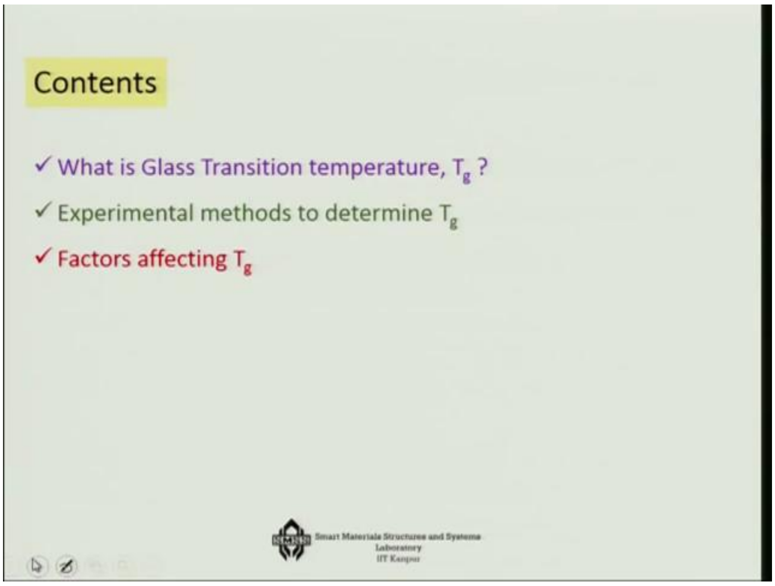

Contents

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

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So we are going to talk about this glass transition temperature because that is what is very important in terms of the nature of the polymers. So we are talking about what is the glass transition temperature, the experimental methods to determine T g and the factors that affect the glass transition temperature. Now, what is this glass transition temperature with actually changes the nature of the polymers very drastically?

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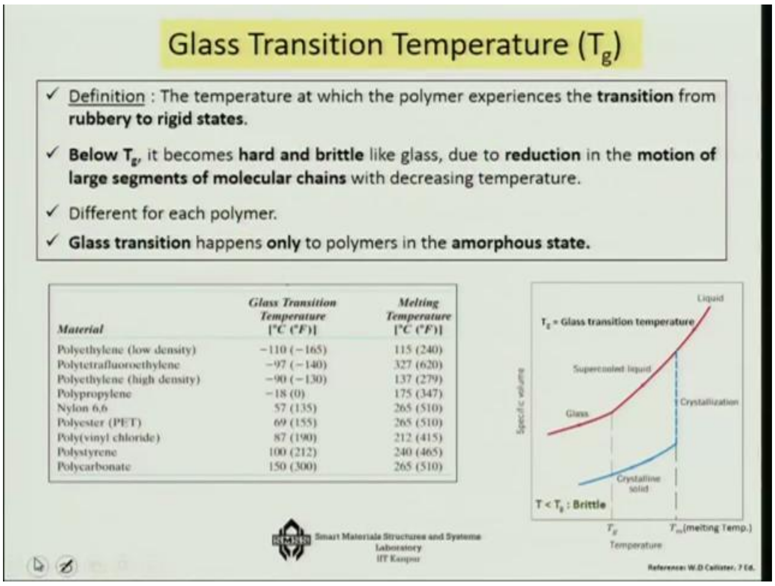

Glass Transition Temperature (T_g)

- ✓ 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.**

Material	*Glass Transition Temperature [°C (°F)]*	*Melting Temperature [°C (°F)]*
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)

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Reference: W.D Callister, 7 Ed.

Well, it is actually the temperature that a polymer the transition happens in a polymer when it goes from rubbery to the rigid states. Now, you need to little bit of imagine this. I told you that polymers has a very long chain, now this long chain if the, if there is enough energy in the long chain, then there will be enough movement between the interlinks.

But if there is not enough energy there, so suppose I consider the polymers like this that you have a long chain system okay. Now, if you have enough energy what will happen is that each one of these links will move against the other, so you can get some kind of a motion that means it can actually kind of adjust itself. If that happens, then the polymer will be in its rubbery state that means the temperature is such that it can actually move links against each other.

On the other hand, if it is a very low temperature level, that very low is of course elative for example, for polyethylene it is like - 110, where as for polyester PET it is only about 69 degree. But at a particular such critical temperature, it will happen that these chains will lose its mobility, it will become rigid, it will not be able to move against each other, at that stage that is below the T g it will behave almost like a glassy material that means it will behave like it is hard and brittle.

