Rheology of Complex Materials
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Lecture – 34
Linear viscoelastic materials

In the discussion on Linear Viscoelastic Materials; we have been looking at several material functions and several simplistic models, and the idea is to understand; what are different types of linear viscoelastic material characterization which are possible?

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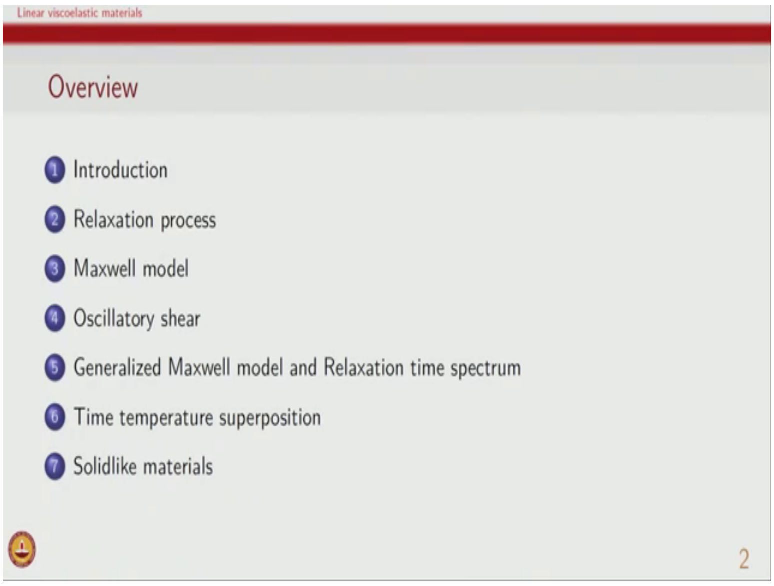

Linear viscoelastic materials

Overview

1. Introduction
2. Relaxation process
3. Maxwell model
4. Oscillatory shear
5. Generalized Maxwell model and Relaxation time spectrum
6. Time temperature superposition
7. Solidlike materials

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So, to this end; we have initially looked at the concept of relaxation process and how a Maxwell model can be used as a simple model to explain relaxation, and then we went on to look at oscillatory shear which is one of the most popular methods of examining rheological response.

And then we also looked at how combination of relaxation processes are involved in a complex material. And therefore, one can use a generalized Maxwell model and capture the overall response of the material. An important aspect in rheological characterization is also to use the time temperature superposition so that one can get response over a wide ranging variety of times as well as frequencies.

And in today’s this segment we will look at the response of more solid like materials. So, quite often we have looked at example materials such as macromolecular solutions or macromolecular melt or we have looked at colloidal dispersions. There are materials which are more solid like; for example, in the introductory classes we saw materials which are gel, materials which are glasses and also we have cross linked rubber for example, which also is a solid like material.

However, whatever we have learned in terms of the viscoelastic response can be used to characterize these materials also. Only thing is simplistic model is an entirely different model because Maxwell model always provides us a fluid like response in the terminal limits, for very long times or very low frequencies Maxwell response is always fluid like.

And then since we have these materials which are either gel or they are rubbery materials then do not have a terminal response which is viscous. And therefore, we call them solid like materials and in this segment; we will examine these solid like materials carefully. And we just should remember that whenever we are looking at the material response, we are trying to look at it qualitatively first then we quantitatively define a material function and parallely we also look at a simplistic constitutive model so that we can understand the response much better.

So, now let us look at the overall response of a solid material and the example solid material that we will have is basically a covalently cross linked network.

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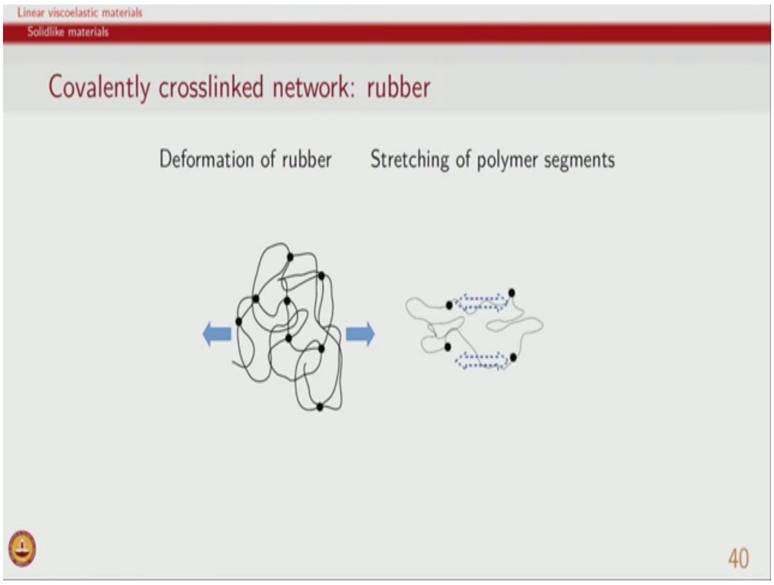

Linear viscoelastic materials
Solidlike materials

Covalently crosslinked network: rubber

Deformation of rubber

Stretching of polymer segments

So, the networks of polymers we have encountered several times in the course so far. We could have a polymer solution which is concentrated and there is very significant polymer-polymer interactions; we of course, discussed entanglements in the context of polymer melts. And in these cases the interaction between polymer-polymer are physical they would be mediated interactions based on hydrogen bonding or electrostatic interactions or Van Der Waals interactions and so on.

