Introduction to Polymer Physics

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Lecture – 20
Viscoelasticity, Dynamic Mechanical Analysis and Rheology

Hello everyone. So, in the last lecture we talked about viscoelasticity of polymeric materials, where we saw that the viscoelastic response typically is a kind of response, which is intermediate to that of a purely elastic response as in purely viscous response. So, we also discussed a couple of mechanical simple mechanical models to describe such viscoelastic behavior. In today's lecture we will carry forward that discussion on viscoelasticity, and we will specifically talk about a couple of other parameters, which are useful in studying the deformation behavior of viscoelastic materials and the corresponding mechanical response.

We will also talk about the dynamic mechanical analysis, where the response to an oscillating load is studied. So, the response of viscoelastic material to let us say sinusoidally oscillating load that is what this dynamic mechanical analysis aims to study. So, we will briefly look at that topic, and towards the end we will again briefly discussed the rheology of a polymeric liquids such as polymer solution sand melts.

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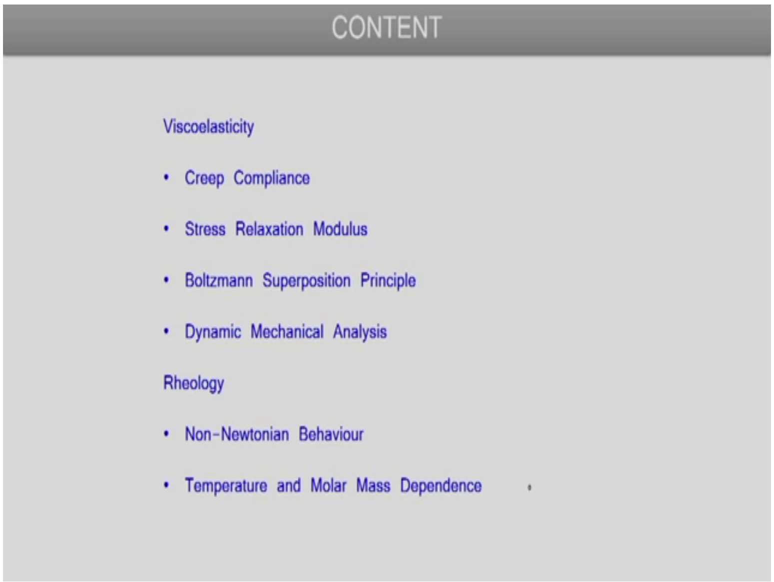

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Viscoelasticity

- Creep Compliance
- Stress Relaxation Modulus
- Boltzmann Superposition Principle
- Dynamic Mechanical Analysis

Rheology

- Non-Newtonian Behaviour
- Temperature and Molar Mass Dependence

So, regarding the content of today's lecture we will start with discussing a couple of parameters related to the viscoelastic response. So, first will be the creep compliance and the next will be the stress relaxation modulus, we will define these parameters. We will also terms talk about what is called the Boltzmann superposition principle, which applies for linear with elastic materials and which allows one to obtain the state of stress or strain in a material at a given time, if the entire deformation history for that material is known and provided the material is linear viscoelastic.

After that we will focus on dynamic mechanical analysis whereas, as we discussed we will talk about, how the viscoelastic materials respond to oscillating kind of load. Then towards then we will focus on rheology and flow behavior of polymeric liquids. So, here we will see that a in many cases that the flow cannot be described using a Newtonian kind of model so, non-Newtonian behavior so, behavior of polymeric liquids will be studied and some simple models that describe such a non-Newtonian behavior that will also be explored. And towards the very end we will briefly look at the dependence of the quantity viscosity on temperature as well as molar mass of the polymer.

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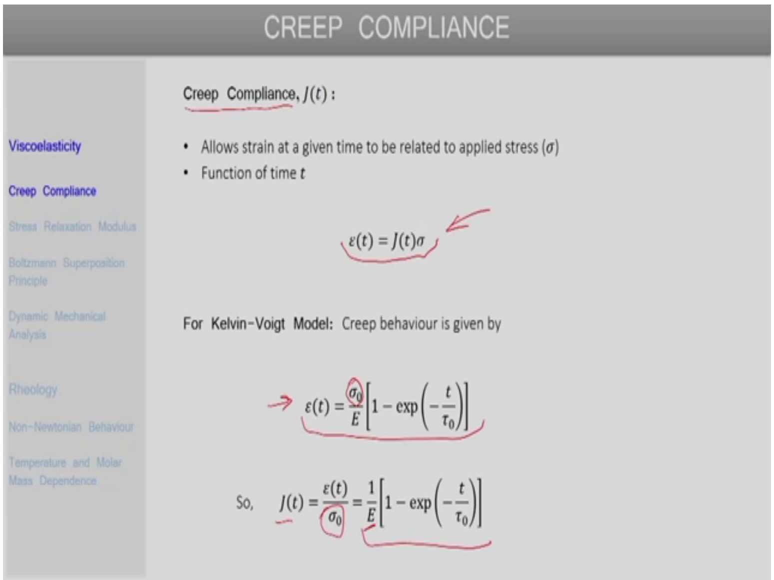

CREEP COMPLIANCE

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Creep Compliance, $J(t)$:

- Allows strain at a given time to be related to applied stress (σ)
- Function of time t

$$\varepsilon(t) = J(t)\sigma$$

For Kelvin-Voigt Model: Creep behaviour is given by

$$\varepsilon(t) = \frac{\sigma_0}{E}\left[1 - \exp\left(-\frac{t}{\tau_0}\right)\right]$$

$$\text{So,} \quad J(t) = \frac{\varepsilon(t)}{\sigma_0} = \frac{1}{E}\left[1 - \exp\left(-\frac{t}{\tau_0}\right)\right]$$

So, to begin with we will start with the quantity creep compliance. So, creep compliance is a parameter, which allows the strain in the material at any given time to be determined provided it is the material is subjected to some stress or some load and it is a function of time. So, creep compliance directly relates the strain developed to the stress applied, and the relationship is simply linear and looks like this. So, epsilon which is a strain induced will be equal to the creep compliance times the stress applied.

So now if we try and see how one of the models that we discussed in the previous lecture for linear viscoelasticity how that model can be used to obtain an expression for creep compliance. So, we discussed in the last lecture that, the creep behavior is modeled in a better way by the Kelvin-Voigt model. So, we will consider that model here. So, if we can say Kelvin-Voigt model then the creep behavior is shown by this expression again there is something that we discussed in the previous lecture and the expression for strain upon application of some fixed stress sigma naught, for Kelvin-Voigt model is given by this relation.

So, now using this expression defining the creep compliance we can obtain an expression for the creep compliance for a Kelvin-Voigt model. So, if we do that this creep compliance is simply the developed by the applied constant stress. So, that is given by 1 over E which is the elastic modulus, then 1 minus exponential of minus t by tau naught where tau naught is the relaxation time. So, in this way we see that for if we have a models of viscoelasticity available, we can obtain expressions for creep compliance from there.

Now, creep compliance is quantity or a parameter that relates the strain developed to the applied stress. In a similar way if we apply a stress if we apply let us say strain to a material a viscoelastic material, then what kind of stress is developed that is given by another parameter, which is called the stress relaxation modulus. So, that is what we will consider next ok.

