

**Rheology and Processing of Paints, Plastic and Elastomer based Composites**  
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**Lecture 12**  
**Master Curve and its Implications**

Welcome to NPTEL online certification courses on Rheology and processing of paints, plastic and elastomer based composites. Today we are in week 2, lecture number 2.6 that means 6th lecture and we will talk about the essence of master curve and its implications. Again the concepts covered precisely will be time temperature relationship or time temperature superposition TTS is called. TTS benefits why and when you should use TTS, when not to use TTS and then guidelines for TTS time temperature superposition, TTS shifting bit on Deborah number and idealized flow curves and shift factor versus temperature shift factors WLF equations. When not to use WLF equation again what is the limitation precisely, age fracture last time we were talking about when talking about the parallel geometry the age fracture when it happens and that is what we try to solve it with some sort of a rotational I mean coolant type of a you know geometry.

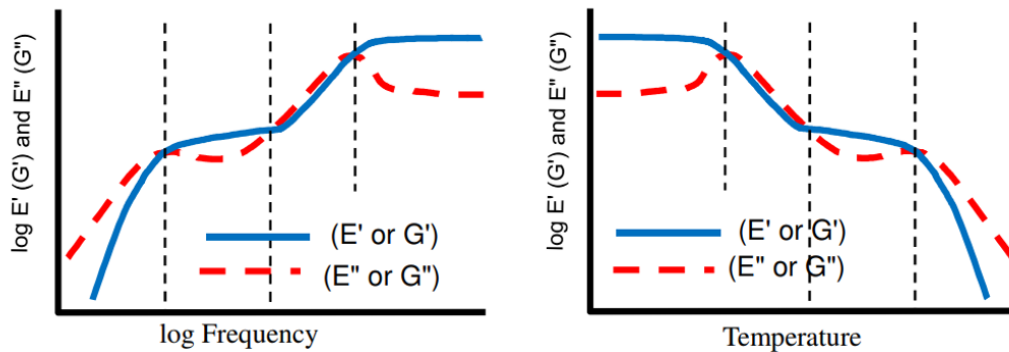
Then Cox-Merz rule that is the most essence of it. So, again some of the keywords which you can look for just to prepare yourself get more about this courses which will be covered today the lectures will be covered today. It starts from viscoelastic properties ends with Arrhenius equations as well as apparent activation energy. So, now coming to the time temperature superposition principle.

As I was mentioning when I was talking about oscillatory you know geometry see what you get I mean either in the form of again storage modulus and loss modulus  $G'$  and  $G''$  and that actually depends on time temperature and frequency and you know simply frequency and time they have a inverse relationship. So, if we look it at the material from the elasticity point of view is better representation is modulus if you look it as fluid point of view viscosity is the parameter. So, either  $\eta'$  or  $\eta''$  that I clarified it. So, however in this plot when I write  $\log E'$  you can read it like  $\log \eta''$  when I write  $\log E''$  you can read it  $\eta'$ . So, likewise you can assume all the way same it is viscoelastic remember it is not purely elastic nor it is purely viscous.

So, there is sometimes you take it as a solidus material sometimes take it makes more sense to consider it as a fluid. So, now if you look it at from frequency wise plot that other day I was talking about temperature or I can write time also here same. So, it

follows it has a glassy state and then glass transition then rubbery plateau then you have a terminal region that means flow so it flows. And if you plot  $G'$  double prime on top of that overlaying that you will find that wherever you get a transition like a glass transition you get a maximum of  $E'$  double prime or  $G'$  double prime and then you have a rubbery plateau then. So, you can often see some crosses over.

### Time and Temperature Relationship



So, initially  $E'$  was more than that of  $E''$  at the glassy state then when the transition sets in commences in you have a transition when I mean  $E''$  becomes more predominant. And then again in the plateau part is subdued by  $E'$ . So, that as if there is a rays going on while traversing from low temperature plus low time to high time. And then finally, you have a another crossover and obviously, when it becomes liquid its  $E'$  subdues and  $E''$  takes over. So, that is the what you call the end of it terminal region.

