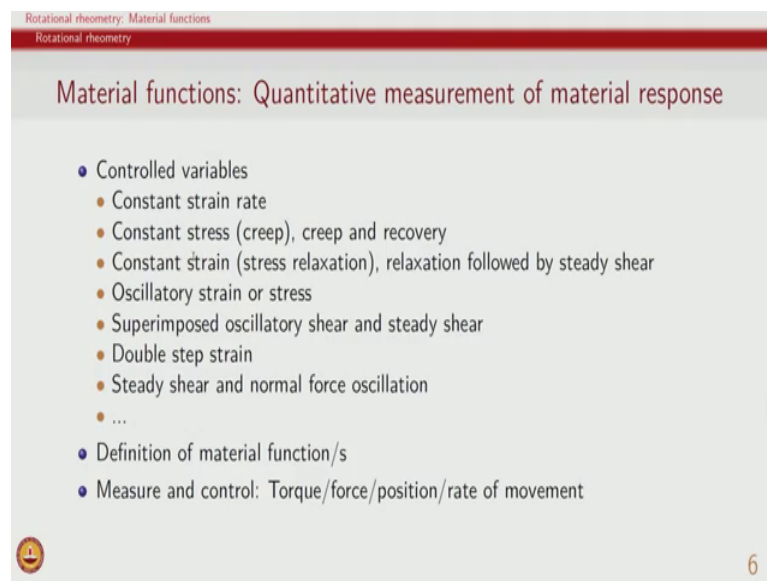


Rheology of Complex Materials
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Lecture – 37
Rotational rheometry: Material functions

In this segment, we are looking at rotational rheometry and the definitions of material functions and how we can achieve as good set of measurement conditions to make sure that whatever are the assumptions related to rheometric flows are being met. And therefore, with that purpose we are looking at first a summary of all the material functions and the material functions are defined for different types of conditions that we impose on the material.

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Rotational rheometry: Material functions
Rotational rheometry

Material functions: Quantitative measurement of material response

- Controlled variables
 - Constant strain rate
 - Constant stress (creep), creep and recovery
 - Constant strain (stress relaxation), relaxation followed by steady shear
 - Oscillatory strain or stress
 - Superimposed oscillatory shear and steady shear
 - Double step strain
 - Steady shear and normal force oscillation
 - ...
- Definition of material function/s
- Measure and control: Torque/force/position/rate of movement

6

For example, one of the control variables could be a strain rate and which is kept constant. So, using constant strain rate, what are the measurements that can be done.

So, what are the measurements that can be done using constant strain rate? Stress relaxation is constant strain. It is there in the list itself. If you maintain constant strain then that is the stress relaxation. So, what is constant strain rate measurement? So, viscosity is a measurement that can be done is constant stress strain rate, what else? In fact, we have discussed two other materials,

Student: (Refer Time: 01:26).

Yes, normal stress differences and one more.

Student: (Refer Time: 01:30).

Yeah. So, first normal, so, what is called primary normal stress difference and secondary normal stress difference or first and second normal stress difference and one more material function?

Student: (Refer Time: 01:40).

That is primary and secondary. n_1 and n_2 are the primary and secondary normal stress differences and then we also have stress growth viscosity. We apply a constant strain rate and then we measure, how does viscosity change as a function of time.

