Rheology of Complex Materials
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Structural materials: yield stress and thixotropy
Lecture - 51
Yield Stress and Thixotropic Materials

So, in this segment of lectures, we are looking at structural materials where the underlying structure and its evolution and especially during the rheological characterization itself is of great importance.

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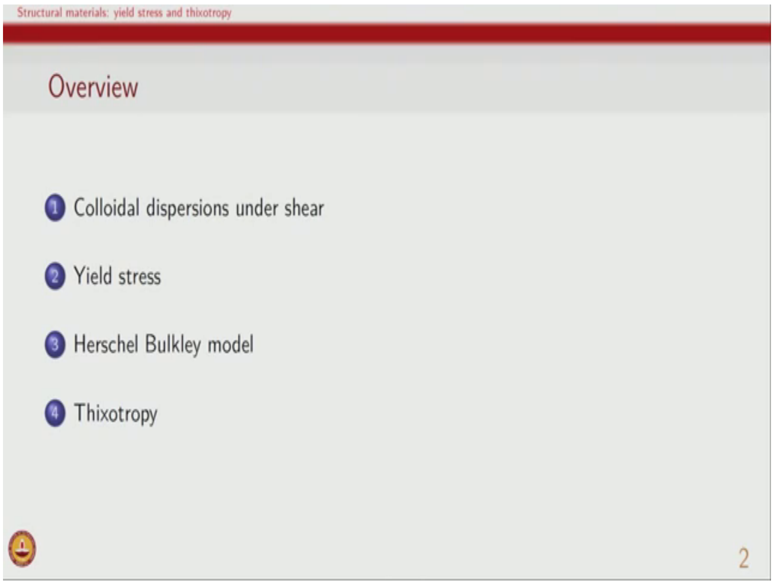

And we are looking at mainly examples of colloidal systems, multi phase systems how they deform under shear or other types of deformations and what happens to particle level phenomena, due to interactions between particles or because of cages which are formed around particles. And we defined yield stress and now in this lecture we will look at the one of the models, which is used to describe such behavior and we will finish the lecture with discussion on thixotropy, and a generic model which is can be used for describing thixotropic materials. Now, let us look at the yield stress, as we said is measured one way of measuring it is to do constant strain rate experiments.

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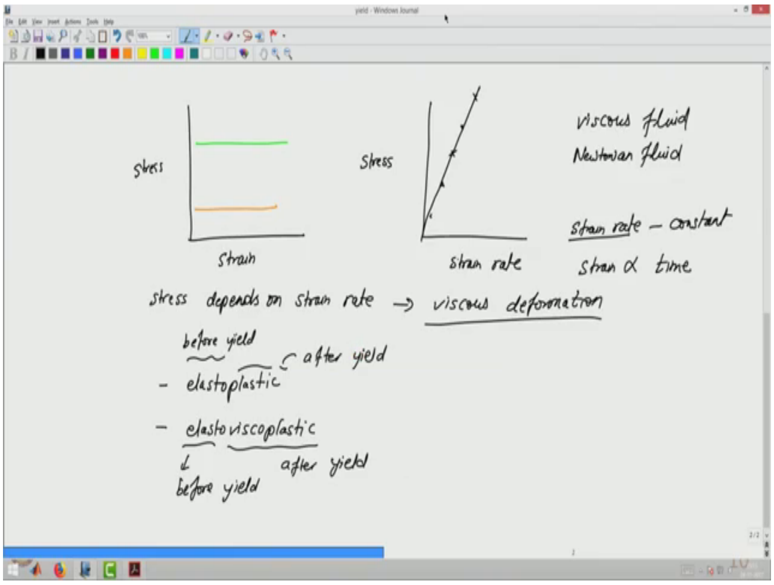

And then look at what happens to material response as strain rate is changed and we only look at steady shear. So, therefore, steady value of stress is measured.

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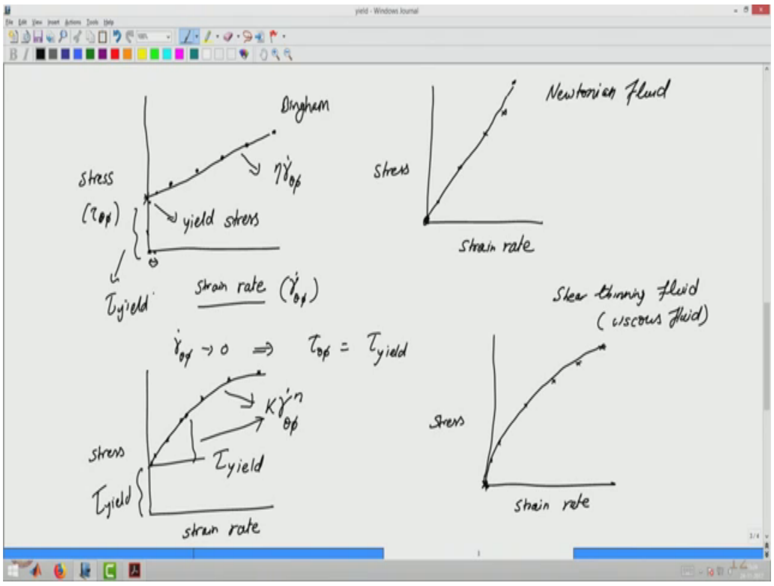

So, in this type of an experiment what we are trying to do is the following that, we subject the material to different strain rates and we are measuring stress. So, what would happen is basically if we choose a one particular strain rate, we may get one value of stress and then if we continue these measurements we may let us say collect these data points. And if we go to lower and lower strains basically what we have is stress decreasing; for a Newtonian fluid if we recall this measurement we were to do we will get basically data which is a straight line going through center.

