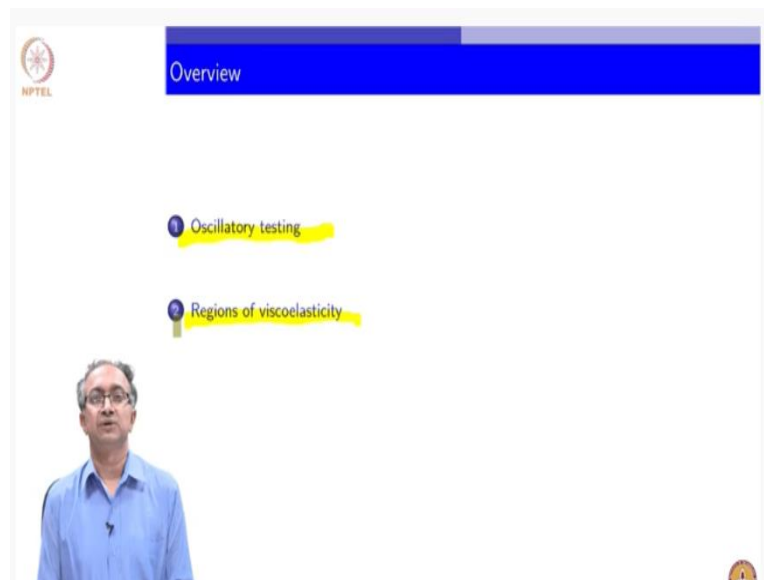


Polymers: Concepts, Properties, Uses and Sustainability
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Lecture – 49
Dynamic Mechanical Analysis

Hello welcome to another lecture on viscoelasticity in polymers there are several aspects of viscoelasticity that we are discussing from linear analysis that is useful for analyzing small deformation viscoelasticity which we term as linear viscoelasticity. We looked at experimental protocols which are used at arriving at an understanding of micro molecular viscoelasticity. We also looked at simple models such as Maxwell and Voigt which are used to compare the real material response with respect to the idealized response that these models represent and all of this can be done in set of instruments which are called dynamic mechanical analysers or rheometers. So, for more solid like materials we generally tend to use the term DMA which we use for analyzing the dynamic response of these viscoelastic polymeric systems for fluid like systems we tend to use the dynamic shear rheometer or just a rheometer. So, our focus now has been to look at properties of these viscoelastic materials and dynamic mechanical analysis is a powerful tool to characterize the properties of viscoelastic materials.

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And we will look at this by first looking at the predominant mode of testing which is used in dynamic mechanical analysis which is oscillatory testing and we look at results of the oscillatory test on a set of polymers and see how the overall response of dynamic mechanical analysis is closely related to what type of polymeric material we have.

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Oscillatory testing

Oscillatory shear

Shear

For small deformations or in linear regime

Periodic mechanical stimulus \rightarrow sinusoidal variation

$$\gamma = \gamma_0 \sin \omega t \quad (1)$$

Stress response

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (2)$$

Elastic $\sigma = \tau_0 \sin \omega t$

$$\tau = G'(\omega) \sin \omega t + G''(\omega) \cos \omega t \quad (3)$$

$\tan \delta = \frac{G''}{G'}$

G' Storage modulus, G'' loss or viscous modulus and δ phase lag

So, let us begin by defining the oscillatory response. In this lecture I am using a notation which is associated with shear deformation. So, as I outlined in the lectures where we talking about experimental protocols the 45th and 46th lectures we talked about different geometries and different sample shapes which can be used and different modes of deformation that can be used. So therefore, tension is used quite often for solid like materials but shear can also be used depending on the application requirements. So, γ is usually indicated as the shear strain and so a sinusoidal input is given where γ varies as a function of time and the amplitude of the variation is γ_0 and the stress response which is the measured quantity is also sinusoidal and because it is a linear response.