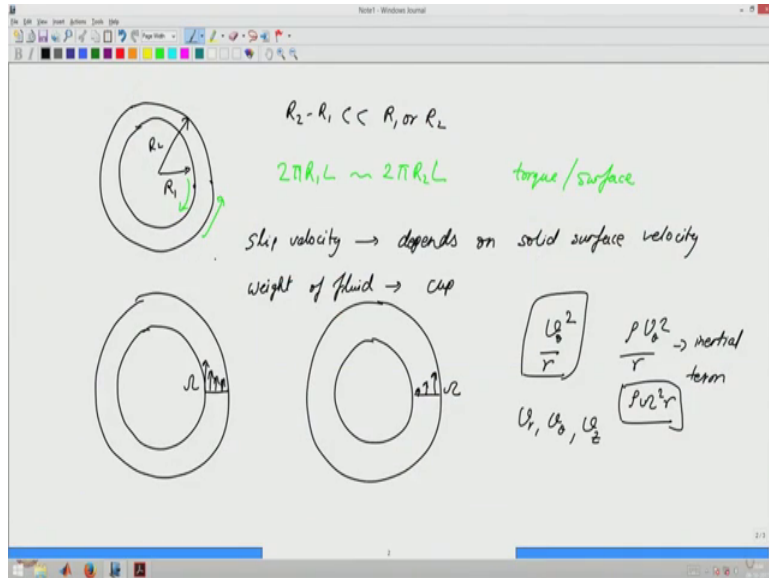
Similarly, we can have constant stress, which is creep and analogous experiment to creep is you apply the constant stress, you measure the creep response and then you remove the stress that was applied and therefore, look at the recovery of the material in case of a solid material we can apply stress the material will deform as soon as I remove the stress the material will come back. So, creep and recover is instantaneous strain and instantaneous recovery in case of a perfect solid material. So, to study viscoelastic response we can not only measure creep we can also measure the recovery.

So, in class we have of course, looked at only constant stress the creep itself, but creep and recovery experiments are quite often done together you anyway apply creep a constant stress measure the response of the material and then remove the instruct rheometer to remove the stress and then look at what happens to the material. So, creep and recovery response.

Similarly, constant strain is where stress relaxation is observed because there is a decay in stress decreases as a function of time and so, you could also do this experiment by instead of saying constant strain because in reality in rheometer it is difficult to achieve a constant strain instantaneously when you say go from 0 to γ_0 , some strain which is let say 10 percent or 4 percent it may not be always feasible. A real instrument may not be able to do this in very small amount of time, for example, it may not be able to do in microseconds.

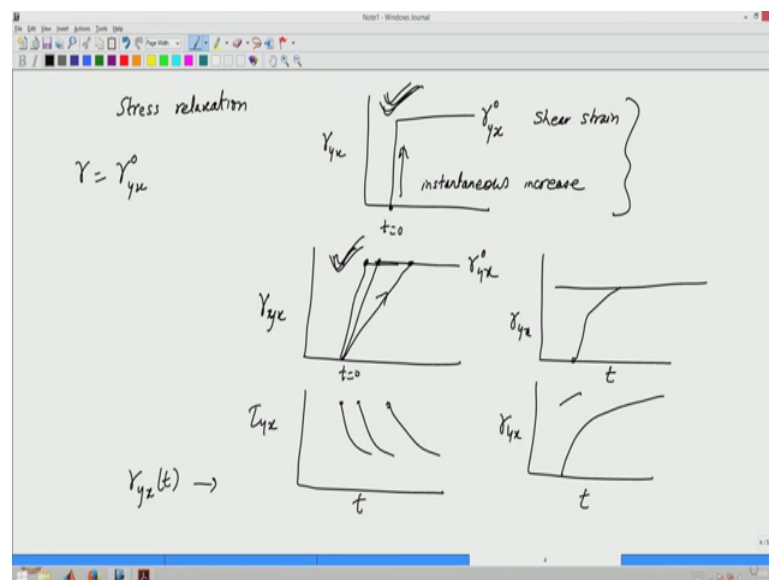
So, then a better approach is to tell the instrument that you go from 0 to a 2 percent strain by different rates.

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And, this we have discussed in one of the earlier segments where we said that you could reach the same strain by applying different strain rates.

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So, for example, a stress relaxation experiment is ideally, so, stress relaxation experiment is ideally only looking at gamma yx, at time t is equal to 0, we apply a constant gamma

naught $\dot{\gamma}$ which is a strain, shear strain. So, it may not be possible to do this instantaneously this change this change is assumed to be instantaneous.

Student: (Refer Time: 04:32).

