Molecular Arrangements and States of Polymers
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Lecture – 22
Glass Transition – I

Hello, let’s continue our look at the structure of polymers and the molecular arrangements and we have looked at the crystalline arrangement as well as the orientational states of macromolecules. And in this lecture, we will start looking at the disordered solid state of polymers, which is the glassy state. And so, we will look at also the transition, which occurs when glassy state is reached or when glassy state the material transforms from to another state.

And so, this is our continuing look at different states of polymers. And the focus of this and the next lecture will be on measurement of properties and its estimation and quantification of it.

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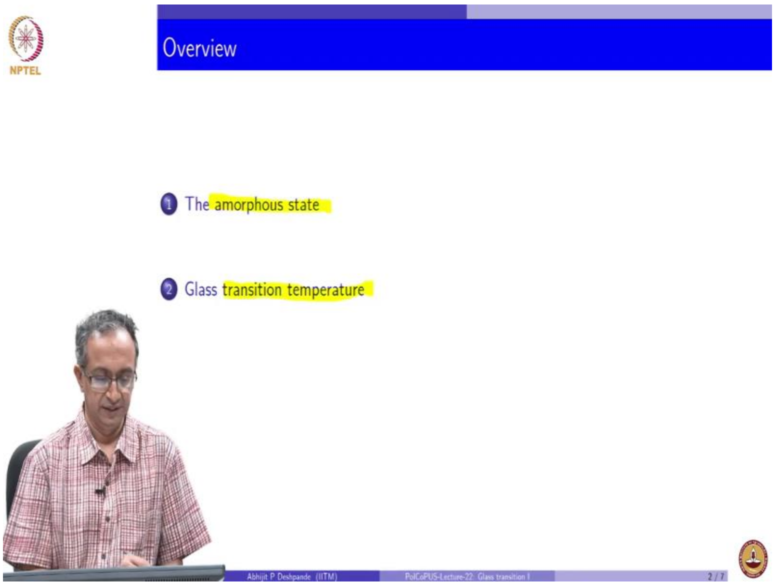

Overview

1. The amorphous state
2. Glass transition temperature

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So, we will do this by looking at the amorphous state itself, what do we mean by it and the transition temperature that characterizes the transition to or from amorphous state.

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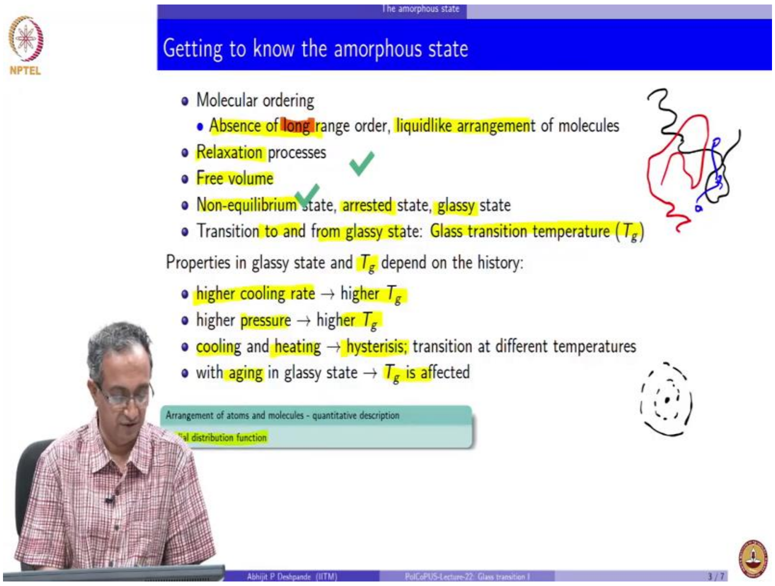

The amorphous state

Getting to know the amorphous state

- Molecular ordering
  - Absence of long range order, liquidlike arrangement of molecules
- Relaxation processes ✓
- Free volume
- Non-equilibrium ✓ state, arrested state, glassy state
- Transition to and from glassy state: Glass transition temperature (T_g)

Properties in glassy state and T_g depend on the history:

- higher cooling rate → higher T_g
- higher pressure → higher T_g
- cooling and heating → hysterisis; transition at different temperatures
- with aging in glassy state → T_g is affected

Arrangement of atoms and molecules - quantitative description

…ial distribution function

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And so, just to know the amorphous state a little better, we have absence of long range order. And the key word here is long range. So, if we were to take a closer look at macromolecular arrangements in amorphous state, periodically, we may end up seeing some segments which seem to be ordered, which looks like a folded chain.