And so, there is the network that is formed in either polymer melt or solution is a temporary network or temp network with temporary junctions. However, a cross linked rubber on the other hand has covalently bonded cross links. So, if you look at the polymer segments they look like randomly distributed just the way they would be in a solution or a melt; however, the polymer molecules are actually cross linked with each other and these cross links are permanent and covalent bonded.

So, therefore, when rubber like material which is cross linked covalently when its heated at high temperatures it the degradation processes will set in, but this material will not really melt because of these covalent bonds. And so, analogously even if we take it to extremely low frequencies or if we examine this material for extremely long times, no flow in the material is possible because of these covalent cross links. And the behavior of this cross linked rubber is due to the behavior of the segments which are there between any two cross links.

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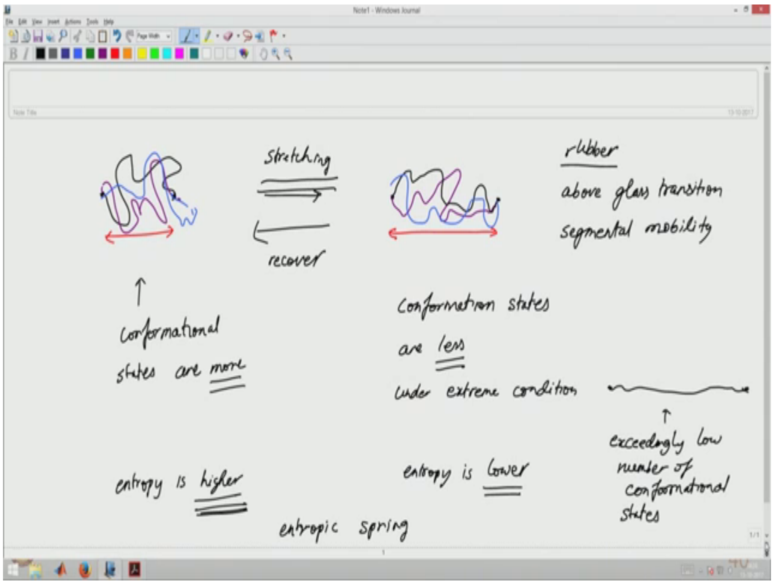

So, for example, if we have two cross links and we have a polymer segment which is connected by the two cross links, if this do cross link points are moved apart; in other words when we stretch the material strain is applied on the material and due to this strain the cross link points would also move further down, so that this distance between cross link point is less compared to the distance in the stretch state.

And because of this now the polymer molecule will also on average get stretched. We should always remember that in the macro molecular state above glass transition since we are talking about a rubber material we are necessarily above glass transition and since we are above glass transition segmental mobility does exist.

So, what that implies is the polymer which is between the two cross link point can actually explore different conformations and so, the polymer molecule can be in another conformation and of course, they will change between the these confirmations. And given that thermal energy is sufficient for these confirmations to take place what we have is segmental flexibility or segmental mobility.

So, due to this, what you can see is in one case the polymer molecule has lot more conformational states possible states are more compared to in the stretch state, where conformational states are less. So, upon stretching the polymer molecule the segment is actually forced to adopt less number of conformation. In fact, the extreme step of this under extreme condition we could visualize that the two cross link point have moved so far apart that the polymer molecule is pretty much completely stretched. So, in this case of course, there is only one conformation possible. So, exceedingly low number of confirmation of conformational states.

So, therefore, in case of a cross linked molecule because of the cross linking point the only possible movement is that of a segment the smaller level length scale motion for example, of a site group or of a smaller maybe 5 carbon atom or 6 carbon atom length scale those motions are certainly possible bond vibrations and the rotations around of site groups these are all possible. However any motion which is larger than the segment is not possible because of the cross link covalently cross link points.

So, when we actually have a stretching of a polymer segment we can see that in general the polymer segments have less number of conformational states. In fact, this is the origin of rubber elasticity the fact that in one case we have entropy is higher and in this case entropy is lower and of course, entropy is lower because the number of conformation states are less, entropy is higher because conformational states are many and because of this whenever rubber is stretched it has a tendency to go back and recover. So, that entropy can be maximized.