And what I told you also for nanocomposites there is yet another plateau that is called terminal plateau, but I am not going into that complication I am just simply considering a simple amorphous material and that has its glassy state glass transition rubbery plateau and terminal flow. So, in this stage is better to consider at as you know oscillatory radiology terms and write rest of the part this is the boundary end of rubbery plateau you consider it is dynamic mechanical properties that is what is the point of confusion you have. Now, the frequency wise if you plot it is just replicate opposite to that. So, here at the you know low temperature it was glassy at high frequency it is glassy and followed

### De Deborah Number

$$De = \frac{\text{Relaxation Time}}{\text{Processing Time}} = \lambda \cdot \dot{\gamma}$$

up to the load. So, your terminal is here.

So, this point here this part portion here is oscillatory radiology part or rheological sense because it is more like liquid and this is the place where you have DMA or solidus part of it. So, that is the cells, but what I call it tell it master cup the whole range of frequency or whole range of you know temperature under consideration. So, suppose if I consider from minus 100 to minus 2 plus 300 that is my you know region or range of temperature of interest. So, that way you may be getting surprised that I am plotting time. So, if I have a rubbery material if I observe it under a load say over 1000 years I may see it flowing.

So, that is what it is called mountain flows before the god. We human being having a lifespan of 90 years we see it is only rubber, but if you keep it some more time some 1000 years it is supposed to show you the fluid like behavior that is what the essence of viscoelasticity is. So, this is called linear viscoelastic properties what we are showing I just last time made you understand what is this linear viscoelastic regimes and LVR I abbreviated and the property you get it linear viscoelastic properties within that amplitude region and are both time dependent and time dependent and temperature dependent. There are two major principles in polymer physics one is Boltzmann superposition principle that takes care of accumulative loads, incremental load, shears, stress or strain and the final part of it you can estimate. Another important part what I am depicting now is called time temperature superposition principle time temperature relationship.

Why we are doing this exercise? Why should we do that exercise? Because all this geometric technique I talked about they have a limitation of frequency or shear rate. I cannot cover continuously the whole range very low very high is very difficult to cover with the realistic instruments. So, we will use this useful principle to interpolate and extrapolate so that I am generate a master curve myself and then I will try to feed in with the rheological formula and that is how the fluid should behave over across the range of temperature and frequency or temperature frequency and time more precisely that is what the essence of it. So, some material so time dependence is proportional to temperature dependence decreasing temperature has the same effect on viscoelasticity as increasing frequency as I said you see decreasing temperature solid is a glassy state and of course increasing frequency is a glassy state. So, as if decreasing frequency and increasing frequency and decreasing temperature is all the lesson.

So, and vice versa that relationship you have to always build it. So, that is the reason if you take a block of rubber or a polymer you try to punch it you may end up breaking your bone. However, if you try to deform it slowly it will give you soft I mean that

texture soft type of a film. The reason is that at when you are punching on that you are deforming it way too fast and it turns out to be a glassy state virtually that is the beauty of it. So, what is the benefit as I mentioned already some of the instruments has a limitation neither you can continuously cover up all whole frequency range together.

So, there your time temperature superposition principle is applied and can be applied I mean that it is generic version generalized form of it from time temperature superposition principle under special circumstances WLF equation which can be strictly applicable or it works for a fully amorphous material unfilled material. So, these are some of the limitations where you should apply I mean where you cannot apply where you can apply that you must know. So, material must undergo thermo rheological one in which all relaxation time shifts as a same shift factor. See relaxation time also is very important. See suppose I have shown you from glassy state to rubber state is undergoing transition which is called segmental motion of glass I mean glass transition.

So, that has a particular time at a given frequency and ultimately you are trying to see that time how it is changing with the effect of temperature. So, that way if you get a modulus say  $g$  at a temperature and time  $t$  and  $t$  there should be a corresponding modulus at a different say  $t_1$  time and at a particular temperature  $t_1$ . So, this is what ultimately we are trying to locate. So, we can shift the data one range to the other. So, that is the beauty of it.

