Polymers: Concepts, Properties, Uses and Sustainability
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Lecture - 51
Time Temperature Superposition

Hello, we are in the week 7 of this course and we are continuing our discussions related to viscoelasticity. We will continue looking at the viscoelasticity and response of polymers through the equivalence of time and temperature or frequency and temperature, through what is called time temperature superposition and the focus will remain on properties, because using time temperature superposition, we can get properties when they cannot be measured. So for example at extremely low times or very, very high strain rates sometimes properties you cannot measure, then you can do superposition and then try to estimate. Similarly for very long times like 25, 30 years of service life, we cannot measure properties and so again time temperature superposition is a very powerful tool for us to do such estimations. There is another way in which time temperature superposition is very useful; is that to characterize the material.

Because we have seen that macromolecule has angstrom level where the bond is all the way till micron and higher length scales in case of blends and composites because of domains and all the other microstructural features. We basically have a material which goes from nanometers all the way till hundreds of microns in terms of the length scales and similarly in case of time scales also, from picoseconds, nanoseconds which is where the bond vibrations and all happen all the way till macromolecular motion which can take up to seconds.

So given this length and time scales involved in the macromolecule, it is useful to also examine them at various different strain rates at various different frequencies and so the experiments that we do may be in limited range, but by doing experiments at different temperature and then shifting the data suitably, so that we can get response over a much longer time scale or much longer frequencies.

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Overview

1. Boltzmann superposition principle
2. Time temperature equivalence

And so that is what is the power of time temperature superposition and it is possible for linear viscoelastic materials to do this, because we also have for linear viscoelastic material this superposition possible, which generally is referred to as the Boltzmann superposition principle, but it is a direct consequence of linearity of the governing system and the time-temperature superposition is based on the idea of the equivalence.

And this we have discussed several times already in the course that higher temperature implies that we give material more time or conversely it is also very low frequency and so there is an equivalence between temperature on one hand and time and frequency on the other.

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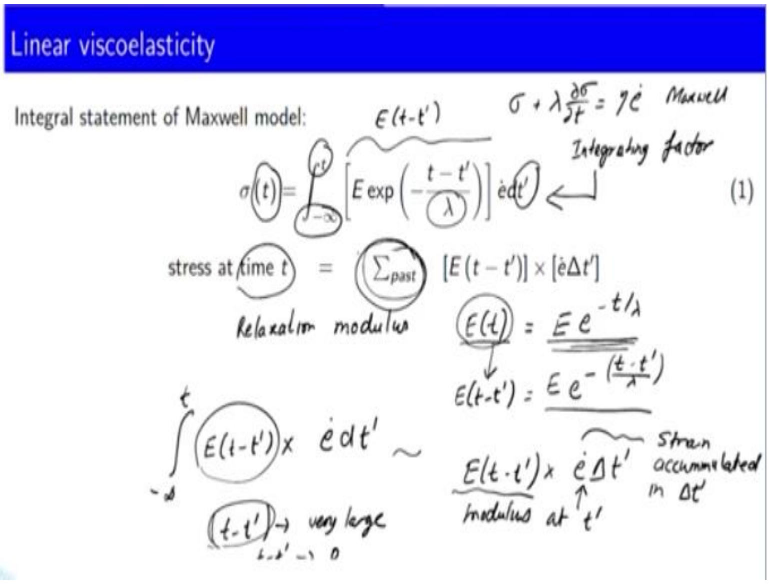

Linear viscoelasticity

Integral statement of Maxwell model:

$$\sigma + \lambda\frac{\partial\sigma}{\partial t} = \eta\dot{e} \quad \text{Maxwell}$$

$$\sigma(t) = \int_{-\infty}^{t} \overbrace{\left[E\exp\left(-\frac{t-t'}{\lambda}\right)\right]}^{E(t-t')} \dot{e}dt' \longleftarrow \text{Integrating factor} \qquad (1)$$

$$\text{stress at time } t = \sum\nolimits_{past} [E(t-t')] \times [\dot{e}\Delta t']$$

