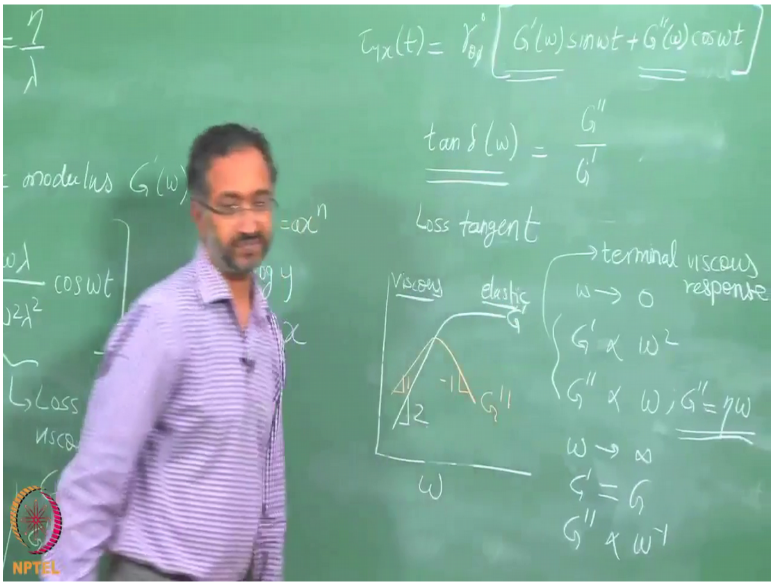
Rheology of Complex Materials
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology, Madras

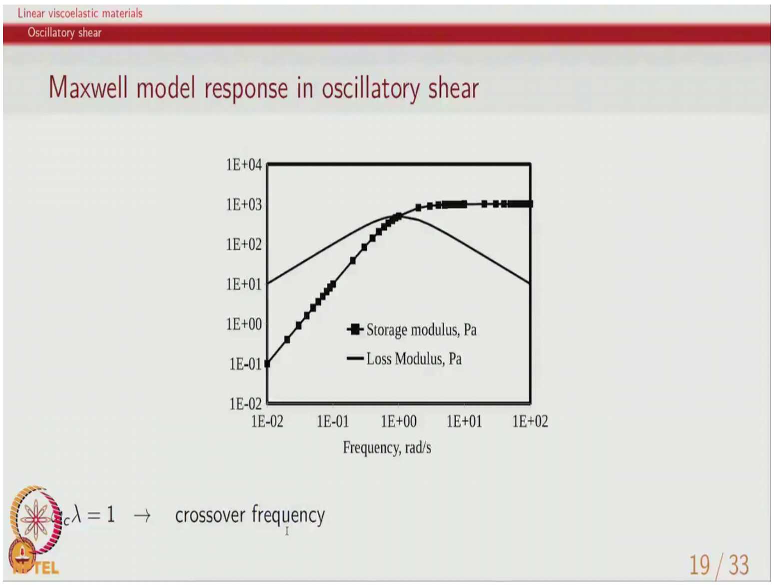
Lecture - 20
Linear viscoelastic materials

(Refer Slide Time: 00:18)



So, so therefore, this is the viscous response, according to Maxwell model and this side is the elastic response and so, this is what is depicted in the graph here.

(Refer Slide Time: 00:26)