You can actually do this test very well if you have a refrigerator in your room. What you need to do is that, you take a for example, a polyethylene packet. For polyethylene let us look at it that is – 90, so that is quite low for you to achieve in the regular system, but something like let us say of course if you cool nylon. You take a nylon rope and you cool it, what you will find is that in fact, that is what you will find in the winter time with nylon is that it will become very hard and brittle, you can break it very easily.

So that means it has reached that glassy stage, where the chains are not able to move against each other. So that is why the glass transition temperature is so important for us because this happens uniquely to polymers and it actually happens in the amorphous state. Now, how we are getting this let us try to look at it that suppose you have a polymer melt in a liquid state. As I am cooling in the super cool liquid form that means cooling at a faster rate, I am going to directly come into the glassy stage.

If you cool it very slowly, then there is a chance of crystallization and then you may get crystalline solid. So the difference between a crystalline solid and glassy solid is that you are actually super cooling the particular solid from the liquid state.

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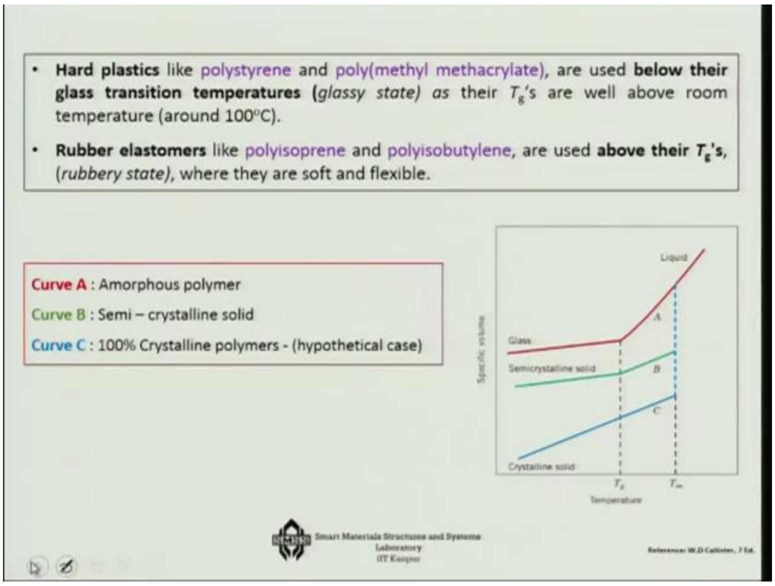

- **Hard plastics** like polystyrene and poly(methyl methacrylate), are used **below their glass transition temperatures** (*glassy state) as* their T_g's are well above room temperature (around 100°C).
- **Rubber elastomers** like polyisoprene and polyisobutylene, are used **above their T_g's**, (*rubbery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

Curve A : Amorphous polymer
Curve B : Semi – crystalline solid
Curve C : 100% Crystalline polymers - (hypothetical case)

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Reference: W.D Callister, 7 Ed.

Now, hard plastic like polystyrene and PMMA, they are generally used below their glass transition temperature that means they are generally used at the glassy state itself because their T g are well above room temperature around 100 degree centigrade. On the other hand, those which we normally use as elastomers like rubbers, poly isoprene, polybutylene, et cetera, they are used above their T g in the rubbery state that is why they are quite soft and flexible.

That means if you really cool them, you will get them in their glassy state. So here is like a liquid you are quickly cooling super cooled, you are getting a glassy state. You are cooling little bit slowly; you are going to get to semi-crystalline solid. And if you are cooling it really very slowly, then you are going to go to the crystalline solid state. So the curve A is for the amorphous polymers, curve B is those polymers which are semi-crystalline, curve C are those which are like hypothetical, but those which are very crystalline.

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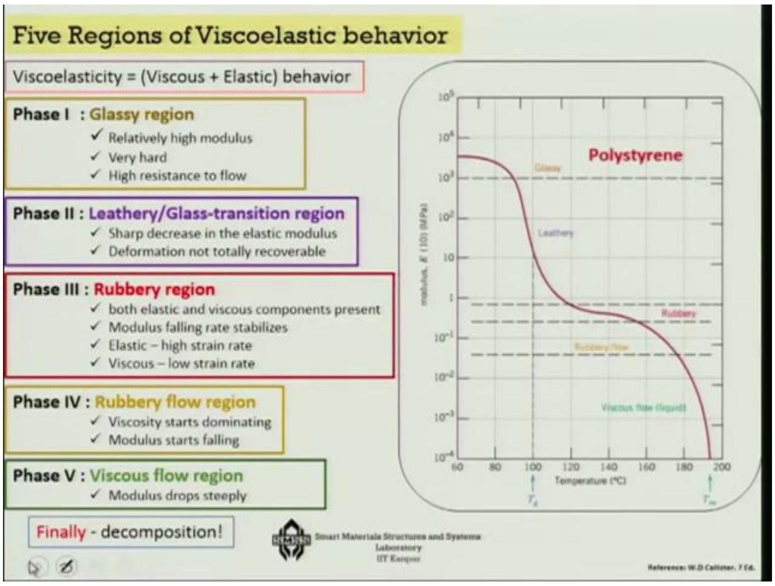

Five Regions of Viscoelastic behavior

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!

