Introduction to Polymer Science
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Module No # 08
Lecture No # 38
Thermo-mechanical Properties, Viscoelasticity

Welcome back, in this lecture, I will discuss about thermos-mechanical properties of polymers and we will start discussing about this viscoelasticity.

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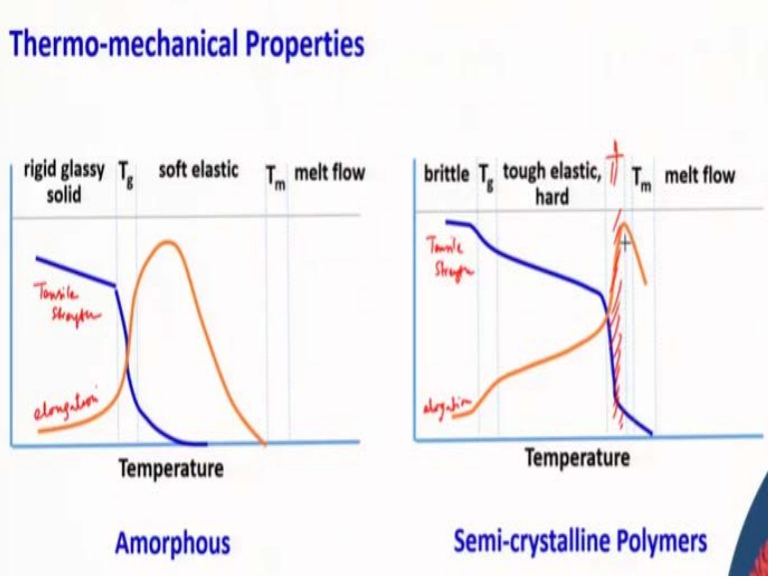

Thermo-mechanical Properties

Amorphous

Semi-crystalline Polymers

When we talk about thermo mechanical properties, we mean that dependence of mechanical properties on temperature. If we look at this diagram, this is for a completely amorphous polymer, this blue line shows tensile strength and this is elongation. With temperature, you can see that the tensile strength slowly comes down before it reaches the region where the temperature is around the glass transition temperature. In this temperature range the tensile strength drops drastically and if it is purely amorphous, it becomes polymer melt. Whereas elongation slowly increases, but at the glass transition region the elongation goes up before it peaks above certain temperature and then again, it drops. If you look about semi-crystalline polymer then we will have similar drop in tensile strength, elongation. So, in this case also we will have some drop in tensile strength around T_g and we will have increase in elongation value around T_g.

But because it has also crystalline regions, the decrease in tensile strength will not be that high as in case of 100% amorphous polymers. Of course, this drop will depend upon the extent of crystallinity present in the sample. Just before the T_m, melting point, this region is where the flow happens, and the tensile strength drop drastically above the melting point, the polymer becomes like a molten polymer.

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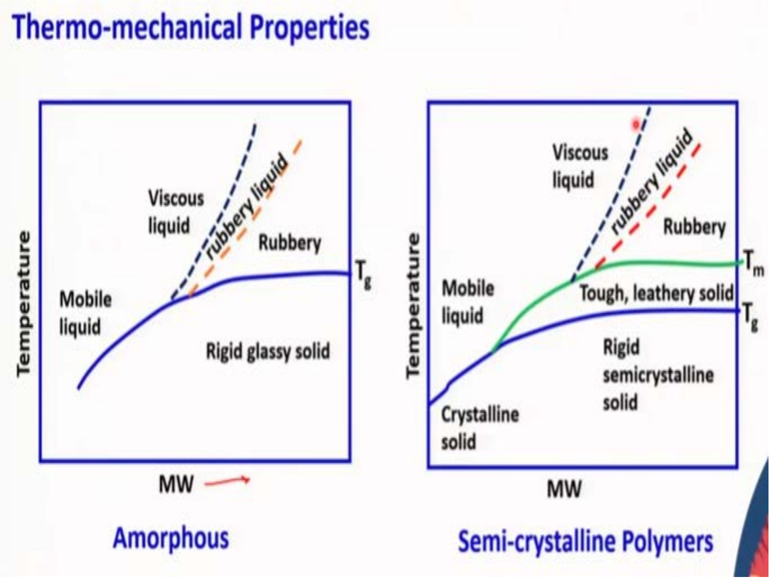

