Introduction To Polymer Science

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Lecture-39
Thermomechanical Properties, Viscoelasticity (Contd.)

Welcome back, in this lecture I am continuing my discussion on viscoelastic properties of polymers.

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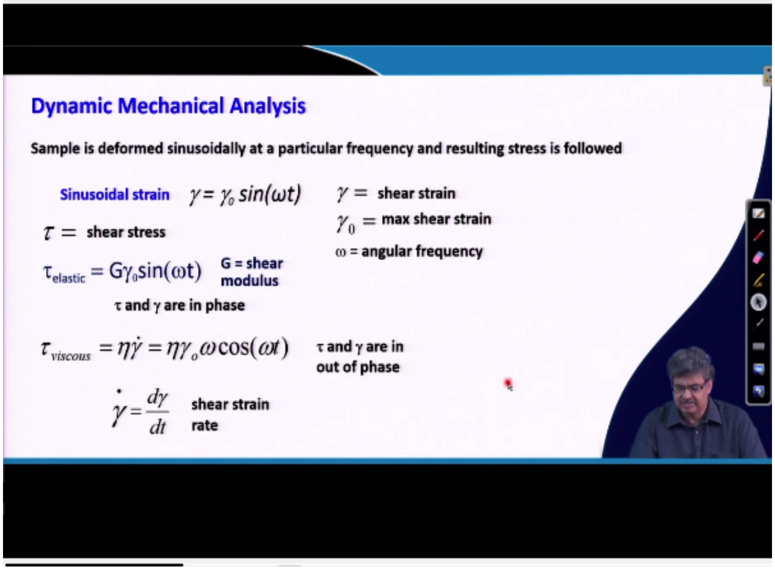

Dynamic Mechanical Analysis

Sample is deformed sinusoidally at a particular frequency and resulting stress is followed

Sinusoidal strain $\gamma = \gamma_0 \sin(\omega t)$

$\gamma =$ shear strain

$\gamma_0 =$ max shear strain

$\omega =$ angular frequency

$\tau =$ shear stress

$\tau_{elastic} = G\gamma_0 \sin(\omega t)$ G = shear modulus

τ and γ are in phase

$\tau_{viscous} = \eta\dot{\gamma} = \eta\gamma_o\omega\cos(\omega t)$ τ and γ are in out of phase

$\dot{\gamma} = \frac{d\gamma}{dt}$ shear strain rate

In last lecture, I have discussed that polymers are generally viscoelastic material, which means that depending upon the temperature and the deformation rate polymers can show a solid like behaviour to a liquid like behaviour. We can quantify this viscoelastic behaviour by experiment called dynamic mechanical analysis. In this experiment, the polymer sample or any other sample is deformed sinusoidally at a particular frequency and the resulting stress is followed.

So, basically you take the sample and you apply a strain sinusoidally at a different frequency. Now, the strain could be a tensile strain or it could be a shear strain, and depending upon that particular experiment, we can define the modulus like shear modulus or a tensile modulus and so on. The other types of deformation can be also applied sinusoidally to the samples as well. Now, if we apply the strain, then we can apply the strain as a function of sine function of angular frequency and time

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

γ shear strain, γ_0 is maximum shear strain and ϖ is angular frequency, we can use other strain as well like elastic strain. In that case, you can just replace this shear strain with tensile strain and corresponding tensile stress as well. Now, if this is strain, then corresponding shear stress can be like this, if this is a complete elastic material perfect solid. Then the stress will be proportional to the applied strain, $\tau_{elastic} = G\gamma_0 \sin \omega t$. So, the stress will be proportional to the strain and G is the proportionality constant, which is nothing but modulus and in this case, we are applying shear strain. So, this G is shear modulus. If we are applying tensile stress and tensile strain, then we can call this as a tensile modulus as well.

Now, if the sample is a viscous, perfect viscous material behaves like liquid, then we can express the resulting stress as a function of viscosity and shear rate, which can be expressed in terms of cosϖt, $\tau_{viscous} = \eta\dot{\gamma} = \eta\gamma_0\omega \cos \omega t$, where $\dot{\gamma}$ is dγ/dt which is shear strain rate.

Now, in this first case, the stress is exactly proportional to the applied strain. We call the stress and strains are in phase. They are overlapping with each other. When in this second case we call, the stress and strain are out of phase, 90° out of phase to be specific. When we talk about out of phase then we generally talk about 90° out of phase. I will explain what does it mean.

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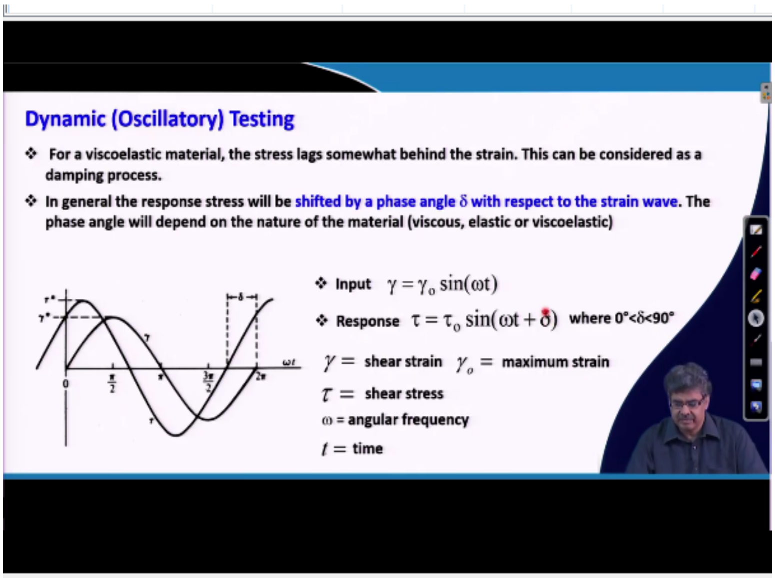

Dynamic (Oscillatory) Testing

- For a viscoelastic material, the stress lags somewhat behind the strain. This can be considered as a damping process.
- In general the response stress will be shifted by a phase angle δ with respect to the strain wave. The phase angle will depend on the nature of the material (viscous, elastic or viscoelastic)

- Input $\gamma = \gamma_o \sin(\omega t)$
- Response $\tau = \tau_o \sin(\omega t + \delta)$ where 0°<δ<90°

$\gamma =$ shear strain $\gamma_o =$ maximum strain

$\tau =$ shear stress

ω = angular frequency

$t =$ time

In the testing, for a viscoelastic material, which is not a perfect solid or a perfect liquid, the stress lags somewhat behind the strain and this behaviour can be considered as a damping process where the stress is lagging behind the applied strain. And in general, the response trace will be sifted by a phase angle δ with respect to strain wave, sinusoidal strain wave, and the phase angle will depend on the nature of the material.

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

If it is perfectly viscous material, phase angle will be 90º, if it is perfectly elastic, it will be 0º, and if it is viscoelastic, then it will be between 0º to a 90º. So, this is the stress and this curve is for strain. You can see in this case that they are out of phase. So, input strain is this and response stress is given by sin(ωt + δ) where angle δ is between 0º to 90º. So, as I explained before, that for a perfect elastic sample, this δ is 0 and viscous a perfectly liquid sample δ is 90º.

