Rheology of Complex Materials
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Lecture – 33
Time temperature superposition

So, in the next few minutes, we will look at the idea of time, temperature, superposition and. So, what is shown here is relaxation modulus with different relaxation times?

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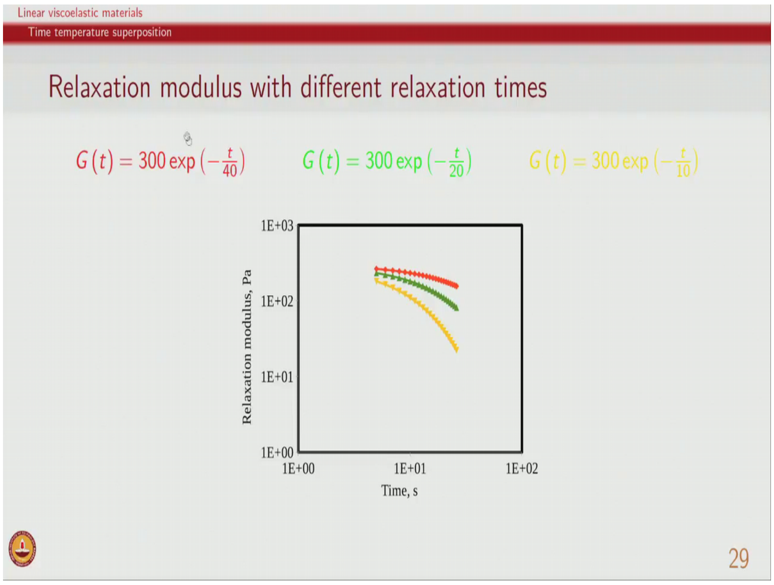

Relaxation modulus with different relaxation times

$G(t) = 300\exp\left(-\frac{t}{40}\right)$ $G(t) = 300\exp\left(-\frac{t}{20}\right)$ $G(t) = 300\exp\left(-\frac{t}{10}\right)$

So, this we have seen that, it is an exponential decreasing function, this is being plotted on a log scale and that is how this is an exponential decrease and it is being done for three different relaxation times, in one case it is chosen to be 40. So, which is a large relaxation time and therefore, relaxation is very slow, while very small relaxation time 10, the relaxation is quite fast.

So, we could also think that it is the same material being represented, but at three different temperatures and this we have discussed earlier that we would expect that at higher temperature, there we can reduce the relaxation times and at lower temperature the relaxation times would increase. So, therefore, if each of these were supposedly with three different temperatures,

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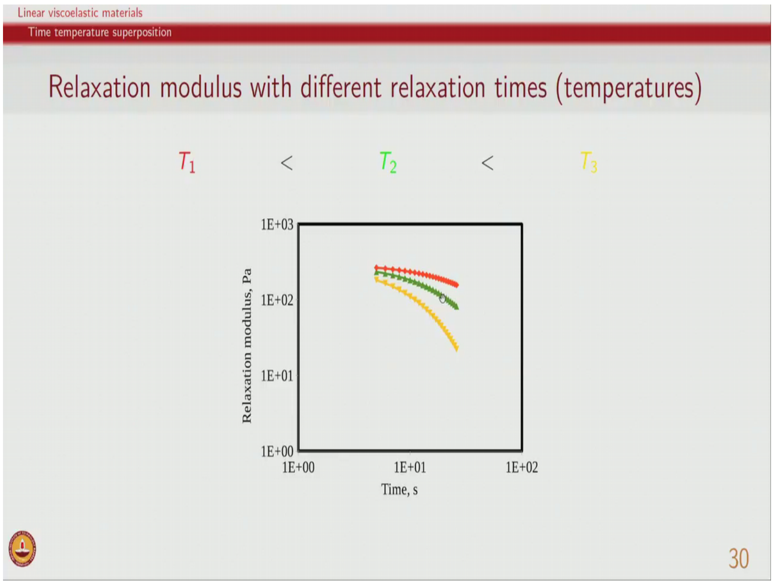

then the green one would be with middle temperature and the red one would be lower temperature, because that is where the material is taking much longer to relax, it is much more solid like, while the yellow curve at temperature T 3, is at a very high temperature, because the material is relaxing somewhat quickly and of course, the extremes are that, if it is a perfectly solid material, no relaxation perfectly fluid material instantaneous relaxation.

So, if we have these three different temperatures which are showing the relaxation modulus given like this, one thing we can notice is let us say, if I talk about this value of about 100 right, if I go and see I can see that if I were to observe 100 as the modulus, as these three different temperature, I just have to wait for different amounts of time. So, therefore, I can get equivalent response, but if I do different times right.

So, the other way also to think of is that now, I have done the experiments for same amount of time, if I were to obtain the response at lower time, but at T 2, what should I do right, if I want to do a material response here, which is much lower time at T 2 I 1 thing is I do experiments at lower time, but that sometimes may not be feasible. For example, microseconds, milliseconds. Similarly, if at green at T 2, I want response, which is at much higher time, again the option is to do experiment for longer time, but again it is not practically always possible.

