Basic Construction Materials
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Module No # 09
Lecture No # 42
Polymers and Composites – Part I

Hello everybody, today we will begin a new chapter in our course on basic construction materials. Now of course when we talk about basic construction materials, we essentially mean concrete, steel and asphalt. However increasingly we see the role of different types of composite which are made not just with these materials but also with other polymers and plastics. So it’s essential for us to understand the basics of polymers and plastics and how they are used to actually produce different types of composite materials.

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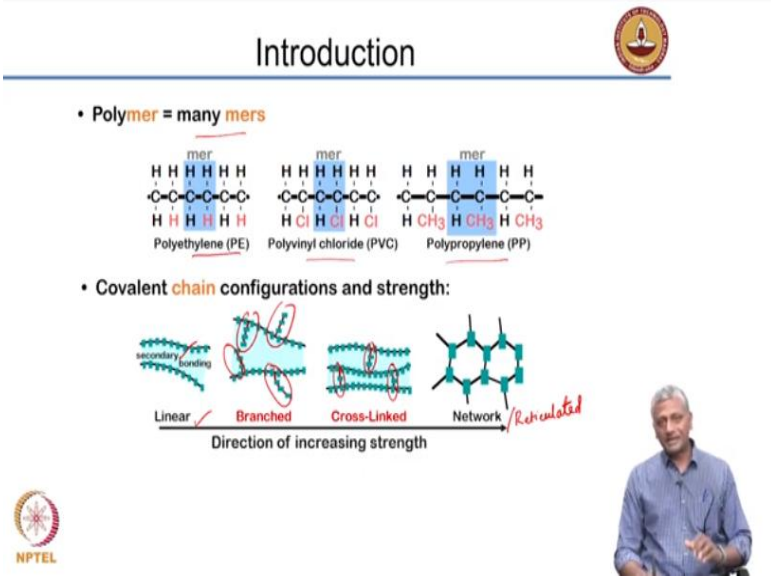

Introduction

- Polymer = many mers

Polyethylene (PE)
Polyvinyl chloride (PVC)
Polypropylene (PP)

- Covalent chain configurations and strength:

Linear ✓ Branched Cross-Linked Network /Reticulated

Direction of increasing strength

So to begin with, it’s just an introduction which probably will take you back to your school days where you learnt about different forms of organic compounds. That’s something that may be fresh in your memory because you would have recently finished your high school. So organic compounds obviously are those which are consisting primarily of carbon and carbon based derivatives.

So polymers are formed out of the combination of smaller units which we call as mers or monomers. A polymer simply means many mers or many monomers joined together. You can have the same type of monomers repeating itself or you can have 2 different types of monomers which combine together to form the polymer. Some of the common examples that you would have already come across in your school days, you have polyethylene.

Polyethylene is basically a polymer made out of chains of individual units of ethylene. You have polyvinyl chloride. The basic building block is still ethylene but then one of the hydrogen is removed and chlorine is substituting one of the hydrogen's. Then you have polypropylene. These are simple addition polymers. You also have condensation polymers where 2 different compounds can join together.

Now depending upon the type of formation, you can get different types of polymer structures and this is extremely important from the point of view of how these polymers actually behave. You have the linear structure where you have individual chains of these polymers which are somewhat loosely held together by secondary bonds. So these chains are mostly set apart from each other but they are loosely held by secondary bonding. You would have already learnt about secondary bonding in science. Here, essentially we talk about Van der Waals bond or hydrogen bonds and things like that.

Sometimes you may have sufficient development of the chain itself and then you may have branches coming out of the chain. That is, from the main chain you have branches. But still individual polymer molecules are still chained with branches. They are not joined to adjacent polymer molecules. So these are called branched polymers. The next higher level of arrangement is basically cross linking. You have one chain here, one chain here and you form a bond or a link between the two chains. That's called cross linked polymers. So you see here, these links are basically connecting the different polymer chains. Now obviously you can realize that this kind of a material will not easily flow. This kind of material, cross linked material will be stronger and stiffer as compared to linear or branched copolymers.

Of course the highest ever order or highest order in terms of polymers is the network or reticulated structure. It's also called reticulated structure. So here in the network structure, you are forming bond across the 3 dimensions. Essentially what this means is, you now have a highly ordered network.

