Physico - Chemical, Mechanical and Electrical Properties of Polymers
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Lecture – 43
Plasticity

So, welcome to this course on polymers, where we are looking at the properties, the usage, the sustainability as well as concepts associated with polymers. In the week which was earlier and this week, we are digging deeper into the understanding related to properties of these polymeric materials. And we focused on mechanical properties and also looked at physico-chemical interactions in case of polymer solvent systems.

And we have looked at conducting polymers as well as the polymers for dielectric response when we use them as insulating materials. In this particular lecture, we will again come back to mechanical performance and look more closely at the phenomenon of plasticity. In fact, given that many kinds of polymeric systems are called plastics. So, it should give you a hint that plasticity is fairly important in the deformation of various polymeric materials. So, our focus will remain of course, on looking at the mechanical properties.

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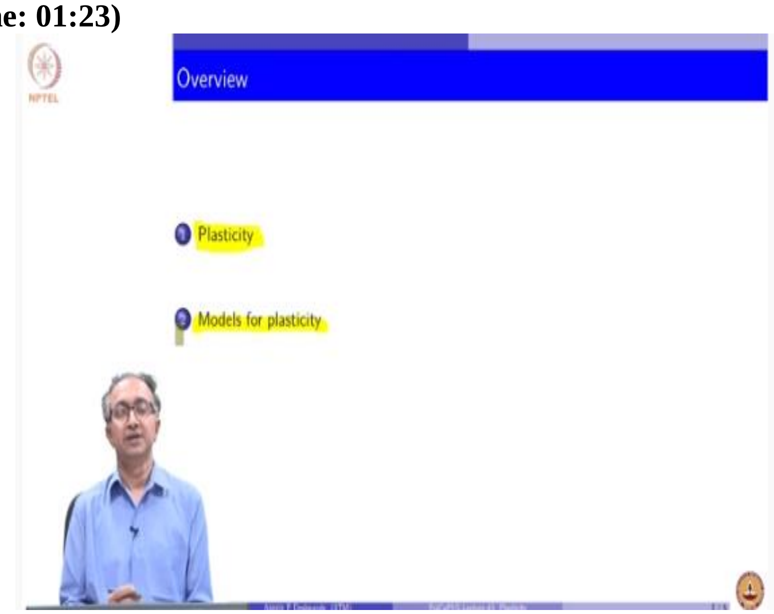

What we will do is look at plasticity, what it means in the context of polymers and then look at the models, simple models which can be used to describe the stress strain relationship in a plastic material.

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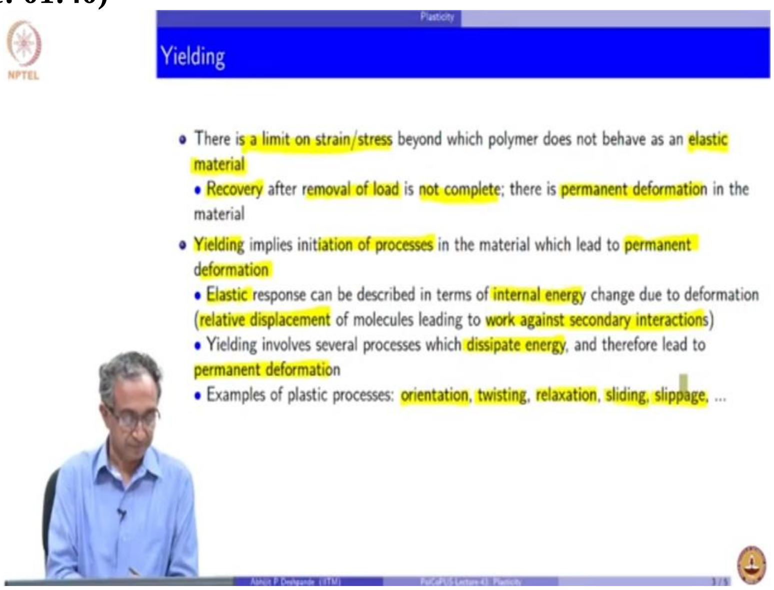

So, yielding is a phenomenon which is central to plasticity. So, what we have in material is that, there is a limit on strain or stress. So, there is an amount of strain let us say 2% or 10s of mega Pascals or a few mega pascal's in case of weaker polymers. So, these materials can withstand only certain amount of strain or stress beyond which the elastic deformation is no longer valid. The elasticity in this case, what we imply of course, is that state of stress is defined by the state of strain alone. And, this also implies that if stress goes to 0, then strain also goes to 0. So, that is what we mean when we say there is a recovery. So, when we go beyond this limit of this strain and stress recovery after the removal of load is not complete. And that implies that there is a permanent deformation in the material. So, plasticity is associated with permanent deformation or deformation which is not recoverable. And therefore, yielding implies initiation of processes in the polymer, which leads to permanent deformation. So, yielding of polymers implies that at the macromolecular level at the microstructural level the deformation leads to phenomena which lead to permanent deformation.