So, is it possible for me to say that given that, I have this response at different temperature. I can say that look this response at T 3 is equivalent to response at T 2, but at some other time, because I have changed the relaxation time, they are showing response like this, but if I somehow interpret this data at T 3, being equivalent to data at T 2, because presumably if I wait long enough at T 2 itself, I should get some response right.

Student: (Refer Time: 04:03) in a particular temperature if you move the equation in, we can see them, see the equation and a with different temperature also we will have a relationship with the different temperature. How the response is changing then?

Student: It will correlate.

Yeah. So, possibly what he is saying is that, if we knew how relaxation time changes as a function of temperature, then we can actually do this exercise, because I know when I go from T 2 to T 3, the relaxation time changes like that and I saw this response. Now, I have to just go back and say no [FL] relaxation time is not that but it is, what is valid at T 2. So, this is what the relaxation time is right now.

So, what if I do this?

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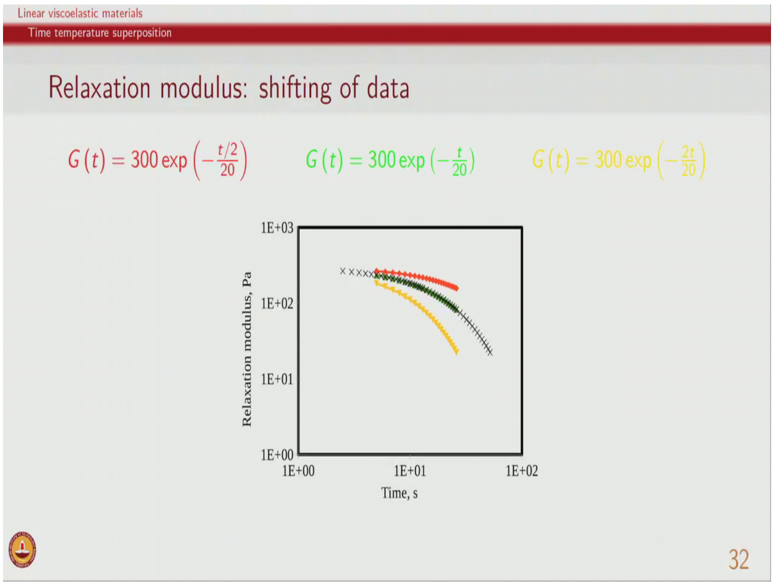

Linear viscoelastic materials

Time temperature superposition

Relaxation modulus: shifting of data

$G(t) = 300\exp\left(-\frac{t/2}{20}\right)$ $G(t) = 300\exp\left(-\frac{t}{20}\right)$ $G(t) = 300\exp\left(-\frac{2t}{20}\right)$

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If I say that the T by 40, I just interpret as T by 2 into 20 and similarly, T by 10, I interpret as 2 T into 20. So, the fact that the response at higher lower temperature is indicative of the response at T 2, but at much lower times; basically I replace time with T by 2 and then I will get response at T 2, but for lower times. So, what we are saying in this graph is, if this red data is shifted to the left, right basically, I change each of the time here, of the red data by T by 2, then I effectively get data, which is like T by 2 by 20.

So, then I have now all the data at relaxation time 20, but I have shifted the time. So, this shifting of the data, the crosses the data points are actually after shifting the data so, but the way I have described it. So, far is also an empirical procedure right, in the sense you shift the data of course, since this was an exponential and there is just a Maxwell model, that I have used, I could write it in terms of exponential functions, but in general, this may not be available.

So, what is done is more empirical procedure; however, what is very useful to note is that the shift factors are not arbitrary functions of temperature shift factors, if shift factor is a known function of temperature, then it becomes a very useful exercise, that time temperature superposition is working with a given set of relaxation times changing with temperature, in a given way and so,

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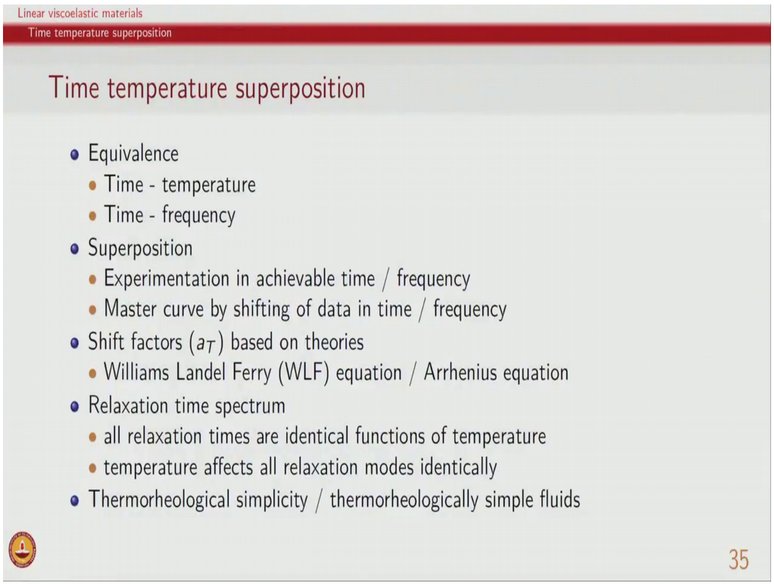

