Polymers: Concepts, Properties, Uses and Sustainability

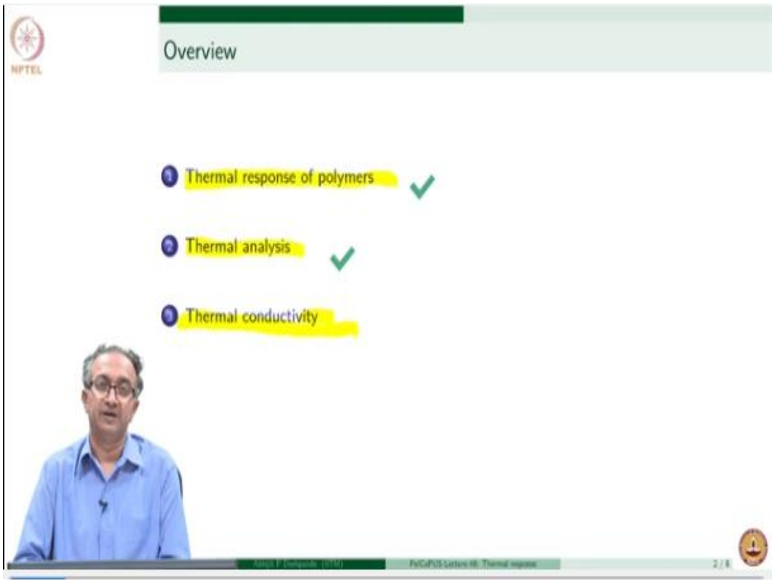
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture – 46
Thermal Response

Hello, welcome to viscoelasticity in polymers, this is the week in which we have been looking at the viscoelastic phenomena in much more detail and the synonymous nature of polymeric materials and viscoelasticity will be brought about in this set of lectures during this week and next week. As I mentioned during introduction to viscoelasticity in the lecture, 45th lecture on introducing the concept of viscoelasticity, the time, rate, frequency, temperature, all of these are intermingled when we try to analyse at viscoelastic response.

So, in this particular lecture we will focus on thermal response to look at the temperature effect in isolation and once having done this, then we will continue our journey towards understanding viscoelasticity little better by quantifying the extent of viscoelastic response by defining response functions, response variables which are useful just like modulus or viscosity is useful for solids or liquids.

(Refer Slide Time: 01:26)

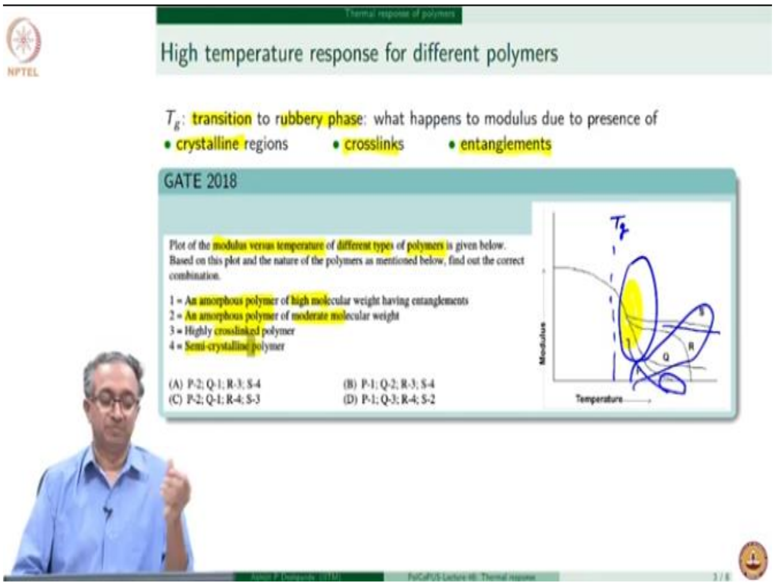


Overview

1. Thermal response of polymers ✓
2. Thermal analysis ✓
3. Thermal conductivity

So, our focus will remain on looking at concepts related to the thermal response of polymers and so we will do this by first quickly looking at what are the different phenomena transitions that happen when we subject polymeric material to different temperatures and how we can use analytical techniques which are called thermal analysis techniques that can be used for characterization of the thermal response of polymers. And finally, we will also look at the conductivity in the polymeric materials, we know polymeric materials are insulating from an electrical point of view but they are also very good thermal insulators, so we look at what is the nature of thermal conductivity for these polymeric system as it is an important thermal characteristic, which is important during application as well as it is important during moulding operations.