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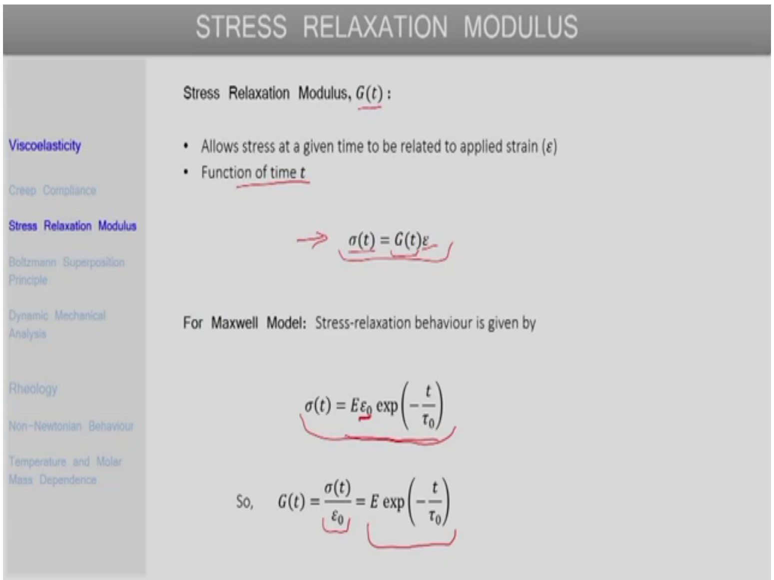

STRESS RELAXATION MODULUS

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Stress Relaxation Modulus, $G(t)$:

- Allows stress at a given time to be related to applied strain (ε)
- Function of time t

$$\rightarrow \quad \sigma(t) = G(t)\varepsilon$$

For Maxwell Model: Stress-relaxation behaviour is given by

$$\sigma(t) = E\varepsilon_0 \exp\left(-\frac{t}{\tau_0}\right)$$

So, $G(t) = \frac{\sigma(t)}{\varepsilon_0} = E \exp\left(-\frac{t}{\tau_0}\right)$

So, the stress relaxation modulus is given by this quantity G t it is a function of time and allows the stress to be determined as a function of the applied strain. So, the relation between stress and strain as given by this stress relaxation modulus is again a linear, and the stress at any point of time sigma t is related to the strain epsilon by this expression where this stress relaxation modulus G t is the quantity, that relates the stress developed to the strain applied.

So, again like in the previous case like in the case of creep compliance we discussed the Kelvin-Voigt model and obtain an expression for creep compliance; for stress relaxation modulus also let us consider simple model that we discussed in the previous lecture and see how an expression for stress relaxation modulus can be obtained. So, in the previous lecture we had discussed that the stress relaxation behavior, where the stress is monitored as time under a given applied strain. So, that is described in a better way by the Maxwell model, the Kelvin-Voigt model is not able to capture the stress relaxation behavior of viscoelastic materials. So, the Maxwell model better captures that behavior. So, we will for the stress relaxation modulus we will focus on the Maxwell model of viscoelasticity.

So, if we have Maxwell model, then from the previous lecture again the expression for the stress as a function of time as developed for the Maxwell model is given here and the constant applied strain is epsilon naught. So again now if we go back to the expression that defines the stress relaxation modulus then from here we can see that the G t is nothing, but sigma by epsilon. So, if we do that. So, sigma by this epsilon naught which is a constant strain applied that ratio is given by this expression e times exponential of minus t by tau naught, and that is the expression for stress relaxation modulus for a Maxwell model.

So, these are a couple of quantities or parameters that are important in the study of deformation response of viscoelastic materials to applied load whether its applied stress or strain. Next what we will do is a study principle known as a Boltzmann superposition principle, which allows one to obtain the stress a state of stress or the state of strain in the material, as a function of its with a knowledge of its deformation history.

So, if a material is deformed in several different steps over a long period of time, then that deform it the entire deformation history for the material is known then the state of stress at occur at a given point of time can be obtained using the Boltzmann superposition principle.

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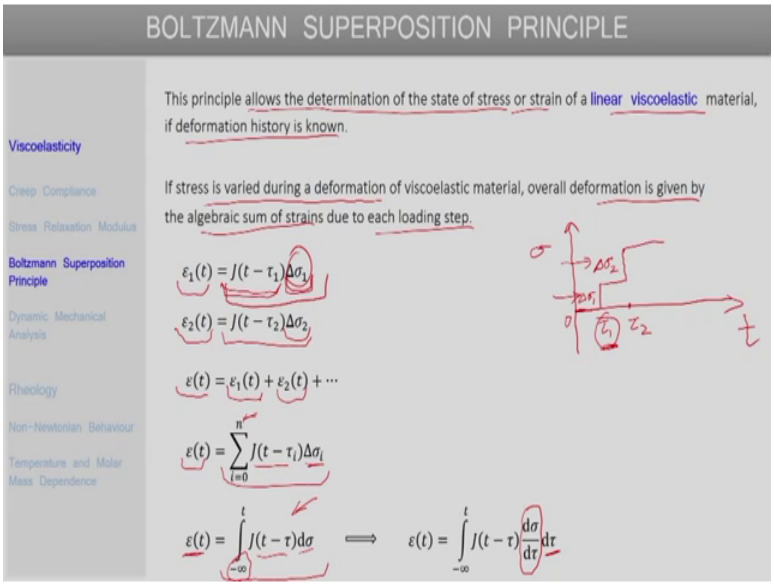

BOLTZMANN SUPERPOSITION PRINCIPLE

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This principle allows the determination of the state of stress or strain of a linear viscoelastic material, if deformation history is known.

If stress is varied during a deformation of viscoelastic material, overall deformation is given by the algebraic sum of strains due to each loading step.

$$\varepsilon_1(t) = J(t - \tau_1)\Delta\sigma_1$$

$$\varepsilon_2(t) = J(t - \tau_2)\Delta\sigma_2$$

$$\varepsilon(t) = \varepsilon_1(t) + \varepsilon_2(t) + \cdots$$

$$\varepsilon(t) = \sum_{i=0}^{n} J(t - \tau_i)\Delta\sigma_i$$

$$\varepsilon(t) = \int_{-\infty}^{t} J(t - \tau)\mathrm{d}\sigma \implies \varepsilon(t) = \int_{-\infty}^{t} J(t - \tau)\frac{\mathrm{d}\sigma}{\mathrm{d}\tau}\mathrm{d}\tau$$

So, the Boltzmann superposition principle as we discussed allows the determination of state of stress or strain in a linear viscoelastic material provided the deformation history is known. So, it must be stressed that this principle works only for linear risk elasticity and of course, if the viscoelastic behavior non-linear it is much more complex and the simple models that we have been discussing they will not apply. So, for linear basic viscoelastic behavior then this Boltzmann superposition principle can be applied.

So, let us consider a case where stress is applied in multiple steps to a given sample of a material, and let us see how the strain varies with time and how the Boltzmann superposition principle can be used to obtain the state of strain in the material at a given point of time, with a continuous application of stress which might be changing with time.

So, if we have stress that is varying during the deformation of viscoelastic material, then what this Boltzmann superposition principle says is that the overall strain or the overall deformation in the material is just given by the linear sum of the individual strains the in the material, that are induced in during the different steps of stresses applied. So, the overall deformation is given by the algebraic sum of strains during each loading step.

So, what we are saying is that the stress is being changed step by step and correspondingly strain will develop in the material and it is a viscoelastic material. So, a kind of creep behavior will be sown shown for each step by the application of stress or load or what is the state of strain or the amount of strain developed in the material at a given point of time, that we can obtain as an algebraic sum of all the strains or deformation the material induced due to each of the loading steps up to that point.

So, if we illustrate try to illustrate this with a graphical kind of approach, then what we can say is that let us say we are plotting time on the x axis, and on the y axis if you are plotting stress first, then let us say initially for some time t equal to 0 initially there is no stress and then at time t equal to some value tau 1, let us say a step stress of magnitude delta sigma 1 is applied.