Linear viscoelastic materials
Time temperature superposition

Time temperature superposition

- Equivalence
  - Time - temperature
  - Time - frequency
- Superposition
  - Experimentation in achievable time / frequency
  - Master curve by shifting of data in time / frequency
- Shift factors (a_T) based on theories
  - Williams Landel Ferry (WLF) equation / Arrhenius equation
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What we have done is the exploited the idea of equivalence of time and temperature or time and frequency, because by changing temperature we modified relaxation time, by changing experimental time we again also perturb the material at different timescales.

So, both can be used higher temperature behavior is like lower time behavior, lower temperature behavior is like larger time behavior, conversely higher temperature, time temperature frequency also, actually time frequency is related and therefore, frequency temperature is also related, low frequency is analogous to higher temperature, high frequency is analogous to lower temperature right.

Student: Sir, temperature.

So, let me just write this down and then maybe, I will take your question, low temperature short times right.

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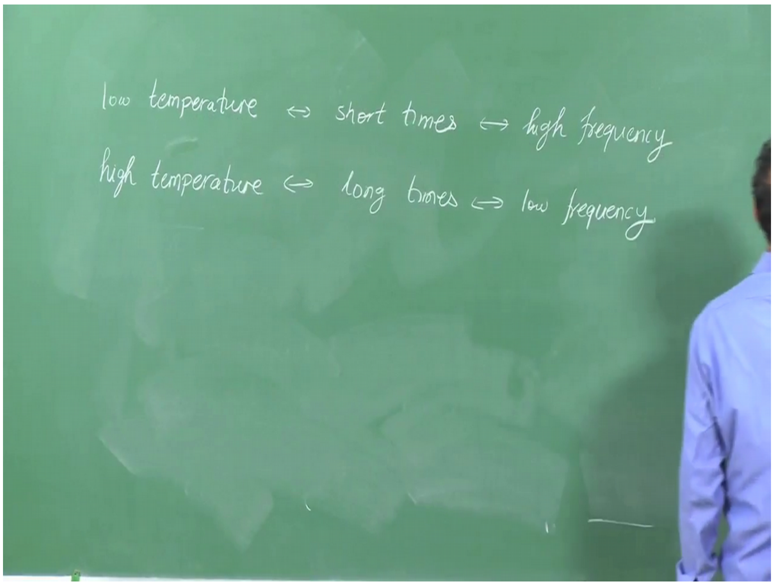

low temperature ↔ short times ↔ high frequency

high temperature ↔ long times ↔ low frequency

If there is a characteristic relaxation time lambda, if I go to lower and lower temperature, then the relaxation time will increase and I get more and more elastic response. Similarly, if I have a characteristic relaxation time lambda, if I subject the material to shorter and shorter experiments, then I will get predominantly elastic response.

So, that is how low temperature and a sorry higher temperature, higher temperature low temperature and short times are related, if you subject the material to higher temperature then it is more viscous response relaxation times are much lower and that is like saying that you carry on the experiment for a very long time. So, high temperature long times is also same thing as low frequency or high frequency right, what was your question?

Student: Temperature is above the crystallization temperature.

So?

Student: So.

Yeah.

Student: It helping the time.

So, why would this time temperature superposition work? Is a good question to ask right. So, what is the, when I wrote something like this for three different temperatures, the same relaxation function is valid. I have written exponential for all three, which means the underlying relaxation process does not change with temperature. Now, if you are talking about a crystallizing material at one temperature it did not have any crystallites, other temperature it had, crystallites or the reverse also melting material at one temperature It did not have any crystal, it had crystals then other temperature crystals are melted away, clearly the relaxation processes which are present, are going to be not there right. When crystals are there, will be one set of relaxation processes, when the melt is there, it is another set of relaxation processes.

So, you would expect that this kind of process will fail empirically, when you do time temperature superposition, it will not work, because the underlying set of relaxation processes themselves have changed. So, material which is structurally changing time, temperature, superposition, would not be expected to be valid.

So, superposition is basically being done, where experimentation is done in achievable time frequency and then by shifting of data, you construct a master curve, which can give you additional time and frequency and as I said what is sort of provides, a little stronger foundation to this empirical exercise is the fact, that the shift factors depend on temperature, in a given way first of all the master curve has to be constructed, if master curve itself is not good, then you clearly know, that look material is undergoing, some changes in temperature.