The response is at the same frequency as the input is however there is a phase lag and so if we were to plot the same response basically, we will get a response which is slightly shifted in phase and so therefore it will be 0 at different magnitudes and depending on the scale how we are drawing again that may also vary. So, therefore there is a phase lag between the stress and the strain if it is a perfectly elastic material then of course we know that

$$\tau = \tau_0 \sin \omega t$$

So, there would not be any phase lag. So, therefore this phase lag is an indicator of the elasticity and viscous contributions and you can using the standard trigonometric formulas of Sin a Cos b you can split the overall stress into two parts one which is in phase with strain and other one which is $\pi/2$ out of phase or 90 degrees phase difference. This coefficient which signifies the in phase response which is like the elastic response is called the storage modulus (G'). Because elasticity implies energy storage and therefore G' quantifies the storage like contributions/mechanisms in the material while G'' quantifies the viscous or the loss like

contributions and δ which is more often represented as $\tan \delta$ so that it varies between 0 and infinity so $\tan \pi/2$ being infinity $\tan 0$ being 0. So, this is basically the ratio of the loss modulus to the storage modulus and all of these are functions of frequency.

So again, the idea behind this oscillatory dynamic test is to vary the time experimental time scale as we saw in case of creep or stress relaxation, I can do creep experiment for 1 hour or I can do it for 10 years or I can do it for milli second. So that is the way the experimental time scale can vary. In case of oscillatory shear by changing the frequency the time scale can vary so if I do very small low frequencies then material gets enough time just the way year would give material enough time to respond if I do frequency very fast high frequency then I am not giving material enough time and that is like doing experiments at short time scales.

So, therefore dynamic tests can be done very easily and nicely using an oscillatory kind of an experiment we can do both shear or flexural or tension any of these only things that generally you will find different is the symbols that are used but otherwise conceptually it remains precisely the same formulation you can also have the same formulation where stress is being applied and strain is being measured.

So therefore, stress may be talked about as

$$\tau = \tau_o \sin \omega t$$

and then strain may be measured as

$$e = e_o \sin(\omega t + \delta)$$

So, in this case we can define compliance for example so here we define G' and G'' which are moduli if we look at stress as an input variable and strain as an output variable then strain divided by stress is compliance and then we can define in phase compliance or storage compliance and out of phase compliance and loss compliance very similar to what we have done.

So, I leave it as an exercise that you can think how viscosity can also be done similarly. So, this we will discuss when we will discuss processing because during melt processing and during moulding operations the polymeric liquids have to be handled and many of them have both viscous and elastic contributions and analysis of that can be done using in phase viscosity and out of phase viscosity. So, just think about how similarly using these variables what would you use as input to define η' and η'' and what would you use as output to define η' and η'' . We will come to this much later when we discuss processing and rheology of materials polymeric materials.

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Oscillatory testing

Maxwell model in oscillatory shear

$$\tau(t) = \gamma_0 \left[\frac{G_{\max} \omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \sin \omega t + \frac{G_{\max} \omega \lambda}{1 + \omega^2 \lambda^2} \cos \omega t \right] \quad (4)$$

in-phase $\frac{\pi}{2}$ phase difference

First term → the elastic contribution to stress, as it is in phase with strain, $G' \propto \omega^{-1}$
 Second term → the viscous contribution. $G'' \propto \omega$

$$G' = \frac{G_{\max} \omega^2 \lambda^2}{1 + \omega^2 \lambda^2}; \quad G'' = \frac{G_{\max} \omega \lambda}{1 + \omega^2 \lambda^2}; \quad \tan \delta = \frac{1}{\omega \lambda} \quad (5)$$

$\omega \lambda \rightarrow \text{very large} \rightarrow G' \sim \frac{G_{\max} \omega^2 \lambda^2}{\omega^2 \lambda^2} \simeq G_{\max}$
 $\omega \lambda \rightarrow 0 \Rightarrow G' \sim G_{\max} \omega^2 \lambda^2 \Rightarrow G' \propto \omega^2$

So, let us look at the oscillatory response of Maxwell model given that we have already seen that it is an exponential decay for stress relaxation and that decay pretty much depends on lambda at the relaxation time and based on the relaxation time the material is predominantly viscous or elastic. So, we will see very similar feature here that depending on the value of lambda and the relative value of omega that is being applied we will again see more relatively higher elastic contributions or lower elastic contributions.

