Rheology of Complex Materials
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Lecture – 54
Review of material functions 3

So, we in this course on rheology, we have reviewed material functions which could be evaluated using rotational geometry. We will continue looking at some of the material functions and summarize them again. And also in this segment of the lecture we will look at some of the material functions which are for not shear flow, but extensional flow. So, we have been following basically this overall framework in which we say that material response has to be characterized.

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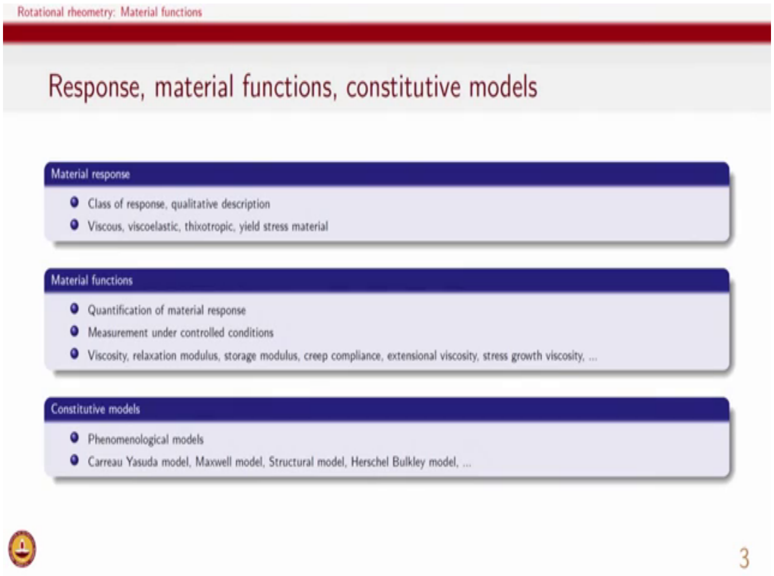

First we recognize the class of material which the response might belong to. then we have quantified the response using a material function, and parallelly we have also been always looking at models and ah. So, earlier we have reviewed already material functions; such as steady shear where we get the viscosity stress relaxation, which is based on a constant strain being imposed on the material.

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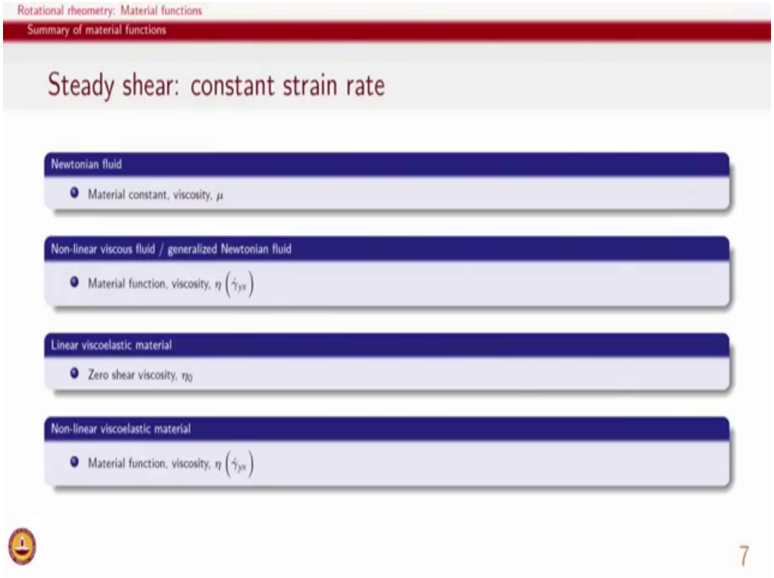

