Medical Characterization of Bituminous Materials
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Lecture-12
Time Temperature Superposition Principle – Part 1

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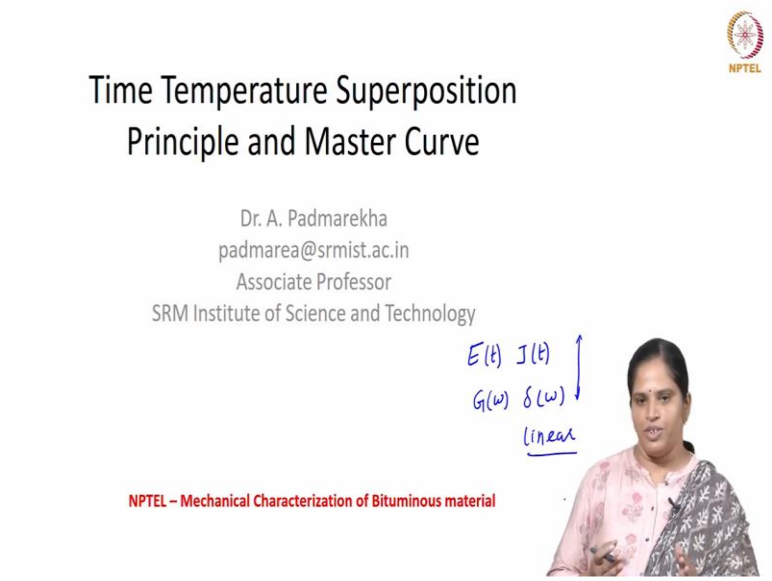

Time Temperature Superposition Principle and Master Curve

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$E(t)$ $J(t)$
$G(\omega)$ $\delta(\omega)$
linear

NPTEL – Mechanical Characterization of Bituminous material

Hello everybody, so far you have learned viscoelastic characterization behaviour in a strain control mode and stress control mode test and in a times sweep testing and in the frequency sweep testing mode. You have also introduced to a material functions such as relaxation modulus which was denoted as E and compliance functions denoted as J and you know that these functions are time control functions and it all depends on time factor.

You also know in oscillatory mode we use dynamic modulus function and the phase angle function to characterize a material behaviour and these functions are frequency dependent. So, these functions are valid only if you test the material in the linear region. So, as of now, we are clear about these functions. Now, the next test in the laboratory when you test the material we have a time constraints.

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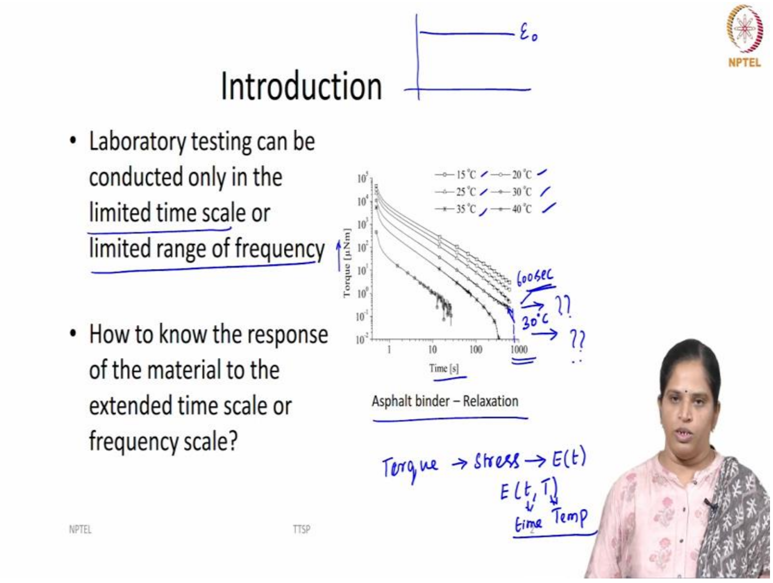

Introduction

- Laboratory testing can be conducted only in the limited time scale or limited range of frequency
- How to know the response of the material to the extended time scale or frequency scale?

Asphalt binder – Relaxation

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So, the testing time or a testing frequency is limited here. For example, if you see a relaxation test result for an asphalt, you see this plot the time scale here is varying from 0, since it is in a logarithmic scale is not starting with 0 and the times maximum time scale is 1000 seconds. So, when you subject a material to a constant strain something like this, let us keep this strain to be an ε_o, the response of a material asphalt binder to this constant strain will be like this.