So, therefore, rubber is an entropic spring and the elastic contribution in rubber arise because of this entropic contribution which comes due to conformational changes in the material. So, therefore, when we have this material compared to polymer melt. In case of polymer melt we had the rotation of side groups we had the born level fluctuations we also had segmental mobility.

But at the same time we also had repetition possible because the entanglement points were temporary in this case we only have the set of relaxation modes which are associated with bond vibration and which and then which are called the glassy modes. Then sub segmental modes which are responsible for motion of segments and then in general, there is a lack of terminal viscous response because there are no there is no bulk motion possible because macromolecules are connected to each other through a covalently cross linked network.

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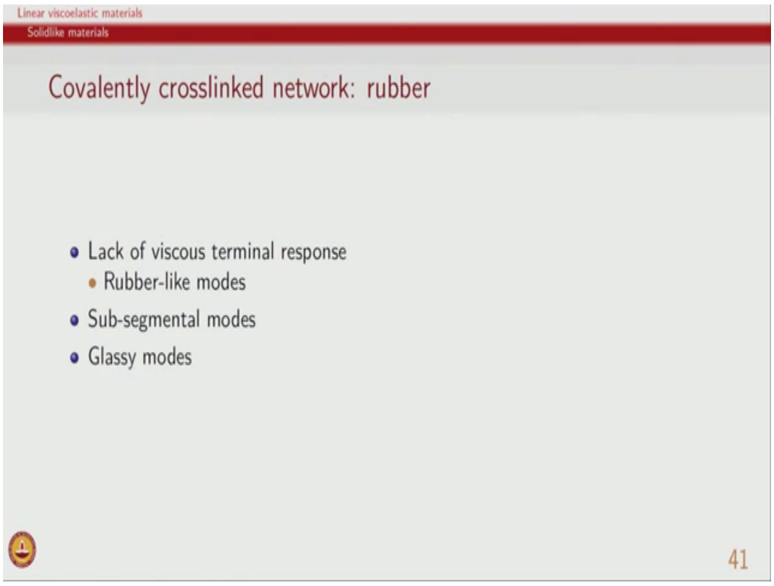

Linear viscoelastic materials
Solidlike materials

Covalently crosslinked network: rubber

- Lack of viscous terminal response
  - Rubber-like modes
- Sub-segmental modes
- Glassy modes

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So, due to this the overall response of a rubber like material is quite different when compared to a polymer melt. If we remember in most of the earlier cases we have seen that there is a viscous terminal response and that would be absent in case of a covalently cross linked rubber.

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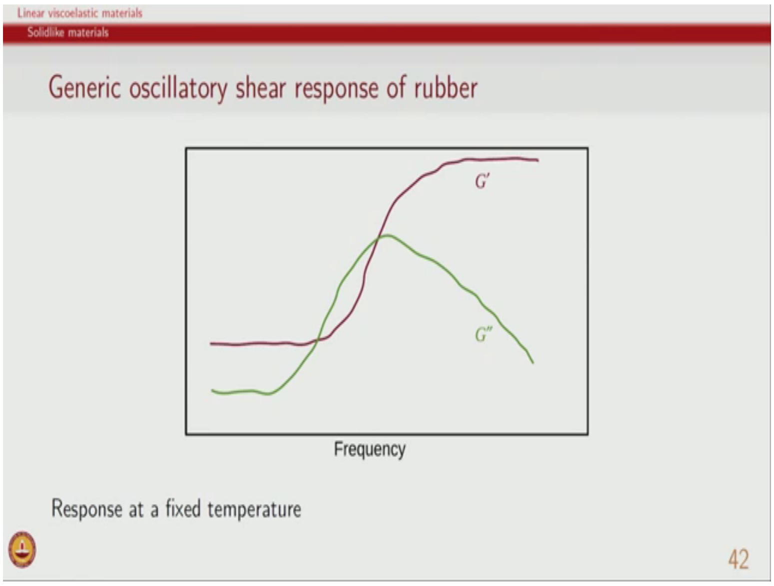

Generic oscillatory shear response of rubber

Response at a fixed temperature

So, if you look at general generic viscoelastic response of rubber what you would see is that at very low frequencies the material would response pretty much elastic in the sense that the storage modulus is order of magnitude higher than the loss modulus and they are generally independent of frequency. And as frequency is increased which means the timescale of probing the material decreases in those cases now even the sub segmental modes start contributing and the overall elastic as well as viscous contributions increase and beyond a certain point the material all relaxation modes basically become frozen and material shows a glassy response.

So, what we have in the frequency domain here which is being shown at a fixed temperature is basically a rubbery response and a glassy response. So, in case of rubber like response there is generally independence of frequency of both storage modulus as well as lost modulus. And in the glassy mode of course, we have G prime again is constant the storage modulus is constant because all the relaxation modes are frozen; however, this dissipated modes contribute less and less and generally therefore, the lost modulus decreases as a function of frequency.