But if we look at this macromolecule, it is of course, is an amorphous state and then, the other macromolecule also is pretty much an amorphous state, but again, it may have just some sections which look like ordering. So, if you focus on a very small portion of the macro molecule, there may be some small ordering. The key feature is that the unit cell which characterizes a crystalline material is absent here. So, that's why we call it the long range order is absent and consequently, the arrangement of molecules can be said to be liquid-like with random ordering. And because of this random ordering and because the possibility of molecular arrangements still non-zero the rate of molecular arrangement is still non-zero, we can still have some relaxation processes, which imply that amorphous state some changes of molecular arrangements are possible.

This is true even in case of crystalline solids if there are defects and if there are vibration around mean position is of course, possible in crystalline solid also, but if there are defects, then atoms can hop across and defects can also move, but the rates that have are exceedingly different in case of an amorphous solid in the glassy state as opposed to a crystalline solid. The relaxation processes are faster in case of amorphous solid.

Just to remind you, that the relaxation processes that we are talking about whether it's defect motion in case of crystalline solid or relaxation processes, in case of amorphous solid are orders of magnitude slower than the rubbery state or the liquid-like states. So, therefore, these are still solid-like states, where relaxation processes are slower, but they are still when we compare the relaxation processes in an amorphous state, we might find the rates to be higher compared to the crystalline state. And the other way of characterizing the given that the relaxation processes are possible to some extent, and also because of these rearrangement of macromolecules there is some amount of free volume present and so, a small molecule when it is present in this macromolecular system, it can also diffuse around.

So, for example, if there is a small molecule, given that there is sufficient gap and some of these macromolecules can relax at a very slow rate, the molecule can hop across and it can diffuse and so, therefore, there is some free volume, which is not really occupied by macromolecule itself, which is available for motion of smaller molecules. Also, the availability of free volume implies that some amount of relaxation processes can happen.

So, one of the implications of saying that there is free volume and there are relaxation processes possible in the material, we are making the assertion that the polymer in the glassy state is not at equilibrium. There are changes taking place in the material which are taking the material from one state to another. And therefore, equilibrium is still to be reached. When we talk about a liquid or a rubber like material, there is dynamicism there also, segments are moving or macromolecules are moving in case of melt. However, the material is in equilibrium. So, the dynamic equilibrium of the material is established in that case and on an average the internal energy or entropy of the material is well defined given temperature and pressure are fixed. When we change temperature and pressure, the volume also changes and similarly, entropy and internal energy or enthalpy or Gibbs free energy any of these thermodynamic quantities change and we say that rubber like material or liquid like material has gone from one equilibrium state to another.

In the case of glassy state, because these relaxation processes are happening and because the material is in a non-equilibrium state, the specification of the state itself becomes a challenging task. And so, quite often therefore, we describe the glassy state as an arrested state. There is a tendency for the material to evolve, there is a tendency for relaxation processes to take place, however, the rate of such relaxation processes are so slow that the material appears to be arrested, the molecules appear to be arrested, though they have a tendency to move. And of course, we also call this state the glassy state. So, transition from this glassy state to a rubbery state or to a more molten liquid like state or transition to glassy state from rubbery state or from the molten state is quantified using glass transition temperature.

So, this is a very key transition as far as macromolecules are concerned. Glass transition is a phenomenon which is observed for a variety of other inorganic and organic solids also, or, for example, glass itself silica, the term comes from there. And so, what we use in windows is basically an amorphous silica and that’s a glassy state of silica. We also have crystalline state of silica which is quartz.

So, therefore, there are many other molecules and atoms which also shows this transition to a glassy or arrested or a non-equilibrium state, where the molecular changes do take place, but at a very, very slow rate. So, for all practical purposes, the material appears to be solid like however, it has a liquid like arrangement as well as relaxation processes, which are still possible. So, the consequence of glassy state being this non equilibrium state, the observation of glass transition also therefore depends on various factors.