Now, if you see this plot, this plot it is given as a torque, you can always convert the torque value to a stress using some constants and this stress can be again converted to a relaxation modulus. So, if you see this relaxation modulus it is a function of time. So, let us pick one temperature data. You have a various temperature data here. Let us pick one temperature data may be corresponding to 30 degree Celsius. So, if you see this plot, the relaxation modulus trend will also be same as the torque trend.

So, at 30 degrees Celsius, the modulus value depends on the time. So, as that time goes on the modulus value is decreasing. Here, while conducting the test, the test was stopped somewhere near 600 seconds. Now, what will be the response of a material beyond this, if you want to know the response of the material above after 600 seconds, so, what to do? Likewise, if you see another factor here, we have different temperatures like measured at 15, 20, 25, 30, 35 and 40 degrees Celsius.

You can see that the modulus function is also temperature dependent, so we can write it as relaxation modulus to be a function of time and temperature. We will use t for time factor and T for temperature. So, we see that the relaxation modulus here depends on time and temperature. And one more thing is our laboratory testing is limited, we limited to a particular time. So, we conduct only to a limited time scale or in case if we conducted in an oscillatory mode or a frequency mode we limit it to a limited frequency.

So, now if you want to extrapolate or if we want to know the response of the material beyond the test conditions, how to project it. So, that is what we are going to do it in this class. So, for doing this, we are going to use a time and temperature equivalency factor. So we call it as a time temperature superposition principle. So, using this time temperature superposition principle, we are going to extend the limit of frequency or a timescale and construct a curve called as a master curve for a bituminous mixture or a bituminous binder.

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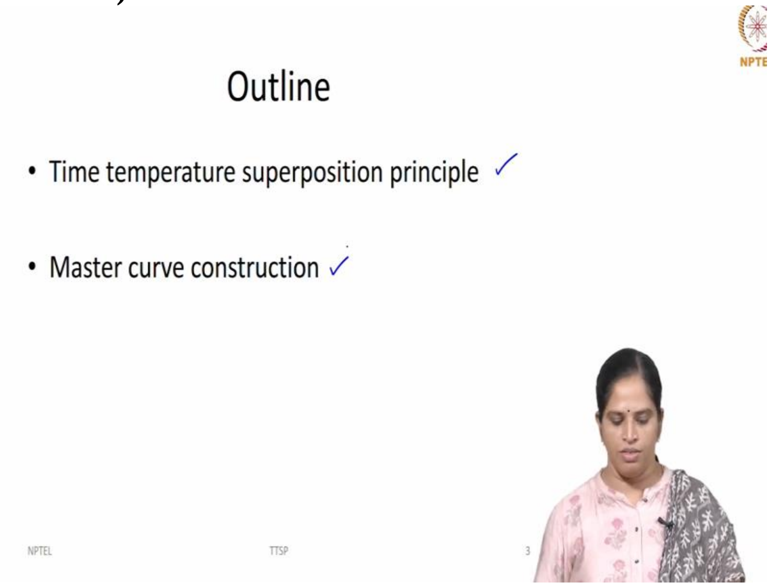
Outline

- Time temperature superposition principle ✓
- Master curve construction ✓

So the outline of presentation is going to be like first we will define what is time temperature superposition and then see the step by step process in constructing a master curve using a time temperature superposition principle.

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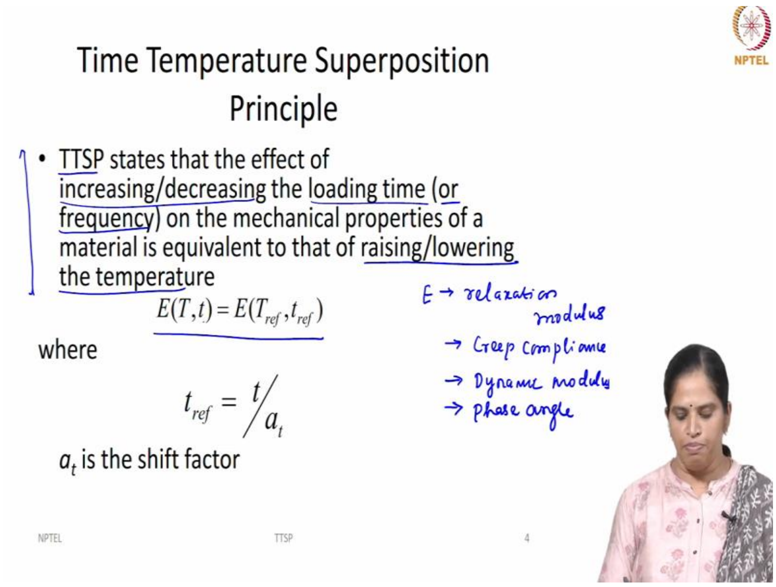