So, instantaneous increase in step strain may not be always feasible and so, what you could tell the instrument to do is the following. You can say that at time t is equal to 0, increase the strain and reach the same $\dot{\gamma}$ naught and this increase could be at different rates. So, you can do a slower rate, you can do a faster rate and then at this point when the strain is reached you can start looking at what is the stress. So, you can start looking at stress as a function of time for all these different experiments.

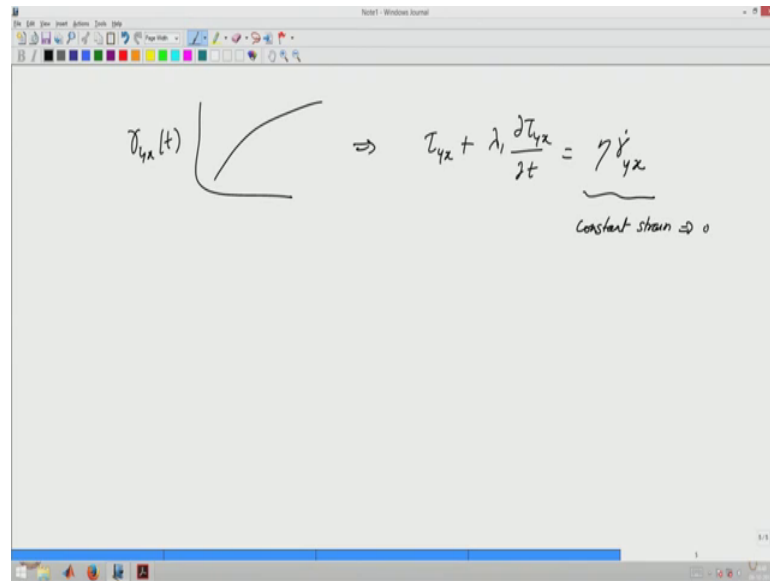
Student: (Refer Time: 05:13) level (Refer Time: 05:15) is it necessary to (Refer Time: 05:17).

That is what. So, you can it is not necessary, but when you instruct the instrument to do this, instrument will anyway take some finite time and you may not have an idea about how much time is taken you could for example, you could say that you will reach the strain in two different linear you could also reach the strain in an exponential manner. So, all these are possibilities, but remember what was our analysis and definition of stress relaxation. Stress relaxation modulus was that on the material you apply $\dot{\gamma}$ naught t x. So, it is a constant strain being applied on the material and then you look at the response. Clearly this is what has to be done.

Given the limitations of the instrument you could do either of these, but most preferably it is better to do this because at least during this period the strain rate is constant. In this kind of things it is even more arbitrary variation remember that in case of viscoelastic material the current response depends on all past histories of deformation. So, the more complicated deformation that you impose on it the more complicated the analysis might be.

Of course, for current research purposes people are engaging with this kind of problem that if I apply an arbitrary time signal, can I analyze and get the material response because I know that instruments cannot really give a step increase why do not I do this I will just apply an arbitrary time signal.

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So, I will say that I will apply a gamma yx which is achievable and maybe it is like this. Now, can I analyze the material response. So, if you remember in case of Maxwell model we had tau yx plus lambda 1 delta yx by delta t is equal to eta gamma dot yx and for a constant strain this was 0, but if you do not have constant strain which is this complicated function then this right hand side is a function of time. So, this therefore, this will be a function of time.

So, clearly, the solution also will be a function of time and for a simple material like Maxwell model you can see that complexity of response increases as soon as you have your input also more complicated function of time and we are mostly working when we are doing many of these experiments we are looking at response of new materials for which we do not know what the responses.

So, therefore, it is far better to first study those materials under much more control conditions. So, our idea is to then therefore, always try to keep a step input. If possible if this is not possible then at least do this type of experiments. So, those are the kinds of things then you can do and then say that at least in the limiting cases I know the response very well.

Student: Yeah.

The other aspect could be that you will see for some materials that the response does not change much. So, then that also gives you enough confidence that look the step increase is happening at short enough time and even though I am applying to three different rates the response is somewhat identical. So, therefore, I will I am not worried about what strain rate is being imposed for the analysis. But, if it is very sensitive to this then you must always then say that look this experiment was done with this strain rate and currently maybe we do not understand why is the material behaving differently, but this is what we need to understand in future. So, it will completely depend on the material and material response.