So, what could be these phenomena which happen at a macromolecular scale? If you remember, most of the plasticity will be associated with polymers which are below their glass transition temperature, which means segmental mobility is absent. In case of rubbers, plasticity is irrelevant because segmental mobility is there and we generally observe largely elastic behavior in the context of stress strain curves, as we saw in the 32nd lecture also.

So, therefore, glassy state and chains in the amorphous material seemed to be amenable to plasticity. Similarly, semi-crystalline polymers in their glassy state where there will be a mixture of amorphous and crystalline states, again plasticity can happen. And so, basically, when we look at it from an energy point of view, the elastic response is described based on internal energy. So, when we deform the material pull the atoms and molecules apart the internal energy changes. And therefore, when we release the load, the material comes back to minimize the energy. So therefore, relative displacement of molecule is involved and this relative displacement happens against the secondary interactions which are there between atoms and molecules. So, therefore, yielding will involve taking these atoms and molecules overcoming the secondary interactions and displacing these molecules such that they do not come back.

So, therefore, yielding necessarily involves dissipation of energy. So, molecules take this energy the mechanical energy which is being imposed on the material, molecules will change their conformations and adopt a new conformation and therefore, they have absorbed the energy which was input. In the case of elasticity, the molecules only get displaced with respect to each other. So, therefore, their secondary interaction has to be overcome. But in this case now molecules or microstructure adjusts itself, changes itself in response to the load which is being applied and because these changes are permanent because the material is after all in the glassy state. So, in general segmental mobility is not there, the crystalline domains cannot move, but because a load is being applied, the chains can start orienting or the crystals can start orienting. Once they orient due to load, they cannot come back because segmental mobility is not there.

So, therefore, permanent deformation is associated with yielding. And so, as I mentioned, we can have orientation of chains, we can have chains twisting, we can have chains relaxing over some amount of deformation, and we can have crystals sliding over each other slippage of different domains with respect to each other. So, these are phenomena which are all dissipative in nature in the sense that the mechanical energy which is put on the material to deform is being taken up by the material and therefore, recovery is not possible.

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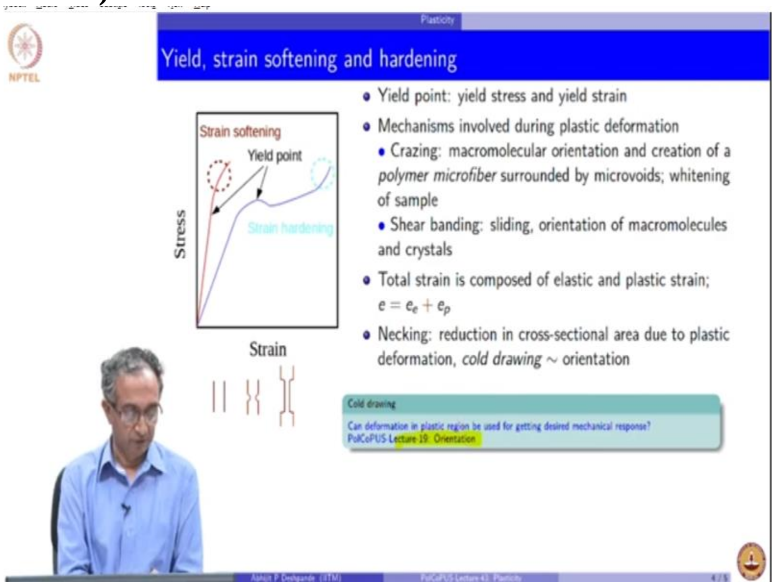

So, if you look at a stress strain graph, we know that the initial low strain limit of course, is elastic, but beyond a certain point, you can see in this case here, the non-linearity starts coming in and what is also evident in such a feature is if I unload the sample from here, it is most likely to come back to a non-zero strain and this is really the permanent deformation that we talked about.

So, this is the permanent strain, which is there in the material. And there are different types of deformation stress strain relationships that can exist depending on the mechanisms of plasticity in the material. So, here for example, there are two types, which is being shown there is strain softening, in which case the stress strain, there is proportionally less stress required for more and more strain. But we can also have strain hardening, in which case more and more stress is required as we apply more and more deformation. So, therefore, these strain softening and strain hardening would depend on what is the mechanism that is at play, while the orientations stretching, twisting or slippage all of those phenomena that are taking place.

