Polymeric Materials of Different Kind

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Lecture - 23
Glass Transition II

Hello, welcome to this lecture on polymers. In this course, we are looking at sustainability, we are looking at uses, we are looking at properties of these materials and we are learning important concepts about these macromolecular systems, another week. And in this week, our focus will remain on macromolecular systems of different kind. By this, I mean, we rarely use polymers in its form where it is pure polymer.

So, we quite often will blend the polymer, we quite often will form composites of these polymers, instead of using a monomer and forming a polymer, we will use multiple monomers and try to form co-polymers. So, therefore, polymeric materials of different kinds are actually used in real applications. And so, this week we will try to look at many of these different kinds of material systems.

However, we still have the unfinished task of looking at simple description of the glass transition through empirical classical theories and try to understand a little bit more about the glass transition. And so, in this lecture, we will look at this property in little more closer detail.

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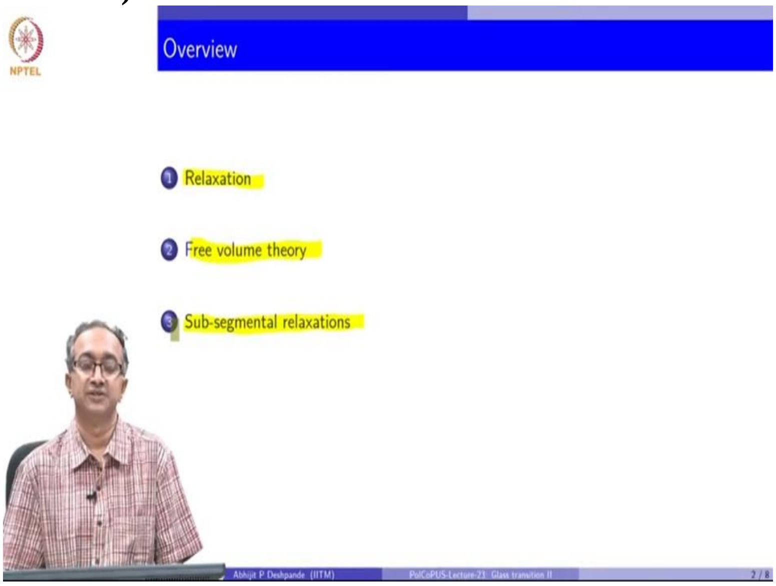

Overview

1. Relaxation
2. Free volume theory
3. Sub-segmental relaxations

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And a lot of what we discuss in glass transition also has relevance related to the viscoelasticity of polymeric systems. So, understanding of glass transition therefore, it is important from the point of view of understanding many properties which are related to polymers. And this is because of these segmental mobility, segmental flexibility and what happens to the segmental flexibility around glass transition. So, it is a very key concept as well as influencing factor in determining the overall polymer response.

So, we will do look at the glass transition by discussing a little bit more about relaxation, this is a term which we have been using at least 3, 4 lectures I have used it and it is something which we must become again much more familiar with for us to understand all aspects related to macromolecular behaviour and its viscoelastic behaviour. We will describe the classical free volume theory which is used to describe the glass transition temperature. And also we will finish the lecture by looking at few other transitions which are exhibited by macro molecular systems in addition to the glass transition temperature.

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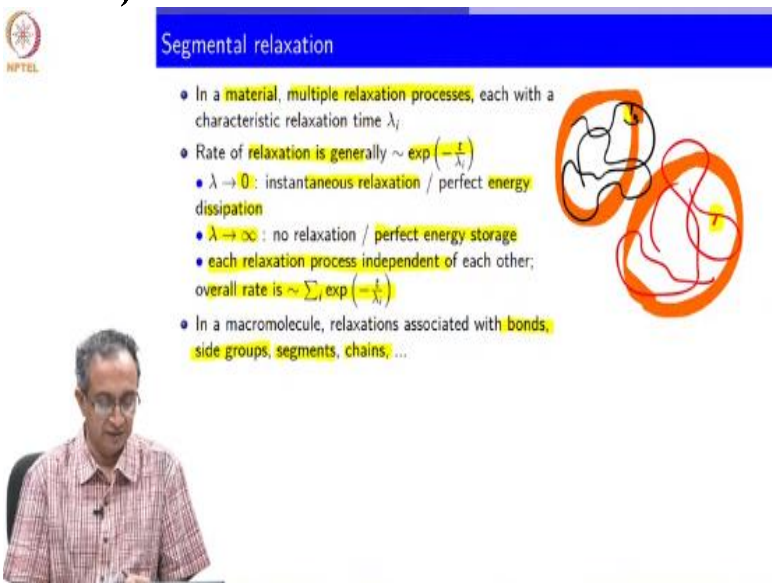