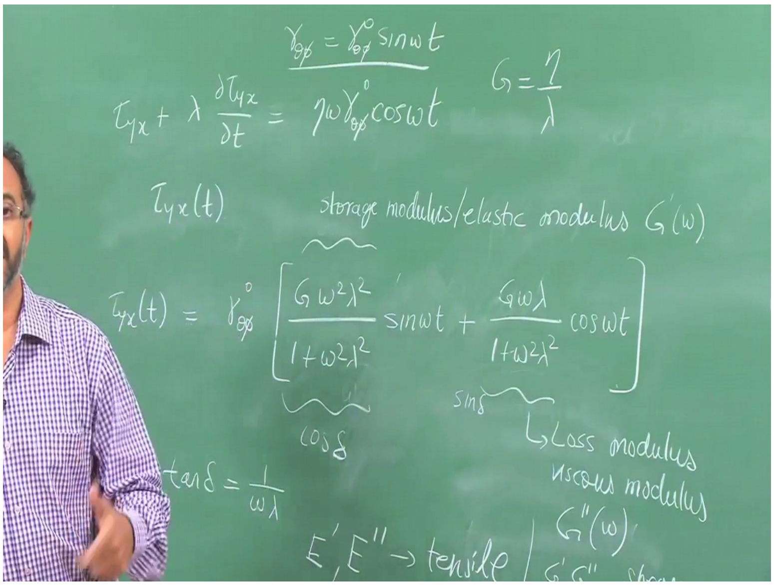

Linear viscoelastic materials
Oscillatory shear

Maxwell model response in oscillatory shear

$\omega_c\lambda = 1$ → crossover frequency

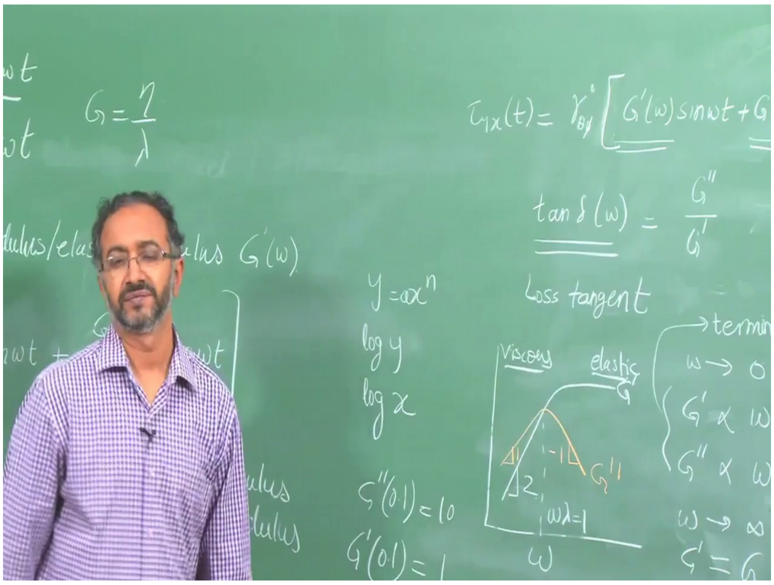
Viscous response is minimal right, once you go to very high frequency, the overall dissipation that can happen in the material all the relaxation modes will be frozen. So, in this case the relaxation mode is frozen. So, it only gives you elastic.

(Refer Slide Time: 00:47)



So, if you look at here, between these two what happens is the stress is almost in phase with strain, since strain is gamma naught theta phi sin omega t. So, since strain and stress are almost in phase this term is 0. So, it is lower and lower as you go to higher and higher frequency. Higher and higher frequency you go, more and more elastic response and what you see is at very low viscous response again this is varies as 2 right. So, the way the graph looks it is likely deceptive. The difference between these two will be orders of magnitude. Does that make sense that if, if let us say value of G double prime at, let us say 0.1 hertz is 10 and G prime at 0.1 hertz is 1.

(Refer Slide Time: 01:36)