So, let us not even at a time type is a superposition, then you should not do tests at some other temperature and try to get deduction about lower temperature, because anyway your material is different at two different temperatures. So, now, point in doing time, temperature, superposition, but let us say, you get a master curve, which appears to be quite continuous, then the next question is how much was shifting was needed to construct the master curve and in this case there are two sets of equations, which generally or two sets of processes, if relaxation processes are of one kind, we get the WLF equation.

So, at each and every temperature, how much shift factor is used prints on temperature and the other condition, it is Arrhenius, any guess on what these two might work. Why do we have these two and I think, we talked about this in earlier class, whenever you have an Arrhenius process, it implies an activated process. So, therefore, what is generally observed is, in more fluid like materials and melts and materials like that, you will see that Arrhenius equation is valid. So, whatever are the basic relaxation modes, which depend, let us say on bond rotation or reputation all of, these are basically, Arrhenius time dependence.

So, relaxation time decreases exponentially, as a function of temperature based on Arrhenius rate process. On the other hand, if you are closer to rubbery material or closer to glass transition, then the WLF equation is, what is observed. In this case the relaxation time increases more rapidly than what Arrhenius would predict.

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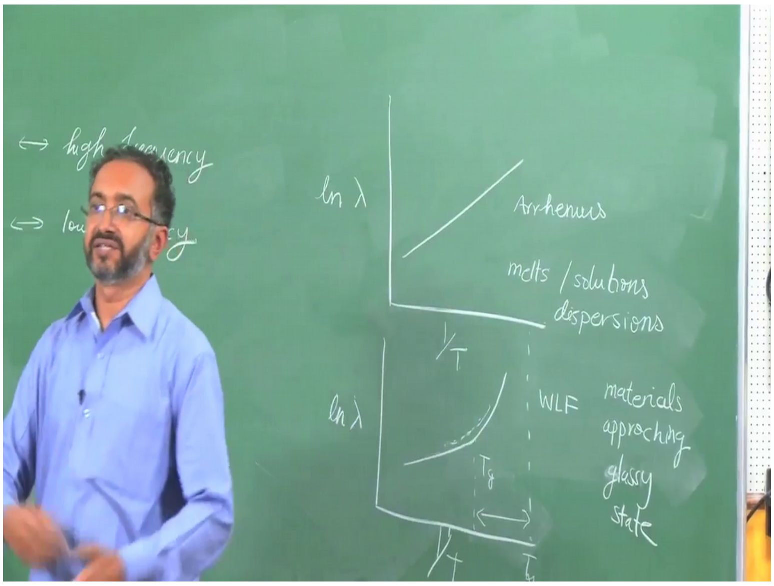

So, for example lambda versus relaxation time right, 1 over T, if the Y axis is, let us say log logarithmic. Write log of lambda, then how would this be for an Arrhenius?

So, relaxation time would continue to increase as temperature goes to 0 and relaxation time will become infinite when temperature is 0. So, at 0 Kelvin basically, no relaxation processes are possible right, that is how the idea of an activated process will be that, there is sufficient thermal energy for activation barrier to cross and this activation barrier will not be crossed, only when you reach 0 thermal energy, which is 0 temperature, but for many materials, when you are approaching the glass transition temperature, the overall response is where the, at lot lower temperature itself the lambda goes to infinite, it starts diverging.

So, lambda that is what I meant, lambda is decreasing much faster than what is predicted by the Arrhenius. So, this straight line portion of the curve is, what is Arrhenius, but then the lambda increases much more rapidly and what I have plotted here is a fictitious temperature, at which all motion ceases. Basically, material is practically, completely frozen and generally about 50 degrees before that; there is the glass transition temperature of the material.

So, near these conditions, the variation is not Arrhenius near around glass transition, for a rubbery material or material which is close to glass, the relaxation time does not change as a function of Arrhenius. So, this is WLF and this is Arrhenius. So, the question is as to why does this happen right. So, there are multiple ways to try to rationalize this. Of course, this is still a very active area of research as to what is meant by the glassy state. What happens to the relaxation time spectrum, when you have these material approaching glass transition and couple of phrases, which can be used to rationalize. This one is the fact that maybe relaxation modes are not independent of each other, they are cooperating with each other.

So, then if the material behavior becomes much more complicated to describe and it is no longer there, for each process and it is activation barrier that is not the only thing. There are multiple relaxation processes, actually cooperating with each other. So, in that case then you cannot explain it, using a simple Arrhenius activated barrier, kind of an explanation in general. For example, relaxation process, we said depends on for example, bond rotation right.

So, in this case, it is as if few sets of bond rotations are responding together and that is why the word cooperativity is used sometime to describe relaxation, near glass transition and. So, WLF William Landel Ferry is an empirical equation. So, in 60s and 70s, when it was observed that miraculously, for large number of materials one equation seems to fit all the data and. So, the main people were thinking that maybe, there is some universal WLF equation, which is valid for all materials we know. Now, that first of all only for materials, which do not undergo large changes as function of temperature, this is valid and. Secondly, the equation, the constants are not necessarily universal.

