Polymer Process Engineering
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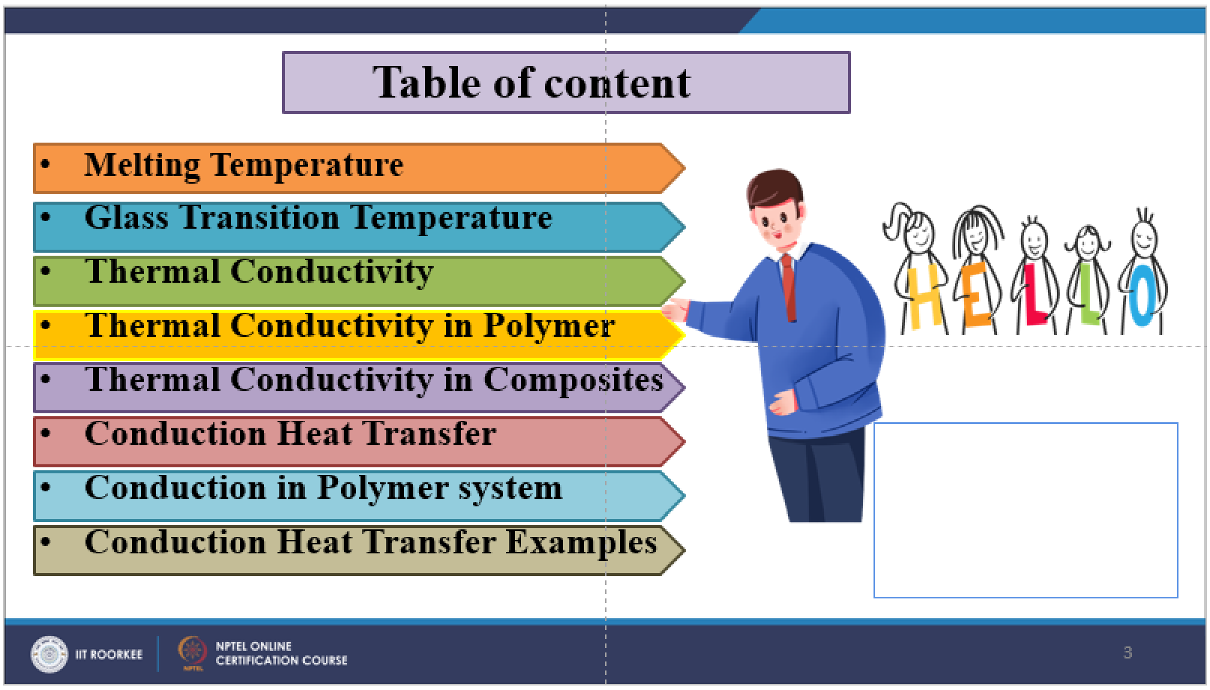
Lecture – 18

Heat Transfer Phenomenon in polymer systems: Thermal properties and conduction

Hello friends, now, if you recall that we are discussing the heat transfer phenomena in polymer systems under the aegis of polymer process engineering. And we are going to discuss about the thermal properties and conduction in this particular lecture. Now, before we go into the details of this particular topic, let us have a brief outlook on what we discussed previously. We discussed the heat deflection temperature, we discussed the wicket softening temperature, then we discussed the heat capacity and thermal expansion, and we discussed the thermal stresses and their importance in the polymeric system. We discussed the thermal shock with the help of certain numerical examples, and we are going to discuss the melting point and the glass transition. Now, here in this particular segment, we are going to discuss the melting temperature, and the glass transition temperature, this is very important in the polymeric system. We are going to discuss this thing and then the thermal conductivity and thermal conductivity especially in the polymers and composites.



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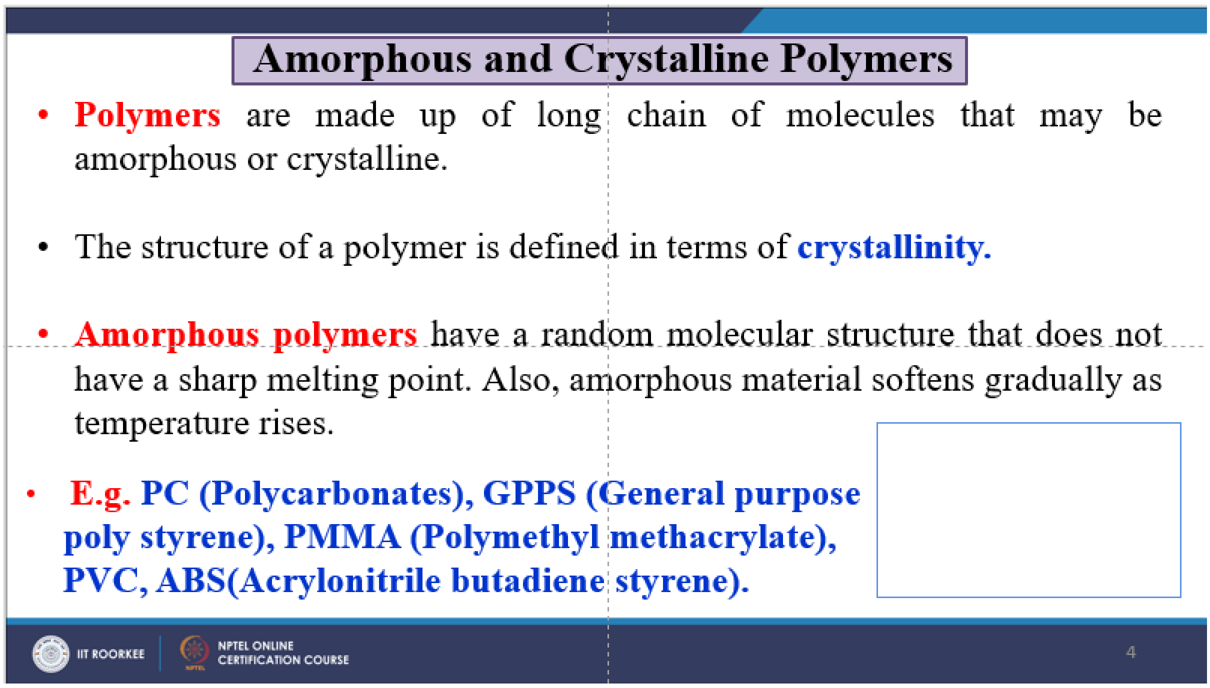
Apart from this, we are going to discuss heat transfer and its heat conduction, conduction heat transfer, and then how this conduction takes place in the polymeric system and we will deal with the several heat transfer examples pertaining to the polymers. Now, let us talk about the amorphous and crystalline polymers. The polymers are usually made up of long-chain molecules that may be amorphous or crystalline. Now, the structure of the polymer is defined in terms of crystallinity.



Amorphous and Crystalline Polymers

- **Polymers** are made up of long chain of molecules that may be amorphous or crystalline.
- The structure of a polymer is defined in terms of **crystallinity.**
- **Amorphous polymers** have a random molecular structure that does not have a sharp melting point. Also, amorphous material softens gradually as temperature rises.
- **E.g. PC (Polycarbonates), GPPS (General purpose poly styrene), PMMA (Polymethyl methacrylate), PVC, ABS(Acrylonitrile butadiene styrene).**

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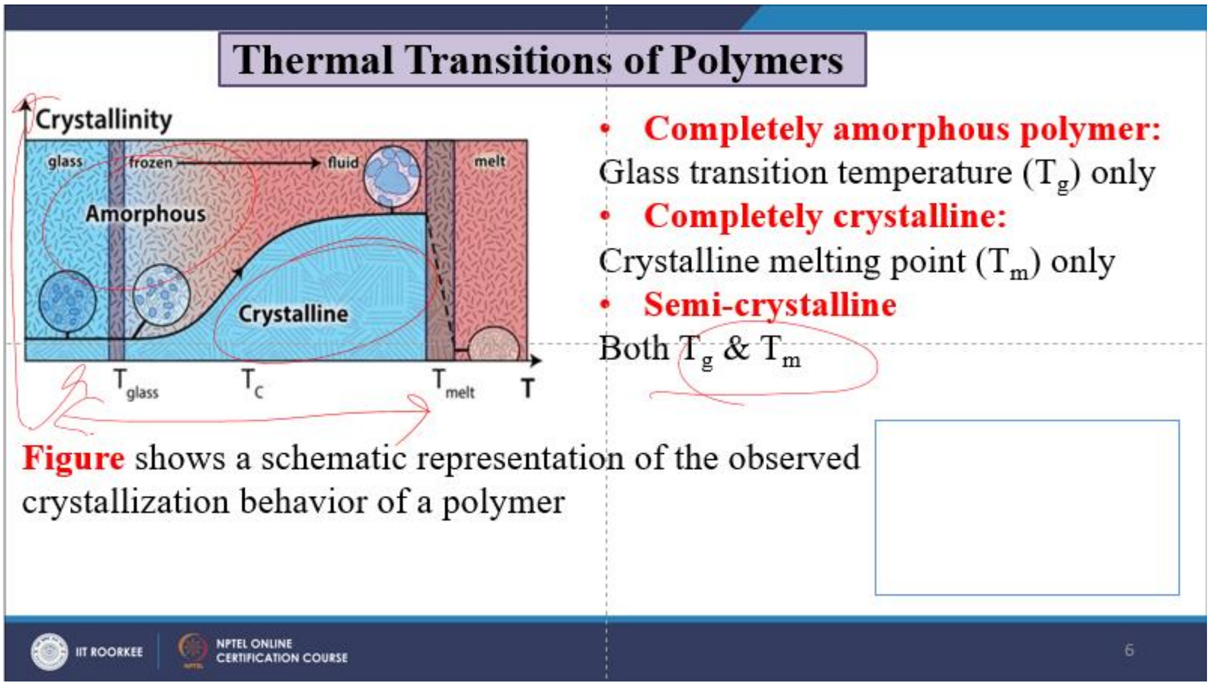
Amorphous polymers have a random molecular structure that does not have a sharp melting point. Also, the amorphous material softens gradually as the temperature rises. For example, polycarbonate, general-purpose polystyrene, poly methyl methacrylate, acrylonitrile, and butadiene styrene all are the best examples of these polymers. Now, the crystalline or semi-crystalline polymers have a highly ordered molecule structure. These do not soften as the temperature rises but rather have a defined narrow melting point. Now, this melting point is generally above that of the upper range of amorphous thermoplastic.

For example, polyolefins, polyethylene ethylates, and polyoxymethylene, all are examples of crystalline and semi-crystalline polymers. Now, completely amorphous polymers possess the glass transition temperature only, and there are the completely crystalline polymers that possess only the crystalline melting temperature or point, and semi-crystalline they possess both glass transition temperature and melting temperature. So, in this particular figure, you see that this is the schematic representation of the observed crystallization behavior of the polymer. Here you see the amorphous range, which is the crystalline range and if you change the temperature, you will observe this type of behavior. Now, crystallization TC occurs above the glass transition temperature at which the amorphous phase in the polymer system can acquire mobility.



Thermal Transitions of Polymers

- **Completely amorphous polymer:**

Glass transition temperature (T_g) only

- **Completely crystalline:**

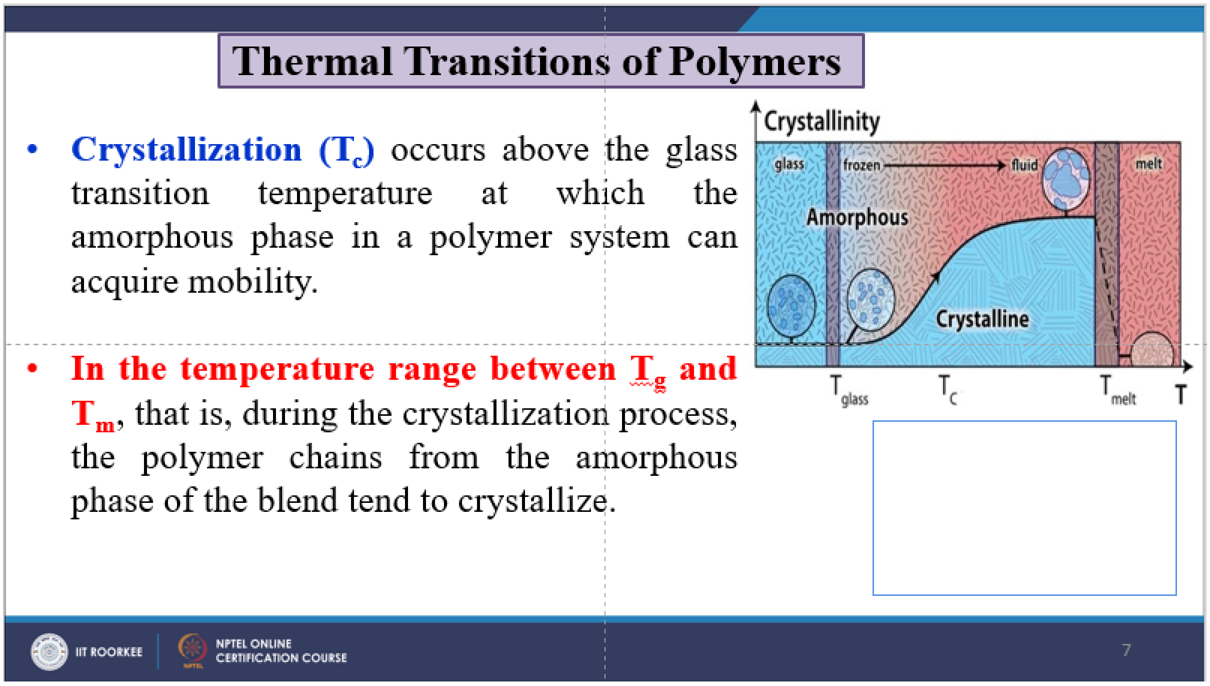
Crystalline melting point (T_m) only

- **Semi-crystalline**

Both T_g & T_m

Figure shows a schematic representation of the observed crystallization behavior of a polymer

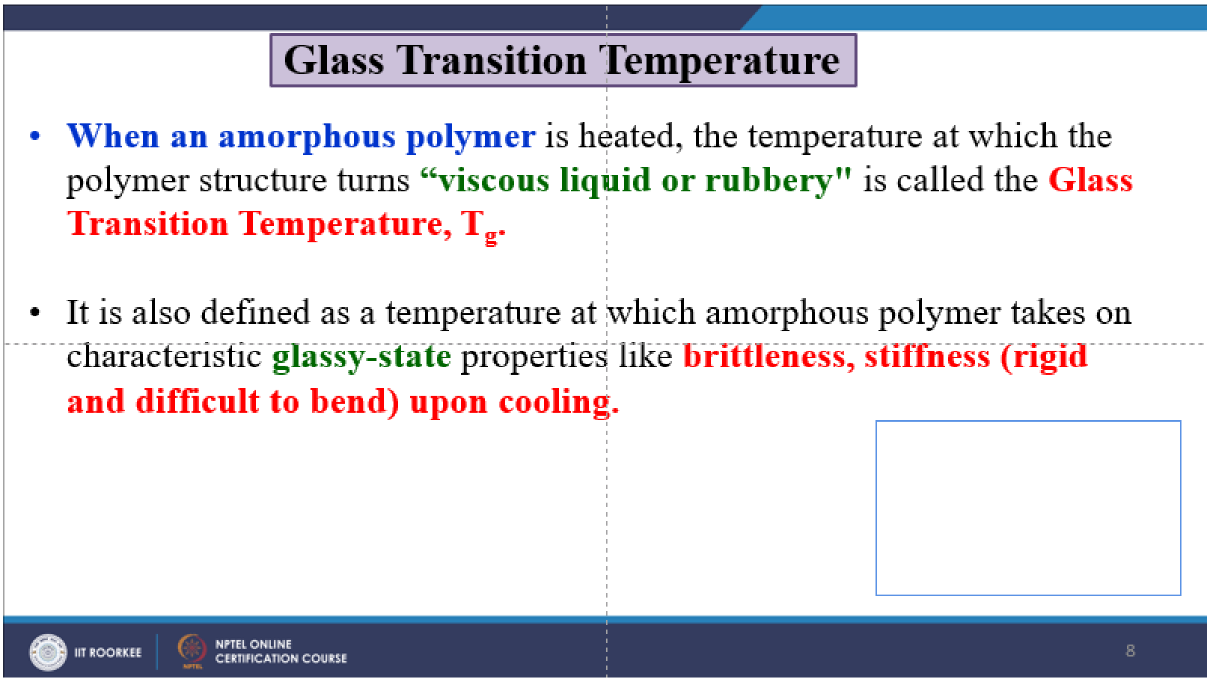
Now, in the temperature ranges between the glass transition temperature and a melting temperature that is during the crystallization process, the polymer chain from the amorphous phase of the blend tends to crystallize. Let us talk about the glass transition temperature because in the previous slides we discussed this TC.



Thermal Transitions of Polymers

- **Crystallization (T_c)** occurs above the glass transition temperature at which the amorphous phase in a polymer system can acquire mobility.
- **In the temperature range between T_g and T_m**, that is, during the crystallization process, the polymer chains from the amorphous phase of the blend tend to crystallize.

So, when an amorphous polymer is heated, the temperature at which the polymer structure turns to viscous liquid or rubbery this is called the glass transition temperature with the TC, and this is because of the polymeric chain and they try to unentangle themselves to align in a particular flow behaviour and that occurs at the glass transition temperature. It is also defined as a temperature at which the amorphous polymer takes on the characteristics of glassy state properties like brittleness, stiffness, rigid and difficult to bend all these things upon cooling. It is named glass is given because glass is a supercooled liquid and this resembles in the amorphous polymeric structures.