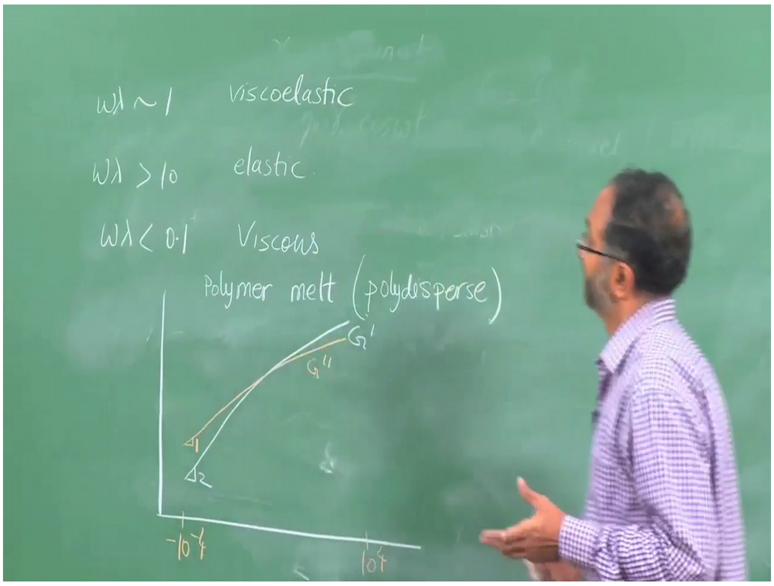
Now, if you go to 0.01, what will be these values? This will go down quit significantly right, this is omega squared this one goes down, while this one only goes as omega. So, when I decrease 10 times this will go to 1, but this will go to 0.01. So, therefore, the difference between them will is the orders of magnitude higher. So, therefore, though we look at these scalings as an approximation, we could always say that G prime is 0 and G double prime only exist. But, because we are trying to measure it as a modulus for a viscous material, what happens is this quantity is reasonably small, viscosity significant, but frequency is very low.

So, therefore, G double prime will ends up being a small number and that is because viscous like material we are trying to measure a modulus from it. So, this is the overall response based on Maxwell model and this is what is plotted here with numbers and one important feature of the Maxwell modulus in terms of, where omega lambda equals 1.

So, wherever omega lambda is 1, is this place and sometimes this is called the crossover frequency. So, omega c is equal to 1 over lambda. So, we can talk about the overall material response with respect to this omega c, if you omega is very less than omega c, then we will observe viscous response and if omega is much larger than omega c, then we would observe elastic response and so omega c captures the material relaxation time it is just 1 over lambda.

Now, the other notice quantitatively what you can notice is, this is the crossover point is at which omega lambda is equal to 1, right. Now let us say if I change omega lambda to 10, what is the response that you can see? I changed frequency in such a way that omega lambda becomes 10. What will be the response of the material? Omega, lambda equal to 10. So now, we are looking at 2 different regimes and with respect to omega c.

(Refer Slide Time: 04:41)



So, we know that, when omega lambda is equal to 1, the material is viscoelastic. If omega lambda is, let us say greater than 10.

Student: Only elastic.

Only elastic response right, so, in fact, even if 10 times with respect to the crossover frequency if I apply I already see only elastic response and similarly if omega lambda is less than 0.1, then I see completely viscous response. You can see right, on the graph by the time I reach 0.1, it is already become straight lines on this log plot and slopes are 2 in 1. Similarly if I go to 10 times, G prime is already become constant and this also is become slope of minus 1. So, just 1 decade this way and 1 decade that way, gives us completely elastic or viscous response.

Now, if I take a material and measure it is G prime G double prime and observe that I do not get elastic response on one side and viscous response on the other side, then what do I conclude. So, for example, if you look at polymer melt and let us say commercially available polymer melt, which means molecular weight distribution is there in the material, not all molecules are of same molecular weight. So, if you have a polydisperse, which means a different molecular weight of the molecules and then if I measure it is G prime and G double prime, this is what generally is seen. So, this is G prime, here the slope is 2 and this is G double prime and here the slope is 1 and the frequencies that we are talking about are 10 to the power minus 4 to 10 to the power 4. So, what should I conclude?

So, we saw the Maxwell model, we saw it is response and now I take a real material like polymer melt and I measure it is G prime G double prime and because somehow I can measure properties from very low frequency to very high frequency, I measure the response and I get response which is like this. So, what does that? Tell me. What are the main features that, given that I know Maxwell very well and I have understood Maxwell model, what can I conclude about this?

Student: Everywhere we are, we will find viscoelastic response?

Yeah, looks like right. So, except maybe 10 to the power minus 4, 10 to the power minus 3 that is small frequency, so if lower frequency 10 to the power minus 3 and lower frequencies polymer melt can be assumed to be a viscous fluid, but any other frequency which is relevant for engineering applications, where I am a moulding specimens or I am making it flow.