Thermo-mechanical Properties

Amorphous

Semi-crystalline Polymers

If we look about the temperature dependence on the behavior of polymers, again we consider at the beginning about 100% amorphous polymer. And in this case, we see the dependence of mechanical property or mechanical behavior on temperature as well as molecular weight. When the molecular weight is very low, the transition happens from rigid glass to mobile liquid above the glass transition temperature. This line is the temperature dependence of glass transition temperature on molecular weight, so when we have sufficiently high molecular weight in which case the T_g almost independent of molecular weight. In that case, if we increase the temperature, we move from a rigid glassy solid to rubbery state and then rubbery liquid and finally viscos liquid as we increase the temperature of the polymer sample.

In case of semi-crystalline polymer when the molecular weight is very low, we cannot call the sample as polymer, we can call this as oligomer, it might crystallize at high extent. Then if we go above this melting point, it goes from a crystalline solid to mobile liquid. Now if we go and take a sample of higher molecular weight, in that case, as we increase the temperature the sample goes from a rigid semi crystalline solid to a leathery tough solid to rubbery region and then rubbery liquid to finally Viscos liquid region.

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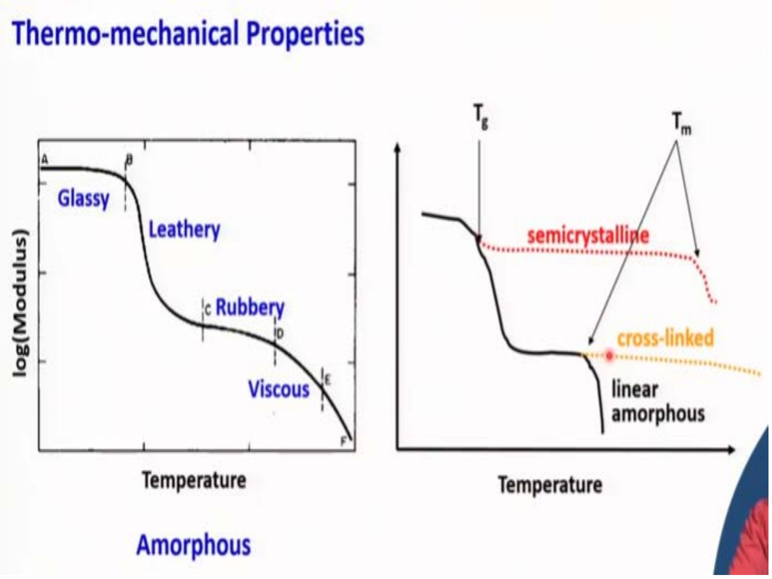

Thermo-mechanical Properties

We can plot this same thing in a different way where we plot modulus or log(modulus) as a function of temperature. And in this case, as you can see, that for a pure amorphous polymer at low temperature it behaves like a glassy polymer, and after the glass transition it behaves as a leathery tough material. After which we have a rubbery plato and then we get a viscos flow of the material.

If you have a semi crystalline material, then as we have seen that this drop in modulus at Tg is not that high because of the presence of crystalline domains. Y- axis is log of modulus, and in this case the rigidity or the tensile strength is maintained till it reaches the melting point after which the modulus decreases sharply and the polymer becomes a polymer melt. If you have a cross-linked polymer then after rubbery region there is no further decrease in modulus, the log of modulus values or modulus values remains little elevated because the flow of the polymer molecule is restricted because of presence of the cross-links between the polymer chains. So, whereas for a linear amorphous polymer the modulus comes down drastically after T_m, for a cross-linked material it will remain slightly elevated and obviously as the cross-linking density increases this might even go up.