Again when not to use TTS if it is crystalline or semi crystalline polymer like polyethylene in a strict sense is not valid. Cross linking decomposition etcetera that is the cases when it is the structural change if it happen because we are only focusing on physical phenomena like relaxation. So, on added to that if anything chemical processes happen WLF equation or time temperature superposition principle as such this principle does not hold good. So, there are many things where it does not really hold good, but principally I told you what is the reason because you are trying to focus on capture on one particular relaxation how it is changing as a function of time and temperature that is the bottom line of it. Else field system you have a some of the fillers already embedded into the you know rubber embedded into the filler their relaxation is pretty much restricted.

So, you do not have a uniform relaxation time. So, it is obviously it will be deviation. And in a strict sense 50 degree below  $T_g$  is not applicable 100 degree above  $T_g$  it is applicable, but not beyond that. So, these are some of the limitation that one must understand before applying it blindly for you know superposition or I mean shifting the data. So, some of the things are written there I am just intentionally leaving it behind because you know when you try to read after this class you try to read those.

If you have any clarification or doubt I will come online that time you get it clarified. So, else you will get it in a standard textbook, but what I mean to say probably by now you might have understood what the essence of it is the shifting of the data. So, you know modulus at a given temperature and time what is going to be the modulus at a another given you know temperature. So, time how much it shifts that shifting you take. So, one temperature you know data another temperature you are estimating the data and correspondingly time axis how it is changing.

So, that is the essence of it. So, you have to have a reference temperature with respect to that left and right all the data should be shifted. Say for example, here you have a data of storage modulus as a function of frequency this is a frequency sweep you can do either in oscillatory rheology again or in DMA it is all the way same. So, these are the data with the frequency from 10 to the power minus 2 to some going to 10 to the power 2 that means 100 Hertz there is a limitation of the you know that particular DMA. You cannot afford to have to use a 4 Hertz in your DMA unless it is very special one.

10 to the power 5 Hertz impossible today's no DMA can take you to that angular frequency because of limitation of the mechanics of the machine basically noise will be important resonance will come into the picture. So, these data you have done at different different temperature 140 degree, 150 degree, 160 degree, 170 degree up to 200 degree you have that data within the given frequency regime. Now, what I am going to do these data I would like to see with respect to one reference point say middle one say take this blue one. So, now correspondingly either this data will go to the left or some of the data above will go to the right. Generally the above data this data will go to the left and this data will shift towards the right and that way you are expanding the window of frequency at a given temperature you will be able to capture what is going to be the data.

So, remember there 10 to the power 5 Hertz I cannot go apparently, but by the shifting process I will be able to access 10 to the power 5 Hertz what is going to be the behavior, but what I did it actually in experimentation different different temperature whatever within the limitation of my instrument I perform the experiment. There are some of the many data's data here see storage modulus at a given set of temperature storage modulus with a frequency of course, and that that those data actually gradually getting shifted and you see when you did the shifting process one by one by one and you see you will finally, capture this much of frequency 10 to the power minus 2 to 10 to the power at least 3 or 10 to the power 4 Hertz you covered the whole data yet some more to be laid off shift data and it superimposes on a single curve that is what you generate a master curve ultimately. However, so far I was talking about the horizontal shift of data of course, because of the temperature effect there will be a vertical discontinuity. So, your