Most of the times when the engineering time scale of interest is seconds or hours and all that, then I will find that viscoelasticity will be very important and it is not completely elastic, it is not completely viscous, it is always a mix of those. The second thing is, what you can see is here when I go change frequency in 100 a relaxation mod goes completely from being viscous to being completely elastic.

So, if I assume that this material is a collection of relaxation modes, then what I will have to say is that there are several relaxation modes which are still giving me this viscous response here. Only when I go to lower frequencies, all the relaxation modes can give me viscous response and other way to put it is if I go to may be 10 to the power 7 hertz or 10 to the power 8 hertz which are not mechanically relevant frequencies, but maybe at those frequencies I might see elastic response in the material.

So, all relaxation modes in that case will give me completely frozen response or overall elastic response. But otherwise, it looks like that under most normal conditions a polymer melt has relaxation modes, which are viscoelastic, which gives us viscoelastic phenomenological response.

So, therefore, we will learn few more things to start interpreting this kind of a response in terms of several relaxation modes and that is the capability which we have to develop and based on just looking at Maxwell model, because Maxwell model as you can see is very limiting if I want to understand this.

(Refer Slide Time: 10:01)

So, right now, the only thing that I will say is, it is it possible for us, to visualise the Maxwell model response like this, where we say that we will have a collection of Maxwell model responses and if I sum all of them up, I will get my overall G prime. Can you visualise that? That every 100, every 1000 thing is this, G prime right, if G prime starts being 2, but it becomes constant. So, what I have drawn here is each of these is that 1 Maxwell mode. If I put several such Maxwell mode and combine at them together, then it is possible for me to then describe the overall relax the storage modulus of a real material.

So, that then immediately gives me this if this is a new material I am working with an I get a response like that, I immediately have to say that there are several relaxation modes, each with a different relaxation time, because relaxation time; which one will be highest relaxation time among these and which is lowest relaxation time, what is this value? This is omega c, omega lambda is equal to 1.

Similarly, for the next mode this is omega lambda equal to 1. So, since omega is increasing this way, lambda is decreasing that way, right. So, each of them is relaxation mode with decreasing relaxation time and in fact, there are still some relaxation modes which are here and therefore, I am still getting viscous response. Only if I go to some hypothetical frequency, then I will get, all of them will become constant. Then only I can hypothetically achieve the completely elastic response from a polymer melt.

Student: On the axis we have cross over frequency.

Ah.

Student: In the (Refer Time: 12:00) are.

Yeah.

Student: X axis.

Ah.

Student: We are having cross over frequency let me (Refer Time: 12:03) omega into lambda.

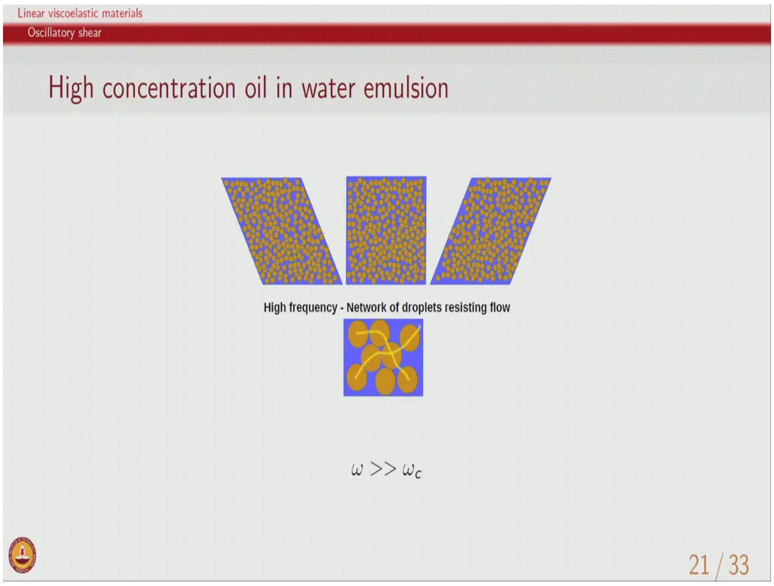
For a single Maxwell mode, all of these are crossover frequencies. The overall crossover frequency for a polymer melt is this, right, but it is not very meaningful because I do not see the overall response which is viscous like, an elastic like. Even though I am going 8 orders of magnitude in terms of frequency, but according to Maxwell model if I just do 2 orders of magnitude I should go from viscous to elastic response, just 2 orders, from omega is equal to 10 to 0.1, 0.1 to 10, 100 right, a factor of 100 and I should go from viscous to elastic.