But still there are large number of theories, which are trying to explain the observation of glass transition and what is meant by state of matter called glass and. So, this is still an active field of investigation, but in terms of the two equations this is what it is.

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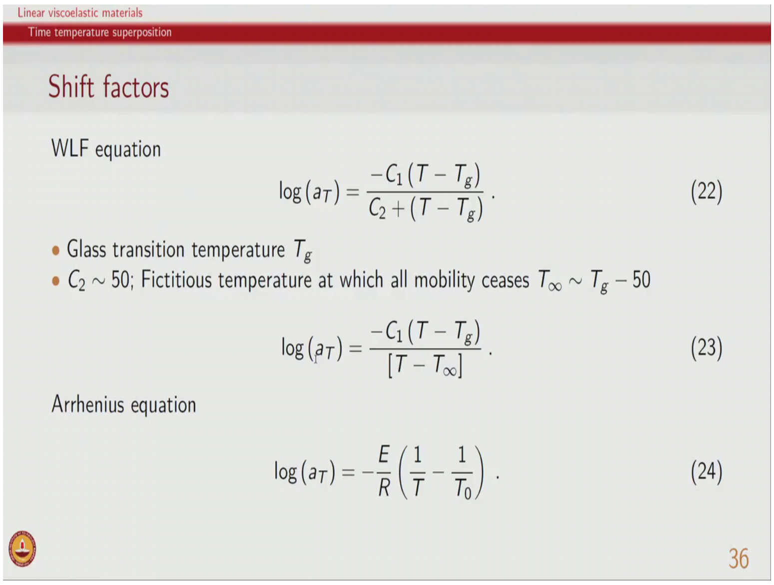

Linear viscoelastic materials

Time temperature superposition

Shift factors

WLF equation

$$\log(a_T) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}. \quad (22)$$

- Glass transition temperature T_g
- $C_2 \sim 50$; Fictitious temperature at which all mobility ceases $T_\infty \sim T_g - 50$

$$\log(a_T) = \frac{-C_1(T - T_g)}{[T - T_\infty]}. \quad (23)$$

Arrhenius equation

$$\log(a_T) = -\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right). \quad (24)$$

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So, in one case the shift factor is dependent on two coefficients C 1 and C 2 and it is a function of how far away from glass transition temperature. You are and generally this C 2 is considered, is as I said a sometimes initially, it was thought to be universal coefficients and many of the C 2s were around 50.

So, you could rewrite this as. So, C 2 plus T minus Tg could be written as T minus.

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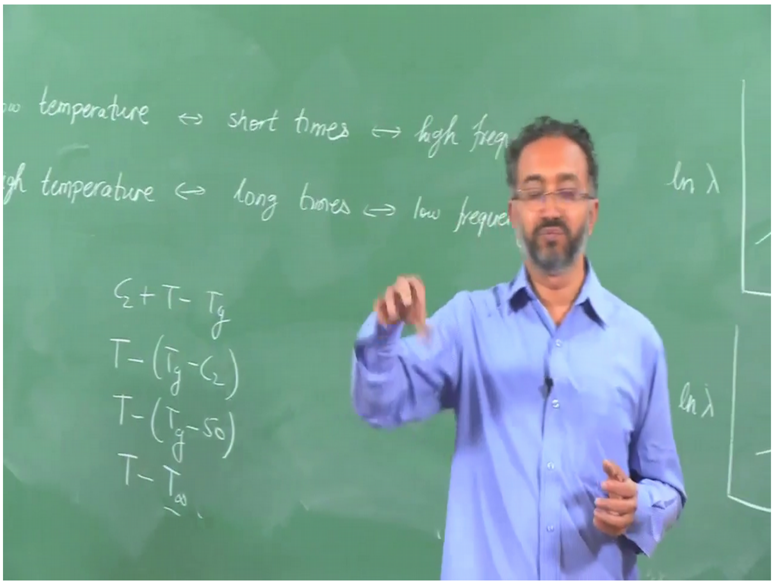

Tg minus C 2 and C 2 is being observed to be generally 50 and therefore, this is T minus T infinity, then it blows up when T approaches, T infinity the denominator goes to 0 therefore, lambda becomes infinite and that is the T infinity that I have drawn here, while in this case T has to go to 0 for lambda to become infinity, in this case at T is equal to T infinity itself. The material can experience very high relaxation times.

Now, for let us say material like a PT polyethylene terephthalate with coke bottles and all Pepsi bottles, they are made up of that. So, the glass transition temperature is around 75 79 around that. So, therefore, below 50 is around their own temperature right. So, 25 30. So, you can expect the material to not really have much of relaxation processes, but if you put 60 degrees, 70 degree water in it, then you are allowing many more relaxation processes to happen in the material at relaxation times, which are if 1 year, 2 years certainly things will happen.

