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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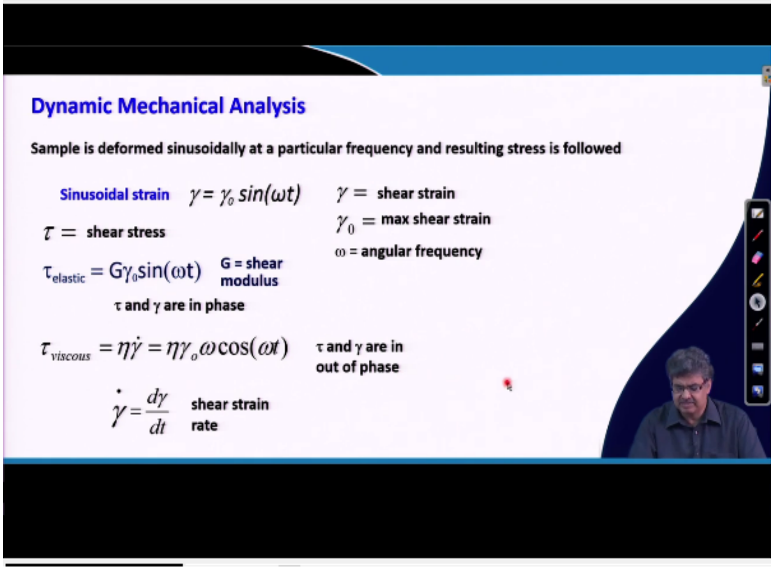

Dynamic Mechanical Analysis

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

ω = 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 viscoelastics material, which means that depending upon the temperature and the deformation rate polymer can be from 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 type of deformation can be also applied sinusoidally to the samples as well. Now, if we apply this strain then we can apply the strain as a function of sine function of angular frequency and time where this is the maximum strain experienced by the sample.

So, this is shear strain, maximum shear strain and omega is angular frequency, we can use other strain as well like elastic strain. In that case, you can just replace these 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.

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 is G shear modulus. So, G 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 cos omega t, where gamma dot is d gamma by dt which is shear strain rate. Now, in this case, the stress is exactly proportional to the applied strain. And we call the stress and strains are in phase. They are overlapping with each other. When in this case we call the stress and strain are out of phase, 90 degrees out of phase to be specific. But when we talk about out of phase then we generally talk about 90 degrees out of phase. I will explain what does it mean?

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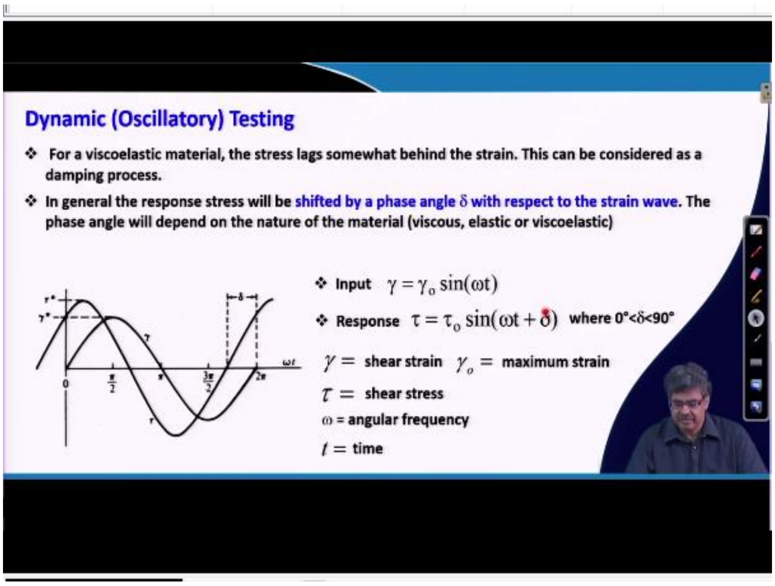

Dynamic (Oscillatory) Testing

- 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

$\omega =$ angular frequency

$t =$ time

So, 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 delta with respect to strain wave sinusoidal strain wave and the phase angle will depend on the nature of the material.

If it is perfectly viscous material face angle will be 90 degree if it is perfectly elastic, it will be 0 degree and if it is viscoelastic, then it will be between 0 to a 90 degree. So, this is the stress and this curve is strain and you can see in this case they are out of phase. So, input strain is this and response stress is given by sine omega t + a phase angle where angle is between 0 degree to 90 degree. So, as I explained before that for a perfect elastic sample this delta is 0 and viscous a perfectly liquid sample delta is 90 degree.

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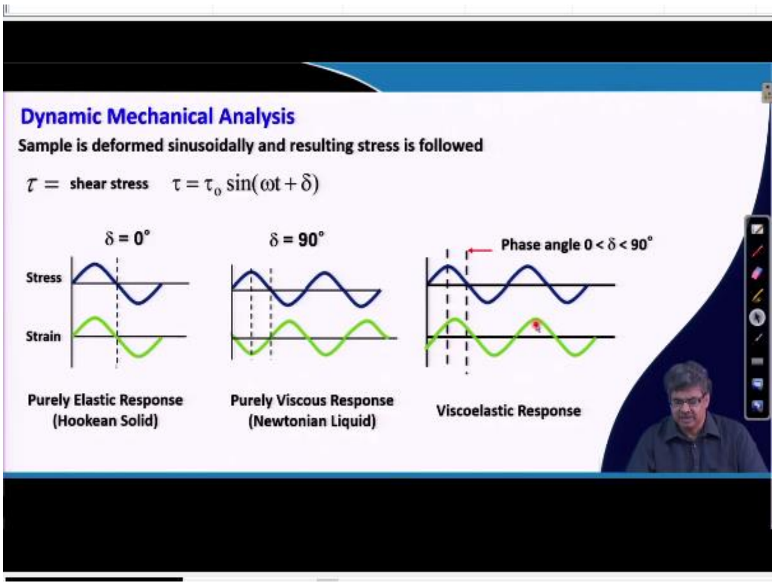

Dynamic Mechanical Analysis

Sample is deformed sinusoidally and resulting stress is followed

$\tau =$ shear stress $\quad \tau = \tau_0 \sin(\omega t + \delta)$

So, in this as I mentioned earlier in dynamic mechanical analysis the sample is deformed sinusoidally and the resulting stress is followed. So, the stress is expressed by this expression. And for a purely elastic response for Hookean solid delta is 0. So, the stress and strain are in phase. If they are like purely viscous response like Newtonian liquid then they are out of phase their delta is 90 degree and for viscoelastic response, they lag with the angle between 0 to delta. The higher is the delta, higher is the viscous component and lower is the delta, higher is the elastic component.