Glass Transition Temperature

- **When an amorphous polymer** is heated, the temperature at which the polymer structure turns **"viscous liquid or rubbery"** is called the **Glass Transition Temperature, T_g.**
- It is also defined as a temperature at which amorphous polymer takes on characteristic **glassy-state** properties like **brittleness, stiffness (rigid and difficult to bend) upon cooling.**

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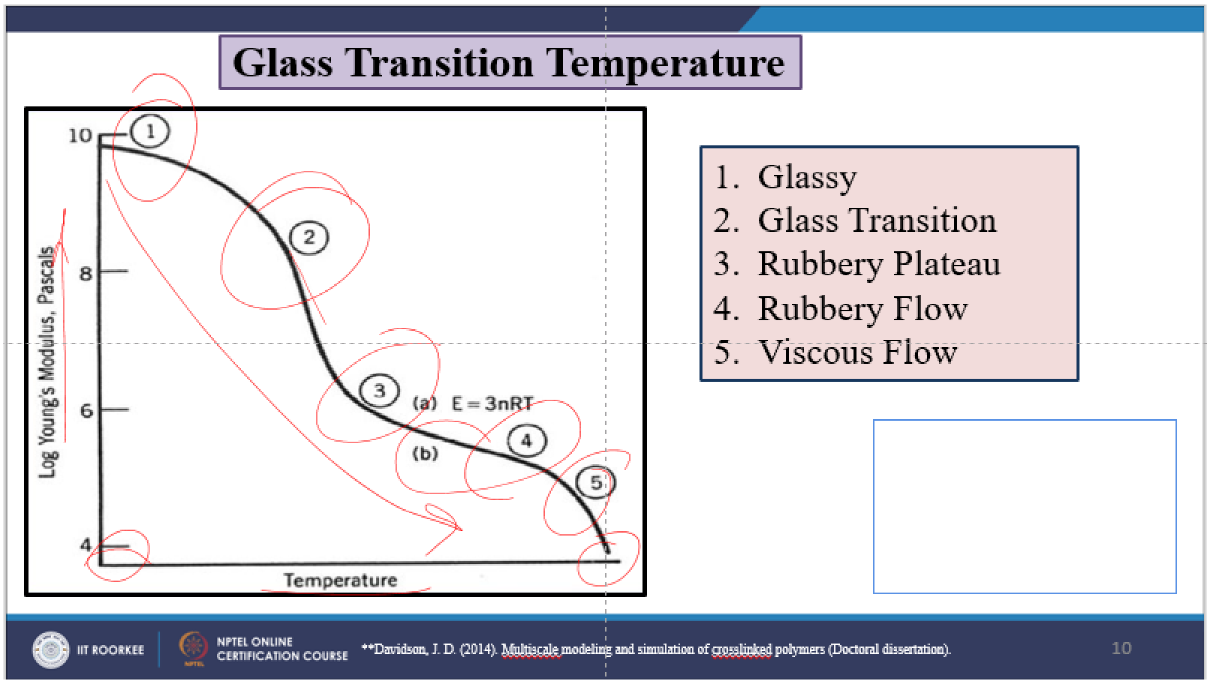
Now, this temperature is usually measured in degree Celsius, this depends on the chemical structure of the polymer and the chain structure and can therefore be used to identify the polymers and this is directly related to the molecular weight distribution. So, the value of glass transition depends on the mobility of the polymeric chain. As I discussed that when you raise the temperature, they try to unentangle and if you lower the temperature, they try to entangle themselves and this is for the most synthetic polymers, they lie between 170 Kelvin to 500 Kelvin. Now, here you see the this is the young modulus versus the temperature. Now, here you see the glass transition temperature variation of different things like this is the glassy, the glass transition temperature and over the period of raising the temperature, the rubbery and the rubbery flow and then the viscous flow.



Glass Transition Temperature

1. Glassy
2. Glass Transition
3. Rubbery Plateau
4. Rubbery Flow
5. Viscous Flow

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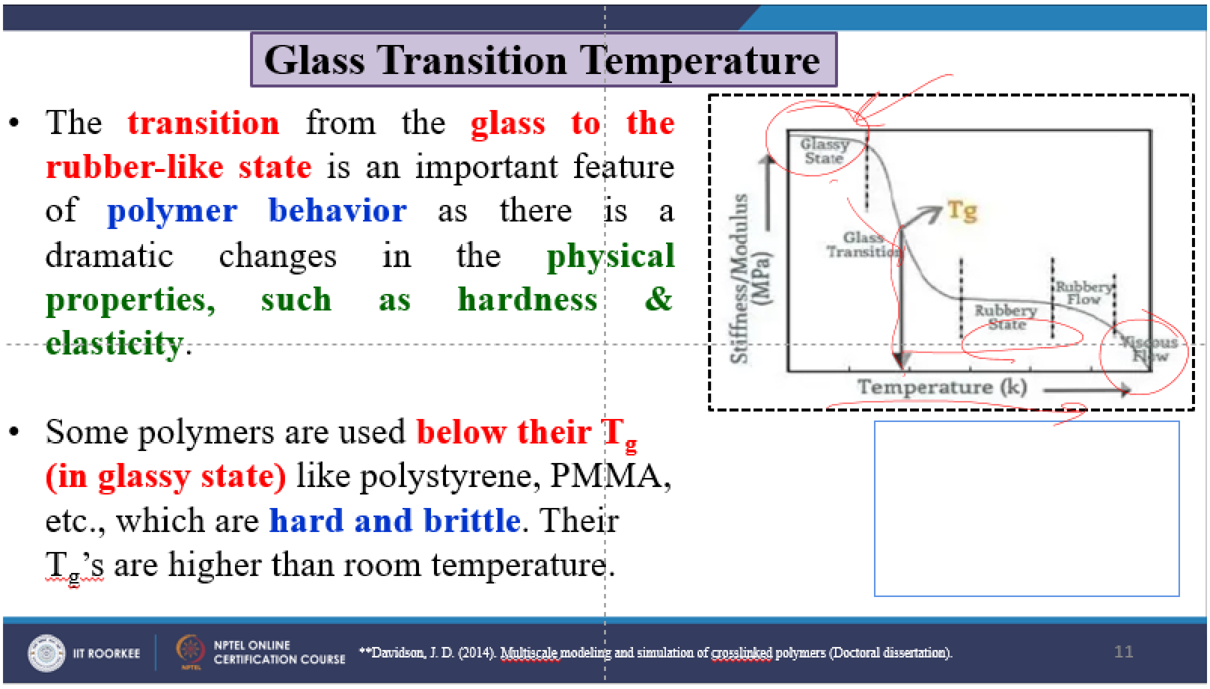
Now, this is because if you raise the temperature, then all the chains they try to align themselves in a particular area and then they try to flow. So, that is why these are the different stages if you raise the temperature from any stipulated point to a different point. Now, this is where you see the transition from glass to rubber a state is an important feature of polymeric behavior as there is a dramatic change in the physical properties such as hardness and elasticity, all these things and some polymers they use are used below their glass transition temperature like polystyrene, PMMA, etcetera which is hard and brittle and their glass transition temperature are higher than the room temperature. So, if you raise the temperature again initially, this is the glassy state, the glassy state is a sub-cooled liquid type of state, then the glass transition temperature where they aligned in the rubbery state, and this is the rubbery state, and then they try to go for the viscous flow. Some polymers are used above their glass transition temperature like rubber elastomers, polyisoprene, polyisobutylene, etcetera, and they are soft and flexible in nature, and their TG is less than the room temperature.

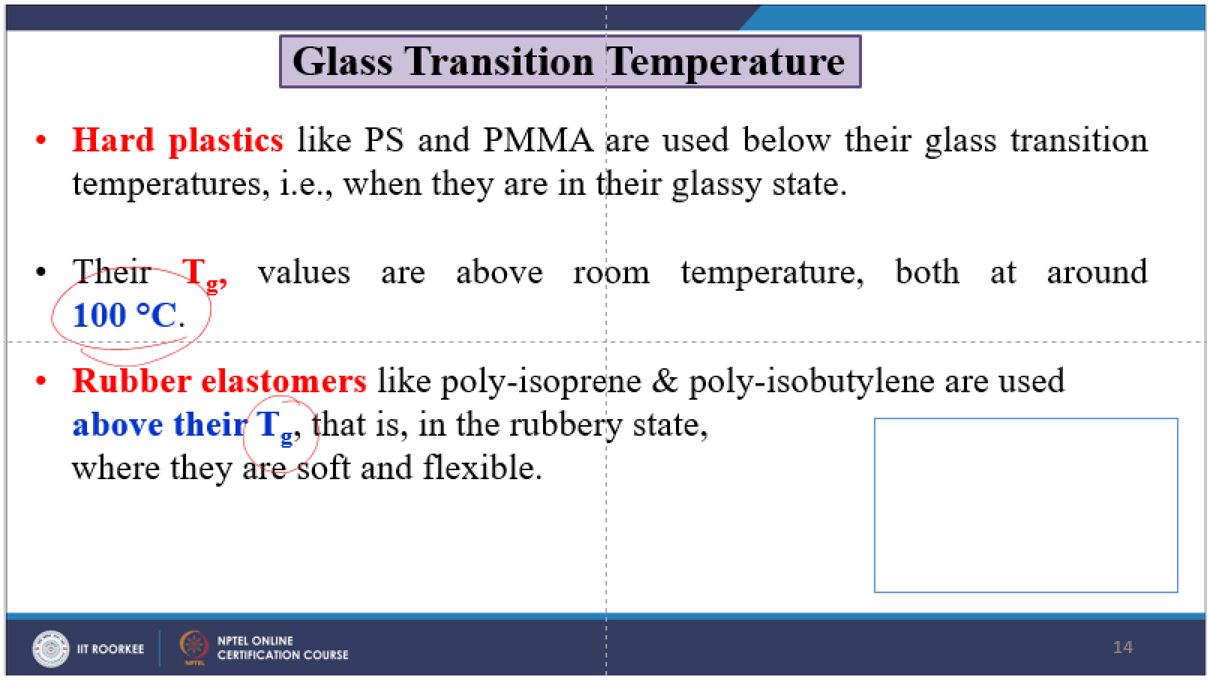


Glass Transition Temperature

- The **transition** from the **glass to the rubber-like state** is an important feature of **polymer behavior** as there is a dramatic changes in the **physical properties, such as hardness & elasticity**.
- Some polymers are used **below their T_g (in glassy state)** like polystyrene, PMMA, etc., which are **hard and brittle**. Their T_g's are higher than room temperature.

**Davidson, J. D. (2014). Multiscale modeling and simulation of crosslinked polymers (Doctoral dissertation).

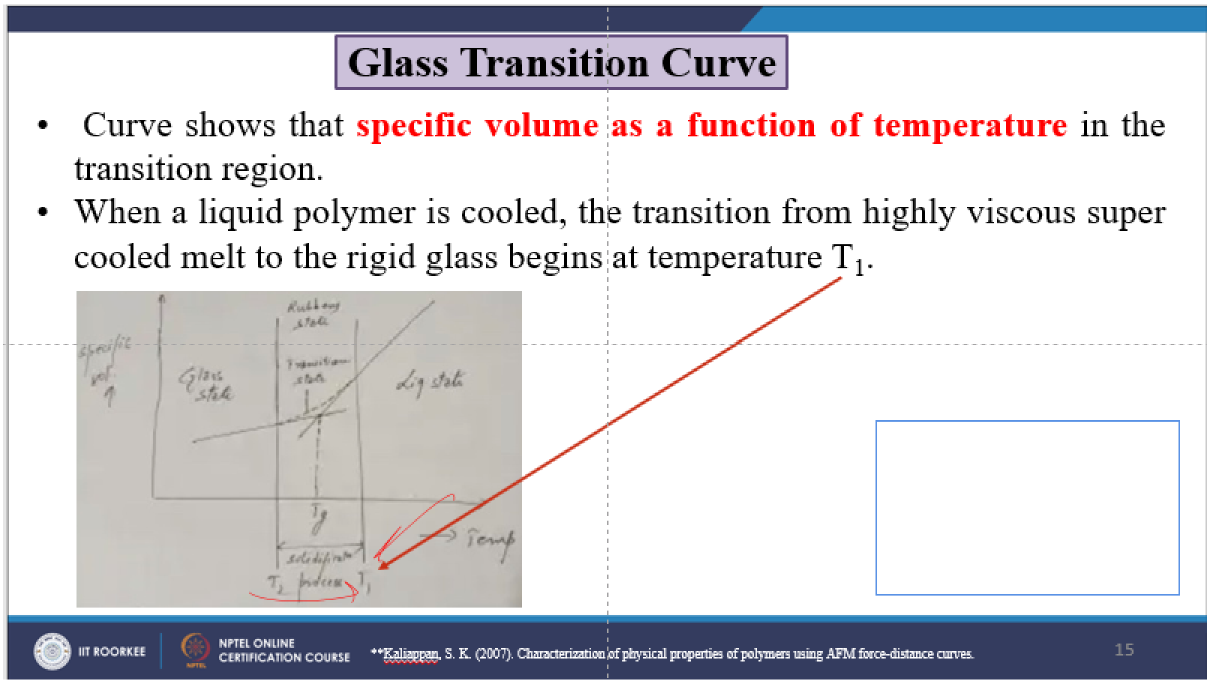
So, this can be used as a soft material and for various purposes like different types of grasses, artificial grasses, then carpets all these things are using this particular type of behaviour. At glass transition temperature, changes in the hardness, volume, percent, and elongation to break of solid they are mainly seen, and glass transition is an important tool to modify the physical properties of the polymer molecules. Now, further improvement in the handling characters, solubility and reproducibility in the dissolution of the solid can be achieved during the increase in the glass transition of the solids. Sometimes hard plastics like polystyrene, polymethane, and methacrylate are used below their glass transition temperature when they are in the glassy states. Now, their glass transition temperature values are above room temperature and around 100 degrees Celsius.



Glass Transition Temperature

- **Hard plastics** like PS and PMMA are used below their glass transition temperatures, i.e., when they are in their glassy state.
- Their T_g, values are above room temperature, both at around **100 °C**.
- **Rubber elastomers** like poly-isoprene & poly-isobutylene are used **above their T_g**, that is, in the rubbery state, where they are soft and flexible.

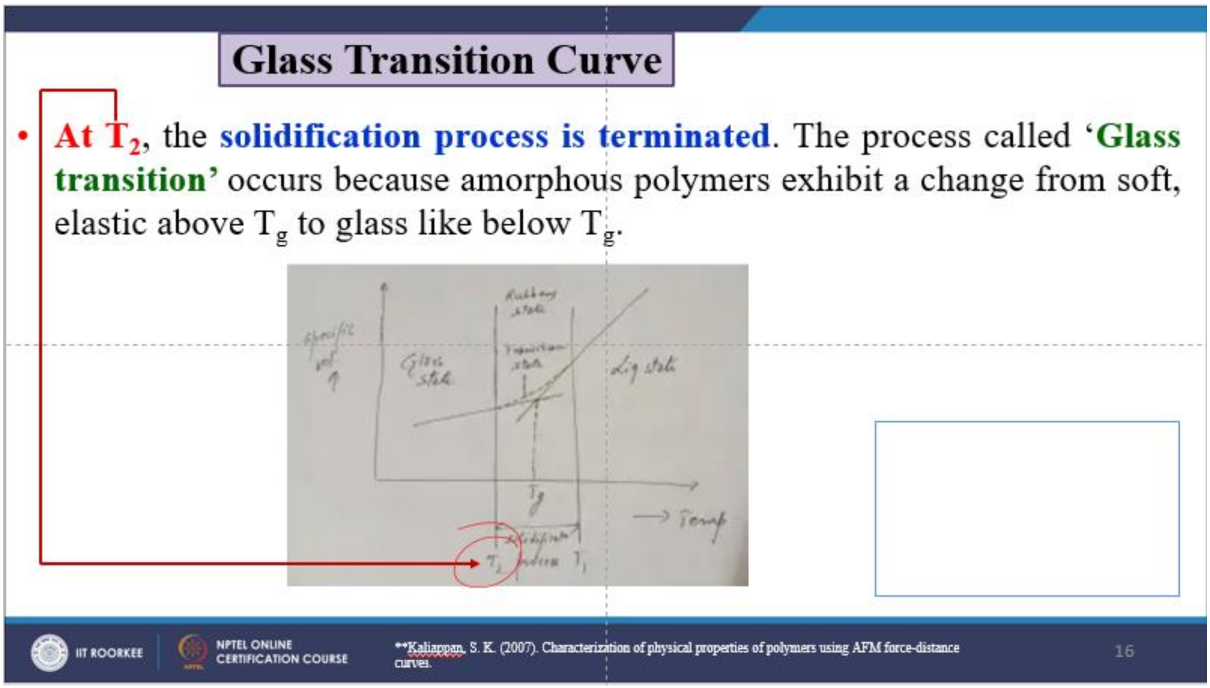
So, very elastomers like polyisoprene, and polyisobutylene they are used above their glass transition temperature as their rubbery state is required or the soft and flexible character is required for those polymers. Now here you see the curve that is a specific volume versus a specific volume as a function of temperature in the transition region. When a liquid polymer is cooled, the transition from highly viscous supercooled melt to rigid glass begins at the temperature 'T' here you see this one. Now this is T 2 where the solidification process is terminated the process is called the glass transition occurs because the amorphous polymer exhibits a change from soft elastic above-glass transition to the glass-like below-glass transition temperature. So, the motion of all the polymeric chains starts this C session.



Glass Transition Curve

- Curve shows that **specific volume as a function of temperature** in the transition region.
- When a liquid polymer is cooled, the transition from highly viscous super cooled melt to the rigid glass begins at temperature T_1.

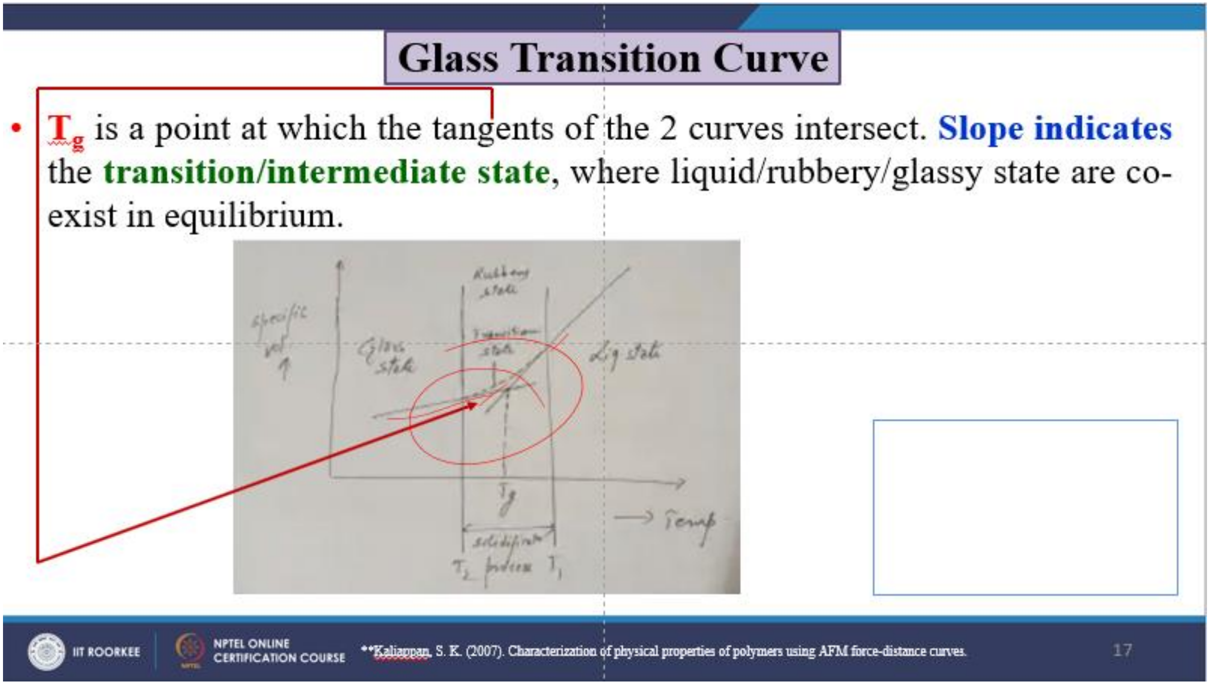
**Kaliappan, S. K. (2007). Characterization of physical properties of polymers using AFM force-distance curves.



Glass Transition Curve

- **At T_2**, the **solidification process is terminated**. The process called '**Glass transition**' occurs because amorphous polymers exhibit a change from soft, elastic above T_g to glass like below T_g.