Segmental relaxation

- In a material, multiple relaxation processes, each with a characteristic relaxation time λ_i
- Rate of relaxation is generally $\sim \exp\left(-\frac{t}{\lambda_i}\right)$
  - $\lambda \to 0$: instantaneous relaxation / perfect energy dissipation
  - $\lambda \to \infty$: no relaxation / perfect energy storage
  - each relaxation process independent of each other; overall rate is $\sim \sum_i \exp\left(-\frac{t}{\lambda_i}\right)$
- In a macromolecule, relaxations associated with bonds, side groups, segments, chains, ...

So, segmental relaxation is the ability of carbon carbon backbone bond to rotate and therefore, leading to different conformations being adopted by a macro molecule. And so, segment conformation changing is called segmental relaxations. So, generally as we are trying to discuss segmental relaxation, we keep on bringing this fact up that you know material generally will have multiple relaxation processes of which segmental relaxation is one example.

So, for example, in case of macromolecule, we may have a bond level relaxations, we will have relaxations associated with side groups, segmental relaxation and the overall macro molecule itself. The whole macro molecule moving and undergoing relaxations are set of relaxations which are at longer timescales as well as larger length scales. Because, macromolecule is much larger compared to segment. So, therefore, for a general material and this is not just true for macromolecules or polymers, this is the way we think of material response.

We say that in a material there are several relaxation processes possible. And, one of the key features of this relaxation phenomenon is the fact that it is a mechanism by which material can dissipate energy. So, therefore, when we think of relaxation, think also of dissipation of energy. The opposite is of course, storage of energy. So, if we have a material where there is no relaxation process, it implies that there is no dissipation and therefore, it will be a perfectly storing, energy storing material.

So, generally the rate of relaxation or the rate of these dissipative processes are given based on what is the relaxation time. So, if relaxation time is 0 or a very small then we have very fast relaxation and therefore, in this case energy dissipation happens in the material and it also happens at a faster rate. The other extreme if we have a relaxation time is infinite then basically that implies that there is no relaxation in the material or it will take infinite amount of time for any dissipative process to happen.

And because of that, these materials then are energy storage materials. So generally therefore, a material depending on the length scale and timescale of the mechanisms which are present will have a spectrum of relaxation times it will have multiple mechanisms. And, our general assumption is also that all of these relaxation processes are independent of each other. So, for example, the way side group rotation happens does not depend on how the overall macromolecule itself is moving.

So, let us say if I look at the macromolecule, and how its state is and how its segments are moving, the side group which is on it, and how it can rotate is not dependent on how where there is another molecule which has a different conformation and then there is a side group. So, the macromolecular motion, which is related to the overall molecule moving is independent of the segment, the side group rotation, which is possible.

So, this is what we mean by each relaxation process is independent of each other. So, if we have several such relaxation processes, the overall rate of relaxation is just summation of all the exponential processes. So, this is generally what we would see in a material with the dissipative mechanisms that are present in the material.