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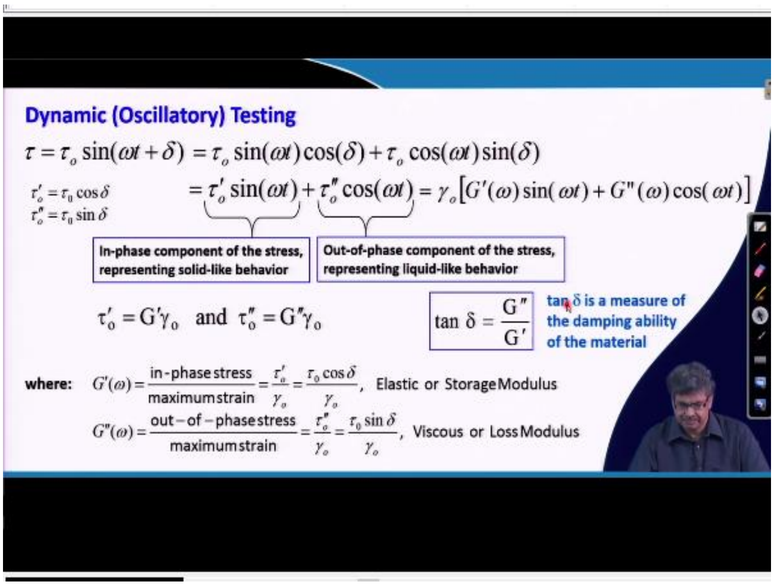

Dynamic (Oscillatory) Testing

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

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

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

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

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

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

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

So, we can express this as before and from omega t we can express this expression in terms of this where we can also take these 2 term and express in terms of tau 0 prime and tau 0 double prime where tau 0 prime is given by this and tau 0 double prime has given by this expression. Now, this first part is related to in phase response of the stress, represent the solid like the area and the second term is out of phase component of the stress representing liquid like behaviour.

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

So, please remember, these G prime is storage modulus and G double prime is loss modulus for a perfect solid, perfect Hookean solid, G double prime will be 0 because there will be no out of phase trace, and this value would be 1. Similarly, for a perfect liquid sample, where G's prime 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 double prime by G prime as 10 delta from this expression and this is basically gives a measure of the damping ability of the material, if G double prime is higher, which means viscous component is higher than the damping behaviour is higher for that particular polymeric material.

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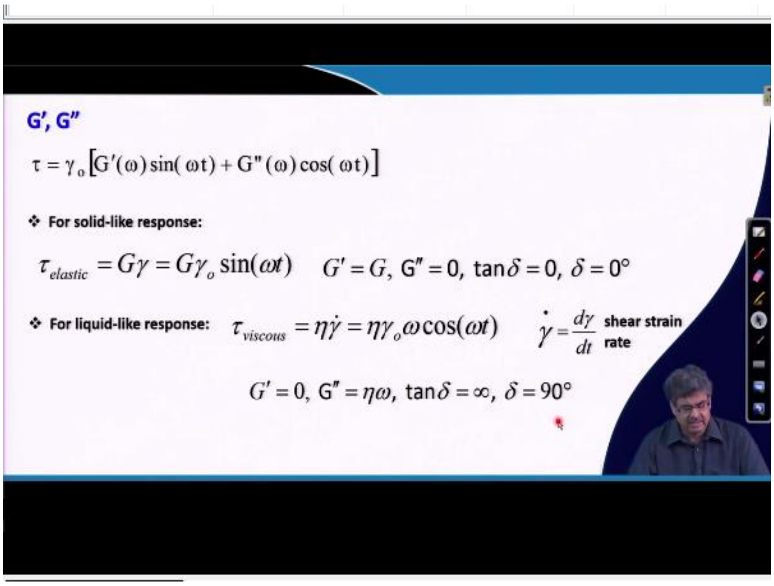

G′, G″

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

- For solid-like response:

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

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

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

Little more about G prime and G double prime, storage modulus and loss modulus, for solid like response we have seen this expression before. So, for a perfect solid G prime is nothing but G, storage modulus is like the shear modulus and G double prime is 0 tan delta is 0 because delta is 0. Similarly, for liquid like response, the shear stress is given by this expression as I have shown before. So, G prime is 0 in that case and tan delta is infinity and delta the phase, phase angle is 90 degree.

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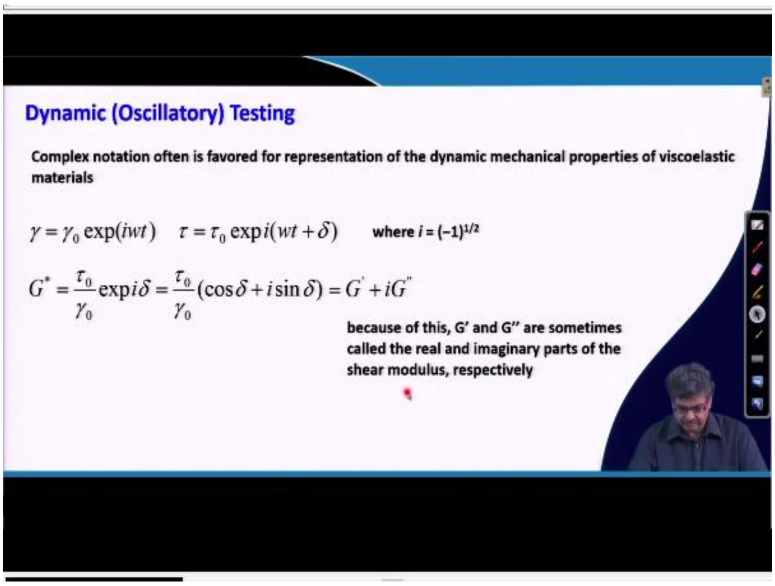

Dynamic (Oscillatory) Testing

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

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

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

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

Sometimes, a complex notation often use for representation of dynamic mechanical properties of viscoelastic material. In that case, the strain is represented by this expression and the stress is represented by this expression where gamma 0 is maximum strain and tau 0 is maximum stress and i is a complex number given by this expression. So, we can express this is complex modulus G star is complex modulus can be expressed in this term. And just comparing these 2 term sometimes G prime is called a real component and G double prime is called the imaginary part of the shear modulus.