Time Temperature Superposition Principle

- TTSP states that the effect of increasing/decreasing the loading time (or frequency) on the mechanical properties of a material is equivalent to that of raising/lowering the temperature

$$\underline{E(T,t) = E(T_{ref}, t_{ref})}$$

where

$$t_{ref} = t / a_t$$

a_t is the shift factor

E → relaxation modulus
→ Creep compliance
→ Dynamic modulus
→ phase angle

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So, I will just read this time temperature superposition as such in the slide. Time temperature superposition principle in short, we can also call it as TTSP. So, it states that effect of increasing or decreasing the loading time or in case if you test it in an oscillatory mode, increasing or decreasing the frequency on the mechanical properties of a material is equivalent to that of either raising or lowering their temperature.

So, in short, you can write it as, E this E can be anything E can be relaxation modulus, any material functions or any mechanical properties of a material, it can be a creep response or a creep compliance or it can be even a dynamic modulus or it can be even a phase lag or the phase angle. So, modulus function or a phase angle function at temperature T and time is equal to the modulus function at some other temperature and time. So, we are going to use this equivalency factor in constructing a master curve.

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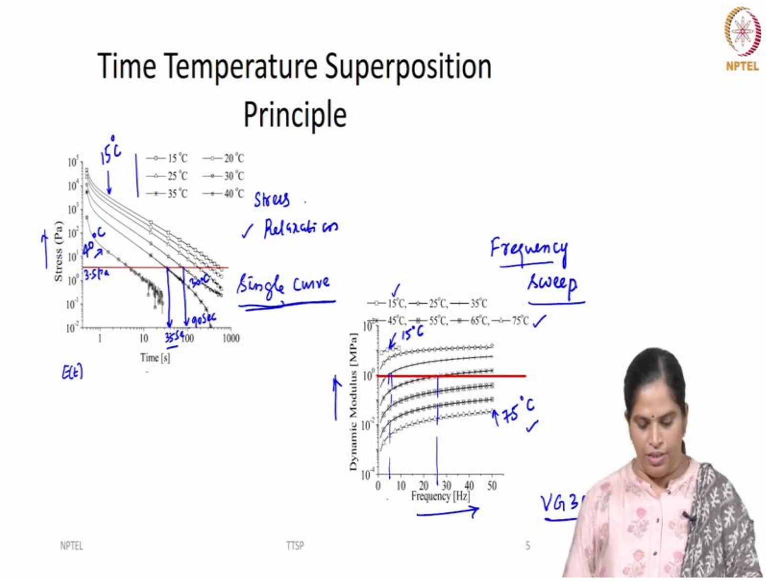

Time Temperature Superposition Principle

So, in otherwise you can see example graph provided here. One is for a time controlled test, this is stress relaxation experiment and this is oscillatory shear testing or frequency sweep test. Now, if you see the stress relaxation experiment, so, the stress is measured at different scale, different time scale and different temperature. This lower one corresponds to a higher temperature 40 degrees Celsius.

As you go higher and higher with the temperature, the material relaxes faster. So, the lower when corresponds to higher temperature and the top one corresponds to lower temperature. So, now, if you see, if you take an example of a stress value here, which is, the stress value here is given in Pascal. So, now this is nearing 3.5 Pascal, so, nearing 3.5 Pascal the stress relaxed from a maximum value to a 3.5 Pascal after if you see the time scale for a 35 degrees Celsius maybe after 90 seconds. The same stress here at this is a 30 degree Celsius and at 35 degrees Celsius, it happened at nearing 35 seconds. So, the stress value here or in terms you can also equate it like equivalence modulus values relaxation modulus. So, the relaxation modulus is same at the time 35 seconds when you measure it at 40 degrees Celsius or at 30 degrees Celsius if you measure it is at 90 seconds.