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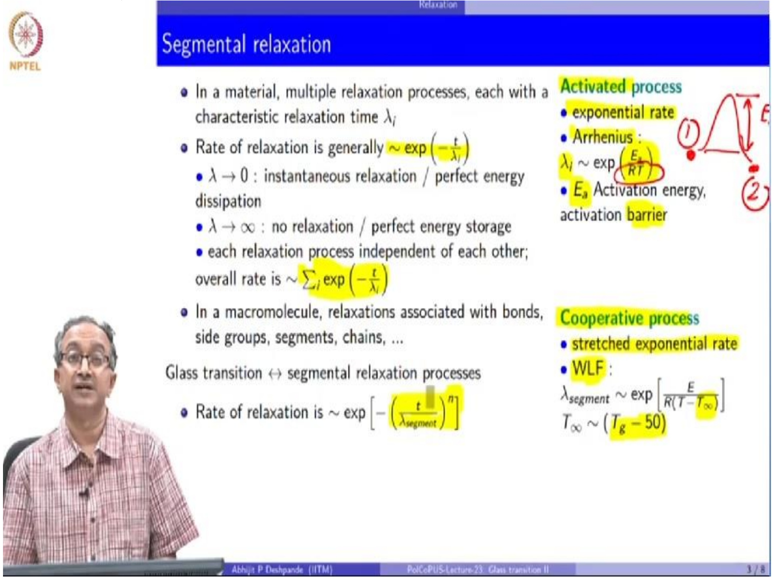

Relaxation

Segmental relaxation

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Glass transition ↔ segmental relaxation processes

- Rate of relaxation is $\sim \exp\left[-\left(\frac{t}{\lambda_{segment}}\right)^n\right]$

Activated process

- exponential rate
- Arrhenius :

$\lambda_i \sim \exp\left(\frac{E_a}{RT}\right)$

- E_a Activation energy, activation barrier

Cooperative process

- stretched exponential rate
- WLF :

$\lambda_{segment} \sim \exp\left[\frac{E}{R(T-T_\infty)}\right]$

$T_\infty \sim (T_g - 50)$

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PolCoPUS-Lecture-23: Glass transition II

3 / 8

And so now looking at glass transition where segment, segmental relaxation processes are occurring around the glass transition temperature. Basically, it is the presence or absence of segmental relaxation. And so, the rate of relaxation in case of the segmental relaxation is not exponential, but it departs from exponential and that is characterised by this exponent n. So, of course, if this exponent is 1, then again this relaxation falls back to exponential.

Given that it is not 1, it implies that the relaxation process which is happening around glass transition due to these segmental relaxations. Even if we identify relaxation time which is associated with the segmental relaxation, we cannot describe it using an exponential. And, so, let us now summarise once more, what we have talked about in terms of relaxation processes. We have said that, if there is a characteristic relaxation time and then there is an exponential rate of that process, then we will term that process an activated process.

The reason we call it activated process is also because we can use Arrhenius relation, when we change the temperature on the material, when the temperature of the material is changed, the rate of relaxation will change. And this rate will change because the relaxation time changes and the relaxation time changes with respect to temperature based on Arrhenius dependence.

And the key factor in this Arrhenius dependence is this activation or the barrier energy. So, the idea of activated process is that material can change the mechanism is there, if we think of let us say a cc bond rotation, so, it is between 2 energy states and this we saw also for butane in our earlier lecture. So, it can go from state 1 to state 2, however, there is a barrier energy. And so, this barrier has to be crossed before it can go from state 1 to state 2.

And so, depending on the thermal energy which is present in the material, also the temperature of the material will determine, what is the rate of change from 1 to 2? And so, this is therefore called an Activated process. An activation barrier has to be hopped based on the presence of thermal energy that is available to the macromolecular system. Now, the other example of process is called a Cooperative process. This is a non-activated process. And in this case, now the rate of the process is stretched exponential.

And if we look at the material and how relaxation time changes as a function of temperature, we will see that free volume theory comes up with this expression which is called the WLF equation. And here the key factor is a presence of temperature, a fictitious temperature which is generally around 50 degrees lower than glass transition temperature. So, this temperature signifies that the λ, the relaxation time will go to infinity if T becomes T_∞.

So, therefore, this is not an activated process where there is an a barrier energy which has to be hopped, but it depends on how far away from a T_∞ temperature we are in terms of the macromolecular segmental flexibility. And why is it also called cooperativity? Because we are looking at segments. And the segmental relaxation cannot be split into several relaxation times and adding them all up as exponential rates, but it is a stretched exponential rate.