So, similarly, we looked at oscillatory shear for quite some time we looked at you can apply oscillatory strain or stress or in fact, strain rate also and then we can look at the material response and these are not all. So, constant strain rate, constant stress, constant strain and oscillatory strain or strain rate are only the basic. So, in fact, it is possible for us to apply superimposed oscillatory and steady shear. So, can you think of a possibility where such experiments will be useful or a material system and an application where, we will measure the material properties while they are flowing also.

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Oscillatory shear \rightarrow small deformation

Steady shear \rightarrow large deformation

$$\dot{\gamma}_{yz}(t) = \dot{\gamma}_{yz}^0 + \dot{\gamma}_{yz}^* \sin \omega t$$

$$\dot{\gamma}_{yz}^* = 0 \Rightarrow \dot{\gamma}_{yz}(t) = \dot{\gamma}_{yz}^0 \rightarrow \text{steady shear}$$

$$\checkmark \dot{\gamma}_{yz}^0 = 0 \Rightarrow \dot{\gamma}_{yz}(t) = \dot{\gamma}_{yz}^* \sin \omega t \rightarrow \text{oscillatory shear}$$

$$\underline{\dot{\gamma}_{yz}^* \text{ amplitude}} = \frac{\dot{\gamma}_{yz}^*}{\omega} \Rightarrow \underline{\dot{\gamma}_{yz}^*} = \omega \underline{\dot{\gamma}_{yz}^0}$$

When we apply steady shear the material is flowing continuously being flown, because in oscillatory shear we are imposing small deformation. So, this is small deformation and

steady shear is basically flow, so, large deformation. So, what we are saying now is can we combine the two?

So, for example, if we have a steady shear experiment and we think of it in parallel plate then basically the plate keeps on moving like this that steady shear, oscillatory shear is we just do this. But, now what we are saying is it is like the plate is moving also, but at the same time it is doing oscillation also. So, if you look at the position of the plate it is continuously moving, but at the same time it is oscillating around its mean position. So, if you write it in terms of let us say a function. So, γ_{yx} as a function of time is some γ_{yx} which is constant plus another γ_{yx} star, let us say, $\sin \omega t$ and let me put this in terms of strain rate. So, if let us say this γ_{yx} star is 0, then what do we have?

Student: (Refer Time: 11:36).

Steady shear. So, if $\dot{\gamma}_{yx}$ is 0, then $\dot{\gamma}_{yx}$ is nothing, but $\dot{\gamma}_{yx}$ which is steady shear and if we have $\dot{\gamma}_{yx}$ as 0, then what do we have? Then, we have an oscillatory shear, which is oscillatory shear. So, why would be of interest to do such a complicated flow? In which situation we may want to say that if I apply only the oscillatory shear then since deformation is small, $\dot{\gamma}_{yx}$ is going to be such that overall deformation of the material is small. Then, what deformation will be basically how much will be deformation is $\dot{\gamma}_{yx}$ is the deformation strain rate? What will be the strain, any idea? What will be the strain if this is the strain rate, integration of that. So, basically ω will come out. So, γ_{yx} star which is the amplitude of strain.

Student: (Refer Time: 13:03).

Amplitude. So, let us forget about the time just the amplitude, what will be the amplitude of strain it will be $\dot{\gamma}_{yx}$.

Student: Into ω .

Divided by ω or into ω ?