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Reference: W.D Callister, 7 Ed.

Now, let us look into the behavior of a in general any viscoelastic polymer, which is not like a thermosetting polymer where actually because for thermosets polymers because of that chemical cross-linking because of the chemical cross-linking thermosets polymers, you will not be able to achieve the rubbery state in a thermosets polymer. But if you consider a thermoplastic polymer, you will find that it is having 5 regions in it.

Phase 1, which is the glassy region you will get it here, and then phase 2, which is like leathery glassy transition region. Then you will get phase 3 which is like rubbery region, then you get phase 4, which is like rubbery flow region and phase 5, which is like a viscous flow liquid. So phase 1, which is glassy region, the tilt signs are that it has relatively high modulus, very hard, high resistance to flow as I told you because chains are not mobilized.

2nd phase, your transition is happening so there is a sharp decrease in elastic modulus as you can see it is falling down, deformation not totally recoverable. Then the rubbery region, where it is both elastic and viscous components are present, modulus falling rate has stabilized, elastic high strain rate and viscous as a low strain rate. Then you have the rubbery flow region, where the viscosity starts to dominate, modulus starts to fall again and you have the viscous flow region where the modulus drops very steeply. Of course, the final phase is the decomposition.

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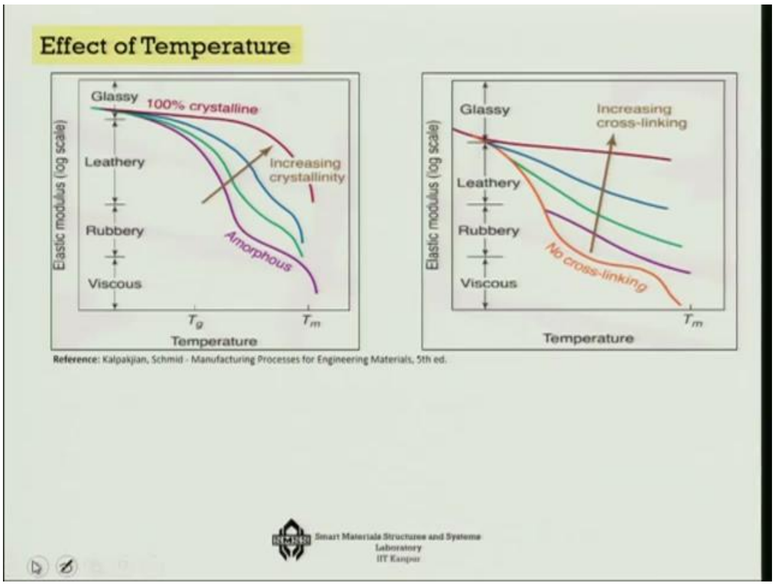

Effect of Temperature

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

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Now, what is the effect of temperature in a viscoelastic material in we consider 2 types, one is totally amorphous. Here you will see that all the regions are present that means from glassy till leathery, rubbery, viscous, you get all the regions. Whereas, if it is 100% crystalline, then you get the glassy state and then you will not get the rubbery transition phase, but it will it will just come down sharply to the flow region, so you get one single melting point and it comes down.

So as the crystallinity is decreasing, this nature is becoming more and more, this type of nature will become more and more predominant for a solid for a viscoelastic material. Similarly, from a cross-linked point of view if there is no cross-linking that means it is like a thermoplastic material, you are going to see all these regions very predominantly.

But as the cross-linking increases like the thermosets here in this case, thermosets material, here you are not going to see these changes anymore why, because I told you since the polymer is already linked heavily networked, so even if you change the temperature you are not going to gain in terms of the mobility of the links. So basically for the thermoset materials you may not even get a melting point, it will straightforward degrade into the gaseous state in many cases. Now how do we measure the glass transition temperature? There are several methods, one of the very popular one is known as DSC Differential Scanning Calorimetry.