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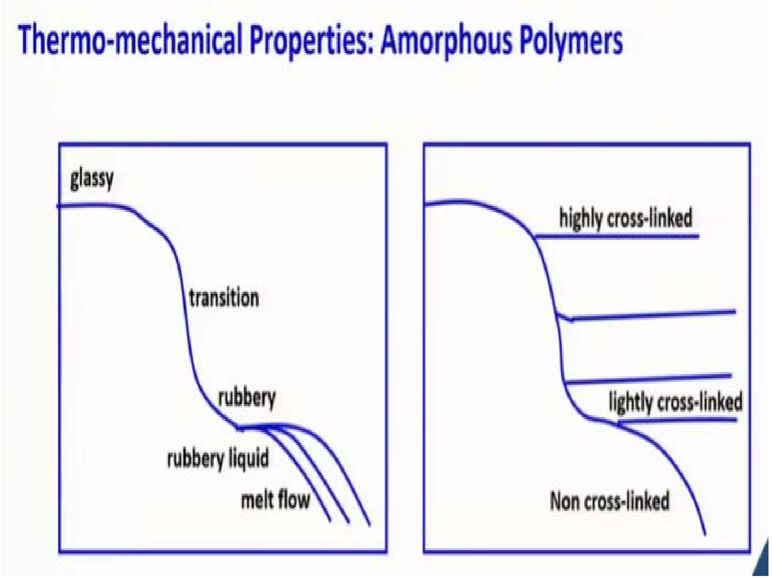

Thermo-mechanical Properties: Amorphous Polymers

So, if we plot the same thing, we plot log E or log of modulus with temperature, in this case we go through the same glassy and then transition region or leathery region, then the rubbery, rubbery liquid to melt flow. In this direction the molecular weight increases, so if we increase the molecular weight, we can increase the temperature at which the melt flow happens. In case of cross-linked systems, as I was discussing in last slide, this drop in modulus is arrested depending upon the extent of cross-link. If it is lightly cross-linked then the value of log E will come down and it will be remain little elevated, whereas if it is highly cross-linked, then the value of log E or the modulus will be quite high. So, in this direction we are increasing the cross-linking density.

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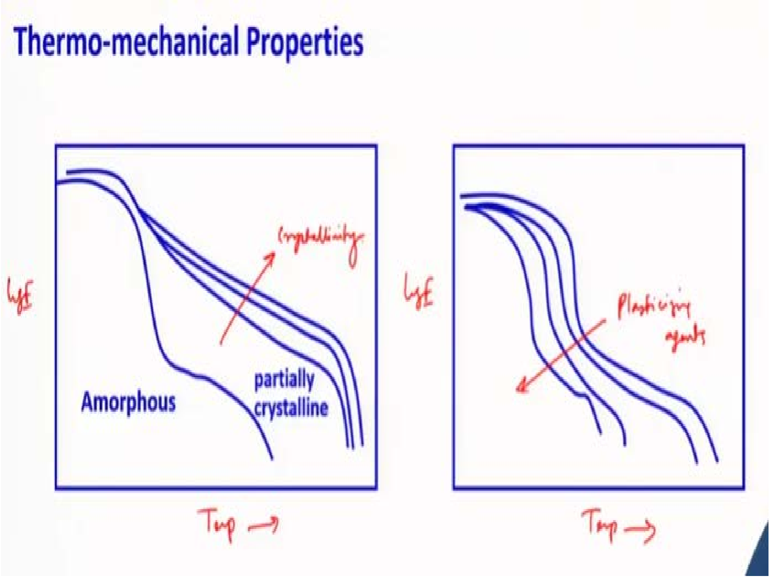

Thermo-mechanical Properties

Similarly, we can also discuss about the crystallinity, effect of crystallinity on modulus or stiffness. So, for a pure amorphous polymer, we had seen this type of decrease in tensile modulus or log of modulus. If we increase or introduce some crystallinity, then the graph will shift like this, as we have seen earlier for semi-crystalline polymers and more the crystallinity it will be move towards this type. So, this is the direction we have increased crystallinity.

Similarly, if we add plasticizing agent or plasticizer, if we increase the concentration of plasticizers in polymer matrix, then the T_g goes down and as a result we get similar sorts of curves of modulus versus temperature, but because in presence of plasticizing agents or plasticizers, the T_g goes down. So, you can see this graph actually moves to lower temperature. So, if we want to decrease the T_g of a polymeric material, we can add plasticizing agent or plasticizer.

