Rheology of Complex Materials
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology, Madras

Lecture – 32
Linear viscoelasticity: generalized Maxwell model

So, what we have been doing over the last few lectures is discussion related to Linear viscoelastic materials and. So, far we have looked at the idea of relaxation process, as central to defining viscoelasticity and the fact, that we use Maxwell model as a very simple model to learn about some of the basic characteristics of viscoelastic materials and then we saw oscillatory shear as a very useful mode of examining material response and then we actually, also looked at few example, materials such as polymer melt or a Wormlike Micellar solution or a soft gel.

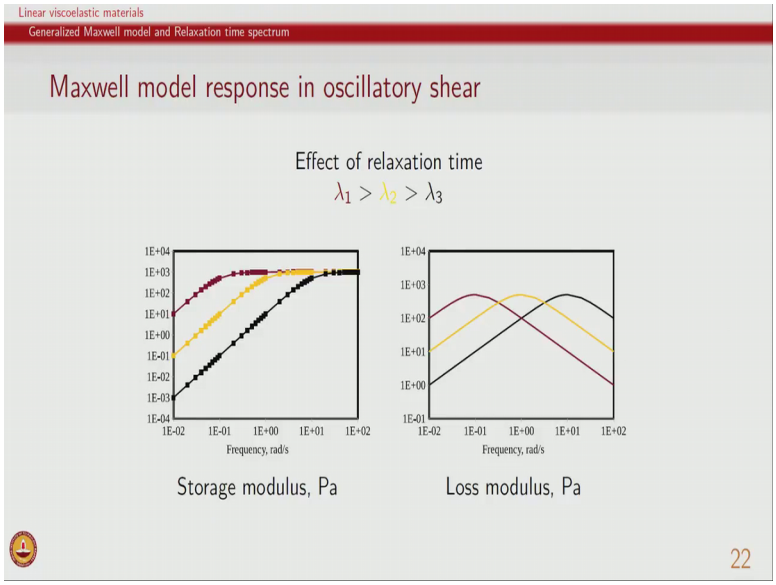
So, how oscillator shear response is for these materials and in what are the underlying mechanisms, which make these materials viscoelastic. So, today we will complete this discussion, related to Linear viscoelastic material by doing two things, the relaxation time and the spread of relaxation times, can be interpreted in terms of what is called a generalized Maxwell model. So, we will just summarize, what is useful to describe the relaxation times that are, there in a real material.

And then we will also look at the idea of time, temperature, superposition, which is useful to get data over much wider time or frequency range and finally, we will look at solid like materials, because some of what we have been discussing are fluids, which like materials, which always give terminal viscous response. So, in oscillatory shear, they would lead to g prime being proportional to omega squared or g double prime will proportional to omega. Similarly, in a relaxation stress, relaxation experiment they would lead to 0 stress the dk would be completely to 0 stress.

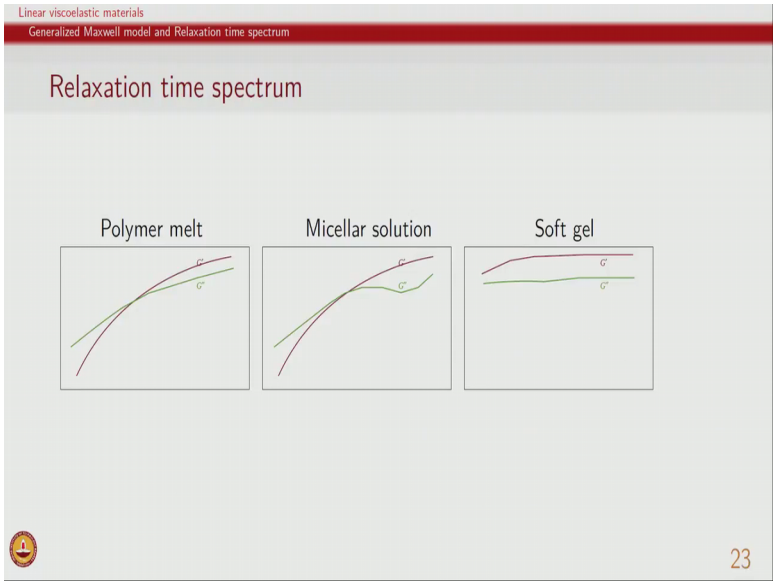
But we have various materials, which are more solid like and they are viscoelastic. So, in such cases, we will not see the terminal viscous response and. So, cross linked rubber is a good example of such viscoelastic material. So, therefore, we will examine it briefly. Similarly, for stress relaxation also, we will see that for solid like materials, the stress will not dk to 0, but to a finite value. So, therefore, there is a simple model called

standard Linear solid model, which is useful to describe these solid like materials. So, we will look at that and that is how we will finish up our discussion of Linear viscoelasticity.