So, this rubber to glass or glass to rubber transition can be observed in the frequency domain by probing the materials at very where different time scales. What this kind of a graph also tells us is that let us say of a material which is at low frequencies a reasonably saw soft material because the modulus storage modulus is much lower also it is a very elastic material in the sense that it will regain any deformation that was given the deformation will be recovered it will regain its shape. So, therefore, this is the qualities of rubber.

The same material if it is examined at much higher frequencies then it will appear with a fairly hard material with a very large storage modulus and this material may also be brittle. So, we have a rubber to glass transition or we also have soft flexible material to a hard stiff and brittle material and clearly we have already discussed that there is an equivalence between the time response of the material and the temperature response. What we saw was that when material is at higher temperature we can expect response times to change the relaxation processes all become much faster or the relaxation times decrease and therefore, the material response becomes more viscous.

So, generally in the case of glass and rubber also if at room temperature the material is rubber like then if we lower the temperature on the material we would certainly be able to see an overall classy response on the other hand if a material is let us say at room temperature a glassy material then we can increase the temperature and therefore, observe the rubber like response.

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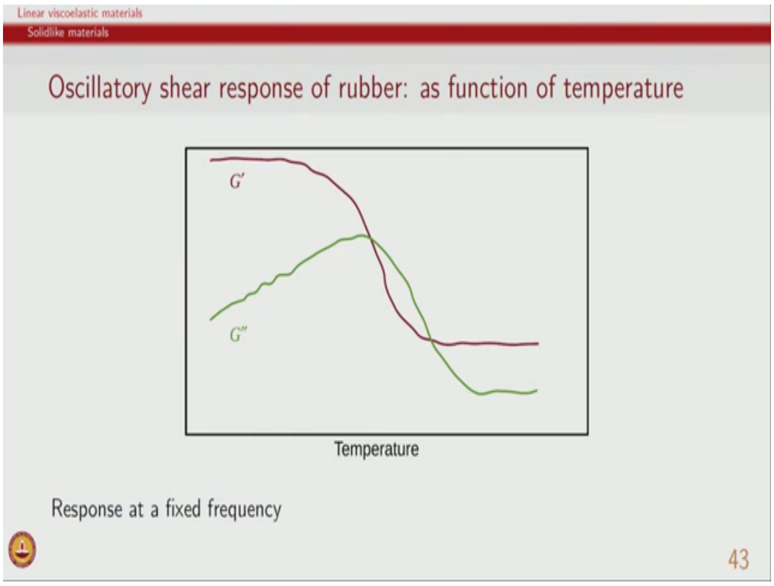

Oscillatory shear response of rubber: as function of temperature

Response at a fixed frequency

And this is what is shown in slight here that if we were to look at the storage and loss modulus at a fixed frequency for a cross linked rubber, then generally what you would see is at lower temperature when the material is in the glassy state the storage modulus would be quite high and then it decreases with temperature and in the rubbery state it would be again become a much lower value than the glassy modulus. We should remember that this level of increase is usually a couple of orders of magnitudes or even more decrease can be observed.

Similarly, in case of the loss modulus at the glass transition when the material goes from a glassy state to a rubbery state there is a strong decrease in the loss modulus. So, what we observed in case of a frequency domain where the material could be either show a glassy response or it can show a rubbery response in this case also we have the material as a function of temperature showing either glassy response or the rubbery response. So, now, this can be captured using a model which is called standard linear solid model.

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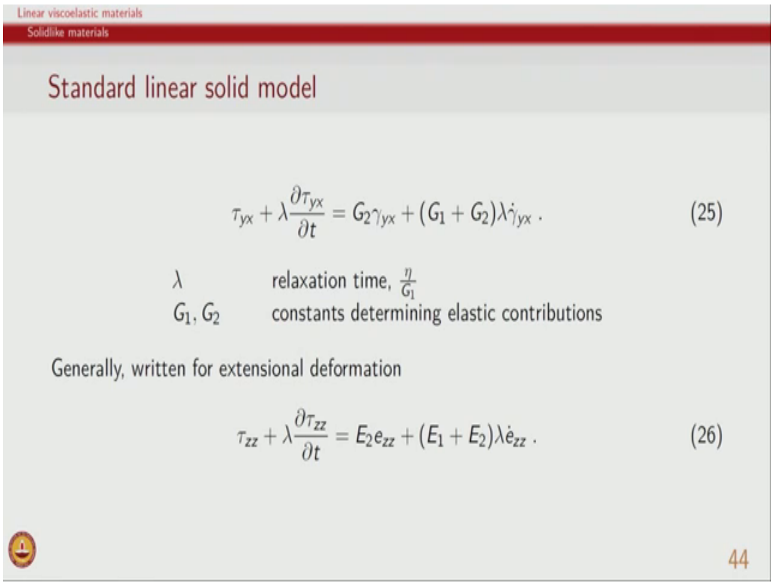