(Refer Slide Time: 02:22)



Thermal response of polymers

High temperature response for different polymers

T_g: transition to rubbery phase: what happens to modulus due to presence of

- crystalline regions
- crosslinks
- entanglements

GATE 2018

Plot of the modulus versus temperature of different types of polymers is given below. Based on this plot and the nature of the polymers as mentioned below, find out the correct combination.

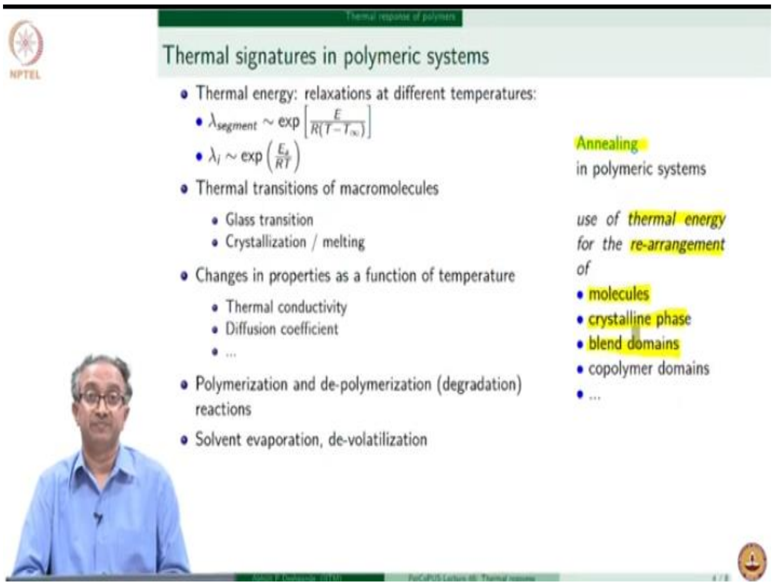
1 = An amorphous polymer of high molecular weight having entanglements
2 = An amorphous polymer of moderate molecular weight
3 = Highly crosslinked polymer
4 = Semi-crystalline polymer

(A) P-2; Q-1; R-3; S-4
(B) P-1; Q-2; R-3; S-4
(C) P-2; Q-1; R-4; S-3
(D) P-1; Q-3; R-4; S-2

So, let us begin by looking at an exam question where we are looking at modulus versus temperature for different types of polymers and so the thermal response of polymers is very sensitive to what happens in terms of the microstructure of the material. So, for example if a transition to the rubbery phase is happening around the glass transition temperature, so I hope all of you can recognize that we have said that around glass transition there is an order of magnitudes decrease in modulus or orders of magnitude increase in diffusion coefficient of small molecules from polymer due to free volume.

So, therefore in this modulus versus temperature graph, glass transition can be located and so rubbery phase seems to have very different class of response which is captured here saying P, Q and R and S. So, the question is; can we know something about the microstructure of the polymer or the type of polymer it is by looking at whether it is decreasing at glass transition but remaining constant or it is suddenly decreasing and falling off to 0. So, do each of these changes with respect to temperature tell us about what type of a polymeric material it is and in fact the question clearly states also that two of them are amorphous polymers, however one of them has high molecular weight, the other one seems to have smaller molecular weight, one of them is a crosslink polymer. So, either a thermoset polymer with reasonably high degree of crosslinking. And then we have a semi crystalline polymer, so is it possible for you to think of what happens when we have thermal energy available to the macromolecule and if macromolecule is constrained by cross link what happens? If macromolecule is constrained by crystallinity, up to what temperature can this constraint remain or if it is only entanglement which is constraining will high molecular weight or high molar mass will have more entanglements compared to low molar mass. So, if you are able to analyse these, then you should be able to answer this question and in all of this the key response is what happens at high temperature, when sufficient thermal energy is available and is there anything constraining the thermal energy in the material from a microstructural point of view.