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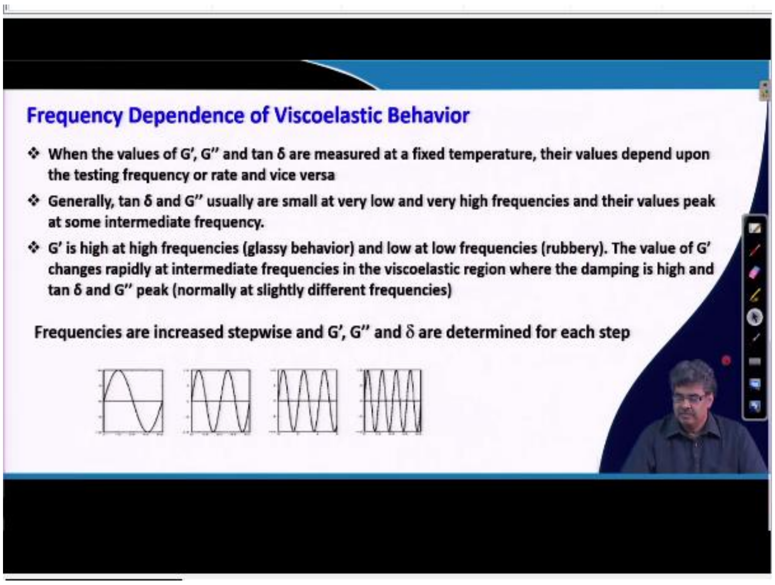

Frequency Dependence of Viscoelastic Behavior

- 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 does dynamic mechanical analysis or DMA experiment is done? In DMA there could be various variables, sometimes frequencies varied, keeping the strain and temperature is constant and sometimes temperature is varied keeping the other 2 constant and something the strain is varied, keeping the frequency and the temperature is constant.

So, when the value of G prime and G double prime and tan delta are measured as a fixed temperature, then their value depend upon the testing frequency or rate and vice versa which means when frequency is fixed, then the value of G prime G double prime and tan delta are dependent on the temperature. So, generally tan delta and G prime are small at low and very high frequencies and their values peak at some intermediate in frequency.

This is related to loss modulus. Whereas, the storage modulus G prime is high at high frequencies glassy behaviour I discussed earlier, that when the frequencies are very high then the polymer chains cannot basically do not have enough time to move fast each other. So, it behaves like a glassy behaviour and at low frequency when the polymers have enough time, they can actually move fast each other and we have a rubbery behaviour that we discussed in last lecture.

So, the value of G prime is high at high frequency and low at low frequency and the value of G prime changes rapidly in the intermediate frequencies in the viscoelastic region where damping is high and as a result tan delta and G double prime loss modulus peak somewhere in between when this transitions happen and they actually normally differ slightly. The temperature for the tan delta peak or G prime peak actually differs a little bit from the maximum decrease in the G prime value.

The frequency experiment which is called frequency sweep, the experiment is generally termed as frequency sweep. In that case frequency sequences are varied stepwise from low to high and G prime G double prime and delta and corresponding tan delta determined for each step.

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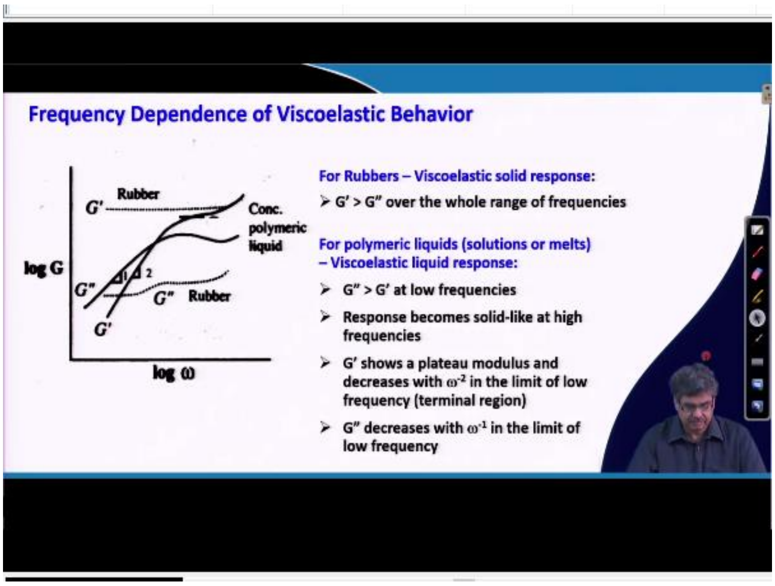

Frequency Dependence of Viscoelastic Behavior

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 behaviour , we can conclude few things like for rubber these values are shown here for rubber. This is G prime and this is G double prime, viscoelastic solid response are dominating which means G prime is always higher than G double prime, storage modulus have higher value than loss modulus in the whole range of frequencies.

But when you talk about concentrated polymer liquid or polymer melt where viscoelastic behaviours are dominated in indirection of liquid side. So, viscoelastic liquid response dominates. So, 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 prime shows a plateau modulus as it shown here and decreases with omega to the power -2 in the limit of low frequencies terminal region in this region whereas, G double prime decreases when omega to the power -1 in this limit of low frequencies.