(Refer Slide Time: 03:15)

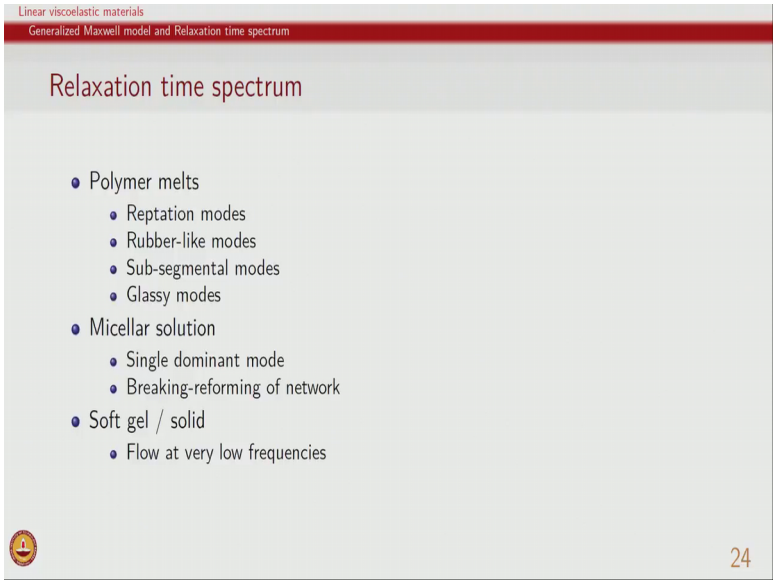


(Refer Slide Time: 03:17)



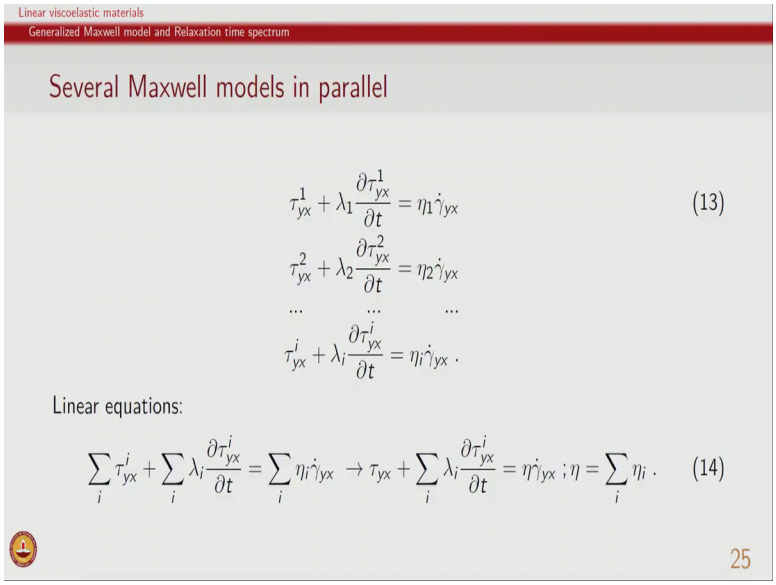
So, let us just look at this response, which we have seen earlier that, there are different classes of materials and in these cases, we saw that in polymer melt case, there was a terminal viscous response, in micellar solution also, there were the terminal viscous response.

(Refer Slide Time: 03:46)

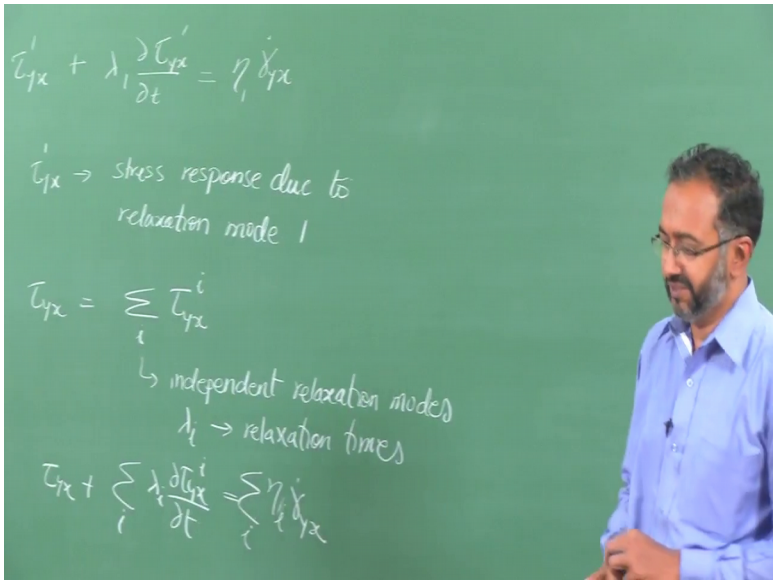


In case of soft gel, it appears, that maybe if you could do material examination at much lower frequencies, you might see the viscous response, but at least it is not seen and therefore, these materials are called soft gels and we saw that how the relaxation modes can be interpreted, as belonging to certain types of responses in the material.

