Rheology of Complex Materials
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Lecture – 30
Linear viscoelastic materials

So, we will continue our discussions on linear viscoelastic response.

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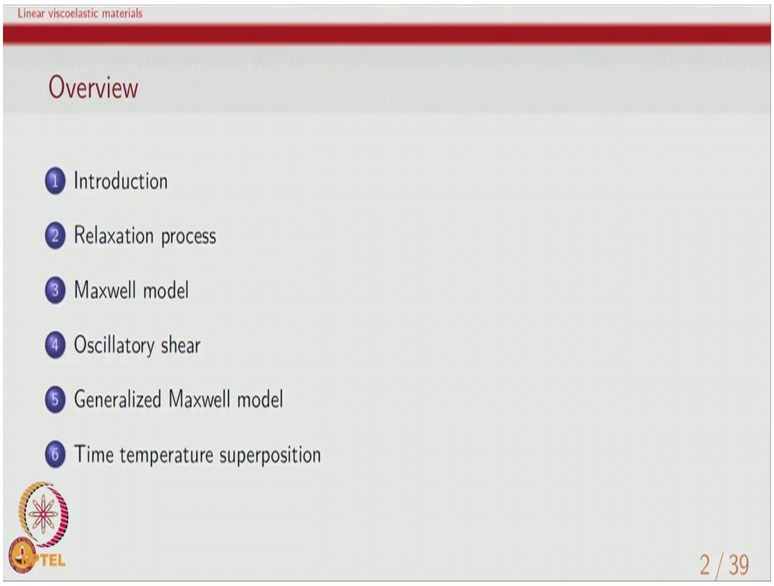

Overview

1. Introduction
2. Relaxation process
3. Maxwell model
4. Oscillatory shear
5. Generalized Maxwell model
6. Time temperature superposition

What we have done so far is familiarized ourselves with an idea of relaxation process, and then we are using Maxwell model as a preliminary model to understand quantitative behavior of viscoelastic materials. We have also looked at oscillatory shear and the response of Maxwell model in oscillatory shear. And so, going on from here what we will do is; we will see that most real materials do not have 1 particular relaxation process; they have collection of relaxation processes.

So, todays class we will look at some example material systems, and how different kinds of relaxation processes those material systems have and we will see that Maxwell model can be extended, 1 Maxwell model is 1 relaxation process or 1 relaxation mode, if you have collection of them then it is called generalized Maxwell model.

So, therefore, most materials can be described using a generalized Maxwell model in their small deformation behavior. So, we will see that and then we will finally, end up looking at time temperature superposition which is accelerated testing that is required whenever we have the requirements of long term prediction of properties. So, therefore, it is an accelerated testing protocol.

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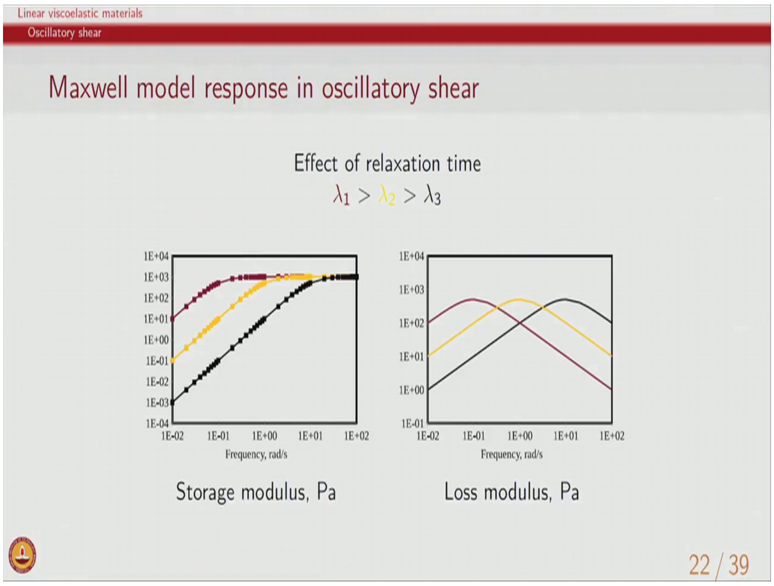

Linear viscoelastic materials

Oscillatory shear

Maxwell model response in oscillatory shear

Effect of relaxation time

$\lambda_1 > \lambda_2 > \lambda_3$

Storage modulus, Pa

Loss modulus, Pa

And so now, let us just last time what we had stopped with is the fact that when you have different relaxation times the Maxwell model response is different, basically one would have to reach for this where lambda 1 is larger, which means it is a more solid like material at lower frequency itself you see elastic plateau, conversely the lambda 3 at very high frequency you have to give go only then you see elastic response.