Standard linear solid model

$$\tau_{yx} + \lambda \frac{\partial \tau_{yx}}{\partial t} = G_2 \gamma_{yx} + (G_1 + G_2) \lambda \dot{\gamma}_{yx} \,. \qquad (25)$$

λ	relaxation time, $\frac{\eta}{G_1}$
G_1, G_2	constants determining elastic contributions

Generally, written for extensional deformation

$$\tau_{zz} + \lambda \frac{\partial \tau_{zz}}{\partial t} = E_2 e_{zz} + (E_1 + E_2) \lambda \dot{e}_{zz} \,. \qquad (26)$$

We have seen that in terms of Maxwell model the response could be captured using this governing equation for a shear deformation. So, we will just see how the standard linear solid model is different compared to this.

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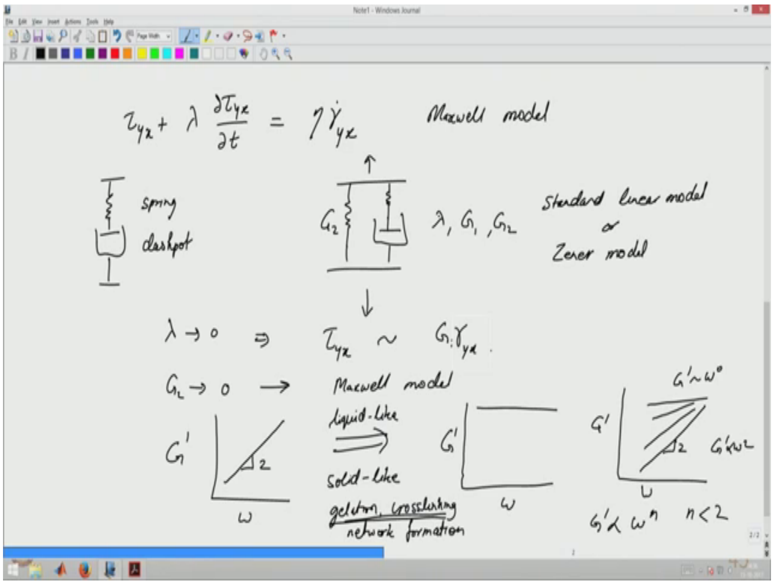

$$\tau_{yx} + \lambda \frac{\partial \tau_{yx}}{\partial t} = \eta \dot{\gamma}_{yx}$$ Maxwell model

λ, G_1, G_2 Standard linear model or Zener model

$\lambda \to 0 \Rightarrow \tau_{yx} \sim G_1 \gamma_{yx}$.

$G_2 \to 0 \to$ Maxwell model

liquid-like $\Rightarrow$ solid-like

gelation, crosslinking network formation

$G' \sim \omega^0$

$G' \propto \omega^2$

$G' \propto \omega^n \quad n < 2$

So, this was the Maxwell model that we have already looked at an examine quite closely and you can see that when you look at standard linear solid model the left hand side is completely identical to Maxwell model. Right hand side also there is some commonality in terms of the dependence of strain rate, but there is also the dependence of strain stress and stress rate are related to strain and strain rate in the material.

And in terms of a mechanical analog the standard linear solid model can also be visualized in terms of combinations of springs and dashpot. We remember that Maxwell model is a combination of spring and a dashpot in series while the standard linear solid model could be visualized as a combination of Maxwell model and a spring in series.

So, therefore, there are two elastic contributions one which is in series with a viscous contribution while one which is parallel and so, the response of this is therefore, characterized based on three parameters the Maxwell model had two parameters here we have lambda G 1 and G 2. So, therefore, lambda G 1 and G 2 are the three responses. And just examining the governing equation we can in fact, see that there are different elastic contributions.

For example, the stress if let us say lambda is very small value then we can see that the material pretty much reduces to a elastic material. So, in case lambda is very small what we have is basically tau y x is just proportional to G 2 times tau y x. So, clearly then what we have is this is the response. So, that at very small lambda the Maxwell element can be eliminated can be eliminated.

So, therefore, this model of course, is if G 2 is 0 then it reduces back to the Maxwell model and if G 2 is 0 then we have it reducing to Maxwell model. So, this model is also called standard linear solid model or the electrical analogue is called Zener therefore, this model is also sometimes called as the Zener model. So, this can be written in terms of shear as we have done for Maxwell model because we are using symbols G to indicate shear modulus responses it could also be written in terms of an extensional deformation in which case on the material we have strain rate which is extensional e dot zz and the therefore, the stress component is tau zz.