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Viscoelastic Properties

Polymers have both elastic and viscous behavior
depending on time and temperature

I will now move to Viscoelastic properties, this is the very important property for polymers and it is based on the fact that the polymers have both elastic and viscous behavior which depends on the time and temperature. That means depending upon how fast the polymer is deformed and what is the temperature of deformation, polymer may behave dominantly as elastic solid or it may be behave dominantly as viscous liquid. We will have more discussion on that from next slide.

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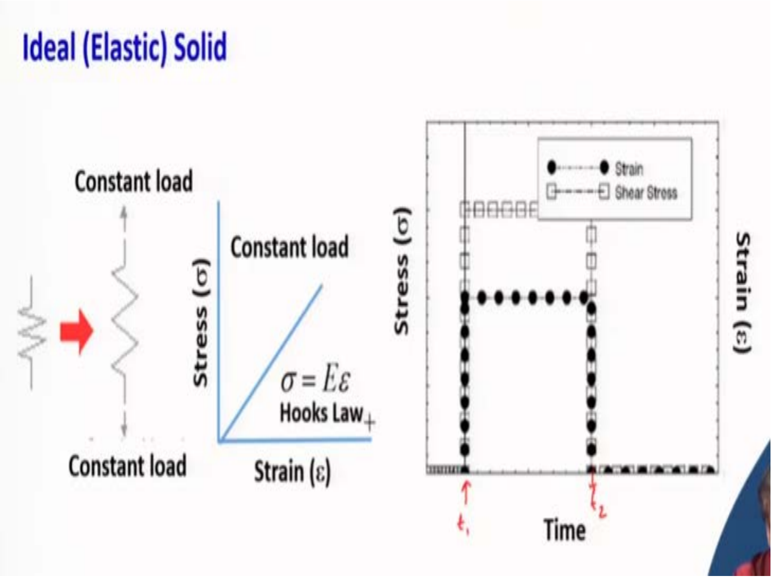

Ideal (Elastic) Solid

Before we go to polymeric systems, let us talk about ideal elastic solid, if we apply a constant load or a stress, in this case, we are just we are applying a strain here and the required amount of stress is followed in this experiment. In this case, for a pure or perfect ideal elastic solid, we get a linear relation between stress and strain and they are related by this equation where E is elastic modulus.

$$\sigma = E\varepsilon$$

This equation is called Hooks law and this type of solid is called Hookean solids. Now let us look at the time dependence of this material under load. This is the time t_1, if we apply some load, the sample will immediately strain without any delay. Now as long as the stress is maintained in the sample the strain will also remain at the same value. But the moment, say at t_2, this stress is removed the sample will come back to the original dimension and the strain will be zero. So, in this case stress and strain will exactly follow each other without any delay and these types of materials are ideal elastic solid and they follow Hooks law.

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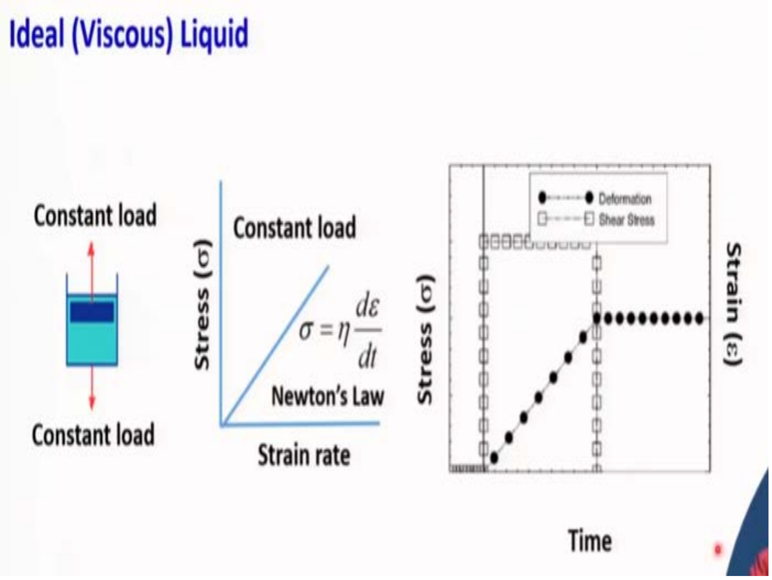

