Mechanical Characterization of Bituminous Materials
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Lecture-13
Time Temperature Superposition Principle - Part 2

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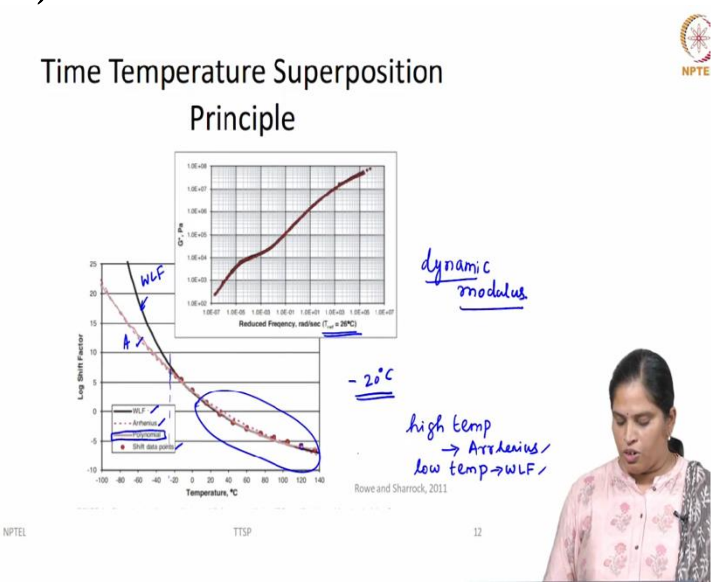
Time Temperature Superposition Principle

dynamic modulus

$-20°C$

high temp → Arrhenius ✓
low temp → WLF ✓

Rowe and Sharrock, 2011

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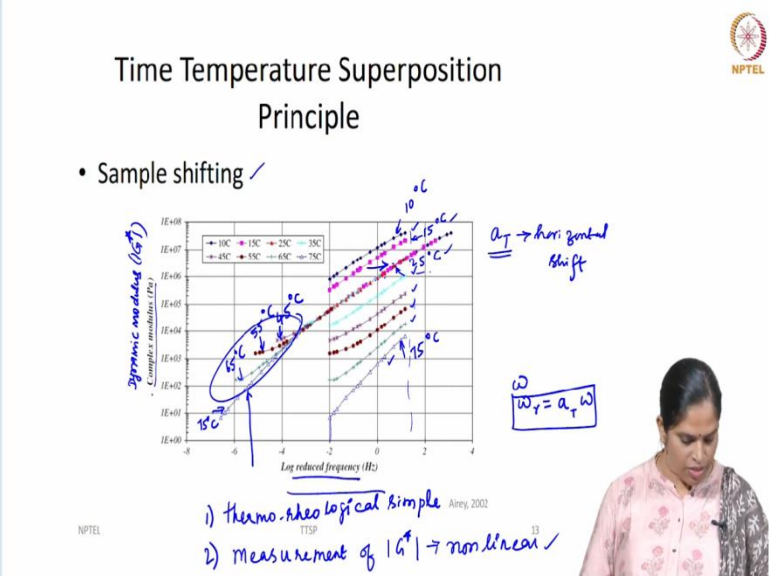
Time Temperature Superposition Principle

- Sample shifting ✓

a_T → horizontal shift

ω

$\boxed{\omega_r = a_T \omega}$

1) thermo-rheological simple
2) measurement of $|G^*|$ → non linear ✓

Airey, 2002

So now we know how to calculate the shift factor. So, after calculating the shift factor, how to shift the data. So, as I mentioned earlier, we shift the data only horizontally only on an X scale and not on a Y scale. Now, if you look into this typical example of shifting, see you have a dynamic modulus, this is dynamic modulus it is not a complex modulus. We call it as a dynamic modulus. As Professor Murali Krishnan already pointed out, dynamic modulus, and the complex modulus were used interchangeably to denote the mod of complex number.

So, Let us take this as a dynamic modulus value. Now, if you see this dynamic modulus value captured at different frequency. These are the direct experimental data. So you have an experimental data here measured at different temperatures starting from 10 degree Celsius to all the way as high as 75 degrees Celsius. So, you have different dynamic modulus data. So, our test frequency region here is very very limited.

So, the one which is red color here is 25 degrees Celsius data. Now, find the equivalent modulus point from a 25 degree Celsius. Now, let us take one case for 15 degrees Celsius. So, this 15 degrees Celsius data knowing the shift factor, we can move in this direction to match the 25 degrees Celsius data. So, once you move this, nicely the pink line and the red line is like it came on the same point same one single line.