So, at when stress is 0 strain rate is also 0. But for these kind of materials as you can see that as the strain rate is lowered the stress does not seem to go to 0 and of course, most instruments will have some limits of how low strain rate can be imposed because lower and lower strain rates would imply it becomes exceedingly difficult to measure whether the material is deforming or not and therefore, beyond a certain strain rate which are the limits of the instrument, we can then extrapolate this and measure the yield stress.

So, as we had seen earlier let us say this is tau theta phi, which are we are measuring because we are doing experiment let us say in a cone and plate rheometer because the strain rate which is being applied is gamma dot theta phi, then as gamma dot theta phi tends to 0 the value of stress tau theta phi becomes tau yield. That is how the yield stress on a material can be measured. For a Newtonian fluid we have obviously, no yield and therefore, the stresses goes to 0 as strain rate goes to 0.

If we have let us say a shear thinning fluid and which is a viscous fluid not a yield stress fluid, then also we would see similar behavior in the sense that we will see that at if there is no stress being applied strain rate will be 0 or as strain rate is going to 0 the stress is also 0, but as we apply higher and higher strain rates, there is a pronounced shear thinning. So, that the material is showing less and less viscosity as strain rate is higher. For this fluid also when we go to lower strain rates we can see that the extrapolation will lead to 0 stress. But these are the kinds of fluids where we have even if we extrapolate the stress does not seem to go to 0.

So, very similar to the shear thinning fluid, but will with yield stress are also there. So, that let us say when we start reducing the strain rate the overall stress decreases significantly, but it still does not seem to go to 0. So, in this case also we can again measure a tau yield.

So, one of the key things as I mentioned is what happens at very small strain rates and experimentally as well as theoretically the phenomena its not very clear whether the yield stress that is being measured is a real characteristic of the material or its some phenomena which can be referred to as an apparent yield stress and used for practical applications. The reason are as follows that we know when we discussed the relaxation processes in the material and the fact that given enough time everything flows.

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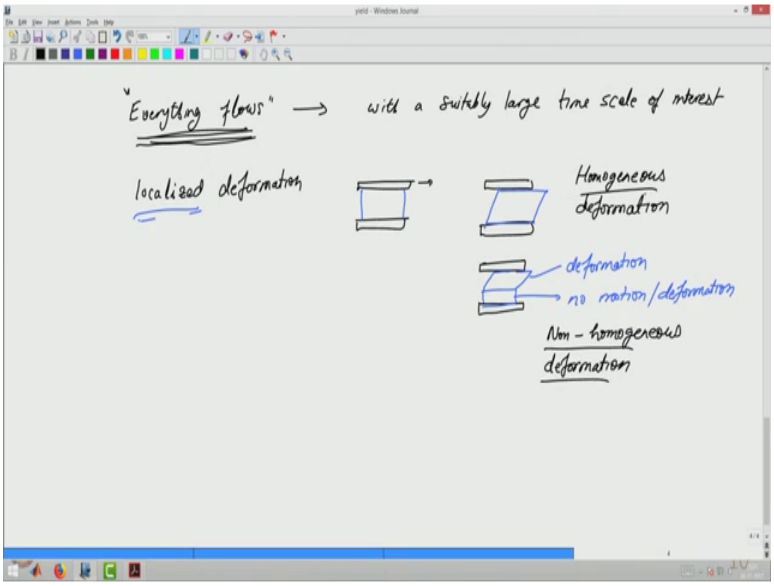

So, this is something which in rheology, we are always very conscious of that it just depends on what is the time scale of interest if we allow large enough timescales, then everything will flow with a suitably large time scale of interest. And Deborah number was basically a way to capture this and so, given that everything flows now if when we go back to this test and see here that we are applying very low strain rates in this range.

So, if we wait long enough surely we will be able to see that there is a stress value and the material will flow. On the other hand what we are saying is if the material has yield stress, then below yield stress value there is no flow possible. So, if we wait long enough we apply a strain rate and wait long enough we will eventually see flow. So, this is one of the possibilities.

So, it just said in many experiments we are not waiting and therefore, we are able to see these phenomena called yield. The other feature that we have come to know because of flow visualization and various other characterization which we can do within the rheological geometry, where we can examine how exactly is the fluid responding to the deformation there are localized deformations, which implies that even though we have imposed a certain deformation because of the motion of one of the plates or let us say in cone and plate it is the cone which is moving or if we take an example of parallel plate.