So, of course, if you take it to 80 or 90 degrees, then you will see that the PT bottle will deform, because you are anyway taking it to a rubbery condition. If you put boiling water, which is around 100 degrees, you have for most often seen right, will completely go out of shape, the other dependence of course, is in terms of Arrhenius. So, which is just exponential, this E by R is the barrier energy right, the activation energy.

So, generally Arrhenius is observed for polymer melts and maybe some dispersions, while this is observed for materials approaching glass transition and for a single polymer, this is quite seen, because let us say for same PT material, if I am trying to understand it's viscosity and relaxation processes around 200 degree Celsius, because its melting point is around 250. So, around 200 180 degree Celsius I can safely use Arrhenius, but our 100 degree 100 and 10 degrees then I will use the WLF equation.

So, if I want to, if I let us say design. For example, just PT is not a material, which can be used for engineering application, but let us say if I were to use PT and ask this question that if I am using it, let us say at 20 degree celsius, will it survive 10 years or not? So, what I can do is, I can do tests at 50 degrees, 70 degrees, 80 degrees, 100 degrees and assume that, it is neither crystallizing nor undergoing any fundamental changes. So, that I can do time, temperature, superposition, and get at 20 degrees, what happens to it, over a much larger period, because higher temperature will correspond to longer times.

So, I can get years of performance, if I go sufficiently high in temperature. And under these conditions, we expect that polymer especially, PT polymer, let us say will remain amorphous. So, whether it is melt state or glass state or rubber state it is amorphous and it is overall molecular structure remains an identical or very similar under these circumstances.

Student: (Refer Time: 22:49) temperature.

Yes, he is just pointing out the fact, that if I let us say cool it very slowly, it is possible that it may crystallize, if I quench it, it may remain amorphous. So, therefore, the nature of crystallization, in the material would depend on how fast or slow we cool it, sometimes for macro molecular system or for colloidal system, depending on the type of monomer or depending on the type of particle. It may not be possible to have a crystalline phase well defined, because for a crystalline phase to be well defined you have to have a unit cell and for example, if you have bulky groups and those bulky groups are random, in case of a macromolecule.

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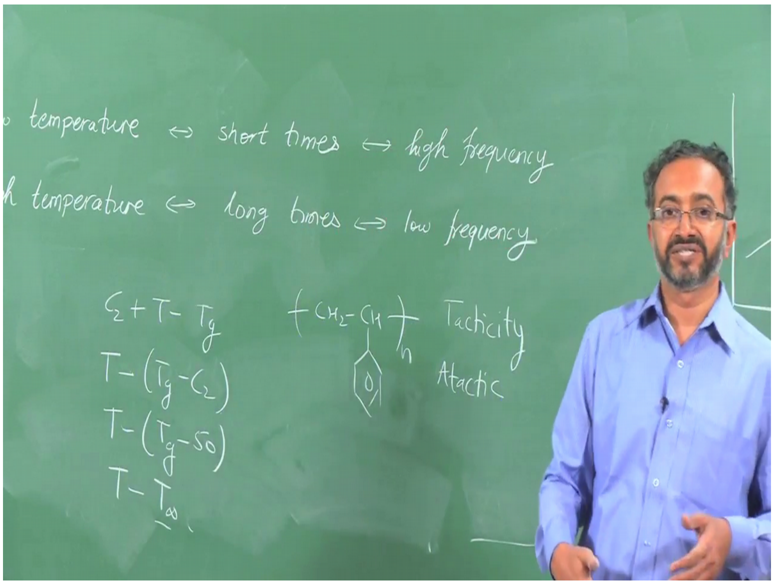

So, let us say polystyrene right. So, for this kind of a molecule, if it has to form crystal, this bulky groups has to basically align. Also it has, there has to be enough space. So, that this bulky group can also be, but what happens is this material is mostly, this bulky group is randomly distributed in terms of, it is position, which is called the tacticity, how this group is. So, generally this material is a tactic, which means how this bulky group is distributed, is completely random.

So, in that case you will never be able to crystallize that material, because the fact, a crystal cannot be formed, because a regular arrangement is not feasible. If you get a material which is isotactic, where there is a well defined position of these groups, then you can get crystallization and then what he said was true, that depending on the cooling rate you can manipulate the crystallinity, just like metals and alloys and so on.