So, now we are going to use this shift all the temperature data into a single curve. Find the equivalency between a time and temperature and shift all the different curves here into a single curve. And that is what that single curve is what we call it as a master curve. Now, here is an example for a frequency sweep test. So, this is a frequency sweep test conducted at different temperature varying from 15 degrees Celsius to 75 degrees Celsius for VG 30 bitumen.

And the variation in the dynamic modulus with the frequency for different temperature is shown in this plot. So, at higher temperature you can see the dynamic modulus value was lower that is this is at 75 degrees Celsius. On the other extreme lower temperature, this is 15 degrees Celsius curve. So, you can see a same dynamic modulus value occurring at different frequencies when the temperature is varied.

So, now, we are going to equate this concept of same dynamic model at different frequency and different temperature for constructing the master curve for a dynamic modulus.

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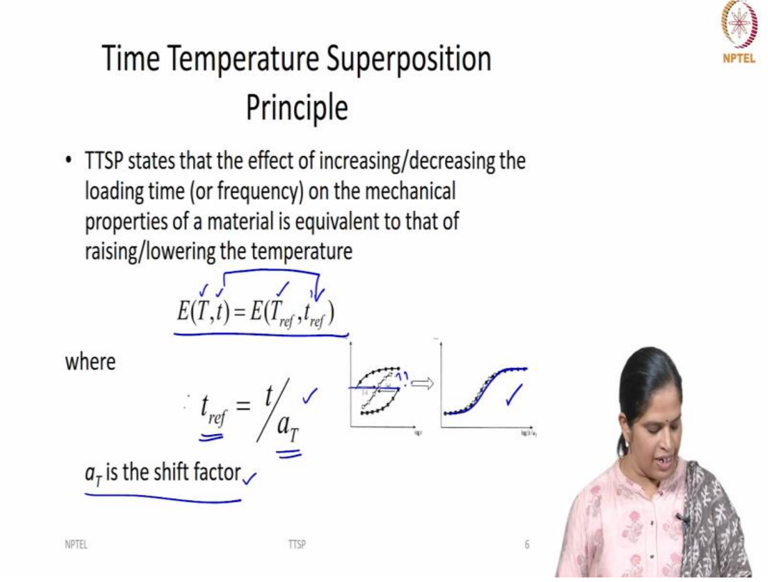

Time Temperature Superposition Principle

- TTSP states that the effect of increasing/decreasing the loading time (or frequency) on the mechanical properties of a material is equivalent to that of raising/lowering the temperature

$$E(T,t) = E(T_{ref}, t_{ref})$$

where

$$t_{ref} = t / a_T$$

a_T is the shift factor

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So, as the time temperature superposition says modulus at specific time and temperature is equal to a modulus at some other reference time and reference temperature. So, now, as I already pointed out, we are going to shift all the data to a single curve to get a master curve. Now, here the question is we are going to match the modulus value for shifting now, how much you need to shift. So, based on the amount of factor which we are going to shift it. This t_r is related to this t.

So, the t_r reference time can be given as t/a_T. This a_T is nothing but the shift factor. So, by applying a shift factors the amount of shift at different temperature once you shifted all these data will merge into a single graph and nicely forms a single plot something like this. So, now, how to calculate this shift factor? See, we know that it is t references equal to t / a_T. This is what time temperature superposition principle says. Now, what is a T?

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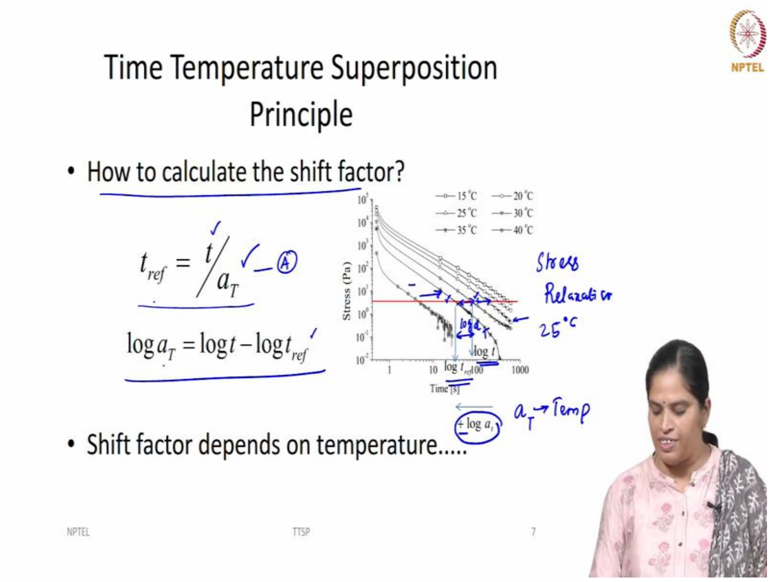

Time Temperature Superposition Principle

- How to calculate the shift factor?

$$t_{ref} = t/a_T \quad \text{— (A)}$$

$$\log a_T = \log t - \log t_{ref}$$

- Shift factor depends on temperature.....