So the type of material that you are dealing with will actually fall into one of these categories. Some of the common compounds that you find as polymers can be one of these sorts of structures. So if you think about the simplest ones like linear polymers, the examples are polyethylene and polyvinyl chloride. When you go towards polymers that are cross linked, one of the common example is the vulcanized rubber. And further when you go to the networked or reticulated structure, you will have compounds like bakelite which are extremely hard and stiff.

So these are examples of different types of compounds. And these structures will actually determine to a large extent what kind of behavior this material has. Primarily with polymers, we want to understand what happens when we heat these polymers. At high temperatures how do they behave? How does the engineering property change when the temperature is increased or decreased? So that's the major aspect that affects polymer behavior and that's what we will talk about for the most part of this lecture.

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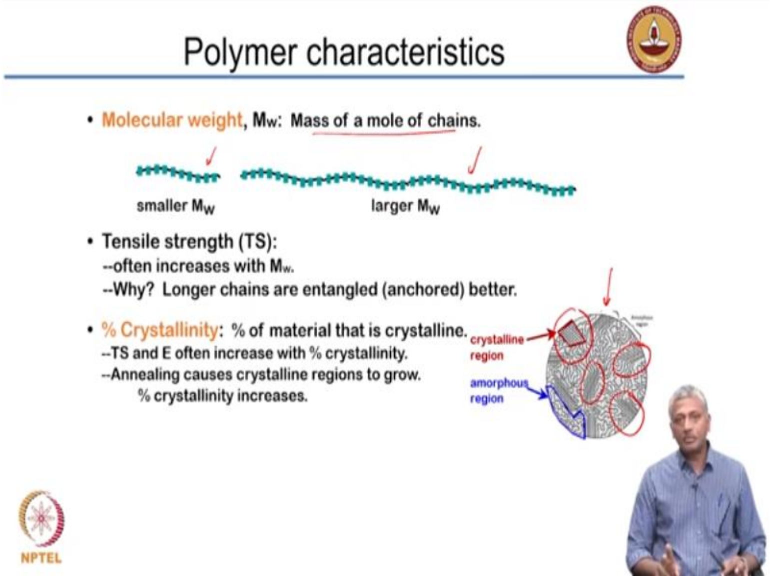

Polymer characteristics

- Molecular weight, M_W: Mass of a mole of chains.

smaller M_W larger M_W

- Tensile strength (TS):
  --often increases with M_W.
  --Why? Longer chains are entangled (anchored) better.
- % Crystallinity: % of material that is crystalline.
  --TS and E often increase with % crystallinity.
  --Annealing causes crystalline regions to grow.
  % crystallinity increases.

Now the number of chains or number of individual units that link together to form a chain contribute obviously to the molecular mass or molecular weight of the polymer. Molecular weight is nothing but mass of a mole of chains. So you have several chains together and if you take one mole of those, you get the overall molecular mass of the material. The individual chains may have smaller number of units together or larger number of units together. But if you take one mole, it will be composed of several chains of different lengths. So you can take the molecular weight as the average represented by all those chains together.

The engineering properties of these polymers depends a lot on the molecular weight. The tensile strength generally increases with increase in molecule weight. So as the molecular weight goes up, tensile strength also goes up. Why is that? Because just imagine a 3 dimensional network of these chains. If you have longer and longer chains, there's a good chance that these chains are anchored or interconnected. Even though there may be linear or branched, they need not be cross linked or networked, but what will happen is they will start intertwining with each other because these are long chains. So this intertwining will tend to increase the extent of strength that you can get out of this material.

So longer chains are entangled or anchored better. Tensile strength obviously depends on molecular mass. The other factor that's very important that governs the response to temperature as well as the mechanical properties is the crystallinity of the polymer. Apart from molecular weight, the other important parameter that you need to think about is the crystallinity.

Now, why we are talking about crystals when it comes to organic materials? A crystal is nothing but an ordered arrangement of atoms. Mostly what we associate crystals with are in naturally occurring minerals or naturally occurring ores or sometimes when we talk about steel, we talk about grains of steel or crystals of steel grains.

Now crystals are having an ordered arrangement of atoms. So in the case of the polymer, whatever section of the polymer shows a large order in terms of the way that the chains are arranged, that portion is called crystalline. When you have these chains in a disordered fashion, we call it amorphous. So if you take a look at the micro structure of polymer, there will be several regions. We have such regions where the chains have very definite arrangements, that is the crystalline region. In between the regions where chains are entangled and sort of disoriented, that is the amorphous region. Now how does this crystallinity affect mechanical properties?