So, the same model in terms of the moduli parameter which are tensile moduli could be E 1 and E 2 could be written and since in case of solid like response we examine them in both extension and shear and in fact, more often they are examined in extension you would quite often see that rubber like materials are reported using E prime and e double prime for oscillatory response and similarly E 1 and E 2 as the material parameters for a standard linear solid model.

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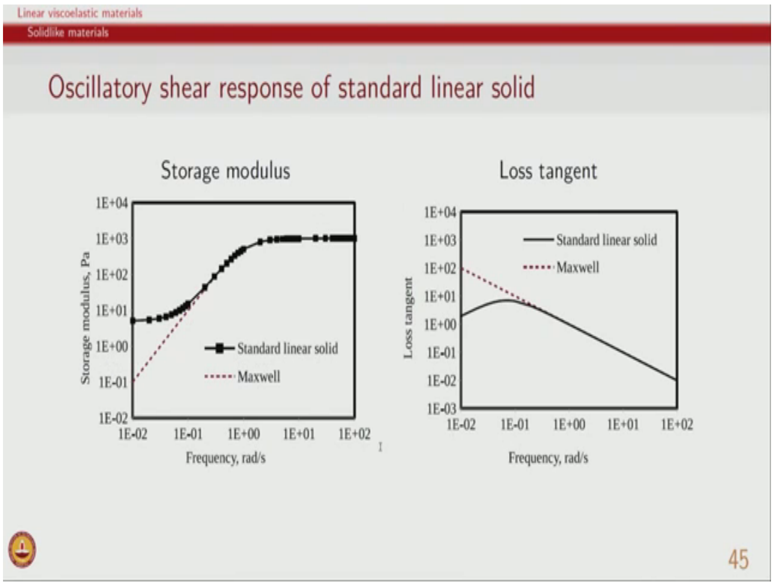

Oscillatory shear response of standard linear solid

When you look at the overall response of the standard linear solid model because of the additional contribution due to elasticity the spring which is there always what we have is at very low frequency there is no terminal viscous response. As we know we have seen that at low frequencies also the storage modulus is constant and of course, there is a glass to rubber, rubber to glass transition as we go to different frequencies.

So, compared to Maxwell model where there is a terminal viscous response we see no such response in case of the standard linear solid model. In fact, in rheology there is a large class of materials which undergo this transition from a fluid like response to a mold solid like response. So, what we have is and one stage when we look at G prime versus frequency at low frequencies the response would be this which is basically the viscous response and at some change in conditions of the sample we eventually reach a sample where G prime becomes constant.

So, this transformation from liquid like to a solid like response is very important in many materials which are this is called either a gelation, this is basically happens when we have cross linking. So, in all these cases whenever a network gets formed we have this transition. So, therefore, examination of the terminal viscous response of materials is very important in terms of characterizing what is the nature of the material.

Of course we also if we examine at different stages of cross linking or gelation what we would see is G prime versus omega basically changing systematically. So, under one condition its G prime with omega squared proportionality and then because the network starts getting formed we will slowly see that G prime becomes a function of frequency and here G prime is omega to the power n and n is less than 2 and of course, finally, going to G prime which is independent of frequency.

So, for many materials even this transition from going from liquid like response to solid like response is very important. And standard linear solid model and Maxwell model basically are two extremes of behavior, one shows the solid like response where G prime is independent of frequency the other one shows G prime which is proportional to omega squared.

Of course since both of these are simplistic models with the help of one relaxation time both of them show the transition to a glassy state most real materials will have a set of relaxation processes and therefore, the overall transition to a glassy state may be over much more orders of magnitude of frequency instead of 1 or 2 orders of magnitude as it is seen in case of a simple Maxwell or a simple standard linear solid model. When we look at the phase lag Maxwell model has an unrealistic phase lag compared to many viscoelastic materials in the sense it goes from very high value to basically 0 as we go from material to a fluid to a solid like response and this is because Maxwell model has only one relaxation process.

Similarly the standard linear solid model also over a same one or two orders of magnitude change in frequency undergoes again change in phase angle. However even at low temperature low frequency conditions the material is elastic and therefore, the phase loss tangent is low then it undergoes a maximum when the transition or viscoelastic response is maximum and then of course, in the glassy state again the loss tangent is less. So, therefore, there is a peak in loss tangent in case of a material which is a cross linked rubber. So, both lost modulus as well as the phase angle show a peak and this is quite often used to measure the glass to rubber glass transition in the materials.