So, I have used all of these is individual things are all in 100 frequency they are going from viscous to elastic and I add all of them up. So, what I am doing is each of these Maxwell modes, I have some G and then lambda, right each of the Maxwell mode has one G parameter and 1 lambda parameter and I keep on choosing different lambdas, I keep on choosing different G, then I can hope to visualise the overall response and why is this important, because even mechanistically this is how we will try to analyse.

What is it? What are the modes, which are at this time? So, generally what we will see in a polymer melt case, is there will be reputation or motion of the macromolecule that we discussed earlier, then there will be segment which is only a part of macromolecules and then, there will be sub segment, even smaller and smaller bonds and of course, polymer melt does not show elastic respond just like water also does not show elastic response, for most mechanical frequencies unless I go to very high frequency, because if we are able to see time scales which are related to bond vibrations of water and things like that, then we can have elastic response.

So, similarly the bond vibration C C bond, C H bond all these things which are there in polymer if we go to very high frequency only then we will see a perfectly elastic frozen response. So, therefore, in general the real materials show a collection of relaxation times, but now let us look at a material which actually shows Maxwellian response. So, this is an emulsion which is extremely concentrated emulsion.

(Refer Slide Time: 14:42)



High concentration oil in water emulsion

High frequency - Network of droplets resisting flow

$\omega >> \omega_c$

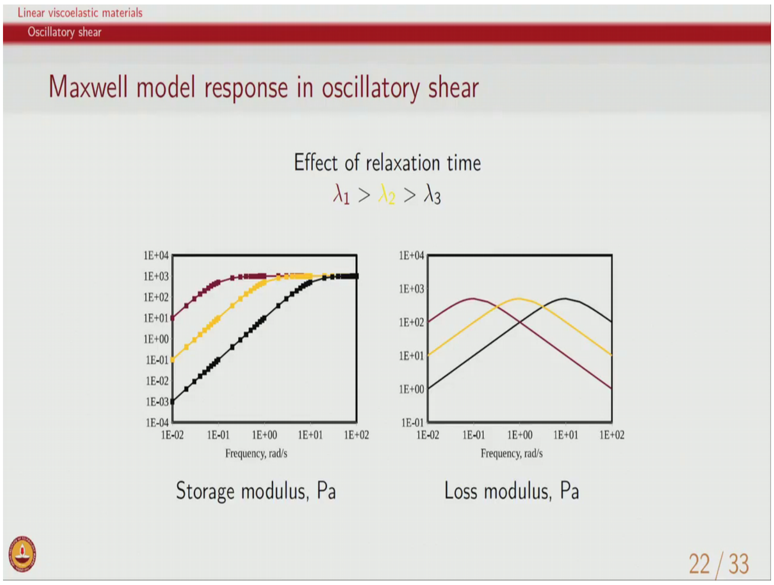
So, what is being depicted here is drops; fine drops of micron size, which are and very high volume of emulsion. How can this be made stable by adding a surfactant, if you have a large amount of surfactant then you can have an oil in water emulsion with fairly large amount of oil, still remaining as dispersed phase and so, if you have such material system and now if I say let us say do an experiment on it which is very, very slow.