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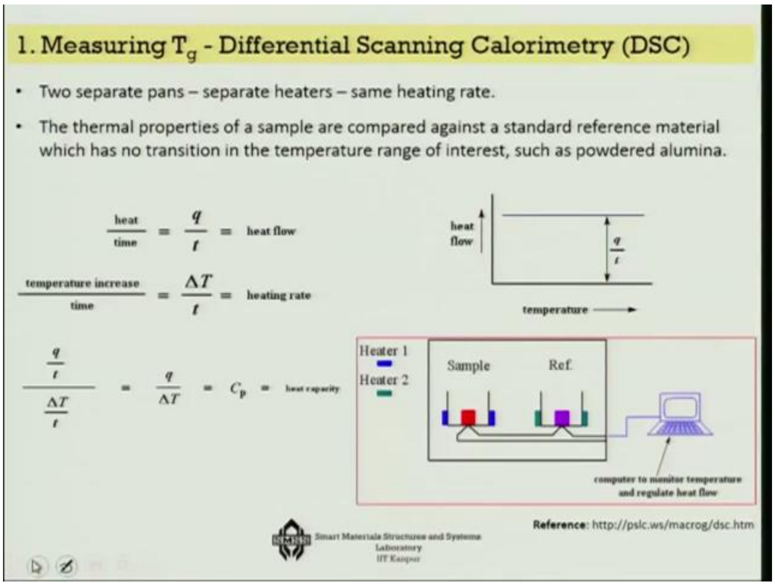

1. Measuring T_g - Differential Scanning Calorimetry (DSC)

- 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.

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

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

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

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

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And here you need to take 2 different materials, one material the sample, which has a glass transition temperature and the particular temperature, when you think this is happening and the other case is the reference material which do not have glass transition at that particular temperature.

Now, because you can control the heating in the pan, so you can find out that what is the heat flow that means heat per unit time. By the help of temperature sensors, you can also measure both for the sample as well as for the reference, what is the temperature increase with respect to time that means the meeting rate. The ratio of the 2 is going to be a Heat capacity and the glass transition if it happens, the heat capacity changes significantly.

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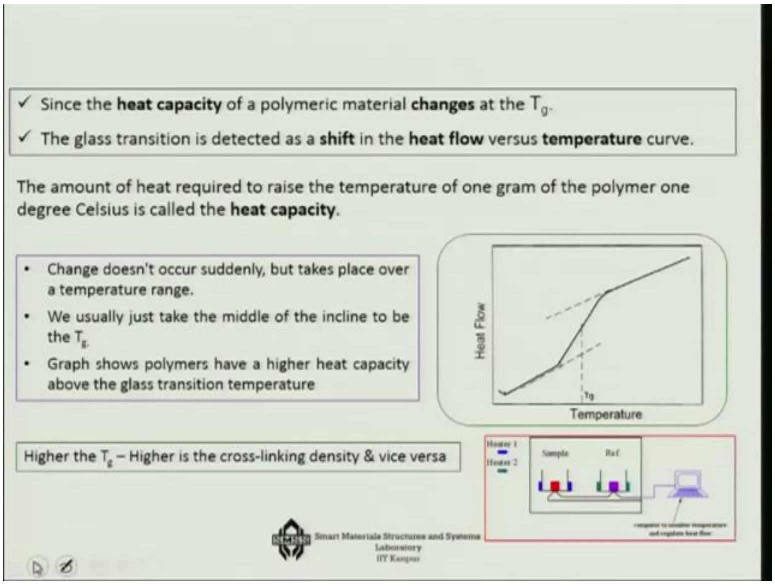

- ✓ Since the **heat capacity** of a polymeric material **changes** at the T_g.
- ✓ The glass transition is detected as a **shift** in the **heat flow** versus **temperature** curve.

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

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In fact, if you look at the curve you would see that if there is a glass transition, then the heat flow is affected and it is significantly changing, so from this you can actually say yes there is a glass transition happening by comparing this with the reference material, which would not show this type of a change or this type of a shape. So you have to keep in mind that this change does not occur suddenly, but takes place over a temperature range.

In fact, that is why we have to take this to tangents and then find out and we usually just take the middle of the incline to be the T g in the graph shows that the polymers have higher heat capacity above the glass transition temperature. So usually higher the T g , higher is the cross-linking density and vice versa, we can say that higher cross-linking density, higher will be the glass transition temperature. So DSC is one way to measure, what are the other ways?