And then again at another time tau 2 another step stress of let us say magnitude delta sigma 2 is applied and so on for different periods of time this the load the stress is being increased in a stepwise fashion. So, for this kind of a loading history Boltzmann superposition principle allows us to calculate the strain at any given point of time, as a linear algebraic sum of all the strains produced by the individual loading steps together and this is something that will allow for apply for a linear viscoelastic material.

So, if we consider this strain at time t you do to this first loading step so, this delta sigma 1 here. So, due to that the corresponding strain produced will be given by a relation that contains the creep compliance that we had just introduced in a couple of slides back, and that creep compliance multiplied by the amount of stress that is applied. So, that is that gives us a strain at any time t after this quantity tau 1; and because this is the time at which this stress delta sigma 1 is applied. So, after at any time t after time tau 1 the strain due to this particular stress delta sigma 1 is given by this expression and this creep compliance will have a value which will correspond to a time of t minus tau 1.

Similarly, for this second load that we are applying the delta sigma to the corresponding strain produced due only to that particular load will be given by again the creep compliance multiplied by the stress ok. So, in a similar fashion if successively further loading is done then for each step the corresponding stress multiplied by the creep compliance, that will give us the contribution of that part of the loading to the strain. So, the overall strain at any time t what the Boltzmann superposition principle says is that that it is the overall strain t at an overall strain at any time t, is given by algebraic sum of all the those individual strains produced by the different loading steps. So, this overall strain epsilon as a function of time is given just by the sum of epsilon 1 epsilon 2 and so, on.

So, if we substitute that then this overall strain is given as a summation over the product of the creep compliance, and the delta sigma corresponding to each loading step and if we have n such loading steps then the overall strain will be given by and the sum of all the corresponding loading steps. So, this is a case if we have a if the stress is being varied in a discreet fashion. So, step wise we are changing the stress. If the stress is changing continuously, then instead of this summation the strain is described using a integral.

So, for a continuous variation of stress, the strain as given me the Boltzmann superposition principle is this integral of again compliance times d sigma. And the lower limit is taken as minus infinity to consider all the entire possible deformation history is that the material has gone through. And this stress that we have; if this stress is changing with time then instead of writing in this rate the strain is more commonly written in a way where the integral is over time. So, that can be done by changing the d sigma to d sigma d tau, and then integrating over this time.

So, that is the expression that we obtain from the Boltzmann superposition principle, if the stress is varying continuously or the loading of the material is being changed continuously. In a similar way the Boltzmann superposition principle can also be applied to obtain the stress developed in a material, if the strain is being changed in either in a stepwise fashion or continuously. So, next let us see how those expressions look like.

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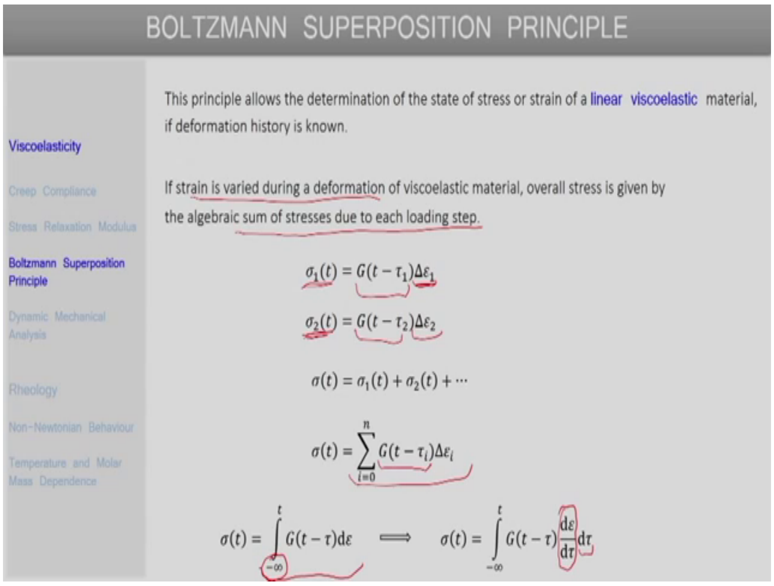

BOLTZMANN SUPERPOSITION PRINCIPLE

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This principle allows the determination of the state of stress or strain of a linear viscoelastic material, if deformation history is known.

If strain is varied during a deformation of viscoelastic material, overall stress is given by the algebraic sum of stresses due to each loading step.

$$\sigma_1(t) = G(t-\tau_1)\Delta\varepsilon_1$$

$$\sigma_2(t) = G(t-\tau_2)\Delta\varepsilon_2$$

$$\sigma(t) = \sigma_1(t) + \sigma_2(t) + \cdots$$

$$\sigma(t) = \sum_{i=0}^{n} G(t-\tau_i)\Delta\varepsilon_i$$

$$\sigma(t) = \int_{-\infty}^{t} G(t-\tau)\,d\varepsilon \implies \sigma(t) = \int_{-\infty}^{t} G(t-\tau)\frac{d\varepsilon}{d\tau}\,d\tau$$

So, if the strain now is varied during deformation of a viscoelastic material, then the state of stress can be defined using this Boltzmann superposition principle as again the linear combination or an algebraic sum of all the individual stresses produced due to due to the individual strains that are being applied so, if each contribution is summed and that gives the overall stress at any time t.

So and the algebraic sum of stresses due to each loading step so, if again for a first loading step strain delta epsilon 1 is there applied when the corresponding stress will be sigma 1, similarly for the next loading step if the strain is delta epsilon 2 then the corresponding stress is sigma 2 and we see that the applied strain and the produced stress they are related by the stress relaxation modulus in this case now. So, the Boltzmann superposition principle again says that the overall stress at any time t is just given with the linear sum of all these individual stresses.

So, that is what we do and for again finite discrete or stepwise change in the strain, we can just write the overall stress as a summation. That summation we can write like this where again the stress relaxation modulus appears here and again as in the previous case if the deformation is history such that the strain is changing continuously, then instead of the summation and integral can be used to describe the state of stress at any point of time t that is given by again this integral, where it is the lower limit in time is from minus infinity to consider the entire possible deformation history again.

And as before if strain is changing with time then the integral is better expressed as an integral over time and that can be done by introducing this derivative d epsilon d tau and then the variable over which integration is carried out is change to this tau. So, these are the couple of ways in which both Boltzmann superposition principle can be applied to obtain either the state of strain on the state of stress in a viscoelastic material provided its entire deformation history is known to us. So, now, what we will do is next we will consider the response of such viscoelastic materials to a oscillating or let us say sinusoidally varying kind of load or deformation.

Till now we have a focused only on loads that are let us say varying linear and linearly or ii let us say if they are constant. So, in a case where the variation of applied load is of an oscillating fashion, then we will see that some interesting kind of behavior is observed and such kind of study forms the area of what is called dynamic mechanical analysis of such materials.