So, in that case what happens is, since all the drops are moving slightly here and there, this drop here for example, will move little bit this drop me also move and therefore, this drop may possibly make way and start moving. So, then the overall response is like a viscous response. That overall drops are able to move, when you have overall viscous response, but same material if I apply high frequency, in this case much higher than the crossover frequency, then what happens is because we are applying now the drops cannot really move there is not enough time given.

So, it appears as s fall the drops are sort of form a network. They are all bound together somewhere and therefore; they only remain in place and therefore, give us an elastic response. So, these are called emulation jells. So, if you form oil in water emulsion both perfectly viscous materials, but because there is a combination of droplet and dispersed phase and continuous phase and dispersed phase is stable and drops cannot move, you eventually get an elastic like response.

So, the material is able to give us some storage capability, energy storage capability and that energy storage capability is embedded because of the droplet network. So, this network formation and in general 3 dimensional networks in materials are always a key to giving us elastic response. Whether it is a case of dispersed phase system or a macromolecular system?

(Refer Slide Time: 16:48)



Maxwell model response in oscillatory shear

Effect of relaxation time

$\lambda_1 > \lambda_2 > \lambda_3$

Storage modulus, Pa

Loss modulus, Pa

So, now let us look at the Maxwell model response for 3 different relaxation times, any question so far on evolution or any other thing, is that ok. Does it make sense? This is where we basically we are shearing right, with oscillatory shear and therefore, at some time scales the droplet us can move and sometimes scales they appear to be bound to each other and they do not cannot really displace each other.

So, therefore, one single droplet does not move at all, same thing is to with what I was saying about polymer melt, which are entangle with each other. If we give enough time, then molecule which is entangle also can move. So, therefore, it moves just like water or fluid like dissipative response.

Of courses the viscosity will not be same as either of the pure phases, right, even if that is very low frequency we have perfectly dissipative response, because we have drops and they are moving in a continuum fluid the effective viscosity of this material will be much higher than the continuous phase, because we have drops moving. So, there is additional dissipation, but the response in terms of normal stresses, the response in terms of any of the features that we talk about we could observe it to be perfectly viscous.

Student: Sir, in case of oil and mercury (Refer Time: 18:12).

Ah.

Student: We are (Refer Time: 18:14) of a top.

Yeah.

Student: So, in that top there will be a only oil molecules.

Ah.

Student: What about water molecules relate (Refer Time: 18:22).

What do you mean on the top there is only oil.

Student: So, it is (Refer Time: 18:29).

Ah.

Student: Density difference oil will be (Refer Time: 18:32).

No, it is a stable right that is what I have been saying, it is a stable emulsion. So, that oil is on the droplet form and there is the surf act coating on the oil droplets. So, that droplets remains stable. What you are talking about is a phase separate mixture of water and oil. We are talking about a stable dispersion of oil drops in water. So, if you look at here the way the top is continuous phase, which is water. It indicated by blue and the yellowish droplets are the oil droplets.

Student: Sir.

Yeah.

Student: If any water and mining water micro reason giving such (Refer Time: 19:13) type or making some aggregate type.

Ah.

Student: At a certain omega.

Ah.

Student: But can be expected if we decrease the omega.

Ah.

Student: It will gives viscous pressure.

Depend, again so that depends on the inter droplet interactions. So, it is possible at times that, if let us say there are sufficient number of charges or there are let us say polymer which are absorbed on the droplets. So, then what happens is the true droplets will, in fact, remain bonded even at low frequency and then what will happen is those emulsion even at low frequency will give us a constant G prime or constant G double prime. So, in fact, that is a very good indication, this so, that is why we do this kind of test right, by measuring G prime and G double prime as a function of frequency I can tell something about the microstructure.

Student: Stability also.

And, not necessarily stability, stability in what way? Stability of the structure you mean.

Student: Yeah, stability also it will not come forward.

You know, in sense see the stability is related to whether that droplet size remain that way or in the end, because the overall thermodynamic driving force for this kind of is terms is to oil to be on top and water to be below, so that is the stability, right.