**Kaliappan, S. K. (2007). Characterization of physical properties of polymers using AFM force-distance curves.

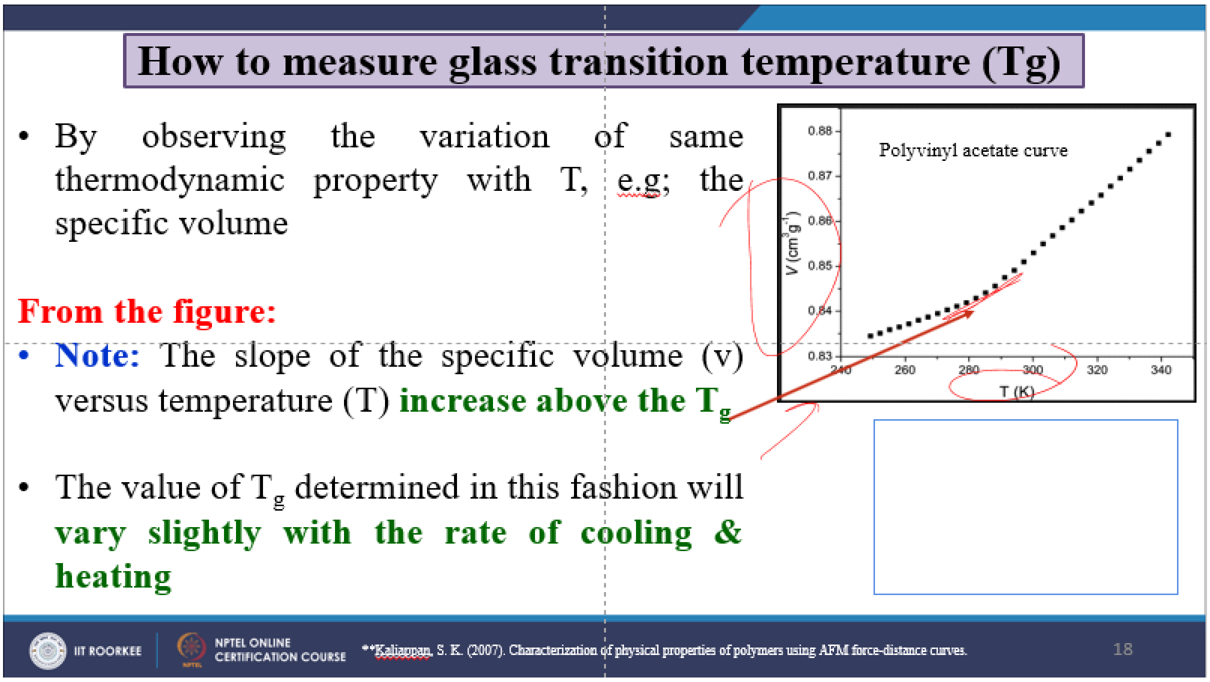


Glass Transition Curve

- **T_g** is a point at which the tangents of the 2 curves intersect. **Slope indicates** the **transition/intermediate state**, where liquid/rubbery/glassy state are co-exist in equilibrium.

**Kaliappan, S. K. (2007). Characterization of physical properties of polymers using AFM force-distance curves.

Now the glass transition temperature or T g is a point at which the tangents of the two curves here you see that the two curves intersect and a slope indicates the transition or intermediate state where the liquid rubbery glassy state coexists in equilibriums. Now, how to measure the glass transition temperature by observing the variation of some thermodynamic properties with the temperature, like a specific volume.



How to measure glass transition temperature (Tg)

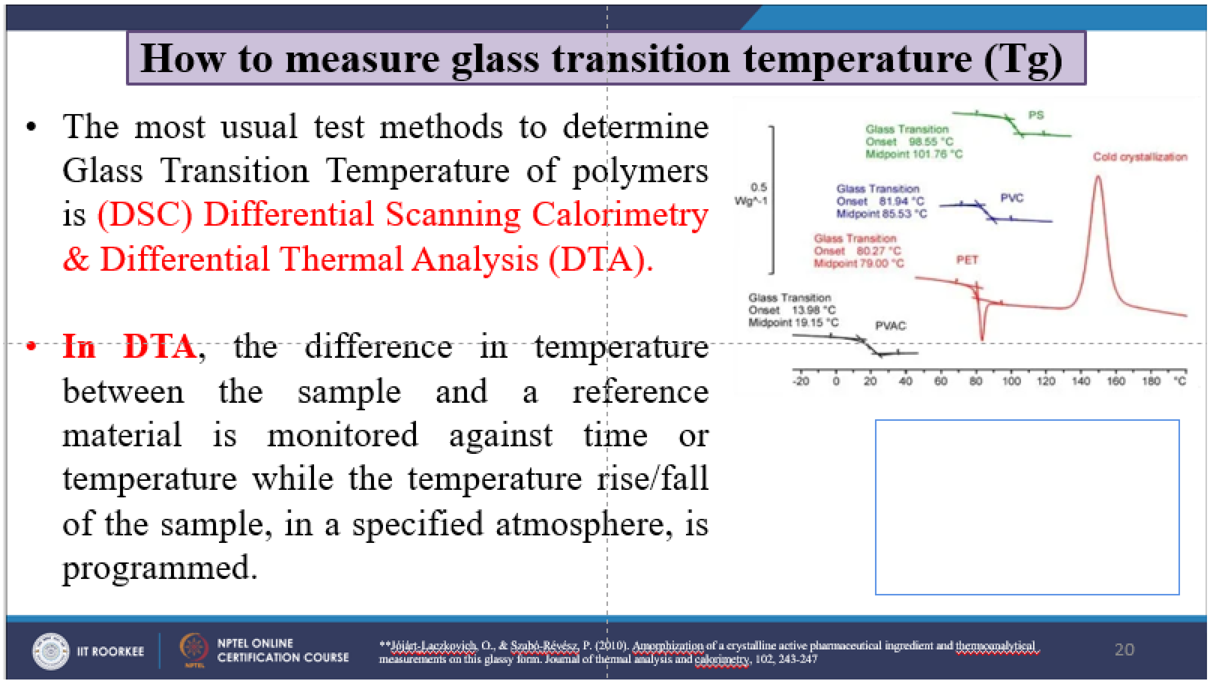
- By observing the variation of same thermodynamic property with T, e.g; the specific volume

From the figure:

- **Note:** The slope of the specific volume (v) versus temperature (T) **increase above the T_g**
- The value of T_g determined in this fashion will **vary slightly with the rate of cooling & heating**

**Kaliappan, S. K. (2007). Characterization of physical properties of polymers using AFM force-distance curves.

If we have a plot or a figure of the slope of the specific volume versus temperature increases above the glass transition temperature the value of T g determined in this fashion will vary slightly with the rate of cooling and heating. This reflects the fact that long entangled polymer chains cannot respond instantaneously to changes in temperature and illustrates because they are bulky in nature and have difficulty in making thermodynamic measurements on the polymer. The most usual test method to determine the glass transition temperature of the polymer is DSC which is differential scanning calorimetry and differential thermal analysis DTA.

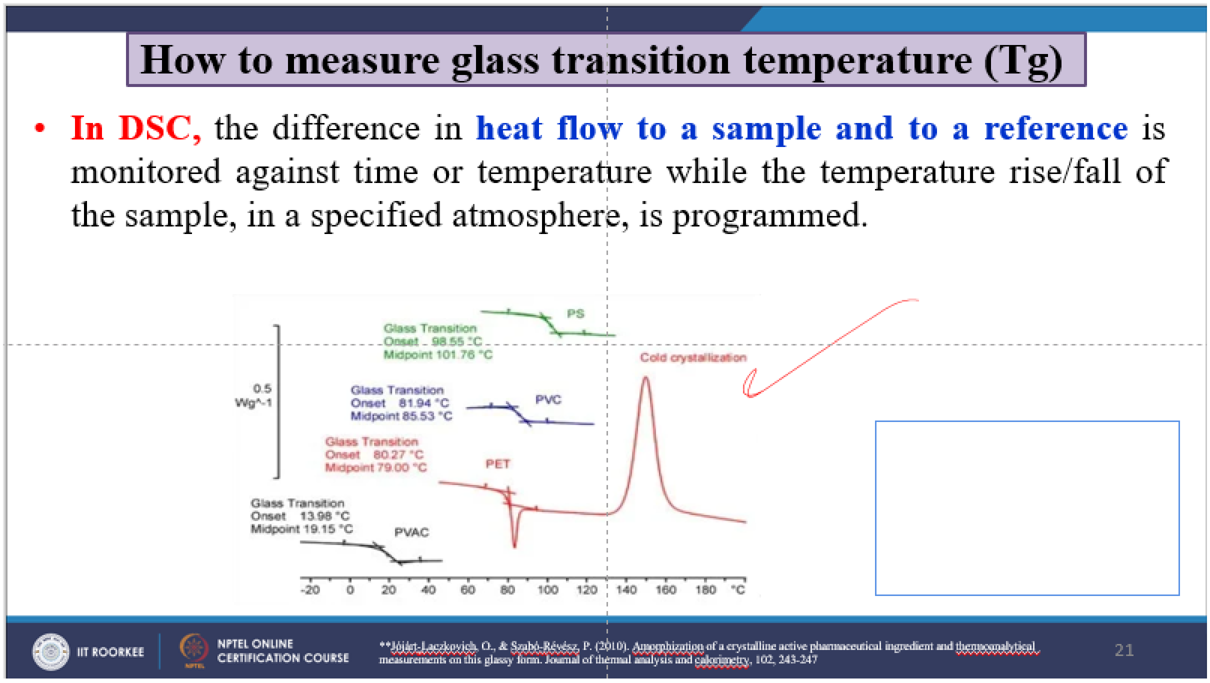


How to measure glass transition temperature (Tg)

- The most usual test methods to determine Glass Transition Temperature of polymers is (DSC) Differential Scanning Calorimetry & Differential Thermal Analysis (DTA).
- **In DTA**, the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.

**Jójárt-Laczkovich, O., & Szabó-Révész, P. (2010). Amorphization of a crystalline active pharmaceutical ingredient and thermoanalytical measurements on this glassy form. Journal of thermal analysis and calorimetry, 102, 243-247

So, in DTA the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature rises or fall the sample in a specified atmosphere is programmed.

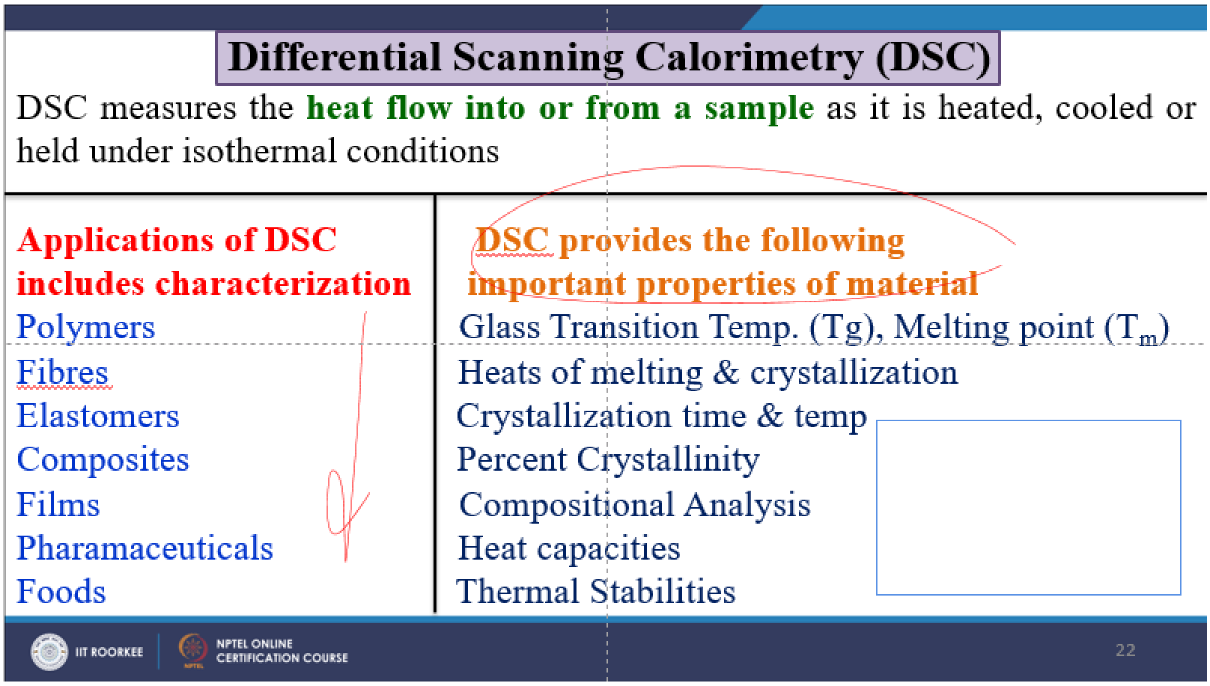


How to measure glass transition temperature (Tg)

- **In DSC,** the difference in **heat flow to a sample and to a reference** is monitored against time or temperature while the temperature rise/fall of the sample, in a specified atmosphere, is programmed.

**Jójárt-Laczkovich, O., & Szabó-Révész, P. (2010). Amorphization of a crystalline active pharmaceutical ingredient and thermoanalytical measurements on this glassy form. Journal of thermal analysis and calorimetry, 102, 243-247

Now in DSC the difference in heat flow to a sample and to a reference is monitored against the time or temperature while the temperature rises or fall of the temperature in a specified atmosphere is programmed. Let us talk about the DSC that is a differential scanning calorimetry. DSC measures the heat flow into or from a sample as it is heated, cooled or held under the isothermal condition. There are various application of DSC this includes the polymers, fibers, elastomers, composites, film, pharmaceuticals, food etcetera.



Differential Scanning Calorimetry (DSC)

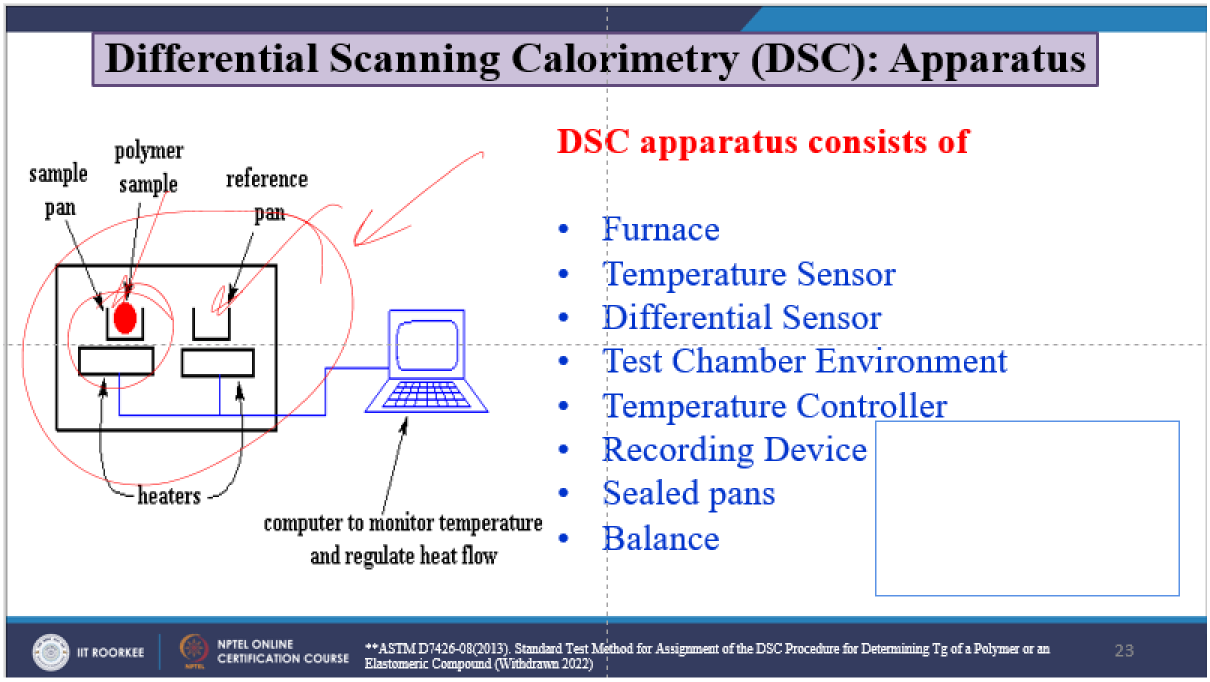
DSC measures the **heat flow into or from a sample** as it is heated, cooled or held under isothermal conditions

Applications of DSC includes characterization

Polymers
Fibres
Elastomers
Composites
Films
Pharamaceuticals
Foods

DSC provides the following important properties of material

Glass Transition Temp. (Tg), Melting point (T_m)
Heats of melting & crystallization
Crystallization time & temp
Percent Crystallinity
Compositional Analysis
Heat capacities
Thermal Stabilities



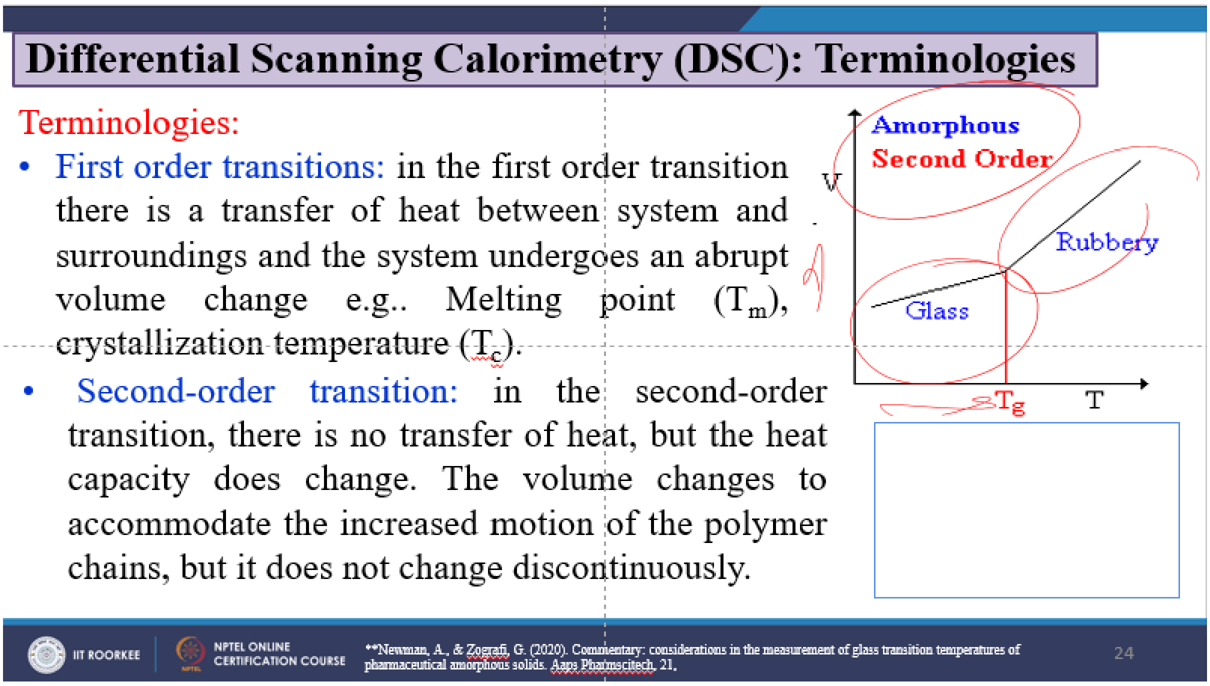
Differential Scanning Calorimetry (DSC): Apparatus

DSC apparatus consists of

- Furnace
- Temperature Sensor
- Differential Sensor
- Test Chamber Environment
- Temperature Controller
- Recording Device
- Sealed pans
- Balance

**ASTM D7426-08(2013). Standard Test Method for Assignment of the DSC Procedure for Determining Tg of a Polymer or an Elastomeric Compound (Withdrawn 2022)

This DSC provides the different important properties of the material like glass transition temperature, melting point, heat of heats of melting and crystallization, crystallization time and temperature, percent crystallinity, compositional analysis, heat capacities, thermal stabilities all those things. Now, let us a brief sketch or a rough sketch about the differential scanning calorimetry. This DSC apparatus broadly consists of a furnace, the temperature sensor, the test chamber environment, the temperature controller, recording device, sealed pans, balance etcetera. So, this is a sample pan here you can put the polymer sample and this is a reference pan and all these things are programmed. Now, there are various terminology been used the DSC, the first order transition, in the first order transition there is a transfer of heat between the system and surrounding and the system undergoes an abrupt volume change that is a melting point and crystallization temperature.