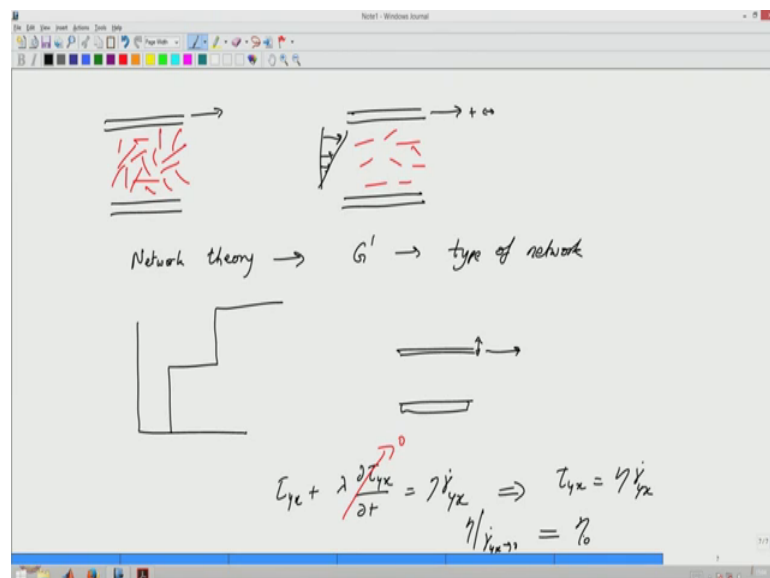
Student: Divided by ω .

Divided by omega right. So, this is the strain. As long as frequencies and gamma dot are maintained in such a way that we do not violate that strain amplitude should be small. So, for example, if I choose my strain rate amplitude to be small enough even if I go to small frequencies my strain will still remain small. Of course, large frequency the strain will automatically remain small because based on this relationship gamma dot star yx is omega times the strain amplitude.

So, if I choose one strain amplitude which is small strain rate will have to be higher and higher at higher frequencies. When I choose this to be constant I have to make sure that my omega range is fixed. So, that this never exceeds a very large value that is all this is essential because remember whenever we did oscillatory shear it was for linear regime, it was for small deformations only. So, that is why oscillatory shear is for small deformation and steady shear is we can impose arbitrarily large amount of deformation.

So, now the question we are asking is can we do put both of these together and why would it be of interest. So, one example is where if the material structure depends on flow itself and this for example, can be there in let us say if you have a crystalline gel a material which has or rod like particles.

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So, if you have material with rod like particles, they will all be dispersed like this and there will be a network of these materials. So, if this is stationary then the material will have one structure. As soon as you impose shear on it right if you impose shear on it then

what happens is on average you will find that many of these rod line particles will start aligning and now, the structure of the material is entirely different. And, if you want to investigate what is the networking points in case under shear then what you can do is you can say that on this I will impose a small oscillatory shear.

So, then I am making the material flow which means it is flowing and there is a constant velocity every where there is a simple shear flow which is being imposed on the material, but on top of then I will also do small oscillation.

So, I will characterize a network here and not the network here because through network theories we can relate the storage modulus to the type of network and the G' that I measure when there is motion is going to be different and this kind of difference may be useful in for me to understand; for example this can be there in let us say if there is a waxy gel will clogs pipeline.

You have a pipeline in which there are it is possibility of some material to crystallize out and form these kind of needle shaped crystals and if they block and the viscosity of such blockages will depend on whether the material is flowing or whether it is stationary. By doing such experiments where you are superimposing two different types of deformation, you may get better idea about how is the structure of the material and what is it is response.

So, in fact, there are multiple such more complicated deformation which are used by researchers to understand the material behaviour it is possible to impose a double step strain also. So, for example, we discuss constant strain. So, instead of just imposing one strain we can impose large strains, but instead of doing it one we can say one and then another one and in fact, polymer melts were studied in eighties using this kind of double strain experiment. A very recent development is where we have steady shear and then normal force oscillation.

So, again by in this case we have a plate which is going up and down little bit at the same time it is doing steady shear also. So, it is like this you are testing the material where it is doing steady shear, but at the same time it is doing little bit of normal oscillation. So, you are what you are doing in all these thing is you are perturbing the material in a slightly more complicated way, but it is still controlled because this oscillation will be small

compared to this steady motion so that you can analyze the material response in a more effective way.

So, of course, in class so far we have discussed only the first 4 ones and 4 more advanced students of rheology the other modes are much more important from today's research point of view and of course, if we do these controlled experiments very well then we based on the definition we can estimate the material functions by the measurement and control. So, now, what we will do is we will quickly go through and review and make sure that we again keep in mind what are the different material functions which are there for each and every mode that we have defined in class.