Ideal (Viscous) Liquid

Next, we will move to ideal viscous liquid. In this case, again, if we apply a load and follow the strain, in that case as soon as the stress is applied the material will strain. And in this particular case of ideal viscous liquid, there is a linear relationship between strain rate, rate of straining with stress. Remember, we talked about stress versus strain relationship in case of ideal elastic solid, but in this case, we are talking about a linear relationship between stress and rate of strain. Rate of strain is written as $\dot{\varepsilon}$, ε is strain, so we have

$$\sigma = \eta\dot{\varepsilon} = \eta\frac{d\varepsilon}{dt}$$

This relation is called Newton's law and η is the viscosity of the material, σ is stress. So, in this case of ideal viscous liquid, stress is linearly related to strain rate and the propositionally constant is viscosity. Now how is the time dependent behavior for this type of material? You can see in this case, say for example at time one, as the stress is applied the material will slowly deform at a steady rate and reach a particular value depending upon the value of stress. But, for example at time t_2, if we release the stress then the material will not come back to the original dimension. It will remain as deformed without coming back or without restoring this strain at all. Which means that the deformation caused by the stress is permanent and this type of behavior happens for ideal viscous liquid, and we call Newtonians liquid in this case. Now in case of polymers, depending upon the time of deformation and the temperature, the polymer actually behaves in between this ideal elastic solid and ideal viscous liquid, and we call that behavior as viscoelastic behavior.

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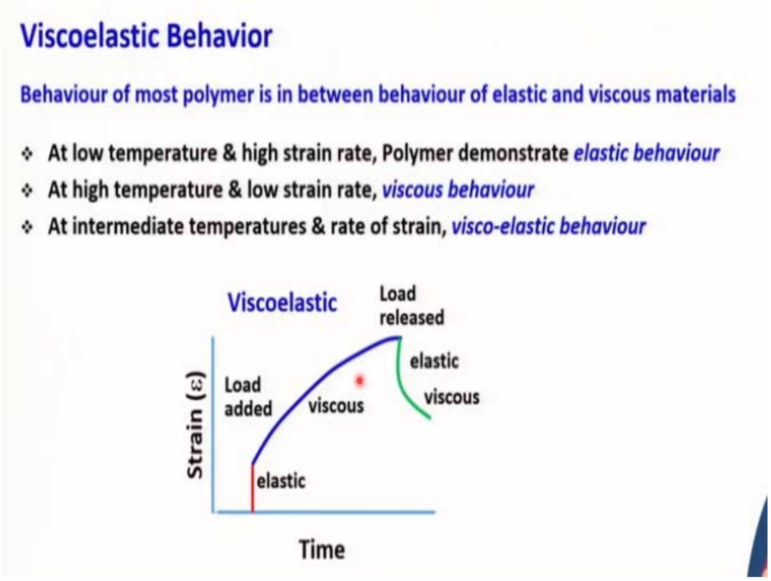

Viscoelastic Behavior

Behaviour of most polymer is in between behaviour of elastic and viscous materials

- At low temperature & high strain rate, Polymer demonstrate *elastic behaviour*
- At high temperature & low strain rate, *viscous behaviour*
- At intermediate temperatures & rate of strain, *visco-elastic behaviour*

Viscoelastic behavior, as I mentioned, this behavior is observed by most of the polymers and it is in between a perfect elastic and a perfect viscous material. At low temperature and at high strain rate the polymers demonstrate elastic behavior. Now what is flow? What is viscosity? Viscosity is movement of molecules past each other. If the sample containing polymers has to show a viscous behavior, then the polymer chains have to move past each other.

Now as we have discussed many times earlier as well, that the polymers in melt are entangled to each other having large molecular weight. If we are deforming at very fast rate or the temperature is low so that the polymer chains do not have any mobility, then the polymer chains may not move past each other and it cannot show any viscous behavior. Rather it shows elastic solid type behavior where there is no movement of molecules passed each other. At high strain rate, there is not enough time for polymer molecules to move around, and at low temperature, there is not enough mobility of the polymer chains to move around. Hence, in this case polymers demonstrate elastic behavior.