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How to calculate this value? So, for calculation of this value, we just use an experimental data and equate the modulus value. So, now, if you take a logarithmic of this equation you will get log a_T = log t – log t_r. So, now, this same plot here which you already see stress relaxation plot. So, in this plot, two temperatures is highlighted here. One is 30 degree and other is 35 degree, the X axis time scale corresponding to 35 degree is taken as t ref and the X axis corresponding to 30 degree is taken as log t. So, now the shift factor here is log t, this log t – log t ref or otherwise this is going to be our shift factor. If it is not a logarithmic scale we can write it as log a T. So, this is going to be our shift factor. We use T here a T because it is it depends on the temperature.

So, you can see that if I want to shift this specific 25 degree curve to a reference of 30 degree, the shift factor value is different the shifting value is different and here from 30 to 35 degrees Celsius the shifting value is different. So, the value here the shift factor, the amount of shift we are going to do it, it depends on the temperature. So, now, if you see, we are shifting it from this is from a lower temperature to higher temperature, so, log t - t ref, so, this is positive.

So, if you shift for example, 40 degree curve towards 35 degree curve, so, now this becomes minus because it becomes t ref – t. So, this becomes minus a T so, it is in the logarithmic scale. So, log a T will be in a minus number. So, it number will be something less than one here.

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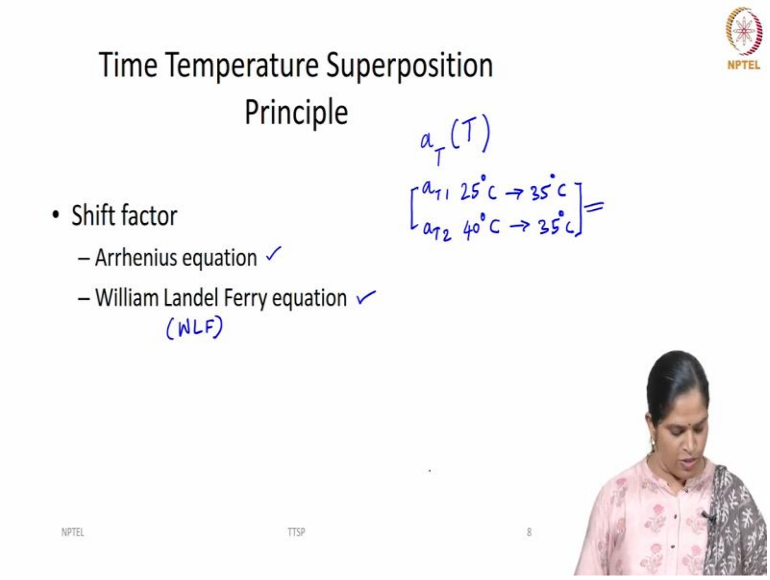

Time Temperature Superposition Principle

- Shift factor
  - Arrhenius equation ✓
  - William Landel Ferry equation ✓

(WLF)

$a_T(T)$

$$\left[\begin{array}{l} a_{T1}\ 25^\circ C \rightarrow 35^\circ C \\ a_{T2}\ 40^\circ C \rightarrow 35^\circ C \end{array}\right] =$$

So, now, the next question is what is the amount of shift. As we already seen that the shift factor a T depends on temperature, if you are going to shift from 25 degree Celsius to 35 degree Celsius, the value is going to be different, if you are going to shift from 40 degree Celsius to the same temperature of 35 degree Celsius, the value is going to be different both this the shift factor is not going to remain the same.

So, now, how to calculate this? So, before even calculating the value of a T, are these two values related. Suppose if I named this as a T1 and a T2 are these 2 values related to each other? The answer is yes. These 2 values are related. For using a time temperature superposition principle, we can calculate the shift factor using 2 approach one is an Arrhenius equation and other is using a William Landel Ferry equations. This in short we call it as WLF equation. So, now, let us see in detail how to calculate the shift factor using Arrhenius equation and WLF equations.