So, therefore, it appears as if they are maybe 3, 4 relaxation processes which are happening which are associated with this segment, but they are all cooperating with each other. Since they are cooperating with each other, we can’t think of each of them as an exponential process and sum them up, like what we did in case of activated processes. However, when we look at the overall rate, instead of it being a sum of exponential, it is a stretched exponential.

So, there is cooperativity of different relaxation modes which are present in the material in during glass transition. So, this is how we describe in words some of these features related to glass transition. Quantification of this is also possible by looking at temperature dependence, by looking at the relaxation times and this is what scientists are doing in order to better our understanding related to glass transition.

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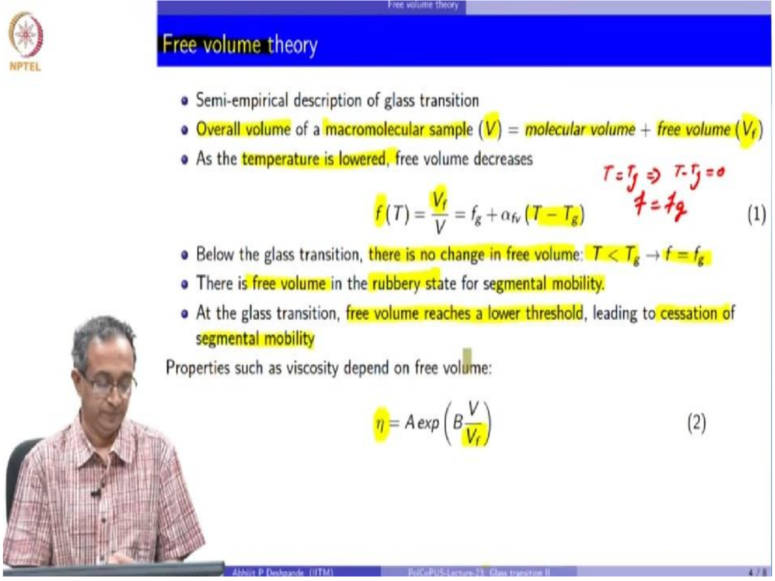

Free volume theory

- Semi-empirical description of glass transition
- Overall volume of a macromolecular sample (V) = *molecular volume* + *free volume* (V_f)
- As the temperature is lowered, free volume decreases

$$f(T) = \frac{V_f}{V} = f_g + \alpha_{fv}(T - T_g) \qquad (1)$$

$T = T_g \Rightarrow T - T_g = 0$
$f = f_g$

- Below the glass transition, there is no change in free volume: $T < T_g \rightarrow f = f_g$
- There is free volume in the rubbery state for segmental mobility.
- At the glass transition, free volume reaches a lower threshold, leading to cessation of segmental mobility

Properties such as viscosity depend on free volume:

$$\eta = A\exp\left(B\frac{V}{V_f}\right) \qquad (2)$$

So, the classical way of describing this is semi empirical theory called Free volume. And I have already alluded to this in the 22nd lecture where we introduced the concept of glass transition. Free volume is basically molecular volume which is above over and above the molecular volume. So the total volume or the overall volume of the macromolecular sample, which we will denote as

$$V = V_f + \text{molecular volume.}$$

And the key observation is that when we lower the temperature, we lower the free volume which is present in the sample. So, if we describe it using a fraction, so, f is basically fraction of free volume in the material, it is lowered depending on how far away from the glass transition temperature you are. And if the material is at glass transition temperature, then $T - T_g = 0$. So, at when $T = T_g$, this $T - T_g$ will be 0 and therefore, $f = f_g$.

And so, what is key about the free volume theory is the assumption that at glass transition temperature, fractional free volume becomes f g and when you go lower than glass transition it remains. So, the amount of free volume becomes frozen in the material. So, a polymer sample, free volume keeps on increasing when we increase the temperature above glass transition, but when we go below the glass transition, the free volume remains frozen.

And so, the free volume is available and it also increases as a function of temperature in the rubbery state. So, therefore, segmental mobility is possible. Since, at glass transition temperature f g is low, such that segmental mobility is not possible. So, free volume reaches a lower threshold and therefore, segmental mobility is completely stopped. Now, how can we use this concept of free volume to describe properties?