(Refer Slide Time: 03:56)



(Refer Slide Time: 04:08)



So, this idea can be captured by using several Maxwell models in basically parallel to each other. So, we have been saying that one particular Maxwell model, in that case we will just have the response, that we have been talking about eta 1 gamma dot yx. So, the idea is that the material is being imposed the same strain rate, which is gamma dot yx, but there are several relaxation processes or relaxation modes in the material and each of them gives a stress contribution. So, therefore, this tau yx 1 is the stress response due to relaxation mode 1 and so on.

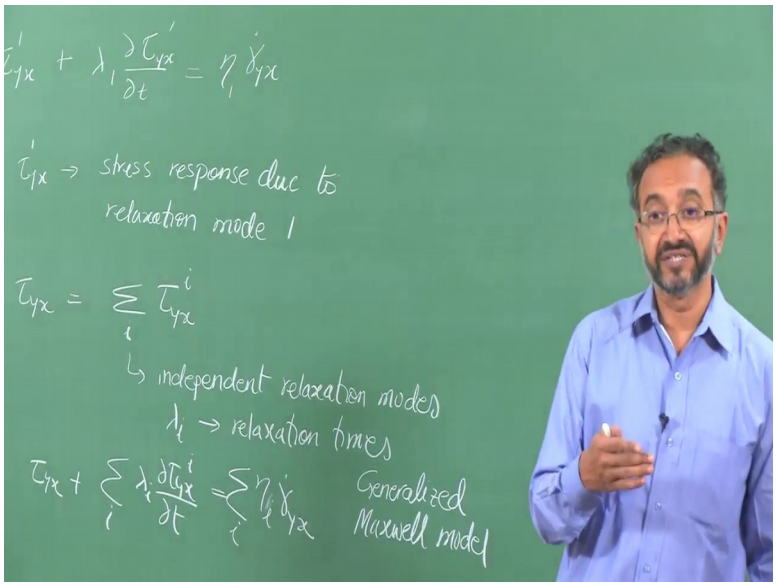
So, we have several such modes. So, each of them give us response and the overall stress response is nothing, but summation of all of these different stress responses. So, each relaxation modes, we are assuming that there are n independent relaxation modes in the material. So, there is a basic assumption involved in writing and visualizing, the overall material response as combination of relaxation modes. So, we assume that there are independent relaxation modes and does, that seem very unrealistic that one relaxation mode is not interfering with another relaxation mode.

So, for example, the vibrations on, let us say a bond is not necessarily interfering with rotation, if that is another or the repetition mode is not really affecting the segmental or sub segmental modes. So, each of them is being considered independent of the other. So, the material is being considered as a set of relaxation processes, which are independent of each other and each has a characteristic relaxation time and which is, what is a lambda i. So, with lambda i as the relaxation times.

So, therefore, we can sum the contribution, due to all such modes and we get, what is called the generalized Maxwell model. So, this description of material is called. So, when I sum all of them tau yx 1 tau yx 2, all of them, sum together will give me this plus summation of lambda i delta yx i by del t is equal to eta 1 gamma dot yx eta i.

So, therefore, all of them are being summed and therefore, this is the, this is what is called a generalized Maxwell model.

(Refer Slide Time: 07:32)

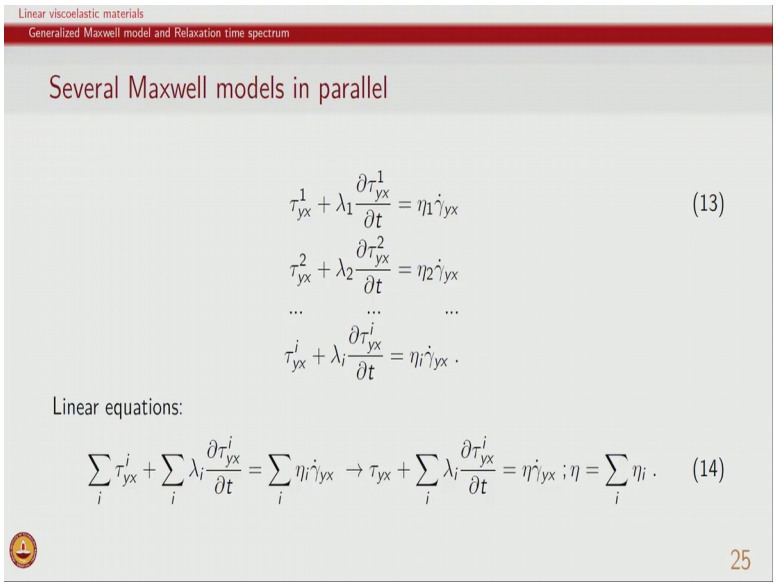


And so this would be useful for fluid like materials, as we will see towards the end of this. In the next class that for solid like materials, we will need an additional set of terms to describe the nonterminal viscous response or non viscous terminal response, the fact that no matter what is the set of relaxation times, we use in this case, at very low frequencies, we will always get terminal viscous response. Of course, that low frequency will depend on the largest relaxation time.