(Refer Slide Time: 04:59)



Thermal signatures in polymeric systems

- Thermal energy: relaxations at different temperatures:
  - $\lambda_{segment} \sim \exp\left[\frac{E}{R(T-T_\infty)}\right]$
  - $\lambda_i \sim \exp\left(\frac{E_a}{RT}\right)$
- Thermal transitions of macromolecules
  - Glass transition
  - Crystallization / melting
- Changes in properties as a function of temperature
  - Thermal conductivity
  - Diffusion coefficient
  - ...
- Polymerization and de-polymerization (degradation) reactions
- Solvent evaporation, de-volatilization

Annealing
in polymeric systems

use of thermal energy for the re-arrangement of

- molecules
- crystalline phase
- blend domains
- copolymer domains
- ...

So, therefore looking at thermal signatures which are there in the material as you go from low to high temperature, the thermal energy which is available basically makes it possible for relaxations to occur and the relaxation rate is higher and higher or relaxation time is lower and lower whenever we are at different temperatures and we have seen that there are 2 types of temperature dependencies around glass transition, we have the WLF. And in melt state or some of the secondary relaxations such as beta or gamma relaxations, we have the Arrhenius dependency, so clearly when thermal energy available to the material changes, the relaxation is possible or not possible. So, the side group for example, rotation which may not be possible at minus 100 degree Celsius but it may be possible at room temperature.

So, clearly the thermal energy available at room temperature is very significantly higher compared to the barrier energy which is there for a side group rotation, so like this thermal energy plays a crucial role in determining which relaxation processes are possible and which relaxation processes are not possible. If the rate of relaxation process is very, very fast, then or the relaxation time associated is very, very slow, then again we get predominantly viscous type of response. So, in case of water for example, water molecules going about the time scales are picoseconds and so therefore, whether it is a millisecond phenomena or a micro second phenomena or hours phenomena, water is a viscous fluid because the time scales over which the relaxation processes are happening in the material are so slow compared to our time scales of interest and so all the relaxation processes happen and therefore water is a perfectly viscous dissipative material.

So, thermal energy plays an important role in determining this and so the other set of transitions which are of interest where the material behaviour, macromolecular behaviour changes from one type to the other is related to glass transition or crystallization melting. In glass transition as we have seen material goes from a segmental mobility possible rubbery state to segmental mobility frozen glassy state or it may go from an ordered crystalline state to a liquid unordered state. Of course most of the properties also change as a function of temperature and that is something important to know in case of polymers for example, we will see that whether thermal conductivity increases or decreases for a polymeric material, depends on what type of polymeric material we are dealing with. So, therefore changes in properties as a function of temperature is an also indication of microstructure and how the material is behaving with respect to its structure and its property.

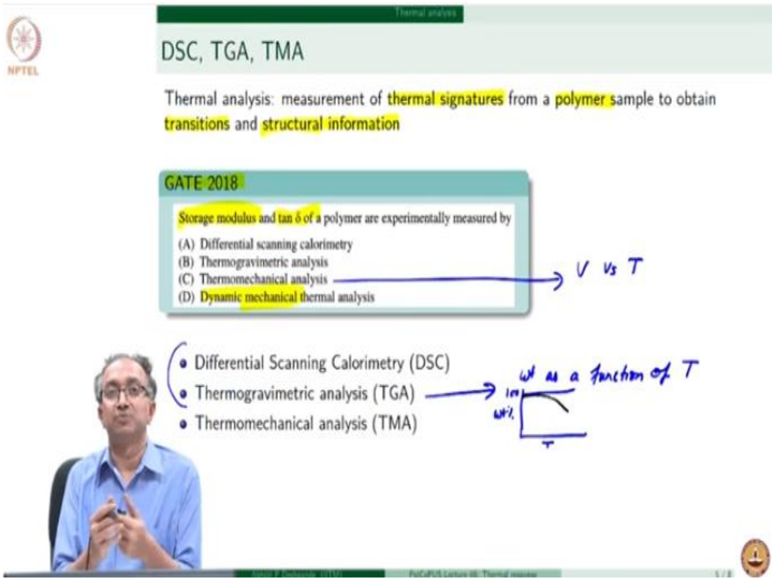
And of course both polymerization and depolymerization are processes which are exothermic and endothermic processes, in the sense that heat is taken or required for these processes to happen. So, can you think in terms of which one will be exothermic and which one will be endothermic, we have monomers joining together to form a polymer and that is polymerization. So, will it be exothermic or endothermic or conversely when we have a polymer which is breaking down into smaller fragments, depolymerisation, will this process be exothermic or endothermic, so think about it while we; we will get back to this later, little later in the lecture. Of course, we may have some solvents or volatiles in the polymeric sample; we have seen that there are many types of additives which are added. We saw in the 33rd lecture that you have many additives which are used plasticizers, UV stabilizers and many of them may volatilize as a function of temperature and time. So, therefore if we look at the thermal response of these materials, there may be devolatilization of small molecules, monomers which is remaining behind or if solvent is there that can evaporate.