So, of course, from a rheological point of view, if you measure, let us say ones the viscosity and then or G prime and then you measure it after sometime, if there is a difference between the 2, then you know that is structurally something is changing in the material. So, that way you can talk of stability, but here what we can talk is, what is the microstructure of the material? So, if I measure it is G prime and at lower frequency I see nice viscous response, then I know that the at low frequency the particle the droplets are not really bound to each other, but if I measure G prime G double prime in it is constant or it is not slopes of 1 and 2, then I know that droplets are very strong interactions and so, even at low frequency I will not observe a perfect viscous response.

Student: Sir, if there any particular frequency above which we say, it is high frequency or low frequency (Refer Time: 21:28).

Depends on the material, but generally, I mean generally 100 and 200, 1000 are considered mechanically significantly higher. So, time scales of milliseconds. Similarly, 10 to the power minus 4, what I have drawn here are usually high and low, very high, very low. So, something around seconds and minutes is moderate and something below seconds and all is low shear rates. So, that is a generic sort of rule of thumb.

Student: This is for high concentration oil, right.

Yeah.

Student: For low concentration oil?

Low concentration oil, what will be the response. Let us try to guess that. So, instead of these many droplets, now if you let us say have just 5 percent oil water emulsion, then what will be it is response.

Student: Viscous.

Just viscous right, because the viscous drops can move around freely and even at very high frequency you will still see that drops can move around, because it is will mostly water and few droplets. Only when I go to 10 to the power 9 hertz or something like that, we are water itself appears. Then maybe I will see more elastic response, but those are mechanically not very relevant frequencies.

So, it is very unlikely that, for low volume fraction emulsions we will see viscoelasticity. So milk for example, that way rheological is not a complex fluid.

Student: Yes sir.

By microstructure point of view it is a complex fluid, but from a viscosity point of view it does not really have any viscoelastic features. On the other hand, a polymer solution even with the 1 percent or 0.5 percent, 8 percent when you add, it shows significant viscoelasticity, because the macromolecule is not a droplet like this, which does not deform and all that right, it stretches it opens up.

So, therefore, it has a very significantly elastic response even at low concentrations. If you had an interface, which was unstable and the droplet rather than remaining spherical were start having different shapes. Then again you can have viscoelasticity in these context also. When we said that dilute, we assume that the show droplets would remain spherical, which is the case observed with most common emulsions. So, the only small chance of getting viscoelastic response is if drop shapes start fluctuating a lot which means the interfacial tensions are such that you can have very close interfacial tension.

So, that the droplet can become a lips oil and then suddenly it can become all the different shapes then it is possible.

Student: Sir, suppose I have (Refer Time: 24:18).

If I have.

Student: (Refer Time: 24:21).

Ah what is that?

Student: penalties against very visco, the molecular rate varieties very highly compare to a.

It is a polymer.

Student: I think so.

Ok, so.

Student: So, suppose I had in the water.

Hm.

Student: So, what about the means (Refer Time: 24:38) response whether it will be viscous have elastic.

Depends on concentration, depends on what is the nature of the polymer, but generally it will tend to be viscoelastic.

Student: Actually, if it is the viscous it densify actually.

Yeah, so, see that is the thing as I said in the previous classes, that many engineering applications even though the fluid is viscoelastic, from engineering point of you it is sufficient to just characterize it is viscosity or for historical reasons people still measure it is viscosity, though it is inadequate. It is like saying that for as asphalt and road design, asphalt is a viscoelastic material and especially temperature range of interest is minus 10 in Himalayas minus 20 and all to 55, 60 degrees in Chennai.

So, that range material is definitely viscoelastic, but if you look at the parameter, which is used to decide which asphalt to use, was viscosity 10 years ago. So, how do people manage, they will say oh I can choose this viscosity, but my experience tells me that if I use viscosity, when there is some problem I will have to do something else.

So, then what you lack by technical information you make up with your expertise. So, then of course, now if you see the asphalt standard will say you please measure G prime, you please measure oscillatory shear and measures the viscous and elastic contributions and use that in the design, to figure out how the asphalt is deforming under realistic road conditions and then if you want to do a good design you must incorporate in your design viscoelastic parameter as supposed to just viscous parameters.