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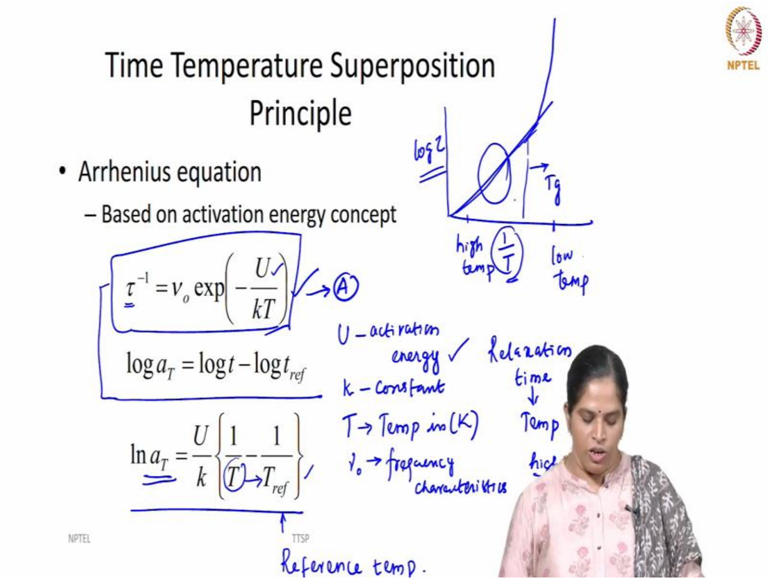

Time Temperature Superposition Principle

- Arrhenius equation
  - Based on activation energy concept

$$\tau^{-1} = \nu_o \exp\left(-\frac{U}{kT}\right)$$

$$\log a_T = \log t - \log t_{ref}$$

$$\ln a_T = \frac{U}{k}\left\{\frac{1}{T} - \frac{1}{T_{ref}}\right\}$$

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So, this Arrhenius equation, this equation given here, equation A is a well known equation to all of us. Here tau given here, this time functions. so the inverse of time function is related to activation energy U by this in an exponential way, U here is an activation energy and k is Boltzmann constant. It is a constant value for a material, T is a temperature measured in Kelvin.

So, we have a Arrhenius equation here. And here one more function is here like mu 0 this is a frequency characteristic function. Now we have this function. So, this function says that inverse of time function you have it here is related to an exponential function. So, if you take a logarithmic value for this equation you will get log tau is related to inverse of temperature.

So, 1 / T inverse of temperature, so, if you take a logarithmic scale, so, this becomes a linear function, so, you get something to be a linear function like this straight line like this. So, time function logarithmic of time function is related to inverse of temperature. See this is the inverse of temperature. So, this is low temperature and this is height this point will be high temperature. So, now we are going to use this Arrhenius equation to determine a shift factor.

So, we know the shift factor is this, when you solve this both the equation you will get log a T which is nothing but to be a function of t and t ref, t ref is called as a reference temperature and t can be any temperature. So, if I want to shift any temperature data to reference temperature, you can use this shift factor as per Arrhenius equations. So, this Arrhenius equation is based on an activation energy concept and it says that logarithmic of time scale, it can be a relaxation time of a material varies in a linear pattern with respect to the inverse of temperature.

See, we know that the relaxation time if we assume this t to be a relaxation time, if we know that the relaxation time depends on temperature. So, at high temperature let us quantify in a relative way high temperature and low temperature what happens. So, at very low temperature, the mobility of a particle ceases or more like a behave like a solid or something like a freezing conditions.

So, at low temperature, this relaxation time will be high relaxation time this will be high at high temperature relatively as you go lower and lower, this high temperature this will become lower less so, now it is Arrhenius equations, when this is validated for a many polymers, it was found that at very low temperature, it is not showing a relaxation time is not showing a linear relation.

But there is a deviation from the linear when it is nearing near when it goes well away from the glass transition temperature TG well away from a glass transition temperature, the Arrhenius equation deviated from a straight line and then the value increased in a drastic pattern. So, now, when to apply this Arrhenius equation is since be assumed to be a linear you have to apply Arrhenius equation only in this region this temperature region.