The tensile strength and modulus of elasticity are seen to generally increase with the extent of crystallinity. The more crystalline polymer or the more ordered the arrangement of polymer, the greater the tensile strength and modulus of elasticity. Now similar to metals, in polymers also you can subject it to heat treatments like annealing. You might have learnt in the chapter of steel that annealing reduces the internal strains and leads to a slightly higher tensile strength of the steel.

Similarly, annealing of a polymer or heat treatment of a polymer can cause a growth in the amount of crystalline regions in the polymer and that will lead to an increase in tensile strength and modulus of elasticity. Very important to remember as far as polymers are concerned, the two major characteristic that determine the engineering properties are the polymer weight and the degree of crytallinity.

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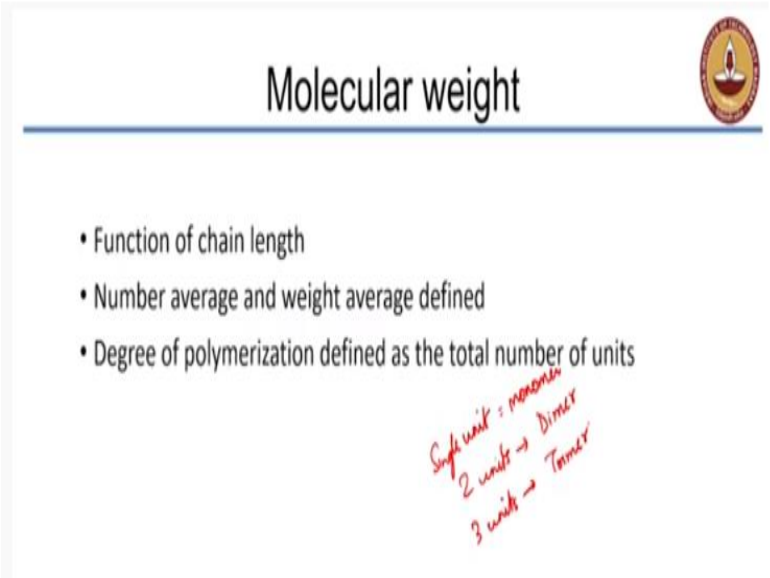

Molecular weight

- Function of chain length
- Number average and weight average defined
- Degree of polymerization defined as the total number of units

Single unit = monomer
2 units → Dimer
3 units → Trimer

Now again molecular weight, just coming back to the same concept, it's the function of the chain length. The number of units linked together in a chain will determine the molecular weight. Since I said you take the bunch of these chains together, you can either take a number average or a weight average. What do you mean by number average? So supposing you have number of units in a chain equal to 20, 30, 40 etc., in different chains. What you can say is, the molecular weight is defined as the number of units on an average in this polymer. Otherwise what you can do is take individual weights of the chains and then take a weight average of the polymer. So that's how you will define a molecular weight of the polymer.

The degree of polymerization is nothing but how many units are joined together. So when two units are joined, we call it a dimer. Of course a single unit is monomer. Three units joined together is called as trimer and so on. So polymer is simply an extension of the number of units that you have. So degree of polymerization just represents the number of units that are joined together.

Interestingly, you can control the properties that you get out of these polymers by controlling the number of units that can join together. And this is usually done during the processing of polymers by application of temperature and pressure and of course creating the right level of alkalinity in the system. We are not going to talk about that here, but just keep that in the back of your mind that you can actually process polymers to get different levels of polymerization.