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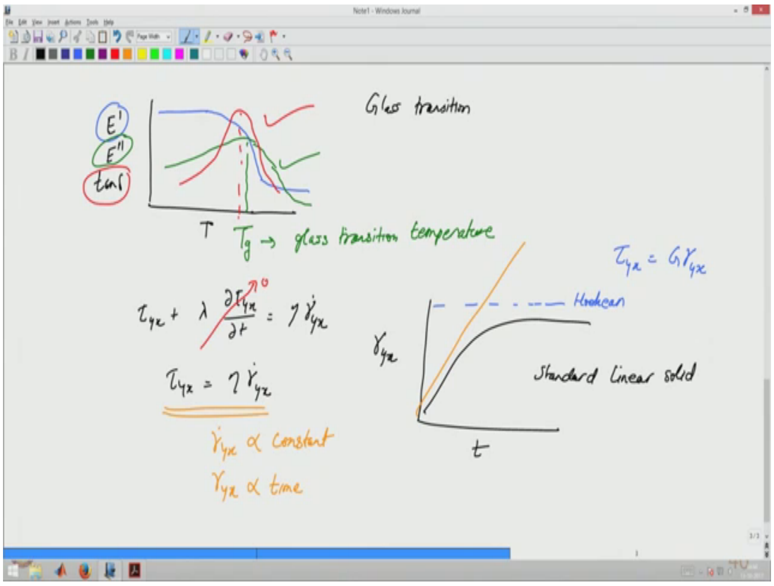

So, glass transition let us say can be measured if we heat the material and measure let us say E prime, E double prime and the tan delta as a function of temperature, what you would see is a E prime would basically be large and then at the glass transition it would decrease as we have seen and in the rubbery state again it would become a constant value, but a smaller constant value. The E double prime on the other hand as we saw earlier goes through a maximum and then it decreases and then in the rubbery state it is lower than the glass transition the storage modulus tan delta also similarly will actually tan delta also will show response which again will be an increase and decrease.

Of course these are all different scales. So, tan delta also shows. So, both the E double prime and tan delta can be used to see the glass transition temperature of the material. So, this is the glass transition temperature that can be measured.

And from the design of polymeric system it is very important to know what is the behavior of the material and where is glass transition with respect to the performance temperature. In case of rubber like materials we have to make sure that the material is being used at temperatures much higher than the glass transition temperature so that the rigid or brittle response which is expected in glassy region can never be observed.

But if on the other hand if you are using the material as a structural material then we have to make sure that the material is being used much lower than the glass transition because if the higher glass higher temperature is seen the soft flexible and modulus being 3 orders of low three orders of magnitude lower will be observed and which will not be suitable for structural applications. So, therefore, glass transition is important for many of the mechanical applications of glassy and rubbery systems.

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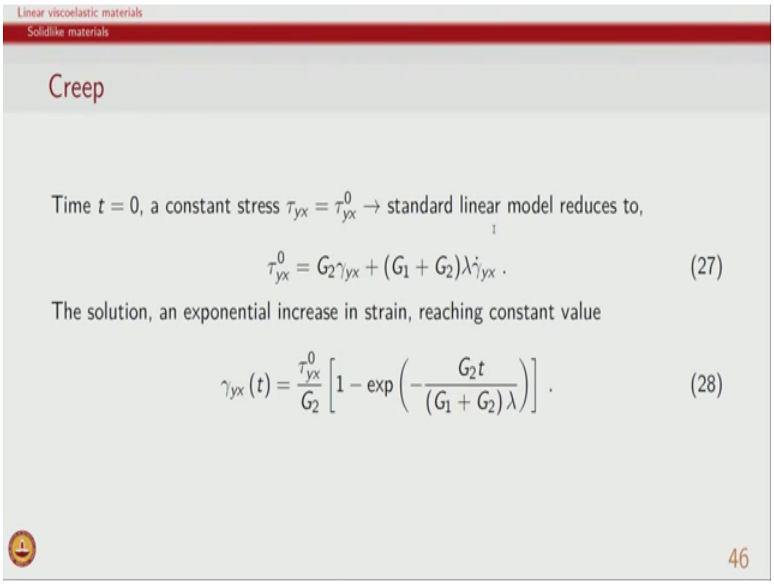

Linear viscoelastic materials

Solidlike materials

Creep

Time $t = 0$, a constant stress $\tau_{yx} = \tau^0_{yx} \rightarrow$ standard linear model reduces to,

$$\tau^0_{yx} = G_2\gamma_{yx} + (G_1 + G_2)\lambda\dot{\gamma}_{yx} . \qquad (27)$$

The solution, an exponential increase in strain, reaching constant value

$$\gamma_{yx}(t) = \frac{\tau^0_{yx}}{G_2}\left[1 - \exp\left(-\frac{G_2 t}{(G_1 + G_2)\lambda}\right)\right] . \qquad (28)$$

So, another examination that can be done for solid like materials is called creep in which case at time t is equal to 0 we apply a constant stress on the material. So, we have examined other modes of viscoelastic characterization. For example, stress relaxation when the strain was kept constant or oscillatory shear where the strain was varied sinusoidally. Now, we have an example of creep where the stress is kept constant.