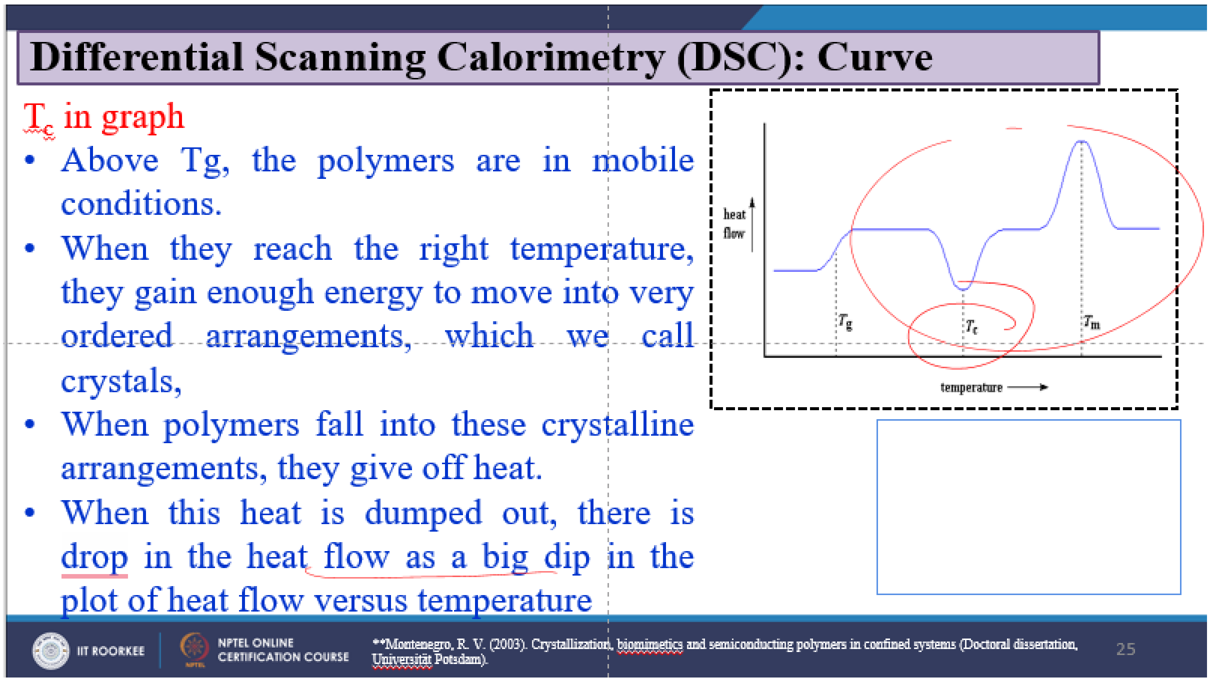
Differential Scanning Calorimetry (DSC): Terminologies

Terminologies:

- First order transitions: in the first order transition there is a transfer of heat between system and surroundings and the system undergoes an abrupt volume change e.g.. Melting point (T_m), crystallization temperature (T_c).
- Second-order transition: in the second-order transition, there is no transfer of heat, but the heat capacity does change. The volume changes to accommodate the increased motion of the polymer chains, but it does not change discontinuously.

**Newman, A., & Zografi, G. (2020). Commentary: considerations in the measurement of glass transition temperatures of pharmaceutical amorphous solids. Aaps Pharmscitech, 21.

So, here you see this is the temperature versus the crystalline solid melt and this is the crystalline first order. Now, second order transition, in the second order transition there is no transfer of heat, but the heat capacity does change, the volume changes to accommodate the increased motion of the polymer chain, but it does not change discontinuity. Now, when we plot the glass transition temperature the Tg, the property usually Tg in graph this provides the property of the amorphous region, below glass transition temperature disorder amorphous solid with immobile molecules and above glass transition temperature the disordered amorphous solid in which the portion of molecules can move back and forth. The second order transition this increase in heat capacity, but there is no transfer of heat. The above glass transition temperature the polymers are in mobile condition, when they reach the rigid temperature they gain enough energy to move into very ordered arrangement which is we call the crystals.



Differential Scanning Calorimetry (DSC): Curve

T_c in graph

- Above Tg, the polymers are in mobile conditions.
- When they reach the right temperature, they gain enough energy to move into very ordered arrangements, which we call crystals,
- When polymers fall into these crystalline arrangements, they give off heat.
- When this heat is dumped out, there is drop in the heat flow as a big dip in the plot of heat flow versus temperature

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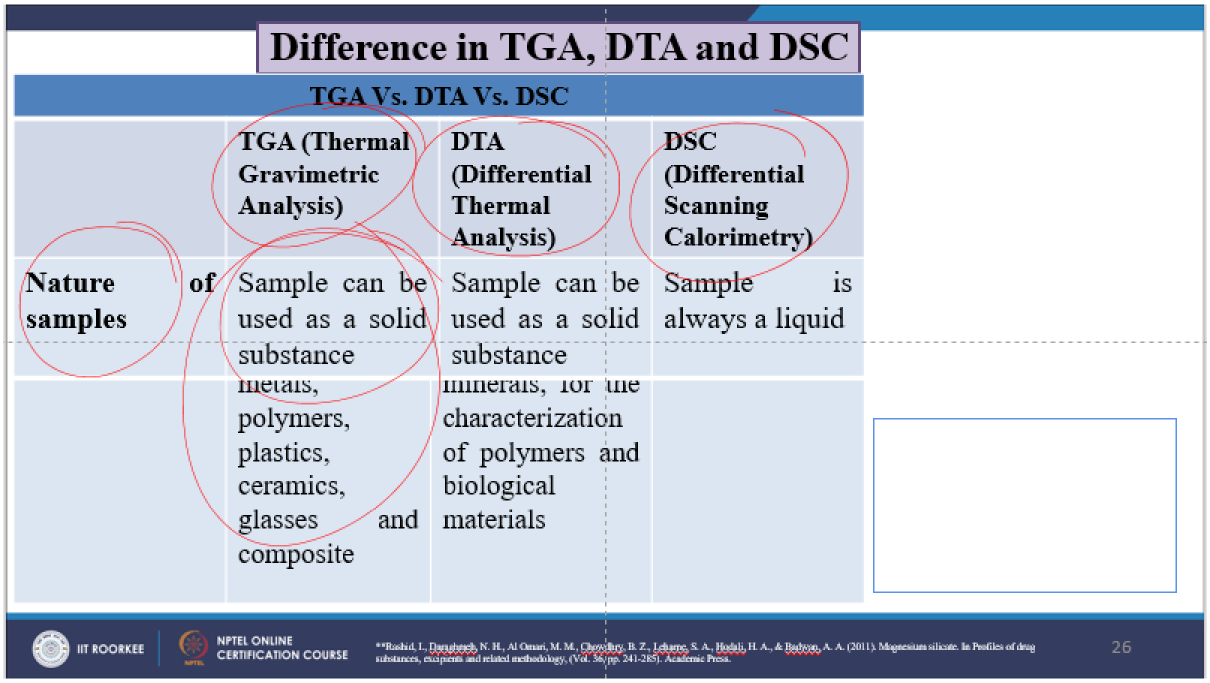
**Montenegro, R. V. (2003). Crystallization, biomimetics and semiconducting polymers in confined systems (Doctoral dissertation, Universität Potsdam).

When polymer fall into these crystal line arrangement they give of heat, when this heat is dumped off there is a drop in the heat flow as the big dip in the plot of heat flow versus temperature. So, above Tc or if we talk about the melting temperature, so above Tc we reach the polymers melting temperature or Tm those polymer crystals begin to fall apart that that is the melt. So, melting temperature is quite essential that the chain, chains come out to of their ordered arrangement and begin to move around freely and melting is a first order transition. Now here you see this is a table where which represents the difference in TGA, DTA and DSC. Now TGA this is a thermal gravimetric analysis, differential thermal analysis and differential scanning calorimetry.



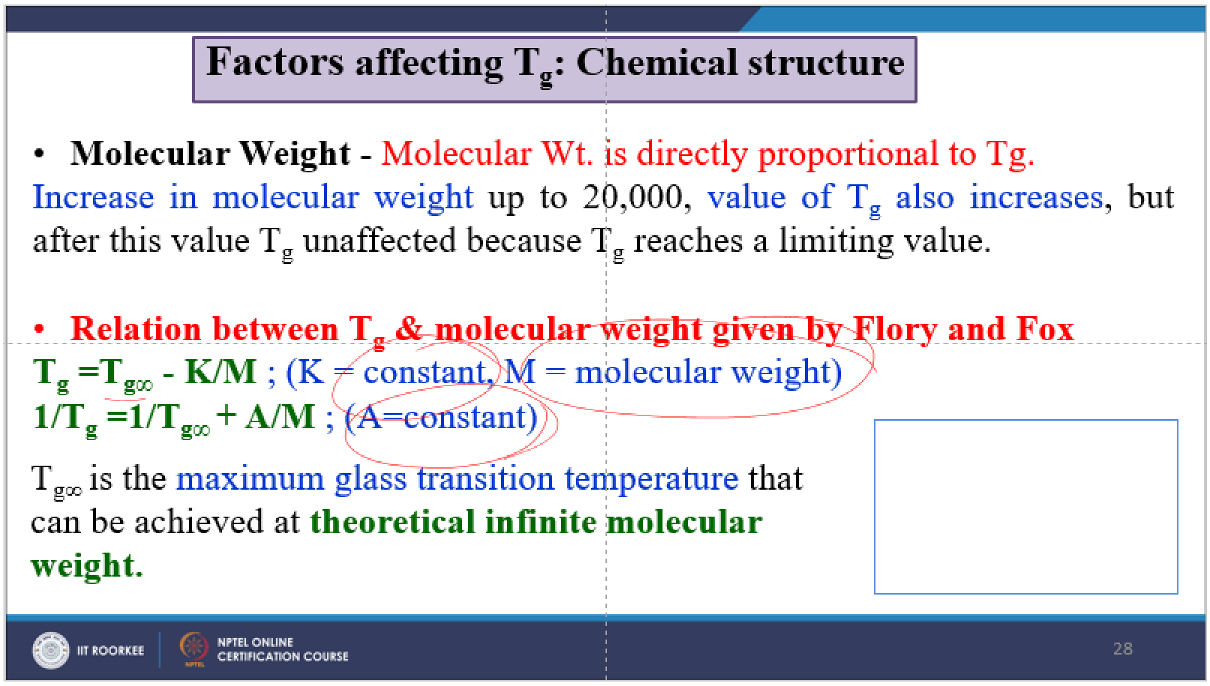
Difference in TGA, DTA and DSC

TGA Vs. DTA Vs. DSC			
	TGA (Thermal Gravimetric Analysis)	**DTA (Differential Thermal Analysis)**	**DSC (Differential Scanning Calorimetry)**
Nature of samples	Sample can be used as a solid substance	Sample can be used as a solid substance	Sample is always a liquid
	metals, polymers, plastics, ceramics, glasses and composite	minerals, for the characterization of polymers and biological materials	

**Rashid, I., Daraghmeh, N. H., Al Omari, M. M., Chowdhry, B. Z., Leharne, S. A., Hodali, H. A., & Badwan, A. A. (2011). Magnesium silicate. In Profiles of drug substances, excipients and related methodology, (Vol. 36, pp. 241-285). Academic Press.

This TGA utilise the technique of the change of the mass of a sample with the change of the temperature. This is usually observed and analysed where in DTA the temperature difference developed between a sample and a reference compound which is measured and identical heat and treatment is been carried out. The DSC the heat flow is measured against the temperature change at a particular time. Then the compound analysed, what compound we analysed this used to analyse the inorganic material metals, polymers, plastics, ceramics, glass composites etc. And in DTA they used to analyse the thermal properties of the minerals for the characterisation of the polymer and biological materials and DSC they used to analyse the protein, antibodies etc.

Now nature of sample is again very important. Then the sample can be used as a solid substance in TGA whereas the solid substance again this can be used in DTA and in DSC the sample is always in a liquid form. Now let us talk about the various factors affecting the glass transition temperature like chemical structure, molecular weight, molecular structure, polarity, chemical cross linking. Apart from this the plasticizer, water or moisture content, enthalpy, entropy of individual polymers, pressure and free volume, chain flexibility, steric hindrance, copolymerization all these factors they affecting the glass transition temperature. Let us talk about the chemical structure, the molecular weight, molecular weight is directly proportional to the glass transition temperature.



Factors affecting T_g: Chemical structure

- **Molecular Weight** - Molecular Wt. is directly proportional to Tg.

Increase in molecular weight up to 20,000, value of T_g also increases, but after this value T_g unaffected because T_g reaches a limiting value.

- **Relation between T_g & molecular weight given by Flory and Fox**

$T_g = T_{g\infty} - K/M$; (K = constant, M = molecular weight)

$1/T_g = 1/T_{g\infty} + A/M$; (A=constant)

$T_{g\infty}$ is the maximum glass transition temperature that can be achieved at **theoretical infinite molecular weight.**

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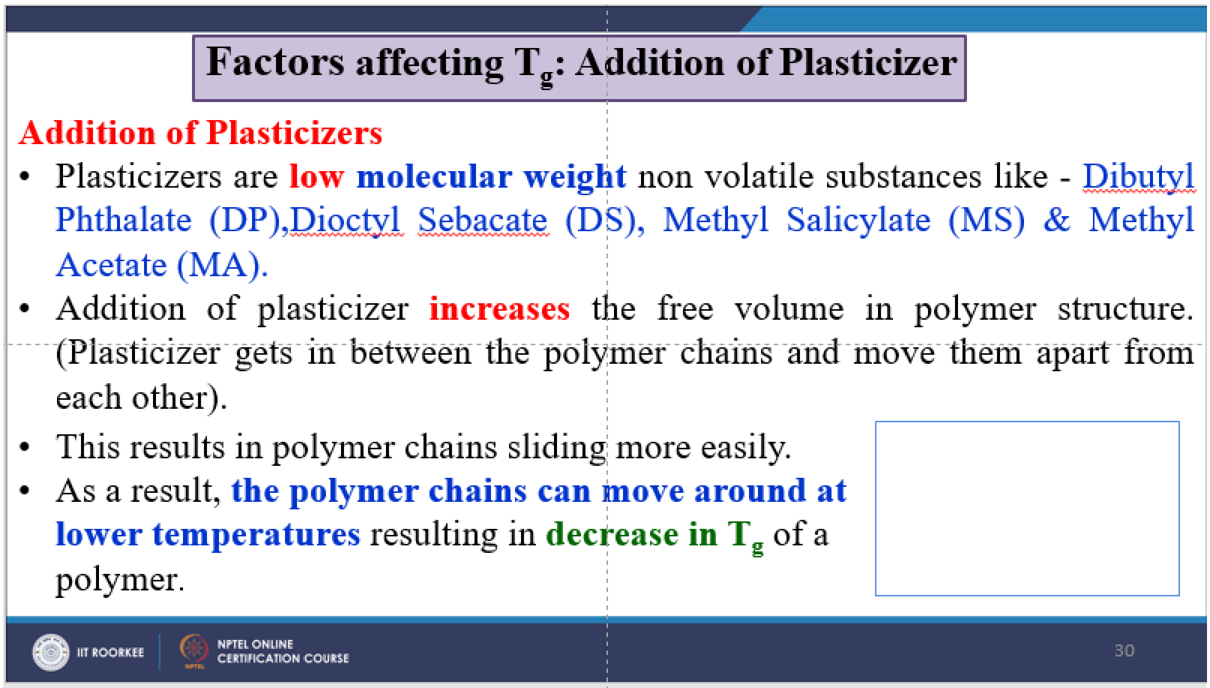
So, the increase in the molecular weight, say up to 20,000 value of TGA, also increases, but after this particular triggering value TG is unaffected because TG reaches a limiting value. There is a relationship between the glass transition temperature and molecular weight. This is given by the PJ Flory. Now here the TG is equal to TG infinite minus K over M, the K is a constant, and M is the molecular weight and 1 over TG is equal to 1 over TG infinite plus A over M where A is constant. So, TG infinite is a maximum glass transition temperature that can be achieved at a theoretical infinite molecular weight.

Then the molecular structure, and insertion of bulky inflexible side groups, increases the glass transition temperature of the material due to the decrease in mobility of those chains. Then the chemical cross-linking, increase in the cross-linking decreases the mobility, which led to a decrease in free volume and an increase in glass transition temperature. Some sort of the polar groups, the presence of the polar group increases the intermolecular forces, interchain interaction, cohesion, this leading to a decrease in the free volume and resulting in glass transition temperature. Sometimes addition of the plasticizer plays a very vital role. The plasticizers are low molecular weight, non-volatile substances like dibutyl phthalate, dioctyl sebacate, methyl salicylate, methyl acetate.