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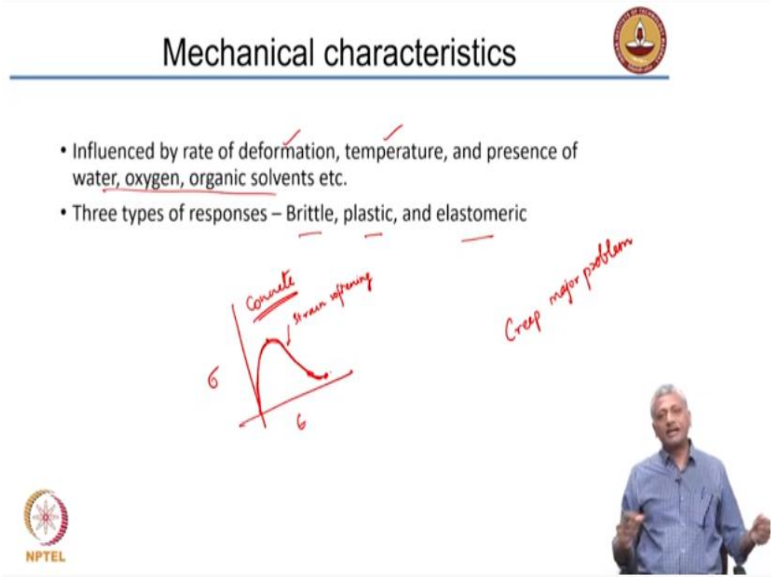

Mechanical characteristics

- Influenced by rate of deformation, temperature, and presence of water, oxygen, organic solvents etc.
- Three types of responses – Brittle, plastic, and elastomeric

Now as I said, the mechanical characteristics like strength and modulus of elasticity are dependent a lot on the polymer characteristics like molecular weight and crystallinity. The other factors that we may affect mechanical characteristics include rate of deformation, temperature and presence of water, oxygen and organic solvents. It is very interesting to know that in the case of metals and concrete none of this is that much of a problem.

Especially the rate of loading and temperature are not huge problem in case of metals. In concrete, the rate of deformation can lead to some interesting effects. The temperature is not so critical as far as concrete is concerned during the time of testing. But for a polymer, when you are testing the polymer, it has to be done at a well-defined rate of loading and at a well-defined temperature so that results can be comparable across labs and it has to be run in the condition that is free from the effect of these impurities. Otherwise you will get results that are completely different. You take the same polymer, you test it in different labs and if you just have a minor change in temperature, you can experience the major change in the mechanical characteristics that you measure.

And where is this applicable? In construction materials primarily we are talking about asphalt or bitumen which is used for road construction. Bitumen is nothing but a polymer. It’s a long chain polymer. If you don’t test bitumen correctly in different labs, you may get completely different results from the same sample of bitumen. That is not really an ideal condition. That’s why we need to define the test environment properly and the rate of loading has to be fixed.

Now why is the rate of loading important? We talked earlier in concrete chapter about creep. Creep is the response to sustained loading. When you continuously load a material for a very long time, you will see that it continues to deform depending upon its characteristics. It’s not so much a problem in metals. In concrete, it can affect performance of concrete structures. But in polymers, the creep can be significant. Creep is a major problem in terms of polymeric behavior because most polymers are extremely stiff. They don’t have a very high modulus of elasticity. As a result of that, they will be subjected to large amount of deformation when there is a sustained load on them.

Based upon the mechanical response that these materials give when you apply a load and test the deformation, you can get 3 different types of behavior. We call it brittle, plastic and elastomeric behavior. Of course we didn’t talk specifically about this with respect to concrete. In steel, you would have come across of course the strain hardening type of behavior that steel exhibits when you subject it to a tensile test. In concrete, if you plot the stress versus strain of concrete, you will see that mostly it is non-linear sort of a behavior and we call that as a strain softening behavior.

This is a subject of slightly different order ofcourse, maybe when you do an elective in concrete technology, you will probably look at all these aspects.

So this is a concrete behavior, it is called strain softening. We have some linear portion but mostly non-linear, it reaches a peak and then there is a drop. And then the material continuous to deform at lower load levels and then finally breaks apart. So that's called a strain softening behavior as opposed to steel which exhibits steel hardening. After yielding there is an increase in the amount of stress as the strain increases. That's because of internal rearrangement, movement of dislocations and so on. Let us not get into that detail here.

So in polymers, we exhibit responses that are brittle, plastic and elastomeric. For the most part, a brittle response simply means that sudden failure happens. Plastic response means that there's got to be a plastic flow or a long yielding before it breaks. And elastomeric response, which we typically see with rubber, is that it exhibits a very high level of strain at very low levels of stress. Let us look at these behaviors in just a minute.