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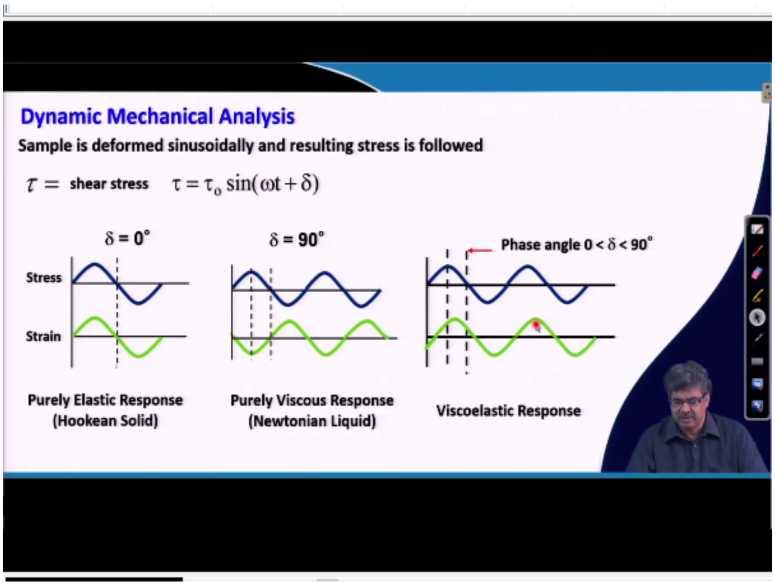

Dynamic Mechanical Analysis

Sample is deformed sinusoidally and resulting stress is followed

$\tau =$ shear stress $\quad \tau = \tau_o \sin(\omega t + \delta)$

So, in dynamic mechanical analysis, as I mentioned earlier, the sample is deformed sinusoidally and the resulting stress is followed. The stress is expressed by this expression

$$\tau = \tau_0 \sin(\omega t + \delta) \;\; where \; 0° < \delta < 90°$$

and for a purely elastic response for Hookean solid δ is 0. The stress and strain are in phase. If they are like purely viscous response, like Newtonian liquid, then they are out of phase, their δ is 90º, and for viscoelastic response, they lag with the angle between 0 to 90º. The higher is the δ, higher is the viscous component and lower is the δ, higher is the elastic component.

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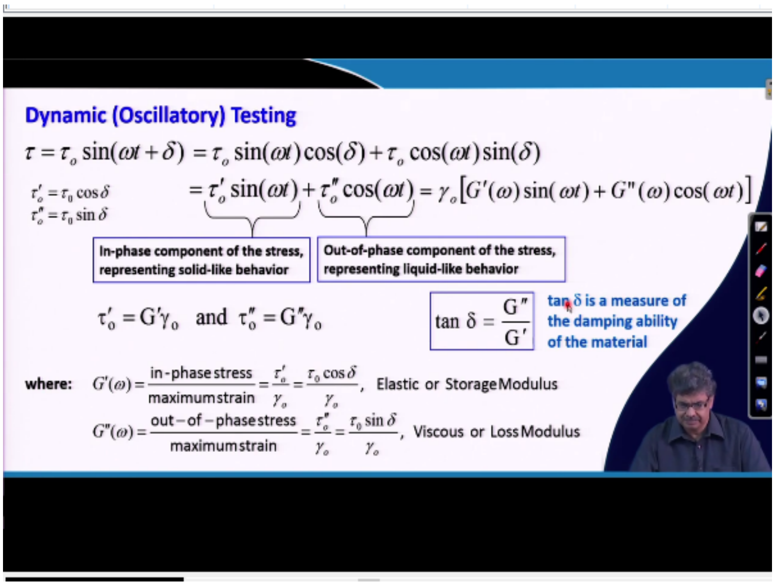

Dynamic (Oscillatory) Testing

$$\tau = \tau_o \sin(\omega t + \delta) = \tau_o \sin(\omega t)\cos(\delta) + \tau_o \cos(\omega t)\sin(\delta)$$

$\tau_o' = \tau_0 \cos\delta$

$\tau_o'' = \tau_0 \sin\delta$

$$= \underbrace{\tau_o' \sin(\omega t)}_{\text{In-phase component of the stress, representing solid-like behavior}} + \underbrace{\tau_o'' \cos(\omega t)}_{\text{Out-of-phase component of the stress, representing liquid-like behavior}} = \gamma_o [G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]$$

$$\tau_0' = G'\gamma_0 \quad \text{and} \quad \tau_0'' = G''\gamma_0$$

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

tan δ is a measure of the damping ability of the material

where: $G'(\omega) = \frac{\text{in-phase stress}}{\text{maximum strain}} = \frac{\tau_o'}{\gamma_o} = \frac{\tau_0 \cos\delta}{\gamma_o}$, Elastic or Storage Modulus

$G''(\omega) = \frac{\text{out-of-phase stress}}{\text{maximum strain}} = \frac{\tau_o''}{\gamma_o} = \frac{\tau_0 \sin\delta}{\gamma_o}$, Viscous or Loss Modulus

$$\tau = \tau_0 \sin(\omega t + \delta) = \tau_0 \sin(\omega t)\cos(\delta) + \tau_0 \cos(\omega t)\sin(\delta) = \tau_0' \sin\omega t + \tau_0'' \cos\omega t$$

$$\tau_0' = \tau_0 \cos\delta \qquad \tau_0'' = \tau_0 \sin\delta$$

$$\tau_0' = G'\gamma_0 \qquad \tau_0'' = G''\gamma_0$$

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

We can express this as before, and from ωt, we can express this expression in terms of this where we can also take these two terms and express in terms of τ_0' and τ_0". Now, this first part is related to in phase response of the stress, representing the solid like behavior, and the second term is out of phase component of the stress representing liquid like behaviour.

$$\tau = \gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]$$

So, this can be expressed, this stress which is in-phase stress, can be expressed in terms of a modulus G', and out-of-phase stress can be expressed in terms of another modulus which is G". So, G' is given by in-phase stress divided by maximum strain and this called elastic or storage modulus, and G" is out-of-phase stress divided by maximum strain, given by this expression, and this is called viscous or loss modulus.

So, please remember, this G' is storage modulus and G" is loss modulus. For a perfect solid, perfect Hookean solid, G" will be 0 because there will be no out-of-phase stress, and G' value would be 1. Similarly, for a perfect liquid sample, where G' would be 0, because there will be no in-phase stress. So, we can express this expression into this, and we also can express from this expression G" divided by G' as tanδ from this expression. This basically gives a measure of the damping ability of the material, if G" is higher, which means viscous component is higher than the damping behaviour is higher for that particular polymeric material.

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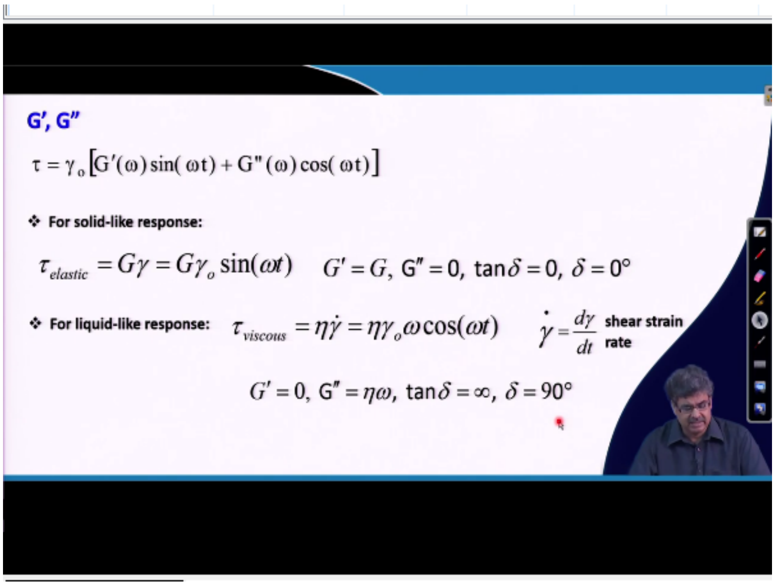