Factors affecting T_g: Addition of Plasticizer

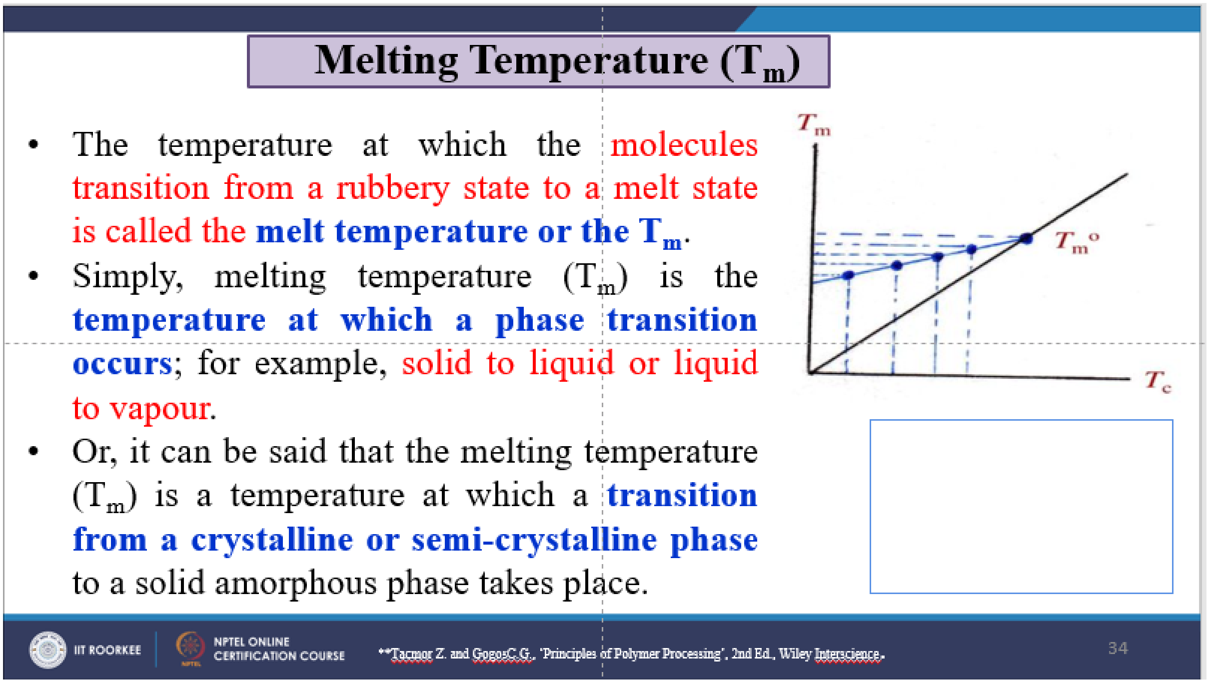
Addition of Plasticizers

- Plasticizers are **low molecular weight** non volatile substances like - Dibutyl Phthalate (DP),Dioctyl Sebacate (DS), Methyl Salicylate (MS) & Methyl Acetate (MA).
- Addition of plasticizer **increases** the free volume in polymer structure. (Plasticizer gets in between the polymer chains and move them apart from each other).
- This results in polymer chains sliding more easily.
- As a result, **the polymer chains can move around at lower temperatures** resulting in **decrease in T_g** of a polymer.

Now addition of plasticizer increases the free volume in the polymer structure and this plasticizer gets in between the polymer chain and move them apart from each other. Now this results in the polymer chain in sliding more easily. So, as a result the polymer chains can move around at a low temperature resulting in decrease in Tg of the polymer. Water content and entropy also plays a valuable factor in affecting the Tg. The water or moisture content, this increase in the moisture content helps in the formation of hydrogen bond that increases the distance between the polymer chain, hence the increase in the free volume and decreases the glass transition temperature.

Effect of entropy, the value of entropy for amorphous material is higher and then and low for crystalline material. If value of entropy is high, the free volume increases and the value of Tg decreases. The pressure and free volume also play a vital role. The increase in pressure of surrounding this leads to decrease in free volume and ultimately high glass transition temperature. The chain flexibility, the polymer with the linear chain, this mainly consists of C-C or C-O or C-N bonds.

They possess the high chain flexibility, therefore shows a low Tg value and usually minus 125 degree Celsius for polyethylene. This is for the sake of an example. The presence of aromatic cycle ring in the backbone chain reduces the flexibility and thereby increasing the glass transition temperature. Sometimes steric hindrance, steric hindrance is also playing a very vital role. The presence of larger and bulky group on the polymeric long chain, this restricts the degree of freedom and free rotation, hence the Tg value increases.



Melting Temperature (T_m)

- The temperature at which the molecules transition from a rubbery state to a melt state is called the **melt temperature or the T_m**.
- Simply, melting temperature (T_m) is the **temperature at which a phase transition occurs**; for example, solid to liquid or liquid to vapour.
- Or, it can be said that the melting temperature (T_m) is a temperature at which a **transition from a crystalline or semi-crystalline phase** to a solid amorphous phase takes place.

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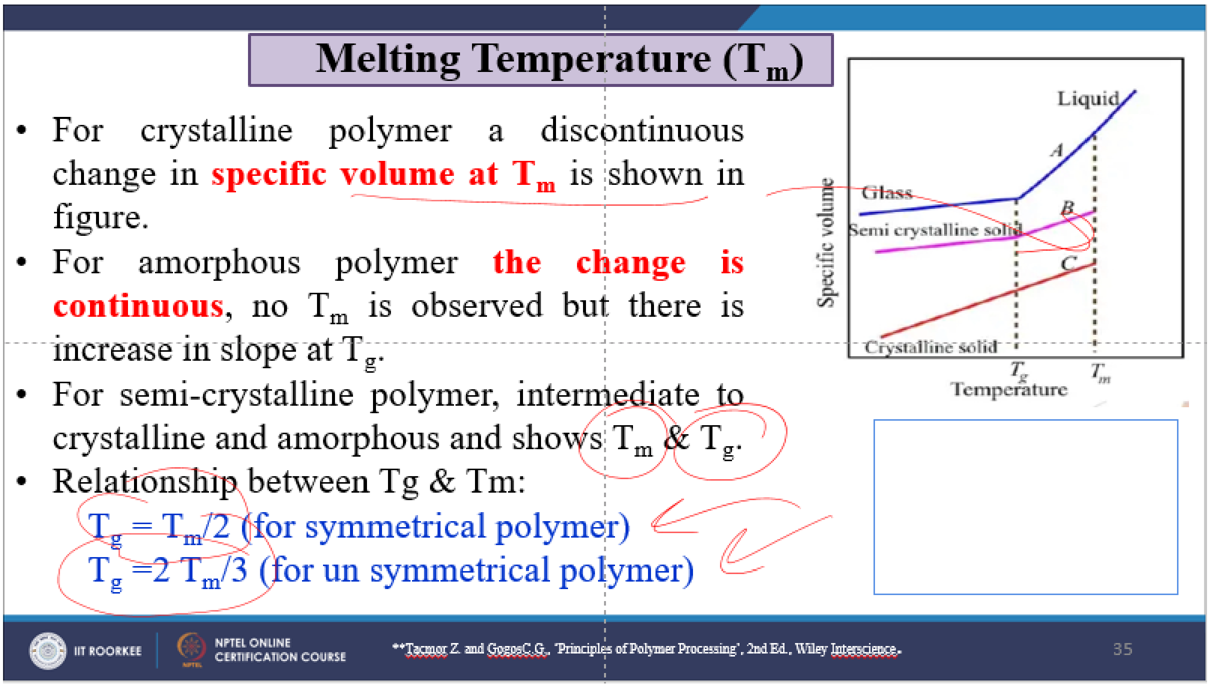
The ortho position restricts the rotation due to the steric hindrance more than the para and meta position, therefore, the Tg value is higher. Let us talk about the melting temperature, the temperature at which the molecules transition from a rubbery state to a melt state, usually, it is called the melt temperature or T_M. This simple melting temperature is the temperature at which the phase transition occurs. For example, a solid to liquid or a liquid to vapor or it can be said to be the melting temperature T_M. This is a temperature at which the transition from the crystalline to semi or semi-crystalline phase to a solid amorphous phase takes place.



Melting Temperature (T_m)

- For crystalline polymer a discontinuous change in **specific volume at T_m** is shown in figure.
- For amorphous polymer **the change is continuous**, no T_m is observed but there is increase in slope at T_g.
- For semi-crystalline polymer, intermediate to crystalline and amorphous and shows T_m & T_g.
- Relationship between Tg & Tm:
  - $T_g = T_m/2$ (for symmetrical polymer)
  - $T_g = 2\,T_m/3$ (for un symmetrical polymer)

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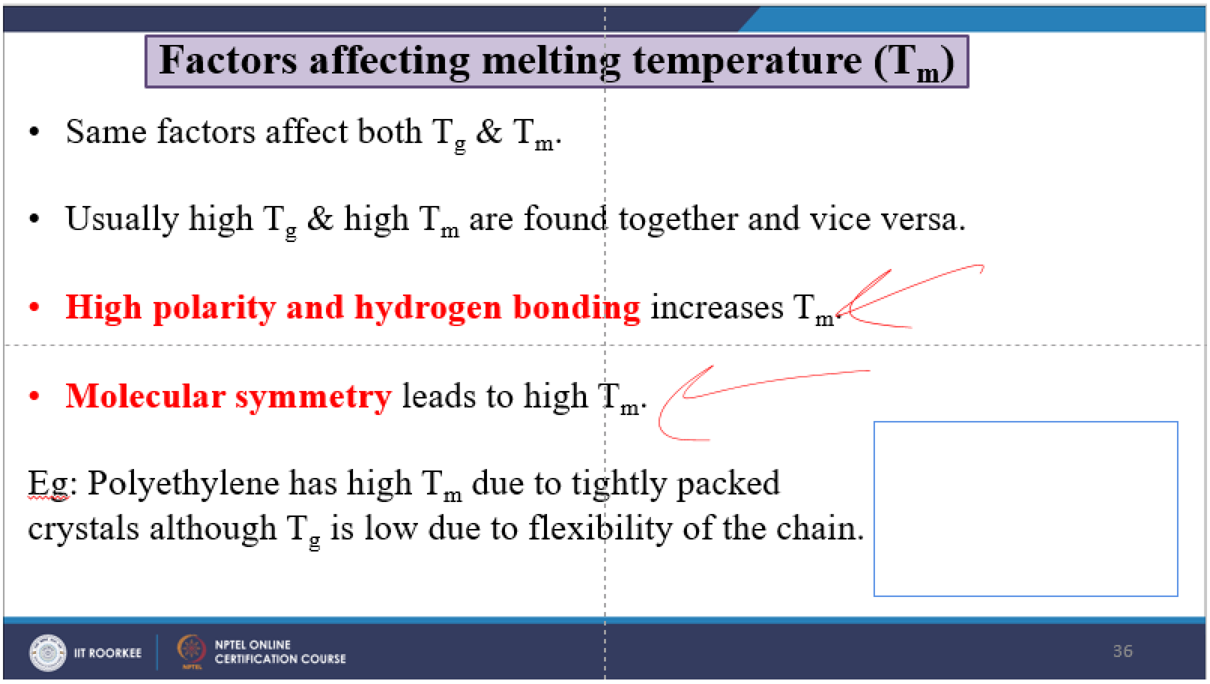
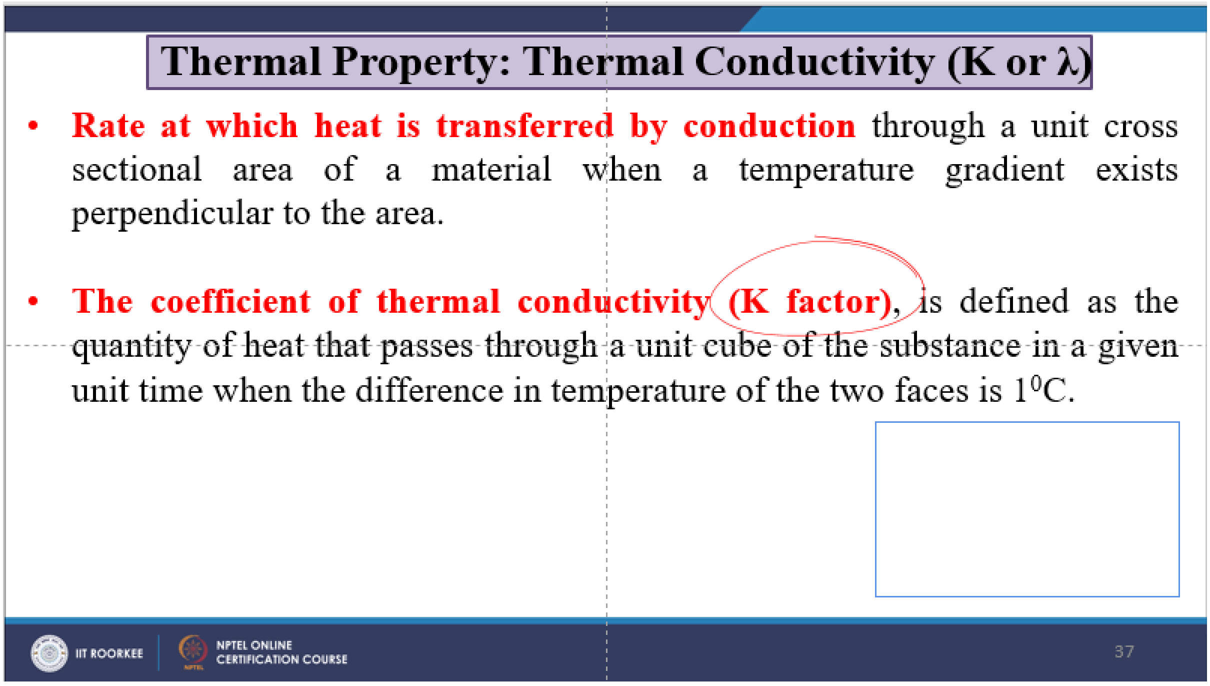
The crystalline polymer is a discontinuous change in the specific volume at T_M. This is as per this figure. Now, for amorphous polymer the change is continuous, no melting temperature is observed but there is an increase in the slope at glass transition temperature. For semi-crystalline polymer, intermediate to crystalline or amorphous and this shows the melting temperature and a glass transition temperature. So, there is a relationship between the glass transition temperature and a melting temperature.



Factors affecting melting temperature (T_m)

- Same factors affect both T_g & T_m.
- Usually high T_g & high T_m are found together and vice versa.
- **High polarity and hydrogen bonding** increases T_m.
- **Molecular symmetry** leads to high T_m.

Eg: Polyethylene has high T_m due to tightly packed crystals although T_g is low due to flexibility of the chain.

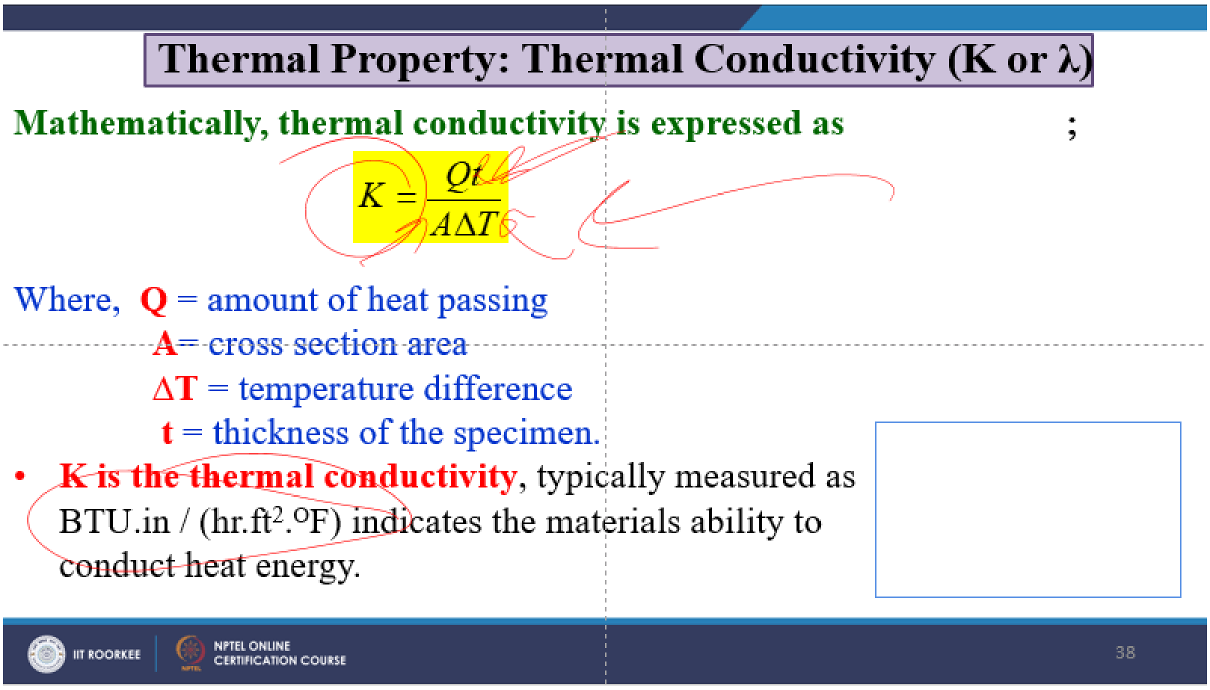


Thermal Property: Thermal Conductivity (K or λ)

- **Rate at which heat is transferred by conduction** through a unit cross sectional area of a material when a temperature gradient exists perpendicular to the area.
- **The coefficient of thermal conductivity (K factor),** is defined as the quantity of heat that passes through a unit cube of the substance in a given unit time when the difference in temperature of the two faces is 1^0C.

This is for the symmetrical polymer TG is equal to T M over 2 and for the non-symmetrical polymers TG is equal to 2 T M over 3. Now, there are various factors affecting the melting temperature. Usually the same factor, they affect the glass transition temperature and a melting temperature. Usually high glass transition temperature, the high melting temperature are found together and vice versa. High polarity and hydrogen bonding, this increases the melting temperature.

Molecular symmetry also led to the high melting temperature. Let us talk about the thermal conductivity K or lambda. The rate at which the heat is transferred by conduction through a unit cross sectional area of a material when a temperature gradient exists perpendicular to the area. The coefficient of thermal conductivity, this is the K factor usually is defined as the quantity of the heat that passes through a unit cube of substance in a given unit time when the difference in temperature of two factor is 1 degree Celsius. Now, this is the mathematical representation of the thermal conductivity K where Q is the amount of heat passing, A is the area of the cross section, delta T is the temperature difference and T is the thickness of the specimen and usually thermal conductivity represented as K.



Thermal Property: Thermal Conductivity (K or λ)

Mathematically, thermal conductivity is expressed as ;

$$K = \frac{Qt}{A\Delta T}$$

Where, **Q** = amount of heat passing

A= cross section area

ΔT = temperature difference

t = thickness of the specimen.