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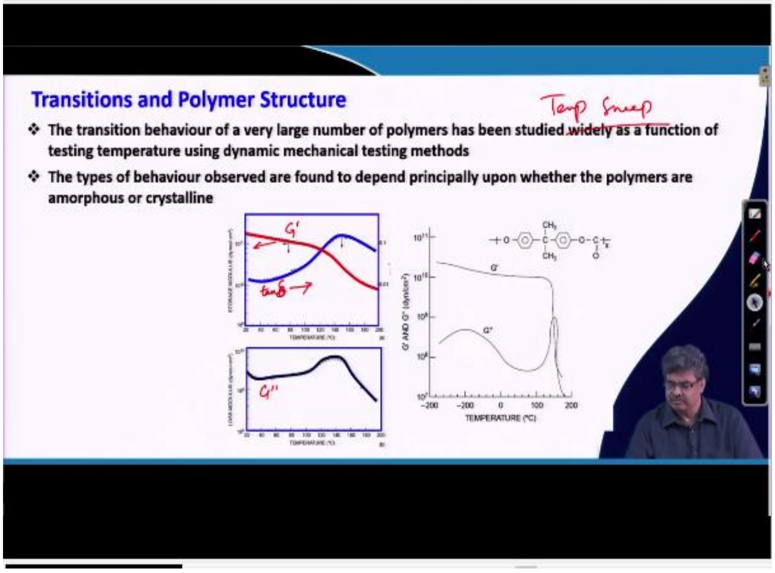

Transitions and Polymer Structure

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

Now, 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 which can change the temperature and measure G prime G double prime tan delta and you can plot those 3 values in as a function of temperature and we call that experiment as temperature sweep. So, 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 following the G prime G double prime and tan delta as a function of temperature. So, in this case the transition behaviour the phase transition behaviour of a very large number of polymers has been studied widely as a function of testing temperature using DMA method.

And the types of behaviour observed are found to depend principally on whether the polymers and amorphous or crystalline. For example, this is a DMA curve, sometimes we call the 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 a storage modulus.

So, this is G prime and this is tan delta tan delta this side and this is G double prime. Now, you can see that G prime decreases with temperature and at a particular temperature around for around 130 or 140 which it dropped significantly. Similarly, G double prime actually increases and it peaks around 145 somewhere there little higher than the drop observed for G prime.

And the ratio of G prime by G double prime actually peaks around 150. So, it is around 150. So, this is the value where we get the peak of tan delta that correspond to the Tg or corresponds to the phase transition depending on the surface we can call this as a first curve transition and second curve transition that we have discussed earlier. So, this is a Tg corresponds of polycarbonate as we measure from a DMA.

Now, if you look at the same experiment when done at from a low temperature - 200 to 200 then you can see this additional peak of tan delta somewhere in - 200. Now, this is generally is not captured in a DS measurement, because these actually related to very small change in enthalpy or heat capacity. Hence, DMA gives us the advantage of capturing even small change in like polymer structure or polymer movement.

And in this case like this as another transition which have at sub 0 and it is believed that because of these transition polycarbonate shows, high impact behaviour or high ductility behaviour in spite of having a completely amorphous structure. So, this is one transition at very low temperature and another transition which we discussed here around 150 degrees centigrade corresponding to that glass transition temperature or T g.

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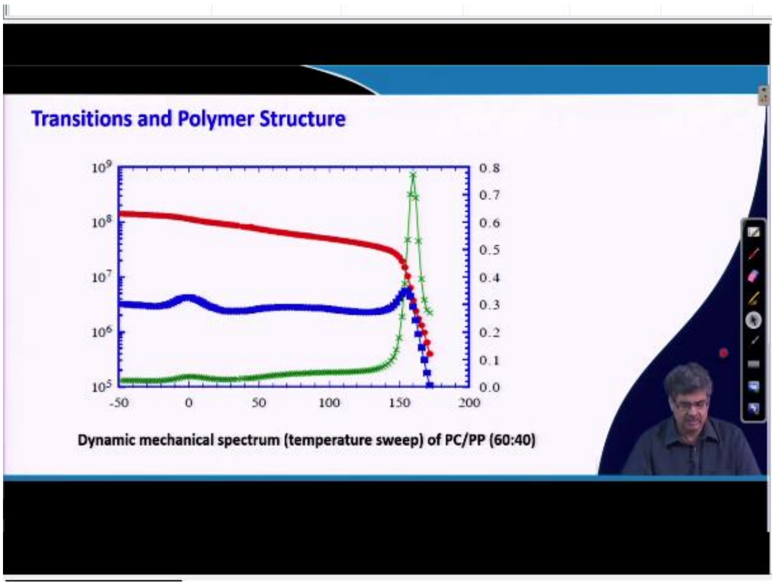

Transitions and Polymer Structure

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 finding temperature keeping the frequency same and you can see this 2 peak corresponds to tan delta. This is G prime, this is G prime, this is G double prime and this is tan delta. So, you can see there is 2 peaks correspond to one around 0 degree for polypropylene and another one around 150 degree that is, because of this is actually filled samples.

So, this is actually a little higher than 150. So, this peak corresponds to around 160 because they are glass filled sample. So, using DMA we can actually measure the temperature correspond to different transitions like glass transition temperature as shown here.

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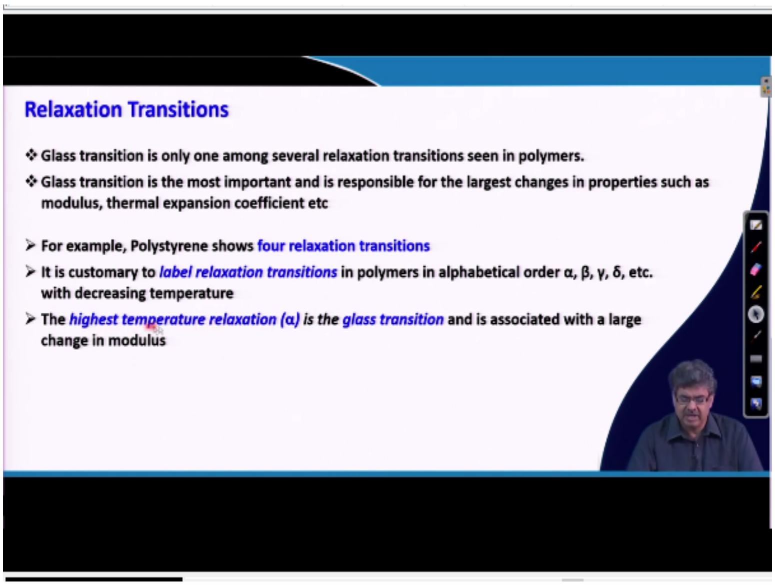

Relaxation Transitions

- 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 conditions are also possible as we described for polycarbonate at sub 0 minus 200 type in the last slide and that is possible to capture or detect those transitions by DMA experiments which are not possible or very difficult to achieve using traditional differentiations colorimetry or DMA experiment as we discussed earlier.