G', G"

$\tau = \gamma_o [G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]$

- ❖ For solid-like response:

$\tau_{elastic} = G\gamma = G\gamma_o \sin(\omega t)$ $G' = G,\ G'' = 0,\ \tan\delta = 0,\ \delta = 0°$

- ❖ For liquid-like response: $\tau_{viscous} = \eta\dot{\gamma} = \eta\gamma_o\omega\cos(\omega t)$ $\dot{\gamma} = \frac{d\gamma}{dt}$ shear strain rate

$G' = 0,\ G'' = \eta\omega,\ \tan\delta = \infty,\ \delta = 90°$

$$\tau = \gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)]$$

For solid-like response: $\tau_{elastic} = G\gamma = G\gamma_0 \sin(\omega t)$

$$G' = G, \quad G'' = 0, \qquad \tan\delta = 0, \delta = 0°$$

For liquid-like response: $\tau_{viscous} = \eta\dot{\gamma} = \eta\gamma_0\omega\cos(\omega t) \qquad \dot{\gamma} = \frac{d\gamma}{dt}$

$$G' = 0, \qquad G'' = \eta\omega, \qquad \tan\delta = \infty, \qquad \delta = 90°$$

Little more about G' and G", storage modulus and loss modulus. For solid like response, we have seen this expression before. So, for a perfect solid, G', storage modulus, is like the shear modulus, and G" is 0, tanδ is 0, because δ is 0. Similarly, for liquid like response, the shear stress is given by this expression as I have shown before. So, G' is 0, in that case and tanδ is infinity and δ the phase, phase angle is 90°.

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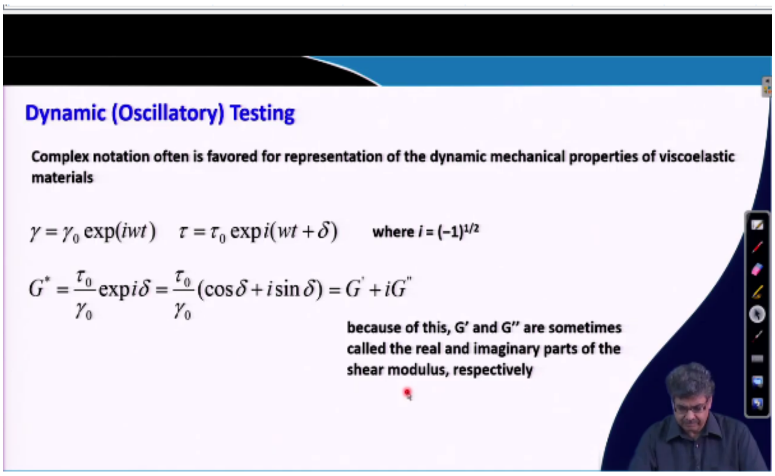

Dynamic (Oscillatory) Testing

Complex notation often is favored for representation of the dynamic mechanical properties of viscoelastic materials

$\gamma = \gamma_0 \exp(iwt) \quad \tau = \tau_0 \exp i(wt + \delta)$ where $i = (-1)^{1/2}$

$G^* = \frac{\tau_0}{\gamma_0} \exp i\delta = \frac{\tau_0}{\gamma_0}(\cos\delta + i\sin\delta) = G' + iG''$

because of this, G' and G'' are sometimes called the real and imaginary parts of the shear modulus, respectively

Sometimes, a complex notation is often used for representation of dynamic mechanical properties of viscoelastic material. In that case, the strain is represented by $\gamma = \gamma_0 exp(iwt)$ and the stress is represented by $\tau = \tau_0 \exp i(wt + \delta)$, where γ_0 is maximum strain and τ_0 is maximum stress and i is a complex number given by $i = (-1)^{1/2}$. So, we can express G*, complex modulus, like this

$$G^* = \frac{\tau_0}{\gamma_0} \exp i\delta = \frac{\tau_0}{\gamma_0}(\cos\delta + i\sin\delta) = G' + iG''$$

And just comparing these two terms sometimes G' is called a real component and G" is called the imaginary part of the shear modulus.

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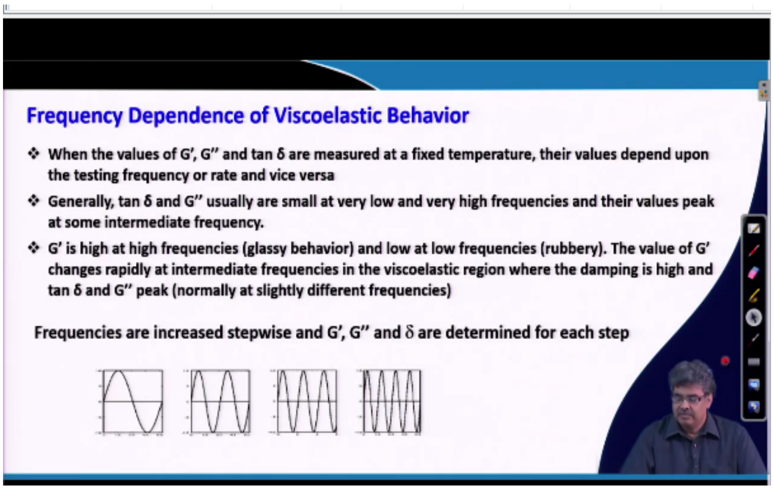

Frequency Dependence of Viscoelastic Behavior

- When the values of G', G'' and tan δ are measured at a fixed temperature, their values depend upon the testing frequency or rate and vice versa
- Generally, tan δ and G'' usually are small at very low and very high frequencies and their values peak at some intermediate frequency.
- G' is high at high frequencies (glassy behavior) and low at low frequencies (rubbery). The value of G' changes rapidly at intermediate frequencies in the viscoelastic region where the damping is high and tan δ and G'' peak (normally at slightly different frequencies)

Frequencies are increased stepwise and G', G'' and δ are determined for each step

Now, how this experiment, dynamic mechanical analysis or DMA is done? In DMA there could be various variables, sometimes frequencies are varied, keeping the strain and temperature constant, and sometimes temperature is varied keeping the other two constant, and something the strain is varied, keeping the frequency and the temperature constant.

When the value of G' and G" and tanδ are measured as a fixed temperature, then their values depend upon the testing frequency or rate and vice versa, which means when frequency is fixed, then the value of G', G" and tanδ are dependent on the temperature. So, generally, tanδ and G" are small at low and very high frequencies and their values peak at some intermediate frequency. This is related to loss modulus. Whereas, the storage modulus G' is high at high frequencies, glassy behavior dominates, I discussed earlier that when the frequencies are very high then the polymer chains do not have enough time to move past each other. So, it shows a glassy behavior, and at low frequency when the polymers have enough time, they can actually move past each other and we have a rubbery behaviour that we discussed in last lecture.

The value of G' is high at high frequency and low at low frequency. The value of G' changes rapidly in the intermediate frequencies, in the viscoelastic region where damping is high, and as a result tanδ and G", loss modulus, peak somewhere in between. The temperature for the tanδ peak or G" peak actually differs a little bit. The frequency experiment is generally termed as frequency sweep. In that case, frequency sequences are varied stepwise from low to high and G', G", and δ and corresponding tanδ are determined for each step.