If we talk of an equilibrium transition, then, as soon as we fix the conditions, for example, boiling point of water, as soon as we say its atmospheric pressure, it is known that it is 100 degrees Celsius, if we change the pressure, the boiling temperature will also change. However, the degrees of freedom in that equilibrium system of water vapour and liquid water, this equilibrium system degrees of freedom are such that, that once you fix pressure, the boiling temperature is fixed.

However, when we are talking about non-equilibrium systems, what happens is the non-equilibrium systems, the state of the material is difficult to specify, we need many more variables to specify the state of the system. And therefore, it’s also not possible for us to fix let us say it just a pressure and therefore, talk about glass transition temperature. So, the glass transition temperature in general depends not only on pressure, it also depends on what was the cooling rate, heating rate. So, therefore, it depends on the conditioning of the sample. So, here we will quickly summarize some of the key features which are known about the glass transition temperature. So, this T g if one cools the sample at a higher cooling rate, we would observe generally a higher glass transition. So, this is another key feature that we have highlighted many times as far as macromolecular systems are concerned.

One of the things that I have said many times is difficult to give a specific set of properties. And it’s difficult to say I will go to handbook and pick up a value of some power property in case of macromolecules and again glass transition temperature is one such property. So, generally when somebody says that you know nylon has a glass transition temperature of 80 degrees Celsius, what we mean is under some conditions the measurement is 80 degrees Celsius.

But if we change the conditions for example, cooling rate, we will observe difference. The thing to note here is it is not that the difference is very large, but easily 5, 6 degrees Celsius difference can be there depending on the conditions of observation. So, similarly, if we pressurize the nylon let’s say, and then cool it and undergo glass transition temperature, then again the glass transition temperature is different, higher the pressure higher is the observation.

Now, one of the things that you can try to consider is why such behaviour? Because it is one thing to say that you know, higher cooling rate higher T g higher pressure, higher T g, but why is it? What is it about this free volume that we talked about? What is it about the relaxation processes that we talked about that when I cool it differently, or when I pressurize the system, and then cool it, what makes the difference? What is this phenomenon of glass transition? Why does it keep on changing? So, we will try to answer these questions as we discuss little more quantitative features of the glass transition. Generally also, if I cool and heat repeatedly, what I will see is there is a hysteresis in terms of where exactly glass transition temperature is observed, because it depends on the cooling and heating, and also it depends on what was the thermal history of the sample, so when the first heating is done or the first cooling that is done, that is going to be different compared to subsequent stages. So, generally hysteresis in heating cooling cycles are observed and the other influences the history of the sample itself. For example, if given that it is a non-equilibrium state and glassy state, if one leaves the sample macromolecules sample for 1 year and then measure the glass transition as opposed to just cooling it and immediately measuring the glass transition, then there will be a difference.

And this is precisely what we meant earlier, when we said that, we have basically free volume and relaxation processes, which are taking place in the material. So, because of this when a sample is brought below the glass transition temperature and is in amorphous state, so, for example, PET bottle, which at room temperature or 35 degrees Celsius or 15 degrees Celsius is in the glassy state.

Now; if it is left for long amount of time, then molecular arrangements can take place and therefore, we call such phenomena aging phenomena. And because glass is a non-equilibrium state such aging processes do take place and because of this aging processes, the glass transition temperature will also get influenced. We should highlight the fact that this aging sometimes is referred to as physical aging, implying that if we leave something for 2 years of course, there may be some chemical changes also there may be some oxidation processes, there may be some chain changes happening where macromolecules get broken down and such changes are termed as chemical aging. So, therefore, the changes which are taking place in terms of molecular structure in the glassy state are due to physical processes, which we call the relaxation processes and they lead to these changes.

So, glass transition that way is a very interesting and I might say also unsolved problem. So, in terms of what exactly is the condition under which glass transition temperature will be observed? How do I quantify the glassy state? These are some of the questions we scientists are still grappling with. That does not preclude us from using many of these materials as engineering materials. So, for example, in aerospace applications, if glass transition is around 170, 180 degrees Celsius, we go ahead with the design and saying that you know, any time the part should not see temperatures around 120 degrees Celsius or higher. So, with such things, we know that we are sufficiently away from glass transition temperature while the part is serving, so, that any of these relaxation processes aging processes will be minimal, the effect of these on the properties of the material will be minimal. And therefore, we can assume constant properties and do our engineering design.