The other way to say this also is even at high frequency you see viscous response for lambda 3, and so on. So, you can also see that the G double prime actually goes through a maximum. So, that us something telling us in terms of dissipation is maximum when the material is viscoelastic for example, when it is in the viscous domain what happens is the magnitude of G double prime is low, even though material is perfectly dissipative; the magnitude of G double prime is lower at very high frequency the material is elastic and therefore, the magnitude of dissipation is lower. It is the in between frequency where the material is viscoelastic where dissipation is maximum relatively.

So, the in general we will see that this maximum in G double prime to indicate dissipated being max and dissipation being maximum. And of course, the maximum shifts and in terms of the idea of a spectroscopy, you might have a heard of molecular spectroscopy techniques like FTIR or NMR. So, most of these techniques we perturb the molecules with certain input radiation; let us say in case of FTIR we are using IR radiation, and we keep on perturbing the material with different frequencies or different wavelength of the IR radiation. And then the material itself consists of several molecules and therefore, bonds and each of these bonds has a characteristic frequency or characteristic time scale of response.

So, whenever the radiation time scale and the molecular time scale the bond time scale they match we have resonance, and that is when we get maximum absorption of energy. So, this is the same thing and therefore, this is the idea of mechanical spectroscopy.

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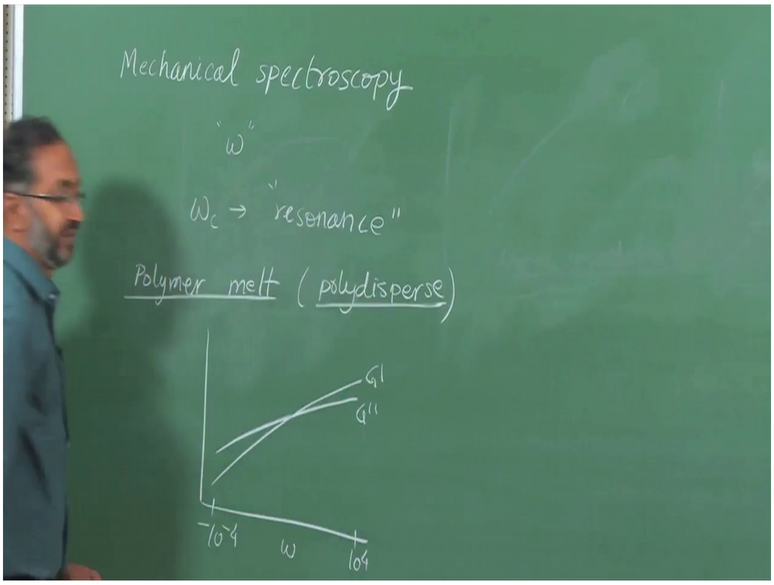

So, what we are doing in fact, is doing mechanical spectroscopy we are perturbing the material at different frequencies and looking at so, omega c is basically the frequencies at which the we can say it is like a resonance, that us where the resonance happened and that us where we see the peak in dissipation.

So, very high frequency if we perturb then the relaxation mode appears to be frozen or whatever is the vibration or segmental motion all of that appears to be frozen. If it is very low then all the material the all the energy is dissipated quickly instantaneously in fact, So, therefore, we go from one extreme to the other when we are looking at these collection of relaxation times.

So, now what we will go through is look at some example materials and how their overall relaxation is. So, for example, we will start with a polymer melt and this is for a commercial polymer melt which means it is a poly dispersed, which implies that molecular weight is not same for all polymer molecule, and when we look at G prime and G double prime. So, we see some feature which is seen in a Maxwell model also that at low frequencies G double prime dominates at high frequencies G prime dominates.

So, the standard idea that higher the frequency elasticity is more dominant is observed, but 1 keep differences this we are going from basically 8 order of magnitude in terms of frequency. So, this kind of data is again obtained using the time temperature superposition that I talked about in the introduction. So, that is why it is very important for us to see how do we get data over such large periods of time or large range of frequencies?