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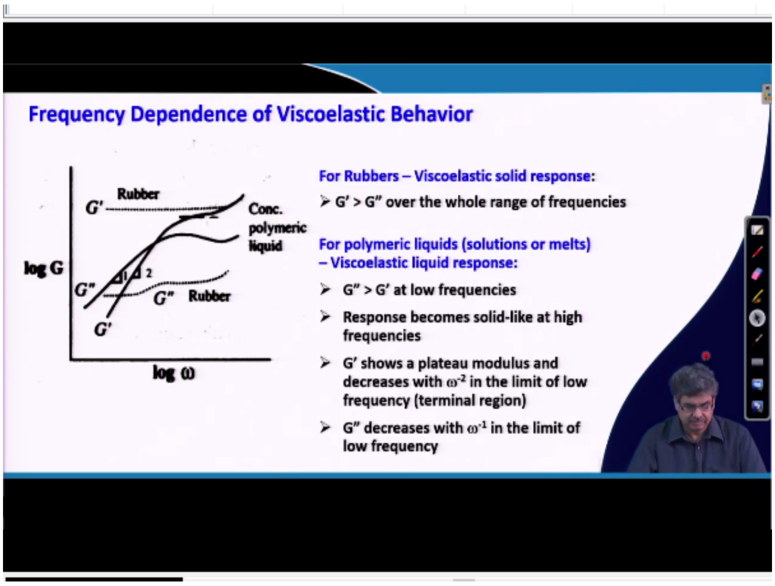

Frequency Dependence of Viscoelastic Behavior

For Rubbers – Viscoelastic solid response:

- G' > G" over the whole range of frequencies

For polymeric liquids (solutions or melts) – Viscoelastic liquid response:

- G" > G' at low frequencies
- Response becomes solid-like at high frequencies
- G' shows a plateau modulus and decreases with ω^{-2} in the limit of low frequency (terminal region)
- G" decreases with ω^{-1} in the limit of low frequency

Now, if we look at the frequency dependence or the viscoelastic behavior, we can conclude few things, these values are shown here for rubber. This is G' and this is G", elastic solid response is dominating which means G' is always higher than G", storage modulus has higher value than loss modulus in the whole range of frequencies.

But when you talk about concentrated polymer solution or polymer melt where viscoelastic behaviours are dominated in direction of liquid, viscous liquid response dominates, especially at low frequency loss modulus is higher than the storage modulus and above certain frequency the storage modulus becomes higher than the loss modulus. So, response becomes solid like at higher frequencies. G' shows a plateau modulus as it is shown here and decreases with ω^{-2} in the limit of low frequencies, terminal region, in this region whereas, G" decreases with ω^{-1} in this limit of low frequencies.

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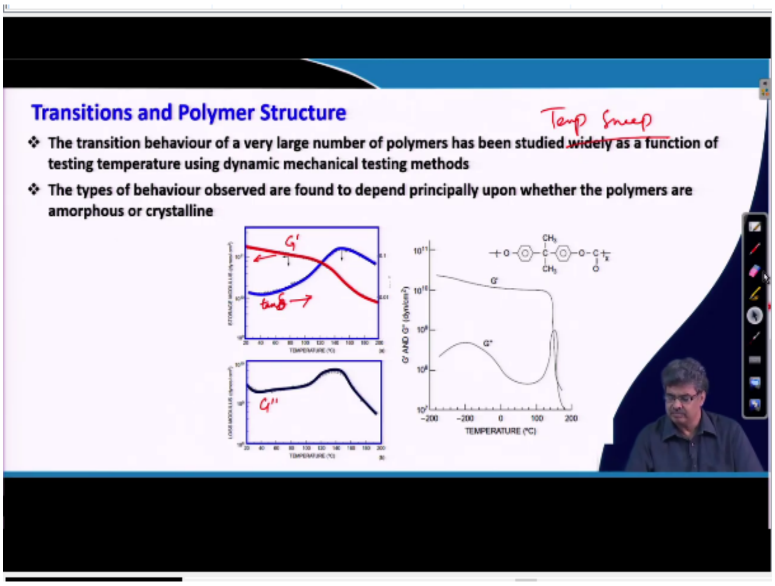

Transitions and Polymer Structure

Temp Sweep

- The transition behaviour of a very large number of polymers has been studied widely as a function of testing temperature using dynamic mechanical testing methods
- The types of behaviour observed are found to depend principally upon whether the polymers are amorphous or crystalline

We have talked about frequency sweep now, we can do the temperature sweep which means, we can keep the frequency and the strain fixed and we can change the temperature and measure G', G", tanδ and plot those three values as a function of temperature. We have talked about frequency sweep, now, we are talking about temperature sweep experiment where temperature is varied keeping the frequency and strain same and G', G", tanδ are plotted as a function of temperature. In this case, the phase transition behaviour of a large number of polymers has been studied widely as a function of testing temperature using DMA method.

The types of behavior observed are found to depend principally on whether the polymers are amorphous or crystalline. For example, this is a DMA curve, sometimes we call DMA spectra or spectrum depending upon whether we are talking about single experiment or multi experiment. Now, in case of polycarbonate, you can see, this is storage modulus. This is G' and this is tanδ, this side and this is G". Now, you can see that G' decreases with temperature and at a particular temperature around 130 °C or 140 °C it drops significantly. Similarly, G" actually increases and it peaks around 145 °C, somewhere there, little higher than the drop observed for G'.

The ratio of G" by G' actually peaks around 150 °C. This is the value where we get the peak of tanδ that correspond to the T_g or corresponds to the phase transition depending on the sharpness we can call this as a first order transition or second curve transition that we have discussed earlier. So, this is a T_g corresponds of polycarbonate as we measure from a DMA. Now, if you look at the same experiment when done at a low temperature from – 200 ºC to 200 ºC then you can see this additional peak of tanδ somewhere at - 200 ºC. Now, this is generally not captured in a DSC measurement, because this actually related to very small change in enthalpy or heat capacity. Hence, DMA gives us the advantage of capturing even small change in polymer structure or polymer movement.

In this case, is considered as another transition at sub 0 temperature and it is believed that because of this transition polycarbonate shows high impact behaviour or high ductility behaviour in spite of having a completely amorphous structure. This is one transition at very low temperature and another transition, which we discussed here around 150 ºC corresponding to that glass transition temperature or T_g.

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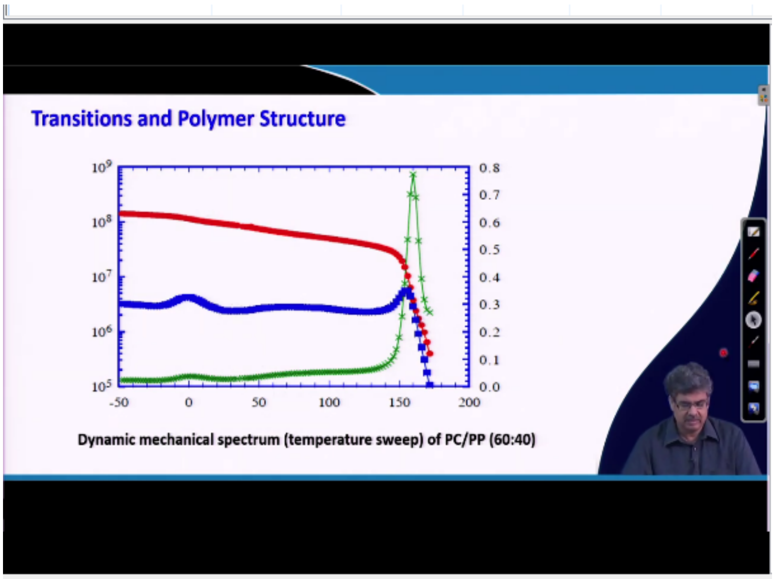

Transitions and Polymer Structure

Dynamic mechanical spectrum (temperature sweep) of PC/PP (60:40)

This is the DMA spectrum for a blend of PC and PP, temperature sweep. So, in this case, we are varying temperature keeping the frequency same and you can see these two peaks corresponding to tanδ. This is G', this is G" and this is tanδ. So, you can see there are two peaks, one around 0 ºC for polypropylene and another one around 160 ºC for PC phase. As this is a glass-filled sample, the Tg for PC phase little higher than pure PC. So, using DMA we can actually measure the temperature corresponding to different transitions like glass transition temperature as shown here.