We saw that in case of a polymer melt, the reptation modes were there related to largest relaxation time and therefore, if you test the material at low enough frequency, then you can get basically, even if reptation is inhibiting, the material flow, if you give enough time, the polymer molecule is able to flow like a liquid and therefore, it gives us terminal viscous response. So, depending on the largest relaxation time available as long as you examine the material at lower frequencies, you can still get terminal viscous response.

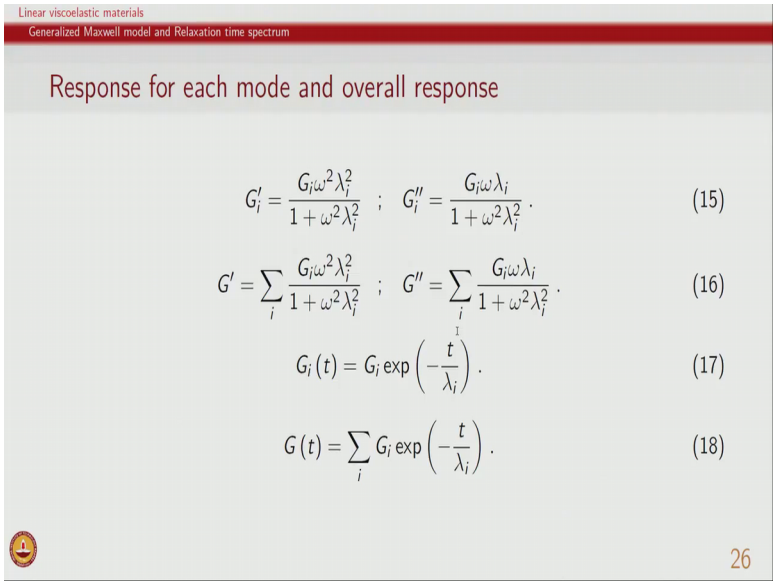
So, if you have a material, which is definite solid like characteristics and a non viscous terminal response, then we will have to add on something else, in addition to the generalized Maxwell model. We will basically need something, which can capture the idea, that there will be a non zero stress relaxation or the material can retain stress for infinite amount of time, in a stress relaxation experiment or in case of frequency is no matter how low you go. The viscous response will not be observed.

(Refer Slide Time: 09:30)



So, they are using this modeling of such kind, you can then try to attempt to describe the estimate, the relaxation time spectrum in a material. So, when you get a G prime, G double prime, for a given material. You can then characterize it and that is what we saw last time, using some of the 10 mode relaxation model, 10 mode Maxwell, model or a 4 mode model. So, those can be used to describe any complicated variation of material properties and even when we look at how the material responses for each and every response is independent of each other, because again these are relaxation modes, which are independent.

(Refer Slide Time: 10:00)



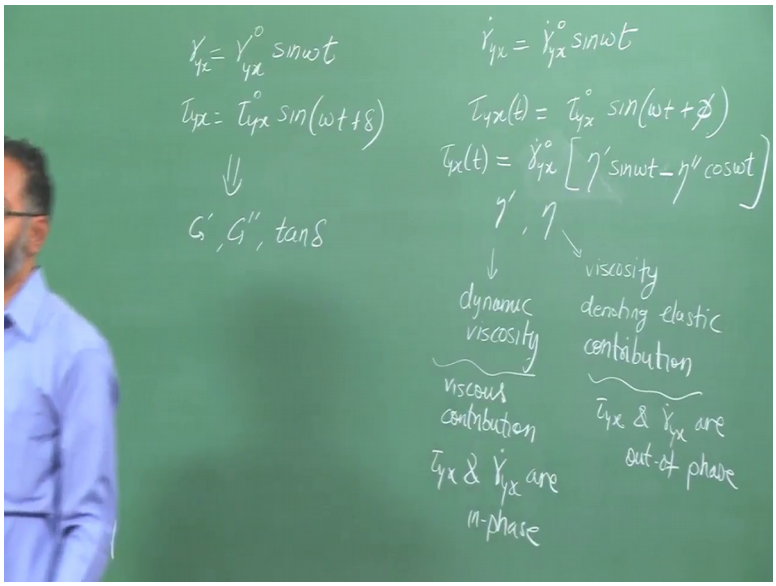
So, therefore, we can, why write the relax, the storage modulus for ith mode, very similar to what we had written earlier and then the overall modulus of the material is nothing, but summation of all of these.