- **K is the thermal conductivity**, typically measured as BTU.in / (hr.ft^2.°F) indicates the materials ability to conduct heat energy.

$$K = \frac{Qt}{A\Delta T}$$

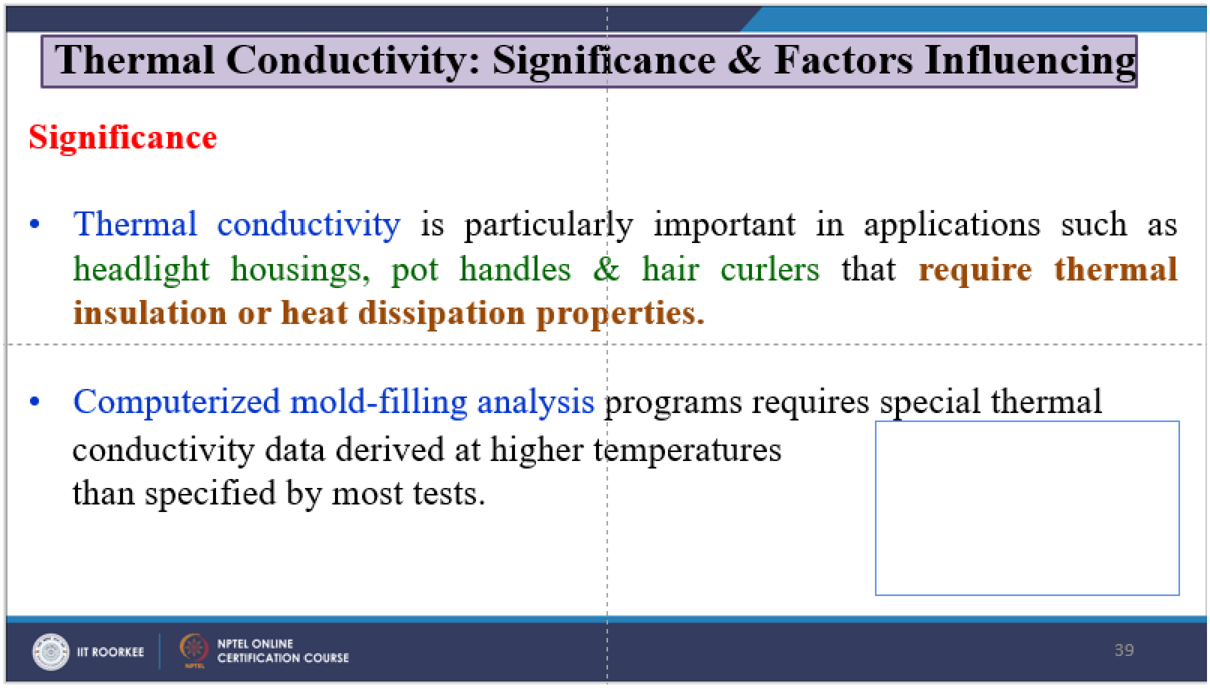
Where, Q = amount of heat passing

A= cross section area

ΔT = temperature difference

t = thickness of the specimen.

So, this is measured in BTU per hour square feet per degree Fahrenheit. This indicates the material's ability to conduct the heat energy.



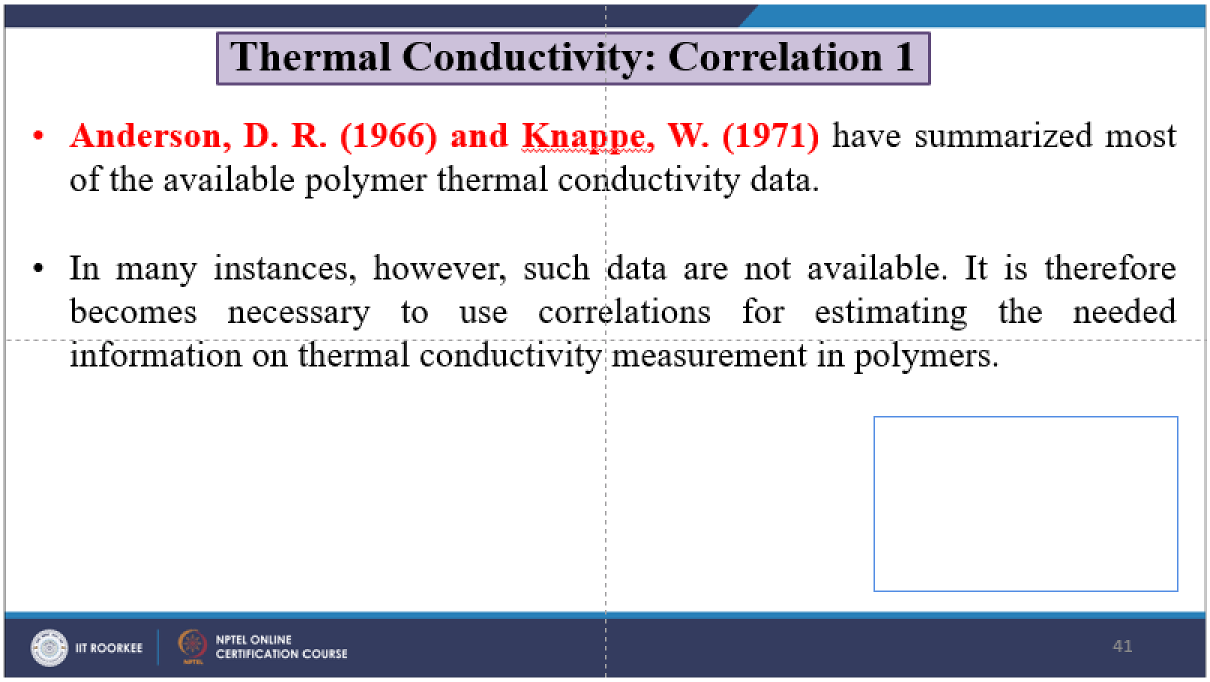
Thermal Conductivity: Significance & Factors Influencing

Significance

- Thermal conductivity is particularly important in applications such as headlight housings, pot handles & hair curlers that **require thermal insulation or heat dissipation properties.**
- Computerized mold-filling analysis programs requires special thermal conductivity data derived at higher temperatures than specified by most tests.

The significance of thermal conductivity is the particularly important in the applications such as headlights, housing, pot handles, hair curlers that require a thermal insulation and heat dissipation properties. Now, for computerized mold filling analysis, the program requires special thermal conductivity data derived at high temperature than a specified mould text. There are various factors affecting in the thermal conductivity, and one is the crystallites they have the higher thermal conductivity.

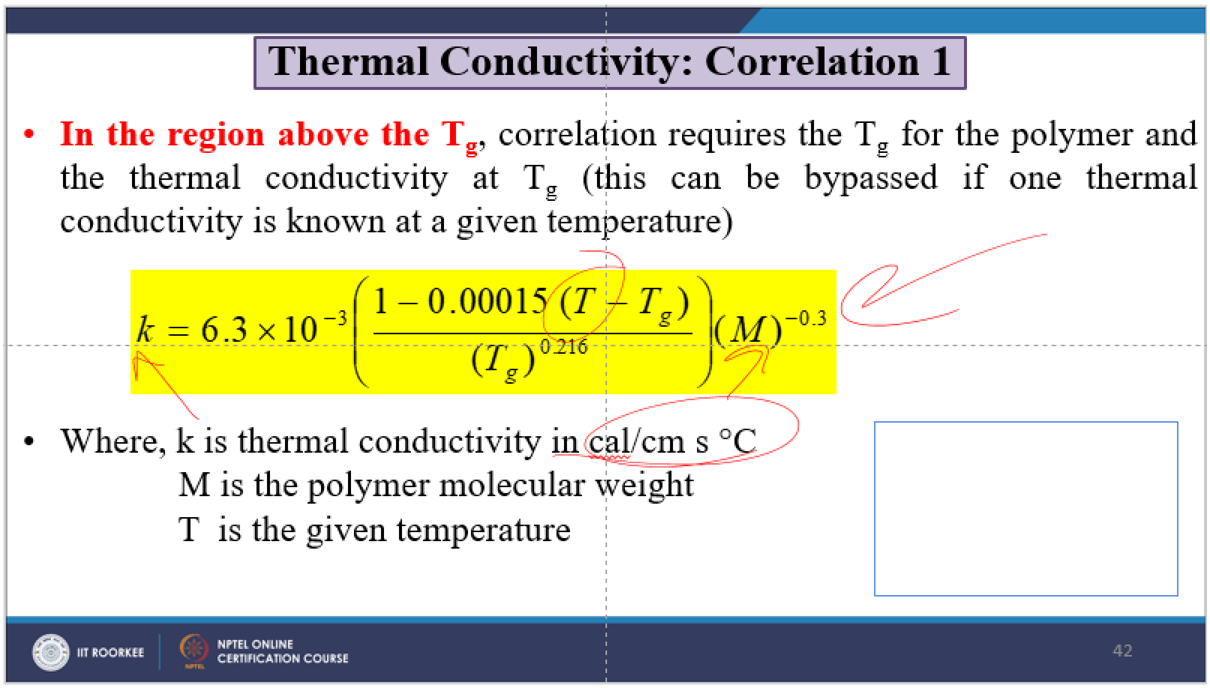
Now, as the density of the cellular plastic decreases the conductivity also decreases up to the maximum value and rise rises again due to the increased convection effect caused by the higher proportion of open cells.



Thermal Conductivity: Correlation 1

- **Anderson, D. R. (1966) and Knappe, W. (1971)** have summarized most of the available polymer thermal conductivity data.
- In many instances, however, such data are not available. It is therefore becomes necessary to use correlations for estimating the needed information on thermal conductivity measurement in polymers.

Now, let us talk about the correlations Anderson and Knapp they have summarized the most of the available polymer thermal conductivity data. In many instances, such data are not available it is therefore, become necessary to use certain correlations for estimating the needed information on thermal conductivity measurement in polymer. So, in the region above the glass transition temperature correlation required for required Tg for the polymer and thermal conductivity at Tg this can be bypassed if one thermal conductivity is known at a given temperature. So, this is the mathematical representation through which you can develop the correlation that is k is equal to 6.



Thermal Conductivity: Correlation 1

- **In the region above the T_g**, correlation requires the T_g for the polymer and the thermal conductivity at T_g (this can be bypassed if one thermal conductivity is known at a given temperature)

$$k = 6.3 \times 10^{-3} \left(\frac{1 - 0.00015\,(T - T_g)}{(T_g)^{0.216}} \right) (M)^{-0.3}$$

- Where, k is thermal conductivity in cal/cm s °C
  M is the polymer molecular weight
  T is the given temperature

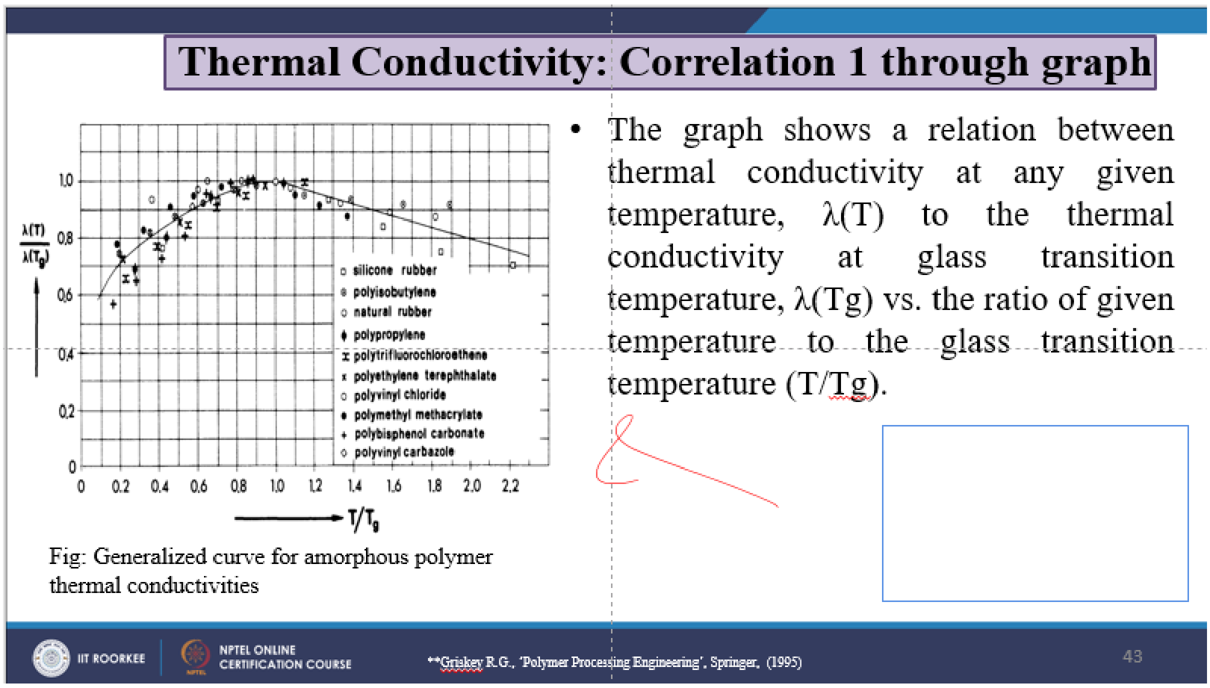
$$k = 6.3 \times 10^{-3} \left(\frac{1 - 0.00015(T - T_g)}{(T_g)^{0.216}} \right) (M)^{-0.3}$$

Where, k is thermal conductivity in cal/cm s °C

M is the polymer molecular weight

T is the given temperature

3 into 10 to the power minus 3 into 1 minus 0.00015 into T minus Tg over Tg to the power 0.216 into m to the power minus 0.3 where k is the thermal conductivity which is represented in calories per centimetre second degree Celsius, m is the polymer molecular weight and T is the given temperature. Now, this graph shows a relation between the thermal conductivity at any given temperature to the thermal conductivity at glass transition temperature versus the ratio of given temperature to the glass transition temperature. Now, in starting there is an increase in the temperature thermal conductivity ratio increases and after attaining the optimum level there is a decrease in thermal conductivity ratio with increase in temperature.



Thermal Conductivity: Correlation 1 through graph

- The graph shows a relation between thermal conductivity at any given temperature, λ(T) to the thermal conductivity at glass transition temperature, λ(Tg) vs. the ratio of given temperature to the glass transition temperature (T/Tg).

Fig: Generalized curve for amorphous polymer thermal conductivities

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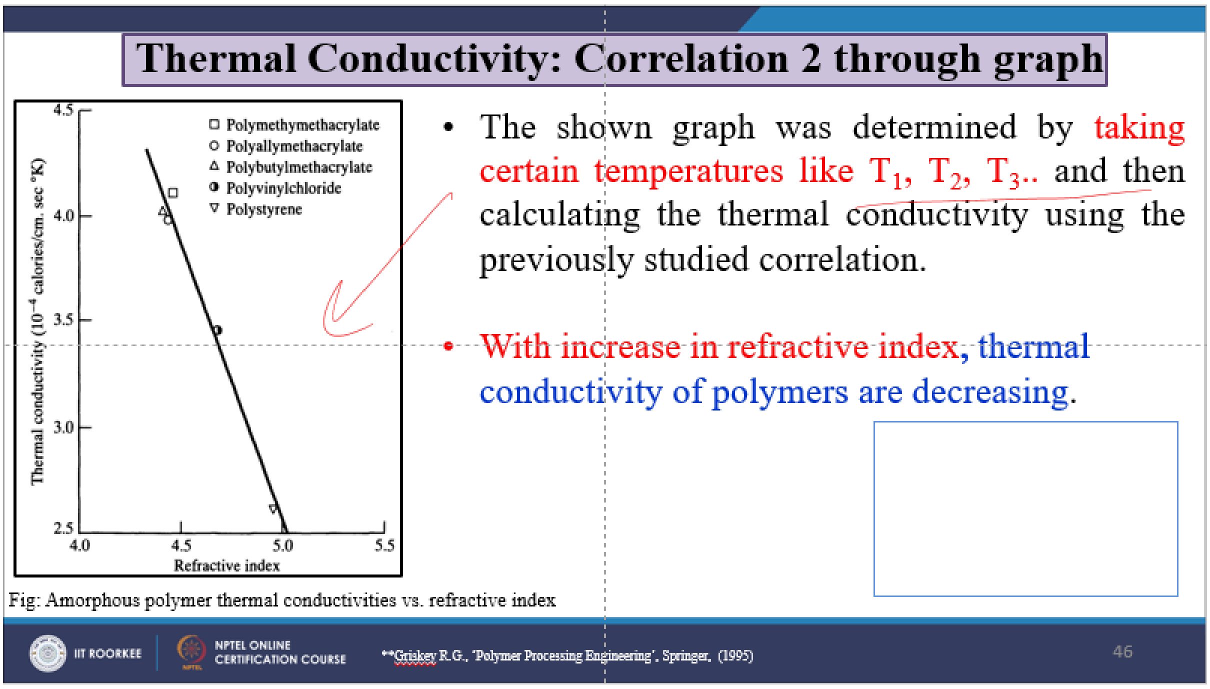
**Griskey R.G., 'Polymer Processing Engineering', Springer, (1995)



Thermal Conductivity: Correlation 2 through graph

- The shown graph was determined by taking certain temperatures like T_1, T_2, T_3.. and then calculating the thermal conductivity using the previously studied correlation.
- With increase in refractive index, thermal conductivity of polymers are decreasing.

Fig: Amorphous polymer thermal conductivities vs. refractive index

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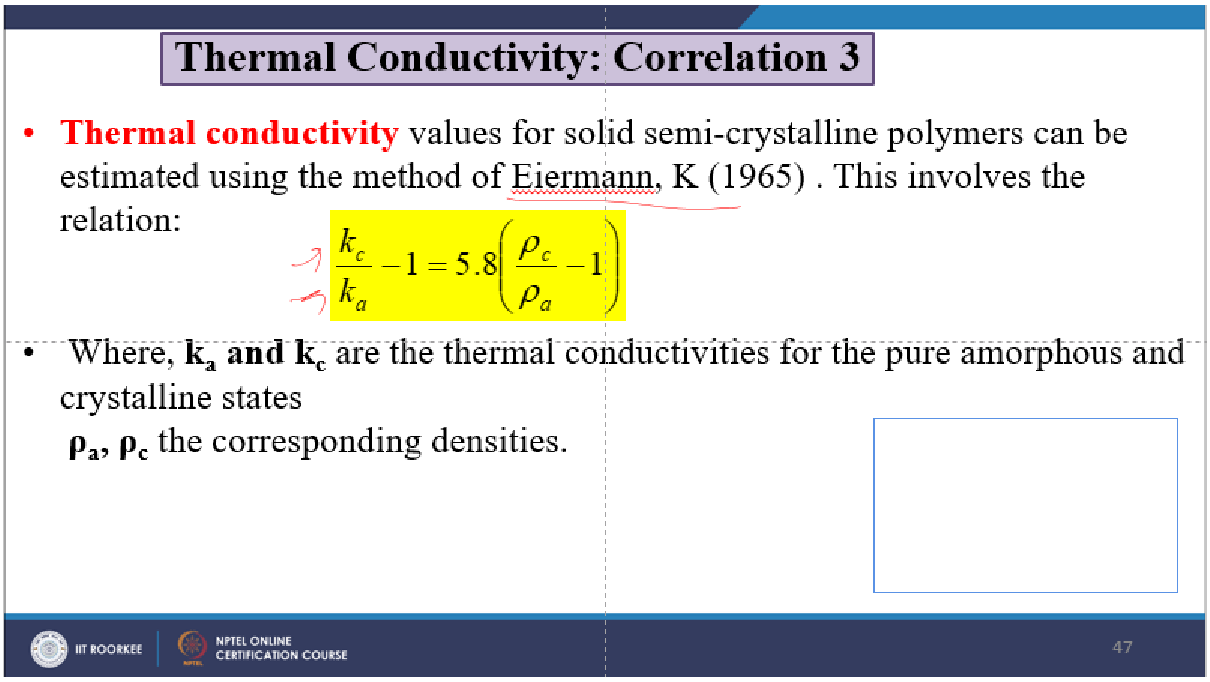
**Griskey R.G., 'Polymer Processing Engineering', Springer, (1995)

Let us talk about another correlation which is through the graph for amorphous solid polymers below glass transition temperature it is found that k correlates well with the refractive index and such correlation this can be used to get the value of k at given temperature. Now, this particular graph was determined by taking certain temperature like T1, T2, T3 and so on and then calculating the thermal conductivity using the previously studied correlation. So, the with increase in the refractive index thermal conductivity of the polymers are decreasing. Another correlation with respect for the thermal conductivity this value of the solid semi crystalline polymers can be estimated by the method of Ironman. This involves the relations kc over ka minus 1 is equal to 5.