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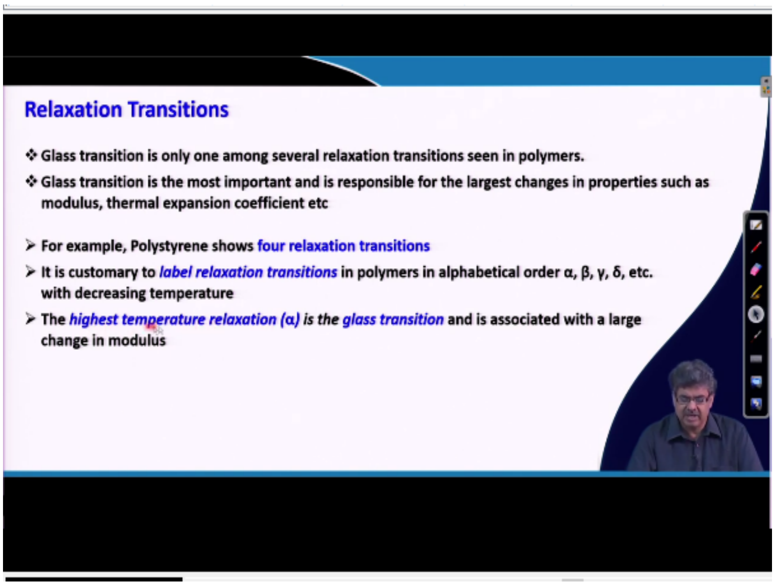

Relaxation Transitions

- ❖ Glass transition is only one among several relaxation transitions seen in polymers.
- ❖ Glass transition is the most important and is responsible for the largest changes in properties such as modulus, thermal expansion coefficient etc

- ➢ For example, Polystyrene shows four relaxation transitions
- ➢ It is customary to *label relaxation transitions* in polymers in alphabetical order α, β, γ, δ, etc. with decreasing temperature
- ➢ The *highest temperature relaxation (α) is the glass transition* and is associated with a large change in modulus

Now, besides the glass transition temperature, other transitions are also possible as we described for polycarbonate at sub 0, nearly at -200 °C in the last slide. It is possible to capture or detect, those transitions by DMA experiments which are not possible or very difficult to achieve using traditional differential scanning calorimetry or DTA experiments as we discussed earlier.

We can talk about relaxation transitions. Glass transition is only one among several relaxation transitions seen in polymers, and it is the most important and responsible for the largest changes in properties such as modulus, thermal coefficient, thermal expansion coefficient etc. But beside glass transition, there are other relaxation transitions in polymer materials. For example, polystyrene shows four relaxation transitions and it is customary to label relaxation transitions in polymer in alphabetical order α, β, γ, δ type, where α is the highest temperature or α corresponding to the relaxation transition corresponding to the highest temperature. So, the highest temperature relaxation, α, is glass transition and associated with the large change in modulus as we have seen earlier. And the other transitions exist and but the change in modulus or other properties are comparably much lower compared to the glass transition.

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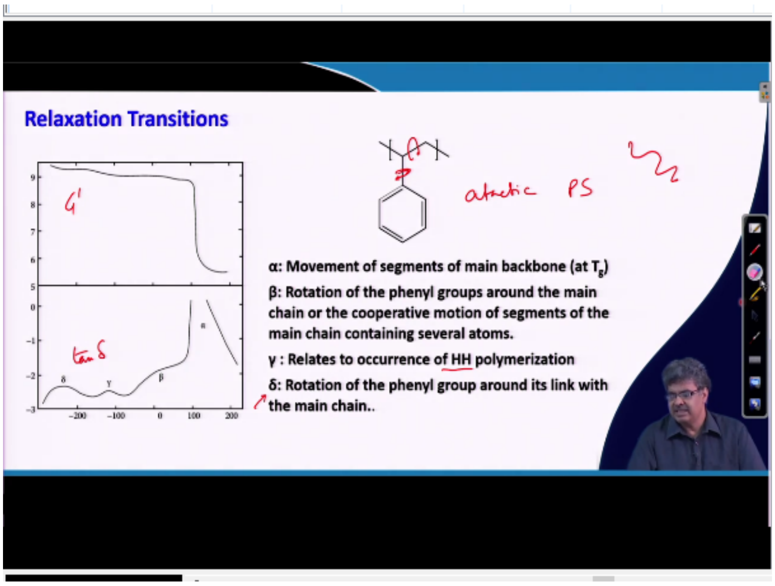

Relaxation Transitions

α: Movement of segments of main backbone (at T_g)

β: Rotation of the phenyl groups around the main chain or the cooperative motion of segments of the main chain containing several atoms.

γ : Relates to occurrence of HH polymerization

δ: Rotation of the phenyl group around its link with the main chain..

This is an example of DMA curve for atactic polystyrene, and this is a G' curve and this is tanδ. So, you can see that we have four transitions, relaxation transitions. Also, these transitions are very weak, only the α transition which corresponds to the glass transition is prominent and very significant that is why the modulus drops significantly. But there are other transitions which are weak transitions. So, the change in modulus is not that prominent, but they exist in polymer systems. As we mentioned for polystyrene, there are four transitions, α transition corresponds to glass transition**,** which corresponds to the movement of polymer segments in the backbone of the polymer backbone. So, the movement of polymer backbone corresponds to the T_g, rotation of this phenyl ring around this single bond corresponds to the β transition. Similarly, rotation of phenyl ring around this carbon corresponds to δ transition, and there is another transition which occurred due to head-to-head polymerization. So, as you can see that these relaxation transitions can be captured with dynamic mechanical analysis.

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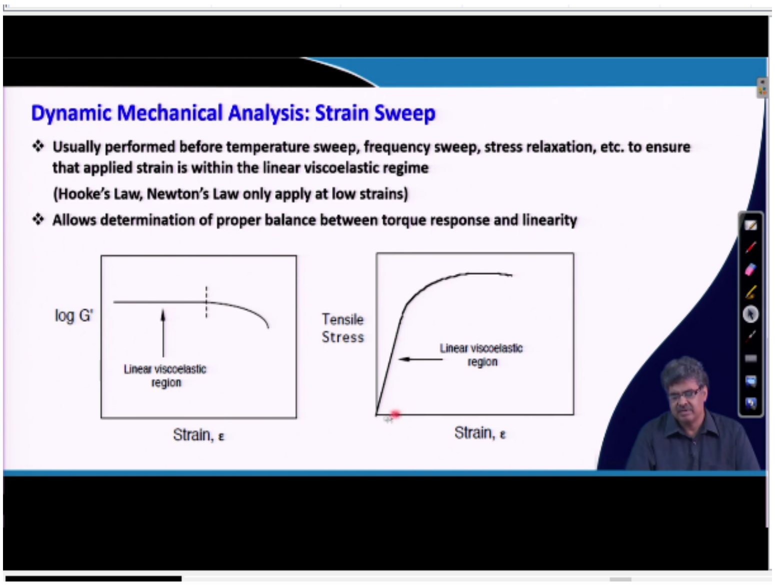

Dynamic Mechanical Analysis: Strain Sweep

- Usually performed before temperature sweep, frequency sweep, stress relaxation, etc. to ensure that applied strain is within the linear viscoelastic regime

  (Hooke's Law, Newton's Law only apply at low strains)
- Allows determination of proper balance between torque response and linearity

DMA can also be used to study other interesting properties as well, like strain sweep, in this case, like we discussed frequency sweep and temperature sweep. In this case strain is varied keeping the temperature and frequency same and this strain sweep is generally performed before the temperature sweep or frequency sweep or stress relaxation etc. to ensure that the applied strain, whatever strain we are applying is within the linear viscoelastic regime. Otherwise, this will complicate the experiment further and for example, if we plot logG' with strain then you can see that up to some strain the sample behaviour is linear. So, we call this region as a linear viscoelastic region, and similarly, for a tensile experiment, you can see that up to some strain, this linear viscoelastic region is maintained. So, when we do a frequency sweep or temperature sweep experiment, we should remain within this strain value, so that we are in the linear viscoelastic region. So, for a shear experiment, we should have the strain within this range and for a tensile experiment we should have the strain within this linear viscoelastic regime.