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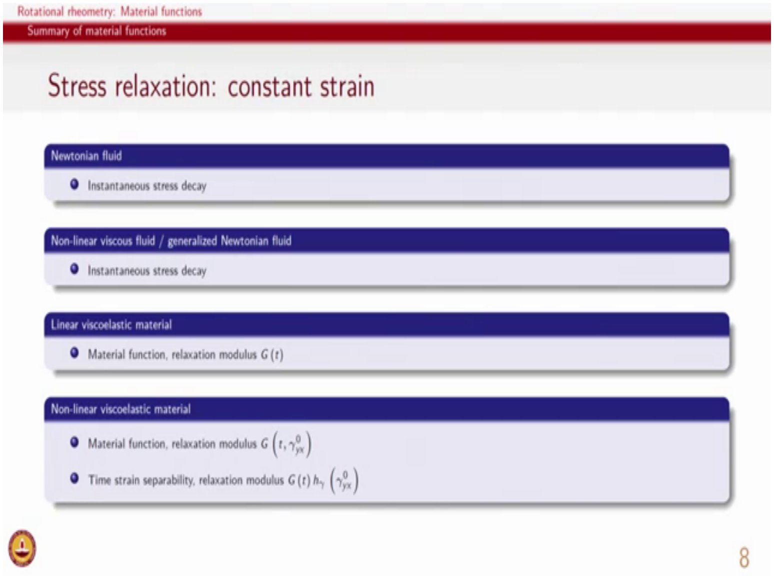

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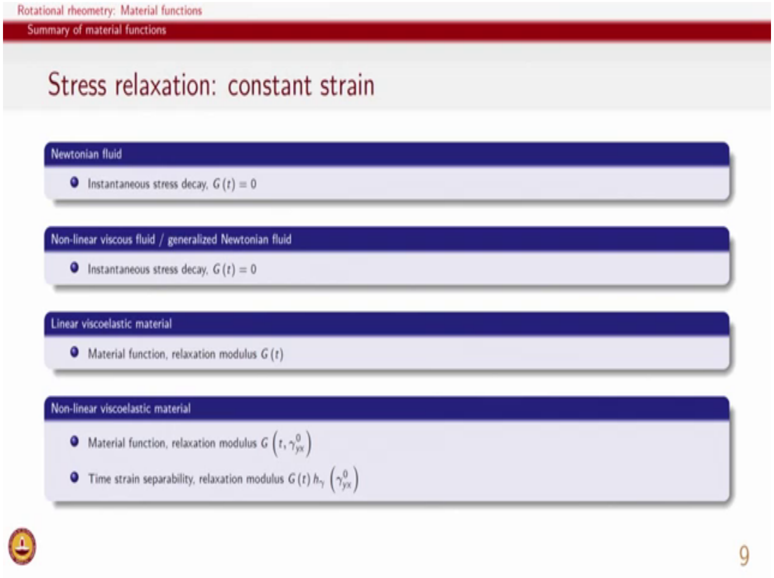

Similarly, we also looked at linear as well as non-linear response, we examined creep where we define the com compliance of the material, and again linear and non-linear response. Then we also looked at oscillatory shear in great detail where depending on.

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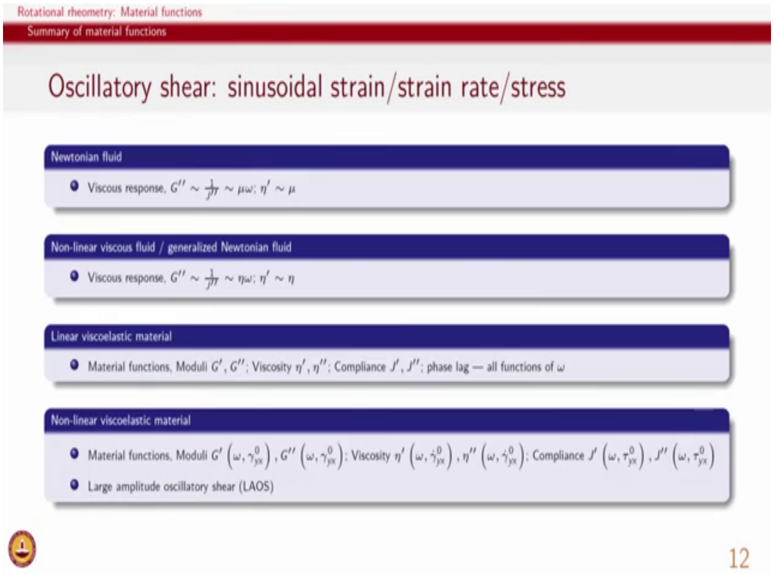

What is the input and output, we could either define the moduli or we could define the compliance or we could define the viscosity.