Relaxation modulus

$$E(t) = Ee^{-t/\lambda}$$

$$E(t-t') = Ee^{-\left(\frac{t-t'}{\lambda}\right)}$$

$$\int_{-\infty}^{t} E(t-t') \times \dot{e}dt' \sim \underbrace{E(t-t')}_{\text{modulus at } t'} \times \overbrace{\dot{e}\Delta t'}^{\text{Strain accumulated in } \Delta t'}$$

$(t-t') \rightarrow$ very large

$t-t' \rightarrow 0$

So going forward, let us first look at the Maxwell model and the integral statement of it. So I am sure you recall that we had looked at Maxwell model and this is the differential equation, which we had written down for Maxwell model and you can quickly look for rewriting this equation in terms of, let us say, the integrating factor approach. So you can search for the integrating factor approach in terms of solution of ordinary differential equation. And then using integrating factor, you can show that this is the governing equation for Maxwell model where lambda is the relaxation time and if you look at this expression little closely, this quantity in brackets is the relaxation modulus. If you remember relaxation modulus for Maxwell model is just an exponential decay. If I take a Maxwell material and apply a constant strain on it, the stress will decay to zero over some time. And that how much time it takes will depend on the relaxation time of the material and you can see that what is written is $Ee^{-((t-t')/\lambda)}$ and so effectively this is E at (t-t'), because we are just substituting t with (t – t'). So this quantity in bracket here is E of (t-t'). So now what we have is this is

$$\int_{-\infty}^{t} \mathrm{E}(\mathrm{t}-\mathrm{t'})\,\dot{e}dt'$$

So it is a relaxation modulus evaluated at (t-t').

While relaxation modulus evaluated at time t is just given by this. So therefore this is nothing but same relaxation modulus, but evaluated at a different time. What does (t-t') imply? t is the present time, because we are interested in knowing stress at the present instance of time, but the present state of stress is determined based on all the past deformation and therefore, this t' which is a dummy variable being used in the integral goes from sometime in the past way back in the past and it comes till the present time.

So therefore (t-t') tells us, how far back in the past this was. At present time, (t-t') will be 0, because t' itself is t at present time. So therefore, this (t-t') tells us the distance from present in terms of time, how away in time was the past deformation. And then we also have this $\dot{e}dt'$and you know the integral definition and so you can think of this as E(t-t') $\dot{e}dt'$.

So we go to some past time t' and we are subjecting at that t' some strain rate. So strain rate into dt gives us the amount of strain that has accumulated in dt time. So this is the strain accumulated in dt' prime interval and this is basically modulus at t'. So therefore, stress can be evaluated at time t by summing up all such past contributions. Now what is the property of the relaxation modulus? You can see that relaxation modulus goes as $e^{-t/\lambda}$. If t is very large, E(t) will be zero. If t is zero, then E(t) is equal to E. So it goes from E which is its maximum value to 0, which is its minimum value. Now just consider what happens when (t-t') is very large. So if this quantity is very large, which means we are much more in the past or if (t-t') is 0, then that means we are in the present instance.

So whenever (t-t') will be 0, this quantity will be E itself. It is the maximum value. Whenever (t-t') is very large, this quantity will go to zero. So therefore, what we have in all of this is basically the present state of stress related to whatever is the past deformation. So in effect what we are saying is, you sum up all the stresses which are there in the material due to past deformation and you get the present state of stress. Effectively, what we are doing is superposition.

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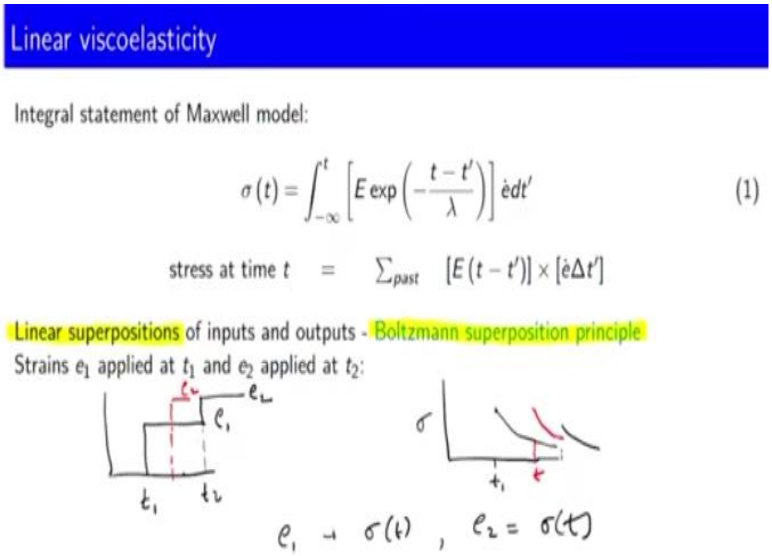