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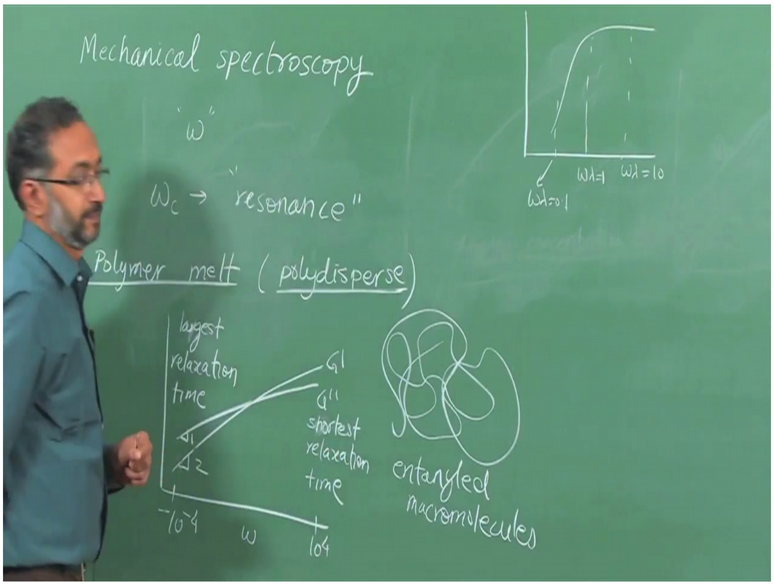

So, in this kind of a case what we clearly see is the fact that if I were to individually do for a Maxwell model we saw that, if this is omega lambda is equal to 1, this is omega lambda is equal to 10 and this 1 is omega lambda is equal to 0.1. So, the material goes from viscous to elastic within only 2 decades itself, and clearly in this case the material is viscous as far as low frequency is concerned, but it is not elastic even at after 8 orders of magnitude in frequency that is because there are multiple relaxation processes that are actually part of the polymeric material.

And in general we can divide the different relaxation regimes in polymer based on the molecular makeup. Since we know that the polymer melt is sort of a entangled mass of macromolecules. So, we have entangled macromolecules; so, in the viscous response cut that terminal regime basically what we have is even though the molecules are entangled, since we are giving it sufficient time the molecules can flow. And so, the time scale the time given here is even more than the molecules to untangle themselves and to flow.

Now, when we start increasing the frequencies we start getting the modes which are to do to entanglement, then we start increasing further then what happens is not just entanglement, but between how the segment between the entanglements point how is that responding so, those are called segmental modes.

And even if we increase frequency higher smaller parts of segments the side groups and so on. So, they also will be so, as you can see as you go from low frequency to higher and higher frequency, you are probing the smaller and smaller length scale of the micro molecule or also you are probing shorter and shorter time scale of the material response.

When you probe the material at low frequency you are probing the material at very high time scales, which means you are probing those relaxation modes of the material which are the largest relaxation time. So, therefore, the relaxation modes here is largest relaxation time, and this side we have shortest relaxation time and later on when we look at the data of real polymer melts and the also. We will look at data of monodisperse polymer melts, which means all the molecular weight is same we will be again clearly able to distinguish between these different timescales.

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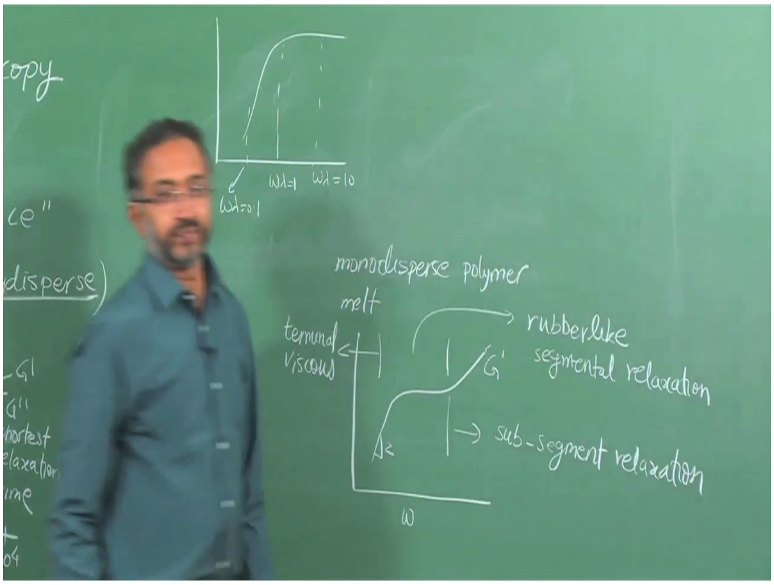

For example if you look at monodispersed polymer melt generally the G prime is seen to be like this. So, at very low frequency we have the terminal viscous response, but in between frequency it appears as if the material is largely elastic like with G prime being independent frequency, and then eventually again it becomes a function of frequency therefore, we have the terminal viscous response and we have the rubber like plateau or it is also the segmental relaxation, and then beyond this frequency we have sub segments.