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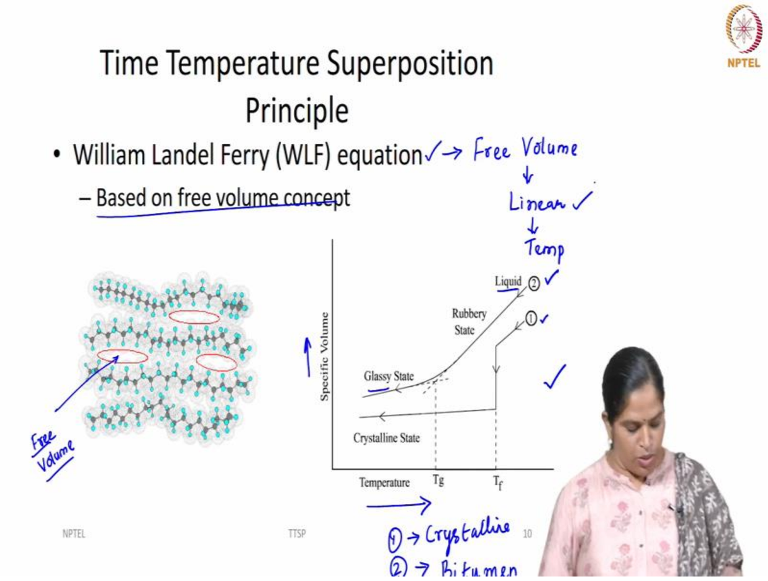

Time Temperature Superposition Principle

- William Landel Ferry (WLF) equation
  - Based on free volume concept

So, generally now the next equation is William Landel Ferry equations, so, this William Landel Ferry equation was initially used for a polymers and it is based on the free volume concept. So, what is a free volume in a polymer? So, you can see a schematic of a picture here, where you have a free space between a molecules and this free space is what we call it as a free volume. Volume of this free space is what we call it as a free volume.

So, this William Landel Ferry equation assumes that free space in the material varies with temperature or free volume varies with temperature and it varies in a linear pattern linear with respect to temperature you can see this well established plot. So, you have a specific volume here and on other scale is a temperature. You have two materials one is written as one another is 2 here. One is a crystalline material and 2 is a amorphous material, you can amorphous material bitumen behave as an amorphous material you can even assume it to be a any amorphous material, See what is the difference is you can see a decrease in means decrease in a free volume as the temperature goes down the in a crystalline material the decrease happens all of a sudden but in an amorphous material, there is a rubbery behaviour between a liquid and a glassy state. So, it is a gradual decrease in a free volume. So William Landel Ferry equations assumes that this decrease in a free volume as the temperature goes down in the linear pattern.

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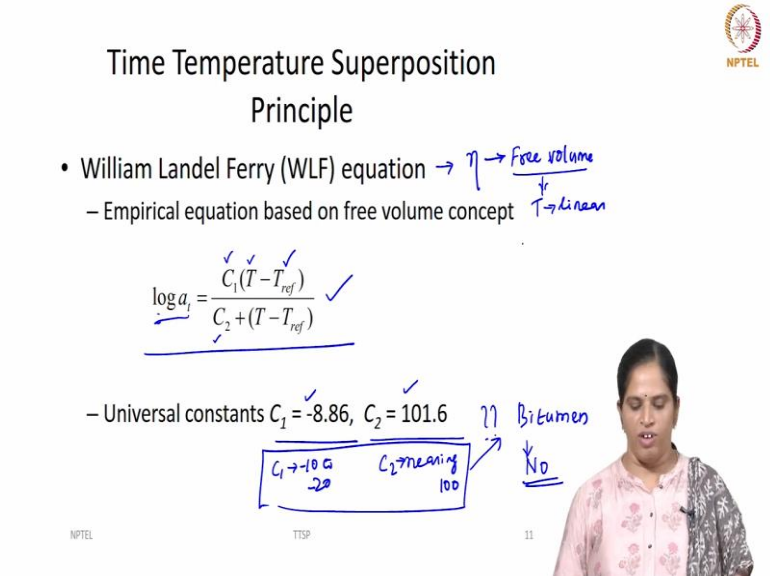

Time Temperature Superposition Principle

- William Landel Ferry (WLF) equation → η → Free volume ↓ T → linear
  - Empirical equation based on free volume concept

$$\log a_t = \frac{C_1(T - T_{ref})}{C_2 + (T - T_{ref})}$$

  - Universal constants C_1 = -8.86, C_2 = 101.6 ?? Bitumen ↓ No

C_1 → -10 G -20 C_2 → meaning 100

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So, this WLF equations is based on the free volume, they equated the viscosity relations means they have related a viscosity with respect to the free volume. And assume that the free volume varies linearly with the temperature with function of temperature and it varies in a linear pattern. With this assumption, this empirical equation was derived. So, the final empirical equations looks like this log a T as a function of two constants C 1 and C 2.