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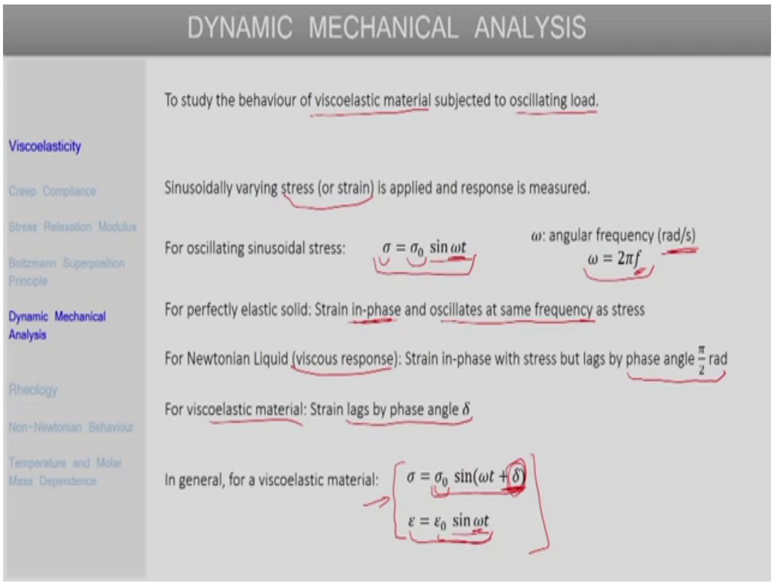

DYNAMIC MECHANICAL ANALYSIS

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To study the behaviour of viscoelastic material subjected to oscillating load.

Sinusoidally varying stress (or strain) is applied and response is measured.

For oscillating sinusoidal stress: $\sigma = \sigma_0 \sin \omega t$

ω: angular frequency (rad/s)
$\omega = 2\pi f$

For perfectly elastic solid: Strain in-phase and oscillates at same frequency as stress

For Newtonian Liquid (viscous response): Strain in-phase with stress but lags by phase angle $\frac{\pi}{2}$ rad

For viscoelastic material: Strain lags by phase angle δ

In general, for a viscoelastic material: $\sigma = \sigma_0 \sin(\omega t + \delta)$
$\varepsilon = \varepsilon_0 \sin \omega t$

And the dynamic mechanical analysis will focus on the behavior of a viscoelastic material that is subjected to an oscillating load as we discussed. So, this oscillating load typically is represented as a sinusoidally varying stress or strain ok. So, in real operation and real applications of viscoelastic polymeric materials also, many times the material or the polymer will be subjected to a load that is changing with time in a kind of with a certain frequency. So, such kind of a load is well replicated by this dynamic mechanical analysis, where a sinusoidally varying oscillating load is considered.

So, the science sinusoidally varying stress or strain is applied, and we measure the strain in these kind of experiments. If we consider a sinusoidally varying stress, then the stress sigma can written simply as a constant sigma naught multiplied by sin of omega t; where this omega is called the angular frequency of variation of this stress and angular frequency the units are radian per second, and its related to the normal the frequency f by this relation omega equal to 2 pi f.

Now, let us see that if the sinusoidal kind of oscillating load is applied then what can we response that can we expect for a different kind of materials. So, if we have a purely elastic material, then in that case the response that we get is that the strain developed also show the sinusoidal kind of a variation and it oscillates with the same frequency as a stress. So, the strain frequency will also be omega and it does not show any phase lag with respect to the stress applied ok.

So, for a perfectly elastic solid the strain will be in phase with the applied stress and it will oscillate at the same frequency of the applied stress. Next if we consider the response of a purely viscous material or purely viscous response to this sinusoidally varying stress then in that case we can consider the case of a simple Newtonian liquid. So, what is observed is that the strain actually lags behind the applied stress in the case of a purely viscous material, and the angle by which the strain or the phase angle which by which the strain lags the stress is 90 degree or pi by 2 radian.

But the strain again also oscillates with the same angular frequency as applied stress. So, the omega is the same, but the strain is not in phase with the applied stress it lags the applied stress by an angle pi by 2 radian. So, that is what we have mentioned here and this is for purely viscous response. Now viscoelastic response what we can expect is that, it will typically lie in between these two extremes of purely elastic and purely viscous response. So, far below viscoelastic materials if sinusoidal kind of load is applied, then the corresponding deformation of strain that also vary sinusoidally used at the same frequency as the applied load, but it lags again lags the stress by some angle.

But this angle typically is between 0 and 90 degrees. So, a lag of 0 degree corresponds to a purely elastic response, a lag of 90 degree corresponds to pure viscous response and for a viscoelastic material this lag or the phase angle by which the strain lags the stress that is between 0 and 90 degrees. So, the strain as we discussed lags by phase angle delta for viscoelastic material.

In general what we can do is that for viscoelastic material we can write the stress and strain variation in this way, where instead of showing the strain by an angle delta we have instead shown that the stresses leading by phase angle delta so, it is equivalent. So, if we consider a sinusoidal stress of this kind then for elastic material the strain will be lagging and we will have to write the strain as epsilon naught sin omega t minus delta; but instead of that what we have done is written the stress as leading the strain by this phase angle delta and both representations are equivalent so, this no issues.

So, the strain is given by epsilon naught sin omega t where again omega is a frequency, and for stress this delta is the phase angle the phase difference between the strain and the stress.

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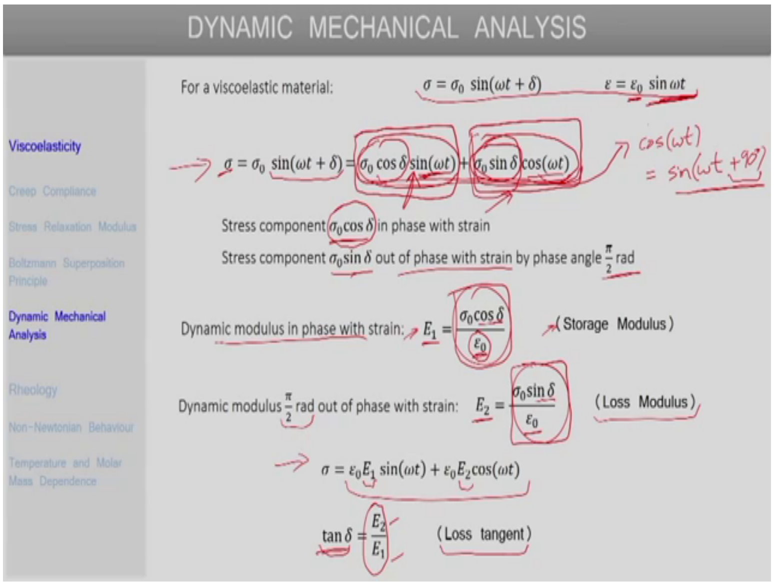

DYNAMIC MECHANICAL ANALYSIS

For a viscoelastic material: $\sigma = \sigma_0 \sin(\omega t + \delta)$ $\varepsilon = \varepsilon_0 \sin \omega t$

$$\sigma = \sigma_0 \sin(\omega t + \delta) = \sigma_0 \cos\delta \sin(\omega t) + \sigma_0 \sin\delta \cos(\omega t)$$

$\cos(\omega t) = \sin(\omega t + 90°)$

Stress component $\sigma_0 \cos\delta$ in phase with strain

Stress component $\sigma_0 \sin\delta$ out of phase with strain by phase angle $\frac{\pi}{2}$ rad

Dynamic modulus in phase with strain: $E_1 = \frac{\sigma_0 \cos\delta}{\varepsilon_0}$ (Storage Modulus)

Dynamic modulus $\frac{\pi}{2}$ rad out of phase with strain: $E_2 = \frac{\sigma_0 \sin\delta}{\varepsilon_0}$ (Loss Modulus)

$$\sigma = \varepsilon_0 E_1 \sin(\omega t) + \varepsilon_0 E_2 \cos(\omega t)$$

$\tan\delta = \frac{E_2}{E_1}$ (Loss tangent)

So, again if we consider these equations for the oscillating load and the corresponding strain produced in a viscoelastic, then this sin omega t plus delta that we can expand. So, if we expand the sin omega t plus delta, this is the expression that we get this is a standard trigonometric expansion sin of a plus b is sin a cos b plus cos a sin b. So, that is what we have done here. And what we can do is now identify these two terms the first term here as well as the second term here as two components of the applied load or the applied stress. So, what we can say is that the first term that we have identified here, that is a component of the applied stress that is in phase with the strain developed the phase difference between this component of the stress and the strain is 0. .