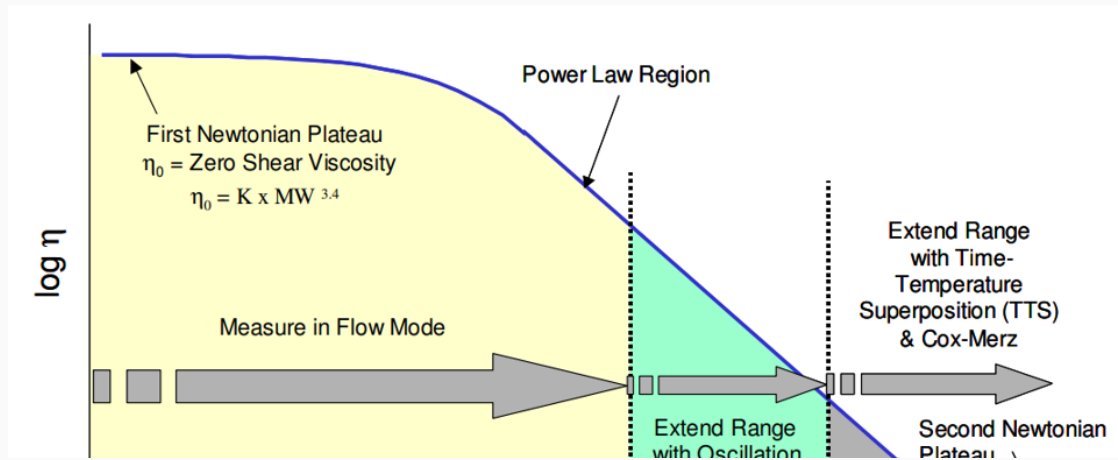
density and modulus also changes as a function of temperature that is the physical effect. So, that if you take care of that is called vertical shift then that then you will get exactly overlaid data points together to generate the master curve.

So, as if this small points they lay over with certain horizontal and vertical shift to a single curve which you call it a master curve. So, TTS helps you generating the master curve in a sense. So, these are the shifting of the data. So, with respect to reference data I mean some data how it is getting shifted. So, you essentially as I mentioned you covered up into 4 and even more the whole range is now covered.

So, you can really now by that process you estimate the data and in this context Deborah number is actually you must understand. So, it is a ratio of the relaxation time. So, you have a relaxation time of the time of the system and when we are deforming with the frequency that ratio gives you the Deborah number basically. Say for example, if a fluid is there, if I allow specific time to flow from some point to the other point, if I allow that time it will flow. If I do not allow that time if I do it deform it very fast it will not flow.

So, it will behave more like a solid material. So, Deborah number that way gives you idea about how the relaxation time changes with respect to the time you are allowing it for in a process or in anywhere. So, rule of thumb for processing make sure Deborah number is as low as possible and processing time is long relative to the relaxation time then only your material will flow get sufficient time to flow. But in this context it is not much that relevance. Now, just try to realize or just try to assume that we understand the essence of it.

### Idealized flow curve- Polymer melts



### When not to use the WLF Equation

$$\log a_T = -c_1(T-T_0)/c_2 + (T-T_0)$$

$a_T$  = temperature shift factor

$T_0$  = reference temperature

$c_1$  and  $c_2$  = constants from curve fitting

- Generally,  $c_1=17.44$  &  $c_2=51.6$  when  $T_0 = T_g$

**In these cases, the Arrhenius form is usually better**

$$\ln a_T = (E_a/R)(1/T - 1/T_0)$$

$a_T$  = temperature shift factor

$E_a$  = Apparent activation energy

$T_0$  = reference temperature

$T$  = absolute temperature

$R$  = gas constant

$E_a$  = activation energy

See this is the master curve here we represented with the viscosity. Like I just put it suppose if we happen to do the measurement in full rotation, no question of storage or loss in that case. So, now if you see is a gross reflection of over the range of shear rate, shear rate is nothing but a frequency actually in essence. I mean in rheology sense we

say shear rate in dynamic mechanical sense we call it a frequency nothing more than that. So, in that you see the gross reflection of the master curve.

Now, if I consider this region what is that region called? Terminal region. In terminal region so far so forth I was talking about your superposition. In terminal region also the data is what is data is classically say it is the rheometric data rheological data. There also you can apply similar to TTS and that follows a rule called Cox-Mertz rule basically. I will come back to what is Cox-Mertz rule, but nonetheless each part of the master curve gives you certain information.