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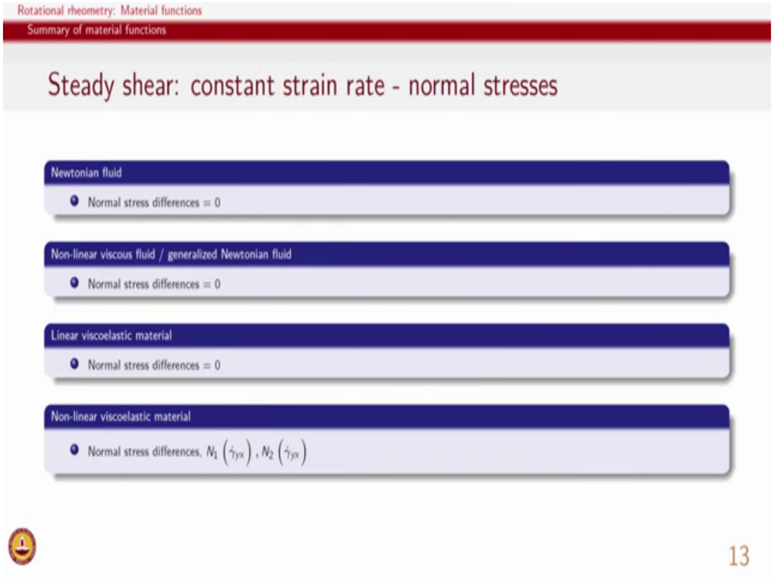

And now, we will continue and look at some of the responses and material functions which belong to the non-linear cha response. for example, normal stresses we saw that normal stress differences as well as normal stress difference coefficient will be non0 for viscoelastic fluids. only if the viscoelastic fluids are subjected to very small deformations or in the linear regime then normal stress differences can be 0. So, for example, of course, this is a simple shear flow again, and a constant strain rate is imposed.

And based on the constant strain rate we wait for a steady state to be achieved, if we measure the shear stress then of course, we define viscosity, we measure the normal stresses and we define the normal stress differences N 1 and N 2. And we know that for Newtonian fluid there is no normal stress difference in simple shear flow. Similarly, for a generalized Newtonian fluid or a non-linear viscous fluid as well, we will not have any normal stress differences even for a linear viscoelastic material because deformations are small the normal stress differences do not exist. Only in case of non-linear viscoelastic materials the normal stress differences would arise and of course,

Both N 1 and N 2 if you recall, N1 is defined based on tau xx and tau yy if x is the direction of the flow and y is the direction of shear. Similarly, N 2 in same situation will be defined as tau yy minus tau zz. And so, both of these is the normal stress differences are functions of this strain rate the constant strain rate which is applied.

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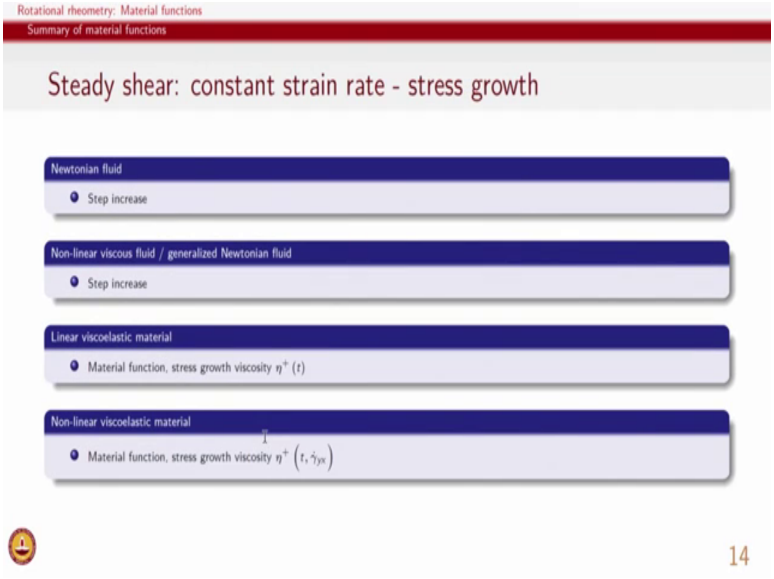

And so, similarly we can also have the next important viscoelastic material function which we have reviewed which we have seen quite a bit we also saw experimental measurements based on that which is called stress growth. in this case if we increase strain rate from 0 to a constant value, for a Newtonian fluid as soon as a strain rate becomes constant the stress becomes constant.