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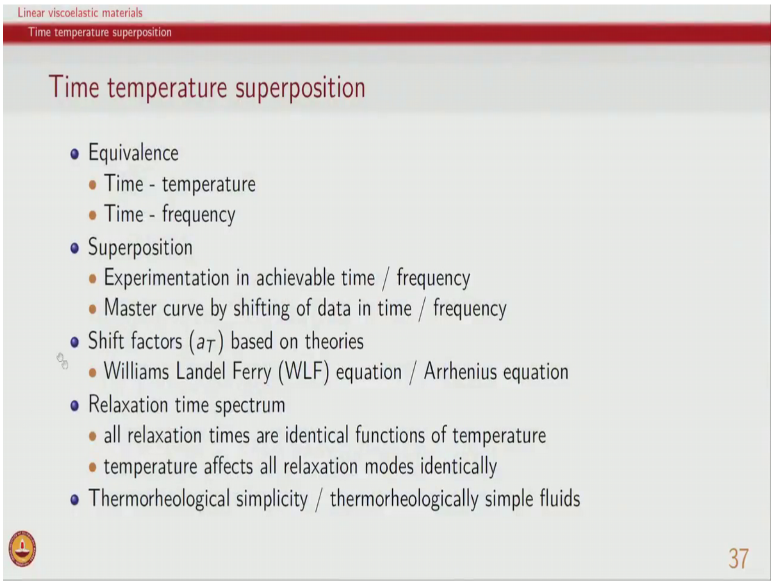

Time temperature superposition

- Equivalence
  - Time - temperature
  - Time - frequency
- Superposition
  - Experimentation in achievable time / frequency
  - Master curve by shifting of data in time / frequency
- Shift factors (a_T) based on theories
  - Williams Landel Ferry (WLF) equation / Arrhenius equation
- Relaxation time spectrum
  - all relaxation times are identical functions of temperature
  - temperature affects all relaxation modes identically
- Thermorheological simplicity / thermorheologically simple fluids

So, just to summarize. So, the shift factors based on either WLF equation or Arrhenius equations are possible and the relaxation time spectrum. We are also assuming, what I showed was a simple relaxation process right, where there was only one relaxation time. Generally, materials will be a collection of relaxation processes and our assumption is that all relaxation processes are being affected in the same way or to the same extent, then only again shifting will work out very nicely.

So, this assumption, that all relaxation times are identical functions of temperature or temperature affects all relaxation modes identically, then these materials are called thermorheologically simple. So, whenever time, temperature, superposition is observed, we say material is thermorheologically simple, the underlying thing is that, all relaxation processes depends similarly, on temperature. So, for example, here,

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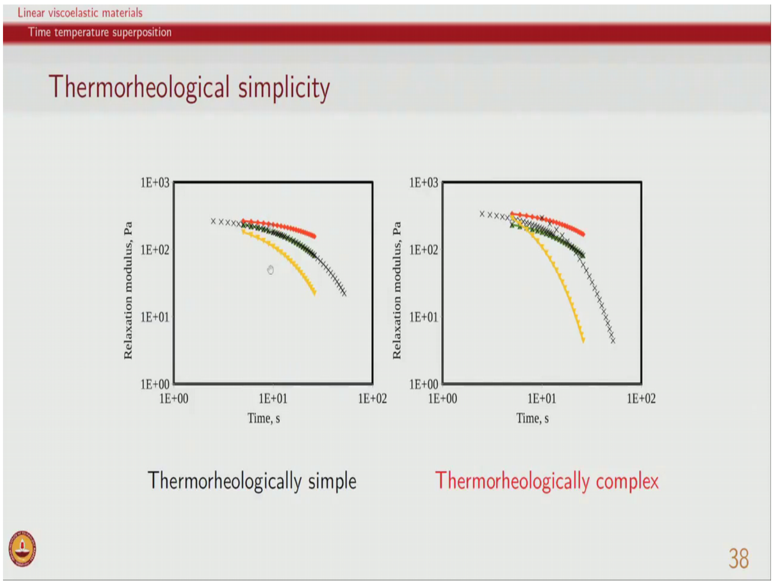
Linear viscoelastic materials

Time temperature superposition

Thermorheological simplicity

Thermorheologically simple

Thermorheologically complex

This is thermorheologically simple, what we saw and if you have three other sets of data and you try to construct and it is not. Now, superimposing nicely, to get a master curve this is the thermorheologically complex material, because either the structure is changing with temperature or relaxation processes are getting affected differently, either way it is the same, because relaxation process depends on microstructure. So, if microstructure keeps on changing with temperature, affecting the underlying relaxation processes, then it will be a thermorheologically complex material.

So, for time temperature superposition to be valid, you would hope that the material is thermorheologically simple and. So, this is again something which is done empirically. You just look at the material response, you try to do time, temperature, superposition and if it gets superimposed, then you say, it is thermorheologically simple material. So, with that we have