Let us say we take material between two plates and our classical example of just moving the top plate basically what we would imply is that the material would deform because of the shear being applied and we would have deformation in the material. But it is possible that when we have materials with very strong bonds or materials with cages as we have discussed in case of yield stress materials then it is possible that, we may have only part of the material moving and part of the material not moving.

So, basically this part of the material no motion or no deformation and this part of the material there is deformation. So, therefore, what we have is a localized deformation even though we have assumed that the material will be flowing throughout it only flows in certain pockets. And so, due to this it becomes difficult to then analyze the overall results because all the analysis is based on what is called homogeneous deformation and we know in various materials that it is possible to have non homogeneous deformation.

So, any measurement of yield stress and any measurement of a character saying that we are trying to quantify the characteristic of material using this value of yield stress has to be done carefully, because many of the values are dependent on how exactly we are doing because in the end it would be expected to flow if we wait long enough and similarly depending on whether its homogeneous or non homogeneous deformation the interpretation of the data is likely to be vary.

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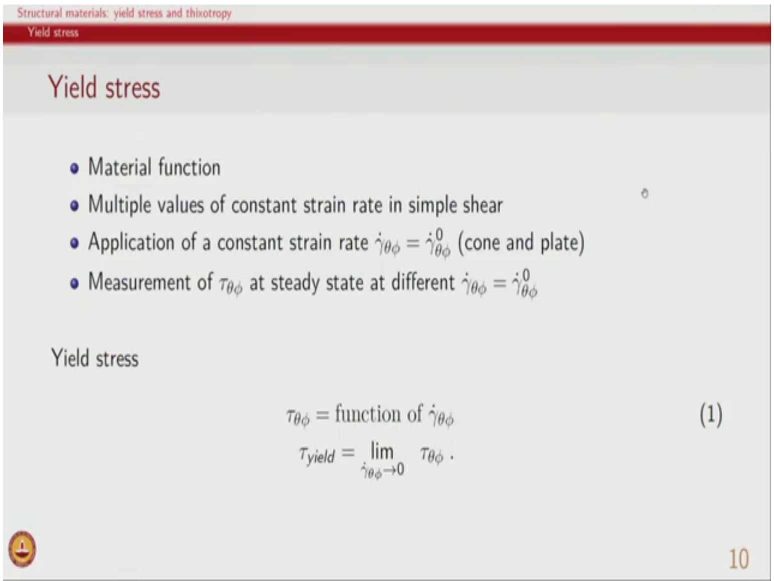

So, therefore, yield stress is a very useful practical concept, but theoretically and from research point of view still being debated very vigorously in terms of what it implies and how do we understand it.

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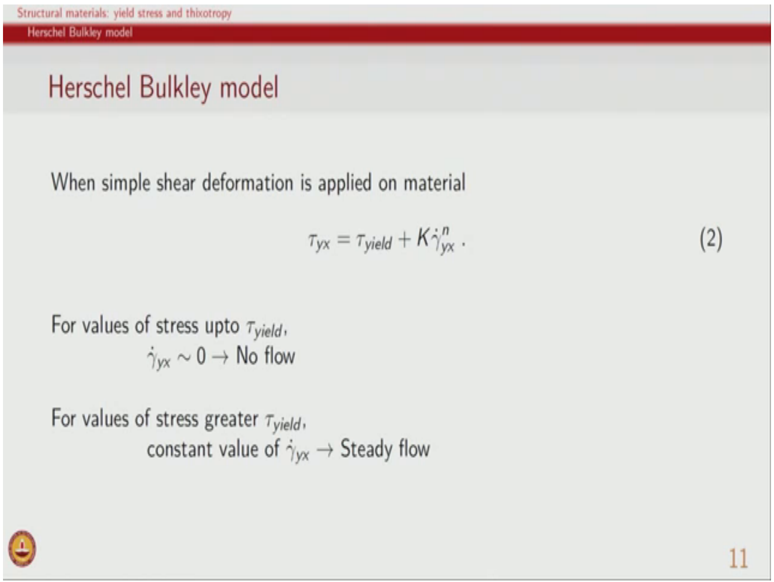

One of the simplest model that can be used to describe the yield stress phenomena is called a Herschel Buckley model and in this model the stress let us say in a simple shear deformation the stress is related to the overall strain rate with a constant and there are two three parameter model, the yield stress itself is a parameter because when gamma dot goes to 0 the stress is equal to yield stress.

So, in this case whenever low strain rates are imposed on the material we only have the yield stress or in other words if as long as the stress remains below the yield value gamma dot will be 0 or the strain rate will be 0 and.

So, for values of stress up to tau yield, we have no flow and for values of stress greater than tau yield we have a constant value of gamma dot yx and the stress of value is tau yield plus given by this and we achieve basically a steady state flow. So, this model is response is basically what is described here. So, so we can see that this part of the curve can be described as gamma dot to the power n and this part of this value is basically tau yield. So, stress at any given point is tau yield plus what is given by k gamma dot to the power n. So, therefore, Hershel Buckley model describes a material which is an yield stress material and beyond yield or post yield the material is a shear thinning material.