So, this C 1 C 2 constants universally we use C 1 value to be minus 8.86 and C 2 value to be nearing 100. So, exact value is 101.6. So, you can see that this a T is a function of C 1 C 2 and T is a temperature at which the data you wanted to shift and T r is a reference temperature, it is the temperature to be shifted. So, this log a T value depends on C 1 and C 2 value. So, you have a C 1 and C 2 value a universal value to be like this.

Now, can we use the same value for bitumen. The answer is, many literature have proved it to be no for predicting the response of a bitumen are applying a time temperature superposition for a bitumen, the C 1, C 2 value we cannot use this universal constant but it will be C 2 value will be somewhere nearing 100 and the C 1 value will be somewhere nearing 10 to 20 but not exactly the same value.

So, -10 to - 20 not nearing the same value, so we have different values for C 1, C 2 for a bitumen and a bituminous mixtures. So, now we have 2 equations Arrhenius equations and WLF equations, we use these 2 equation to find a shift factor.

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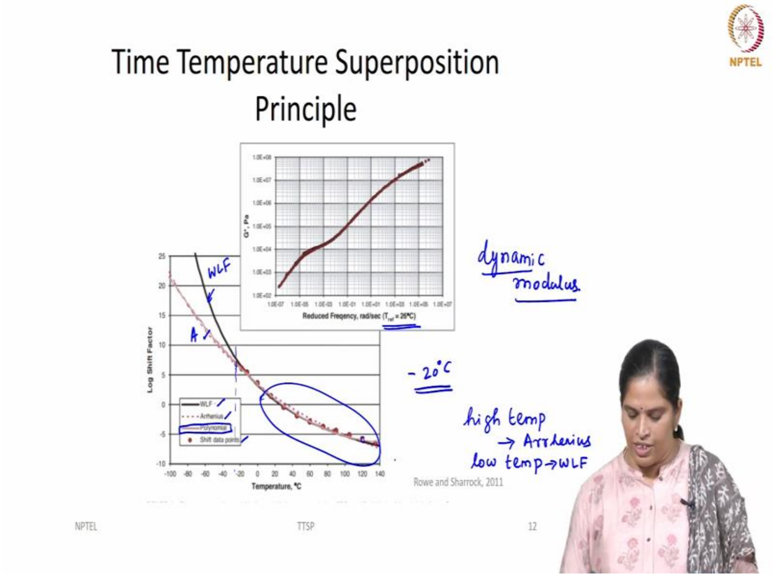

Time Temperature Superposition Principle

Rowe and Sharrock, 2011

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So, once we find a shift factor now, next is to shift the value along that X axis. So, before doing that we will see a relation between the Arrhenius equation and WLF equations. So, Arrhenius equations you can see in a dotted line. So, this is Arrhenius equation let me mark it as A on the thick black 1 is WLF equation. So, we saw only these 2 equations Arrhenius equation and WLF equation. So, let us not worry about what is this polynomial fit.

So, now if you see the dotted line the red colour bigger dots here are the shift factor obtained from the experimental data. So, if you see Arrhenius equation here deviated from the data from the WLF equations when the temperature is less than - 20 degrees Celsius. See this is the shift factor obtained while constructing the master curve for a bitumen at the reference temperature of 26 degrees Celsius. So, this master curve was constructed for a dynamic modulus value.

So, the dynamic modulus value was measured at different frequencies and at different temperature and the master curve was constructed, master curve was constructed and the shift factor was estimated and it is fitted to a WLF and Arrhenius equation. So, let us not worry how master curve was constructed as of now, we will just look into the deviation from Arrhenius equation and a WLF equations.

So, there is a common temperature range here where both Arrhenius equations and WLF equation is applicable. So, generally, as their temperature goes higher and higher, at high temperature range we prefer Arrhenius equation and at low temperature range, low temperature range, we prefer WLF equations.Yyou can see a common temperature range where both the Arrhenius and WLF equations are applicable.