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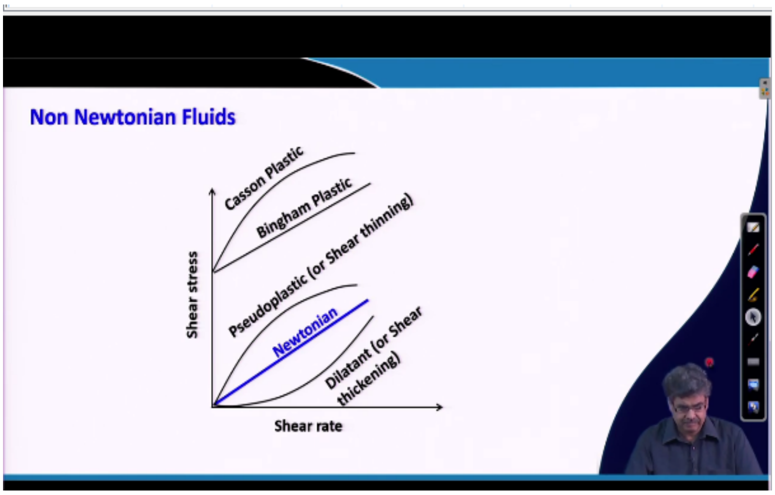

Non Newtonian Fluids

The polymer samples can also behave like a non-Newtonian fluid, and we can basically classify these behaviors into different types of polymer materials. For example, if the shear stress and shear rate are linearly related then we call this a Newtonian fluid as we described earlier, but often this is not the case. Sometimes, at higher shear rate, the stress actually comes down; we call this a shear thinning behavior, actually, viscosity comes down at higher shear rate. We call this also as pseudoplastic. Similarly, this is the case for a shear thickening, the viscosity goes up, stress goes up, and we call this as dilatant. There are two more possible behaviors, in this case you can see the stress remains zero. After a value, it starts behaving linearly, it is called a Bingham plastic, if a behaviour is like this as shown in this graph. And this is a casson plastics, where it starts from a high stress and behave like a shear thinning polymer after that. So, these are different types of viscoelastic or non-Newtonian behaviour possible for polymer sample. Sometimes, there is an advantage associated with this type behavior for example, as I explained, this shear thinning behaviour help us in processing. During processing if the shear rate is higher, the melt viscosity actually decreases, which helps the polymers to flow. Otherwise, if there is no shear thinning behaviour at high shear rate than the melt viscosity will be very high and we need to apply a very high energy to process polymer. So, sometimes this type of behaviour like shear thinning actually helps in saving energy during polymer processing.

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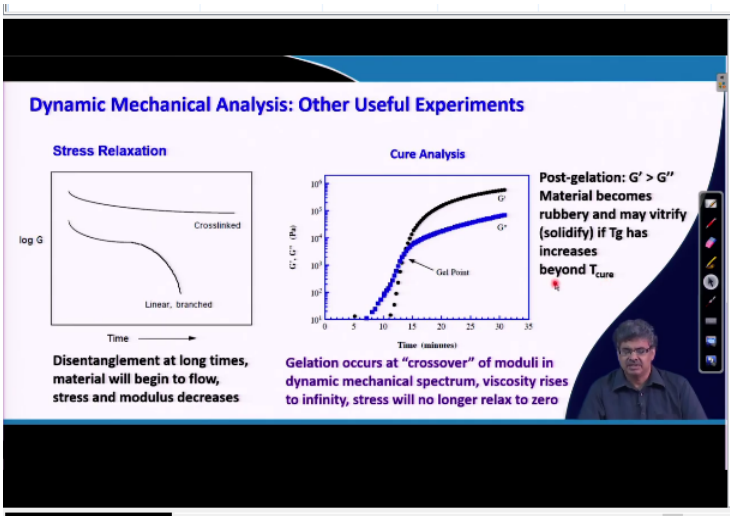

Dynamic Mechanical Analysis: Other Useful Experiments

Stress Relaxation

Disentanglement at long times, material will begin to flow, stress and modulus decreases

Cure Analysis

Post-gelation: G' > G"
Material becomes rubbery and may vitrify (solidify) if Tg has increases beyond T_{cure}

Gelation occurs at "crossover" of moduli in dynamic mechanical spectrum, viscosity rises to infinity, stress will no longer relax to zero

As I said that, using DMA, dynamic mechanical analysis, we can do other useful experiments. For example, we can do stress relaxation measurements, where we plot G with time and we can compare the linear or branched polymers with the cross-linked polymers. For a linear or branch polymer sample, the shear modulus actually comes down after some time as the polymer chain that are entangled with each other starts moving past one another and the value of G actually decreases and approaches to 0. Whereas, for cross-linked material, as the polymer chains are cross-linked, they cannot get separated from each other. So, the value of G does not decrease beyond a certain value even you keep the sample under the stress for a much longer time. So, for linear polymers, as disentanglement happened under stress, materials will begin to flow, the polymer chains will move past each other and the stress and modulus decreases and approaches 0.

Similarly, we can use DMA experiments to find out curing like isothermal curing, where we do the curing experiment at the same temperature. In this case, as you can see, this is a possible scenario where at the beginning when the time is less, we start the experiment with low molecular weight sample and in this case G" is higher than G' because we are talking about liquid behaviour. After some time, when the curing starts, the modulus increases drastically, and at certain point when the network formation take place, G' crossovers G" and that is the point we call gel point. Above this gel point, G' is higher than G" and this happened due to cross-linking during curing process. This G" do not come back to lower value because the polymers cannot move past each other because of the cross linking. If the temperature, at which the curing experiment is done, is below the T_g of the polymer samples, then the cured sample become glassy in nature. So, gelation occurs at this crossover of moduli, G' and G", in dynamic mechanical spectrum, viscosity raises to infinity because we have polymer samples with a cross-linked network structure. So, stress will no longer be approaching to 0 and post curation, as I explained, G' would be greater than G", materials become rubbery and may become solidify or may be vitrified if the T_g of the resulting sample increases beyond the temperature of curing.