So, one of the ways of quantification of the arrangement is called radial distribution function. This is something you can read about and you can see that, because of the experimental techniques, such as scattering techniques, which are present today and also the modelling tools, which are from molecular simulations to coarse grained simulations, this is something microscopic quantity which is accessible to us, both experimentally as well as theoretically.

So, therefore, one way to capture quantitatively, the state of glass is to look at the radial distribution function. And in this case, you can read about it more. Basically, what we say we pick one particular atom or molecule, and then we start asking the question that at some distance away from this molecule, what are the other sets of molecules? So this way that is why it is called radial distribution function, given point of reference how are the other entities atoms and molecules in the system distributed with respect to the point of reference. So, you can read about it to know get to know about arrangement and how to quantify the arrangement of atoms and molecules.

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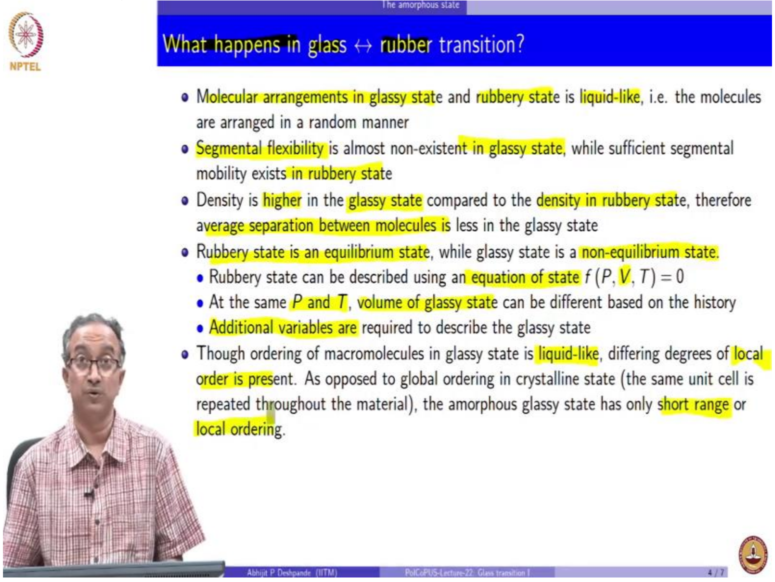

The amorphous state

What happens in glass ↔ rubber transition?

- Molecular arrangements in glassy state and rubbery state is liquid-like, i.e. the molecules are arranged in a random manner
- Segmental flexibility is almost non-existent in glassy state, while sufficient segmental mobility exists in rubbery state
- Density is higher in the glassy state compared to the density in rubbery state, therefore average separation between molecules is less in the glassy state
- Rubbery state is an equilibrium state, while glassy state is a non-equilibrium state.
  - Rubbery state can be described using an equation of state $f(P, V, T) = 0$
  - At the same P and T, volume of glassy state can be different based on the history
  - Additional variables are required to describe the glassy state
- Though ordering of macromolecules in glassy state is liquid-like, differing degrees of local order is present. As opposed to global ordering in crystalline state (the same unit cell is repeated throughout the material), the amorphous glassy state has only short range or local ordering.

So, let’ just rephrase and state it again clearly as to what happens when this glass to rubber transition takes place. So, the implication is also clear that we have a glassy state and amorphous state where the relaxation processes are exceedingly slow and the state appears to be completely solid like. We also have a state which is rubber like where there is flexibility and there is segmental mobility possible and but there is a transition between these two.

So, molecular arrangements in glassy state and rubbery state are both liquid-like, so molecule arrangement remains liquid-like which means random and disordered. And so, from a point of view of this molecular arrangement, there is very little to distinguish between the glassy state and rubber like states. Segmental mobility or the ability of conformational changes as we have discussed several times in this course, is possible in rubbery state however, it is non-existent in the glassy state. So, this is a key feature of when a glassy state is reached is when segmental flexibility ceases to exist. Because we are at a lower temperature in the glassy state, the volume specific volume or volume per unit mass is lower. So, the volume of the polymer system as the temperature is lower will of course, start becoming lower and lower. So, density is higher and higher. So, the density is higher in case of glassy state compared to the density in the rubbery state.

And that of course, can also be looked at a molecular picture by saying that the separation between molecules is higher in case of rubbery state as opposed to in case of glassy state. This we have also said again that rubbery state there is an equilibrium state and implication is that, if I specify pressure and temperature, in case of a rubbery state I can specify the volume also. So, therefore, the equation of state can be provided for a rubbery state.