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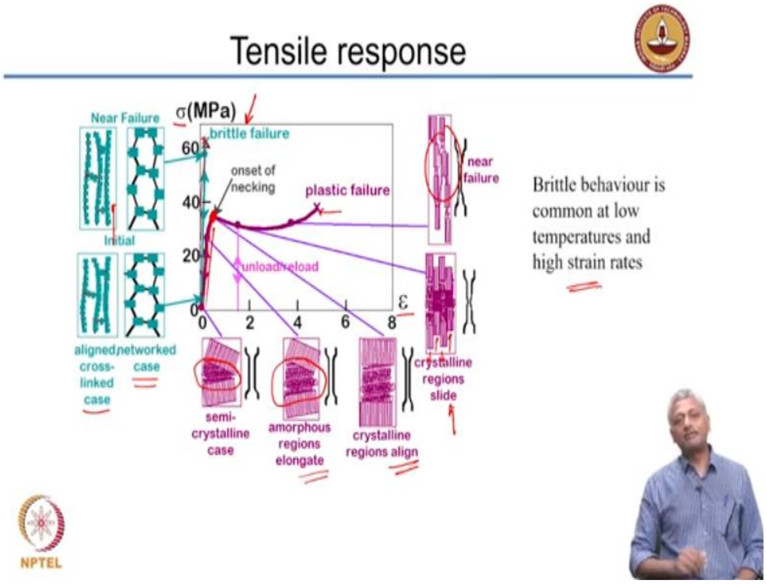

Tensile response

Brittle behaviour is common at low temperatures and high strain rates

So what is commonly plotted is a brittle and plastic behavior. This brittle behavior simply means that you have an almost linear stress strain relationship. What is plotted in the y-axis is the stress and x-axis is the strain. And what you see here is that, for brittle material you have a continuous increase in the stress and then finally the rupture happens when you exceed the strength capacity of the material.

Mostly what you will see is that this kind of a behavior is exhibited by aligned cross linked polymers as well as networked polymers. So the higher the degree of order in the polymers, the more brittle they become. It's easy to imagine because these are highly connected structures. So if you have to deform that, you may have to break the bond.

On the other hand, when you talk about linear or branched polymers, you have sufficient pliability and these chains can move past each other. And because of that, you get a lot of plasticity or flow from the linear and branched copolymers. On the other hand, for cross-linked and reticulated materials, as you near failure, the bonds starts breaking. The bonds between the atoms will start breaking and as a result you get a brittle failure.

Let us see what happens in a linear and branched polymer. In the case of linear and branched polymers, there are amorphous regions and then there are crystalline regions. In some regions, the branches or the linear chains are arranged quite nicely and in other regions they are entangled and don't really have a good shape. So what happens now? In this case, as you load, you are going up in terms of level of stress but what starts to happen at that point of time is that you start aligning, that is, during this process you start aligning the entangled chains.

So you have some crystalline components which are not deforming but the amorphous region on the polymer where you have an entangled chain basically starts to stretch. And that is what it is happening in this pre-peak region. So what is happening is amorphous regions are elongating and causing and leading to the distribution of the stress better. And then you have an alignment of the crystalline regions at the point of the peak. When you have an alignment, the next step is that you have a continuous deformation and then the crystalline regions that have so formed will start to slide against each other. So you will have the sliding of the crystalline regions as you continue to load.

Once the sliding comes to a level which cannot be contained further, you have a rupture. That's what you see here in the case of a rupture. So that's a plastic behavior. You have a slow growth up to the point of maximum stress and that is where your polymer has been completely aligned, that is, it is taking maximum load at this point. Beyond that, the polymer is almost entirely crystalline and the region starts sliding past each other. Please remember these are connected by weak bonds, so there will be sliding between the chains. There's not going to be any breakage of the bond but sliding between the chains. But near failure, you will probably get close to a breakage sort of behavior. So that's essentially a plastic failure.

Now brittle behavior is common at low temperatures and high strain rates. Even a polymer that would otherwise exhibit plastic behavior, if you test it rapidly, if you test it very fast, it will exhibit brittle behavior. A polymer that is still flowable if you test it at very low temperature, it becomes hard enough and rigid enough that it starts exhibiting brittle behavior. And this is a problem.

Now when you deal with common polymers, let us say you have your water bucket, you will see that with multiple uses the buckets starts cracking. Why does it start cracking? It's because the material has been more and more brittle. In response to age, it has become brittle; age implying exposure to ultra violet radiation. That's another aspect that can change the properties of the polymers significantly. But then as far as elastic response is concerned, brittle behavior can be commonly observed in low temperatures and at high strain rates.