Similarly, at high temperature when the mobility is very high for the polymer molecules and at low strain rate, we are giving enough time for polymer molecules to move around, the polymer chains can move past each other and viscous behavior will dominate. In intermediate temperature and rate of strain, there is an intermediate behavior between elastic and viscous, we get a viscoelastic behavior. If we apply a load, then it deforms partly, if it was perfect elastic solid probably it would have deformed immediately to a higher extent. But because it is a viscoelastic it partly deforms immediately and part of the deformation continues till we apply the load. Once the stress is released, it immediately recovers some of its deformation like elastic solid. But because of its viscous behavior, it shows some permanent deformation within the sample. It shows both elastic component and viscous component within its behavior. So, it recovers partly and show permanent deformation partly as well.

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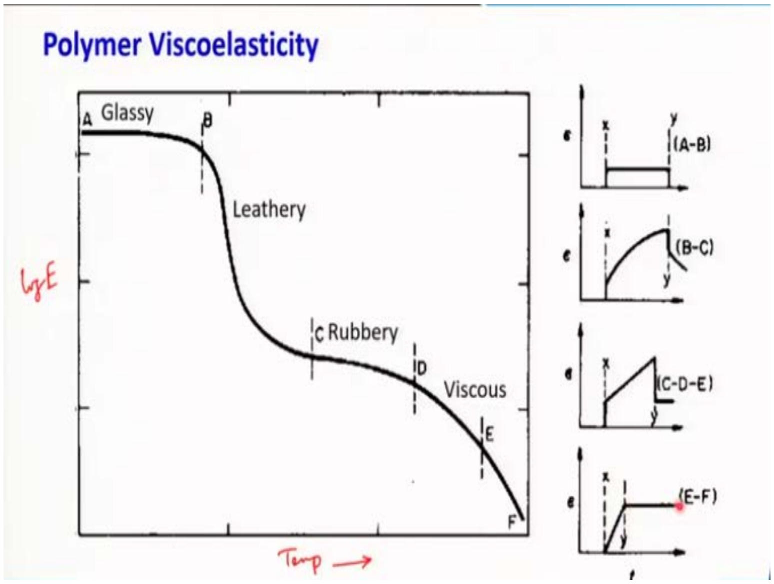

Polymer Viscoelasticity

Now if we go back and look at these regions. Y-axis is log E and x-axis is temperature. At low temperature polymers behaves like a glassy solid, then it is a soft leathery, and then it is rubber plate, and then viscous. Look at the corresponding time dependent behavior, this x is where a strain or stress is applied and y is where the stress is removed or the load is removed and this is how strain behaves with time.

The polymer is deformed in this time, and the load is removed in this time, and how this strain is followed is shown here. How the strain behaves, as the polymer is deformed, is shown in this curve. In this case between A and B when the polymer is glassy solid, you can see that it behaves like a perfect elastic. As soon as you apply the stress it deforms and as long as the load is maintained, it maintains the deformed behavior, and as soon as the load is removed it comes back to the original dimension, so it behaves like perfect solid, elastic solid.

But in the range of this leathery region, you can see it shows part of elastic behavior, so as soon as you apply the load it partly deforms immediately and then it partly continues to deform as long as the load is maintained. When the load is removed, it recovers partly and it remained deformed permanently to some extent. So, it is a viscoelastic behavior, but if you compare between this and this region and you can see that the viscous part, this linear deformation is dominating. And as soon as you remove this load it comes back partly and remained deformed partly without trying to recover some of this deformation behavior. So, both this case, viscoelastic behavior is expressed by the polymer but in this case, this is more elastic compared to this. Otherwise, this is more viscous compare to this but when we compare or when we discuss this region which is like a polymer melt it is behave like a completely viscos material. As you can see, the deformation happens linearly as the load is maintained and once the load is removed the deformation is permanent.