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Rotational rheometry: Material functions
Summary of material functions

Steady shear: constant strain rate

- Newtonian fluid
 - Material constant, viscosity, μ
- Non-linear viscous fluid / generalized Newtonian fluid
 - Material function, viscosity, $\eta(\dot{\gamma}_{yx})$
- Linear viscoelastic material
 - Zero shear viscosity, η_0
- Non-linear viscoelastic material
 - Material function, viscosity, $\eta(\dot{\gamma}_{yx})$

7

So, the first one is for example, steady shear; steady shear implies constant strain rate and what is the material function that is defined?

Student: Viscosity.

Viscosity. Now, what we are going to do here is to summarize the behaviour for these four different broad class of materials that we have seen; Newtonian fluids, non-linear viscous or generalized Newtonian fluid, linear viscoelastic material and non-linear viscoelastic material. So, we have seen that for a newtonian fluid this viscosity is a material constant. It can depend on temperature, but it does not depend on anything else; temperature, pressure and those variables it can depend on, but it does not depend on for

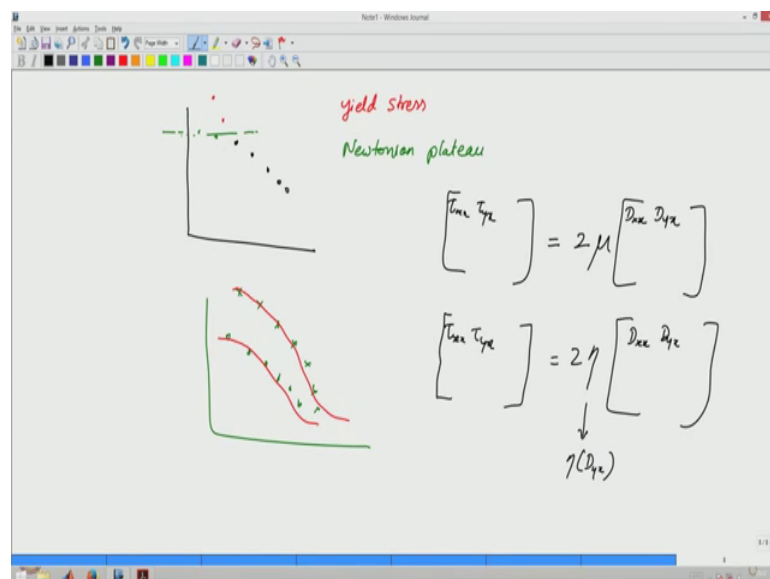
example, the strain rate that is being applied on the other hand non-linear viscous fluids we define a material function viscosity and it depends on the strain rate which is being applied and based on this we decide define material whether there are shear thinning or shear thickening and so on.

For a linear viscoelastic material the viscosity, in fact, is a constant. I hope you remember that for Maxwell model viscosity is constant, because and at steady state this derivative goes to 0 and therefore, we only have τ_{yx} is equal to $\eta \dot{\gamma}_{yx}$ and. So, viscosity is constant for a linear viscoelastic material such as Maxwell model.

So, therefore, for linear viscoelastic materials we call it zero shear viscosity. This is recognizing the fact that most viscoelastic material will not have a constant viscosity, but at low strain rates they are likely to have a Newtonian plateau or a constant viscosity and therefore, that viscosity is called zero shear viscosity, the strain rate is tending to 0. So, η_0 is defined when strain rate tends to 0. So, η as $\dot{\gamma}_{yx}$ tends to 0 is defined as η_0 . Now, so, that depends on the different materials. So, for example, we will see later on that materials let us say which are yield stress fluids, in fact, do not have a zero shear viscosity.

So, lower and lower strain rate you go the viscosity still keeps on increasing and. In fact, it seems to be diverging. So, in that case then we will say that viscosity is not zero shear viscosity, it does not exist.