So, if I fix any two quantities, the third quantities get fixed. This we are familiar with of course, in case of thermodynamics when we look at liquids and gas and gas liquid equilibrium vapour equilibrium, we study equation of state. And in the presence of equation of state implies that equilibrium states are possible and degrees of freedom for a single material is two. So, therefore, if we fix two variables, all the other variables of the equilibrium states are fixed.

So, when we fix pressure and volume, let’s say temperature gets fixed, and all the other thermodynamic variables which describe the state, whether it’s internal energy or entropy or any of the free energies, all of those things are fixed. However, in case of glass, since it’s a non-equilibrium state, even if we fixed pressure and temperature, volume in the glassy state can be different.

So, if I use two different cooling rates and arrive at the same pressure and temperature, so, let’s say atmospheric pressure 25 degrees Celsius, but I use different ways of cooling and subjecting the material to pressure and so, so, therefore, different thermal and mechanical history and so, they bring down the condition to 25 degrees Celsius and atmospheric pressure, the volume will be different.

So, this is another indication of the state being a non-equilibrium state. So, therefore, generally to specify the state of the system, additional variables are needed. Can you think what may be one possibility of additional variable what do we mean by additional variable when we think that we cannot specify the overall volume of a glassy state, if I just fixed pressure and temperature, what else may I need?

So for example, in crystalline state we ordering is perfect, but in case of amorphous, glassy state, we say that the ordering is random, but there may be a presence of local order. So this presence of local order can be different in different samples. And so therefore, there is a degree of local ordering that if we can quantify, then we can say that you know, that can be included as a way of specifying the state. So, this is one possibility and there are several such possibilities. And that’s why I have made the remark that as scientists, we are still grappling with the phenomenon of glass transition as well as characterization of the glassy state. So, though the ordering is liquid like local order is present. And because of this local order, the short range order, we can try to quantify some of the behaviour of the glassy state.

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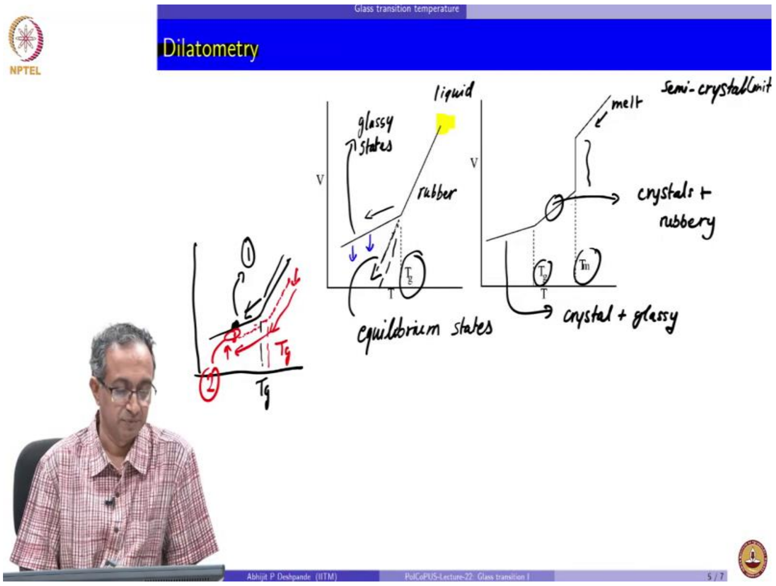

Glass transition temperature

Dilatometry

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So, let’s look at this qualitatively looking at how does volumes change as a function of temperature. And so, the technique is just measurement of volume dilatometry and if we start from a higher temperature, where the material is in the molten state, so, this is a liquid state, when we lower the temperature, we will reach the rubbery state of a macromolecule and then at a given temperature, which is the glass transition temperature, what we see is the volume does not go decrease as it would decrease for a liquid like arrangement, but it start decreasing at a lesser amount. So, therefore, this if we were able to obtain, these set of states if we were able to obtain then they would be the equilibrium states. And since, we cannot reach there, what we end up having is the glassy state. So, there is always a tendency for the material to go from these glassy state towards the equilibrium state and that is what we meant by the glassy state being a non-equilibrium state and possibility of relaxation processes however slow they may be the possibility of aging processes however slow they may be, they are definitely present and that leads to evolution of the material. Now, if we look at the same kind of behaviour for a semi crystalline material, so, we know that many of the polymers will have some amount of crystallinity, the semi crystalline material, we can be in the melt state and then when we cool the temperature at melting or fusion temperature, as we have already discussed, there is a first order transition, which is the crystal melt transition melt to crystal transition. And then we reach a state where we have crystals plus rubbery state combination. And then at the glass transition, we reach a state which is crystal plus glassy state. And melt of course, neither crystal nor glassy state exists, it is just one random set of macromolecules.