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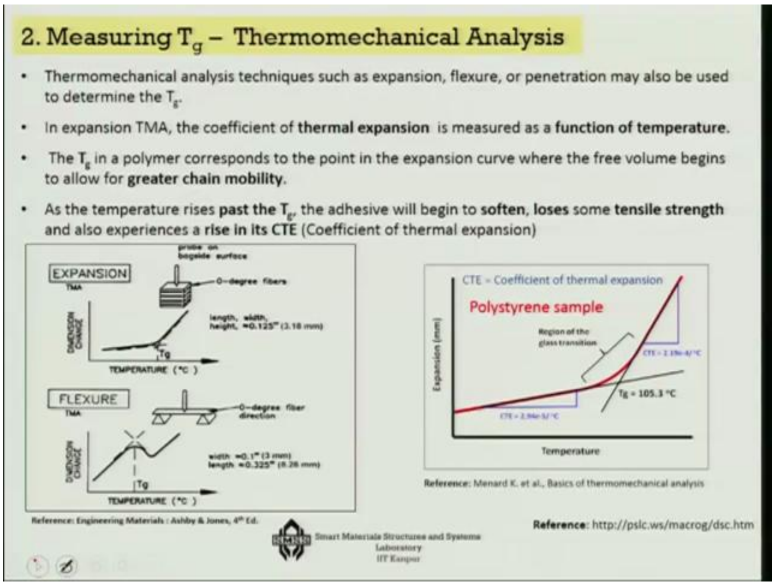

2. Measuring T_g – Thermomechanical Analysis

- 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

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The other very popular way is called Thermo Mechanical Analysis or TMA. Now unlike the heat capacity, what we measure here is actually the coefficient of thermal expansion because that also with respect to the glass transition you would see that the coefficient of thermal expansion either you test it in a longitudinal expansion or in flexure, in both the cases you will see that the coefficient of thermal expansion changes a lot.

And by drawing similarly 2 tangents, the intersecting point will be able to find what the glass transition temperature is in this particular case. So Thermo mechanical analysis techniques such as expansion, flexure or penetration, they can be used for T g. And in expansion TMA is the coefficient of thermal expansion which is directly measured as a function of temperature.

And 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 or lose some tensile strength and also experience arise in the CTE the Coefficient of Thermal Expansion. The 3rd method, which is also very interesting method, is known as Dynamic Mechanical Analysis or DMA.

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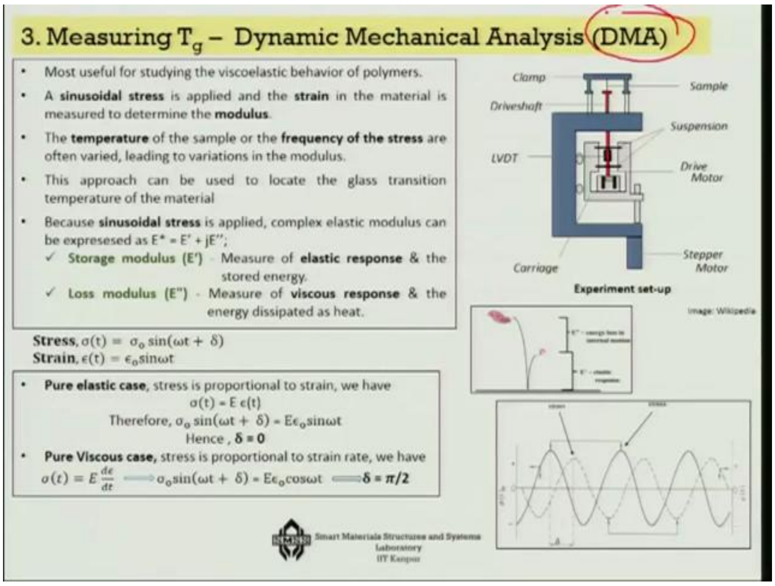

3. Measuring T_g – Dynamic Mechanical Analysis (DMA)

- 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 expresesed 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
  $$\sigma(t) = E\,\epsilon(t)$$
  $$\text{Therefore, } \sigma_0 \sin(\omega t + \delta) = E\epsilon_0 \sin\omega t$$
  $$\text{Hence, } \delta = 0$$
- **Pure Viscous case,** stress is proportional to strain rate, we have
  $$\sigma(t) = E\frac{d\epsilon}{dt} \Longrightarrow \sigma_0 \sin(\omega t + \delta) = E\epsilon_0 \cos\omega t \Longrightarrow \delta = \pi/2$$

Experiment set-up

Image: Wikipedia

What we will do here is that much unlike the change of temperature, here we generally change the temperature in a very small scale, but we actually subject this polymer to stress and it is the sinusoidal stress that we apply and we try to find out that what the strain is. So here is the stress for example, you are plotting and you are also measuring the strain and you are plotting it, you see there is a phase difference between the 2.