So, therefore this is also will require enthalpy of evaporation or enthalpy of volatilization, so therefore again there is a heat requirement in these cases also. So, these are different types of thermal events that can happen in a polymeric material and lot of this analysis can be done using thermal analysis as we will see shortly. One of the important term which is used quite often in case of polymers is annealing.

And annealing is nothing but the use of thermal energy for the manipulation of microstructure of the polymeric material and this microstructure manipulation could involve rearrangement of molecules, rearrangement of crystalline phase, what do we mean by rearrangement of a crystalline phase? For example we could cool the polymer at a certain rate and therefore form certain lamella of a thickness. But when I anneal the polymeric sample the thickness can increase, so therefore annealing can be used as a way of improving properties of materials. If there are blend domains, the blend domain sizes can change due to annealing, so in each of these cases annealing implies that we make segmental motions or macromolecular relaxations possible, so that some of these rearrangements can take place.

So, quite often therefore annealing would involve taking the material close to or slightly higher than glass transition temperature because much below glass transition temperature, segmental motion as well as many other polymeric macromolecular relaxation mechanisms are frozen. So but once we take the polymer to glass transition or slightly beyond, then annealing can happen and because of segmental mobility many of these rearrangements can take place.

(Refer Slide Time: 11:28)



Thermal analysis

DSC, TGA, TMA

Thermal analysis: measurement of thermal signatures from a polymer sample to obtain transitions and structural information

GATE 2018

Storage modulus and tan δ of a polymer are experimentally measured by

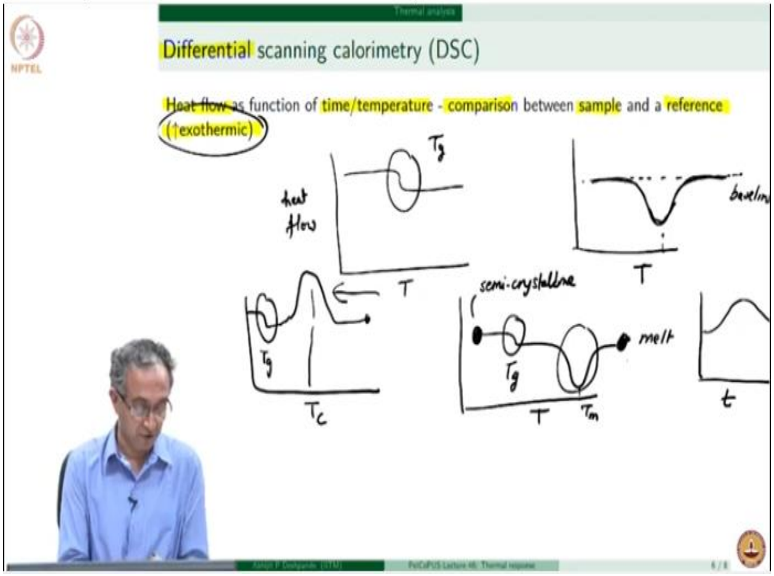
(A) Differential scanning calorimetry
(B) Thermogravimetric analysis
(C) Thermomechanical analysis
(D) Dynamic mechanical thermal analysis

- Differential Scanning Calorimetry (DSC)
- Thermogravimetric analysis (TGA)
- Thermomechanical analysis (TMA)

So, the thermal analytical techniques basically is to measure thermal signatures from a polymer sample and the idea is to look at transitions as we talked about or phenomena such as polymerization or solvent evaporation and so on and also by way of characterization, we get back what is the structure of the underlying polymeric system and so just to highlight there is the question related from exam, where storage modulus and tan delta are experimentally measured using all of these techniques. And the answer to this is; this is the one mechanical which can measure this modulus, while these 3 others predominantly measure the thermal signatures however, the thermomechanical analysis which is nothing but measuring volume as a function of time or it is also called dilatometry, so that can also measure some mechanical response. So, let us look at the differential scanning calorimetry and TGA in a little bit more detail.