One way is to look for properties, how do they change with respect to free volume. So, this is an expression which is also referred to as do-little expression, which tries to describe viscosity of any material and this was also done for simple liquids. So, how does it change on free volume? So, you can try to think about it as to why V_f is in the denominator. So, if V f is higher or lower, is viscosity higher or lower? So, think about it and then what we need to do is we need to combine the equations 1 and 2 to basically get an expression for viscosity as a function of temperature.

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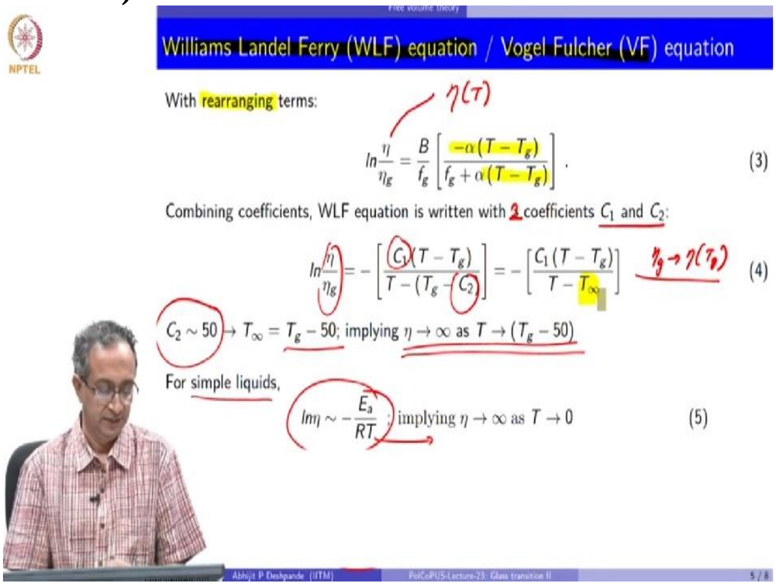

Free volume theory

Williams Landel Ferry (WLF) equation / Vogel Fulcher (VF) equation

With rearranging terms:

$\eta(T)$

$$ln\frac{\eta}{\eta_g} = \frac{B}{f_g}\left[\frac{-\alpha(T-T_g)}{f_g+\alpha(T-T_g)}\right]. \quad (3)$$

Combining coefficients, WLF equation is written with 2 coefficients C_1 and C_2:

$$ln\frac{\eta}{\eta_g} = -\left[\frac{C_1(T-T_g)}{T-(T_g-C_2)}\right] = -\left[\frac{C_1(T-T_g)}{T-T_\infty}\right] \quad \eta_g \to \eta(T_g) \quad (4)$$

$C_2 \sim 50 \rightarrow T_\infty = T_g - 50$; implying $\eta \to \infty$ as $T \to (T_g - 50)$

For simple liquids,

$$ln\eta \sim -\frac{E_a}{RT}; \text{ implying } \eta \to \infty \text{ as } T \to 0 \quad (5)$$

So, if you do a little bit of algebra and arranging of terms we get what is called Williams Landel Ferry equation. And when you do rearrangement, you are basically getting a factor T – T_g. And this is the factor that I talked about when I described glass transition as a cooperative process segmental relaxation as a cooperative process, where the temperature difference from the glass transition with respect to glass transition is the key feature as opposed to the activation energy.

So, we can combine these α and B and all these coefficients f_g and the 2 coefficients which are C_1 and C_2 are basically describing the relationship of viscosity at any given temperature with respect to viscosity at glass transition temperature. So, here now η_g is viscosity at glass transition temperature. While η is the viscosity at any other temperature. So, what we can see is, depending on these coefficient C_1 and C_2 or C_1 and T_∞, the behaviour will be different.

One key thing you can observe is if $T = T_g$ then, η will be equal to η_g. So, therefore which is by definition. And if $T = T_\infty$ then, η becomes infinite. So, therefore, this fictitious temperature which is around 50 degrees celsius below glass transition, because for many of the polymeric systems, C_2 is around 35, 40, 50, 55. So, it is a temperature below the glass transition temperature basically, segmental mobility completely seizes.