So whereas if we consider the second component of this stress; then that component can be thought of as lagging. So, if you consider the second component that component can be thought of as out of phase with the strain by an angle of 90 degree so, leading the strain by an angle of 90 degrees. So, this component is in phase with the strain and this component of stress is out of phase with the strain by an angle of 90 degrees and that we can say observe by identifying that cos of omega t is simply equal to sin of omega t plus 90 degrees ok. So, that is again a standard trigonometric identity.

So, the second component where this cos of omega t is there is that we can write as sin of omega t plus 90. So, we see that now this component has this extra plus 90 degree that extra phase angle compared to the strain that we have. So, this component leads the strain by an angle of 90 degrees. So, where that whereas, this component of the stress is in phase with the strain. So, the component of stress sigma naught cos delta, that is what we have written that is in phase with the strain whereas, the second component sigma naught sin delta, that is out of phase with the strain by this angle pi by 2 radian.

So, now these two components we can basically write in terms of certain moduli or dynamic moduli and that is what will define next. So, the dynamic modulus that is in phase with the strain now then can be defined as E 1 is equal to this in phase component of stress divided by the amplitude of strain. So, sigma naught cos delta divided by and this dynamic modules that is in phase with the strain that is called the storage modulus usually. Similarly dynamic module that is that is in phase with or out of phase with the strain by an angle pi by 2 radian, that we can define as the second component of this stress by the amplitude of the strain. So, sigma naught sin delta by epsilon naught and that is represented as E 2 and that is usually referred to as a loss modulus.

So, the in phase modulus is a storage modulus and that corresponds elastic response to the deformation whereas, the E 2 which is which we are referring as a loss modulus that corresponds of viscous or dissipative kind of response to the diff deformation applied.

So, these two moduli we can express the overall stress again in terms of E 1 and E 2 in this way based on these two definitions as well as this equation, we can write sigma in terms of E 1 and into E 2 like this.

And also the ratio of E 2 and E 1 that if we take the ratio E 2 and by E 1, then that ratio will be equal to the tangent of the phase angle delta. So, that ratio is the actually an important quantity and that is referred to as a loss tangent. So, this tan delta which is just E 2 by E 1 so, if we divide this expression of E 2 by the expression for E 1 we will get tan delta. So, this ratio of loss modulus to storage modulus is tan delta and this tan delta is referred to as a loss tangent.

So, the two moduli that we have defined here they usually in many cases are combined as a single complex moduli of this form modulus of this form.

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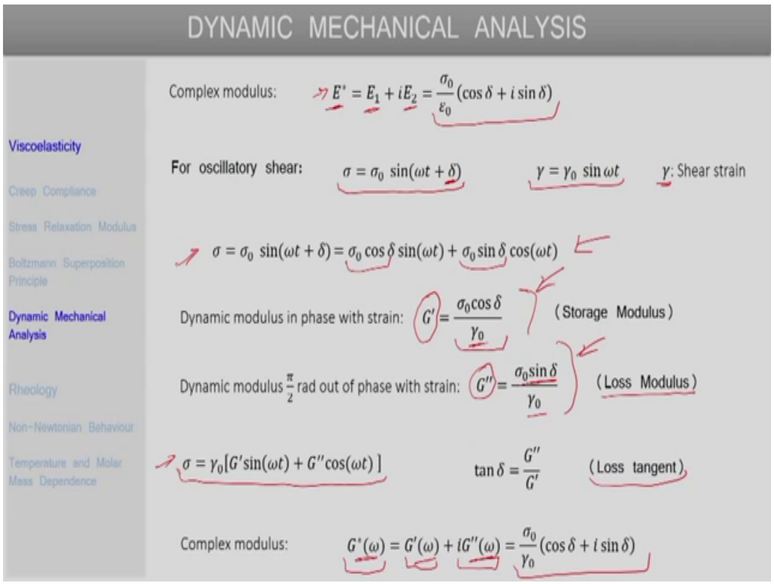

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Complex modulus: $E^* = E_1 + iE_2 = \frac{\sigma_0}{\varepsilon_0}(\cos\delta + i\sin\delta)$

For oscillatory shear: $\sigma = \sigma_0 \sin(\omega t + \delta)$ $\gamma = \gamma_0 \sin\omega t$ γ: Shear strain

$$\sigma = \sigma_0 \sin(\omega t + \delta) = \sigma_0 \cos\delta \sin(\omega t) + \sigma_0 \sin\delta \cos(\omega t)$$

Dynamic modulus in phase with strain: $G' = \frac{\sigma_0 \cos\delta}{\gamma_0}$ (Storage Modulus)

Dynamic modulus $\frac{\pi}{2}$ rad out of phase with strain: $G'' = \frac{\sigma_0 \sin\delta}{\gamma_0}$ (Loss Modulus)

$\sigma = \gamma_0[G'\sin(\omega t) + G''\cos(\omega t)]$ $\tan\delta = \frac{G''}{G'}$ (Loss tangent)

Complex modulus: $G^*(\omega) = G'(\omega) + iG''(\omega) = \frac{\sigma_0}{\gamma_0}(\cos\delta + i\sin\delta)$

So, where E star is a complex modulus and even the storage modulus is expressed as the real part of this complex modulus, and the lost modulus E 2 is represented as the imaginary part of this complex modulus E star. So, if we substitute the expression for E 1 and E 2 we get this expression for the complex modulus.

So, till now we have discussed dynamic mechanical analysis considering the application of certain kind of oscillatory stress. So, if we focus specifically on the application of oscillatory shear stress. So, under oscillatory shear conditions, this expressions that we have developed is known the same expressions will apply only thing is that instead of the strain that we are using specifically the shear strain will appear, and instead the storage and loss moduli that we have discussed, they will be defined in a similar way, but their notations are typically different for studies under oscillatory shear.

So, if you have oscillatory shear then the stress again is the sinusoidal function leading the strain by an angle delta, and for strain we will specifically look at the shear strain the represented by gamma and again stress can be expanded as done previously and we can identify the in phase component and the outer phase component of the stress with respect to the strain.

And the dynamic mod modulus that is in phase with the strain which is the storage modulus that is represented in the case of oscillatory shear by this symbol G prime usually. So, that is again define a sigma naught cos delta by gamma naught. And the modulus that is out of phase or out of phase by pi by 2 radian from the strain that is defined as sigma naught sin delta by gamma naught and this is represented by G double prime typically and this is the corresponding loss modulus.

So, the tan delta again can be defined as a ratio of the lost modulus to storage modulus, and the overall stress also can be expressed in terms of the storage and loss modules like this. So, they are all stress if we just combine these two equations with this equation, we will get the overall stress in terms of G prime and G double prime and tan delta as we discussed is just a ratio of loss in storage modulus, and this is the loss tangent tan delta.

So, this is G double prime by G prime and finally the complex modulus in this case of oscillatory shear can also be defined as that was on previously, and this complex modulus is just G prime plus i times G double prime that is given by this expression. And we see that the moduli that we have these are written as functions of omega or the functions of the applied frequency.

We see in these two equations that G prime G double prime has functions of delta the phase angle. So, it is observed that the phase angle actually is a function of the applied frequency. So, that is why moduli that we have since they are functions of the phase angle they are correspondingly also functions of the applied frequency. So, now, that we have discussed the dynamic mechanical analysis of viscoelastic materials where an oscillatory load is applied and the response is studied, let us briefly discuss a physical significance of some of these quantities.