Linear viscoelasticity

Integral statement of Maxwell model:

$$\sigma(t) = \int_{-\infty}^{t} \left[E \exp\left(-\frac{t-t'}{\lambda}\right)\right] \dot{e}\, dt' \qquad (1)$$

$$\text{stress at time } t = \sum_{past} \left[E(t-t')\right] \times \left[\dot{e}\Delta t'\right]$$

Linear superpositions of inputs and outputs - Boltzmann superposition principle

Strains e_1 applied at t_1 and e_2 applied at t_2:

So all this is possible because of the linearity of Maxwell equation and because of the linearity, what we can do is superimpose inputs and outputs and this is stated as Boltzmann superposition principle. So for example, if let us say have a material in which I apply, let us say, e_1 at a given instance of time. So at t_1, I apply a strain e_1 what I would expect is stress to remain 0 till t_1, because there is no strain and then there may be a decay of stress.

Now let us say at time t_2, I apply another strain over and above this. So therefore, let us say at time t_2, I increase the strain to e_2. So then what would happen is at time, this stress would decay and then at time t is equal to t_2, again it will increase and then decay. So what I can do is, whenever I change t_1 and t_2 the overall stress response will keep on changing, but I can solve this problem first by just looking at e_1 and then looking at sigma as a function of time. And then looking at e_2 and then looking at sigma as a function of time and then knowing when e_1 and e_2 are applied, I can just add and subtract or shift these stresses and I will get. What I mean by shifting is, instead of let us say t_2 being here, if let us say t_2 was here and this is where the e_2 was applied, then in this case also what will happen is we will get t_2 to be here and then suitably there will be again a change in sigma. So the shifting and superposition of inputs and outputs is possible because of linear viscoelastic systems.

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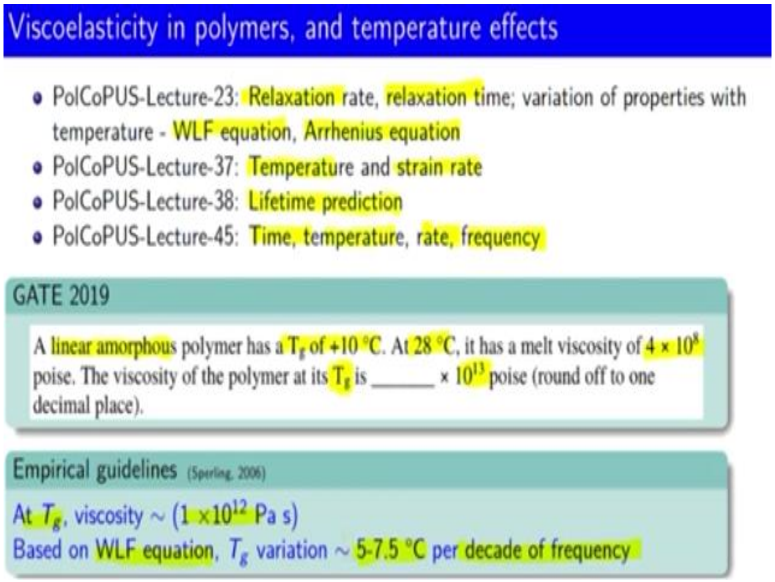

Viscoelasticity in polymers, and temperature effects

- PolCoPUS-Lecture-23: Relaxation rate, relaxation time; variation of properties with temperature - WLF equation, Arrhenius equation
- PolCoPUS-Lecture-37: Temperature and strain rate
- PolCoPUS-Lecture-38: Lifetime prediction
- PolCoPUS-Lecture-45: Time, temperature, rate, frequency

GATE 2019

A linear amorphous polymer has a T_g of +10 °C. At 28 °C, it has a melt viscosity of 4×10^8 poise. The viscosity of the polymer at its T_g is ______ $\times 10^{13}$ poise (round off to one decimal place).