Now this phase difference, if you look at the amplitude here and if you look at the amplitude here of the strain, then there is a phase difference delta, this phase difference delta is a measure of the loss of viscoelasticity in the material. And the frequency at which this happens is known as the critical frequency and the temperature when this happens is known if you actually plot this loss factor with respect to temperature, you would see that Tan Delta if you plot with respect to temperature or frequency, we will see there is a glass transition temperature T g, where this loss will be maximum.

At this juncture I need to tell you that much unlike the metallic or the ceramic counterparts, the modulus of elasticity for a polymer is actually always complex. It has 2 parts, one is the Storage modulus E prime and another is the loss modulus, which is E double prime. So if you find out the stress in a cycle, Sigma 0 Sine Omega T + delta, strain is sine omega T, then there is a difference.

You can do it the other way also that means you can put Sigma T as sigma 0 sine Omega T and you can observe the change in Epsilon depending on whatever you like, it will become sine Omega + Delta, so the phase difference either from the strain or from the stress. Now for a purely elastic case this delta is actually 0, so that means stress and strain, they are exactly at the same phase.

For a purely viscous case, this delta is actually pie by 2, which means this stress and strain are actually in a 90 degree no opposite phase. And for viscoelastic materials it is always in between the 2. Now this Tan Delta which is also a measure of the loss, the energy that is dissipated in the system can be actually expressed as a ratio of the E prime to E prime that is the loss modulus to the storage modulus of the sample.

So if Tan Delta is high that means the material is highly viscoelastic, it can actually enormous amount of energy it can dissipate and particularly that happens at the glass transition temperature, when the chains have just reached enough mobility. So the Delta value changes between 0 to 90 degree and as Delta approaches 0 degree, you get purely elastic behavior, as Delta approaches 90 degree, purely viscous behavior and Delta in between the 2 is actually viscoelastic material.

At the glass transition temperature, the storage modulus decreases dramatically I told you and the loss modulus reaches a maximum, so this is the real modulus or the storage modulus, at the glass transition the storage modulus is decreasing. On the other hand, at the glass transition, so E prime is decreasing.

On the other hand, just like the Tan delta, at the glass transition you will find that if you plot it, E double prime you will find it is going to be a almost the same manner as the Tan Delta that means at the glass transition temperature, the E double prime, so this is the E double prime that is actually showing that peak, so that is kind of comparison between the 2. What are the factors that affect this glass transition temperature? The one is the chain length, the higher the chain length the more will be this. Chain stiffness, plasticizers, cross-linking and copolymers, let us look at them one by one.

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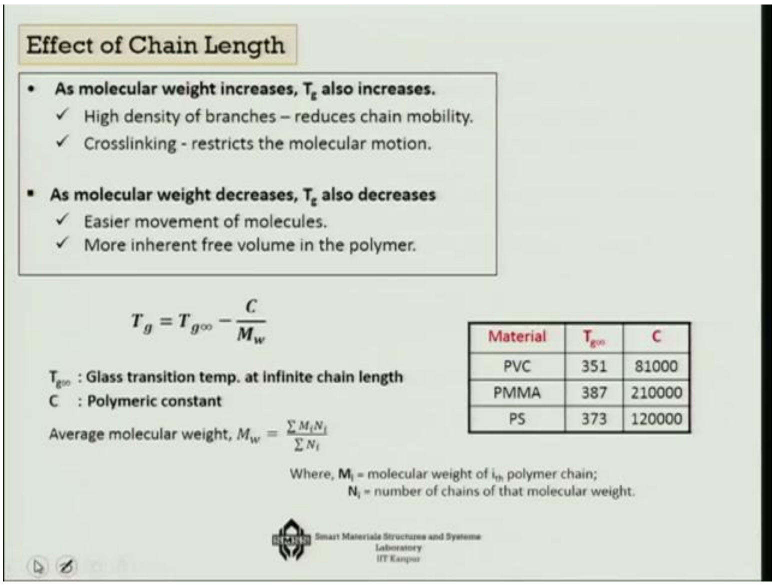

Effect of Chain Length

- **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, $\mathbf{M_i}$ = molecular weight of i_{th} polymer chain;
$\mathbf{N_i}$ = number of chains of that molecular weight.