So, a measurement of these quantities like the storage or loss modulus as well as the loss tangent delta, as a function of the applied frequency allows one to obtain information about the molecular motions that are taking place inside the polymeric sample that is being explored. So, if we have a purely amorphous material, then its relatively more convenient to identify the different types of motion that are taking place with the behavior of these quantities the tan delta as well as E 1 and E 2 with respect to changing frequency.

If you have semi crystalline materials crystalline fraction is also present there, there the analysis becomes more complex so, but for a general let us say amorphous polymeric material, what is observed is that corresponding to molecular motion say taking place inside the polymeric material; the characteristic frequency of that those molecular motions if they correspond to the frequency at which the load is being applied, then quantities like tan delta show characteristic peaks.

So, if we plot 1 tan delta as a function of frequency some peaks are usually observed. So, the large peak in tan delta corresponds to a glass transition in polymeric material, where which marks the onset of significant molecular motion of polymer chains.

Similarly, if we have a small range segmental motion of few bonds concerted motion of a few wants. So, a polymer chain or let us say motion of the side groups of a polymeric material, then such motions will also get reflected in the tan delta graph as some small maxima. And typically instead of studying the variation of this tan delta or E 1 E 2 as a function of frequency, what is done is the variation studied as a function of temperature?

So, temperature can also be varied and variation in temperature actually can produce similar effects as variation in frequency, and again there the temperature at which tan delta shows a maximum that will correspond to the glass transition temperature. So, a glass transition temperature which marks the significant onset of molecular motion, this tan dent delta shows a strong characteristic peak ok.

So, what we see is that these quantities that a study near dynamic mechanical analysis, allows us to explore and study the molecular motion of the polymer chains inside groups.

So, that is why this technique dynamic mechanical analysis is a powerful technique, and useful for studying all the characteristics of polymer molecular motions. So, next let us see if we consider that such a sinusoidal kind of load and use a simple kind of viscoelasticity model that we had developed in the previous lecture, we let us try and see what kind of predictions are made or what kind of for expressions that we obtain.

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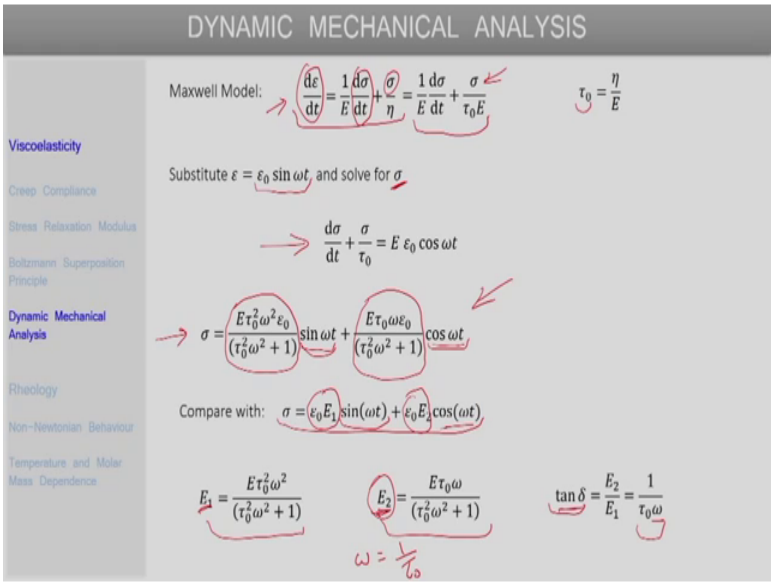

DYNAMIC MECHANICAL ANALYSIS

- Viscoelasticity
- Creep Compliance
- Stress Relaxation Modulus
- Boltzmann Superposition Principle
- Dynamic Mechanical Analysis
- Rheology
- Non-Newtonian Behaviour
- Temperature and Molar Mass Dependence

Maxwell Model: $\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\tau_0 E}$ $\tau_0 = \frac{\eta}{E}$

Substitute $\varepsilon = \varepsilon_0 \sin\omega t$, and solve for σ

$$\frac{d\sigma}{dt} + \frac{\sigma}{\tau_0} = E\,\varepsilon_0 \cos\omega t$$

$$\sigma = \frac{E\tau_0^2\omega^2\varepsilon_0}{(\tau_0^2\omega^2+1)}\sin\omega t + \frac{E\tau_0\omega\varepsilon_0}{(\tau_0^2\omega^2+1)}\cos\omega t$$

Compare with: $\sigma = \varepsilon_0 E_1 \sin(\omega t) + \varepsilon_0 E_2 \cos(\omega t)$

$E_1 = \frac{E\tau_0^2\omega^2}{(\tau_0^2\omega^2+1)}$ $E_2 = \frac{E\tau_0\omega}{(\tau_0^2\omega^2+1)}$ $\tan\delta = \frac{E_2}{E_1} = \frac{1}{\tau_0\omega}$

$\omega = 1/\tau_0$

So, if we consider the Maxwell model that we have we had developed in the previous lecture, there the rate of change of strain is related to the rate of change of stress as well as the stress by this expression. And if we introduce that the quantity tau naught as eta by E, where tau naught is the relaxation time corresponding to this model, then we can write the Maxwell model; equation for this Maxwell model in this way.

So, now let us see what happens if an oscillatory kind of load is imposed on this Maxwell model. So, if we consider epsilon as epsilon naught sine omega t so, an oscillatory kind of strain and try to solve for this quantity sigma that is the stress using Maxwell models.

So, we will get this ordinary differential equation again, and this equation is also a first order linear ordinary differential equation, which can easily be solved by the method of integrating factors. So, by applying that method and solving this equation the expression for stress that we get, looks something like this and it contains these two terms when having the sin omega t and the other having cos omega t terms present.

So now if we compare the expression that we obtained from the Maxwell solution of the Maxwell model to the expression for this oscillatory shear stress which as discussed a couple of slides back is this so if we compare these two and try to relate the sin omega t term here with the sin omega t term here. So, we will see that this term we can say has been equal to this term here, similarly this term which is the pre factor for the cos omega t that we can say is has been equal to this term here. So, using this kind of comparison, we can obtain expressions for E 1 and E 2 which are the storage and loss moduli.

So, the storage mo modulus as predicted by the Maxwell model is given by this expression loss modulus by this expression, and if we take the ratio E 2 by E 1 that gives the loss tangent tan delta and in Maxwell model, that tan delta is given by 1 over tau naught omega. If we now try to let us say plot these quantities E 1 E 2 which is the story in loss moduli or the tan delta as a function of omega, then what we will see is that E 1 actually shows an increase with increasing omega which is reasonable representation of the behavior observed in actual viscoelastic materials.

E 2 actually shows a peak or a maximum at a certain tau omega value tau naught omega value. So, at omega is equal to 1 by tau naught at that condition or at that value of frequency, in this E 2 shows a peak the fact that E 2 verses omega plot shows a peak for this Maxwell model that is also inline with experimental observations.

However, if we see tan delta as a and if you plot it as a function of omega will see that, tan delta continuously decreases as omega is increased, and that is something which is not very consistent with experimental findings where tan delta is shown to exhibit a maximum particularly at the corresponding to the glass transition. And for some other transitions in molecular motions also some other maximum values of tan delta peaks in tan delta can be obtained. So, we see that the maximum model although it captures the behavior of change in storage and loss moduli with omega to a reasonable extent, but it is not able to capture the behavior of tan delta with omega ok.