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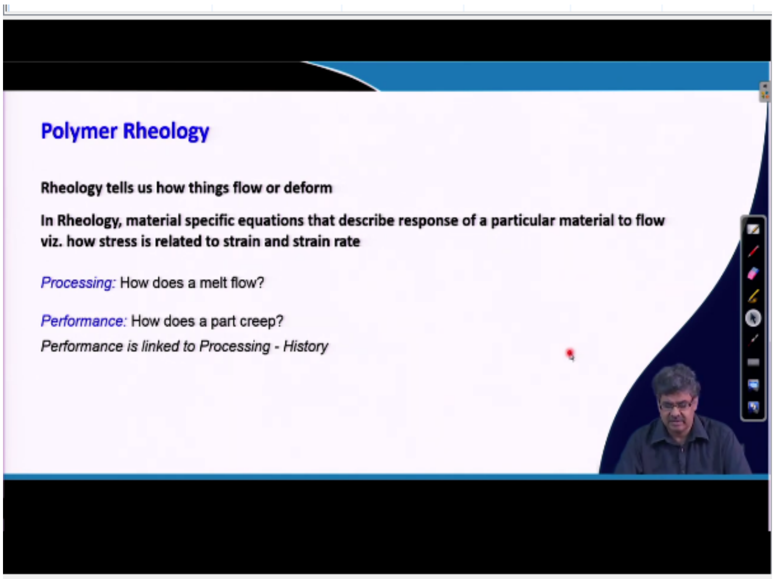

Polymer Rheology

Rheology tells us how things flow or deform

In Rheology, material specific equations that describe response of a particular material to flow viz. how stress is related to strain and strain rate

Processing: How does a melt flow?

Performance: How does a part creep?

Performance is linked to Processing - History

I just discussed about dynamic mechanical behavior, which is related to the flow properties of polymer samples. Actually, the flow behavior of polymer samples is formally called rheology. The science of studying flow behaviour of any material is called rheology and if we use the polymer sample, then we talk about polymer rheology. Rheology tells us how things flow or deform and we discussed the deformation behaviour or flow behaviour in details during our discussion on viscoelastic properties. So, in rheology material specific equations that describes response of particular materials to flow are derived. For example, how stress is related to strain and strain rate, and we discussed most of it during our discussion of viscoelastic properties.

Polymer rheology is important for polymer processing, because, to understand the processing behaviour or how to conduct the polymer processing, we should know how the polymer melts flow. The performance of the final products is actually linked to the processing history. The performance of the final products also depend upon the deformation behaviour like how does a part creep. So, we also need to find out the flow behaviour other than the dynamic mechanical analysis.

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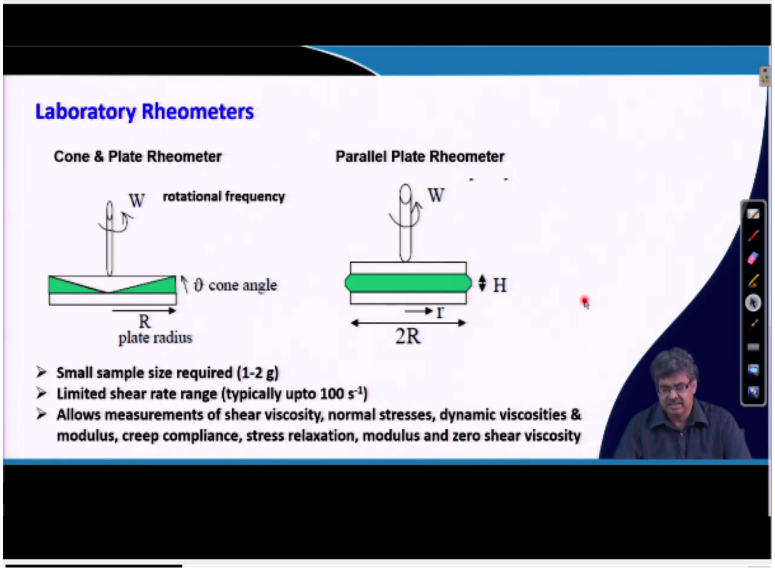

Laboratory Rheometers

Cone & Plate Rheometer

Parallel Plate Rheometer

- Small sample size required (1-2 g)
- Limited shear rate range (typically upto 100 s^{-1})
- Allows measurements of shear viscosity, normal stresses, dynamic viscosities & modulus, creep compliance, stress relaxation, modulus and zero shear viscosity

Examples of the typical laboratory rheometers are cone and plate rheometers, parallel plate rheometers, etc. I am not going into the details about the principle of action, if you require you can go through any literature. So, this cone and plate rheometer or parallel plate rheometer or capillary rheometer can be used to measure the flow properties of polymer in lab and these rheometers require small size of sample, 1 to 2 g. These laboratory rheometers can be used for a limited shear rate range, typically, up to 100 s^{-1}. This allows the measurement of shear viscosity, normal stresses, dynamic viscosity and modulus, creep compliances, stress relaxation modulus and zeros shear viscosity. For high shear rate, we can use capillary viscometer and dynamic mechanical analysis as I discussed earlier.

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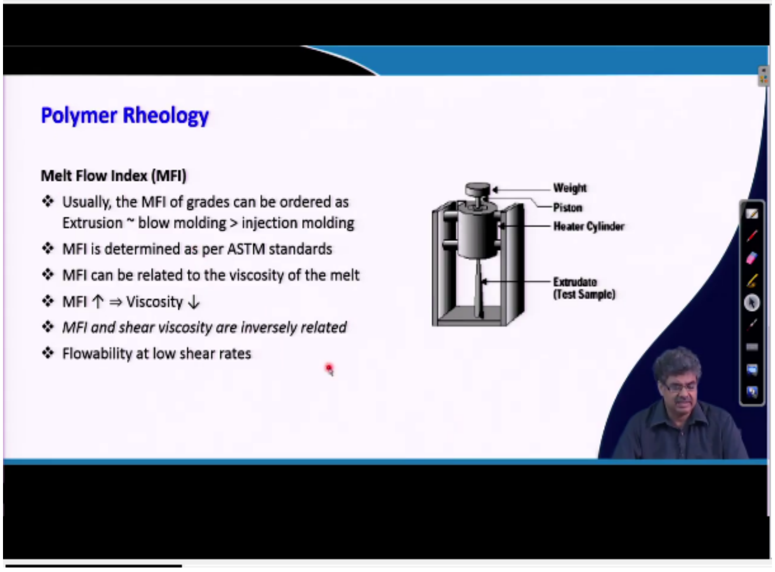

Polymer Rheology

Melt Flow Index (MFI)

- Usually, the MFI of grades can be ordered as Extrusion ~ blow molding > injection molding
- MFI is determined as per ASTM standards
- MFI can be related to the viscosity of the melt
- MFI ↑ ⇒ Viscosity ↓
- *MFI and shear viscosity are inversely related*
- Flowability at low shear rates

This is another important practically used technique called MFI measurement, melt flow index measurement. In this case, a sample is basically allowed to flow under a certain load. In this case, as we know, the flow behavior also depends on the applied stress or load. The sample is heated and it is allowed to flow through an orifice under a particular load.

This MFI values of different grades of polymers can be in the ordered - extrusion, blow molding, injection molding; which means that MFI of injection grade has the highest value. MFI is determined as per ASTM standard. So, which temperatures would be used, what would be the load, those are described in these standards. MFI can be related to viscosity of the melt, obviously, as MFI is higher, flow is higher. MFI and shear viscosity are inversely related as I discussed, lower shear viscosity means more and more sample pass through the orifice during MFI experiment, so MFI goes up. This melt flow index measurement can be utilized to find outflow at low shear rate.