And so, if we are measuring stress as a function of time, basically there is a step increase in stress. Stress is 0 when strain rate is 0 stress is constant when con strain rate is constant. So, therefore, there is a step increase. A similar step increase is also there for generalized Newtonian fluid and non-linear viscous fluids. For a linear viscoelastic material, the stress growth viscosity is a function of time. And if you recall for Maxwell model we had shown that this is an exponential function.

So, if Maxwell model is subjected to a constant strain rate, then the stress increases exponentially and eventually in each is a steady state. And for a non-linear viscoelastic material the material function that we define is again the stress growth viscosity. And however, it will be function of not only just the time, but also the strain rate which is being applied. And so, this is also the non-linear where viscoelastic response is very useful in characterizing, the overall mechanisms in the material which lead to elastic behavior.

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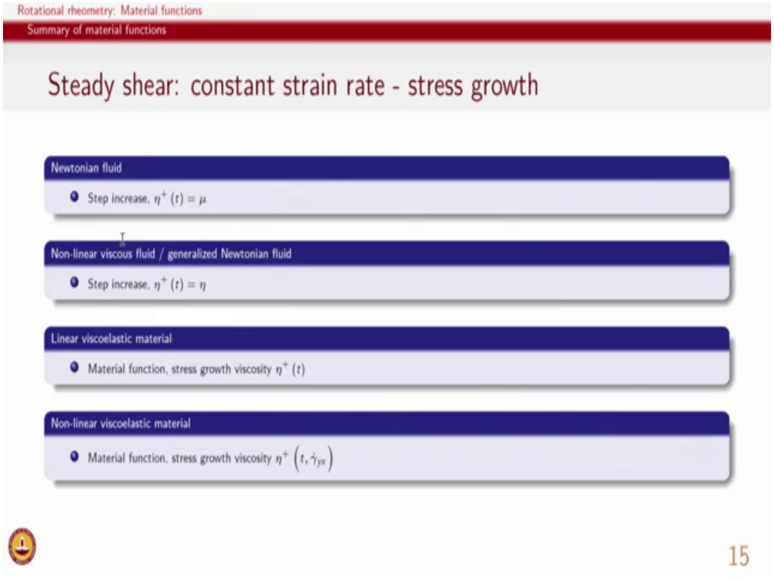

Now if we look at the overall response in terms of definitions, for a since there is a step increase for Newtonian fluid the stress growth viscosity is nothing but just a constant which is the viscosity itself, for a non-linear viscous fluid it is the again viscosity which is a material function because this depends on the strain rate, but it is constant there is no dependence on time. as far as a linear viscoelastic material goes it is a material function which is a function of time itself, and as I have mentioned for Maxwell fluid it is an exponential function.

And of course, it is a generic function for a non-linear response. Now just the way we saw that normal stresses could be are generally evaluated in steady shear, you could also evaluate normal stresses in oscillatory shear.

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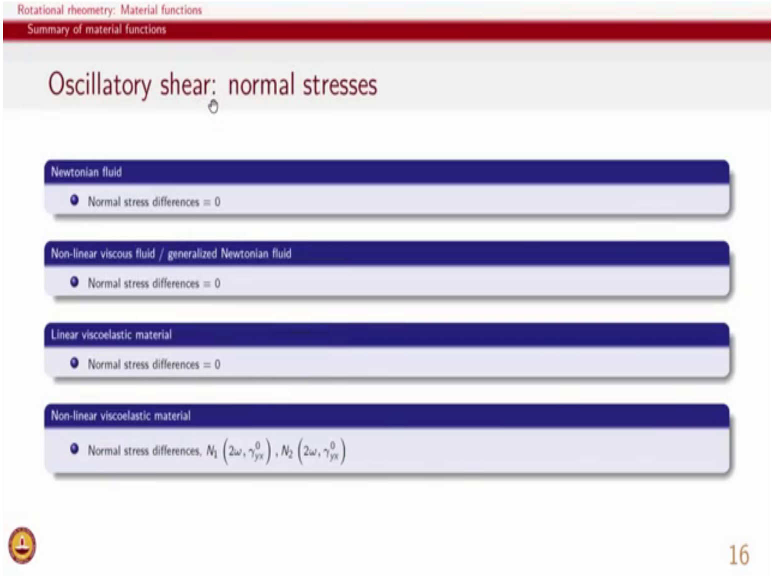