TGA is basically where we look at weight as a function of time or temperature, so we can heat the polymer sample and at a given heating rate and then let us look at weight percent and initially of course, the polymer sample will have 100 weight percent and as the time goes by, as the temperature is increased on the sample, the degradation reaction sets in volatilization happens and therefore weight reduction happens. And so thermo gravimetric analysis therefore is a technique to look at stability of polymeric system, it is an aggregate technique because we are only looking at weight and weight change can be associated with various phenomena which are together. So, therefore quite a few times thermogravimetric analysis is coupled with some other spectroscopic technique, so that we can identify the molecules which are coming out, the degradation products which are coming out, so that can give us clues about what may be the chemical changes that are happening in the macromolecular system.

(Refer Slide Time: 13:47)



Thermal analysis

Differential scanning calorimetry (DSC)

~~Heat flow~~ as function of time/temperature - comparison between sample and a reference (↑exothermic)

So, let us look at DSC in much more detail because it has a very good correlation with the aspects related to the structure of the polymer. So, DSC is a technique in which we focus on the heat flow as a function of time or temperature and it is called differential because what we do is compare the heat flow requirement for the polymer sample and a reference sample and the reference sample we choose in such a way that transitions taking place there are completely known.

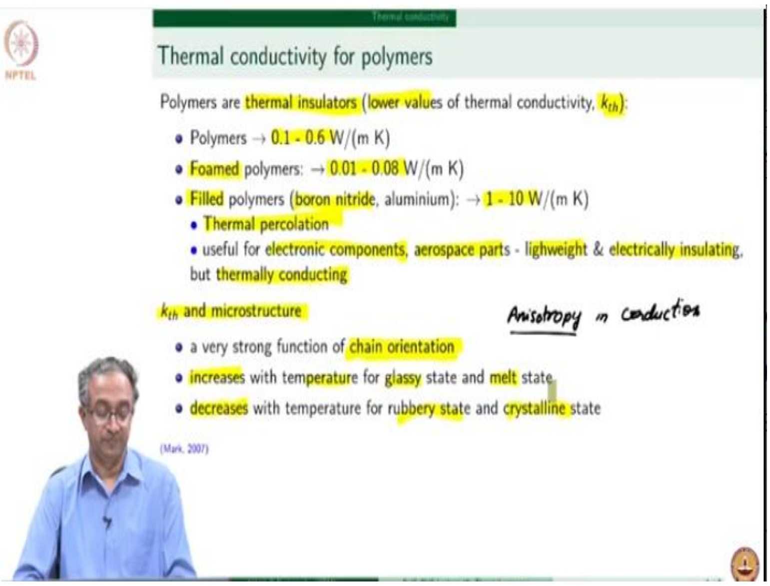
So, we know what is the amount of heat flow required for a given rate of change of temperature let us say, so if I heat the sample, reference sample at 5 degree Celsius a minute, I know what is the heat requirement there and then if the sample, polymeric sample is undergoing glass transition or it is undergoing crystallization or melting, then the heat requirements will be completely different. Because many of the processes will involve change in heat capacity as we see in case of glass transition or it may involve enthalpy changes which is either exothermic or endothermic process. So, therefore generally, DSC curves are also plotted by talking about which side implies exothermic. So, for example if I take a polymer sample and look at let us say, heat flow as a function of temperature and if this is the overall heat flow curve this implies that this is step change and this is associated with glass transition temperature.

On the other hand, if I take a sample and see a endothermic peak because remember exothermic is up and so therefore, with respect to and this heat flow is basically with respect to whatever happened in the reference, so since heat flow requirement is more in case of endothermic sample, we get a difference and so generally, this is also called the base line. So, I can draw what would be the reference response itself which is called a baseline. So, with respect to baseline, the heat flow requirement for the sample are different and this is an endothermic peak and so what are the endothermic processes that you know of and especially, in case of a macromolecular system what may be set of endothermic processes that you can think of. So, one possibility is of course melting because when we have to melt the crystal, we have to supply heat.