Empirical guidelines (Sperling, 2006)

At T_g, viscosity ~ (1×10^{12} Pa s)

Based on WLF equation, T_g variation ~ 5-7.5 °C per decade of frequency

And we have discussed the temperature effects several times and we know that for example, relaxation rate, relaxation times are all dependent on temperature and we have a WLF or Arrhenius equation, which describes this change. We have also discussed that temperature and strain rate are analogous when we look at stress strain curves. So properties at higher strain rates can give us equivalent response at lower temperature or the vice versa. So if we go to higher temperature, we get properties at lower strain rates. Similarly in case of aging and lifetime prediction and accelerated aging we again saw that instead of doing a long term testing, which is not feasible we can do short term testing, but at more stringent condition. So if we think in terms of temperature, then we do testing at higher temperature and get the material response and then we say that okay. During service life the temperature will be lower, but material will be able to withstand for much longer and in lecture 45 also, we looked at you know all the interrelation between time, temperature, rate and frequency. So we have discussed this several times in the course. So because of all of this time-temperature superposition as a concept works; that we do tests at whatever can be done in short amount of time in lab conditions. And then we extrapolate it to either very high frequency low frequency or a very large time or small time and just to again let you think about what happens to the properties when you change temperature on the material and how shifting of properties happens; is this question asks that for an amorphous polymer there is a T_g of 10 degree C and at 28 degree C which is higher than the glass transition, it has a certain viscosity. Now what happens to that viscosity when you go to the glass transition temperature? I will give you couple of empirical guidelines. These are generally what is observed for many polymer systems. For example at glass transition the viscosity is about 10 to the power 12 Pas. So therefore, how the viscosity decreases as you increase temperature is generally based on the WLF equation and at glass transition itself the viscosity is very high. Remember, that viscosity will go to infinity at the fictitious temperature, which is 50 degrees below glass transition and again based on WLF equation, if we were to do the measurement of glass transition at different frequencies. So I can do the glass transition measurement at 1 Hertz or 10 Hertz or any of the frequencies. So generally the glass transition measured is different at different frequency.

So I hope you can quickly rationalize this that if I perturb the material very fast, I will get one glass transition, but if I perturb the material very slow, I will get different glass transition temperature and I hope you can see that if it is higher frequency, I will get low or high glass transition temperature. So just think about it. In the next couple of minutes, we will answer this question.

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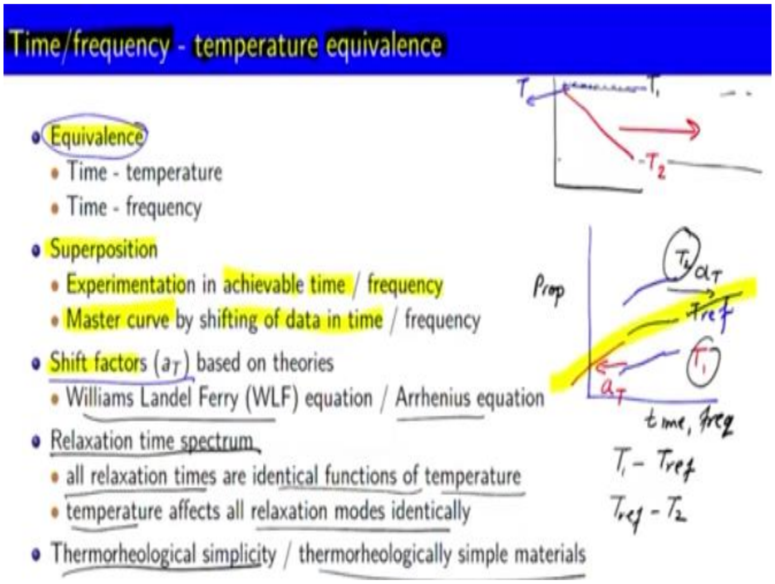

Time/frequency - temperature equivalence

- 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 materials

So generally, what we are exploring is the equivalence between temperature on one hand and time and frequency on the other and so this equivalence lets us do superposition in which what we do is we do experiments in whatever is the time that can be achieved or the frequency in which we can realize in the experimental conditions and then we prepare a master curve by shifting of the data. As I showed this, when we were doing accelerated testing that if I do test at a very, very service life condition, it may take years for the property to decrease and therefore I may not be able to assess whether the service life is 15 years or is it 20 years, what can I guarantee; but what I can do is, I can do the tests under lab condition under much more stringent, more pH, more temperature and then I can get a property change, which is much more significant.