So, we can talk about relaxation transitions, and glass transition is only one among several relaxation transitions seen in polymers and glass transitional is the most important and responsible for the largest changes in properties such as modulus, thermal coefficient, thermal expansion coefficient etc. But besides glass transition, there are other relaxation transitions in polymer materials.

For example, polystyrene shows 4 relaxation transitions. And it is customary to label relaxation transitions in polymer in alphabetical order alpha, beta, gamma, delta type, where alpha is the highest temperature or alpha corresponding to the electrician transition corresponding to the highest temperature. So, the highest relaxation temperature relaxation is always alpha is a glass transition and associated with the large change in modulus as we have seen earlier. And the other transitions existed and but the change in modulus or other properties are comparably matched lower compared to the glass transition.

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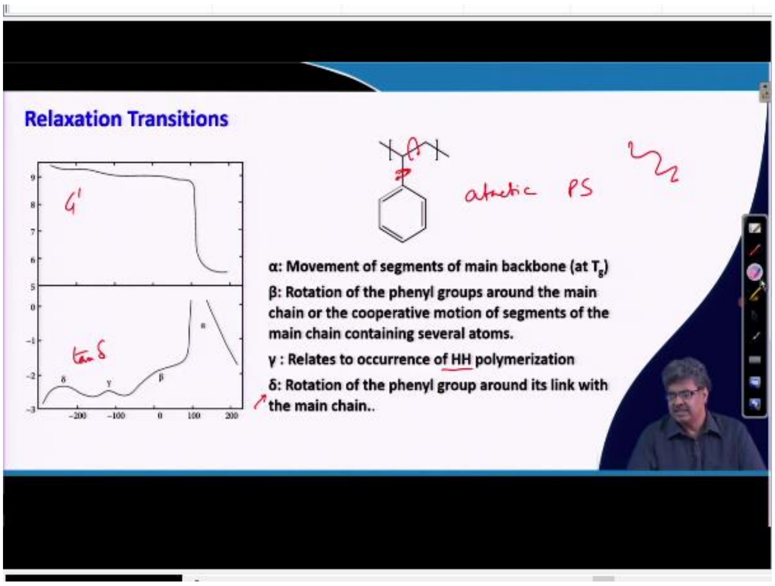

Relaxation Transitions

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..

So, this is a example of DMA curve for a tactic polystyrene and this is a G prime curve and this is your tan delta. So, you can see that we have 4 transition relaxation transitions. And obviously, you can see that reflects in the G prime values also, there are the conditions are very weak the alpha condition which corresponds to the glass transition is very sharp and very significant that is why the modulus drops significantly.

But there are other transitions which are weak transition. So, the change in modulus is not that prominent, but they exist in polymer system. As we mentioned for polystyrene there are 4 transition alpha transition corresponds to glass transition**,** which corresponds to the movement of polymer segment 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 represent or corresponds to the beta transition. Similarly, rotation of phenyl ring around this carbon and phenyl ring corresponds to delta transition and there is another transition which occurred due to head to head polymerization. So, as you can see that these electrician transition can be captured with dynamic mechanical analysis.

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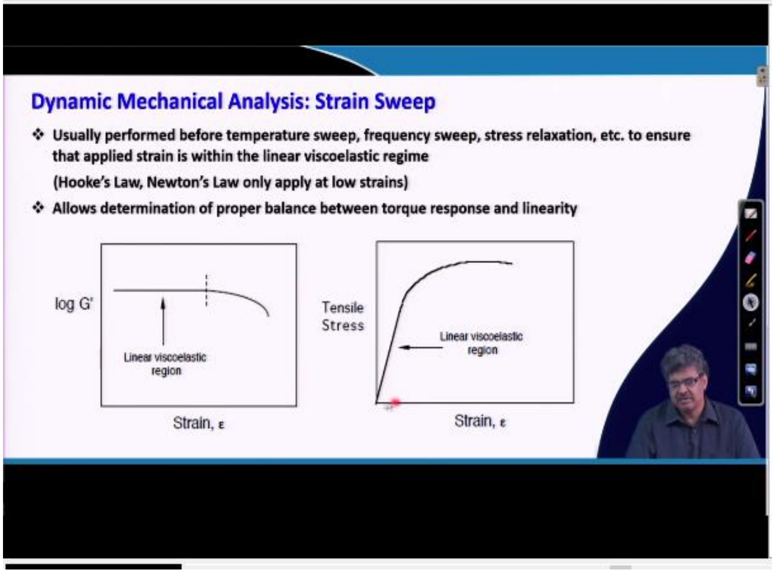

Dynamic Mechanical Analysis: Strain Sweep

- 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 trace relaxation etc. to ensure that the applied strain, whatever stream we are applying is in within the linear viscoelastic regime.

Otherwise, this will complicate the experiment further and for example, if we plot log G prime with strain then you can see up to some strain the sample behaviour is linear. So, the call this region as a linear viscoelastic region and similarly, for a tensile experiment you can see there are up to some strain, this linear viscoelastic region is maintained. So, we need to do a frequency sweep or temperature sweep we should remain within a 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 between these linear viscoelastic regime.