And therefore, viscosity becomes infinite. If you look at the other sets of materials, and if you have a Arrhenius dependence, then in this case only when temperature goes to 0, when temperature goes to 0 this η will become infinity. So, you can see the difference between how the relaxation processes rate changes in case of WLF dependence as opposed to Arrhenius dependence. And this T_∞ is also referred to as equations temperature where dependent on Vogel Fulcher equation.

So, just to complete the definition, the this equation is also called Vogel Fulcher equation in certain literature and T_∞ is the temperature which is crucial to the definition of the WLF or Vogel Fulcher dependence.

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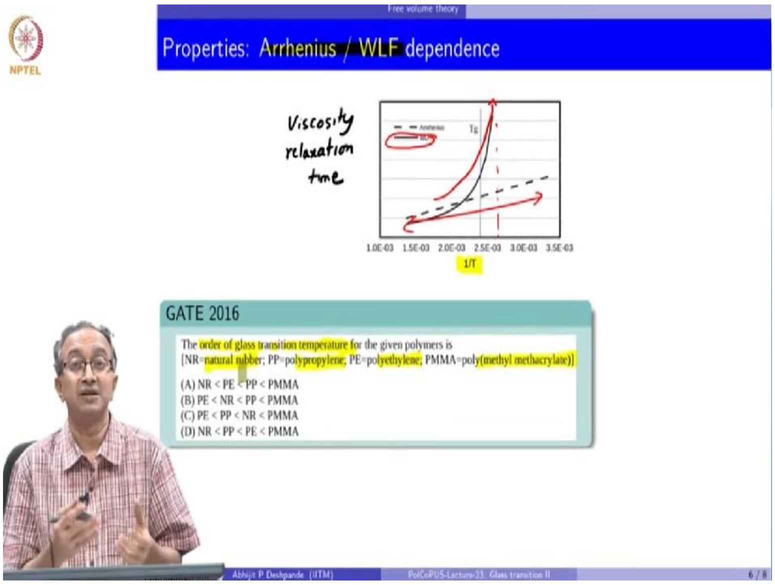

Free volume theory

Properties: Arrhenius / WLF dependence

GATE 2016

The order of glass transition temperature for the given polymers is
[NR=natural rubber; PP=polypropylene; PE=polyethylene; PMMA=poly(methyl methacrylate)]

(A) NR < PE < PP < PMMA
(B) PE < NR < PP < PMMA
(C) PE < PP < NR < PMMA
(D) NR < PP < PE < PMMA

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Just to highlight how different this transition is, we can look at how do properties change as a function of temperature when we have Arrhenius dependence or WLF dependence. So, in this case, what we have plotted is the rate of change of a property as a function of temperature. So, this property could be viscosity as we have seen, it could be the relaxation time. So, it could be many of these things which depend on temperature.

And as the temperature is higher, the thermal energy present is higher and if it is just an activation barrier hopping, then e / r t is the dependence and therefore, then Arrhenius is straight line. So, as we increase the temperature the rate of relaxation processes keeps on becoming higher and higher. On the other hand, for WLF dependence, what you can see is, it goes to infinite at a temperature which is T_g - 50 around there.

So, therefore, the rate of change of any of the properties is much stronger with respect to temperature when we approach glass transition. And this is something which we will see later on also, when we look at time temperature superposition in case of polymers, we have shift factors which are describing the time temperature superposition procedure. And we will see that shift factors can be WLF or shift factors can be Arrhenius.

Based on this description, I do not know if you can think and see if I look at polymer melt and look at shift factors there or if I look at polymer material near rubber transition and look at it shift factor. Can you try to reason out as to shift factors will be WLF for melt or shift factors will be WLF for rubbery material. Other way to ask the question is also, will shift factor be Arrhenius for the melt material or will shift factor be Arrhenius for rubber like material.

So, based on we have discussed you should be able to reason out and see that why melt we will have Arrhenius dependence and why for rubbery material which is closer to glass transition, we will have WLF dependence or Vogel Fulcher dependence. So, just to think of this specifically also for a set of polymers in this question which is from the exam, we are being asked to look at what is the order of glass transition.