So, the since the Maxwell model is relative simple model, we do not expect it to capture all the physical phenomenon and the tan delta behavior is not captured well. Instead if we used the standard linear model and try to again solve the equation for an oscillatory kind of load then the tan delta p can other characteristics may be observed as well. So, this here was just a simple illustration of what happens when an oscillatory load is imposed on a simple model of polymer viscoelasticity and with this discussion we will conclude our discussion on viscoelasticity of polymeric materials, and move on to briefly discuss the rheological and flow behavior of polymeric liquids particularly polymer melts.

So, if we consider the polymeric liquids like polymer solutions or polymer melts, in general at reasonable reasonably large values of shear rates these materials show what is called non Newtonian behavior. So, to understand on it and behave it let us just first recap what the Newtonian behavior looks like mathematically.

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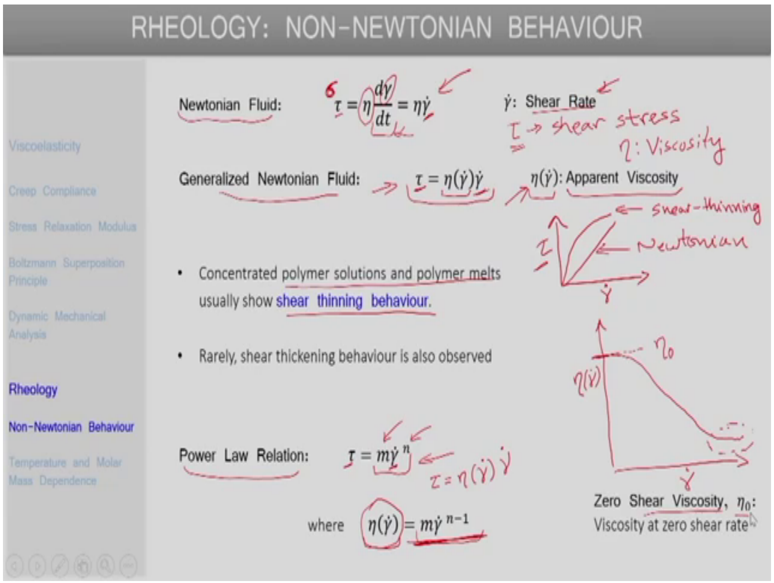

RHEOLOGY: NON-NEWTONIAN BEHAVIOUR

Newtonian Fluid: $\tau = \eta \frac{d\gamma}{dt} = \eta\dot{\gamma}$

$\dot{\gamma}$: Shear Rate

$\tau \rightarrow$ shear stress

η: Viscosity

Generalized Newtonian Fluid: $\tau = \eta(\dot{\gamma})\dot{\gamma}$

$\eta(\dot{\gamma})$: Apparent Viscosity

- Concentrated polymer solutions and polymer melts usually show shear thinning behaviour.
- Rarely, shear thickening behaviour is also observed

Power Law Relation: $\tau = m\dot{\gamma}^n$

$\tau = \eta(\dot{\gamma})\dot{\gamma}$

where $\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1}$

Zero Shear Viscosity, η_0: Viscosity at zero shear rate

So, Newtonian fluid is defined by a fluid where the shear stress tau. So, here we are using tau for the shear stress. So, instead of tau we can also use sigma, we have been using sigma in general for the stress in our discussion. So, whether its tau sigma it is equivalent. So, so for a Newtonian so, it that is proportional to the shear rate. So, this gamma is a shear strain and if tau is the shear stress. So, here let us say we are representing the shear stress by tau, with the knowledge that previously we have used the symbol sigma for the shear stress as well so, but in the discussion of flow behavior of liquids typically shear stress is many times expressed as tau. So, that is what we will use here.

So, it is proportional to directly proportional to the shear rate or rate of change of shear strain with time that this quantity and the proportionality constant is this quantity eta which is referred to as a viscosity of the Newtonian liquid. So, we can write this tau or the shear stresses simply eta times gamma dot, where gamma dot is there a time derivative of gamma which is the shear strain. So, gamma dot is referred to as shear rate.

So, for Newtonian liquid the viscosity of the quantity eta is a constant it does not change with the shear rate. So, for many liquids with non-Newtonian kind of behavior is observed where the viscosity actually changes with shear rate. So, an extension of this Newtonian kind of behavior is what is called the generalized Newtonian fluid behavior.

The relation between the shear stress and the shear rate is given by a form that is similar to the Newton's law of viscosity. But now the viscosity eta is allowed to be a function of the shear rate. So, for a generalized Newtonian fluid, the viscosity is a function of the shear rate, but the mathematical form of the relation between shear stress and shear rate that is identical to what we have for the Newton's law of viscosity.

And this viscosity which is a function of shear rate, that is referred to as the apparent viscosity and this kind of a model can capture the behavior of non-Newtonian many non-Newtonian fluids. So, for the case of polymeric fluids that is the polymer melts, it what is typically observed is that the behavior non-Newtonian behavior that the exhibit is of the shear thinning kind. So, constant polymer solutions and melts typically show shear thinning behavior, in some cases in rare cases shear thickening behavior can also be observed. So, for some polymeric liquids, but mostly shear thinning behavior is observed. So, we will focus on the shear thinning behavior

So, by shear thinning what we mean is as the shear rate is increased, the viscosity of the material actually decreases. So, this decrease in viscosity with increase in shear rate that is characteristic of a shear thinning fluid. And for a shear thickening fluid correspondingly the viscosity increases as the shear rate is increased. So, if we try to let us say plot the shear stress tau against the shear rate gamma dot, for a Newtonian fluid it will be straight line, for a shear thinning fluid it will be a curve that looks like this. So, the slope of this curve keeps decreasing as a shear rate increases. So, correspondingly the viscosity keeps on decreasing as the shear rate increases.

So, this is the shear thinning behavior and many polymeric liquids are shown to exhibit this kind of a behavior. So if we now try and plot the change in viscosity with shear rate ok so, here we have plotted chain in the shear stress with shear rate, and this straight line is Newtonian. So, if you plot the change in viscosity or the apparent viscosity with shear rate this apparent viscosity, then for Newtonian fluid this viscosity will be a constant so, we will get a horizontal line; but for a shear thinning fluid like a polytypical polymeric fluid let us say. Initially we will get a horizontal line at small shear rates and at higher shear rates it will decrease at very high shear it might also again become horizontal.

So, at very low shear rates polymeric liquid can behave kind of like a Newtonian fluid, but as the shear rate is increased and the polymer chains tend to elongate, and that will lead to a shear thinning kind of behavior where the viscosity of the material decreases. And at very high shear rates almost all polymer chains are well aligned in the flow direction, again the viscosity becomes pretty much constant, but the viscosity value will be very low and that is what is shown by this constant at very high shear rates. The shear thinning kind of behavior of polymeric liquids can be well captured by a model that is called the Power Law relation so, a power law fluid model.

So, here the shear stress tau is related to the shear rate gamma dot by this power law kind of expression where the m and n are characteristic parameters of this Power Law equation. So, now, if we try to identify the apparent viscosity in this equation, then apparent viscosity eta as a function of gamma dot we can just write it as m multiplied by gamma dot to the power n minus 1. Because if we write apparent viscosity in this way, then for a power law fluid also we can then write the shear stress as just this apparent viscosity multiplied by the shear rate ok.

So, apparent viscosity for power law fluid is defined like this and finally, the viscosity at very small or almost zero shear rates here, that is denoted many times via the symbol eta naught and that is called the zero shear viscosity it corresponds to the viscosity of the fluid at almost the zero shear rates.