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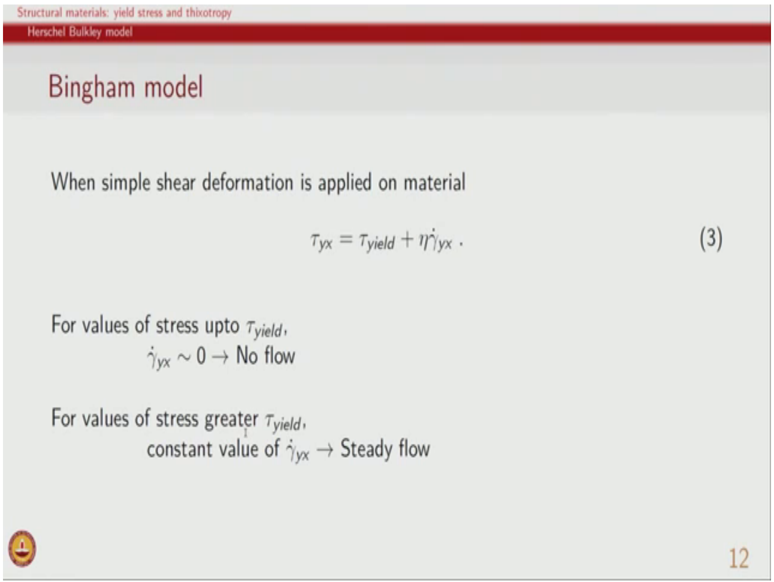

A simpler model which was proposed by Bingham and in fact, now this is an idea which is about 100 years old. So, Bingham proposed that stress in the material is related to yield stress, and the overall stress beyond an yield point is basically like a Newtonian fluid. So, we have also seen example of this.

So, this is a Bingham plastic material, because in this the velocity is related to gamma dot theta phi while this is the tau yield. So, both bingham model and Herschel Buckley models can be used to describe the yield stress behavior of materials. However, there are other possibilities in terms of trying to examine this behavior of yielding what we have already seen is steady shear.

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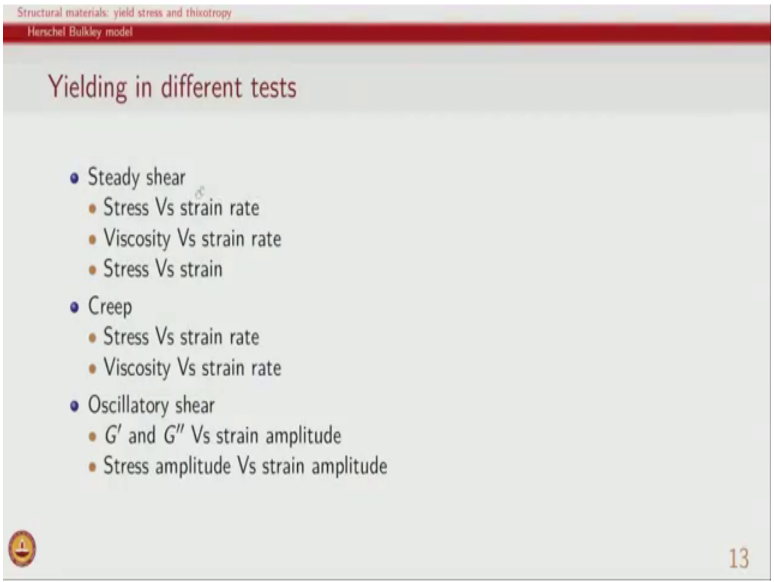

Where we looked at stress versus strain rate we could re plot some of this data in terms of viscosity versus strain rate. So, what we will see is in let us just look at the overall data again.

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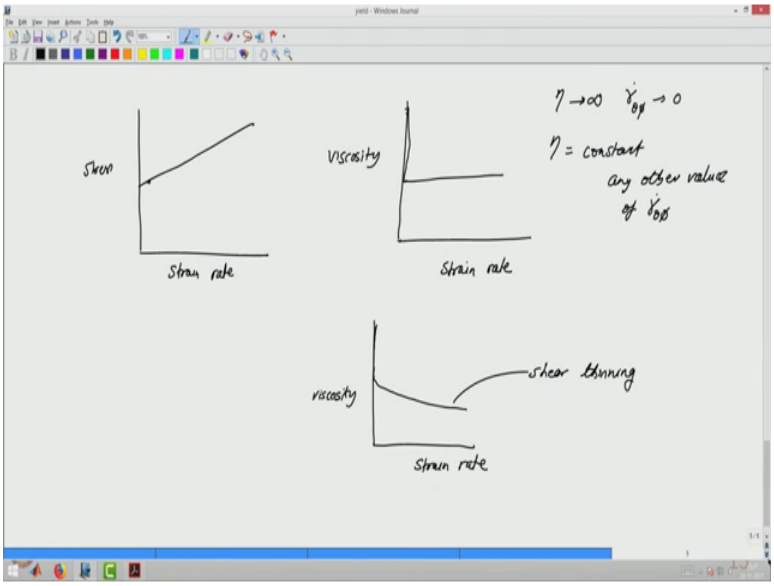

So, where we have stress versus strain rate since we saw that the overall behavior is like this. So, in this region viscosity is constant. So, if I were to plot viscosity as a function of strain rate, what I would see is viscosity is constant and then at strain rate going to 0 there is a finite stress value. So, stress divided by strain rate which is 0 the viscosity is infinite.