The other possibility could be also degradation, so just by looking at this, it is not easy to say what may be the sample undergoing, so therefore quite a few times we may have to do multiple techniques or we need to have some hypothesis regarding this material. So, for example if it is a polyethylene sample and this change is happening around 200 degree Celsius, then we know that it is could be a degradation or a depolymerization process. But let us say, if the same peak is around 110 degree Celsius, then we know that it is associated with the melting of polyethylene crystals, so therefore some idea about what may be the mechanisms involved and what is the stability of bonds in these systems is required for us to analyse such behaviour and so if we look at another sample and if we see some response like this, then can you state something about what was the state of the material here and what was the state of the material here.

So, as we increase the temperature we undergo a step change which is the glass transition temperature, then there is an endothermic process which is associated with melting temperature and so here the material is basically, disordered melt and here the material was a semi crystalline glass, semi crystalline polymer but in a glassy state because it has glass transition associated with the amorphous state and it has melting temperature associated with the crystalline state. So, therefore you can see that this way the DSC has a technique is very useful to characterize all these thermal transitions that are happening. One can also start from melt and then cool it down. So, for example the same sample if it is cooled down, what we will see is the, an exothermic peak because crystallization now happens and then as we reach closer, we will again have a glass transition.

So, therefore we have the glass transition and we defined the crystallization temperature and if this is done at different rates, so if you recall our discussion related to glass transition temperature, glass transition depends on the heating rate similarly, the cooling rate will affect what temperature does crystallization happen. So, all of these things can be studied using DSC, the crystallization kinetics, the effect of heating rate on glass transition, so variety of these phenomena can be studied based on observing heat flow as a function of temperature or time as the case may be. Because we could do an isothermal experiment also where we take the material to a given temperature let us say, T1 and then observe heat flow as a function of time, so temperature is constant and therefore heat flow may show some trend like this and this implies that there is crystallization taking place in the material and this is the isothermal crystallization that we discussed earlier. So, all these phenomena can be studied using DSC and looking at these DSC curves and these transitions, we can make out about what the material is like. **(Refer Slide Time: 20:06)**



Thermal conductivity for polymers

Polymers are thermal insulators (lower values of thermal conductivity, k_{th}):

- Polymers → 0.1 - 0.6 W/(m K)
- Foamed polymers: → 0.01 - 0.08 W/(m K)
- Filled polymers (boron nitride, aluminium): → 1 - 10 W/(m K)
  - Thermal percolation
  - useful for electronic components, aerospace parts - lighweight & electrically insulating, but thermally conducting

k_{th} and microstructure

Anisotropy in conduction

- a very strong function of chain orientation
- increases with temperature for glassy state and melt state
- decreases with temperature for rubbery state and crystalline state

(Mark, 2007)

So, we will finish this lecture by looking at the thermal conductivity of polymeric materials of course, we know that polymers are generally thermal insulators, their value of thermal conductivity is quite low. So, for example it is about 0.1 to 0.6 in many of the polymeric material systems and since we use polymers also for even better insulating purposes, we have the foamed polymeric materials whose conductivity is even an order magnitude lower.

But at the same time, there are applications such as an electronic components where heat has to be dissipated away, many of the electronic components when they operate there is lot of heat dissipation and heat increase and of course, we know how mobile phone gets becomes hot or how laptop becomes hot. So, this heat dissipation has to be taken away and so many of the material requirements in these is to have higher thermal conductivity.

But at the same time, other advantages of polymeric materials, so similarly in aerospace parts where the light weight is required and electrically insulation material is required but at the same time, thermal conduction is required. So, for such materials we can prepare a composite as we have seen because composites can be prepared not only to improve mechanical performance but to induce a property which otherwise was not there.