Again applying this to the example of pavements or roads where bitumen is used. If the bitumen in the pavement serves in a condition where temperature can change significantly between 30 to 40 degrees Celsius to all the way to negative temperatures, what will happen in that case when you go to negative temperatures? The behavior of asphalt will become very different. It will have low temperature thermal cracking or brittleness will be introduced and there will be cracking in the pavement because of the cracking of the polymer, that is the bitumen.

So all these are practical connotations. Whatever you learn in the basic understanding of construction materials will have connotations to how these materials actually behave in real life applications.

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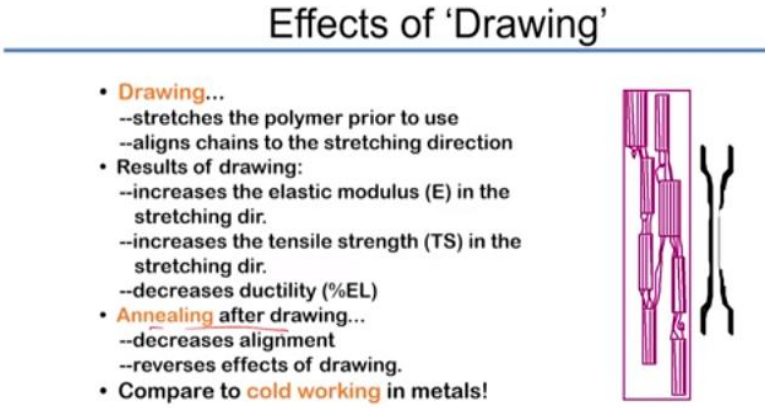

Effects of 'Drawing'

- Drawing...
  - --stretches the polymer prior to use
  - --aligns chains to the stretching direction
- Results of drawing:
  - --increases the elastic modulus (E) in the stretching dir.
  - --increases the tensile strength (TS) in the stretching dir.
  - --decreases ductility (%EL)
- Annealing after drawing...
  - --decreases alignment
  - --reverses effects of drawing.
- Compare to cold working in metals!

Now, we talked about the fact that in the case of linear and branched polymers, you have a slow alignment of the polymer chains. What if you take this polymer and do this alignment process before and then subject it to loading? In metals, in steel especially you would have talked about a concept called cold working. So what is done in cold working? You have your steel and you are basically stretching it and increasing the extent of strain in the material so that it overcomes the yielding and then you unload it. So what happens the next time you load it? you directly make the material enter the strain hardening region.

Now similar to cold working, there is a concept called drawing in polymers. Drawing is basically stretching the polymers prior to the use. So what you end up doing as a result of this is that you make the materials stronger and stiffer. That is, you increase the elastic modulus and you increase the tensile strength.

However just like cold working in steel, the effect of drawing on ductility is negative. You make the material less ductile. Please remember the cardinal truth in more materials is that when you increase the strength, you will generally compromise on the ductility. When you increase strength ductility will be compromised. You will be reducing ductility when strength increases.

Again in polymer, you can also do annealing after drawing. That means heat treatment after you do the stretching. That will tend to remove some internal strains and that may tend to reverse the effects of drawing and that may increase the extent of ductility you can get from these systems. But for polymers we are not really that highly worried about ductility as we are with steel.

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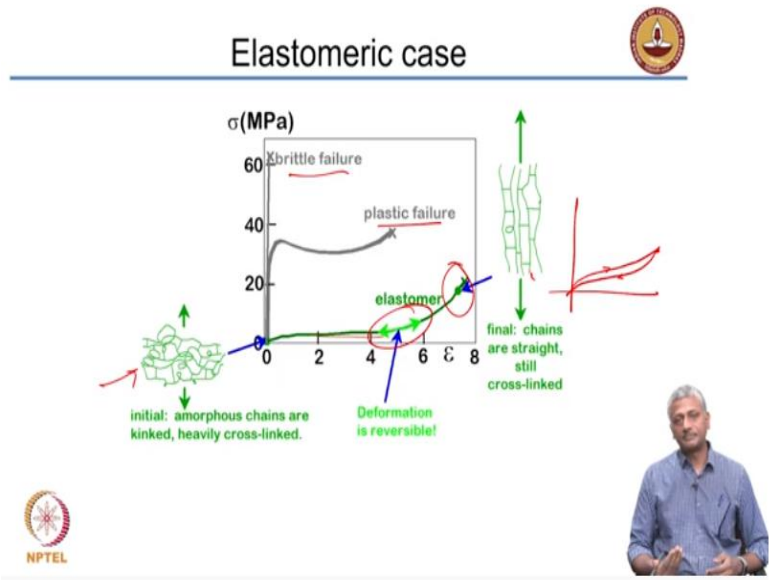

Elastomeric case

initial: amorphous chains are kinked, heavily cross-linked.