So, the overall stress if we solve that ODE of Maxwell model with the condition that we just talked about here that we are applying a strain which is

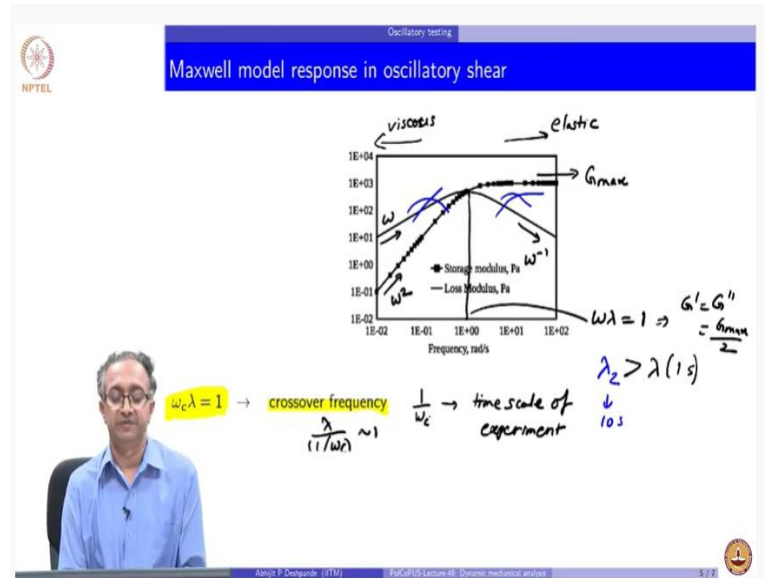
$$\gamma = \gamma_0 \sin \omega t$$

the solution is given in equation 4. So it is a time series with both Sin and Cosine function so there is an in phase part with the input strain and there is out of phase or $\pi/2$ phase difference part and so this of course is G' and G'' is the loss modulus which is signifying the viscous contribution and if you look at how G' varies we can look at this $\omega \lambda$ as a combination because if you see everywhere it appears as a combination. So if $\omega \lambda$ is very large what happens then you can pretty much ignore this one $\omega \lambda$ let us say is 100 then 100 and 101 is very similar so in therefore in that case what happens to G' will become $G_{\max} \omega^2 \lambda^2$ divided by $\omega^2 \lambda^2$ because we can pretty much ignore 1 and so therefore this becomes G_{\max} .

So, G' becomes constant and that is an sign of elastic response. So higher frequencies we get elastic response from the Maxwell model what happens at very low frequencies when we have very low frequencies then $\omega \lambda$ is very small so in that case what we will have is $\omega \lambda$ can be ignored as comparison to 1 and so therefore G' will be $G_{\max} \omega^2 \lambda^2$.

So actually, in this case G' is proportional to ω^2 . So, for a viscous response G' will be proportional to ω^2 and so this is a Maxwell model response if you look at the G'' you will see that G'' is proportional to ω^{-1} and its proportional to frequency when it is very high frequency and very low frequency. So, you can again do the similar exercise and try to justify this.

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And we can look at the overall response where G' increases as ω^2 then it becomes constant which is the G_{\max} value. G'' on the other hand increases with ω but later it decreases as ω^{-1} and in between we have a point where $\omega\lambda = 1$. In this case G' is equal to G'' and both of them are actually equal to $G_{\max}/2$. Because if you have $\omega\lambda = 1$ then G' as well as G'' are $G_{\max}/2$. So therefore, one side of the frequency we have elastic response from the Maxwell model this side of the frequency where $\omega\lambda = 1$ we have the viscous response. So, that is the meaning of time scale of experiment and the material time scale. So, if ω is very small then because λ is a given value, we see largely viscous response.