So 15 and 25 degree matched, you can likewise match the 2 pairs of data to a reference temperature knowing this shift factor value. Shift factor is nothing but the amount of shift we do it horizontally. So, it is just an horizontal shift. So, the modulus value will never change only the X scale will change. If the X scale changes after shifting we call it as a reduced frequency. So, it is reduced frequency not just a frequency. It is reduced frequency.

We generally denote a frequency by ω, reduced frequency we denote it as ω_r. See this reduced frequency, since it is in the logarithmic scale. So, it is a $T \times \omega$. So, we are shifting it we are adding it, either plus or minus. So, since it is in the logarithmic scale, the reduced frequency can be calculated from this a $T \times \omega$. So, now after shifting, you can see that no calculations have been done, it has just shifted either to the left or right keeping a reference temperature to be 25 degrees Celsius. Now, you can see that there is a discrepancy in few data in this temperature region. If this corresponds to 65 degrees Celsius, this corresponds to 55 degrees Celsius, and this data corresponds to 45 degrees Celsius. So you can see a discrepancy in the data from the curves, main curve, so, this discrepancy in the data happens, if the response of the material is not thermo rheologically simple - one condition is. Other is if the measurement goes out of nonlinear region. So, we measure modulus this modulus measurement, measurement of E value or a dynamic modulus value here, if we represented by G*, measurement of G* if it goes in that nonlinear or any other testing artifacts. But we cannot use this data. We have to remove these data before we do a master curve fitting.

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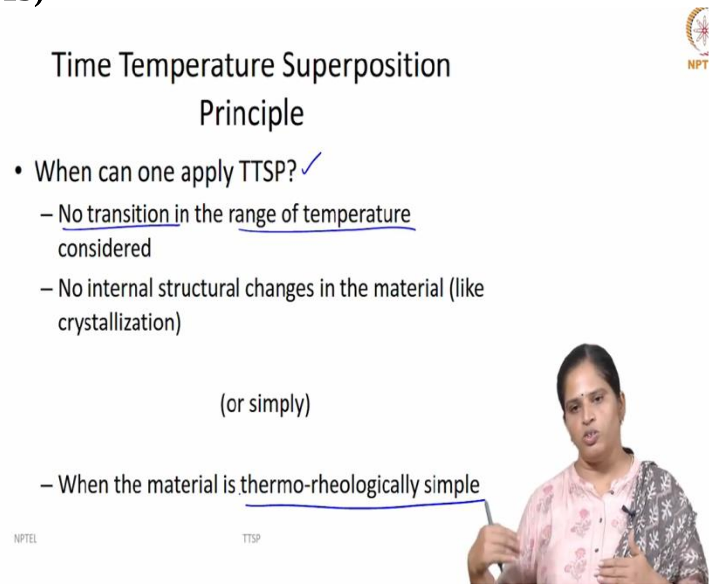

Time Temperature Superposition Principle

- When can one apply TTSP? ✓
  - No transition in the range of temperature considered
  - No internal structural changes in the material (like crystallization)

(or simply)

  - When the material is thermo-rheologically simple

So, now the next question is we have defined what is time temperature superposition principle can we applied time temperature superposition principle for all cases? The answer is no, as I said, we can apply the time temperature superposition principle when the material exhibits the thermo rheological simple response. So, when the material is thermo rheologically simple. What is this thermo rheologically simple. Let me define it in terms of a relaxation modulus or a relaxation time.

So, if material at 2 different time exhibits the same relaxation process, we can call it as a material to be thermo rheologically simple at both the temperature. Or otherwise, there should not be any transition when you move across a different temperature. So, if there is no transition in the range of temperature we are looking for, then we can apply a time temperature superposition principle or if you want to describe in terms of internal structural changes in the material, there should not be any structural changes in the material like crystallization etc. to happen within the temperature range. Then we can call as the material to be thermo rheologically simple. So, we study the response of a material over a wide range of temperature. Within this wide range of temperature, if the material exhibits the same relaxation process or there is no transition in this region, transition in the flow behavior or no transition in the internal structures. This transition in the internal structures induces the rheological changes. So, if there is no any transition occurring in this wide range of temperature, we call that a material response to be thermo rheologically simple.