So, this power law fluid model is reasonably good model to describe the shear thinning behavior of many polymeric liquids, and the study of the flow behavior of polymeric liquids is important particularly in polymer processing operations where, the molten polymer is subjected to high shear rates, and the flow behavior can actually affect the quality of product that we get. So, the rheology and the flow behavior of polymer liquids it study is important from that perspective.

Finally let us look at how the viscosity of this polymeric materials or polymeric liquids um changes with temperature, and what is the dependence on the molar mass of polymer as well ok. So, if we are talking about a polymeric material and it is above its glass transition temperature, then the change in viscosity can be related to the glass transition temperature using an equation called the Williams Landel Ferry equation or the WLF equation.

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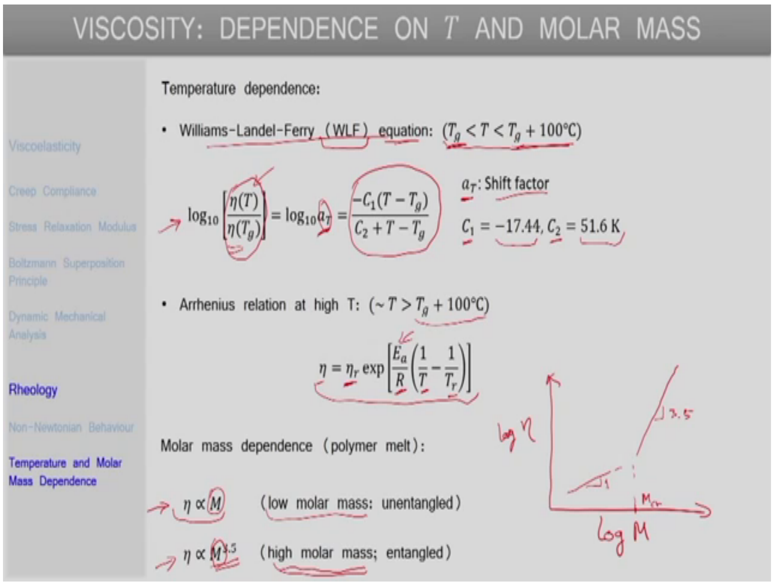

VISCOSITY: DEPENDENCE ON T AND MOLAR MASS

Viscoelasticity

Creep Compliance

Stress Relaxation Modulus

Boltzmann Superposition Principle

Dynamic Mechanical Analysis

Rheology

Non-Newtonian Behaviour

Temperature and Molar Mass Dependence

Temperature dependence:

- Williams-Landel-Ferry (WLF) equation: $(T_g < T < T_g + 100°C)$

$$\log_{10}\left[\frac{\eta(T)}{\eta(T_g)}\right] = \log_{10} a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g}$$

a_T: Shift factor

$C_1 = -17.44, C_2 = 51.6\ \mathrm{K}$

- Arrhenius relation at high T: $(\sim T > T_g + 100°C)$

$$\eta = \eta_r \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right]$$

Molar mass dependence (polymer melt):

$\eta \propto M$ (low molar mass: unentangled)

$\eta \propto M^{3.5}$ (high molar mass; entangled)

And it is typically valid for a temperature range between the glass initial temperature of the polymer and up 100 degrees above the glass transition temperature.

So, the expression for this via WLF equation is something like this; log 10 of eta or the viscosity at any given temperature by the viscosity at the glass transition temperature that is equal to this quantity here. Where the C 1 and C 2 are observed to be constant for most many polymers and the universal values of these constants are minus 17.44 and 51.6 Kelvin. Now this ratio that we have here this ratio is also referred to as a Shift factor 80. So, 80 is nothing, but the ratio of the in this cases this particular case is a ratio of the viscosity at temperature t by the ratio of the viscosity of the polymeric material that its glass transition temperature.

So, this shift factor 80 is actually an important parameter and the WLF equation that we have written specifically for viscosity it is a more general kind of equation which appears in the study of what is called time temperature superposition behavior of polymeric materials. So, will not go into the details of such behavior, but it is important to know that this WLF equation is, more general in applicability; and one can specifically apply it to the viscosity change with temperature, but other effects can also be captured using this WLF equation.

So, for this viscosity change the shift factor 80 is just the ratio of the viscosity. If the temperature is much higher than the glass transition temperature so, if we are much higher above more than 100 degree celsius above glass transition temperature, then it is proposed that an Arrhenius kind of relationship actually better describes the viscosity change with temperature. So, this Arrhenius relationship is given by the relation of this kind where R is the universal gas constant, E a is some kind of activation energy, eta r is the viscosity at some reference temperature T r and eta is the viscosity at temperature T. So, these are some expressions relating viscosity to temperature.

We can also discuss the relationship between viscosity and molar mass of polymers, because it is observed that the polymer molar mass actually has a very strong effect on the viscosity of polymers. So, if you are talking polymer melts then at for low molar mass polymeric materials, where the entanglement of polymer chains is negligible; such cases the viscosity is seen to be proportional directly to the molar mass itself whereas, if the molar mass is crosses above some critical value of molar mass value, the viscosity actually is seen to depend very strongly on molar mass.

So, for high molar mass polymers the viscosity is seen to be proportional to M to the power 3.5 or 3.4 something in that approximate range. So, for this high molar mass polymers were where entanglement effects are strong, there the viscosity scales very strongly with the molar mass. Typically there is some critical molar mass below which entanglement effects are negligible and we have this kind of relation between eta nm and above this critical molar mass where entanglement effect of long polymer chains started to dominate the stronger relationship between the viscosity and molar mass is observed.

So, if we plot let us say this log of eta versus log of molar mass, then at for small molar mass values low slope is observed and, but at higher molar mass values that the slope of this curve will be much higher, it will be around 3.4 or 3.5 that will be the slope and low molar mass will have around a slope of 1; and these slopes correspond to the exponents of this quantity I mean these relations. And at some critical molar mass let us say some m critical molar mass this transition behavior is observed and that typically marks the onset on scent of a chain entanglement because that molar mass increase leads to longer chains which have a greater tendency to get entangled.

So, with that we will conclude this discussion of polymer viscoelasticity as well as brief discussion of polymer rheology and non-Newtonian flow behavior; and what I will do is leave you with this video which is a very nice illustration of the interesting effects that can be observed because of the viscoelastic and non-Newtonian nature of polymeric liquids.

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Source: https://nnf.mit.edu/home/billboard/topic-5 (accessed on 20 July 2018)
(Hatsopoulos Microfluids Laboratory, MIT)

So, if we look at this video, we have a liquid filled inside a beaker and it rod is placed inside the liquid and the rod is being rotated at high speed. So, for a Newtonian liquid what one would observe is that, if the rod is rotated at high speed then the liquid will typically move towards the periphery of the beaker and rise and get depressed at the center near the rod, because of inertial effects.

But for polymeric liquids because of the viscoelastic nature, there is some normal stresses present which lead to rise in the polymeric liquid on the rotating rod that we have. So, this effect is known as the rotating rod or Wiesenberger effect; in this particular video as mentioned is taken from a source which is the website of Professor Hatsopoulos at MIT. So, it very nicely illustrates very interesting kind of flow behavior of a viscoelastic polymeric liquids where the liquid tends to climb on top of a rotating rod.

That will conclude our lecture for today and hopefully these last couple of lectures have introduced you to the concept of viscoelasticity as well as how it applies to the mechanical response of polymeric materials.

In the next lecture we will look at another interesting kind of mechanical behavior of polymers, in particular that of rubbery cross link polymers, and that behavior is what is called a rubber elasticity.

Thank you.