Again in oscillatory shear we apply a constant strain or a constant stress depending on what is the controlling parameter or even a constant strain rate. And then we measure the other variables, and for a Newtonian fluid in oscillatory shear again there would not be any normal stress differences. This is again because let us say if we apply shear then in case of rectangular systems, what we have is only tau xy present. So, this we have seen earlier that because we have a simple shear flow and even if it is oscillating the fact that it is going back and forth.

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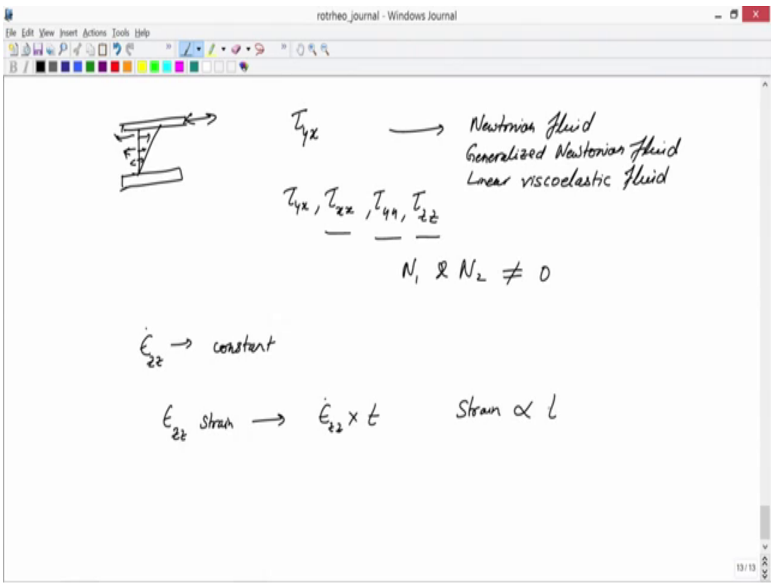

The only stress which will arise in this case is tau yx which is the shear stress. For a general a general viscoelastic fluid, we saw that we could have all the normal stresses as well as the shear stress tau xy non0. So, this is for the Newtonian fluid, this is also for generalized Newtonian fluid. And this is will also be the case for linear viscoelastic fluid. And so, what we have is for a non-linear viscoelastic fluid normal stress differences will be there which implies that tau xx tau yy and tau zz may be non zero.

And therefore, N 1 and N 2 may not be 0. And in that case, these are functions of the frequency. And we have seen that in upper convected Maxwell model can be used to describe the normal stresses in steady shear ah. So, upper convected Maxwell model is the simplest of the model's which shows normal stress differences. So, for using the same model if we were to apply oscillatory shear, we can show that the overall normal stress in fact, varies as twice the frequency which is applied. So, therefore, both N 1 and N 2 are functions of 2 omega. So, where omega is the frequency of strain that is being applied and since it is a non-linear regime the overall normal stress difference would also be a function of the strain amplitude which is being applied.

So, therefore, what we have seen is many of these material functions which are all defined based on rotational rheometry where shear is the predominant mode of deforma deforming the material. And of course, this can be used very effectively to characterize the visco elasticity of the material. Now going forward, we will also quickly summarize the material functions which are used in extensional flows. So, continuing on the extensional material functions are very similar in terms of the set of constant quantities that are kept. For example, we saw that you can evaluate oscillatory shear functions or you could also look at stress relaxation, what we will see is in spirit some of the material functions which are defined for extensional flows are also similar.