So, basically what we have is the whole molecule response part of the molecule response, and even smaller and smaller fragment of molecule response. And if I go to extremely very high frequency which is let us say then everything will even the bond fluctuations, and all will appear to be frozen. So, then I am probing the material at the shortest relaxation time.

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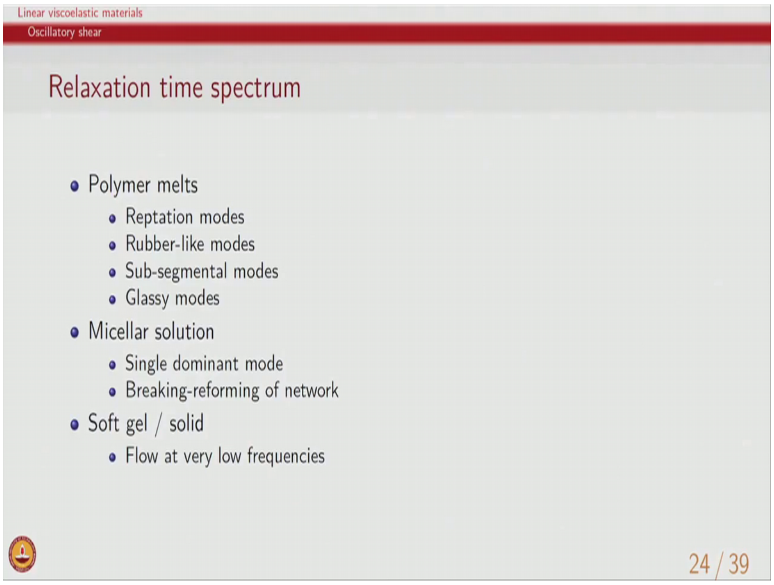

Relaxation time spectrum

- Polymer melts
  - Reptation modes
  - Rubber-like modes
  - Sub-segmental modes
  - Glassy modes
- Micellar solution
  - Single dominant mode
  - Breaking-reforming of network
- Soft gel / solid
  - Flow at very low frequencies

So therefore, this is the case of a polymer melt, in which case as a summary what we are saying is that the relaxation times which are longest or material takes So, reputation modes are basically the longest relaxation times, the sub segmental modes and the glassy modes are of course, shorter and shorter relaxation times.

So, therefore, we have to go to higher and higher frequency to observe the response from them. So, in this case the solid like response is given because the materials are entangled and there are repetition modes.

For example, if you have water then there are only.

Student: (Refer Time: 13:23)

Glassy only molecules those modes right and therefore, material is completely viscous under most normal condition. So, that is why the largest relaxation time in a polymer is only reputation modes which are only hours, and maybe beyond on the other hand a material like steel or concrete has relaxation times which is even larger therefore, it appears completely solid at room temperature.

So, but presumably if to steel or concrete if I subject it to a frequency of 10 to the power minus 10 hertz, then I might start probing some dissipative responses from them which is basically nothing, but 10 to the power nine seconds or 10 to the power 10 seconds right. So, we are talking about years multiple years then yes that it is possible.

So therefore, in this case what we are talking is when you say shortest relaxation time this is what is there in the material. And so, the longest relaxation time of polymer melt is likely to be somewhere around hour's right polymer melt. Now if I say let us say for a material the longest relaxation time is infinity, then what can you conclude from that if longest relaxation time is infinity, then no matter how lower frequency I go.

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I will still see elastic response, I will still not see this terminal viscous response.