So, basically at strain rate equal to 0 we have infinite viscosity. So, we can say that viscosity is in finite as gamma dot tends to as gamma dot theta phi tends to 0 and then eta is a constant value for any other value of gamma dot theta phi. Similarly for a Herschel Buckley kind of a material, what we will see is viscosity at a certain strain rate is at 0 strain rate is in finite and then beyond it is a decreasing this is a shear thinning

So, many real materials if we examine their behavior show the behavior which is then based on which then we can try to guess whether this is a yield stress material.

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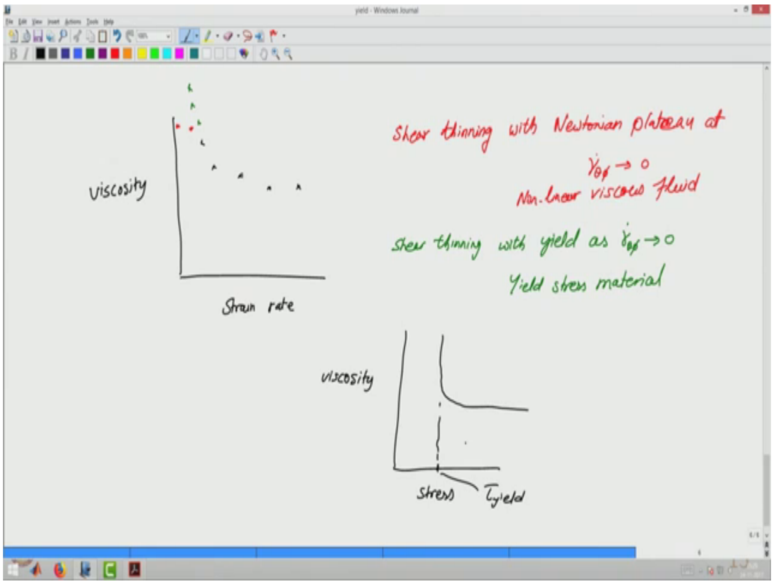

So, if we are trying to (Refer Time: 15:10) a plot viscosity as a function of strain rate for an unknown material and we start measuring data, and we see that viscosity is. So, up to this point if you are trying to measure we can clearly make out that this is a shear thinning material, now there are two possibilities that the material at low strain rates may have viscosity like this and so, this is then shear thinning material with Newtonian plateau.

So, it is a viscous fluid plateau at gamma dot theta phi tending to 0 and so, this is therefore, a non-linear viscous fluid and there is other possibility where the data points beyond this may look something like this where viscosity increasing higher and higher.

So, this is now again a shear thinning fluid because viscosity does decrease as a function of strain rate with yield as gamma dot theta phi goes to 0.

So, therefore, this is an example of yield stress material. Now we can also look at the similar feature in terms of either viscosity versus stress or stress versus strain, generally many times the data is also presented for viscosity as a function of stress and in that case what we would see is till the value of tau yield the viscosity will be in finite and then you have depending on whether it is a shear thinning or a Hershel Buckley kind of a fluid or a Bingham plastic we will have the variation in this range.

So, but the key th feature is that the viscosity is go diverges and it becomes infinite as we approach the yield stress. So, therefore, we can use steady shear to look at yielding in materials and we can analyze the data by looking at them in several different ways. We can also look at creep; creep is a measurement in which we apply a constant stress on the material. So, therefore, we can apply the constant stress and wait for steady strain rate to evolve and again look at stress versus strain rate response. Since we wait for the steady state and measure strain rate we can again look at viscosity versus strain rate.

So, we could apply a constant strain rate and look at the response or we could apply a constant stress and then look at the response. These days a fair number of researchers and industrial characterization is done using oscillatory shear and again in oscillatory shear we look at how they do the moduli, the storage and the loss moduli vary as a function of strain amplitude. So, generally we saw that for a linear response the moduli were only function of frequency.