Can you think of why would the strain hardening occur in case of semi crystalline polymer or also in case of an amorphous polymer. So, what would be the reason that it becomes progressively more difficult to deform the material as plastic deformation takes place? The other feature you can think of is this there seems to be a prolonged the large amount of deformation which the material takes in while the load relatively remains constant. So, the load is pretty much remaining constant in this region while deformation continues to happen. In fact, this is perfect plastic behavior. And if you can think of the mechanism that we talked about whether when there are crystal planes crystallites in the material and of course, they will be attached with each other with some amorphous polymer. Now, if they start sliding, so, one crystal starts sliding with respect to each other, what happens is a certain amount of load is required before the slippage can happen. But once the lead that loads is reached, slippage can continue to happen. So, this is a perfectly plastic phenomenon. So, therefore, many polymeric materials show this reasonably less change in stress for a reasonably large amount of deformation. So, this is where those untwisting of chains or slippage of crystal planes and all of those phenomena happen. And once these phenomena happen, the orientation in the sample is such that everything gets oriented in the direction of which the stress is being applied.

And therefore, then the strain hardening happens, because now it requires since everything is oriented in the direction of the sample, so it becomes harder and harder to pull the sample. So if you think of it in case of rubber, strain hardening is also observed. Initially, it is easy to pull a rubber band, but when you stretch it more and more, it becomes more difficult. So, in that case, also, it is the chain orientation, which leads to strain hardening. In this case, it is also crystal orientation or chain orientation, which leads to strain hardening. So, therefore, yield point is associated with the yield stress. So, in this case, we can look at the two yield stresses which are there. So, this is somewhere there is a yield stress and yield strain. And similarly, in this case also we have generally, depending on the definition and the material and the type of response that’s there, we will have yield stress or yield strain associated with the material.

And generally this is reasonably large for many of the polymeric materials. For example, 3%, 4%, 5% strain is there before elastic limit is exceeded, and the mechanisms that are also involved during the process is orientation of and sliding of crystals, which is valid more in the case of semi crystalline polymer, but also in case of amorphous polymers, we have the phenomenon of crazing. Actually, this leads to whitening of a sample. And I am sure a lot of you have seen this that if you take some polymer films and if you stretch it, it starts becoming white, and what that is due to is the macromolecules start orienting themselves. And due to this orientation, there all of macromolecules which are starting to get oriented towards each other, they form a fibril. And because the chains are coming together and getting oriented, there is a micro white formed between the microfibers and that is what leads to whitening, because whenever you have these density fluctuations, so, we have a region of polymer and then there is gap and then there is another fiber. So, therefore, due to these density differences in the material, light scattering takes place and material becomes white. So, both the crystal sliding and chain orientations and such phenomena are important during plastic deformation as well as crazing, depends on the polymer.

So, the total strain generally in the material is composed of the elastic and plastic strain. So, general understanding we have is there is an amount of strain which is elastic and it can be recovered and then there is a permanent deformation. And one of the important phenomena that we ought to understand during this because of all these sliding orientation and because of the phenomena that is happening, what happens is the polymer sample starts reducing in cross section and this phenomena is called necking. So, reduction in cross sectional area due to plastic deformation. We also use the term cold drawing to describe this. So, sometimes if we have made a fiber and we would like to make it even stronger, what we can do is basically do plastic deformation. So, we can stretch the fiber to much more extent than what its original diameter was.

$$e = e_e + e_p$$

And then due to orientation that happens in the polymer fiber, we can get a much stronger fiber. So, therefore, cold drawing is a standard way of improving mechanical properties of fibers and sheets by achieving a specific orientation. And of course, this we have already seen in lecture 19, where we looked at how orientation in a polymeric sample can be influenced.

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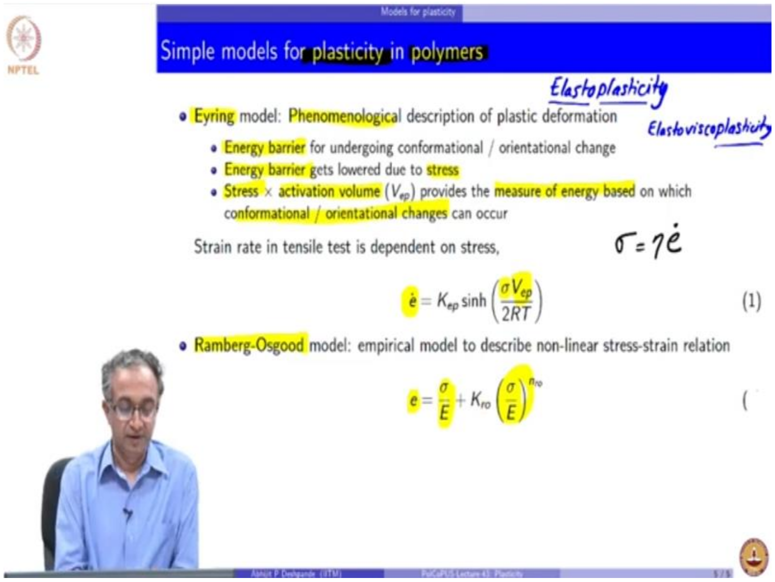