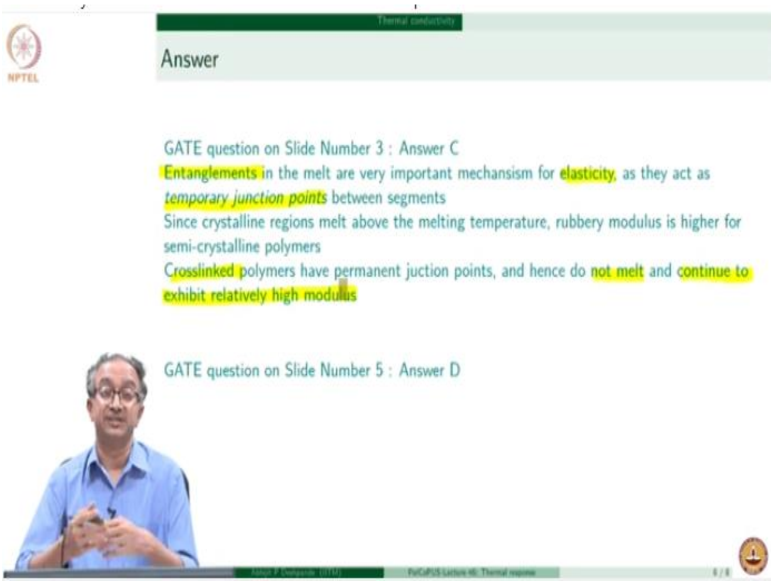
So, fillers like boron, nitride or aluminium can be used and then the conductivity can be order or 2 magnitude higher than the conductivity of the polymers and just the way we discussed the mechanical percolation or electrical percolation, thermal percolation is also possible. Whenever the particles and fillers start touching each other, then the conductivity increase will be very significant, if they are isolated in well dispersed in matrix, then the increase will be lower. And as we can see, there is an orders of magnitude increase in conductivity possible, if we add more and more filler, so therefore thermal conductivity of polymers though low can be modified based on addition of fillers. Just to end with this discussion, we will look at briefly how does the conductivity effect of temperature tell us about the microstructure, so the conductivity is a very strong function of chain orientation.

If you recognize what is the basic mechanism of thermal conductivity, so either from schooling or your earlier studies, how does conduction; heat conduction happen and part of it you would say is related to electronic interactions between neighbouring atoms, so its vibration of neighbouring atoms and so on is the explanation that you have read about. Now, if you look at a macromolecule, the interaction between 2 macromolecules is through secondary interactions and electronic interactions are much weaker.

The electronic interactions around macromolecule chain is much higher because of the covalent bond and so therefore, conduction along the polymer chain is much stronger than across the chain and so therefore, if a sample has oriented chains then the thermal conductivity will be very different and so therefore, many of the polymeric sample, if chain orientation is there, there is also anisotropy which means different thermal conductivity in different directions.

So, conduction behaviour of many of the polymeric films which are oriented will have anisotropic conduction, second aspect is related to what happens with respect to temperature. So, if we increase the temperature in glassy state or in a melt state, the conductivity increases, why would this be the case? This is because when we increase the temperature we allow higher thermal energy and easier for phonons to conduct heat. The other aspect is related to decrease, so when we have rubbery state or a crystalline state, then if we increase the temperature, then the thermal conductivity decreases. So, you can see that based on the temperature dependency, we can understand what may be the underlying structure of the material.

(Refer Slide Time: 24:44)



Thermal conductivity

Answer

GATE question on Slide Number 3 : Answer C

Entanglements in the melt are very important mechansism for elasticity, as they act as *temporary junction points* between segments

Since crystalline regions melt above the melting temperature, rubbery modulus is higher for semi-crystalline polymers

Crosslinked polymers have permanent juction points, and hence do not melt and continue to exhibit relatively high modulus

GATE question on Slide Number 5 : Answer D

So, with this we will close this lecture, we have looked at the thermal response, different signatures and different phenomena which happen as a function of temperature and we know of course that all of this is related to the viscoelastic and dielectric response of the polymeric system because thermal energy which is available for macromolecular relaxation is an underlying mechanism for all such responses.

And as far as the modulus variation with temperature is concerned, entanglements play a very important role of providing elasticity because they act like temporary junction points. So, therefore elasticity if its there, if we have very high molar mass and very high set of entanglements and of course, crosslink polymers will not really melt and therefore they will continue to have relatively higher modulus even at higher and higher temperature.

Only beyond a certain temperature degradation sets in and then the depolymerization would happen, molar mass will come down and then the overall modulus will also go down but that happens during degradation. So, with this you can arrive at the answer which is related to the question and of course, dynamic mechanical analysis was the answer to the other question. So, with this we will close and we will continue looking at viscoelasticity of polymers in much more detail in a future lecture. Thank you.