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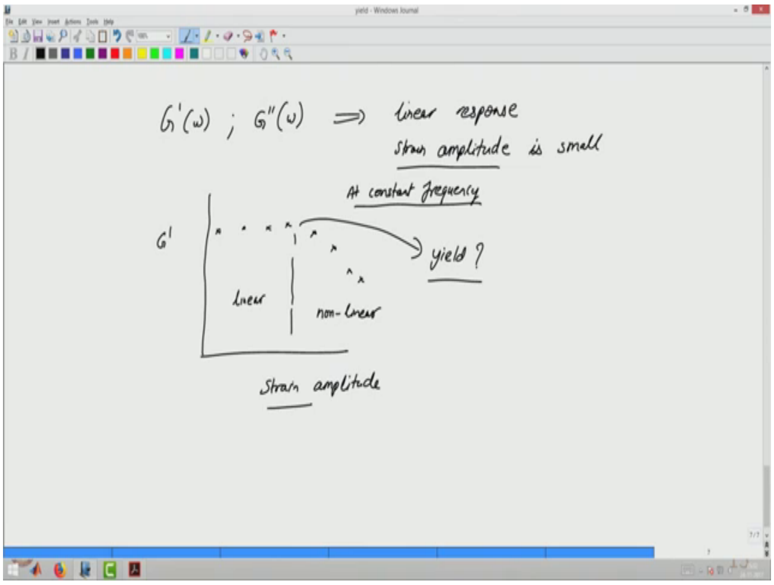

So, we saw that G prime omega and G double prime were functions of only the frequency and this is what we characterized as the linear response. And we also saw that linear response is observed whenever strain amplitude is small. So, the question is happens to the behavior, when we apply arbitrarily large strain amplitudes. So, this measurement is done where we measure let us say G prime as a function of strain amplitude and we look at the measurement. What we will see is at low strains basically the G prime will be independent of strain amplitude because its only a function of frequency this measurement is being done at let us say a constant frequency.

So, given that its being done at constant frequency the G prime will only have one value, but beyond a certain strain then the G prime would start decreasing. And so, whether this kind of a test can be used to characterize yield phenomena. One should remember that we are looking at the transition between linear and non-linear response in this case. So, whether this transition is associated with yield or not is has to be a (Refer Time: 20:11).

Generally the guideline is if the g prime value decreases very strongly with strain amplitude then there is a possibility that we can characterize yield using oscillatory shear. So, in general for practical situations steady shear or creep is used to look at and characterize the yield stress value, though in some cases even oscillatory shear is used, but as I said one must be careful in terms of looking at the order of magnitude change in these quantities, because in general when we increase strain amplitude we will observe non-linear behavior where G prime is a function of strain amplitude for all materials and G double prime is a function of strain amplitude at large strain amplitude for all materials.

So, therefore, whether the change in G prime in G double prime is a signature of yield or because of non-linear response of materials is not clear just based on experimental data. So, little more information about the material itself will have to be known before we can use the analysis and try to characterize yield stress from such measurements.

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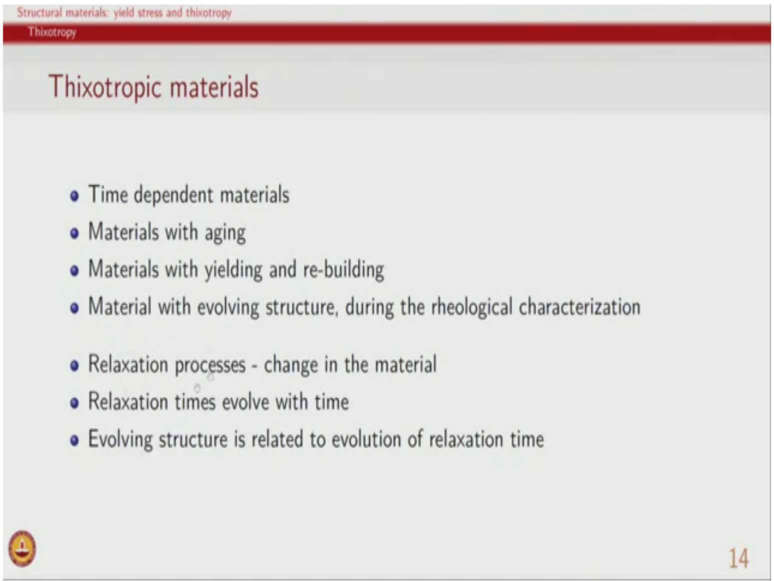

So, this gives us an idea about the yield stress materials very closely linked to yield stress materials though they are generally thought of as two different classes of materials are thixotropic materials. Thixotropic materials are sometimes called as time dependent materials they are also called materials with have aging or materials which have yielding and rebuilding. So, this rebuilding is a key concept which is has to be considered when we look at thixotropic materials. So, the let us go and look back at what happened let us say when we had Herschel Buckley kind of a material being measured.

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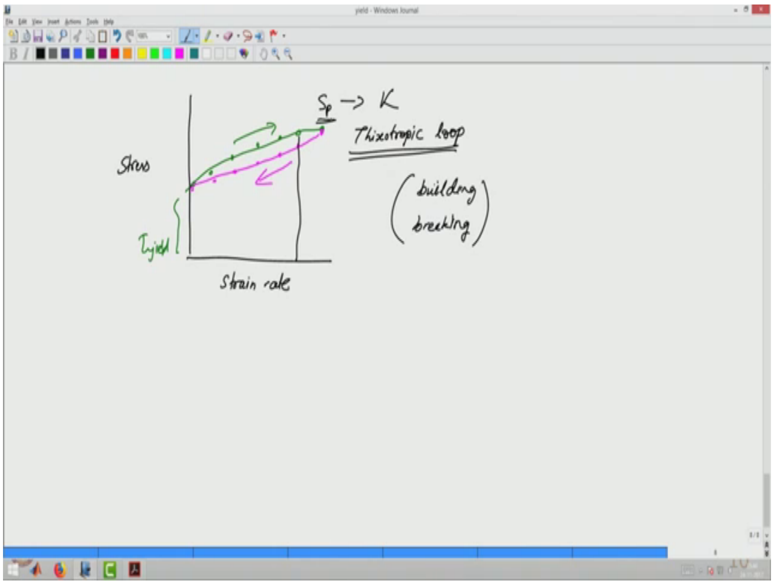