So this is at a very high temperature, while this other one earlier test is whatever is the service temperature. So now the question is can I do shifting, can I do time temperature superposition? So what you can clearly see is, if I take this T_2 data to very high times, basically at very large times this will also decrease and eventually read this value. So that is the time I want to know through this time temperature superposition. So generally we have to shift curves and in this case, this data will have to be shifted. Similarly, if I do the same test at a much more lower stringent condition, so let us say a colder temperature T, then the change will even be much less gradual and so this will have to be shifted to the left, because it gives me the performance at much lower time. So I can choose generally a reference temperature and then I shift the data to the left or right depending on this idea of the equivalence. So equivalence is central to the time temperature superposition and so how much we shift by is a shift factor and generally what happens is let us say in case of frequency, we will get maybe data like this. I will just show 3 sets of data and so what we end up doing is shifting, so that all these three superimpose on each other and let us say this is the reference temperature. So what we do is this data will shift to left and it may come like this.

And this data which is here will shift to right and so there is a shift here and there is a shift here. So this is also 80 and this is also 80 and then what I have got effectively is a master curve. So this is the idea of shifting data and getting a master curve and how much can I shift by will depend on the temperature difference. So if let us say this is the T_1 and this is T_2, then basically $T_1 - T_{ref}$ or $T_{ref} - T_2$ will tell me how much is the shift.

And generally that can be predicted by either Arrhenius or WLF and if these are predicted based on these well known equations, then we enhance our knowledge of what may be the basic mechanism. So if there is a glass rubber transitions and glass transition involved, then WLF dependence will be there. If there is some activation process, which has to be overcome in terms of relaxation processes, then Arrhenius will be involved.

So generally given that several relaxation times are there in the material, this time temperature superposition can be carried out if all relaxation times are identical functions of temperature, because if the relaxation modes change their way at different temperatures, then time temperature superposition cannot be done. Fortunately, because of the way the material relaxations are related to macromolecules, quite often this assumption holds. And given that temperature affects all the relaxation mode identically and that is why they are all identical functions of temperature, such materials are therefore called thermorheologically simple and for these time temperature superposition can be carried out. There are few materials where let us say there may be structural changes, then what happens is material crystallizes, let us say. So then clearly there will be a relaxation mode associated with crystal, crystal amorphous interface, which was not there earlier. So clearly due to changing temperature, the material has undergone structural differences which leads to changes in relaxation modes and in that case clearly, they are thermorheologically complex materials and time temperature superposition will not be easy to do. Given that it is such a powerful tool, there are many empirical procedures used by practitioners to somehow still use master curve preparation and time temperature superposition.

This shift factor that we are talking about is a horizontal shift, which means we shift in terms of time or frequency. So the property is measured and then the property is shifted in time and frequency at higher and lower times that is why the master curve here has now effectively information for much lower time, which we had not measured and much higher time, which we had not measured, but our initial measurement was done at all different temperatures. And then the data was shifted to get response at one temperature for different times. So therefore, we get this information at extended periods of time or extended frequency, because of this time temperature superposition principle and given that this is such an advantageous feature, whenever we are looking at practical performance related issues, practitioners try to do shifting horizontally, vertically everything and try to come up with master curves. And so applicability of any such master curve and whether it is useful or not will depend on the judgments and experience of that particular application, but for thermorheologically simple materials time temperature superposition holds, because the relaxation processes are all identical functions of temperature.