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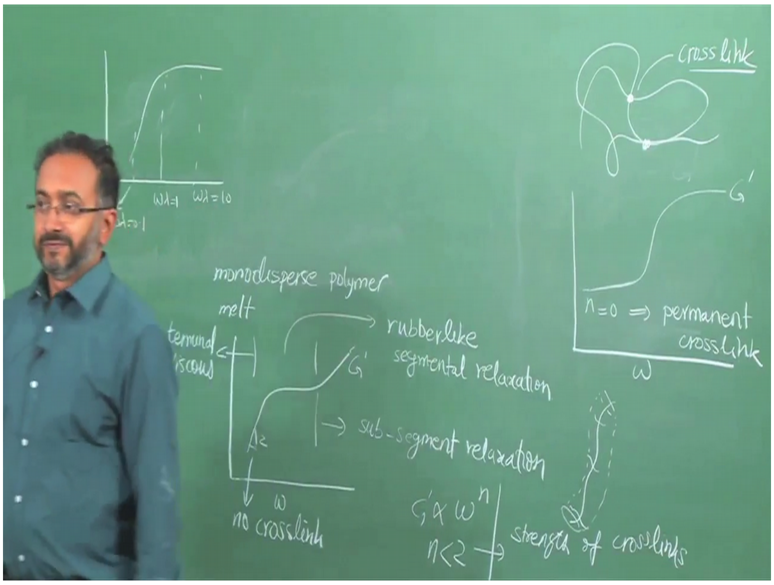

So, one easy way to do that for a polymer is to say that I have this polymer, and then let us say I do cross linking. So, I get a rubber or I get a hydrogel which I discussed in the first class, that if you have a polymer, but you link it using a cross link, then in thus this case what happens is now the material is solid like and. In fact, no matter how small a frequency that I go to I will observe the material response to be actually solid like.

Student: Solid like.

And in that case we say that the largest relaxation time of the material has diverged or it has become infinity.

Student: (Refer Time: 15:47) case cross linking.

Yeah only in the if we do a cross linking, if the cross linking is if the cross linking is permanent then what happens is I will see this signature like this. So, if I look at G prime I will see it something like this, that no matter what how low frequency I go I will never go to a terminal viscous response. The material will always remain solid like and it will still give me an elastic response, which is what a rubber is right no matter how slowly I deform it gives me an elastic response.

So, what we are saying is the following if I probe the material at very low frequencies, then basically I am allowing the material to the molecules to un entangle and flow right because the entanglement is a process we saw basically entanglement is where if I have a molecule there are other molecules right which are it is entangled with.

So, effectively what happens is each and every molecule is basically confined to what what is called a tube right, so molecule can only move in that tube because other side it is being constrained or entangled by the other, but in this direction the molecule can move right it can move like a snake that us what we call the motion called reputation.

Similarly, these molecules are also actually moving themselves right this is a melt. So, there is sufficient thermal energy so therefore, this tube is also a changing function. Now if we probe the material very slowly what happens is there is sufficient time for some of these entanglements to go away and for this molecule to also move like a snake.

So, let us say for example, we have polyethylene where the interactions is mostly van der Waals and so, we will observe this kind of a case, but let us say instead of that I maybe include some hydrophobic hydrophilic kind of interactions or hydrogen bonding which may be a little stronger, then what I will start seeing immediately is the fact that instead of this terminal viscous response I will start seeing.

Student: some elasticity.

Some elasticity coming in so in fact therefore, not observation of no terminal viscous response and a slope of G prime; so, G prime tending to omega to the power n where n is less than 2 is an indication of some structure in the material or some stickiness of the cross linking.

So, that us a very good indication if most polymer melts we will see that you will observe the terminal response because there is sufficient time, but if I make those entanglement points to be more stronger with hydrogen bonding or with hydrophilic hydrophobic interactions, I will start seeing departure from 2 and n will be less than 2. If I make that cross linked permanent which is what rubber is then in that case n becomes 0.

So, basically in the low frequency regime you have n going from 0 to 2. So, n equal to 0 implies permanent cross link, n is equal to 2 implies no cross link basically and n less than 2 depending on what is the value of n it tells me the strength of those cross links. So. In fact, polyvinyl alcohol right as a material it has strong hydrogen bonding, and many times when you work with such materials then you will see that n need not be necessarily 2. So, that indicates that there is some structure in the material even if I prove it at very low frequencies.

So, this is an indication of strength of cross links, and this in between region is where we are probing the material over segmental. So, that is less than because now we are probing the material at short enough times, that now it does not matter whether there is cross linked or there is only entanglement.