Deformation is reversible!

final: chains are straight, still cross-linked

What about elastomeric? Again the brittle and plastic have been plotted here just for an example to show you the stress levels. But if you look at the elastomeric case like for example when you have amorphous chains that are kinked and heavily cross linked like in rubber, if you increase the load, the strain increases significantly. There is an anomalous increase in the strain for very small increases in the stress.

And this deformation that you see, that is, the increase in the strain is actually reversible. So when you unload, the material will go back. So as the material will go up like this and if you unload at this point, it will come back. It may not come back across the same path, it may exhibit what we call as hysteresis but it will come back to the point 0. That means it will have no deformation when you remove the load. So there is no plastic flow happening here but there will be ultimately failure when you straighten up the chain significantly and then the chain starts rupturing.

So rubber, which is cross linked or vulcanized rubber, which is a cross linked polymer, there you are producing basically an elastomeric material which exhibits high levels of strain at low stress levels. And these strains are recoverable, reversible.

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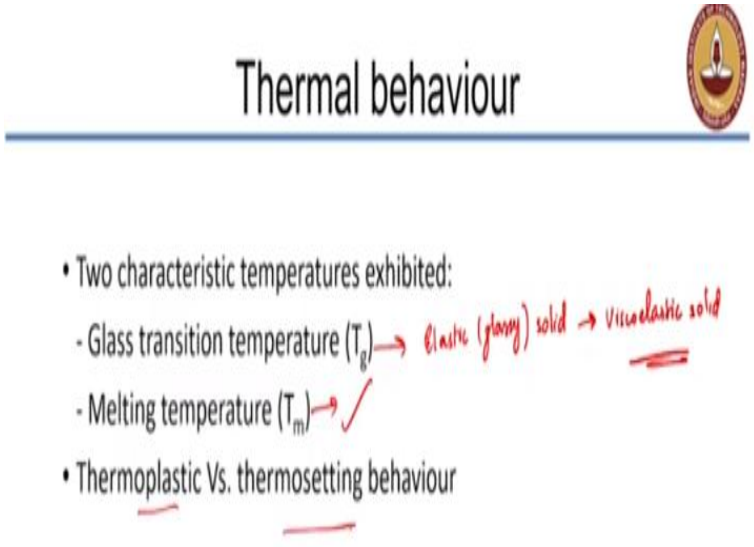

Thermal behaviour

- Two characteristic temperatures exhibited:
  - Glass transition temperature (T_g) → Elastic (glassy) solid → viscoelastic solid
  - Melting temperature (T_m) → ✓
- Thermoplastic Vs. thermosetting behaviour

So we looked at mechanical behavior of polymers. Now let’s talk about another important characteristic that is the thermal behavior. Most polymers which have crystalline and amorphous regions would exhibit two characteristic temperatures. You will have a glass transition temperature and a melting temperature. Now just let us define this. Ofcourse melting is something that you are all familiar with. You know melting simply means that the material becomes almost liquid like and starts flowing.

But a glass transition temperature is very interesting. So what does glass transition temperature mean? Let us say you have material at room temperature which is extremely solid, which is a real solid almost an elastic solid type material. When this material undergoes an increase in temperature, at one particular temperature it may start becoming more deformable. And then you continue to heat the material, at one particular temperature it may start becoming almost liquid like.

So what is happened is there are 2 transformations that have taken place. One is from an elastic solid to a viscoelastic solid. That means it starts flowing, it is still solid but it starts flowing. But the other temperature, much higher temperature is the melting temperature where this viscoelastic solid has become a liquid. But of course materials usually exhibit several ranges of transformations but these are the 2 important transformations.