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If you look at the chain length, as molecular weight increases the T g increases you know that. So high density of branches will actually reduce the chain mobility, cross-linking will actually restrict the molecular motion. And as the molecular weight decreases, T g also decreases because there is easier movement of molecules and more inherent free volume in the polymer.

So in any polymers, there is something called T g infinity that is the glass transition temperature at infinite chain length. There is a polymeric constant and molecular weight of a particular polymer, so if you know T g infinity, C and the molecular weight, you can actually find out what is T g. For example, for PVC T g infinity is 351, C is this, like that for PMMA or polystyrene.

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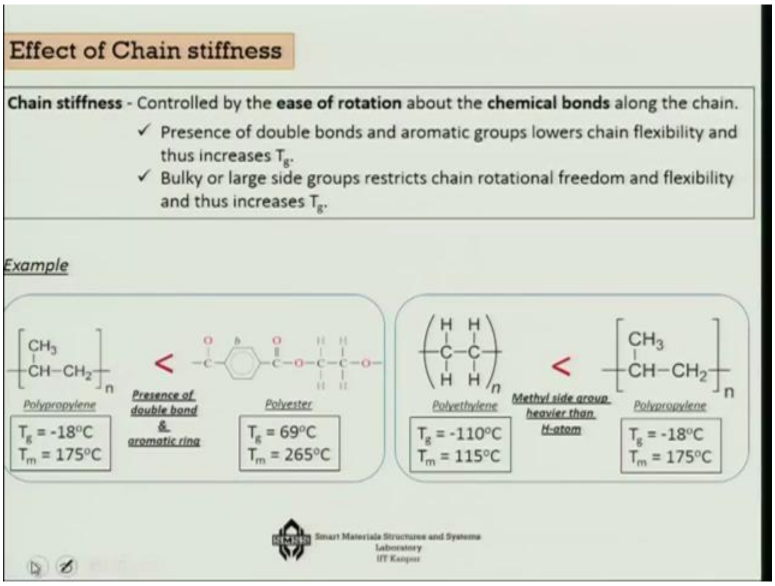

Effect of Chain stiffness

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
T_g = -18°C
T_m = 175°C

<

Presence of double bond & aromatic ring

Polyester
T_g = 69°C
T_m = 265°C

Polyethylene
T_g = -110°C
T_m = 115°C

<

Methyl side group heavier than H-atom

Polypropylene
T_g = -18°C
T_m = 175°C

Now for the chain stiffness this is controlled by the ease of rotation about the chemical bond. So if you have presence of double bonds or aromatic groups, this will definitely lower the chain flexibility and thus it will increase the T g. If you have bulky large side groups that will restrict the chain rotational freedom and flexibility, so you are going to get an increase in terms of T g.

For example, you consider polypropylene, you check the presence of double bonds and aromatic rings, so if you consider polypropylene with polyester, you will see that polyester has actually higher T g or higher melting point temperature mostly because it has actually more number of double bonds and aromatic rings, you can see the aromatic rings and double bonds.

Similarly, if you consider methyl side group which is heavier than hydrogen atom between polyethylene and polypropylene, you can see here that the polypropylene has this particular heavy side group, so its T g is actually higher in comparison to the T g of polyethylene. So thus the chain stiffness definitely changes the t g.

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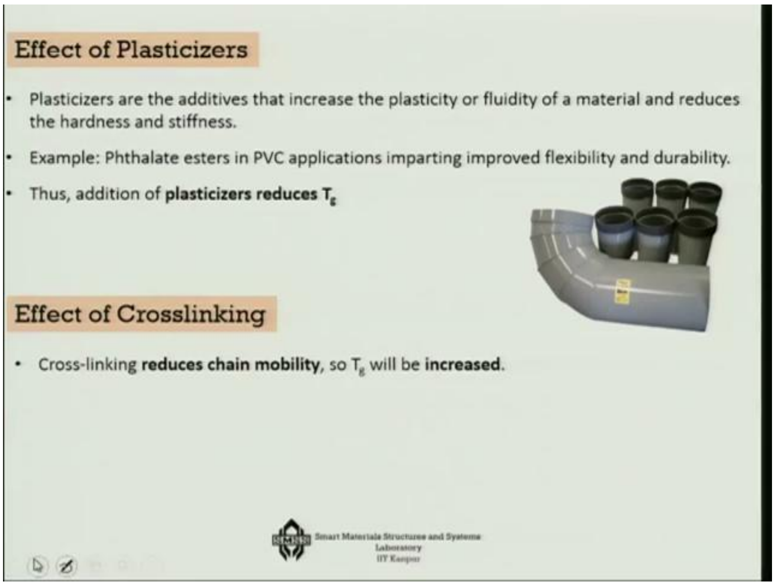

Effect of Plasticizers

- 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**.