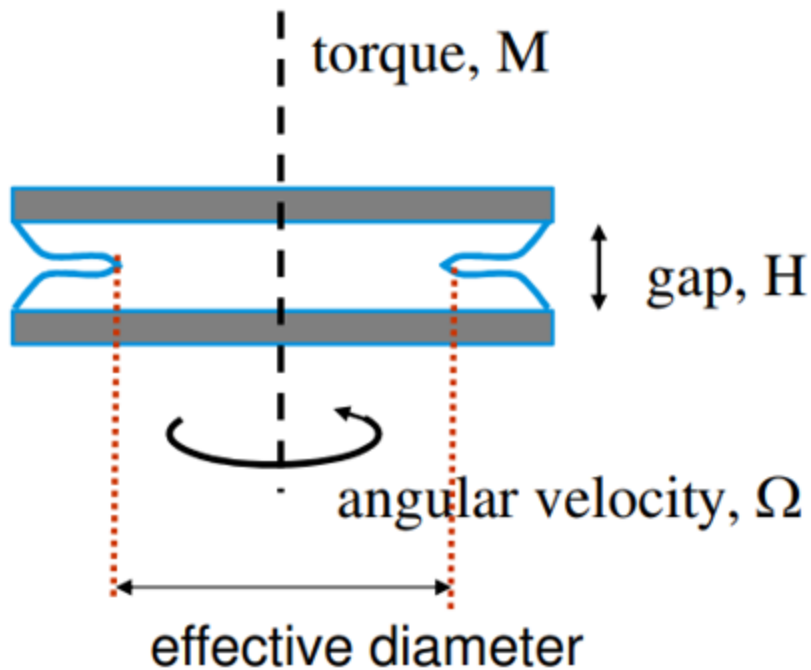
Since this viscosity is a zero shear viscosity basically. And that viscosity is proportional to molecular weight to the power 3.4. So, if you do that measurement you know interpolate it to the frequency 0 and then you get approximate measure of the molecular weight side of a high polymer. So, you can understand you can use in the flow mode also you have several regimes the EOLO regimes measure in flow mode, extend it in oscillation the next region and is a Newtonian plateau where classically it behaving like a fluid, but whole data can be superimposed basically using extended form of TTS.

As I said WLF equation TTS is a generalized principle. At certain condition if you impose it upon you end up having a WLF equation which actually is a shift factor I was talking about shifting the time the shift factor  $\log AT - C_1(T - T_G)$  by  $C_2 + T - T_G$ . Initially people thought  $T_G$  is the reference temperature by the way. When you consider  $T_G$  as a reference temperature is more of in the WLF form, William Lendel Ferry form. So, again so this shift factor actually roughly with the temperature varies this way.

So, I am not going into the details of it actually WLF equation comes from Dolittle equation. Do-Litley equation is a how viscosity changes with temperature and there is a theory called fractional free volume theory. So, if you combine fractional free volume theory with the Dolittle equation and you are remember your relaxation depends on the viscosity. From maximum model actually what you get to see relaxation time  $\tau$  equals to viscosity by viscosity of the you know dashpot modulus of the spring.



## Edge Fracture



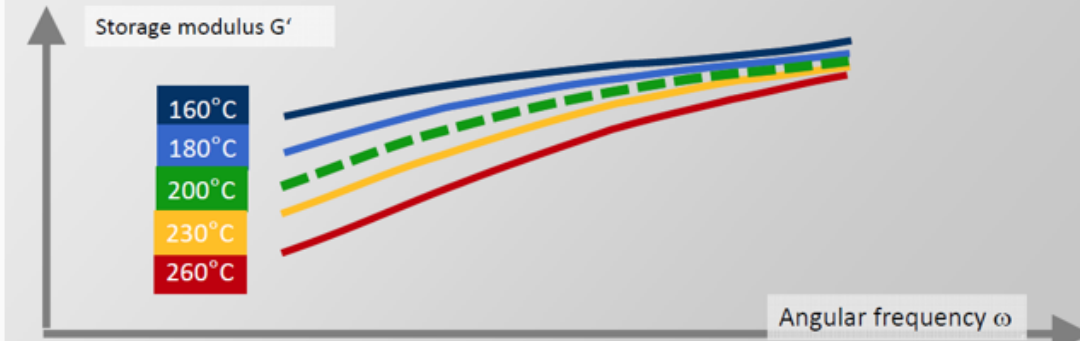
So, this you consider time independent. So, your time will depend more of viscosity and the viscosity is governed by Doolittle equation and put in the fractional free volume theory and from there you arrived at what you call it WLF equation it takes this form as I told you. So, I am not going into the details for the timing initially people thought of  $C_1$  and  $C_2$  are universal constant, but it varies from polymer to polymer. So, in my last class last NPTEL courses I have given a very good depiction of WLF equation. So, please refer to that or else you can refer to any book introduction to viscosity by Aklonis book you can refer to any other standard viscosity book you will get how it is derived off.