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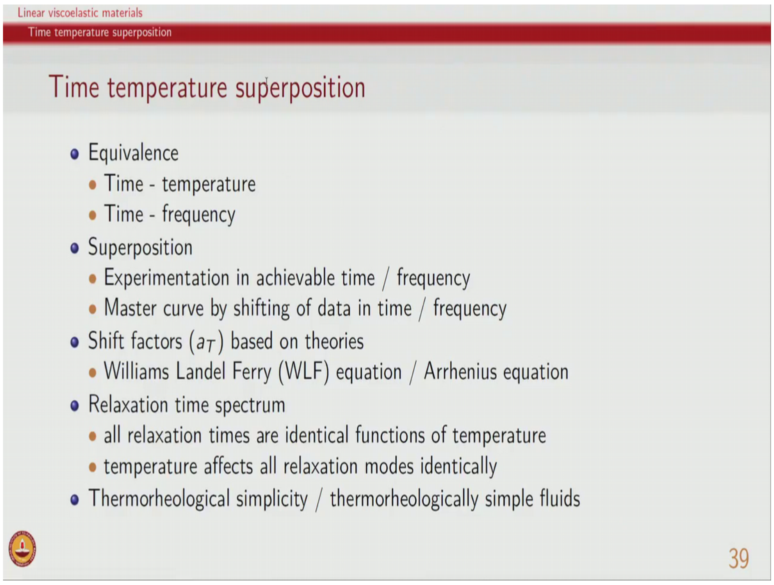

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Now, covered the aspects of time, temperature, superposition. Now, in the, there is still one more class remaining on the solid, like materials so, that we will do next time.

Student: Sir (Refer Time: 26:54) we were going to a experiment a higher temperature.

Yeah.

Student: And I want to compare to (Refer Time: 27:00) longer time. How can I received that, during higher temperature material is not changing and also for long time of periodic, will not changing. How can I received?

So, what will happen is let say, he is pointing to another possibility, that let us say, if PT itself right. If I am testing it at, let us say, my processing temperature is to 50 degree Celsius right. So, I want to or understand behavior, but again I do not want to do too much long term testing, I will just take the material to 300 degree Celsius and test it and then see, but at 300 degree Celsius maybe, some oxidation and some few other things may happen. So, some degradation reactions may happen.

So, am I sure that when I do? So, what you will see is when you do time temperature superposition of 300 and 290. You will see that the 300 data is not superimposing well, because of the degradation reactions, the polymer chain length is changing, molecular weight is changing, because of that, the way entanglement, that has changed. So, the fundamentally, there is a structural change in the material. So, that is a good indication and of course, you will need to have a hypothesis, on the other side as to what might be happening.

So, at 300 for PT, you will say that yes, some chain session, some oxidation reactions are happening, then you can do a spectroscopic analysis to see right. A material which was subjected to 300 is it showing any other bonds or you can do a calorie metric measurement to see, if there was any heat of reaction and to say that there was some other, because melting and all is finished by 250. So, at 300 no other temperature, thermal event should be there, but if there are chain scission reaction, those are exothermic. So, will get heat of reaction. So, things like that.

So, you will always have to you, we always have to supplement rheological analysis with other things, but this will give you a clue, if time temperature superposition is working, it still does not mean that, processes are not happening. Sometimes, the cancellation of two processes can give you some result right. So, that of course, we always have to worry about.

Student: Sir, suppose it is (Refer Time: 29:08) some part. And that is how it is a.

Yeah. So, it is I mean by the way, there are what we talked about time, temperature, superposition can be taken, once it is a procedure and once you want to exploit a utility, you can also say that even for crystalline sample, I will use it, but I will use a vertical shift, I will say that when crystal gets formed, there will be an additional elastic contribution and I will use a vertical shift to say that the elastic contribution is changing. So, there will be vertical shift added on and I can a priori tell you by doing DSC or some other method, that how this vertical shift will change as a function of temperature.

So, you can attempt that right, I mean once it is a procedure available to engineers, we can try exploiting it. Similarly, they for biomaterials, you can modify the response with ph instead of temperature. So, you can do ph time, something which is solid like at some ph may be fluid like at another ph. So, because you are changing the interactions and therefore, you are changing the relaxation times. So, just the way with temperature, you change the relaxation time; you can change it to ph. So, people can do ph time superposition and so on.

So, once the idea is there, then you can all of, this is basically saying that by modifying a parameter like ph or temperature, you are modifying the underlying relaxation processes by only modifying the relaxation times, you are not modifying the nature of relaxation processes, then it will work if it works only for part of the time, they part of the records, then you are free as an engineer to say I will look at only that part and I will throw away the rest, because it is not of my interest. So, some other changes are happening there, but I am not going to look at it.

Let us say you are using a seal for a high temperature, application to in some machine right. Let us say oil drilling, there you are using some rubber seal and it is being used at for 10 years. It should work, nobody has the wherewithal to do a test for even a year, even 3 months and all industry will say too much cost. So, then what do you do? Time, temperature, superposition try to. So, accelerated aging, actually accelerated aging is done in all fields given here, what is somewhat more robust about this is that the Arrehenius and WLF equations.

So, we understand something about the physics of these materials and therefore, we are able to say a priori, how would shift factor B in industries, when accelerated testing is done, they can have their arbitrary time dependence of shift factors and that will be. In fact, a closely guarded secret then they may not understand it, but it will work it has shown to be work working. So, it will be used