So, this is again, because of Linear governing equations and given that we are confining our attention to small deformations and Linear viscoelasticity, if this G prime are functions of the strain amplitude itself, then we will not be able to do such method. We will not be able to use, such summation to get the overall response. Similarly, the stress relaxation modulus, for one particular mode is again in exponential and the overall relaxation modulus is summation of all the exponential functions.

So, using this generalized Maxwell model, we can describe a fairly large number of fluid like materials and. So, as long as our analysis is limited to small deformations, this way of analyzing materials is quite useful, the idea of doing oscillatory shear or a relaxation stress, relaxation experiment, try to capture what are the relaxation modes, which are there in the material and try to explain both the oscillatory shear and the stress relaxation modulus of the material. So, the of course, limitation is that, we will only have to work with small deformations or do not perturb the material very much away from equilibrium. So, under those conditions, this is quite useful.

So, now in the just closing, we will also look at the other material function, which can be defined, which is the viscosity.

(Refer Slide Time: 12:08)



So, we had earlier defined the G prime and G double prime, using this response, where we had seen that tau ix sine omega T plus delta was used to define G prime and G double prime and tan delta.

So, similarly, instead of saying that we are applying defined strain on the material, we could say that we are applying a defined strain rate on the material and. So, in that case, we apply gamma ix dot. So, it is a constant amplitude strain rate being applied and since we are dealing with small deformation, these two are derivatives of each other, but since we are doing the experiment in a strain rate control modes.

So, this is something which in Rheometers and their construction of Rheometers, there are different controls possible. So, we can either control the torque or the stress, we can either control the rotation amount of rotation or strain or we can control the rotation rate or strain rate depending on what is available and of course, lot of this is also done with feedback loop, and control loops, and the usual instrumentation procedures, which we use for any instrument.

So, therefore, if we apply a constraint with this strain rate amplitude, we apply a sinusoidal strain rate, then again the response can be generally written as tau ix, which is a function of time will be tau ix naught sine omega t plus let us say phi. So, some phase difference and. So, out of this, then we can define the viscosity of the material and we

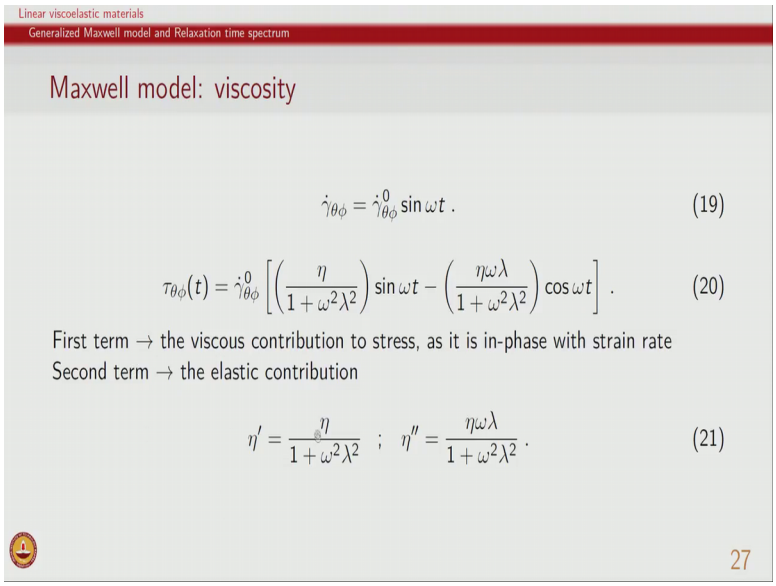
can again define, this is called the dynamic viscosity and this is just the viscosity, which denotes the elastic contribution.

So, just away here, we had the storage modulus, which denotes elastic and storage modulus was where stress and strain were in phase. Now, we have the dynamic viscosity and the dynamic viscosity denotes the viscous contribution of the material where. So, this denotes the viscous contribution, where stress and strain rate are in phase for Newtonian fluid or a perfectly viscous fluid of course, these two are in phase.

So, therefore, that part of overall stress response, which is in phase with gamma dot yx is called dynamic viscosity and this contribution is, where the part of tau yx and gamma dot yx are out of phase. And so we can substitute this particular condition in the Maxwell model and again, we will get an ordinary differential equation and we can solve for the stress response and we can write the overall stress as in terms of the amplitude yx divided by gamma dot naught yx stress itself. We will need to do, this to define the viscosities. So, let me first define the stress itself.