Even I.M.O. Wards book by mechanical properties of polymers introduction to mechanical properties of polymers you will get it. But in the anyway there are certain limitation of WLF equation as I mentioned  $T_g$  plus 100  $T_g$  minus 50 that is the limit and that too it is valid for purely amorphous polymers unfilled polymers and so on and these are the temperature window over which it is applicable. See Arrhenius case also I mean roughly about you can use Arrhenius equation also. See Arrhenius equation which says it is rate dependent process here rate dependent relaxation process and your modulus or viscosity derives from the relaxation processes and combination of it. And in fact, indeed this relaxation are distribution of relaxation time.

## Frequency Sweep – Master Curve

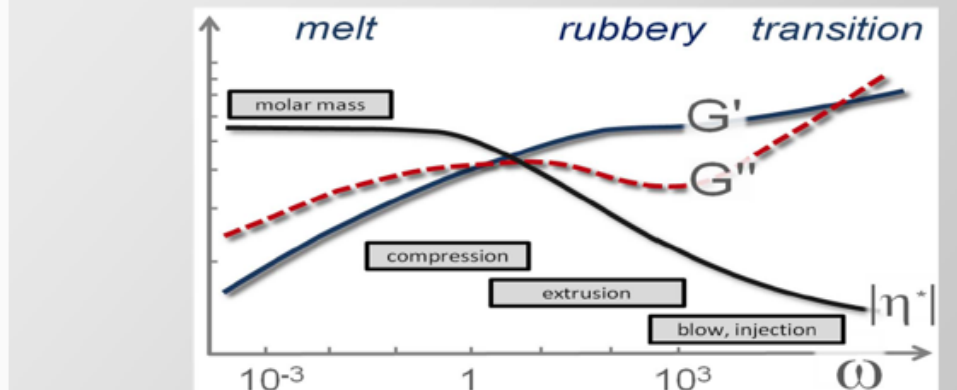
Horizontal shift towards the reference temperature  $T_0$