And so, what we saw is if you are measuring let us say stress versus strain rate, in that case what we saw was the measurements were done such that we saw that at low strain there was a finite yield stress value, and even if you extrapolate there is a finite yield stress value. Now once the strain rate is increased and now the same sample if we start measuring the material response.

So, what we what is seen in case of thixotropic materials is that there is a different viscosity. So, the viscosity is different while decreasing the strain rate and viscosity was different while increasing this strain rate or the stress was different when we change the strain rate in one direction and this sometimes is called the thixotropic loop.

So, we know that the phenomena of yield is associated with breakdown of structure; for example, cages or bonds breaking, but if in the material rebuilding can also happen during the rheological testing, then what we have is a combination of building. So, there is a building process which goes on where cages can be built, bonds can be rebuilt and then there is a breaking process which is on which also is a function of strain rate. So, if these two processes happen in the material simultaneously, then we have what is called a thixotropic material. And one characteristic feature of a thixotropic material is this kind of a loop which is observed when we do this stress versus strain rate tests.

So, therefore, the thixotropic material is a material which has an evolving structure the structure is evolving because there is continuous breaking and rebuilding going on and we saw that yielding is a process which is closely related to breaking and therefore, we should think of thixotropic materials in combination with yield stress and for both of these materials underlying structural changes are key in terms of understanding their behavior.

So, during rheological characterization itself the structure is evolving and so, in general we can think of this also in terms of relaxation processes, and what we are seeing because the structure is evolving the relaxation processes in the material are changing when we when we look at a macro molecular solution or when we look at a colloidal dispersion when its not a yield stress or a thixotropic material then we know that the material has a set of relaxation processes and depending on the our examination time scales the relaxation process contribute either by dissipating or storing energies and therefore, we have the viscoelastic response. But now imagine in the same material due to some reason structure keeps on changing and therefore, the relaxation processes themselves will keep on changing.

So, for example, if you have rebuilding of clusters going on in a colloidal dispersion, then we would certainly have the relaxation processes changing. And so, effectively what we are saying is the relaxation times which are associated with these relaxation processes they also change with time and so, evolving structure is related to evolution of the relaxation time.

So, in the thixotropic materials we cannot make a hypothesis of an underlying relaxation processes which are independent of the material being sheared or material being deformed. So, the set of relaxation processes depend on what is the nature of shearing or deformation, which is being imposed on the material. Polymer melt for example, has several relaxation processes starting from bond level vibrations to repetition where the overall molecule macromolecule itself moves, but all of these relaxation processes do not evolve in time or in as a function of strain rate they just contribute differently. So, the underlying processes remain the same, but they contribute differently depending on the time scale of or the deformation that is being imposed on them.

On the other hand for thixotropic materials the relaxation processes itself are we make a hypothesis that the relaxation processes themselves change and therefore, it is then natural to say that the relaxation times, which are characterizing these relaxation processes they themselves change and so, the evolving structure is related to the evolution of relaxation time and so, then its natural to try to think of in which way is the structure evolving.

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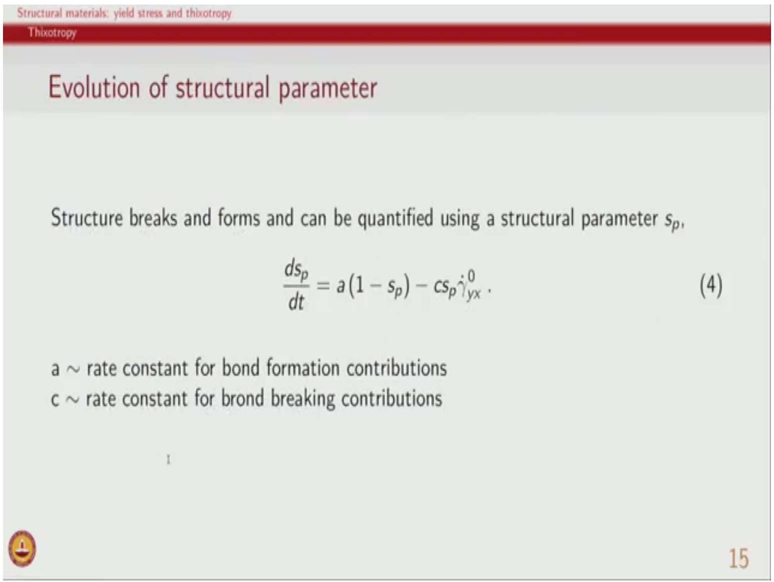

So, we generally make hypothesis of a structural parameter. The structural parameter basically characterizes the extent of structure in the material. This is more like a any kinetic equation whether there is a forward rate which is let us say building and a back which is breaking and a backward rate which is building. And so, structure breaks and forms and can be quantified using a structural parameter.