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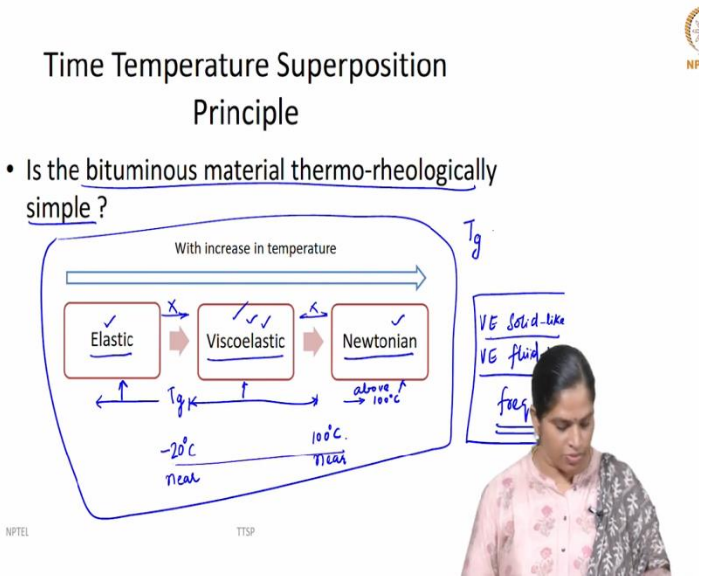

Time Temperature Superposition Principle

- Is the bituminous material thermo-rheologically simple ?

So, let us come back to a bituminous material. Now, is the bituminous material, thermo rheologically simple? So, for this next question, whether the bituminous material is thermo rheologically simple, let us look into a behavior of bitumen over a wide range of temperature. So, right from a glass transition temperature or will start well below a glass transition temperature. You know what is glass transition temperature. So, for glass transition temperature of a bitumen, we will take it as T_g. So, well below the glass transition temperature of a bitumen, the bitumen will behave as a elastic material. Generally, this occurs near -20 degrees Celsius it is near -20 degree and this value is not fixed, it varies with a binder type it varies with the aging conditions, many other factors testing equipment we use and many other factors. Let us assume like that T_g is near minus 20 degrees Celsius and the response of a material below T_g will be typically elastic. So, above T_g, when you process, the response of the material will be viscoelastic. So, as a temperature further increases, there will be a transition from viscoelastic to a Newtonian temperature. This temperature, this transition may happen near, say 100 degrees Celsius. Again, it is a near temperature. It is not exact value here. So, this is the viscoelastic range of temperature below T_g elastic range of temperature and above 100, in this case above

100 that is Newtonian. So, you have, as we change the temperature, we increase the temperature from as low as minus 50 to go even up to 160, 170 degrees Celsius, bitumen exhibits 3 kind of response. At very low temperature, it is elastic. At the intermediate temperature, it is viscoelastic and at very high temperature it is Newtonian behavior. So, now, if you have 3 different response of a bitumen, if you consider as such as a whole, the bitumen is not thermo rheologically simple. But you can assume that the material is thermo rheologically simple within this viscoelastic temperature region or you can assume that the bitumen is thermo rheologically simple in this elastic range or in this newtonian range not from one to other. So, in this transition range, bitumen if you consider over a whole temperature, bitumen is not thermo rheologically simple. So, if you just consider only the viscoelastic behavior, we can assume that bitumen is thermo rheologically simple. Even here, you might have learned already viscoelastic solid like behavior, viscoelastic fluid like behavior. So, as the temperature increases in this viscoelastic range from T_g to high temperature, there will be a transition happening from viscoelastic solid to fluid like behavior. This solid like to fluid like behavior we have already seen in small amplitude oscillator shearing that this transition is frequency dependent. There are many other factors that the solid to fluid like behavior varies. So, there is no fixed method to identify what is the solid like behavior or a fluid like behaviors. As of now, let us not move in detail about whether this solid like behavior and fluid like behavior has to be considered as a transition. So, we will as of now, we will take it as viscoelastic material, bitumen behaves as a viscoelastic material in this temperature range. So, from near minus 20 to near 100 degree and we can apply a time temperature superposition principle and this is the temperature range where all payment engineers is also interested in.

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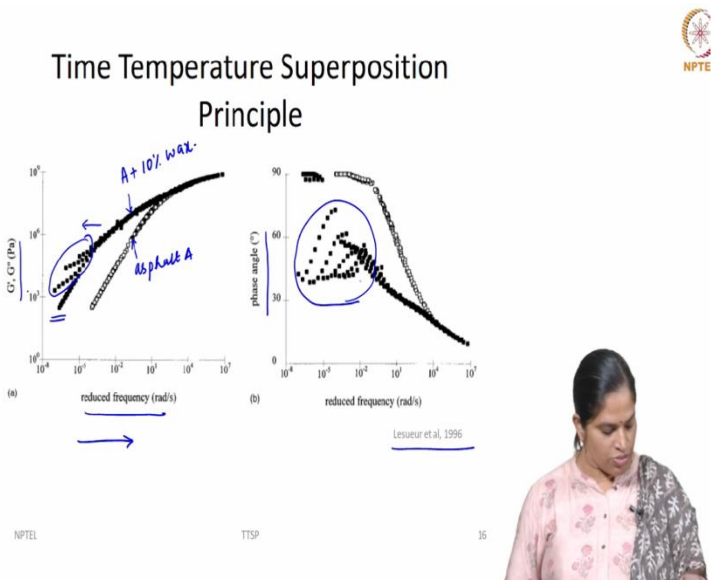