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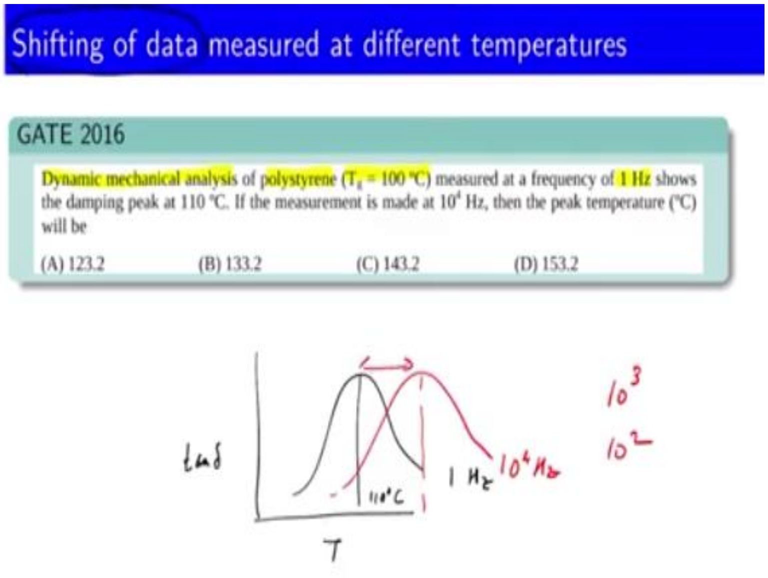

Shifting of data measured at different temperatures

GATE 2016

Dynamic mechanical analysis of polystyrene (T_g = 100 °C) measured at a frequency of 1 Hz shows the damping peak at 110 °C. If the measurement is made at 10^4 Hz, then the peak temperature (°C) will be

(A) 123.2 (B) 133.2 (C) 143.2 (D) 153.2

So we can close by looking at this idea of shifting of data through a question, which says that you know there is dynamic mechanical analysis for polystyrene, where glass transition temperature is about 100 was measured at 1 Hz and so if you do this test what it says is you get a damping peak. So if you look at let us say tan delta as a function of temperature, you get a peak and this peak is at 110 and now the same measurement, if it is done at 10^4 Hz, what happens to the peak temperature?

Now just the way the answer is, you clearly see that all the temperatures are above 110. So can you first justify that why do I have to go to higher temperature, if I do the test at higher frequency. What I am expecting is, when I am applying load at a certain frequency the macromolecules to respond with all their relaxation modes. So if you just let us say think in terms of segmental relaxation because this is a peak has associated damping. Peak is associated with segmental relaxation. So at 1 Hz, I am giving material enough time for all the segments to do relaxation processes, but now when I go to higher frequency now segments will appear to be frozen, because I am doing too fast a test; but again if I go to higher temperature, then what happens is the relaxation time comes down. The relaxation time associated with segmental relaxation comes down.

And so then again I can observe the stamping peak, because at higher frequency at higher temperature, there is sufficient segmental mobility for us to observe the damping peak. So what you would see is that at another frequency, which is 10^4 Hz, the peak would have shifted and this is what is meant by shifting of data and time and temperature equivalence. So what I could do is I could say that same response is observed at 10^4 Hz but at another temperature. So if I do test it 10^4

Hz and if I know that the temperature is there, using WLF I can find what is let us say the peak at 10^3 Hz or 10^2 Hz by shifting and that is what we do in time temperature superposition. So this question is in fact asking us about what will be the shift and this is just an application of WLF equation and using that we can know what s this shift of temperature.

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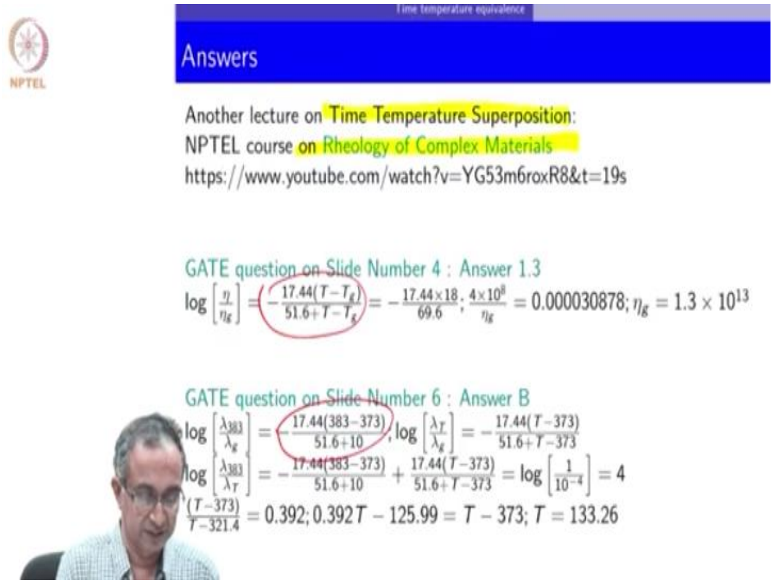