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So, for example, you may get some set of data points like this when you do the measurement. If you get such measurements you need to definitely repeat and say that I will try to measure at lower strain rates. If you get data points which are, let us say, like this there seems to be now a possibility of zero shear.

So, even if it is not feasible let us say to do the measurement it is possible for you to say that maybe this might be the zero shear viscosity, but if let us say the data points are like this, then you say that in this case there is no zero shear viscosity and then we will see that this kind of a material is more likely to be an yield stress kind of a material which is a different class of behaviour which we have not discussed in the lecture so far, while the green ah this thing the data are hint at a Newtonian plateau.

So, for linear viscoelastic material the behaviour prediction is that there is going to be a constant viscosity. So, we say that therefore, linear viscoelastic material can only predict the Newtonian plateau or the low strain rate response and this makes sense because at low strain rates strain is also likely to be low. Remember, these are state steady flow, which means we are imposing a constant strain rate. If you have a very high strain rate then the deformation on the material is very large. If we have a very low strain rate then even if we perform the experiment for some time, the overall deformation that is being imposed on the material is low and therefore, linear viscoelastic material can only predict zero shear viscosity.

Other way to remember this is also the fact that linear visco-elasticity relates to the equilibrium structure of the material we are not perturbing the material very far away and by applying very small deformation rate and by keeping deformation small we are only perturbing the material so much that it does not really go away from its equilibrium state. So, therefore, zero shear viscosity is a good measure of material structure, it is a good indicator of material structure.

On the other hand, if we impose any arbitrarily large strain rate then the material function will be dependent on the strain rate. Now, what is the difference between non-linear viscous fluid and non-linear visco elastic material? At least if you look at the definition here they are identical, it is in our choice. If we want to ignore the elastic contributions if we want to ignore the elastic mechanisms and we just need a viscosity as a function for pumping purposes or largely steady purposes, then we can go ahead and adopt non-linear

viscous fluid as a model which is what was done traditionally in earlier days, in sixties whether it is paint or coal slurry or variety of such materials were assumed to be either power law fluid or Carreau–Yasuda model or any such model where we say that underlying mechanisms may be is elastic, but we will ignore all that and assume as if material is only behaving, the only feature it has is viscosity which is dependent on strain rate there is no other feature which is interest.

Student: (Refer Time: 25:17).

Not necessary. We are only saying that we do not know the mechanism of shear thinning and all that. We are capturing that using empirical models which are power law or such models. So, we are it is not necessary for us to confine to low strain rates or high strain rates we are confining ourselves in terms of explanations and understanding of the basic mechanisms as to, for example, we are not really saying why is there shear thinning in the material.

For example, if I do experiments and if I find one cement slurry and another cement slurry and in both cases I will get let us say shear thinning response. So, I have two compositions of cement slurry and one case I get data like this and the other case I get data like this. So, is there why is there a difference between the two? What I could do is, I will say that look I am not really interested what I will do is I will fit both of these to a model which is Carreau–Yasuda model, I will get all my parameters and I will use that only this information for some pump design where viscosity is an important parameter in viscosity is not constant, but if at all let us say I am interested in the mechanisms then I must think about what is the structure and then I will have to say that the material is a non-linear viscoelastic material.

There are different contributions there are different relaxation processes which all respond at different times and depending on which strain rate I apply some mechanisms are more active and therefore, I get different response at different strain rates. So, then I am saying that I will have to look at material as a non-linear viscoelastic material and if I look at the material as a linear viscoelastic material again I am constrained to only small deformations in which case, I cannot really explain the shear thinning or shear thickening nature of the material. So, this is one example.

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Rotational rheometry: Material functions
Summary of material functions

Stress relaxation: constant strain

- Newtonian fluid
 - Instantaneous stress decay
- Non-linear viscous fluid / generalized Newtonian fluid
 - Instantaneous stress decay
- Linear viscoelastic material
 - Material function, relaxation modulus $G(t)$
- Non-linear viscoelastic material
 - Material function, relaxation modulus $G(t, \gamma_{yx}^0)$
 - Time strain separability, relaxation modulus $G(t) h_\gamma(\gamma_{yx}^0)$

8

Just to summarize for the viscosity, so, the next experiment is stress relaxation which we define where a constant strain is applied on the material and we saw that Newtonian fluid case there is a instantaneous stress decay. Basically, because we are applying a constant strain you do not have to apply any stress to maintain the fluid in the new position. So, therefore, stress has immediately only while the time applying strain there was a small stress which was needed, but beyond that no stress is needed just remember that contrasting with a elastic solid we will always need to keep constant stress on the material if we apply a constant strain.