So, let us begin the review by looking at first the steady extension, we have defined the extensional viscosity earlier, in which case if we impose a constant strain rate and wait for steady state to reach and measure the stress which is the normal stress and that divided by the strain rate that is being applied gives us the extensional viscosity. And we know that for a Newtonian fluid this is just the trough tons viscosity or extensional or elongational viscosity and it is 3 times mu. For a generalized Newtonian fluid again the behavior remains similar, in the sense that the extensional viscosity is 3 times the quote unquote shear viscosity.

So, sometimes mu and eta are also referred to as shear viscosity to just distinguish it from the extensional viscosity, but they are one in the in the sense one coefficient characterizes the overall behavior of the material in both shear and extension, which is not the same case in case of non-linear viscoelastic materials. As we have seen in terms of the when we were doing review of the material functions we saw that, there is no correlation between the viscosity measured in steady shear to viscosity measure in such steady extension for a non-linear viscoelastic material. for a linear viscoelastic material, extensional viscosity is just related to again the 0-shear viscosity, and there again it is 3 times eta 0.

So, therefore, these are the this is how the extensional viscosity varies for different materials, and of course, for most polymer melts and solutions and multiphase systems non-linear viscoelastic responses of great use. For example, if a colloidal dispersion is being used in inkjet printing, then how is it is extensional behavior at large deformation is of interest. And given that drops may be injected from inkjet printer at various different velocities, leading to different strain rates we may have very different values of extensional viscosity.

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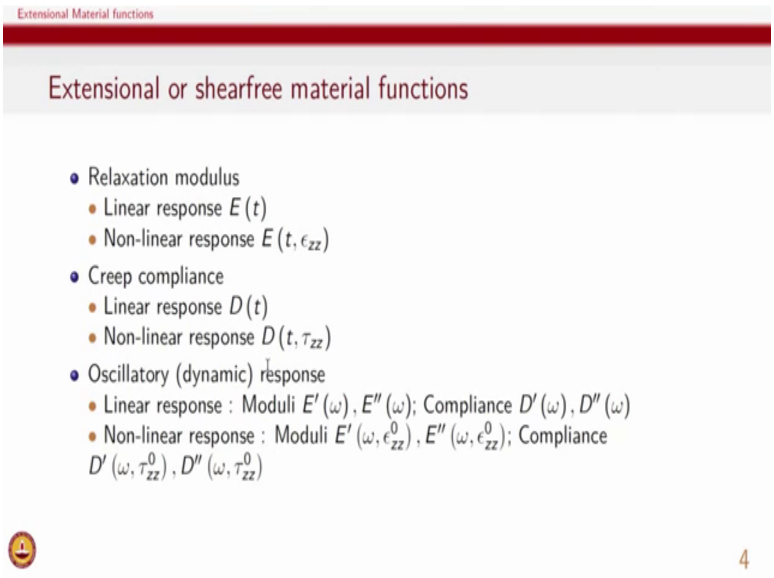

Now similar to the oscillatory functions in case of shear or creep functions in case of shear or relaxation modulus in case of shear we can define extensional or shear, free material functions we say shear free. Because as you recall the overall strain rate tensor in this case has only diagonal components and off diagonal elements are 0.

So, therefore, the overall flow field can be described as shear free. And so, relaxation modulus we had G of t earlier is indicated same way as E of t. The difference between the extensional material function and sheer material function will be in terms of the type of deformation which is being imposed; however, the overall methodology remains the same.

So, in relaxation modulus a constant tensile strain would be applied, and the stress would be measured as a function of time, and the measured stress divided by strain applied will be give us the will give us the relaxation modulus. And in linear response of course, the relaxation modulus is only function of time, but in the non-linear regime the relaxation modulus is a function of the strain that is applied on the material as well. Similarly, the creep compliance is designated as D when we define the compliance in shear mode we had defined it as j.

So, again they are functions of time only when we are looking at small deformations and for large arbitrarily large deformations we have the creep compliance; which is extensional mode function of time as well as the stress the normal stress which is applied to basically make the extensional flow possible. Similarly, for oscillatory response which is also called the dynamic response as the stress strain or strain rate vary sinusoidally as a function of time. we could apply a tensile strain and then measure vary it sinusoidally, and then again carry out the analysis very similar to oscillatory shear.