So glass transition means that material changes from elastic or glassy solid to viscoelastic solid. That’s the glass transition temperature. Again it has got practical connotations. For example if you are using plastic pipes to carry hot water. Depending upon the type of plastic and its glass transition temperature, you may actually not be able to push hot water through certain types of pipes. Why is that? Because at some temperature of the hot water, let us say you are putting boiling water at 100 degree Celsius through the pipe. At that temperature, some polymers may undergo this glass transition. That means they are changing their behavior from a hard elastic solid to a viscoelastic material. So your pipe will start getting bent and warped because your shape is going to change when it starts flowing at that high temperature.

Again something very commonly observed when you actually take a PTFE bottle or water bottle, you empty the bottle and fill up hot water in it. What you see happening? You see that the material gets deformed and it is very easy to press the bottle. When you have cold water in it, the bottle will rather become stiff and hard. But when you fill hot water in it, the plastic basically undergoes a change in its temperature. That is why you should not fill up extremely hot water in the regular plastic water bottles. There are specialized bottles available which are a lot more temperature resistant.

Another behavior that you would have learned before is the thermoplastic versus thermosetting behavior. Thermoplastic simply means materials that exhibit flow as you increase the temperature. A thermosetting behavior relates to those materials that do not show any change with an increase in temperature until a point where they simply burn off. So those are the two characteristics that are exhibited by different types of polymers. Let us take a look at what types of polymers exhibits what characteristic?

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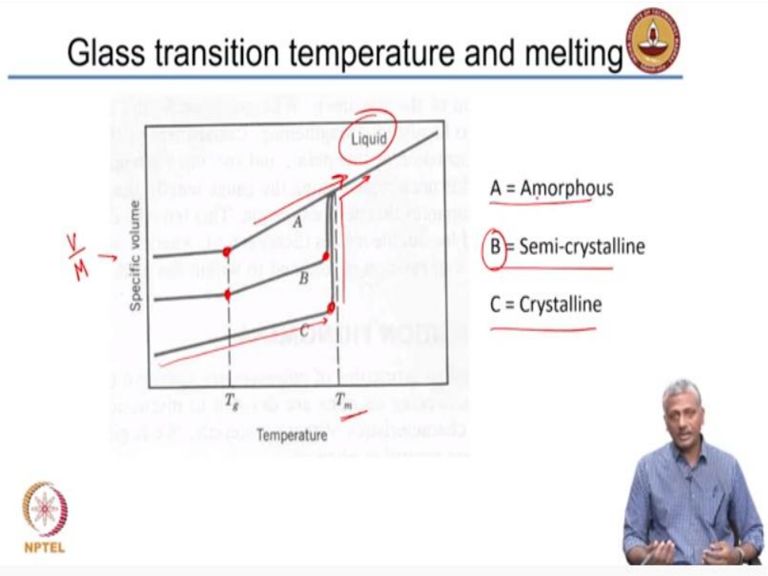

Glass transition temperature and melting

A = Amorphous

B = Semi-crystalline

C = Crystalline

Again just to reemphasize this aspect about glass transition temperature, what is plotted in the y-axis is specific volume (Specific volume is nothing but volume divided by mass. It is the inverse of density) against temperature. Now you know very well when solids change to liquid what happens? Solids have a smaller volume for the same mass. In liquids, you have a greater volume for the same mass. That means as the material turns into a liquid, the specific volume which is inverse of density should go up.

So let us look at the 3 different cases. A is amorphous, B is semi-crystalline and C is crystalline. In the case of crystalline material, as you increase the temperature, you do experience some increase in specific volume but you do not see any transition happening in the material until you reach this temperature and it suddenly transforms to a liquid phase. And that is your melting temperature.

In the case of an amorphous material where all the chains are disordered, you will experience the glass transition. The material will experience the glass transition but beyond that it will have almost a liquid like behavior.

On the other hand in most polymers which are semi-crystalline, you will exhibit both glass transition as well as melting. At glass transition you will have a sudden change in the rate of increase of specific volume and at melting obviously you will have the most major change in the rate of increase of specific volume.

So when you consider different types of polymers, you will experience different types of behaviour. Again just to think about the example of this, amorphous would relate to linear or branched polymers. Now the same linear and branched polymers could also exhibit semi-crystalline behavior, assuming that there has been some heat treatments and some drawing and all done with these materials.

But in the case of cross linked and reticulated structures or networked structures, you will mostly exhibit the crystalline behavior where you just see melting. There is no glass transition happening there.