So, all these features that we have described in terms of segmental mobility, these get affected due to the physical chemical interactions at the macromolecular level. And the concept of chain flexibility that we learned during our second week of lectures becomes very useful in terms of analysing these phenomena. Because just by understanding segmental mobility or chain conformations, we can immediately understand how is glass transition temperature different.

So, in case of polypropylene or polyethylene or poly methyl methacrylate or natural rubber, which one will have a higher glass transition temperature? So, again things to think about are in terms of, is there anything along the macromolecular chain which makes it difficult for conformations to change, which means are there any features which make the macromolecule more rigid and therefore, segmental mobility will have to be achieved by taking the material to higher temperature.

Converse is also there that if cc bond rotation is very easy and there are no bulky side groups and there is not much of an interaction then the material will be observed in rubbery state or segmental mobility will be observed at a much lower temperature. So, we can think look at all of these polymers and then look at answering this question.

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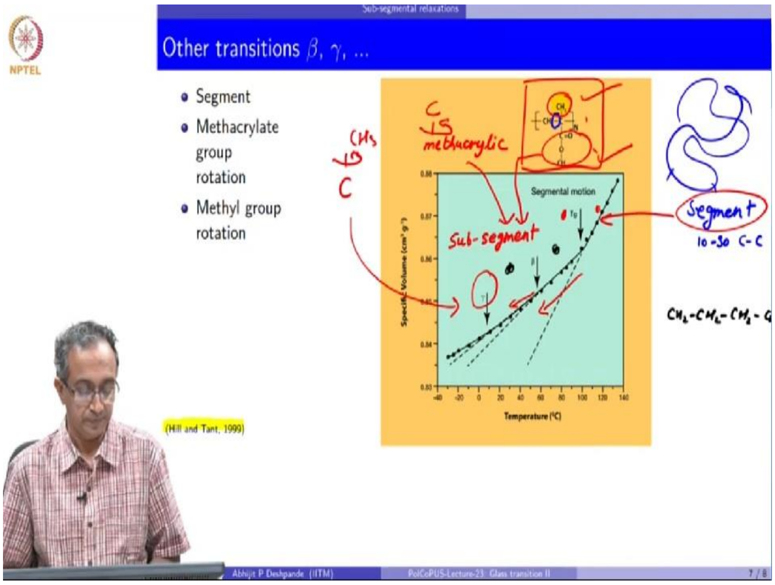

Sub-segmental relaxations

Other transitions β, γ, ...

- Segment
- Methacrylate group rotation
- Methyl group rotation

(Hill and Tant, 1999)

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We will close this lecture by just looking at what are the other transitions possible and we will look at this based on some very nice data which is from the literature which is related to poly methyl methacrylate PMMA. So, it has this methyl group and also it has this methacrylate group. So, now, you can try to figure out as to what are the different relaxation modes which are present in this.

So, one relaxation mode is of course, the overall macromolecule moving. So, which happens when the material is in the melt state. So, that we are not really concerned about while we are discussing glass transition. But when we are discussing glass transitions we are looking at segmental. So, if we look at a segment and the segment may have anywhere from 10 to 30 cc bonds and the cc bonds we are talking about are these.

So, there is rotation around the cc bonds and like we described in case of butane, 3 different conformational states are possible. So, now, the 3 different conformational states how easy are they when there is a bulky group like methacrylic group which is present here. So, given that these groups are there, both methyl as well as methacrylic acid groups, so how does this change.

And so, the glass transition temperature of PMMA therefore, is observed at reasonably high temperature as opposed to polypropylene or other materials where the side group is only methyl, its smaller side group. Now, when we lower the temperature further, what we see is at transition which we identify as beta, there is again a small change in volume versus temperature phenomena. And so, this beta and further down gamma, they are relaxations, which are associated with sub segment motion.

So, can you guess as to what might be the sub segment motion looking at what is the set of groups which are present. So, the cc bond rotation and the segment is associated with T_g. Now, what you can see is the rotation of methacrylic acid group will be it is a bulky group which can rotate. So, this C, C and so, instead of writing C, I will just write this as methacrylic group.