So, the simple models which are useful to describe the plasticity in polymers, it's a plasticity by itself is a fairly complicated phenomenon for two reasons. One, we have to look at all the dissipative mechanisms that take place and though inwards it seems fairly easy to describe that you know, there is orientation of chains or there could be crystal slippage and crystal orientation. To describe them mathematically using equations is quite challenging because how do we quantify orientation, how do we quantify the extent of slippage, if there are defects in crystals, if the defects are themselves also migrating then how do we quantify that? So, in general the phenomena of plasticity is quite challenging to describe. The other aspect related to plasticity in case of polymers is that the viscous nature is also always there.

So, you might hear the term in metal context describing elasto-plasticity and as the name suggests, it is a combination of elastic and plastic behavior. But in case of polymers, what we need to really look at is elasto-visco-plasticity. So, plasticity implies that the phenomena that we talked about, where we have chained twisting or crystal orientation and things like that, viscous phenomena will imply the segmental relaxations and segment conformation changing and so on, so which are very important in case of polymer. So, many times it is difficult to ignore viscous effects during understanding of the plasticity in case of polymeric materials. And of course, elasticity is always involved because at small deformations, the material is elastic and even when we impose large deformation part of the deformation is elastic. So, one of the ways in which we can make hypothesis regarding plasticity modeling and both the models which are discussed here are used for a variety of materials including polymers.

So, these are both phenomenological descriptions by which we mean is since we know the shape of stress strain curves and since we know the kind of stress strain behavior that is shown by many plastic materials, we can try to capture it using mathematical equations. So, the hypothesis behind Eyring model is that there is an energy barrier for undergoing the plastic processes. So, for example, for a slippage to happen, there is an activation energy barrier or for a conformational change to happen, twisting of the chain or unravelling of the chain, for these phenomena to happen, there is an activation energy barrier and this activation energy barrier is lowered because of stress. So, the material is always has a tendency to have plastic deformation, but when no stress is applied or when less amount of stress is applied, these plastic mechanisms do not really take place because of the energy barrier, but as soon as stress is increased beyond the point, the energy barrier is lowered and then what happens is these phenomena start happening. So, therefore, there is a hypothesis of an activation volume and that multiplied by the stress gives you the measure of energy based on which these changes these plasticity mechanisms can happen. And so, based on such hypothesis of the material response, the strain rate in the material is related to the stress and of course, the activation volume as the hypothesis is.

$$\dot{e} = K_{ep} \sinh\left(\frac{\sigma V_{ep}}{2RT}\right)$$

So, here you can see clearly one aspect as soon as we are discussing non-elastic response rates start playing a role. So, in this case, we have strain rate dependent on stress. Similarly, in case of Newtonian fluid also, we will see of course, that sigma is related to viscosity times strain rate. So, viscous and plasticity effects, the rate effects play a significant amount of role, while in case of elasticity, only the present state of strain matters and therefore, rate effects are completely irrelevant.

Now, the complication with polymers is that they can show elastic behavior under some strain conditions and they may show plastic behavior under some other strain rate condition and therefore, we always need to look at what are the timescales of our experiment in relation to what is the timescale of the material. And this idea of course, we will discuss lot more when we discuss phenomena of viscoelasticity.

The Ramberg-Osgood model is a simpler model, which just says that the overall strain is summation of an elastic strain and then just power law nonlinear strain and when you sum both of them, you can get the overall strain. So, with this we have scanned the mechanisms associated with plastic deformation in polymeric materials. It is important for both amorphous as well as semi crystalline thermoplastic materials.

$$e = \frac{\sigma}{E} + K_{ro}\left(\frac{\sigma}{E}\right)^{n_{ro}}$$

In thermosets, we will not observe plastic deformation and I hope that you can try to rationalize this as why would this be the case that thermoset polymers will have mostly elastic deformation and then there will be failure, there will not be any plastic deformation. So think about it. We will resume our journey of polymers in the next lecture. Thank you.