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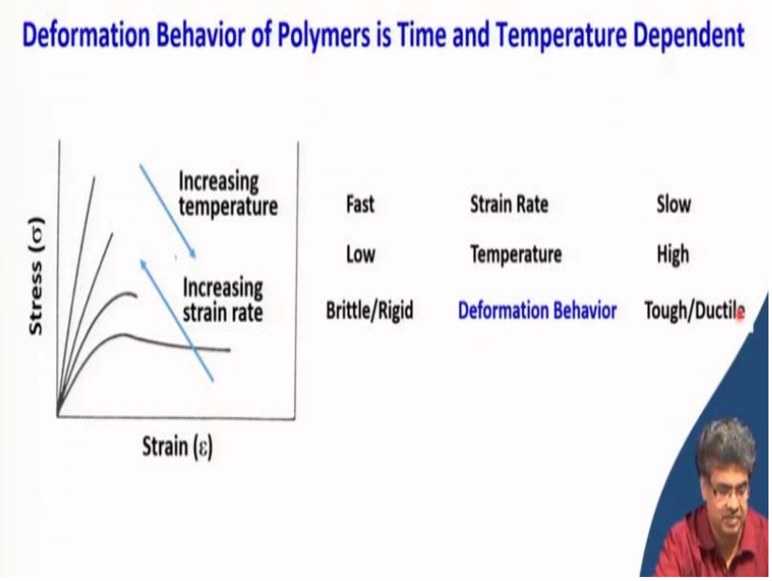

Deformation Behavior of Polymers is Time and Temperature Dependent

Fast	Strain Rate	Slow
Low	Temperature	High
Brittle/Rigid	Deformation Behavior	Tough/Ductile

You can see the deformation behavior of polymers is time and temperature dependent. We see that the stress-strain plots vary with the temperature at which we are doing the measurement or at which strain rate we are doing the measurement. If we do the deformation at a very high strain rate then polymer behaves like a solid, brittle or rigid solid. And if we do an experiment at low strain rate then it behaves like a more viscous sample.

And if we increase the temperature then the extent of viscous behavior goes up. If the strain rate is fast or the temperature is low, we see a brittle or rigid behavior. Whereas if strain rate is low and temperature is high, then we see more viscous behavior which basically gives the toughness or ductility in the polymer sample.

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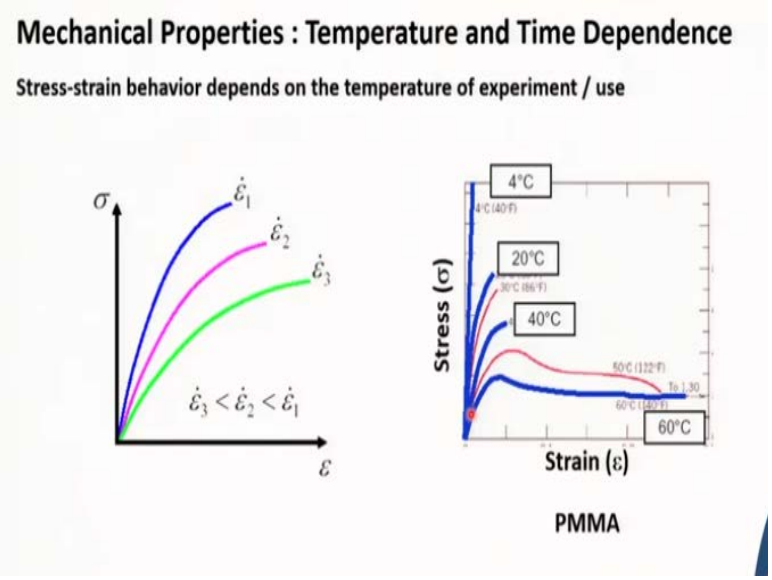

Mechanical Properties : Temperature and Time Dependence

Stress-strain behavior depends on the temperature of experiment / use

This is the example for a poly(methyl methacrylate) sample, you can see that in this case the deformation is done at three different strain rates, where this has the highest strain rate and this is the lowest strain rate $\dot{\varepsilon}_3 < \dot{\varepsilon}_2 < \dot{\varepsilon}_1$. And this case this shows more elastic behavior compared to at a lower strain rate. Similarly, if we see the plots at different temperatures, you can see that at high temperature it behaves more like a viscous material.

So, it can elongate for longer time and it shows ductile behavior and the area under the curve also increases so its toughness also increases. Whereas in this case, the modulus is low as you can see from the slope of this line, whereas at lower temperature, it is much more stiff and the modulus is high. Now remember once again, I have mentioned this earlier also, as the temperature is low polymer chains are frozen, they cannot move past each other. Hence, they behave like solid, elastic solid. Similarly, if the deformation rate or the strain rate is high then we are not giving enough time to polymer molecules to move past each other. Hence the polymer molecule behaves like elastic solute. But if we give the polymer chains enough time that means if we do the deformation at slower rate than it can actually show more viscous behavior.