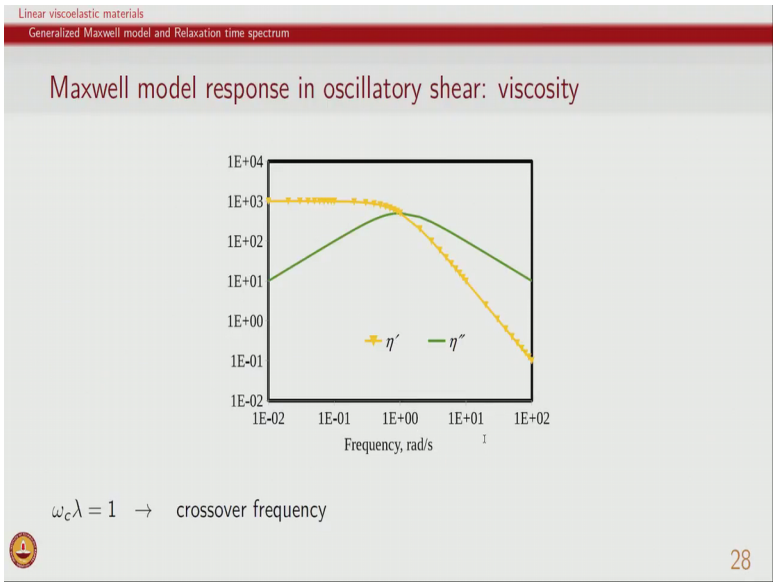
So, we will get two terms basically, eta prime sine omega t plus and minus eta double prime cos omega t does, that make sense. Now, write, this needs to be gamma right. So, therefore, eta prime is where gamma dot yx and tau yx are in phase, while eta double prime is where they are completely out of phase and. So, the solution of this for a Maxwell model is given by this where eta is eta prime, is eta over 1 plus omega squared lambda squared.

(Refer Slide Time: 17:26)



So, it starts out being a constant value, because if omega is very small, then basically eta prime is eta and then it goes down as a function of frequency, while eta double prime has increasing and decreasing trend, which is, what is shown here.

(Refer Slide Time: 17:47)

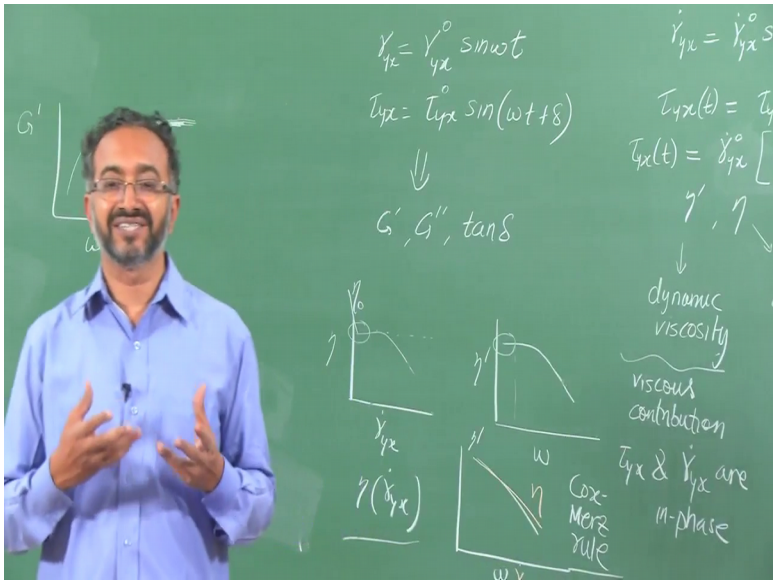


So, eta prime initially is constant and then it decreases as frequency increases and the eta double prime of course, goes through a maximum. So, in general in terms of usage, what we will see is G prime, G double prime is used quite a lot or tan delta, all of these are used quite heavily. When we generally, look at the viscosity as a material function from

oscillatory shear, most often only the dynamic viscosity is analyzed well, because one is interested in looking at the viscous contributions of viscoelastic materials, using oscillatory shear.

So, you can do that of course, looking at G double prime also, but you can look at it, using dynamic viscosity also and an important comparison, usually is in terms of, if I get viscosity, which is this dynamic viscosity, using oscillatory shear and then the viscosity, that is obtained using steady shear right. So, if you look at it, the response of eta prime as a function of omega, at least according to Maxwell model, seems like this.

(Refer Slide Time: 19:00)



So, for many materials you would expect this kind of a behavior, that at very low frequencies, since the material is given enough time to respond all the relaxation modes, can provide you dissipative response and you get basically, a viscous response and then, when you go to higher and higher frequencies, then the material shows more viscoelastic response and in terms of the viscosity, that we had talked about, we also saw many fluids show a similar response.

So, is there a correspondence between these two contributions, of these two measurements, of viscous response of materials, in both, in this case of course, we are characterizing both viscous and elastic contribution, but eta prime is only talking about viscous contributions, in this case, we look at only the steady state. So, therefore, we only look at the overall viscous contributions and as we saw that in making the material

shear thinning. Of course, there are elastic mechanisms, the fact that a macromolecule can orient or the fact that the particles can agglomerate and break.