So, in this case again non-linear viscous fluid when we say or generalize it will again have instantaneous decay, because when we assume a fluid to be generalised Newtonian fluid we are assuming that it has no elastic features and just to remind you of the detailed model again, if you remember the stress with all it is nine component was related to $2\mu D$. So, this is d_{xx} this is τ_{xx} and so on, τ_{yx} , this is d_{yx} . So, if we impose d_{yx} we are only going to get τ_{yx} and if d_{yx} is constant τ_{yx} has to be constant, because there is no other dependency.

Similarly, the non-linear viscous model is also 2 eta same thing. Only thing is this is a function of shear rate, but otherwise there is no difference. So, again if d_{yx} is constant eta may be a different value because it depends on, but τ_{yx} has to be constant. So, therefore, there is no elastic feature at all both of these are completely viscous fluids and

that is why we call it as a generalized Newtonian fluid one is a Newtonian fluid which has constant viscosity the other one is generalized Newtonian fluid which can have viscosity which varies, but it still is the same model stress is proportional to strain rate. Proportionality constant is a function of strain rate in case of generalized Newtonian fluid and so, the material function for a constant strain is instantaneous stress decay for both of these and it is relaxation modulus and if you recall for Maxwell model the relaxation modulus was, what was the functional form for relaxation modulus for Maxwell model?

Student: (Refer Time: 29:58).

It is an exponential decay. An exponential decay depends on what is the lambda value right and so, however, if it is a non-linear visco elastic material then the material function will be relaxation modulus which is a function of time as well as the strain which is imposed on the material.

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The image shows a whiteboard with the following handwritten equations and notes:

$$\tau_{yx}(t) = \gamma_{yx}^0 G e^{-t/\lambda}$$

$$G(t) = \frac{\tau_{yx}(t)}{\gamma_{yx}^0} = \underline{\underline{G e^{-t/\lambda}}}$$

γ_{yx}^0 is small

$$h_Y(\gamma_{yx}^0) \rightarrow 1$$

$$G(t, \gamma_{yx}^0) \rightarrow G(t)$$

So, if you remember for stress relaxation experiment for Maxwell model, we had got that tau yx as a function of time will be gamma naught yx which was applied on the material times e to the power minus t by lambda, this is the exponential decay. So, the relaxation modulus which is going to be tau yx time divided by gamma naught yx is going to be G e to the power minus t by lambda.

So, the relaxation modulus does not depend on the input strain, it only depends on time and this is our definition of what is a linear response scaled response. If I increase strain twice the overall stress response also increases twice so that the relaxation modulus remains independent of the strain input. But, in case and this is again by saying that with the material structure is pretty much the same; whether I apply γ_0 or two times γ_0 both of them are still small deformation material structure is the same therefore, the response which is measured using relaxation modulus remains same.

On the other hand, if I apply very large deformation then the relaxation modulus will be a function of time and also function of the strain which is being applied. The overall relaxation modulus can be split into two functions; one which is a function of time and another one which is a function of strain and this is called time strain separability. The fact that overall material response can be split into the response, which is function of time alone and the other one which is function of strain; so, what happens to $h(\gamma)$ at very small deformations?

So, what value will it take? 1, right? It will become 1 at small deformation so that at small deformation for when γ_0 is small $h(\gamma)$ which is a function of γ will tend to 1 and therefore, G will tend to just $G(t)$ and which is the linear visco elastic response and linear visco elastic response is observed whenever we have strain to be very small.

So, therefore, now we have looked at two of the material functions and reviewed them in the next segment we will review the remaining material functions.