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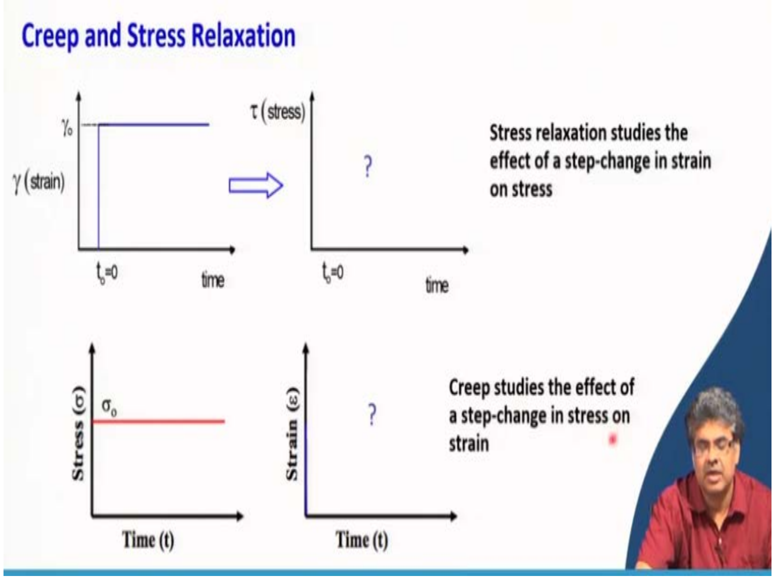

Creep and Stress Relaxation

Stress relaxation studies the effect of a step-change in strain on stress

Creep studies the effect of a step-change in stress on strain

Generally, these viscoelastic experiments are done two ways, one is creep experiment, another is stress relaxation. In case of stress relaxation, the strain is applied, a predefined strain is applied at some time and the strain is maintained, and the instrument follows the stress with time. So, at some time a certain strain is applied which is maintained with time but the instrument follows how the stress is changing with time keeping the strain same. This experiment called stress relaxation studies, the effect of step change in strain on stress. Reverse is creep where we apply a predefined stress and continue that stress with time and then you follow how the deformation or strain behavior happens with time. So, in creep studies the effect of a step change in stress on strain.

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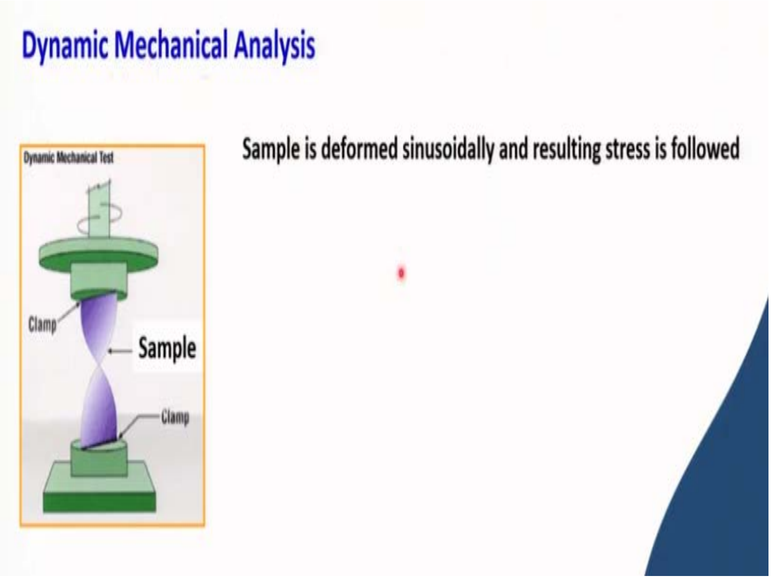

Dynamic Mechanical Analysis

Sample is deformed sinusoidally and resulting stress is followed

In next lecture, I will talk about the quantitative aspect of viscoelastic behavior and we will start dynamic mechanical analysis.