So, while visualizing we had seen that when you look at oscillator a shear the bottom plate is fixed and the top cone may be doing oscillation like this, when we are looking at extensional we are basically doing something like this, where we apply a tensile strain on the material and then do an oscillation. So, in such cases again we can either define moduli or the compliance, and the modulis are indicated in E prime and E double prime and compliances are indicated in D prime and E double prime. So, this is the general convention follows.

So, you might notice that in some of the papers talk about G prime and G double prime, and some other papers talked about E prime and E double prime and quite often. The difference could be in terms of whether it was an extensional mode of rheological examination or was it a shear mode of experimental examination. And of course, for the linear response these moduli and compliances will be function of frequency only, at which the strain is being applied, for non-linear response they will of course, be function of either the strain which is being applied or the stress which is being applied, and therefore, they are far more complicated responses.

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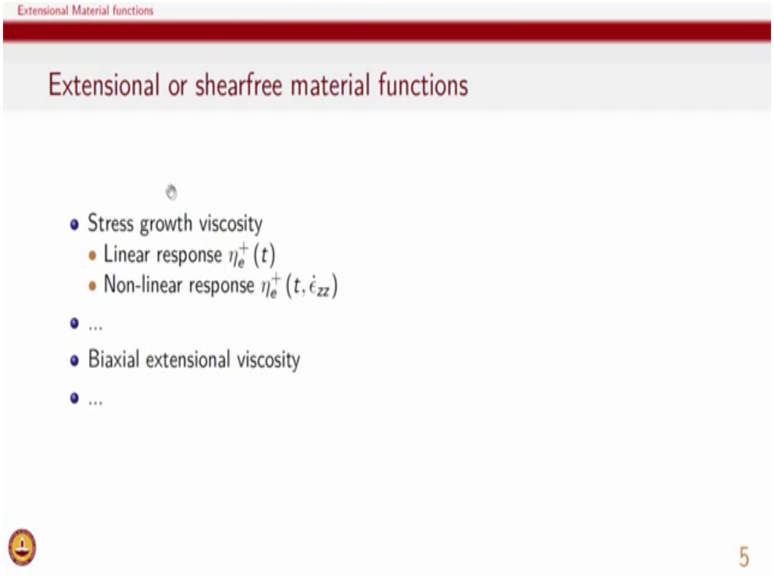

Now, similar to the stress growth viscosity that we saw in case of shear, we also have the overall stress growth viscosity in case of extensional flows. So, as we apply a constant strain rate on the material, the stress evolves and therefore, if you measure the stress as a function of time divided by the applied strain rate we get the extensional viscosity which is the stress growth viscosity. And it is a function of time for the linear response, and for non-linear response it would be a function of the time as well as whatever is the strain rate being applied.

So, as we saw many of the extensional material functions are counterparts of their sheer material functions. The at a micro structural level; however, the response of microstructure and material may be very different in the 2 cases. And therefore, we have always emphasized this point that characterizing and understanding the material response in shear will not be in any way always complete so that we can also predict what might happen in extensional flow.

So, therefore, we have to examine the materials in the extensional mode also and understand their behavior and the microstructure in extensional mode, and then reach at a more complete understanding of the overall rheological response of the material. depending on specific set of experiments there are additional material functions also possible.

For example, rather than doing a uniaxial extensional flow one could also look at biaxial extensional flow and therefore, a viscosity which is defined as biaxial extensional viscosity. So, over and above the material functions that we have reviewed in these course both for oscillatory and extensional flow, there are more specific material functions sometimes defined either for research or for applications purposes which are far more valuable for that particular situation. And now just to summarize and look at some experimental data we will look at the extensional viscosity growth for certain polymeric melts.