So, this rotation is what is related to beta. Now, similarly, there is also C and CH 3. So, this rotation is also possible. There is another CH 3 group here also and so, these rotations are basically responsible for gamma transition. So, you can see that it is a set of transitions depending on what are the mechanisms which are present in the material. If we have polyethylene, then in that case of course, these transitions will again depend on what are the bonds which are present.

So, there is cc bond along the chain and there is CH CH bond along the side groups. In so, in case of PMMA we have different sizes, therefore, length scales and different timescales associated with each of these subunits. And therefore, they lead to transitional conditions. And properties will again change across a beta transition or gamma transition. So, if I measure let us say modulus, we will look at for example, storage modulus as a function of temperature for these kind of material systems.

Or if I measure Youngs modulus at temperature, let us say at around minus 20 and at around 25 degrees celsius, there will be a difference. And that is because of the processes, relaxation processes associated with these side groups are present or absence. And so, therefore flexibility of the overall macromolecular system is lower or higher. The difference in properties though is smaller, when we go from higher than beta lower than beta.

So, if we are at this point or at this point there will be a difference in properties, but much less compared to if we are at 2 points across glass transition temperature. So, we already said that orders of magnitude 3, 4 orders of magnitude property change will be there when we are across glass transition. When we across beta or gamma transitions property changes will be much smaller.

They will be same order of magnitude but there will be a difference. So, therefore, these relaxations which are associated with subunits of a segment with a single group rotation or change in conformation of smaller groups, they are important for certain applications and certain quantitative differences in terms of property changes. But they are not as crucial in terms of practical considerations as glass transition temperature is.

So, generally when we look at engineering prescription of a material, we generally will specify either heat deflection, heat distortion temperature or a Vicat softening point or the glass transition temperature itself. But from a finer understanding many of these additional transitions are also very useful.

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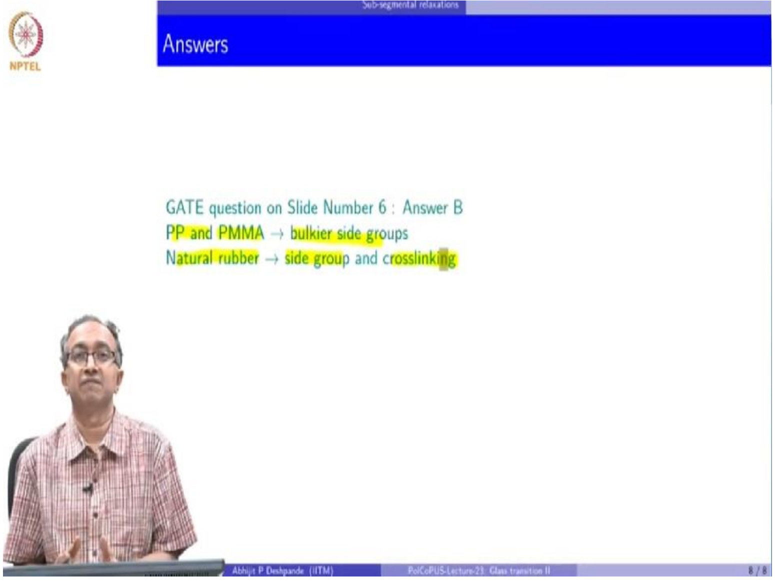

Sub-segmental relaxations

Answers

GATE question on Slide Number 6 : Answer B
PP and PMMA → bulkier side groups
Natural rubber → side group and crosslinking

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So, with this we will close this lecture thinking back about the answer related to which one will have a higher glass transition temperature and you can see how each of the answers now, related to bulk behaviours such as glass transition depends on macromolecular interactions related to chain flexibility. So, p polypropylene and poly methyl methacrylate have of course, bulkier side groups and therefore, they will have higher glass transition temperature.

Natural rubber will also have isoprene side group, and also there will be cross linking. So, therefore, you can go and justify to yourself the correct answer based on these descriptions of different macromolecular interactions and macromolecular gene architecture which is responsible for observation of segmental flexibility in the material. So, with this we will close this lecture. Thank you.