Time Temperature Superposition Principle

Lesueur et al, 1996

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This is an example where the oscillatory shear data was shifted using a time temperature superposition principle, taken from Lesueur. So, this compares a master curve after shifted, master curves of 2 samples, one is an asphalt A. Let us not worry about what is A. Another is asphalt A plus 10% Wax. One plot here gives you the modulus, storage and the loss modulus and the other plot is a phase angle.

So now if you see asphalt, asphalt exhibits a nice, smooth master curve, but with wax here, you can see a discrepancy here, deviation in the data from a main curve and you can very well see it in the phase angle. So phase angle is very sensitive function. So if you want to check whether the material is thermo rheologically simple or not, you can use a phase angle function.

So, you can see a discrepancy in the data at lower frequency. So, lower frequency corresponds to a lower temperature data. So, as a temperature increases from low to high we know that the wax melts. So, when you move from high to low temperature, there is a crystallization happening. In the presence of wax, material may crystallize and you can see, as the material crystallizes or there is a change in the internal structure of a material, you can see a discrepancy in the data when you construct a master curve.

Now, after conducting an experiment, now if we wanted to construct a master curve with our experimentally available data, so, before even attempting to construct a master curve, you may want to know whether I can use the entire data in constructing a master curve.

You can use or construct black diagram or you can use Kramer-Kroning relation and check the consistency in the data and filter your data based on the results and then construct a master curve. So, what is this black space diagram? So, this black space diagram is nothing but the relation between a dynamic modulus and the phase angle. So, this dynamic modulus and a phase angle is obtained from the oscillatory shear testing after conducting a frequency sweep test, so you have a different temperatures, you can see from 25 to 75 degrees Celsius. So, this is 25 degrees Celsius and the maximum here 75 degrees Celsius. The dynamic modulus and the phase angle functions and not an independent functions. So if it exhibits a smooth trend, we can use that data for the construction of the master curve. Now here, for this case 65 degrees Celsius data and 75 degrees Celsius data do not follow a smooth trend. So, once you remove the 65 and the 75 degrees Celsius data, you can see a smooth trend in the dynamic modulus and a phase angle data. This is based on the concept that dynamic modulus and phase angle are not an independent function. We already saw this.

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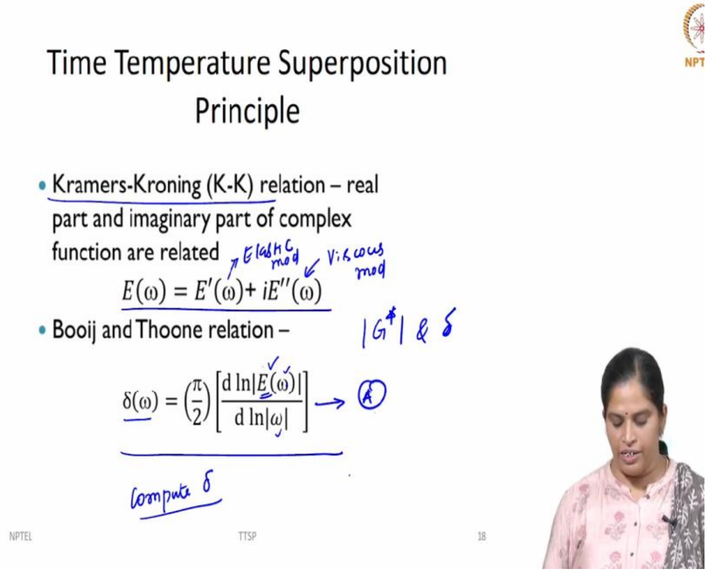

Time Temperature Superposition Principle

- Kramers-Kroning (K-K) relation – real part and imaginary part of complex function are related

$$\underbrace{E(\omega) = \overset{\nearrow \text{Elastic mod}}{E'(\omega)} + i\overset{\swarrow \text{Viscous mod}}{E''(\omega)}}$$

- Booij and Thoone relation –

|G*| & δ

$$\delta(\omega) = \left(\frac{\pi}{2}\right)\left[\frac{d\ln|E(\omega)|}{d\ln|\omega|}\right] \rightarrow \text{Ⓐ}$$