So, those kind of features are present which can lead to shear thinning, but when we do a steady shear experiment, we are only characterizing the steady response and therefore, only the viscous response of the material. So, is there a correspondence between these two and does it sort of make sense, the two tests are being done under very different conditions. In one case the deformation is kept small, but it is a time dependent test where oscillatory shear is being applied,

The other one is a time independent, a steady state and deformation is not kept small. In fact, you apply constantly, keep on applying strain rate on the material, you wait for steady state to be reached and then you measure.

Student: Sir in steady state, we are assuming, there is only viscoelastic response. There is no (Refer Time: 21:24)

No it is. So, it is not that, we are assuming there is only elastic response. We are only characterizing the steady response.

Student: There is no viscoelastic contribution (Refer Time: 21:33)

No. So, we realize that underlying contribution, underlying mechanisms, are necessarily viscoelastic, but if I choose to model, this using a viscous model, I can do that right. So, if I use let us say a carry, you see that kind of a model that we discussed, if I use that then I am ignoring the viscoelastic, the mechanisms and I am saying, I am only interested in looking at viscosity as a function of gamma dot yx, if I do that then I am looking at viscous response only and we said that, this kind of use response is useful, if we are looking at mainly pipeline transport or those kind of problems, where things do not change much. So, only for those situations, it may be useful to do this.

So, but we know that this is only a partial picture there and in the last part of the course, we will discuss a non-Linear viscoelastic model, which when you apply in full, it will give you this shear thinning behavior. So, that you do not have to assume an empirical model or model like power law to say that I will just assume eta is related to gamma dot y x, using some equation, what we will have is a full fledged constitutive model, which

describes all viscoelastic mechanisms, in the material and then on that, if you say gamma dot yx is constant, it will give you the response and that response will be also shear thinning for that.

For example, for a Linear viscoelastic model, that is not true, because for Linear viscoelastic model if I say gamma dot yx is constant, then steady state response is only constant viscosity. So, Linear viscoelastic models, even though they are viscoelastic, can give us only this part of the steady shear response. No matter, how high the strain rate, we go to, we will get only and therefore, we had said that this is the 0 shear viscosity.

So, is there given, that these two are very different set off examining, the material qualitatively at least both of them, seem to have similar response, that there is, it looks like that, there is a constant viscosity, up to certain time scale, because both frequency and strain rate are controlling the time scale, this left hand side, the time scale is larger and larger that is being given to the material, when you go to higher frequency or higher strain rates, we are giving much less time for the material to respond.

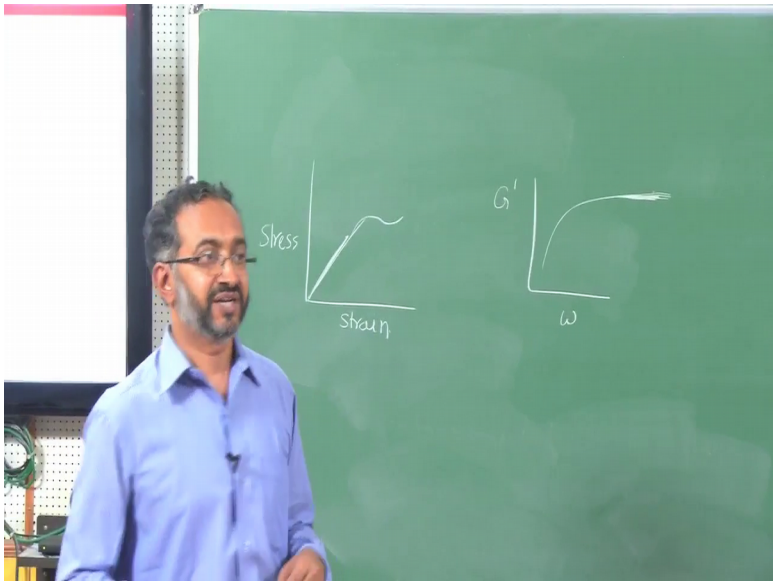
So, do you think that there might be a correspondence between these two? If a material is shear thinning, let us say in this you would expect it to be shear thinning here also or if the material has, for example, one of you was asking about a Boger fluid, which is an example of a fluid, which has constant viscosity. If you do steady shear on, it shows constant viscosity, but. In fact, if you do oscillatory shear, you can characterize the elastic contributions also. So, it has elasticity, but it is a constant viscosity elastic fluid.

So, such possibilities are there. So, is it possible for us to say that there we should not really look at correspondence between these two or maybe there is some Indian. We are trying to characterize a viscous like response. So, when we do steady shear, we are largely looking at the viscous response of the material. The fact that, because it is a steady measurement, whether we ignore all elastic contribution and look at it this way or actually look at it as a response of a larger viscoelastic model, there those are two ways, but in the end the method, is only trying to characterize a steady response.

So, any thoughts on given, that we now, we have looked at these two different viscosities, will there be correspondence between them? Would you expect any correspondence between them? Any thoughts. In fact, you could also think of this in another possible way, is to say that you know, you do a what is called a standard test for

solids, a uniaxial extension in which case, you apply the strain on the material and measure stress versus strain graph and then you get a modulus usually.