Now, we are probing the material at in between time scale. So, both rubber as well as polymer melt will show similar behavior that us why this is called a rubber like plateau. So, what is happening here in a polymer melt is very similar to what is happening here, for a rubber because we are in both cases we are probing a length scale or a polymer segment which is smaller. It does not matter whether that segment is entangled or not because anyway we are not giving enough time for the entanglements or to relax, and therefore this is called a rubber like plateau.

Beyond this in fact, again they will have similar response. So this increase here, and this increase here, is again similar because we are probing even smaller segments. And then this of course, if I do eventually I will again see what are called the glassy modes. So, that is what is written here so, the longest relaxation time is associated with reputation because it is associated with the overall motion of a molecule, then we have rubber like modes which are related to segments between to entanglement points or between 2 cross links that us called a segment .

If we go to still higher frequency we have sub segmental modes, and if we go to higher frequencies that is glassy modes. If we perturb the material beyond glassy modes then basically everything is frozen, and we will see completely elastic response right under those conditions the material will appear to us hard and brittle material.

So, the same polymer material at very low frequency appears to be a fluid in fact, a perfectly viscous fluid right this is Newtonian fluid also has the same response, Newtonian fluid G prime is proportional to omega squared G double prime is proportional to omega. So, that us the same response that even a polymer melt shows at very low frequency, but on the other hand at very high frequency it shows and glossy response.

So, now let us look at another material this is what we do when we are doing this mechanical spectroscopy, we are probing the material at different frequencies and trying to understand what mechanisms are underlined. So, now, let us look at the next material which is a micellar solution.

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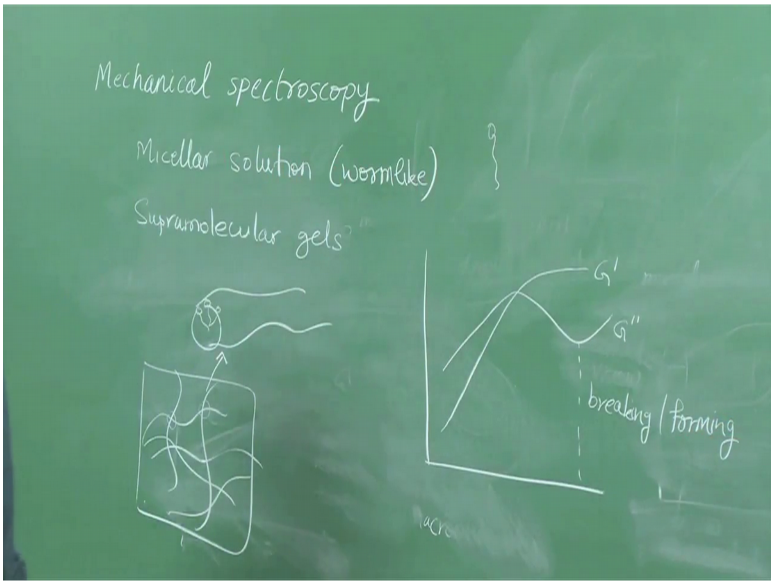

And also supramolecular gels there are several materials which belong to this class. In fact, it is a warm like micellar solution or it is also some materials which are supramolecular gels they show these kind of response. So, we will just look at quickly the warm like micelles what we have is basically it is a micellar solution so, it is surfactants are there and the surfactant basically form a spherical micelle at low concentration.

But if you keep on increasing the concentration of surfactant then they form what are called the cylindrical or warm like micelles. So, in that case what happens is you have basically a cylindrical micelle like this, where the all along the cylinder the surfactants are all basically arranged.

So, any cross section you take there is a circle of surfactants. So, it is a tube and that is why it is called like a worm, and the overall worm like micelles solution is nothing, but so each and every warm is drawn like this. So, this is a worm like micelles solution. So, each and every line that I have drawn here if you magnify it is a collection of surfactant molecules. Now, what you can clearly see is in this case the joining and rejoining of these points is dynamic there is no entanglement here, because in this case of polymer 1 polymer molecule on the other the only way this molecule could move was if this molecule went away.

But in this case we are talking about small surfactants which make this worm also this worm also and surfactant molecules can in fact, exchange each other from. So, therefore, this particular thing can also break and reform. So, therefore, these kind of systems do not have entanglement modes, but they only have breaking and reforming off the worm like micelles.

So, if you probe these materials and look at their. So, G prime is somewhat similar to a maxwellian response and G double prime in fact, under is and in fact this time scale is associated with the breaking forming. And so, these are examples of a material which are called so supramolecular gels or also small molecules which assemble themselves, in this case also surfactant assembles itself in warm like micelles; these warm like micelles are assembled themselves, right into a chain mass of to many worms which are next to each other and so, in case of a breaking and reforming you have.