- TTS example: horizontal shift of storage modulus  $G'$



Horizontal shift towards the reference temperature  $T_0$

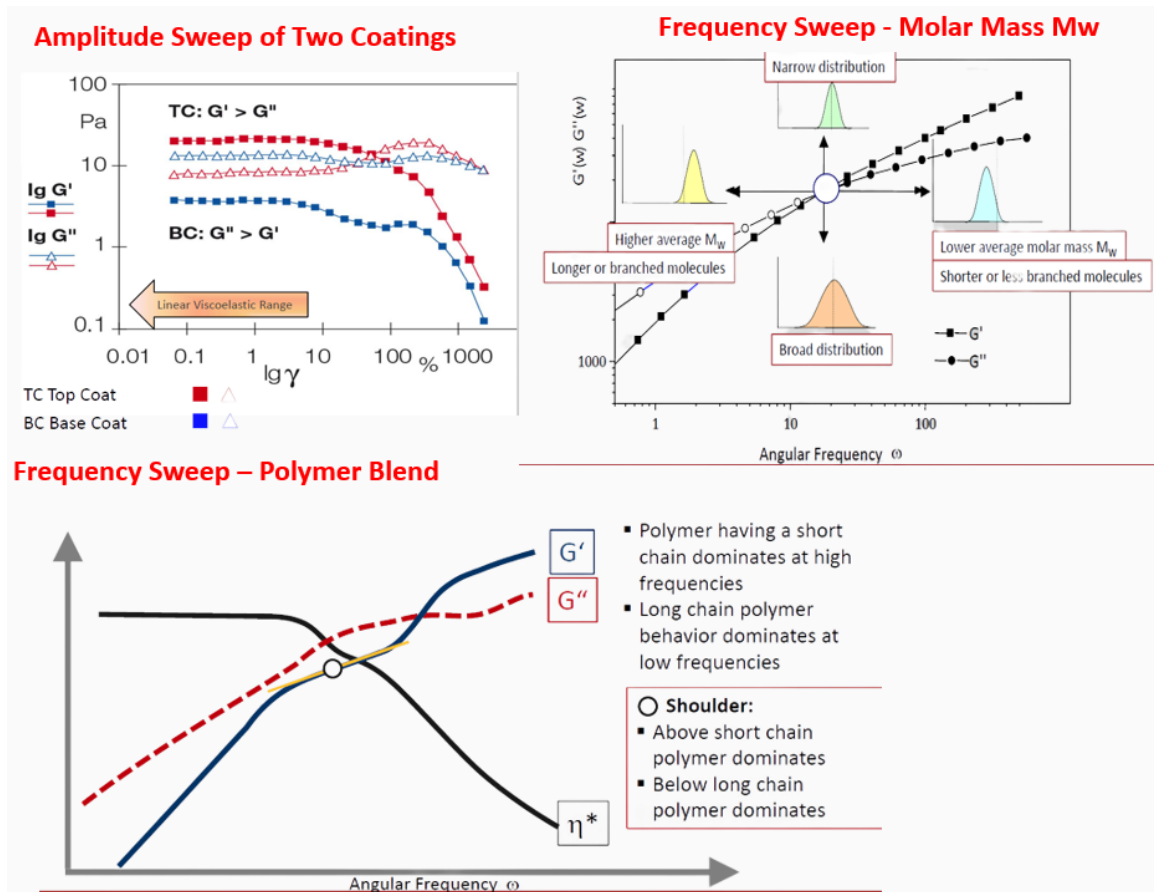
- TTS example: shift of storage modulus  $G'$
- The range above the transition region is called glassy region



So, your modulus or viscosity is a function of distribution of relaxation time. So, that is the origin of it. So, you can either apply a Arrhenius equation or else you can apply you know Arrhenius equation is based upon the activation energy barrier the process goes and here is based upon the you know some dulittle equation of viscosity and change of relaxation time in a sense. So, once again if I ask you the question why you would like to do TTS again my answer will be the same what I told you just to capture the entire range of temperature or frequency or shear rate number 1. Number 2 our rheometry has some limitation I cannot continuously using a single rheometer capture the whole region very low to very high.

So, we get discrete data that data can be overlaid together using superposition principle

WLF and Cox's merge is a special type of it it is applicable for the oscillatory rheometry vice a vice with the you know capillary rheometry which you capillary rheometry you get it high shear rate data oscillatory rheometry you get it the data at lower shear rate the whole data can be superimposed a single viscosity versus shear rate plot that is the essence of Cox-Merz principle. So, edge fracture that they are just talking about is caused by elasticity of the fluid see remember between two plates if you put a fluid from the edge it will try to undergo fracture remember this thing. So, the result will be apparent viscosity will be decreased. So, you have to minimize the edge factor. So, you have to reduce the measurement gap and you use the partition plate.



So, we have why we are covering here we could not cover it there as such. So, just to give you an idea it is elasticity governed phenomena edge for fracture and you can really take care of while doing geometry in parallel plates. Nonetheless this is the TTS you know with the frequency you captured the  $G'$  you can write I do not mind if you write it with a double prime at different temperatures overlay within a master curve where you have a wide range of angular frequency here all the way same either frequency or shear rate and then what you get  $G'$   $G''$  again you see the crosses over as I mentioned it to you while describing the usual DMA from different

transition you have a cross over between  $G'$  and  $G''$  and remember one thing all this frequency regimes are important for different processing. See the lower frequency you get more idea about the molar mass molten stage in the frequency and one hertz is close to the compression in between extrusion very high is either injection or blow molding techniques. So, these are the essence of the frequency free essence of what I described you.