Compute δ

The next approach for checking the data is, you can use Kramers-Kroning relations. So, this is also widely used to for bitumen and bituminous mixture, to check the consistency in the dynamic modulus and the phase angle value. See, we know that complex modulus has 2 parts, the real part is what we call it as a elastic modulus and the imaginary part is what we call it as a viscous modulus. So, this elastic modulus and viscous modulus is not an independent function, Kramers-Kroning equation gives the relation between this elastic modulus or a viscous modulus or otherwise dynamic modulus and phase angle. So, the Kramers-Kroning relations is as given in this equation A. Let us not worry about how this equation is derived. Now if you see, the delta value here is phase angle as a function of frequency, depends on the modulus value and the frequency here.

So, delta is related to a dynamic modulus using this equations. So, now, what you can do is, use the dynamic modulus value obtained experimentally, compute delta value from the experimentally obtained dynamic modulus value, compare this computed delta value with an experimental delta value and check whether there is a consistency in a dynamic modulus and a phase angle recorded.

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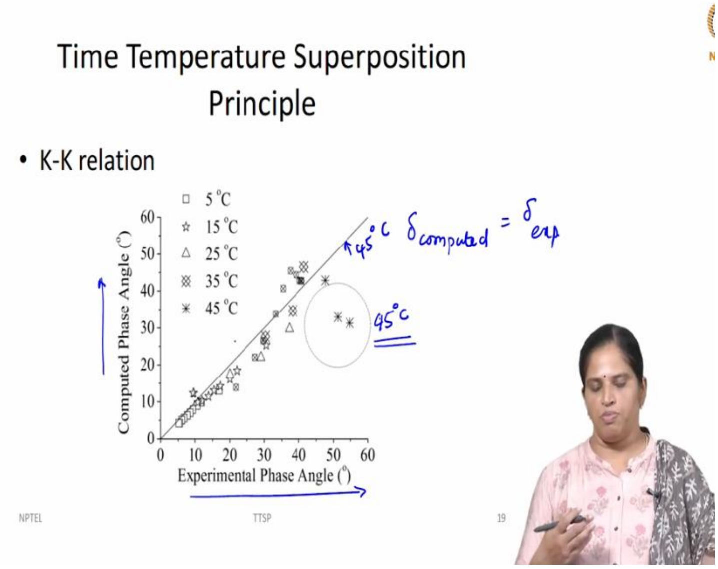

Time Temperature Superposition Principle

- K-K relation

One such an example is given here. So, if you see X scale, it is an experimental phase angle and Y scale is computed phase angle, computed from the dynamic modulus value using a Kramers-Kroning relations, Booji and Thoone relations which was given here. So, this equation was derived by Booji and Thoone. Booji and Thoone equation as given here is used in computing the delta value and it is plotted here.

So, now if you see this, comparing a computed phase angle and experimental phase angle, you can see that at a higher temperature, may be around 45 degrees Celsius, there is a discrepancy from the 45 degree line, This line is 45 degree. Along this line, computed value is equal to experimental value. So, if data deviates more from this, it indicates that the Kramers-Kroning relation is not applicable. So, you can see that at 45 degrees Celsius there are some data where it does not fall into a Kramers-Kroning relation. So, while fitting a master curve, you remove these data from the experimental data and then start fitting the master curve.

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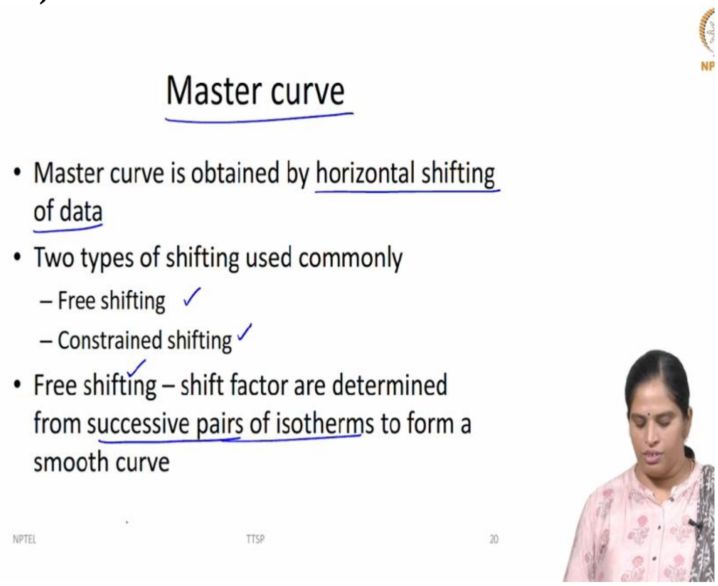