So, this is the transition, which happens when we go from one temperature to the other. And what I have already highlighted if we change the pressure, then actually some of these transitions will change. And so, just to as an exercise, you can think about this, that if I have let's say this an amorphous solid or a material, which has no crystallinity, this is where T g is observed. Now, if I take the material in the liquid state, molten state and increase the pressure on it, and when I increase the pressure on it, the volume will be lower. And now, if I start cooling it, so, the question is what happens, how does the volume will start decreasing and at what temperature is glass transition observed. So, what we already said was that the glass transition will be at a higher temperature.

And so, what we will see is the glass transition temperature will be observed at higher temperature and what we can also see is if I stopped the cooling and now revert back the pressure to atmospheric pressure, the sample will again recover, but it will not come back to exactly the same point which it would have been here. So, what happens is the sample here, which is the one which was this path and same sample but in another state2 where the path followed was this, then this and then release of pressure actually the volume of the sample is different. So, this is what we meant by non-equilibrium nature of glass and the fact that just because pressure and temperature is fixed, we cannot say what is the volume of the sample it depends on whatever is the thermal history and the other deformation history of the sample.

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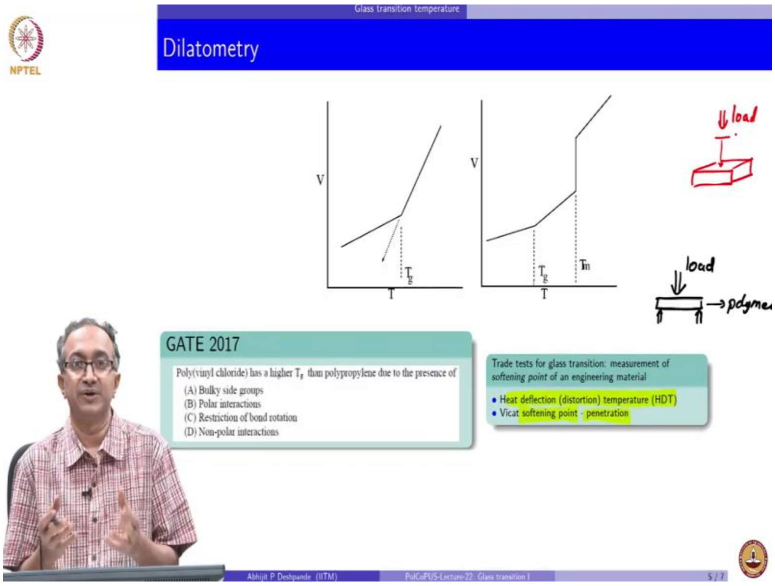

Dilatometry

GATE 2017

Poly(vinyl chloride) has a higher T_g than polypropylene due to the presence of
(A) Bulky side groups
(B) Polar interactions
(C) Restriction of bond rotation
(D) Non-polar interactions

Trade tests for glass transition: measurement of *softening point* of an engineering material

- Heat deflection (distortion) temperature (HDT)
- Vicat softening point - penetration

So, therefore, this is just to highlight that at a qualitative level glass transition temperature is due to segmental mobility and due to the changes in volume of the sample and it appears that at one particular temperature called the glass transition temperature, the volume versus temperature graph suddenly departs. And so, the question that we can ask is, you know, what leads to this glass transition temperature being higher or lower for a given polymer?

When we talk at a generic level all the polymers will have this glass transition temperature, but why for example, a polymer such as vinyl chloride has a T g which is higher than polypropylene? Is it because, the vinyl chloride has a bulky side group? Is it because there are polar interactions in this? Is it because there is some way there is a restriction of bond rotation and or is it because of some other interactions which are non-polar?