So, now, is somebody wrong in saying I will just go ahead and use viscosity, when they are not, know wrong necessarily, but they will have to make it up by using their expertise, so which is, what is done in many of the engineering applications. So, when somebody is using at the viscosity modifier, their primary purpose is to change viscosity. Viscosity is a study property. So, therefore, viscoelasticity is irrelevant, but surely if that material let us say being used in porous media for example, surfactant solution or a polymer solution which is used in enhanced oil recovery, again the purpose is to increase viscosity, but the material goes through porous media which is things like this.

So, fluid flow is happening where geometry is small, geometry is large. So, clearly extensional flow, shear flow everything is involved, time dependent flow is involved. So, even though 2 viscosity modifiers, which are identical in terms of giving you the viscosity rise, in the end when you do the experiments with porous media will do different jobs, because for the real application viscoelasticity is also relevant, but many times the engineering applications have not caught up, with the rheological information that is out there.

Now, we look at the response for 3 different relaxation times. So, lambda 1 which is the brownish colour is larger, compared to yellow, compared to lambda 3 which is the black. So, since lambda 1 is larger at low frequency itself. Does it make sense?

Student: (Refer Time: 28:09).

At low frequency itself, you get elastic response. While the black which is very low relaxation time you have to go to very high frequency to see elastic response or in other words for most of the frequency range it shows viscous response.

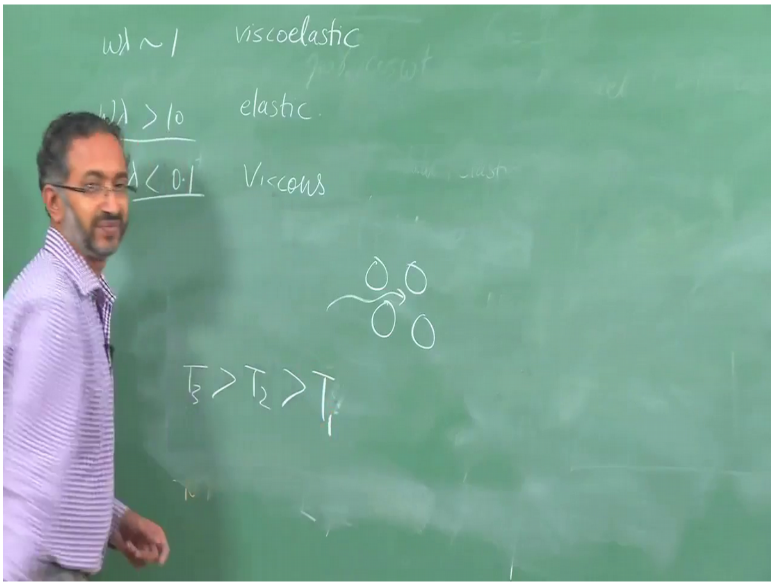
Now, just for a thought, these could be 3 different materials right. So, that I am talking about a material with relaxation time which is more than the other material and so on, but this could also be the same material, but at 3 different temperatures, right. So, which one will be at high temperature and which one will be at low temperature if you assume yellow is the room temperature.

Student: Black will be viscous, high temperature.

High temperature, right, the black will be viscous and therefore, high temperature and the brown will be low temperature response, right. So, this is a fundamental idea that we also have to get used to it. Why does that happened, because when we increase the temperature we decrease the relaxation time, right. Most of the relaxation processes are dependent on thermal energy of vibration and fluctuations.

So, higher the thermal energy easier relaxations become faster or in other word relaxation time decreases. So, therefore, in this graph we would be able to say that T 3 is greater than T 2 greater than T 1.

(Refer Slide Time: 29:40)



If it is the same material at 3 different temperature, right. So, if I take material like a jell or a polymer melt or a colloidal dispersion by changing temperature I could see the response which I could also see by changing frequency. So, there is some correspondence between times, temperature, frequency. With that thought we will stop now.