Time temperature equivalence

Answers

Another lecture on Time Temperature Superposition:
NPTEL course on Rheology of Complex Materials
https://www.youtube.com/watch?v=YG53m6roxR8&t=19s

GATE question on Slide Number 4 : Answer 1.3

$$\log\left[\frac{\eta}{\eta_g}\right] = -\frac{17.44(T-T_g)}{51.6+T-T_g} = -\frac{17.44\times18}{69.6};\ \frac{4\times10^8}{\eta_g} = 0.000030878;\ \eta_g = 1.3\times10^{13}$$

GATE question on Slide Number 6 : Answer B

$$\log\left[\frac{\lambda_{383}}{\lambda_g}\right] = -\frac{17.44(383-373)}{51.6+10},\ \log\left[\frac{\lambda_T}{\lambda_g}\right] = -\frac{17.44(T-373)}{51.6+T-373}$$

$$\log\left[\frac{\lambda_{383}}{\lambda_T}\right] = -\frac{17.44(383-373)}{51.6+10} + \frac{17.44(T-373)}{51.6+T-373} = \log\left[\frac{1}{10^{-4}}\right] = 4$$

$$\frac{(T-373)}{T-321.4} = 0.392;\ 0.392T - 125.99 = T - 373;\ T = 133.26$$

So with this, we will close the lecture. Both the questions of the exams were related to direct application of WLF equations. So I leave you to look at these and try to first attempt the problem yourself and then rationalize based on the solution given here, but use of WLF because that is what is useful around glass transition temperature in case of polymer. In case you are interested in more discussion related to time temperature superposition, you could look at another NPTEL course on rheology of complex materials and that also gives a detailed discussion of this shifting of curves and the time temperature superposition.

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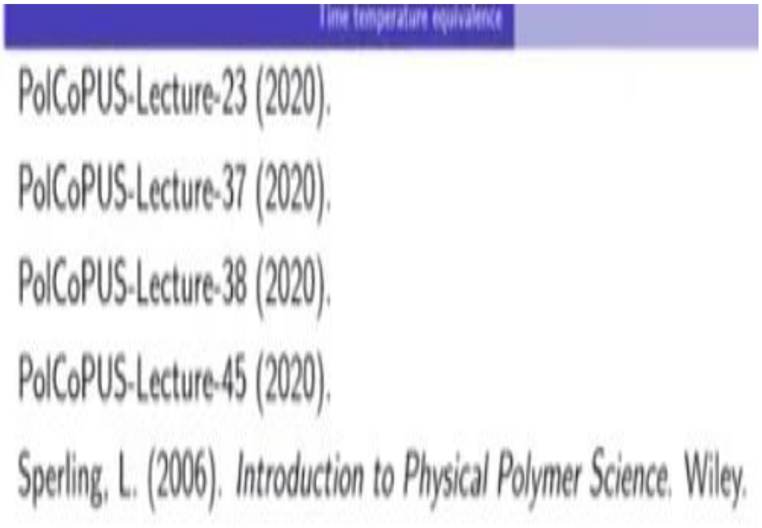

Time temperature equivalence

PolCoPUS-Lecture-23 (2020).

PolCoPUS-Lecture-37 (2020).

PolCoPUS-Lecture-38 (2020).

PolCoPUS-Lecture-45 (2020).

Sperling, L. (2006). *Introduction to Physical Polymer Science*. Wiley.

So with this, we will close this lecture and we will continue our discussions related to viscoelasticity and various other properties of polymeric materials. Thank you.