So, if I do the same experiment on a material where λ is different then what will happen is the overall set of curves will shift to the left or right. So, let me ask this question let me pose this question and you think about it if I now let us say choose a material which has a different relaxation time let us call it λ_2 and let us say this $\lambda_2 > \lambda$ so we have already plotted this curve for λ . So now let us say λ is somewhere around 1 because at frequency of 1, $\omega\lambda=1$. So, λ is basically nothing but 1s. So now let us say λ_2 which is greater is 10. So, according to the Maxwell model how would the G' , G'' look like and you can think about it the overall shape and overall because G_{\max} is let us say remains the same overall shape will still remain the same the value of G' , G'' at the crossover point will also remain the same.

So the question that you have to try to answer is will the curve come here and this is where the crossover point will be or will the curve come here and this is where the crossover point will be and this if you are able to answer then you will know what is meant by time temperature superposition also. Because different value of λ also implies same material but at different temperature. So, if I decrease the temperature on the material the relaxation time may increase from 1 second to 10 second. So, I can do the experiment on the same material at different temperatures and I will get different responses but I can shift them parallelly with respect to each other and obtain a master curve. So, this is the idea which is exploited in time temperature superposition as we will see later on.

So, this value where $\omega\lambda$ is 1 is called the crossover frequency because it indicates the time scale of experiment which is $1/\omega_c$. So $1/\omega_c$ which is the time scale of experiment and the λ is the material time scale. So, $\lambda/(1/\omega_c)$ this is equal to one at the crossover frequency. So, therefore both of them are similar orders of magnitude.

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So, in a dynamic mechanical analysis we are able to do this experimentally and a dynamic mechanical analyser can do this oscillatory testing on polymeric and other samples and generally we have all the different modes that we spoke about there can be flexural mode which is quite common we can have basically tensile mode or shear mode.

So, depending on the application any of these modes are possible geometry is quite often a rectangular sheet so with a very small thickness and significant width and much higher length generally the frequency of a dynamic mechanical analyser goes from a millihertz to somewhere around 100 to 200 hertz because this is a mechanically vibrating system we cannot achieve

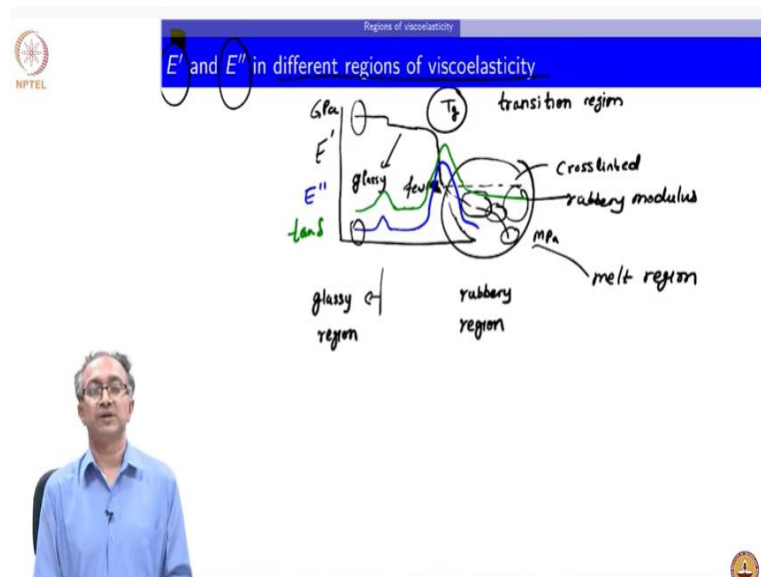
much higher frequencies if you want to achieve higher frequencies then you require much more specialized instruments that can do testing at around kilohertz.