Master curve

- Master curve is obtained by horizontal shifting of data
- Two types of shifting used commonly
  - – Free shifting ✓
  - – Constrained shifting ✓
- Free shifting – shift factor are determined from successive pairs of isotherms to form a smooth curve

So, now, we know what is time temperature superposition principle, we know how to calculate the shift factor, once you know how to shift it amount of shift, now, how to do a shifting process or construct a master curve. So, as pointed out earlier master curve has shifted using a horizontal shifting, only we do a X axis shifting. So, for shifting that, we follow a 2 approach one is a free shifting and other constrained shifting. So, in a free shifting of a data, what we do is, we take a successive pair of dynamic modulus value or a relaxation modulus value. So, we take a successive pair of isotherms and make it a smooth curve as given here.

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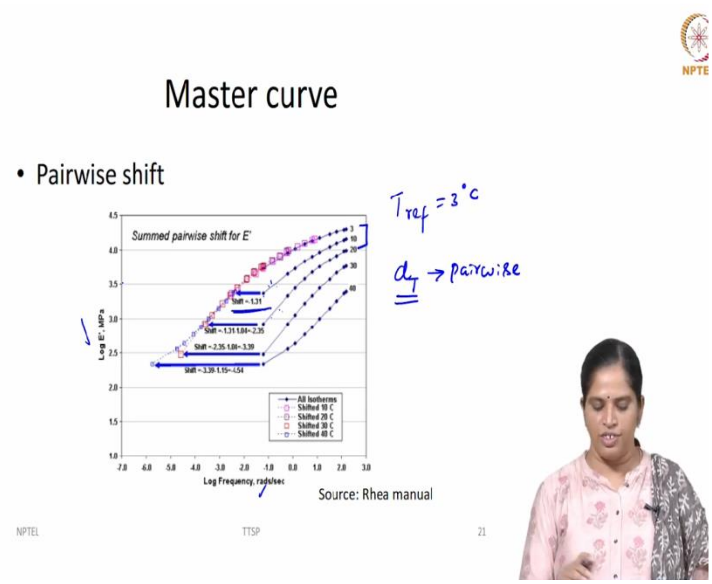

Master curve

- Pairwise shift

$T_{ref} = 3°c$

a_T → pairwise

Source: Rhea manual

In this example, again it is a dynamic modulus data as a function of frequency. You have a different temperature data varying from 3 to 40 degrees Celsius. Suppose if we need to shift all the data corresponding to 3 degree. So here reference temperature is 3 degrees Celsius. So, now, find out a pairwise, just take first 3 and 10 degrees Celsius, find out amount of shift. Now, next is from 10 to 20 degrees Celsius, what should be the amount of shift? So find out a pairwise do a pairwise shifting and find out what is the value of a_T based on a pairwise shifting and shifted data. So this is one method. We call this as a free shifting. So in this free shifting process, we do not assume or give any trend for a final master curve we just find out what is the shift factor between 2 pairs of isotherm and then just shift the data.

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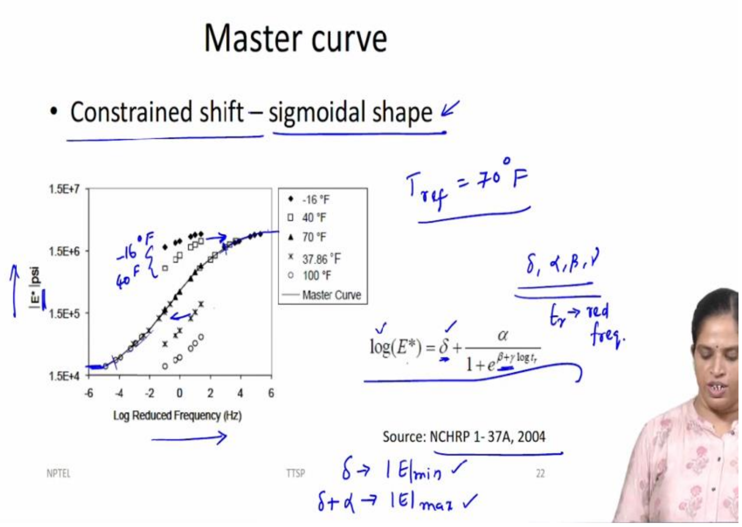

Master curve

- Constrained shift – sigmoidal shape

$T_{ref} = 70°F$

$\delta, \alpha, \beta, \gamma$

t_r → red freq.