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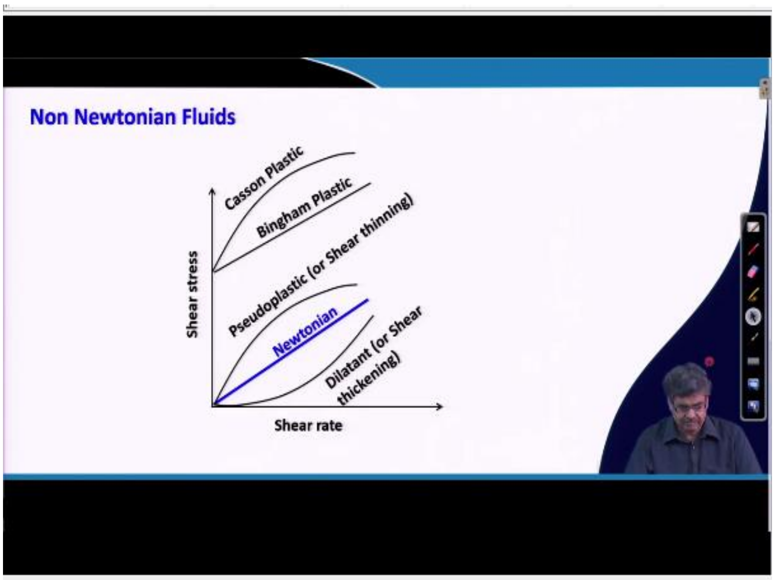

Non Newtonian Fluids

The polymer samples actually can also be of like a non Newtonian fluid and we can basically classify these behaviour s into different type of polymer material. For example, if the shear stress and shear rate are linearly related then we call is 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 behaviour.

Actually, viscosity comes down as a higher shear rate. And 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 and there is also possibly 2 more possible is behaviour, in this case you can see the stress remains 0. And after a value then it start behaving linearly. So, it is called is a Bingham plastic, if a behaviour is like this as shown in this graph.

And this is a casson plastics, where it start 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 and there is an advantage also associated with this type behaviour as I explained this shear thinning behaviour help us in processing. During processing if the shear rate is higher than actually the melt viscosity actually drops 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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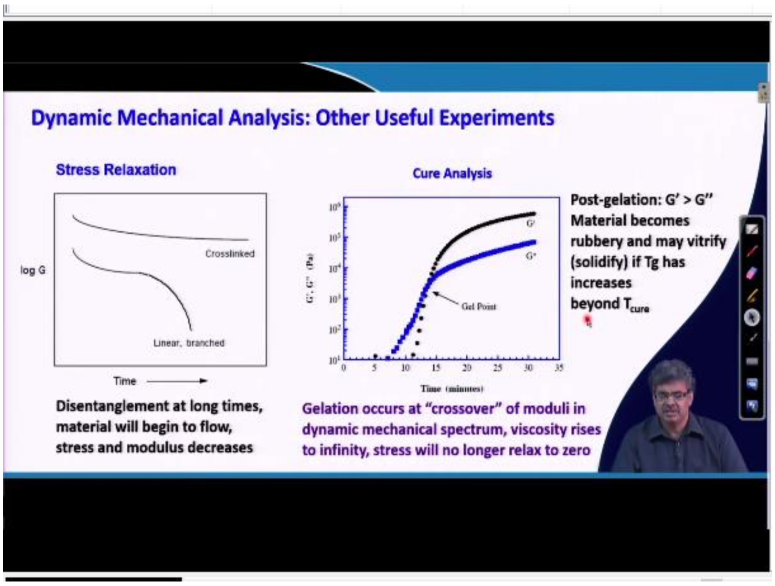

Dynamic Mechanical Analysis: Other Useful Experiments

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, where we plot G with time and you can compare the linear or branched polymer with the crosslink polymer. For a linear or branch sample, the shear modulus actually comes down after some time as the polymer chain entangled with each other and starts moving past one another and the value of G actually decreases and approaches to 0.

Whereas, for crosslink material as the polymer chains are cross-linked they cannot get separate from each other. So, the value of G does not decreases beyond a certain value even you keep the sample or the stress for a much longer time. So, this entanglement at long time 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 cure curing like isothermal cure, where we do the curing experiment at the same temperature. And 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 double prime is higher than G prime 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 happened in that time, basically G prime crossover G double prime and that is the point we call gel point and above this gel point G prime higher than G double prime and because this happened due to cross linking for curing these G double prime do not come back to lower value because the polymers cannot move fast each other because of the cross linking.

And due to this curing, if the T g of the polymers sample increases, then the experiment at which the experiment is done curing experiment done if that becomes lower than the Tg of the sample, then this sample the cured sample become glossy in nature. So, gelation occur at this crossover of moduli G prime and G double prime in dynamic mechanical spectrum viscosity raises to infinity at because we have cross polymer samplers are becoming cross linked and they have a network structure.

So, stress will no longer be approaching to 0 and post duration as I explained G prime would be greater than G double prime materials become rubbery and may become solidify or maybe vitrified. If the T g of the resulting sample increases beyond the T temperature of curing.

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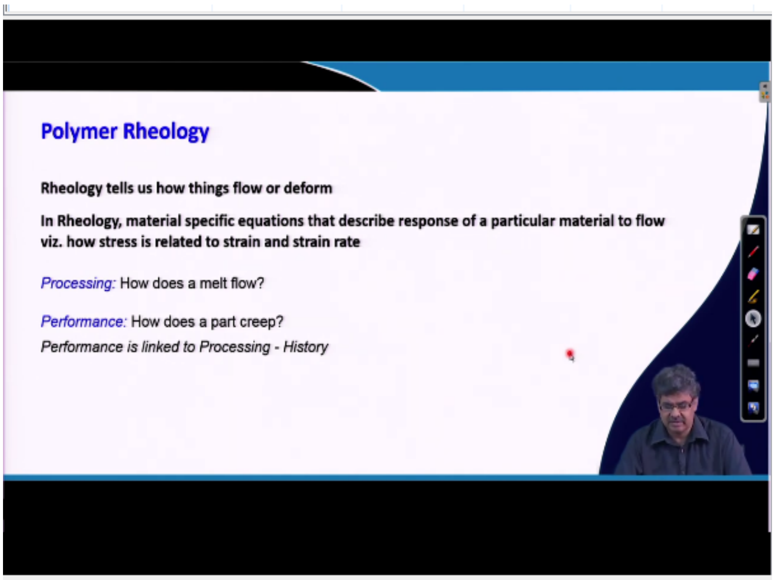

Polymer Rheology

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 behaviour which is related to the flow properties of polymer samples. And actually the flow behaviour of polymer samples are formally called rheology. The science of studying flow behaviour of any material is called rheology and we use the polymer sample then we talk about polymer rheology. So, rheology tells us how things flow or deform and we discussed the deformation behaviour or flow behaviour in details during studying our discussion on viscoelastic properties. So, in rheology material specific equations that describes response of particular materials to flow.