Thermal Conductivity: Correlation 3

- **Thermal conductivity** values for solid semi-crystalline polymers can be estimated using the method of Eiermann, K (1965) . This involves the relation:

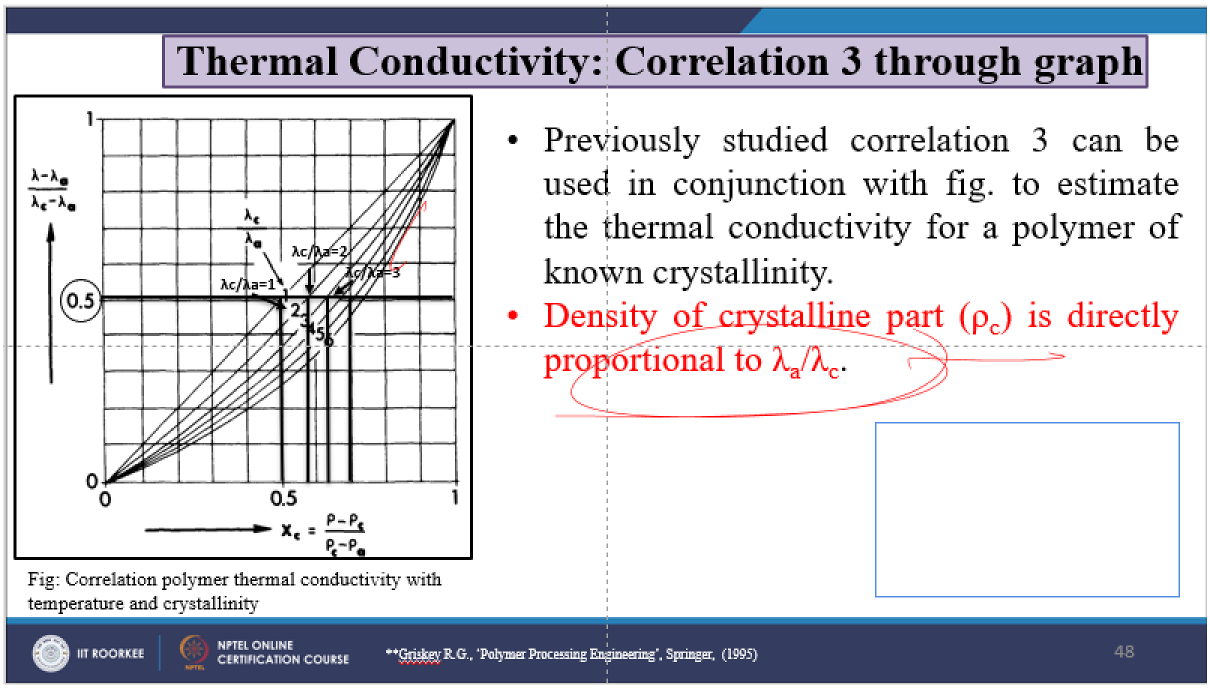
$$\frac{k_c}{k_a} - 1 = 5.8\left(\frac{\rho_c}{\rho_a} - 1\right)$$

- Where, **k_a and k_c** are the thermal conductivities for the pure amorphous and crystalline states

  ρ_a, ρ_c the corresponding densities.

$$\frac{k_c}{k_a} - 1 = 5.8\left(\frac{\rho_c}{\rho_a} - 1\right)$$

8 into rho c, over rho a minus 1 where this ka and kc they are the thermal conductivities of the pure amorphous and crystalline state. So, that can be used as a reference material, and rho a and rho c is the corresponding densities. So, the previously studied correlation can be used in conjunction with this particular figure to estimate the thermal conductivity for a polymer of known crystallinity. Density of crystalline in the part rho c is directly proportional to rho lambda an over lambda c. So, therefore, the density of the crystalline material increases the thermal conductivity of amorphous part lambda a this also increases. In contrast, the thermal conductivity of the crystalline part is decreased with lambda c.



Thermal Conductivity: Correlation 3 through graph

- Previously studied correlation 3 can be used in conjunction with fig. to estimate the thermal conductivity for a polymer of known crystallinity.
- Density of crystalline part (ρ_c) is directly proportional to λ_a/λ_c.

Fig: Correlation polymer thermal conductivity with temperature and crystallinity

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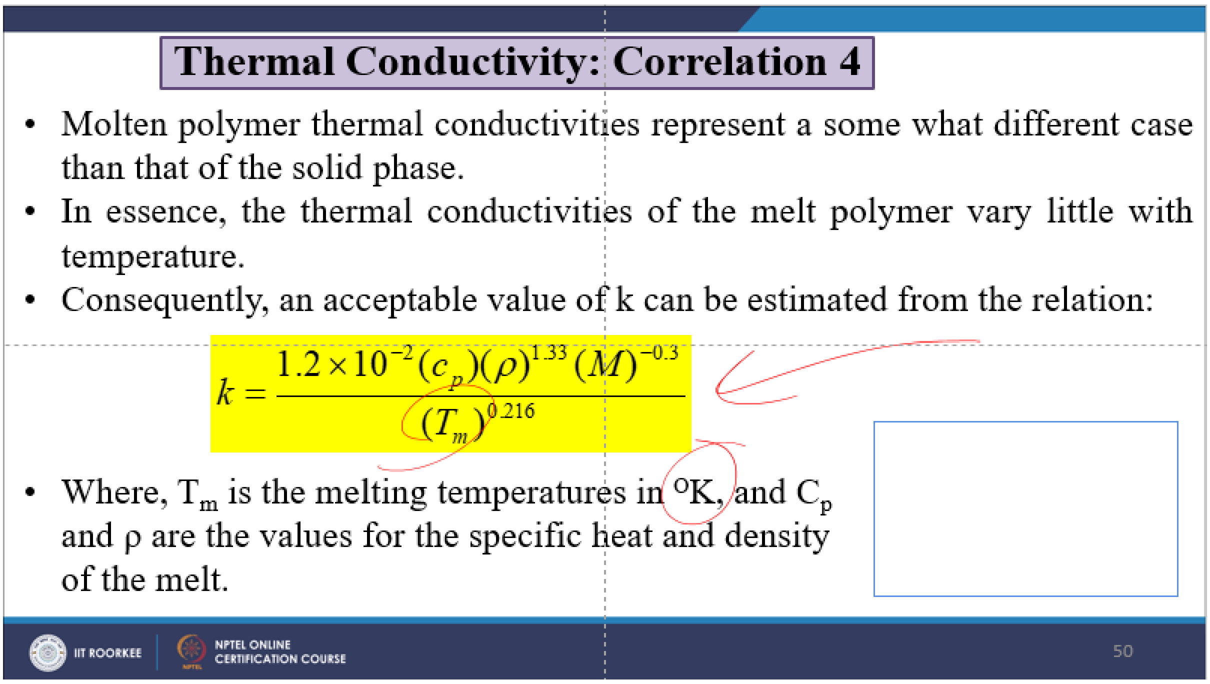
**Griskey R.G., 'Polymer Processing Engineering', Springer, (1995)

Another correlation and that is the molten polymer thermal conductivities this represent to somewhat different case than that of solid phase. So, the essence of thermal conductivities of the melt polymer vary little with the temperature and consequently the acceptable value of k this can be estimated from the relation that is k is equal to 1.2 into 10 to the power minus 2 C p into rho to the power 1.33 into m to the power point minus 0.

an acceptable value of k can be estimated from the relation:

$$k = \frac{1.2 \times 10^{-2} (c_p)(\rho)^{1.33} (M)^{-0.3}}{(T_m)^{0.216}}$$



Thermal Conductivity: Correlation 4

- Molten polymer thermal conductivities represent a some what different case than that of the solid phase.
- In essence, the thermal conductivities of the melt polymer vary little with temperature.
- Consequently, an acceptable value of k can be estimated from the relation:

$$k = \frac{1.2 \times 10^{-2} (c_p)(\rho)^{1.33} (M)^{-0.3}}{(T_m)^{0.216}}$$

- Where, T_m is the melting temperatures in ^{O}K, and C_p and ρ are the values for the specific heat and density of the melt.

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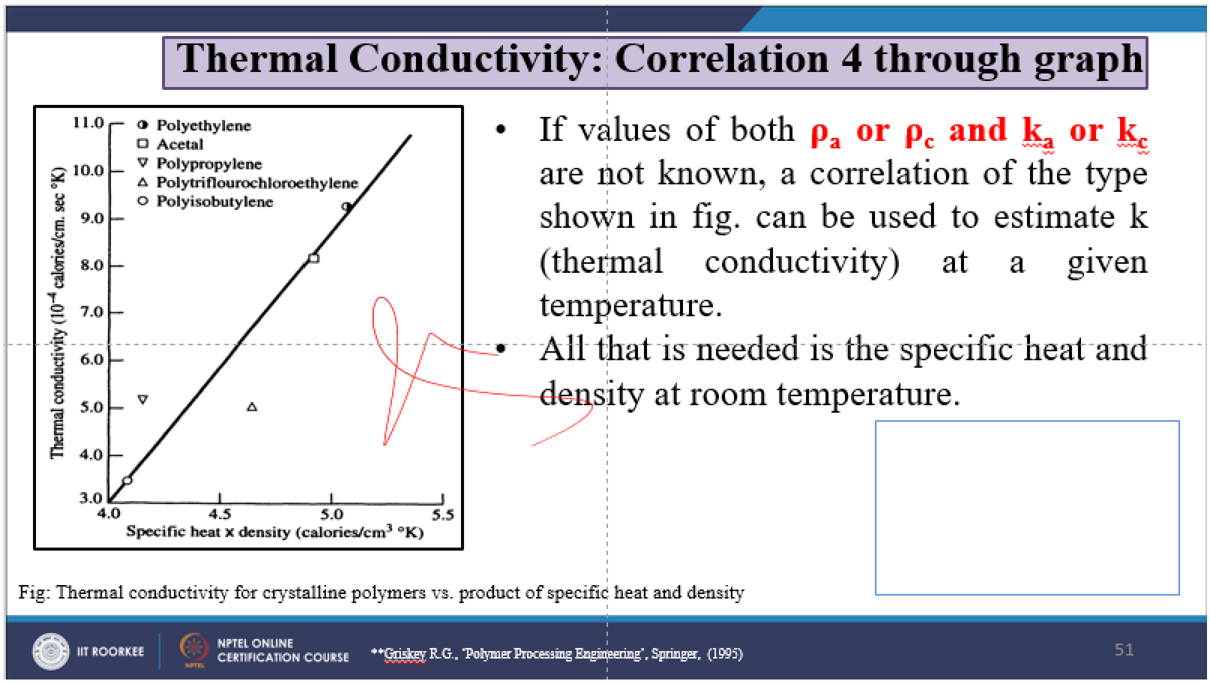


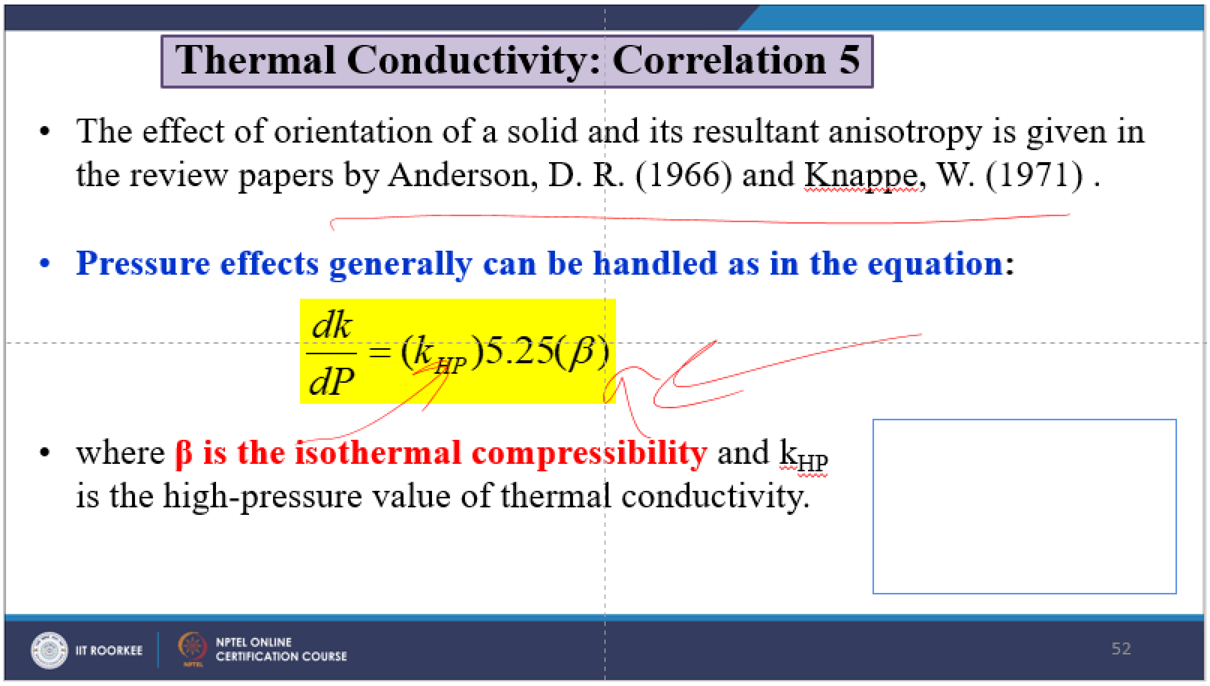
Thermal Conductivity: Correlation 4 through graph

- If values of both **ρ_a or ρ_c and k_a or k_c** are not known, a correlation of the type shown in fig. can be used to estimate k (thermal conductivity) at a given temperature.
- All that is needed is the specific heat and density at room temperature.

Fig: Thermal conductivity for crystalline polymers vs. product of specific heat and density

**Griskey R.G., 'Polymer Processing Engineering', Springer, (1995)

3 over t m to the power 0.216 this t m is the melting temperature and degree Kelvin C p and rho are the values of a specific heat and density of the melt. So, the values of both rho a and rho c are k a or k c are not known a correlation of the type shown in this particular figure can be used to estimate the k or thermal conductivity at a given temperature all that is needed that is specific heat and density at a room temperature. Correlation number 5 the effect of orientation of the solid and the resulting anisotropy is given in the review paper given by the Anderson and Knapp and this usually utilizes the pressure effect and the pressure effect generally can be handled as in this particular mathematical relations d k over d p is equal to k H p 5.25 beta where beta is the isothermal compressibility and k H p is the high-pressure value of thermal conductivity. Now, let us take some of the examples of thermal conductivity.



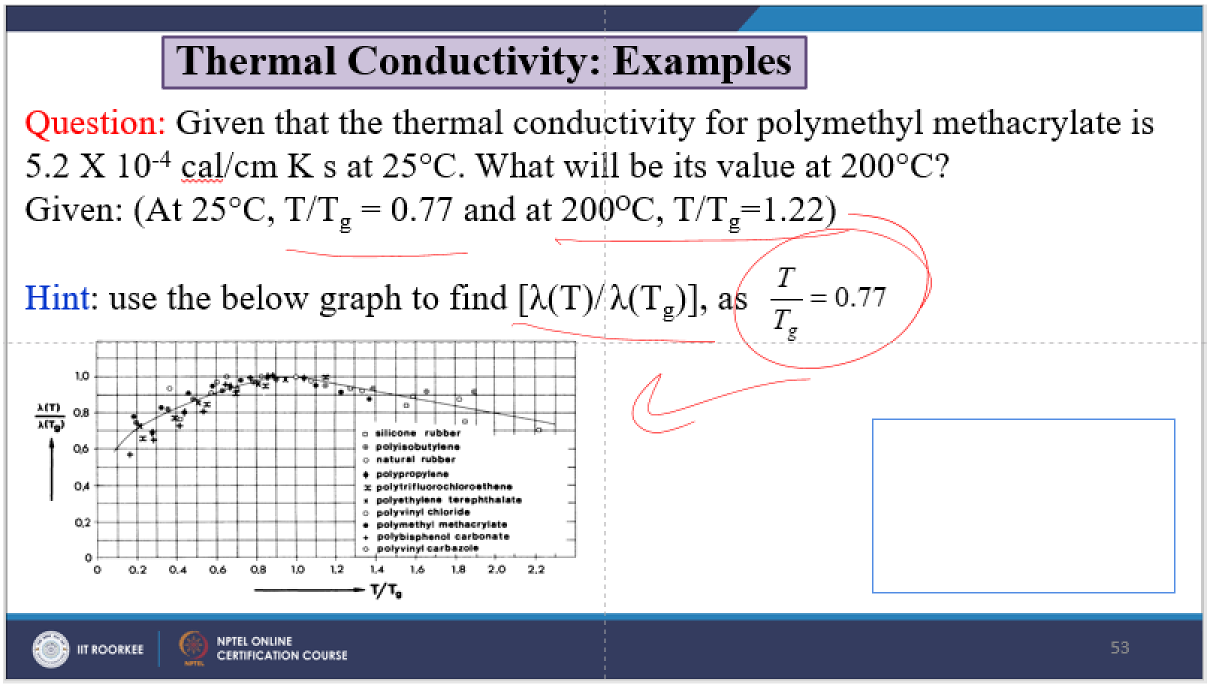
Thermal Conductivity: Correlation 5

- The effect of orientation of a solid and its resultant anisotropy is given in the review papers by Anderson, D. R. (1966) and Knappe, W. (1971) .
- **Pressure effects generally can be handled as in the equation:**

$$\frac{dk}{dP} = (k_{HP})5.25(\beta)$$

- where **β is the isothermal compressibility** and k_{HP} is the high-pressure value of thermal conductivity.

Now, here is one question that is given that the thermal conductivity for poly methyl methacrylate is 5.2 into 10 to the power minus 4 calories per centimeter Kelvin at 25 degree Celsius. So, what will be its value at 200 degree Celsius? So, obviously requires certain statistical data and that is at 25 degrees Celsius t over t g is equal to 0.



Thermal Conductivity: Examples

Question: Given that the thermal conductivity for polymethyl methacrylate is 5.2 X 10^{-4} cal/cm K s at 25°C. What will be its value at 200°C?