So, you can see now there is a slightly different characteristic feature another thing to notice, we are going let us say from 10 to the power minus 1 to about 100. So, we it is not very high in terms of frequency range unlike a polymer molecule.

And so in terms of what are the relaxation modes available for this kind of material they are narrow, the material goes from viscous to an elastic like in very small frequency range. So, because that us because the overall comp the constitution of the material is not very complex in terms of what type of relaxation modes that are available. And so one more material that we will look at is called the soft gel.

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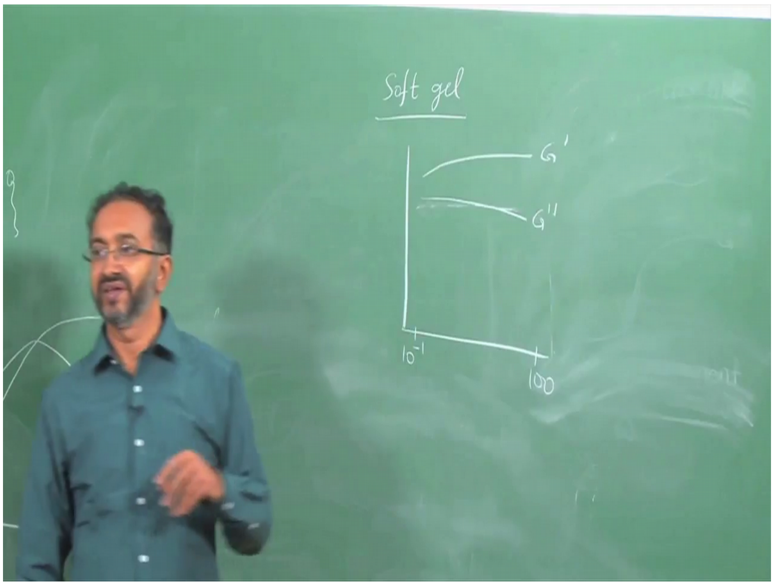

And many dispersions or emulsions show this kind of behavior, where you have a collection of these particles and there is a strong network between these particles as we discussed earlier in case of emulsions, then what we see is it appears as if almost G prime and G double prime are almost independent of frequency.

So, clearly as soon as we see that G prime even if you go to lower and lower frequency, and let us say it here now we are talking about again 2 n to the power minus 1 2 100, and by the way this is the usual frequency range at which we usually probe the materials to begin with because, these are the mechanically most relevant time scales of interest and therefore, whenever we get a new material we try to probe it at these, and then depending on our interest we can say that can I get hold of some technique. So, that I can get maybe beyond hundred or less than 10 to the power minus 1 by doing superposition.

So, in this case what I can clearly see is both G prime and G double prime there is nowhere near terminal viscous response. If at all it appears to have a more elastic like response G prime is more than G double prime elasticity dominates over, the viscous response. If there is a hint that if at all if I can go maybe there is something like this right if I go to, but then I need to do those experiments and in fact, I see it to see that.

Student: Longer time is required.

Yeah longer time may is possibly required, but one thing which we always have to be concerned about whenever we subject the material to lower and lower frequencies is the stresses involved or the stalks involved from the instrument, we always reach the limits of the instrument response what whatever is the least count of the instrument.

So, the data gathering in low frequencies is always tricky. So, sometimes it may be possible to go to lower frequencies and do some other times it may not be possible, the other thing you must realize is that when I say 10 to the power minus 3 1 cycle itself is going to take 1 hour.

Student: (Refer Time: 29:42)

Right so, if I go to 10 to the power minus 4 it quickly climbs up right. So, therefore, again experimentation is not achievable in our time scales, we are trying to answer some questions by doing a research project and so, or we are trying to do let us say in industry some of the product development. So, we cannot say give me 4 months for testing and I will do 1 test for 1 month that kind of things are not feasible.

So, therefore, soft gel is a material which again has a overall possible terminal viscous response at the lower frequencies, but what we see in most common thing is mostly the elastic. So, again these are therefore called the gel like materials. So, with this we have a now reviewed three different materials, and seen the observation of these three different materials with three different types of relaxation times.

Now what we will do in the next class is look at can I explain the overall these three responses by combining, the different relaxation modes that we talked about.