One can see what happens in case of Maxwell model for creep since we have Maxwell model and since stress is constant this term would go to 0 and therefore, Maxwell model is similar to a Newtonian fluid model in case of creep. So, therefore, we have said that the Maxwell model can be used mostly for fluid like materials and it is inappropriate for solid like materials. On the other hand standard linear solid model since it captures the low frequency or long time response it also gives a more realistic response for creep.

So, if we substitute the condition for creep in the standard linear solid model the derivative of stress goes to 0; however, we still have terms which are related to strain and strain rate and which is equal to the constant stress. And when we solve this we get strain as a function of time and what we see for a standard linear solid model is the fact that strain in the material as a function of time increases exponentially and then become constant.

If you look at for a Hookean solid material which is for example, would have tau y x is equal to G gamma y x. So, therefore, strain if stress is kept constant then strain would also become constant and this would be the response of a Hookean material. On the other hand the response of a fluid we have already seen Newtonian fluid. So, if stress is kept constant the gamma dot y x will be proportional to time.

Because sorry gamma dot y x will is constant and therefore, constant and therefore, gamma y x will be proportional to time. So, you would see a response which is like this. So, you can see that the standard linear solid model gives a response which is a combination of viscous and elastic response and in creep it provides an appropriate qualitative response. So, using this concept we can define creep compliance for the material.

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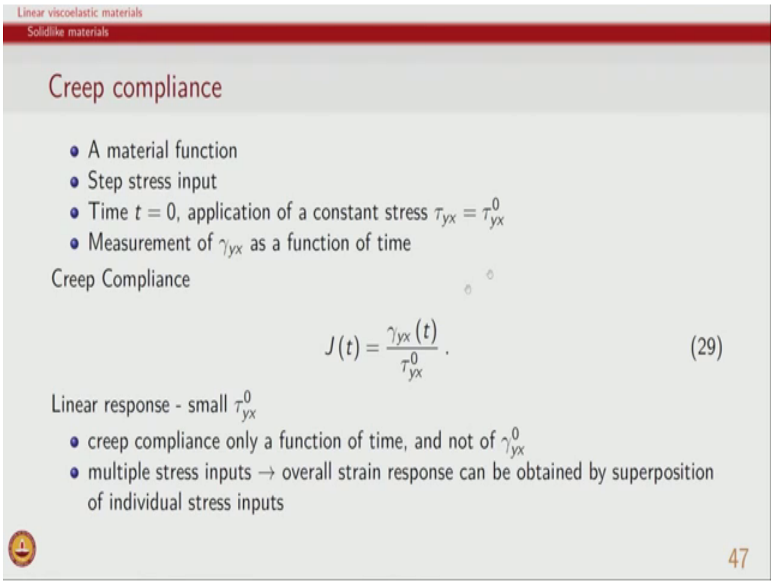

Linear viscoelastic materials

Solidlike materials

Creep compliance

- A material function
- Step stress input
- Time $t = 0$, application of a constant stress $\tau_{yx} = \tau_{yx}^0$
- Measurement of γ_{yx} as a function of time

Creep Compliance

$$J(t) = \frac{\gamma_{yx}(t)}{\tau_{yx}^0}. \tag{29}$$

Linear response - small τ_{yx}^0

- creep compliance only a function of time, and not of γ_{yx}^0
- multiple stress inputs → overall strain response can be obtained by superposition of individual stress inputs

Again this is a material function were a step stress input is given to the material at time t is equal to 0 we apply a constant stress and we measure the strain as a function of time. And then we define a creep compliance which is in some sense inverse of modulus because it is strain over stress strain is of course, a function of time because we are measuring it as the stress constant stress is applied and of course, we expect linear response when small stress is applied the creep compliance will only above function of time and it will not depend on what is the level of strain.

And of course, because the linear response is observed we can apply multiple stress inputs and overall strain response can be calculated by superposition of individual strain increases and then becomes constant for a standard linear solid model. More generally for different materials we would have different strain responses and therefore, we can define a material function which is called creep compliance.

So, in this case a step stress input is applied at time t is equal to 0 for example, we would apply a constant stress tau y x naught. Then measurement of strain is carried out as a function of time and creep compliance is defined which is inverse of the modulus as the ratio of strain over stress and since strain changes as a function of time the creep compliance is a function of time. And for a small stress we would be in the linear regime in which case the creep compliance would only be a function of time. And when multiple stress inputs are applied we could actually obtain the overall strain response by combining or superposing the individual responses.

So, with this we have now over viewed all the relaxation, stress relaxation, oscillatory, shear, creep and 0 shear viscosity all these material functions which are very useful in terms of characterizing the linear viscoelastic response. Just the way we define compliance to define the creep response the creep the oscillatory response could also be described in terms of compliance. So, therefore, in general there are a variety of these material functions which are reported depending on the context of the material and the study.