Given: (At 25°C, $T/T_g = 0.77$ and at 200°C, $T/T_g=1.22$)

Hint: use the below graph to find $[\lambda(T)/\lambda(T_g)]$, as $\frac{T}{T_g} = 0.77$

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77 and at 200-degree Celsius t over t g is equal to 1.22. Now, you can utilize this particular graph to find lambda t over lambda t g now as t over t g is 0.77. So, the to obtain the value of delta t over delta t g we should first go through the x axis using a scale bar determining the value of 0.77 for your convenience it is already marked in this particular figure. Then we will trace the vertical line from this value to the point where the dark circle of the point of the poly methyl methacrylate is indicated and then we will trace the horizontally to obtain the desired value which is determined as 0.

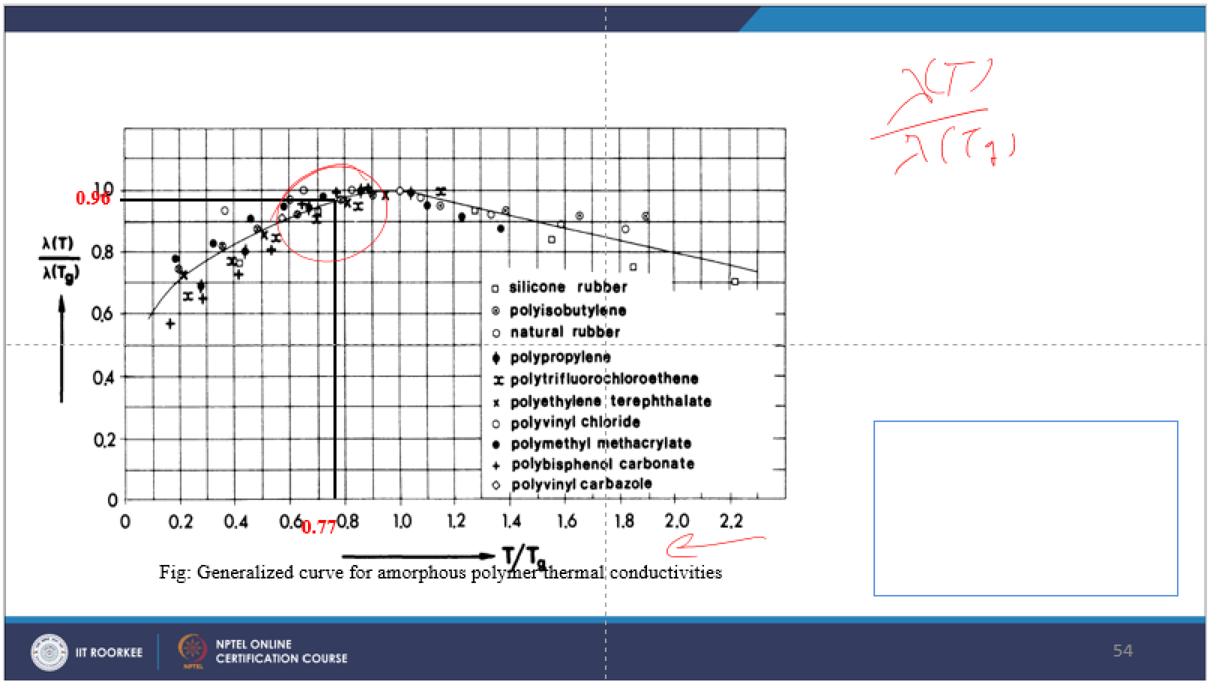

Fig: Generalized curve for amorphous polymer thermal conductivities

$\frac{\lambda(T)}{\lambda(T_g)}$

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Hence the value of $\lambda(T_g)$

$$\frac{k(298k)}{k(T_g)} = 0.96 = \frac{5.2 \times 10^{-4}\ \frac{Cal}{Cm\ K.S}}{k(T_g)}$$

$$\rightarrow k(T_g) = 5.4 \times 10^{-4}\ \frac{Cal}{Cm\ K.S}$$

96. So, hence the value of lambda t g this can be determined as ‘k’ this is equal to 0.96 5.2 into 10 to the power minus 4 calories plus centimetre Kelvin over k which is comes out to be k t 5.4 into 10 to the power minus 4 calories centimetre this one. Now, as we have obtained the value of thermal conductivity at the glass transition temperature we can use this value to obtain the thermal conductivity of a material at any temperature if the ratio between the temperature and the glass transition temperature is provided.

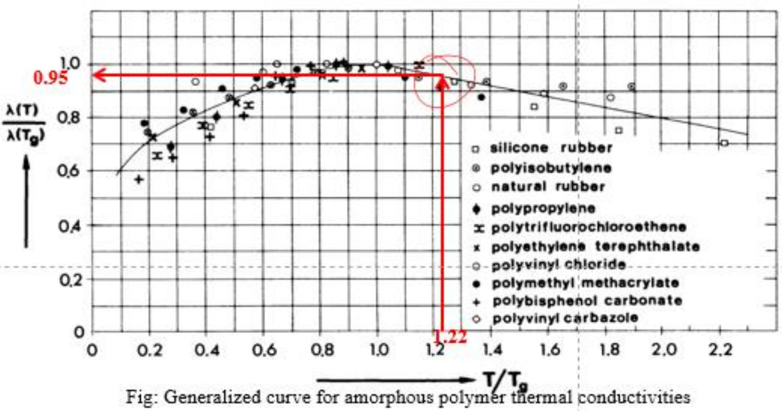


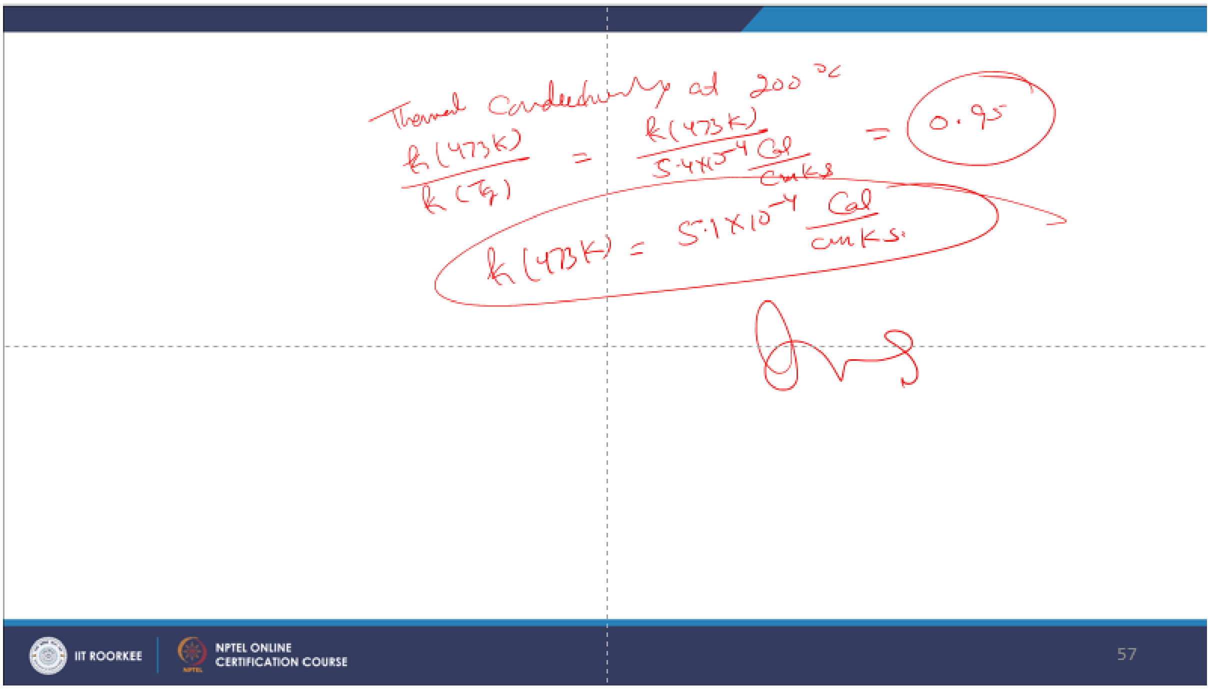
Fig: Generalized curve for amorphous polymer thermal conductivities

$200°C \quad \frac{T}{T_g} = 1.22$

$\frac{\lambda(T)}{\lambda(T_g)}$ @ 200°

$200 + 273 = 473K$

So, if you look like the into the question data you will find that at 200-degree Celsius t over t g is given as 1.22. So, therefore, we will again use the same graphical tracing strategy to obtain the value of lambda t over lambda t g at 200 degree Celsius that is 200 plus 273 473 Kelvin. So, here you see that this value is given over here and by this way you will find that this one is 0.



Thermal Conductivity at 200 °C

$$\frac{k(473K)}{k(T_g)} = \frac{k(473K)}{5.4\times10^{-4}\ \frac{Cal}{cm\,K\,s}} = \boxed{0.95}$$

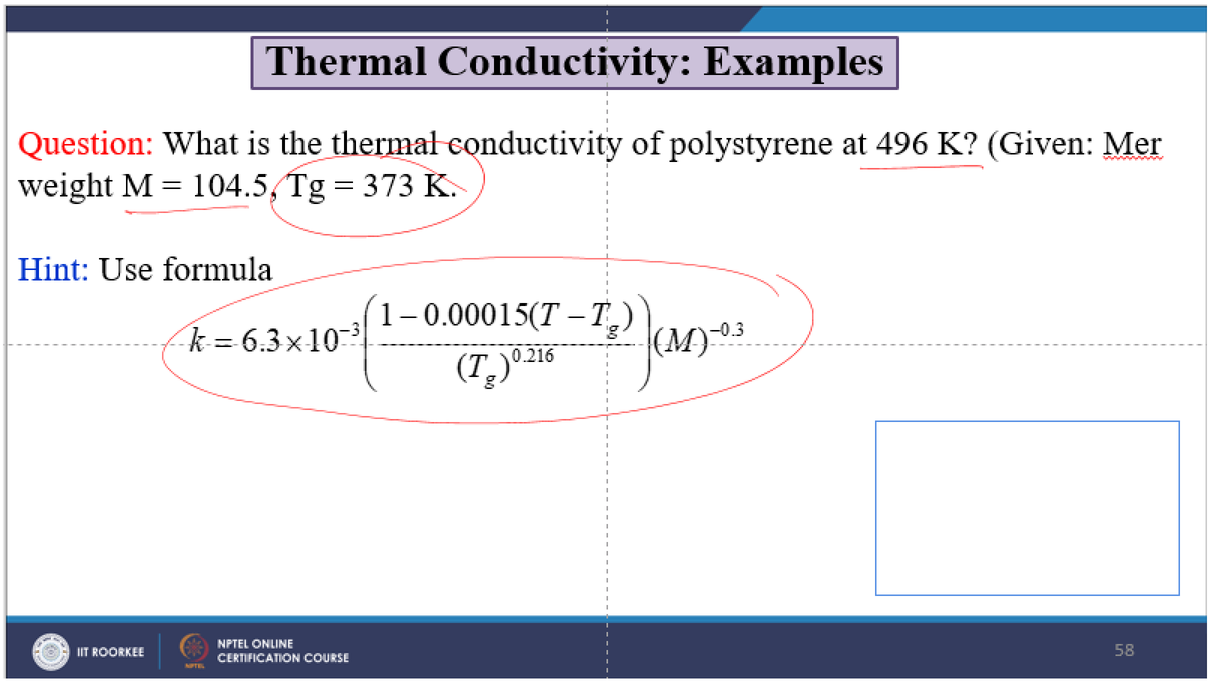
$$\boxed{k(473K) = 5.1\times10^{-4}\ \frac{Cal}{cm\,K\,s}}$$

Thermal conductivity at 200°C

$$\frac{k(473K)}{k(T_g)} = \frac{k(473K)}{5.4\times10^{-4}\,\frac{cal}{cm.K.s}} = 0.95$$

$$k(473K) = 5.1\times10^{-4}\,\frac{cal}{cm.K.s}$$

95. Now, thermal conductivity at 200 degree Celsius is given as k 473 this is k 473 Kelvin 5.4 into 10 to the power minus 4 which is comes out to be which is equal to 95 as we calculated in the graph. So, k equal to 5.1 into 10 to the power minus 4 this is the answer. Now, let us take another question what is the thermal conductivity of a polystyrene at 496.

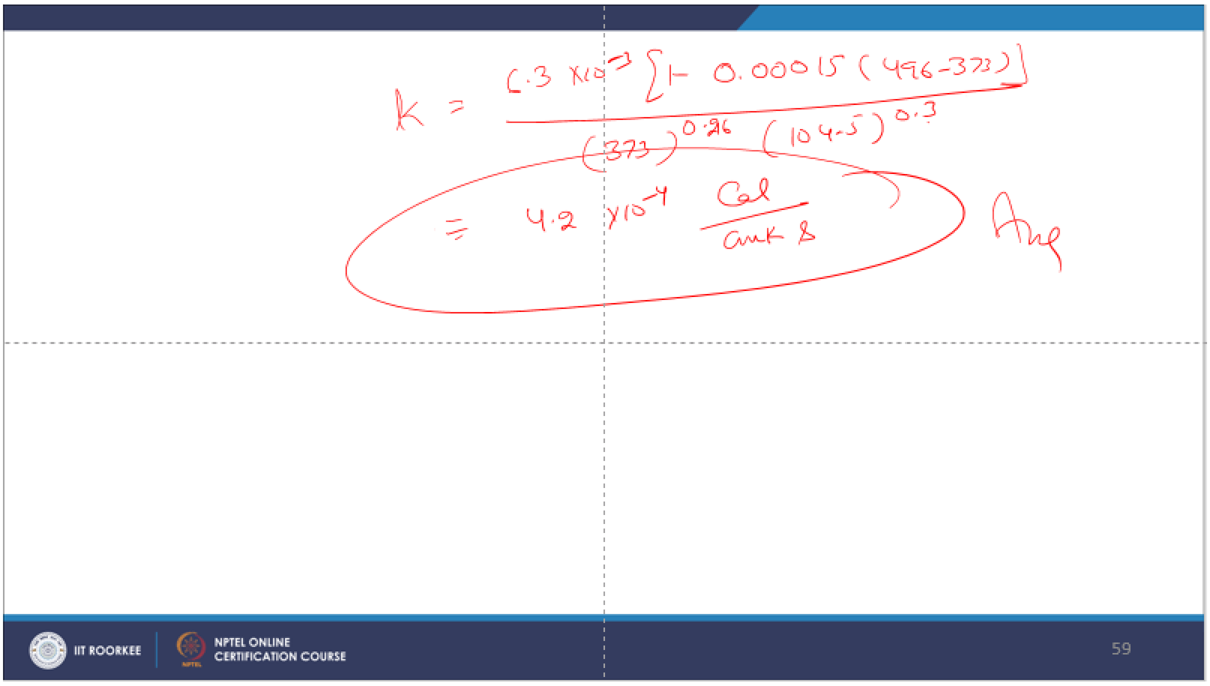


Thermal Conductivity: Examples

Question: What is the thermal conductivity of polystyrene at 496 K? (Given: Mer weight M = 104.5, Tg = 373 K.

Hint: Use formula

$$k = 6.3 \times 10^{-3}\left(\frac{1-0.00015(T-T_g)}{(T_g)^{0.216}}\right)(M)^{-0.3}$$



$$k = \frac{6.3 \times 10^{-3}\{1-0.00015(496-373)\}}{(373)^{0.216}(104.5)^{0.3}}$$

$$= 4.2 \times 10^{-4}\ \frac{Cal}{cm\,K\,s}$$ Ans

$$k = 6.3 \times 10^{-3}\left(\frac{1-0.00015(T-T_g)}{(T_g)^{0.216}}\right)(M)^{-0.3}$$

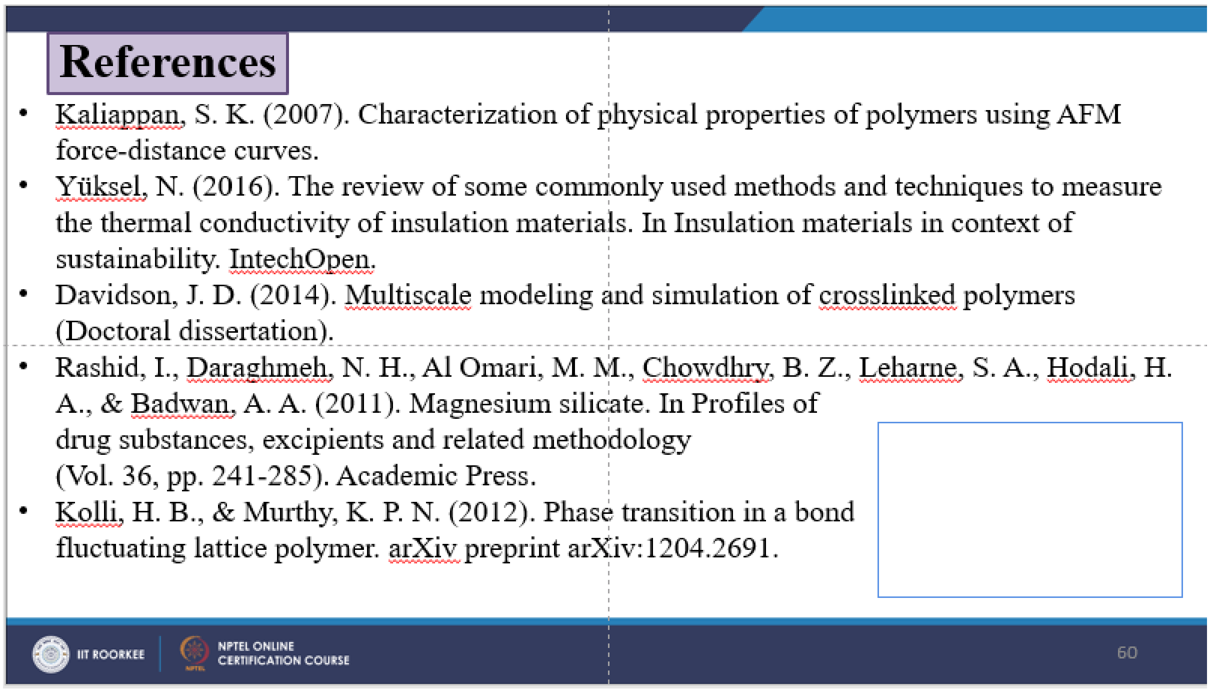
Solution:

$$k = \frac{6.3 \times 10^{-3}[1-0.00015(496-373)]}{(373)^{0.216}(104.5)^{0.3}} = 4.2 \times 10^{-4}\frac{cal}{cm.K.s}$$

Now, it is given that the molecular weight is m is equal to 104.5 and glass transition temperature is 373 Kelvin. Now, here you can use the formula which is which we have already discussed that is k is equal to 6.3 into 10 to the power minus 3 into 1.0015 into t minus t g over t g to the power 0.

216 m to the power minus 0.3. So, just only you need to put the values and this is 6.3 into 10 to the power minus 3 into 1 minus 0.00015 into 496 minus 373 over 373 into 0.

216 into 104.5 to the power 3 which is comes out to be 4.2 into 10 to the power minus 4 calorie per centimetre Kelvin second and this is our answer.



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So, dear friends in this particular segment we discussed the various aspects of thermal conductivity with a couple of examples and for your convenience we have enlisted various references and these references are very useful for further studies. So, in case if you wish you can utilize these references for your further studies. Thank you very much.