$$\log(E^*) = \delta + \frac{\alpha}{1 + e^{\beta + \gamma \log t_r}}$$

Source: NCHRP 1- 37A, 2004

$\delta \rightarrow |E|_{min}$ ✓

$\delta + \alpha \rightarrow |E|_{max}$ ✓

Now, in the constrained shift process we define a final form of a master curve. It can be a sigmoidal shape or an any shape. MEPDG design uses a sigmoidal shaped master curve. So, let us just look into what is sigmoidal shape master curve. Now, again the same kind of a data dynamic modulus data as a function of frequency you have it here. Now, we have at a different temperature. If we want to shift that data to our reference temperature, here it is given as 70 degree Fahrenheit. So, shift the data to a reference temperature of 70 degree Fahrenheit. You have a low temperature data minus 16 degree F and a 40 degree F and a higher temperature data high temperature data here, So, now here if you want to shift this data along as marked directions, so, what you do is define first curve shape and shift the data accordingly. So, sigmoidal equation states this log of dynamic modulus value is a function of this delta, delta here is not a phase angle. So, this is a equation as such given an NCHRP, this delta is not a phase angle which we used to previously. So, you have a delta, alpha, beta, gamma these are all some material functions. Now, if you take this delta value, this delta value is G minimum, as such it has given as E here, so, E minimum value, minimum value here so, lower frequency asymptote functions and delta plus alpha value together will be an higher frequency asymptote function. So, now, this equation becomes a sigmoidal functions with the minimum value was delta and maximum value as alpha plus delta this beta and gamma functions describes the slope functions in this range and t r here as a reduced temperature here it is reduced frequency. So, now, you fix the form of a curve and shift the data to that form we call it as a constrained shifting.

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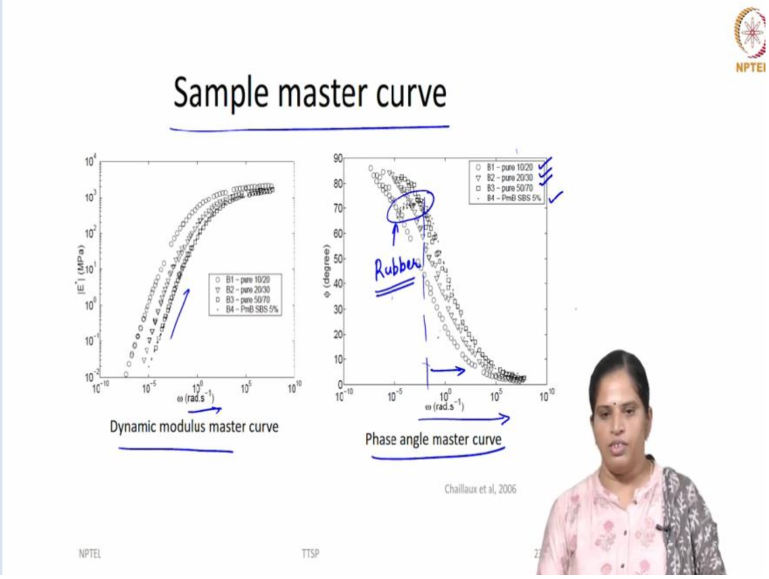

Sample master curve

Dynamic modulus master curve

Phase angle master curve

Chaillaux et al, 2006

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So, if you do a shifting, you can see a sample master curve, we will get it so, dynamic modulus master curve and a phase angle master curve. So, for a different bitumen, you can see a dynamic modulus varying smoothly as a frequency increases there is an increase in the dynamic modulus value. Here again, as the frequency increases, so, at high frequency material will become more elastic like. So, we expect the phase angle to decrease as the frequency increases. So, that is what happening in bitumen B1, sample B2 sample and B3 sample. Now, if you take a B4 sample so, you have a range of a frequency where they expected trend is following. There is a range here another where you expect an increase but you have a rubbery kind of a region here, where the phase angle is almost constant or just reducing. So, this is due to a internal structural change that is happening at this frequency reduced frequency. So, this kind of a rubbery behavior, material behavior that happens for this particular material, do not worry about what this material is. So, our focus is not what the material is, our focus is only what kind of a phase angle master curve we may get it. So, this kind of behavior can be captured when you construct a master curve. This is an another advantage or an application of a master curve.