So, this Cox-Merz rule I already talked about the essence is two data one is your rotational data in parallel plate you are getting. So, another or capillary data what you are getting another is the oscillatory measurement you are doing this data can be superimposed. So, for materials that exhibit wall slip or edge fracture one alternative way to obtain viscosity information over shear rate is to use Cox-Merz principle that can be actually you know corrected and Cox-Merz rule is an empirical rule and it was observed that many polymer system the steady shear viscosity plotted against the shear you know the shear rate is correlated with the complex viscosity oscillatory viscosity actually steady shear viscosity oscillatory viscosity against the frequency in the LVER. Sometimes you call LVER or LVR it is all the way same linear viscoelastic regions. With the again to remind you if you plot modulus with the amplitude the nonlinearity comes.

So, within that linear range I mean rather I my representation will be stress. So, dynamic frequency sweep you do it here you get it you know composite viscosity you do steady flow you get  $\eta$  versus shear rate. Here you get it  $\eta'$  versus  $\omega$  you get  $\eta''$  two different measurement techniques and then finally, you can use Cox-Merz to overlay them. And you once you overlay whatever discontinuities you get it in the flow curves that you can eliminate and consider it as a edge fracture basically as simple as it is. So, that is it about the Cox-Merz principle I can show you some case studies while doing oscillatory measurement and use of TTS.

See here the first one is about a coating system top coat and bottom coat. You see the measurement  $G'$   $G''$  across the you know regimes and you see it is a it is a amplitude sweep basically and you see it is stiffer and it breaks down faster. Both the  $G'$  and  $G''$  to plot is shown, but while the bottom coat is softer and it is breakdown process is also different in a given adhesive. I am not going into the details of it, but nonetheless you just try to capture because this crossover many times gives you a lot of sense. Sol to gel as I mentioned it to you change in orientation change in entanglements those will be grossly reflected in terms of angular frequency versus  $G'$  and  $G''$  if you plot.

So, you can see it polymer having a short chain dominates at the high frequency frequencies. So, your contribution from the short chain at high frequency will be more

influential and long chain behavior dominates at low frequency. So, in a given polymer how much or long how much is short by geometry you will be able to estimate, but for that you need to use TTS to have an extended window of frequency and try to have a gross behavior of it correct. So, that way and the solder is also important whenever you are getting solder why you are getting solder above the short chain polymer dominates below the long chain dominates in the solder is a quasi part of it where both of them are not that dominant basically.

This makes more sense from rheology to molecular picture. Here in this case also is a gross depiction of this. So, you have a that way frequency if I plot it in log scale a wide range of frequency you see somewhere you see the dominant part contribution from the higher molecular weight side and longer branch side whereas, in the other frequency region the contributors are more from those molecules those are having lower average molecular weight and shorter or less branches there. So, that way if you have a wider range of so what I have tried to see you do rheometry you do direct mechanical properties over whatever your machine allows try to put it in a time temperature superposition principle have a gross wide range of temperature or frequency behavior of it and try to give its interpretation. So, then it makes your life easier even if you do not have that broad data or you have a limitation capturing the data you can use WLF equation both for dynamic mechanical point of view as well as from the point of view of rheology. So, with that these are the books I have given you and quickly to sum up what I in a sense try to convince you with the idea about time temperature superposition principle although I did not go details about that I make you aware of the fact that when and how it has to be used to get a broader you know behavior of it across a whole range of temperature and frequency of your interest and then try to use it and not only that what I did not tell you once you have that master curve you can fit it into the rheological model and you can use it for simulation or designing a machine for processing of those particular polymers of your interest.

So, with that you refer to Cox-Merz principle WLF equation shift factor etcetera with that thank you very much.