What you can see is each of this interaction is trying to highlight the fact that because of the interaction the segmental mobility is affected, and so, the temperature at which segmental mobility becomes negligible differs for polyvinyl chloride compared to polypropylene. So, you can think about it and try to reason out as to which of these may be the reason for polyvinyl chloride to have a higher Tg.

One thing about glass transition temperature is also that there are many trade tests, which can be used to quantify it and here I have just given two, one is called the heat deflection temperature and many times when we look at the datasheet of polymers, they will not mention a glass transition, but they will say HDT of the polymer is such and such, and from a practical designing point of view, this quantity is very useful. What is done in this case is you can just take the sample and apply some load on it, so, this is the polymer sample and certain load can be applied on it and one can start heating the sample and we can see at what temperature does the polymer sample start deforming, and that is why it is called a heat deflection or heat distortion temperature. Temperature at which there seems to be a significant amount of distortion and all of these things are fixed based on the trade test, the amount of load that is put the amount of deflection that has to be observed for the given size of sample.

So, it is a standardized way of measuring, softening of the material. Similarly, there is also Vicat softening point, which is taking a polymer sample and then just measuring penetration in it. So, you can take a polymer sample and then you can put a needle like system and then again you can apply load on it and you can measure the amount of penetration that happens and again change the temperature and whenever softening happens, the penetration will be higher and therefore, you can then quantify the characteristic glass transition thats happening in the material. Glass transition of polymers and these are whether HDT or Vicat softening points are related to each other. They are of course proportional to each other, but they will be at different temperatures, because in the end, volume versus temperature is a precise measurement, while load and deflection of a given size of polymer, they depend on the way the measurement is done. But however, trade tests are useful for engineering design purposes.

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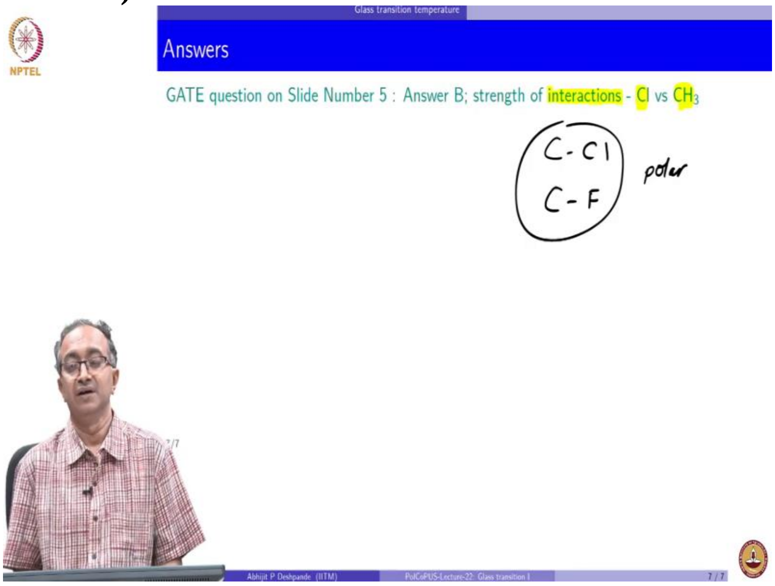

Glass transition temperature

Answers

GATE question on Slide Number 5 : Answer B; strength of interactions - Cl vs CH_3

C - Cl

C - F

polar

So just looking at the answer to the question, which was posed related to the glass transition temperature of PVC versus the polypropylene, so you can see that the side group, you can look at the sizes of these 2, and conclude for yourself that maybe size is not the factor which leads to PVC being higher glass transition temperature, so it is due to interactions.

But given that PVC has the higher glass transition temperature, the nonpolar interactions would be present in methyl group and CH2-CH2 chain also. So therefore, it’s the polar set of interactions ad CCL bond is known to be one of the polar bonds, CF of course, also is polar, strongly polar. And so, these are examples of polar bonds which are available in macromolecular system and these interact through electrostatic interactions because of the partial charge separation which is there and that leads to the reduction of segmental mobility.

Therefore, one has to go to higher temperature to get segmental mobility in case of PVC as opposed to polypropylene. So, with this we will close this lecture and we will continue the next lecture we will where we look at one of the classical theories called the free volume theory for glass transition and try to understand some more details about the glass transition. Thank you.