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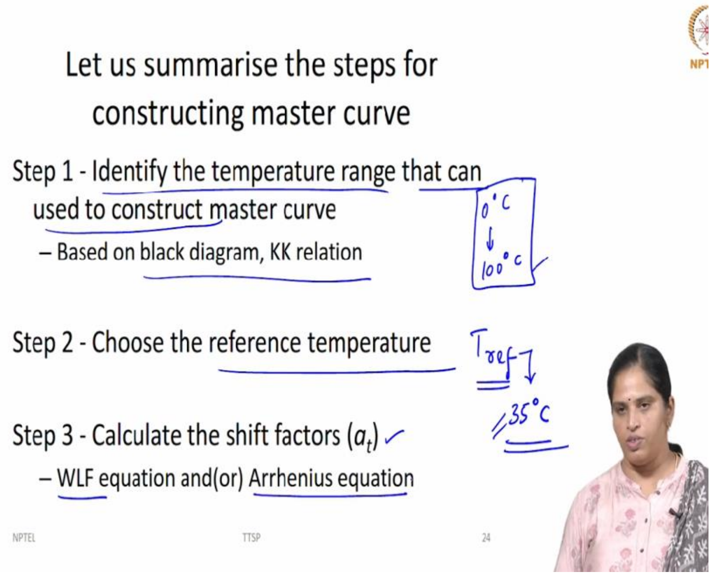

Let us summarise the steps for constructing master curve

Step 1 - Identify the temperature range that can used to construct master curve

– Based on black diagram, KK relation

0°C ↓ 100°C

Step 2 - Choose the reference temperature

T_{ref} ↓ 35°C

Step 3 - Calculate the shift factors (a_t) ✓

– WLF equation and(or) Arrhenius equation

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So, now, let us summarize the steps that we use to construct a master curve. So, for constructing this, you have to do an experiment, frequency sweep test in a frequency mode or relaxation test or a creep and recovery test at different temperatures. So, now you have a different temperature data as a function of frequency or a function of time. If you have a different set of data, identify a temperature range that can be used to construct a master curve.

So, you may have a data from may be from, all the way from 0 degrees Celsius to 100 degrees Celsius, but we may not be able to use all the set of data. You have to check whether you can use it, using either a black space diagram or using Kramers-Kroning relations. So filter the database using a black space diagram and Kramers-Kroning relations, after filtering that, now select the reference temperature and shift all the data to this reference temperature.

So, this selection of reference temperature is based on our requirement. If you want to know the response of a bitumen maybe at 35 degrees Celsius, you select it to be 35. So it is based on the user requirement and there is no fixed scale to select the reference temperature. So after selecting a reference temperature, find out the shift factor for each isotherm. For finding out the shift factor, you can either use a WLF equation or you can even use Arrhenius equations.

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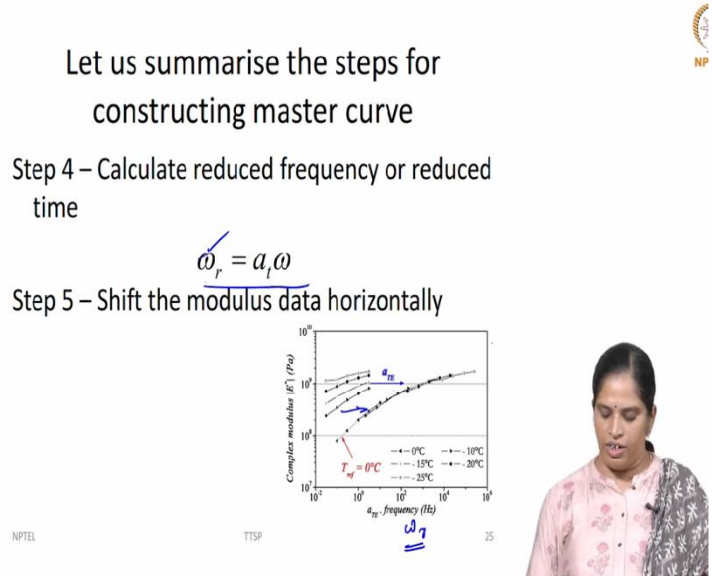

Let us summarise the steps for constructing master curve

Step 4 – Calculate reduced frequency or reduced time

$$\omega_r = \underbrace{a_t\omega}$$

Step 5 – Shift the modulus data horizontally

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So, once the shift factor is determined, find the reduced frequency or reduced time in case of a timescale testing using this relations. Once a reduced frequency or reduced time is determined, using this reduced value, shift all the modulus value in a horizontal scale, keeping the X scale as reduced frequency or reduced time in case of a time domain testing. So, once you shift all this data, you will get a nice smooth master curve.

So, far we have seen what is time temperature superposition principle and how to use this time temperature superposition principle in constructing the master curve. In a next lecture we will see what are the different model that is available to predict the response of bitumen. Thank you.