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Many times we use plasticizers that means some kinds of additives, which increases the chain movement like Phthalate esters in PVC improves the flexibility and durability. So addition of plasticizer can actually reduce the T g significantly. And in terms of cross-linking, if you can reduce the chain mobility, then the T g will be increased. So thus you can add chemicals to do this process.

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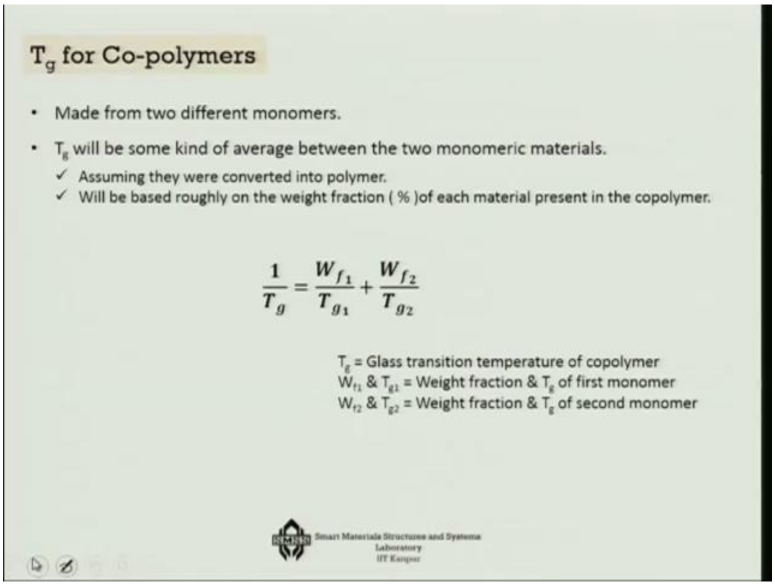

T_g for Co-polymers

- 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.

$$\frac{1}{T_g} = \frac{W_{f_1}}{T_{g_1}} + \frac{W_{f_2}}{T_{g_2}}$$

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

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If you add copolymers, now every copolymer or so to say every copolymer has its own glass transition temperature, so if you have 2 polymers, then you have 2 glass transition temperature and if there are 2 different weight fractions, by using this formula you can actually find out what is the T g and naturally the T g will be different from T g 1 and T g 2. So thus copolymers can affect the glass transition temperature.

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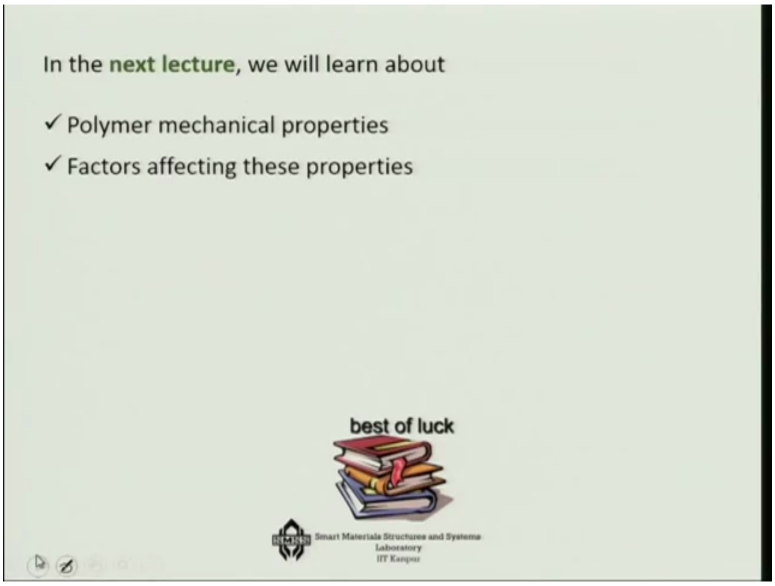

In the **next lecture**, we will learn about

- ✓ Polymer mechanical properties
- ✓ Factors affecting these properties

best of luck

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So this is where we will put an and about the affects of these things various things like the chain length, the chain stiffness, okay the presence of the side groups for example okay. And also along the point I did not tell you that the torsion and tacticity they can also affect the glass transition temperature. In the next lecture we will learn about the polymer mechanical properties and the factors that affect these properties, thank you.