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? Especially the main processing we should know how the polymer melt flow? Also and as a result, the performance of polymer sample final product is actually linked to the processing history.

And also the performance of final polymers 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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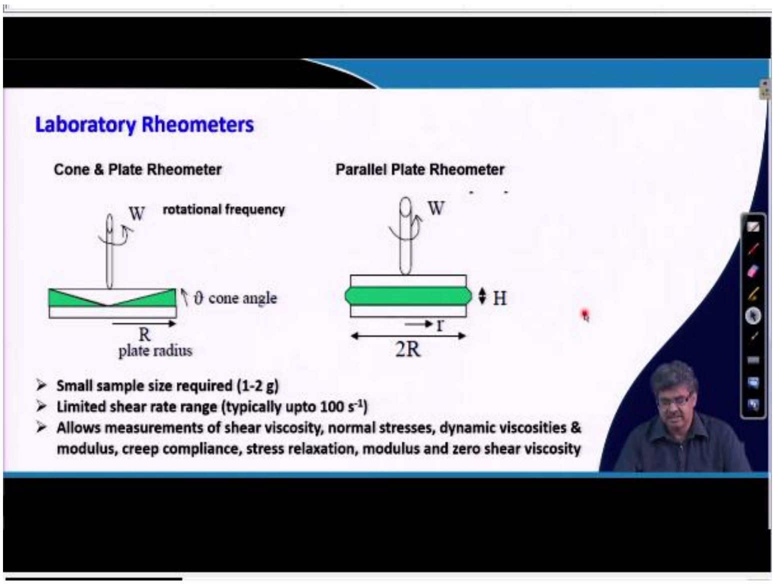

Laboratory Rheometers

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

And the typical laboratory rheometers which are used like cone and plate rheometers, I am not going into details about the principle of an action if you require you can go through any literature. So, this cone and plate rheometer or panel plate rheometer or capillary rheometer can be used to measure the flow properties of polymer in lab and these rheometers requires small size 1 to 2 gram.

And these lab rheometers can be used for a limited shear rate range typically, up to 100 second inverse. This allows the measurement of shear viscosity normal stresses dynamic viscosity and modulus keep 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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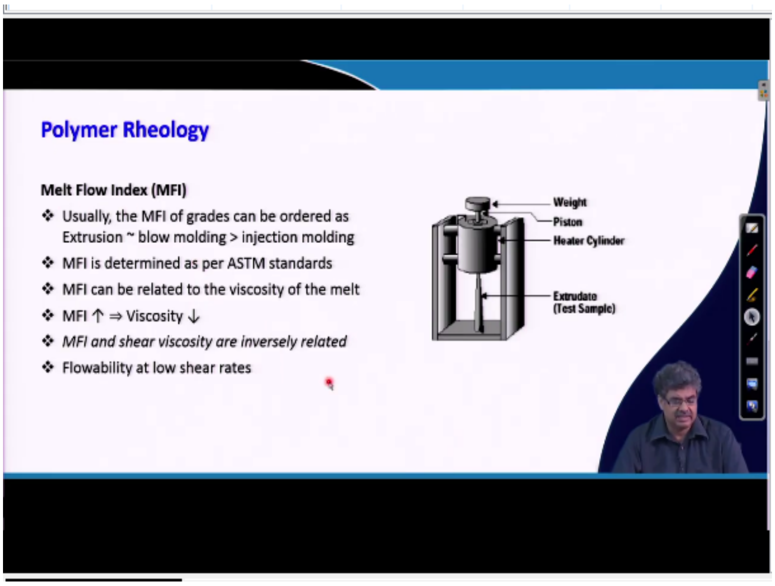

Polymer Rheology

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 is called a MFI measurement melt flow index measurement. In this case, a sample is basically allowed to flow under a certain load. So, in this case, as we know, there is the flow behaviour also depending upon the applied stress or load. So, in this case the sample is heated and it is allowed to flow through a basically a orifice under a some particular load.

So, this MFI of grades or different gates of polymers can be ordered as extrusion blow simulated blow only greater than injection molding, which means this MFI injection liquid means the higher value of MFI. 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, MFI is higher.

That means it flows better. So, the viscosity is lower. MFI and shear viscosity are inversely related as I discussed, when the shear viscosity comes down, more and more sample actually comes out. So, MFI goes up and flowability at low shear rate can be basically determined by this main flow index measurement.

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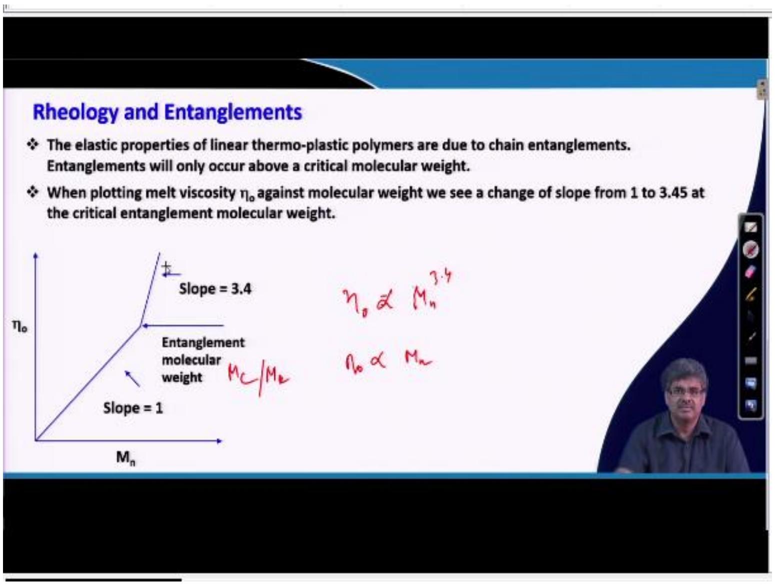

Rheology and Entanglements

- 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.