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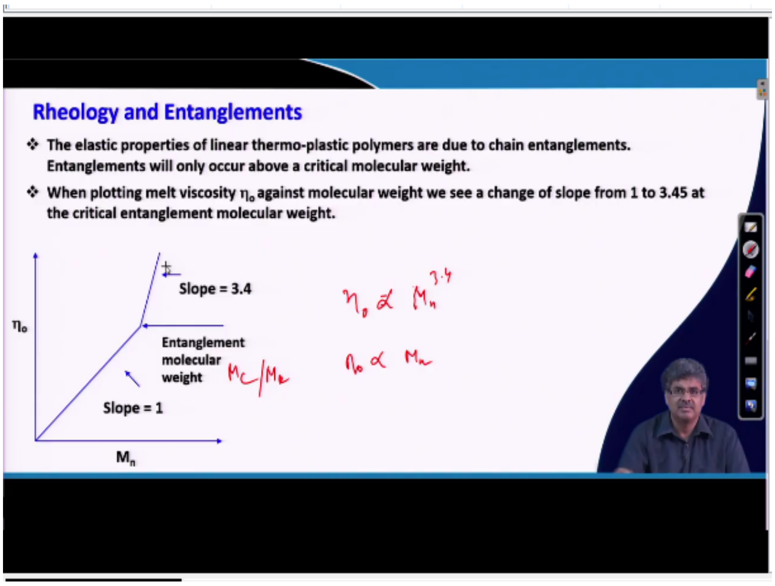

Rheology and Entanglements

- The elastic properties of linear thermo-plastic polymers are due to chain entanglements. Entanglements will only occur above a critical molecular weight.
- When plotting melt viscosity η_o against molecular weight we see a change of slope from 1 to 3.45 at the critical entanglement molecular weight.

Rheology and entanglement are important aspects of polymer flow behaviour, the elastic properties of linear thermoplastic polymers are due to chain entanglement, that I have described several times. Because of the entanglement of polymer chains, when the frequency is higher, chains cannot de-entangled and cannot move past each other, as a result, the elastic or solid-like behaviour happens. Entanglements will only occur above a certain critical molecular weight, obviously, to have this entanglement, the polymer has to have a minimum size or molecular weight so that they bend and entangle with each other. For example, if you are talking about a chowmin sample, if we break the chowmin strands in small pieces, then they do not entangle with each other, we can easily take out from the bowl. But if we do not break and we use large size chowmin, then we can see that they are entangled with each other, it is very difficult for takeout the samples from plate using, say a spoon or fork. So, when plotted, melt viscosity against molecular weight, we see that a change in slope from 1 to 3.4 at a critical entanglement molecular weight. The molecular weight below this critical entanglement molecule weight or M_e,

Below this critical entanglement molecular weight, M_c, sometimes it is called M_e, the viscosity increases linearly with the slope of 1 with respect to number average molecular weight, above a certain critical molecular weight the entanglement happens and as a result, the viscosity shoots up very sharply, and viscosity, η_0 varies with $M_n^{3.4}$. Below the critical molecular weight, η_0 varies with M_n.

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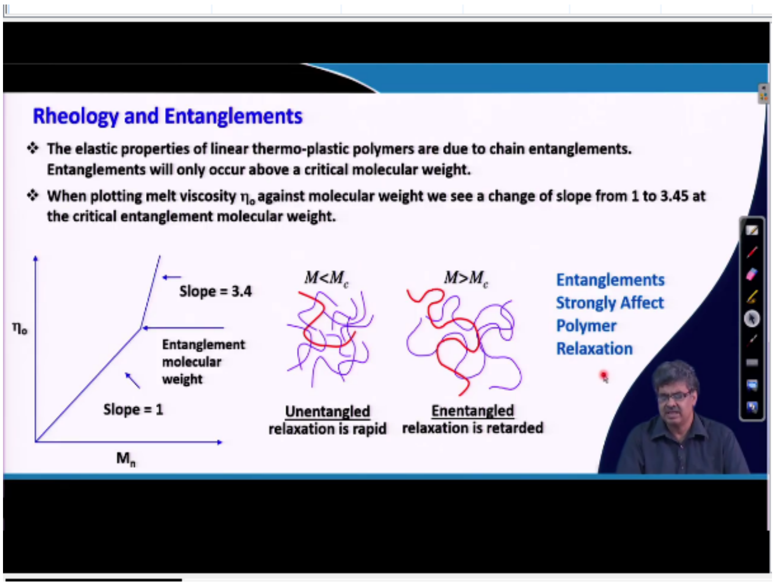

Rheology and Entanglements

- The elastic properties of linear thermo-plastic polymers are due to chain entanglements. Entanglements will only occur above a critical molecular weight.
- When plotting melt viscosity η_o against molecular weight we see a change of slope from 1 to 3.45 at the critical entanglement molecular weight.

Entanglements Strongly Affect Polymer Relaxation

So, the polymer chains are un-entangled when Mn is less than M_c. These un-entangled polymers can relax rapidly, so viscosity is low. But, when the polymer molecular weight is higher, the chains are entangled with each other. So, the relaxation is retarded, they cannot move past each other, as a result viscosity is higher. So, entanglements strongly effect the polymer relaxation.

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The Great Dilemma in Polymers

- ❖ Polymers must have good properties
  - ➢ Good properties are favored by high molecular weight
- ❖ Polymers must have good processebility
  - ➢ Good processing is favored by low molecular weight

And this causes a dilemma. Now to have good properties of polymers, the molecular weight actually has to be high. The mechanical property, for example, increases sharply with molecular weight before it levels off above a certain molecular weight. So, ideally you should have high molecular weight to have good properties. Similarly, flow behaviour actually decreases and the viscosity increases very much with increase in molecular weight. So, ease of processing actually decreases with molecular weight, the higher is the molecular weight, higher is the viscosity. As a result, the processing becomes difficult. So, ease of processing becomes lower with increasing molecular weight.

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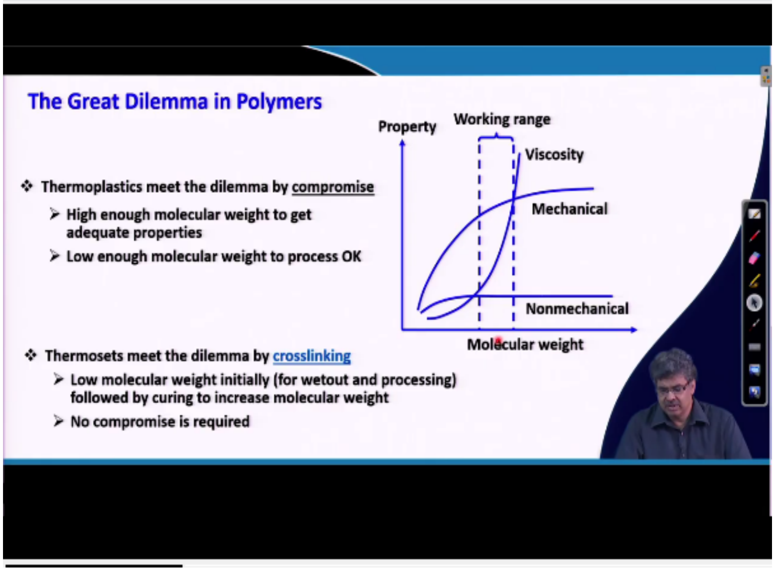

The Great Dilemma in Polymers

- ❖ Thermoplastics meet the dilemma by compromise
  - ➢ High enough molecular weight to get adequate properties
  - ➢ Low enough molecular weight to process OK
- ❖ Thermosets meet the dilemma by crosslinking
  - ➢ Low molecular weight initially (for wetout and processing) followed by curing to increase molecular weight
  - ➢ No compromise is required

For thermoplastics, this dilemma is met by a compromise. We choose a molecular weight range. So, this is the working range, there is a compromise between the ease of processing, which is governed by the viscosity, and the property like mechanical property. So, this is the working range of the molecule weight which balances between the ease of processing and the property.

For thermosets this balance, or this dilemma is met by cross-linking, for low molecular weight, obviously processing is easier because viscosity is low, and on cross-linking you do not require any further processing. Basically, curing increases the molecular weight. So, no compromise is required if the cross-linking is done, and on cross-linking value of the properties increases. With this, I will stop for this lecture.