In this case if you see the rate of change of dSp by dt is proportional to 1 minus Sp. So, this rate depends on if Sp is small value this rate is higher and if Sp is 1 then this rate is lower. So, clearly this is the building rate because if sp is one then structure is already built and there is no further building to happen if Sp is 0 which means let us say the structure is completely broken down then the building rate is very high similarly. So, therefore, this will be the breaking rate if Sp is 0 there is no further breaking that can happen and if Sp is one then the breaking rate is maximum. So, therefore, you have breaking and forming rates and. So, a and c are the rate constants which talk about breaking and formation in these materials.

So, basically in all the thixotropic materials we make a hypothesis of a structural parameter and we have to write an equation, which is similar to this in terms of saying that how the structural parameter evolves structural parameter changes as a function of time because there is shearing happening. This is one example of an evolution equation essentially what we are saying is the structural parameter depends on several parameters and the structural parameter value itself.

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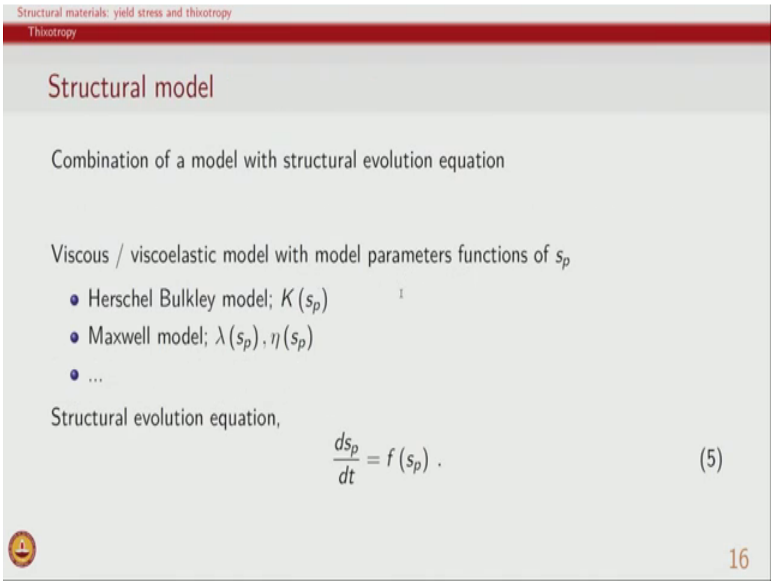

So, a structural model which characterizes the overall thixotropy in the material, is basically a combination of an existing model or otherwise model which relates stress or strain or strain rate basically what we mean by either viscous or viscoelastic model along with an evolution of structural parameter. So, what we are saying given that the underlying processes in the material change as a function of time, the relaxation time or any other parameter which is associated with the material behavior also changes with time and shearing and therefore, structural parameter is influencing all the parameters of a model. So, for example, if we choose a viscous model such as Herschel Buckley model then the parameter k in the Herschel Buckley model will be assumed to be a function of structural parameter.

So, that when we have an evolution equation for structural parameter, which will depend on structural parameter and various other variables which are possible such as strain rate, stresses and all of them can influence and so, a functional form of this kind will determine the evolution of structural parameter; knowing at any point given point of time or a given application of strain or strain rate we can find out what is structural parameter and then substitute that in Hershel Buckley model to find out the stress value.

So, therefore, these are coupled equations which have to be solved for us to get an idea about stress and strain and strain rate in the material. Similarly if we let us say use a viscoelastic model such as Maxwell model, then the two model parameters of maxwell model the relaxation time and eta are again assumed to be functions of structural parameter and then this in combination with the structural evolution equation will become the structural model. So, therefore, with such structural models we can then capture the thixotropic response of materials and the loops that I we talk discussed can also be shown to behave shown to according to the structural model.

So, given that now at any particular strain rate we need to know what is the S p and that sp will determine the Hershel Buckley model k. So, therefore, we can get different Hershel Buckley behavior from the same material depending on what is the value of sp. Therefore, these kinds of loops can be described using combination of Furcal Hershel Buckley model and a structure evolution equation and similarly for a viscoelastic materials where elasticity is dominant our elasticity plays an important role Maxwell model or any other viscoelastic model is used along with the structure and evolution equation.

So, in general the yield stress materials and thixotropic materials are practically very relevant, but because of this very close connection with the underlying structure and the need to describe them these materials are far more challenging from a theoretical point of view, and lot of research is going on in the last few years to understand these materials to a much closer degree. However, from some of the basic guidelines like using stress versus strain rate response, we can capture both the thixotropic loops as well as yield stress in the material and using these quantified characteristics we can do design and all the other relevant engineering decision making based on these numbers, but from an understanding point of view lot needs to be done.