What we will see in damping applications is many times the vibrations have to be damped which are at kilo hertz and those kinds of frequencies. So, that those kinds of measurements cannot be done in a dynamic mechanical analyser however since we can do time temperature superposition or frequency super frequency temperature superposition, we can by doing this superposition we can obtain response at variety of frequencies.

And we can as we discussed have stress as an input or a strain as an input and therefore conversely strain can be the output or stress can be the output and generally the temperature ref difference is from - 150 to about 600 degree Celsius which is the temperature of interest for most polymeric system I do not know if you can think of why would one want to measure properties at - 100 degree Celsius for a polymeric system and that depends on cryogenic applications.

And let us say if it is a gasket being used, we would make sure want to make sure that the gasket remains in rubbery state at even lower temperatures and so for many rubbers like samples it is of great interest to measure properties at extremely low temperatures.

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So, now we will close this lecture by just looking at both this storage modulus and the loss modulus as a function of temperature for some variety of polymers. So, for example if we look at E' and we start from a very low temperature and start measuring we may see that there is a small change in E' and as soon as there is associated with a small change, we know that this is not associated with glass transition temperature.

Because loss transition temperature because of the segmental mobility being allowed the change in storage modulus is magnitude is higher. So, therefore this could be a sign of beta gamma transition which is their secondary transitions and when we have a very drastic change this is where the glass transition of the material is and then as we saw in the previous lecture where depending on the type of material that exists we could have a variety of responses and so all of these responses indicate whether the material is cross linked polymer.

Because in case of crosslink polymer the cross links will make sure that no macromolecular flow is possible and therefore there is a rubbery modulus which will continue. So, this is the glassy modulus and this is the rubbery modulus and if we have crystalline sample then again the crystalline samples will play the role of junctions and therefore again some amount of modulus will be there but if it is an amorphous polymer the decrease may be much more rapid because molten polymer will not really have a higher amount of E' .

So, we are looking at basically giga pascals of modulus when we have the glassy state and then when we look at the molten state it is mega pascal so therefore there is an order of magnitude change and this also could be in terms of few mega pascals. So, there is a drastic change in modulus as temperature increases correspondingly if you look at E'' . So, that also shows changes where associated with secondary relaxations there will be a maximum and then there will be another maximum associated with the glass transition.

So, whenever there is dissipation associated with a relaxation mechanism we see a corresponding peak in E'' and similarly if we look at tan delta also tan delta may also show some features which are very similar in qualitative way to so this is how we can look at different regions of viscoelasticity in a polymeric material we have basically glassy state or the glassy region. Then we have a transition region and this transition region can be about 20, 30 degree Celsius because of the kinetic effects associated with the glass transition temperature this is not a sharp thermodynamic transition like a melting temperature and therefore the changes can happen gradually and the transition region itself is reasonably wide for many of the polymeric system then we have the rubbery region. And then finally we have the melt region and depending on the type of melt it is we can have a flow which is more restricted flow and a flow which is more allowed flow because if crystalline portions are there then the flow is restricted and if more entanglements are there then flow is restricted. So, therefore the melt region itself can be split in further regions depending on the microstructural features which are present.

So, you can see that different regions of viscoelasticity can be used analysed using this dynamic mechanical analysis and other feature that you can see is the domination of elastic in the glassy region and domination of the loss modulus in the viscous region. So, as the temperature goes

up as thermal energy becomes more and more accessible to the macromolecules more and more relaxation processes can happen and dissipative response is observed while at lower thermal energy at lower temperature more elastic response is observed.

So, therefore DMA is very excellent instrument to try to analyse the viscoelastic response using oscillatory as well as creep and stress relaxation experiments that we talked about earlier and is basically a workhorse to try to characterize the overall viscoelastic response of polymeric systems. So, with this we will close this lecture and we will continue our discussion related to viscoelasticity with looking at damping response in one of the next lectures. Thank you.