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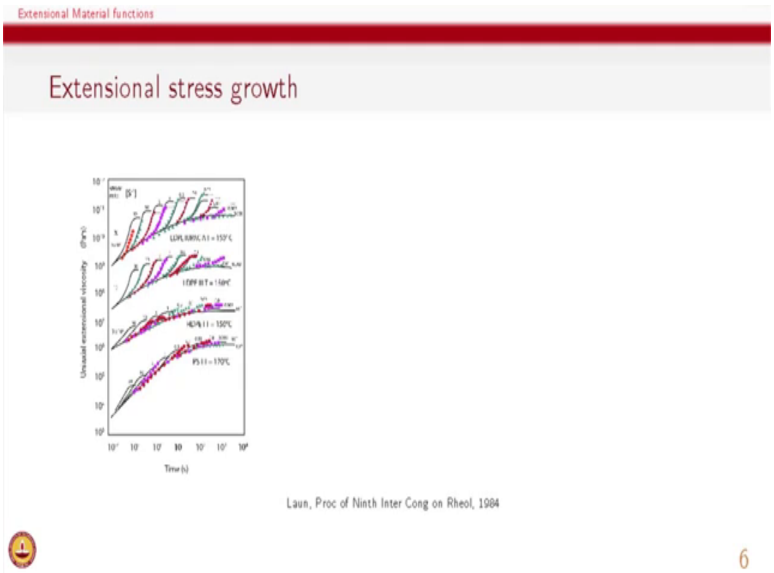

So, in this graph we have the uniaxial extensional viscosity as a function of time. remember that extensional stress growth is being observed at a constant strain rate. which means strain is directly proportional to time. So, since strain is constant and quite often it may be just let us say epsilon zz, then the strain will be the strain rate times t. So, therefore, strain will be proportional to time. So, quite often you might see experimental measurements or information about extensional stress growth as a function of time or strain.

Because they are both directly related to each other and what you can see is there is a melt material which is linear, both polystyrene and high-density polyethylene are linear macromolecules. And their behavior is qualitatively different compared to LDPE which is branched polymer low density polyethylenes. And what is very noticeable in the branched cases is a pronounced increase in stress. If you see here there is a small increase and then the values become constant, but in this case, there is a 2 orders of magnitude increase in stress. And in fact, this stress growth in branched polymers is key to processing films from these materials.

So, the fact that we are able to see so, many of plastic films around us is because of the stress growth that can be achieved in case of processing a branched polymer. Because of this stress growth, you can do effective stretching and therefore, achieve very fast processing and still control thickness to as low levels as possible. And therefore, quite often these days even if we are processing linear melts, linear macromolecular melts, we add small amounts of branched polymer to it to improve it is rheological response.

So, that is how many times looking at the rheological response much more closely will give us insights as to how to modify the processing conditions for many of these polymers. You can see that as strain rate is lower and lower, the overall response is related to almost an exponential increase which is what is very similar to what would be in case of a Maxwell model. since this is over a large decades of time, it is very likely that this increase can be explained only by using a generalized Maxwell model or a combination of relaxation times. And that should not surprise us because polymer melt will have several relaxation times which include the repetition modes or the the segmental modes or sub segmental modes.

So, therefore, using them we can incur describe many of these increases, where the overall stress seems to be only a function of time with very small sets of excursions where the stress does not seem to fall on an overall function which is only a function of time; however, in branched polymer cases, you can clearly see non-linear response, as each and every strain rate the stress is very different. And the other thing that one can notice also is it does not seem like that a steady state is reached. In this case the stress increases and eventually reaches a constant value. And therefore, a steady state is reached in which case the strain keeps on increasing strain rate is constant, stress is also constant. So, the viscosity reaches a constant value.

So, therefore, steady extension can be done and you can measure a steady extensional viscosity in these cases; however, in these cases you can see that the stress continues to increase and many of the data suggests that it is also diverging. And therefore, a steady state may never be reached. So, in this cases rather than looking at the steady extensional viscosity we look at the overall stress growth itself to understand; what are the mechanisms, which are responsible for the rheology of the material.

So, with this now we have reviewed all the set of material functions which are very commonly used And we have also done a survey of most of these material functions for realistic materials and now in the remaining part of the course we will look at some of the more advanced models which are useful for describing some of the more complex material function behavior that we saw for both polymer melts as well as multi-phase systems.