(Refer Slide Time: 26:54)



So, you measure the stress and strain and then you get a modulus, the response may be complicated, but initial part of the elastic portion you get, what is called the modulus, the Young's modulus of the material.

And then we are now measuring this g prime. So, are these two related right. So, in one case, we are doing the material test only, under elastic part of the response and then we are also not doing a time dependent test. We are assuming that the material response is going to be independent of the strain rate. We only talk of stress strain, though the real experiment is always done at different strain rates, but we assume that the response will be independent and. So, therefore, we always talk of a modulus value. Now, is that modulus value and this g prime that we measure which, again is characterizing the elastic contribution, of the material, will these two be related under some conditions.

So, in this case this is a fluid test generally what is used this is something we are doing for viscoelastic material, but viscous contribution of a viscoelastic material this is a test which is done for solid and then, but we get some response like this. So, this is a test being done for viscoelastic materials. So, this G prime that we are getting which supposedly where material is largely elastic only will that be related to this modulus. So, that is the question.

So, what are your initial thoughts on is it useful to relate like this is it useful to think like that and/ or should we be careful in comparing properties of these kind in the end, we are measuring modulus and modulus elastic contribution elasticity modulus of Young's modulus of elasticity viscosity dynamic viscosity which is viscous contribution to viscoelastic to material stress.

So, we are not really comparing quantities which are signifying different, but they are being examined in different types of tests. So, what would you expect any

Student: (Refer Time: 29:42) elastic to solid like behavior.

Ha.

Student: Prime distance should be higher and higher (Refer Time: 29:48) same type of distance.

Student: (Refer Time: 29:52).

No. So, that is I am saying, let us compare only this g prime. When we the material is largely elastic. So, at least can this be compared with this modulus. Similarly, this eta 0 and this eta prime can that be compared, will we get the same response? So, under those circumstances at least we should get the same response, given that now, even in oscillatory modes, sufficient time is given and you get a constant viscosity, which is only viscous. What you would expect is, at very low frequencies, it to be terminal viscous response.

Student: Yes.

Which means, it is going to be just constant viscosity. Similarly, here at very low strain rates, you get only viscous response. So, in both cases, the material is being examined beyond the largest relaxation time of the material. So, those ought to be similar.

Student: No deformation (Refer Time: 30:58).

Ha.

Student: In both cases we will not (Refer Time: 31:00).

Yes.

Student: Large.

So, even though, you are doing steady shear, you will confine yourself to load deformation. So, therefore, both in the end being become identical type of material response. So, the eta 0 that you measure from here and eta 0, that you measure from here ought to be same. Similarly, here the modulus, that you measure of course, what usually we will do is, we will measure tensile modulus, from which we can calculate shear modulus and this is usually shear, the way we are defining. Of course, we could also measure e prime, which is in tensile mode. So, those are to be related to each other, but that is again at a very limit, because we are also going to do this test at extremely high frequency and low and deformation and this also is low deformation behavior.

So, this is some of these expectations are usually reasonably observed. So, the two materials, which will show. Let us say young's modulus to be one higher than the other, it is E prime or G prime, will also be higher than the other, because it is signifying the same elastic contribution or the two materials, which have a different eta 0 1, higher than the other in steady shear, will also show here.

Now, the question is of higher frequencies and higher strain rates. So, there the picture is not. So, clear clearly because in one case we are applying large deformations and waiting for steady state in the other case we are continually deforming the material, but it. So, happens that there are several materials which actually show that if you impose you plot eta prime and eta. So, let us say this is eta prime and then you plot eta and function of gamma dot yx or function of omega they seem to show very similar behavior and. So, this is called Cox Merz rule.

As you can see, this is not a theoretical sort of principle based on which, we can say why in some cases? It is observed, we only have an empirical observation and some arguments for the class of fluids, which show this kind of behavior. So, whenever you have a material, whose equilibrium structure does not get disturbed a lot, then you will observe this correspondence between the steady shear and the oscillatory shear viscosities right, because the structure is such that, it is not very subject to deformation and does not get really perturbed away from the equilibrium structure.

But in general, most materials, you will not observe this Cox Merz rule, but generally again, if you are interested in a new material, like a dispersion, this is one of the useful

thing to do is to look at it. An oscillatory shear characterized eta prime, put it in steady shear, look at characterize eta and then compare the two, if they do not compare well at all, you know, you have a task at hand to try to say what are the, a mechanisms which are valid for large deformations. How is the material structure changing under deformation? Is there orientation? Is there agglomeration breakage? What are the basic mechanisms, which are taking place.

So, therefore, it becomes important for us to compare these different responses, in order to understand the underlying material structure. So, with this we will stop now and in the next lecture, we will look at time, temperature, superposition.