$\eta_o \propto M_n^{3.4}$

$\eta_o \propto M_n$

Rheology and entanglement is a important aspect of polymer flow behaviour, the elastic properties of linear thermoplastic polymers are due to chain entanglement, that I have described several times that because of the entanglement of polymer chain, when the frequency is higher, it cannot be entangle and move forth polymer chains cannot move fast each other as a result, the elastic or solid like behaviour happens.

And entanglements will only occur above a certain critical molecule, obviously, to have these entangled means the polymer has to have a minimum amount of size or molecular weight so that the bend and entanglement with each other. For example, if you are talking about a Charmin sample, if we break this Charmin sample in small pieces, then they do not entangled with each other we can easily take out from the wall.

But if we do not break and we use large size Charmin then we can see that they are basically entangled with each other, it is very difficult for takeout the sample from plate using say a spoon or something. So, when plotted melt viscosity against molecular weight, we see that a change in slope from 1 to 3.45 at a critical entanglement molecular weight. So, when the molecular slope below this critical entanglement molecule with MC, we call this is MC critical entanglement molecule weight or ME sometimes it is called ME**.**

Below this 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 the results the viscosity shoots are very sharply and viscosity become the factor of into the cos eta 0 varies with varies Mn to the power 3 to the power 4. Below the critical molecular weight eta 0 varies with Mn. And that result because of the entanglement of polymer chains, with each other.

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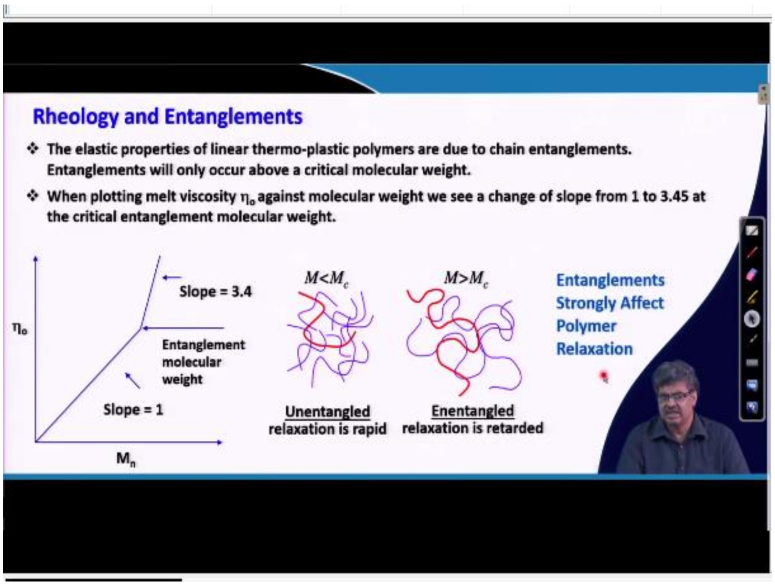

Rheology and Entanglements

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Entanglements Strongly Affect Polymer Relaxation

So, this un entangled when M is less than M c. This un entangled, they can relax rapidly. So viscosity is high, low, but when the polymer molecule weight is higher, the chain entangled with each other. So, the relaxation is retarded they cannot move fast each other as a result viscosity is higher. So, entanglements are 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 polymer the molecular weight actually has to be high. So, the mechanical property for example increases sapling molecular weight before it levels up above certain molecular weight. So, ideally you should have high molecular weight to have high poverty similarly flow behaviour actually decreases, the viscosity increases very much with molecular weight.

So, ease of processing actually decreases with molecular weight, the high is the molecular weight viscosity is very high. As a result, the processing becomes difficult. So, ease of processing becomes lower with increasing molecular weight.

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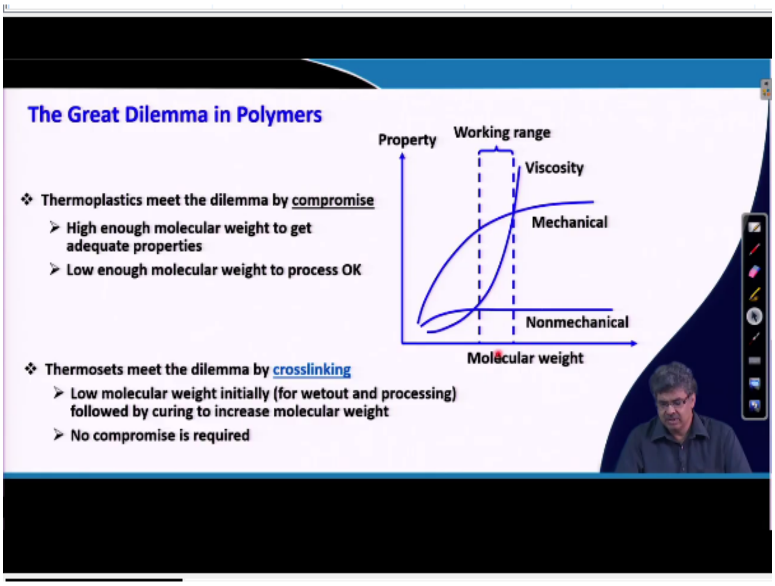

The Great Dilemma in Polymers

- 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 made by a compromise. So, basically we choose a molecular weight range. So, this is the working range. So, there is a compromise between the ease of processing, which is governed by the viscosity, and the property like mechanical properties. So, this is the working range of the molecule weight which balances between the ease of processing and the property.

And for thermosets this balance, or this dilemma is made 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. So, basically, curing increases the molecular weight. So, no compromise required if the cross linking is done, and on cross linking value of the properties increases. With this I will stop for this lecture.