PolCoPUS
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Lecture No -57
Viscoelastic response: examples

Hello, we are in the week 9th of this course on polymers and viscoelasticity is still with us given the importance of viscoelasticity in polymeric systems we have at least spend two weeks trying to analyze different aspects. In this lecture we will look at a couple of examples which highlight many of the concepts that we have seen. So by focusing on properties of polymeric materials we will get further insights into viscoelastic response of polymers.

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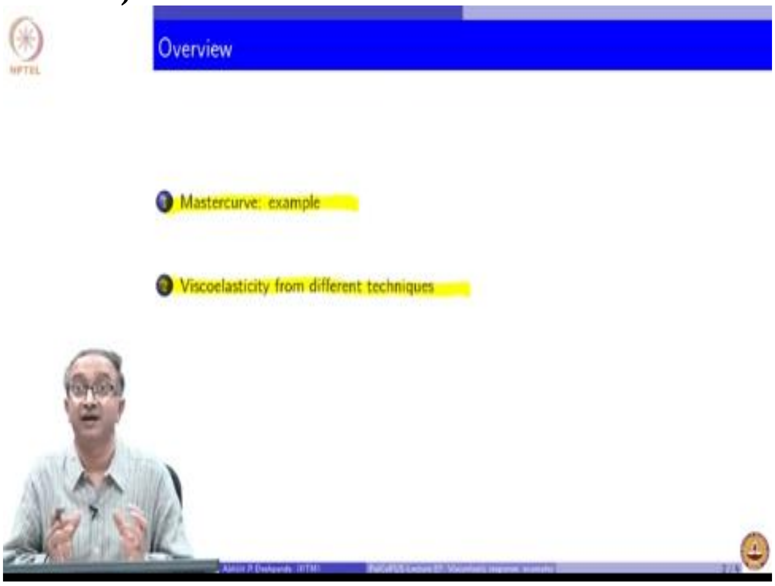

Overview

- Mastercurve: example
- Viscoelasticity from different techniques

And this will do by doing two things we will look at an example of a master curve which is obtained during time temperature superposition as we discussed earlier and we have discussed dielectric response we have discussed mechanical response, so can we not look at viscoelasticity and compare and contrast behavior obtained from different techniques. So we look at one example related to viscoelasticity from different techniques.

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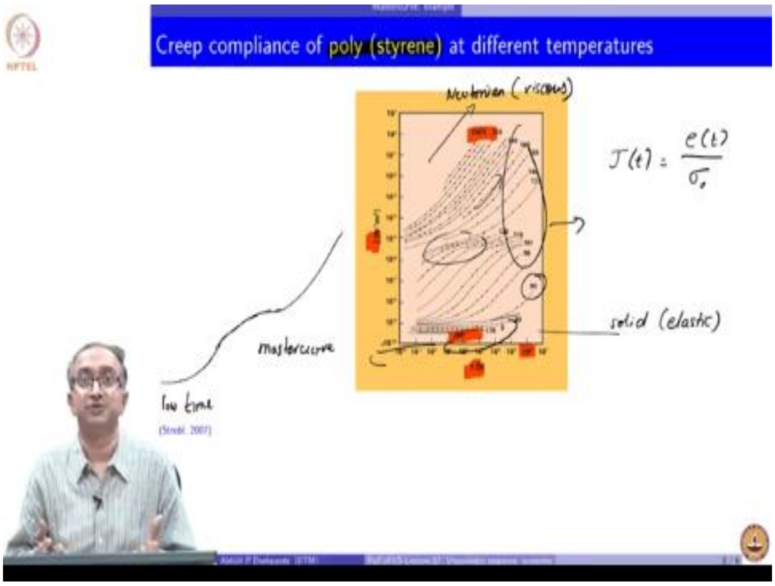

Creep compliance of poly (styrene) at different temperatures

$J(t) = \frac{e(t)}{\sigma_0}$

(Strobl, 2007)

So let us begin by looking at this classical data which is for polystyrene and again what we can do is do experiments in lab for time scales which are up to 10^6 seconds, 10^7 seconds. So this is basically some days and that is doable and what you can see is the experiment is done at several different temperatures and look at the range of temperature and that is why such data is part of all the textbooks related to polymers.

The temperature is varied from very low temperature to very high temperature and what we can see is the compliance, right compliance varies from very low which means the material is stiff and does not comply as much the strain in the material is very less. Remember that compliance is related to strain in the material divided by the constant load that is being applied in a creep experiment.

So strain is very high at high temperature again something which is easy for us to understand. Now you can see that there is all different types of qualitative response we have basically constant compliance which implies an elastic Hookean elastic behavior we also have pretty much constant increase in compliance which pretty much implies Newtonian viscous response and again at lower temperature we would expect the solid like response elastic.

And at very high temperature we would expect Newtonian. So it is very nicely captured in the data here now what we can do is shift these curves, so we can let say pick any one of the temperature as our reference temperature and then start shifting the curve. So let us say if we are interested in looking at the material response at 90 then what we can do is these curves can be shifted to the left and all these curves can be shifted to the right and what you can see is initially the stress is compliance is constant then it increases.

And then in this region you can again see that when we stack different curves like this preparing a master curve what we will see is there is again a plateau and then again it starts increasing, so therefore again it so this is will be the type of master curve that we will get and why do we get a master curve like this? What do the different regions in this master curve imply? Basically what we are trying to suggest through this master curve is very low time we have material elastic.

If you do not give them as a chains enough time to untwist or do any deformation there is no segmental mobility in that case basically we have no compliance and very large time if we give then the material will deform and this is a curve which is prepared at 90, but the time because we will do the shifting and it may happen that the time will be 10^{15} seconds. So it basically requires years not just some years we may require thousands and millions of years for it to actually start flowing.

And that is again the concept of Deborah number that we talked about that the material relaxation time and the experimental times the relationship between the two we will have to look at while analyzing elastic response of polymeric materials.

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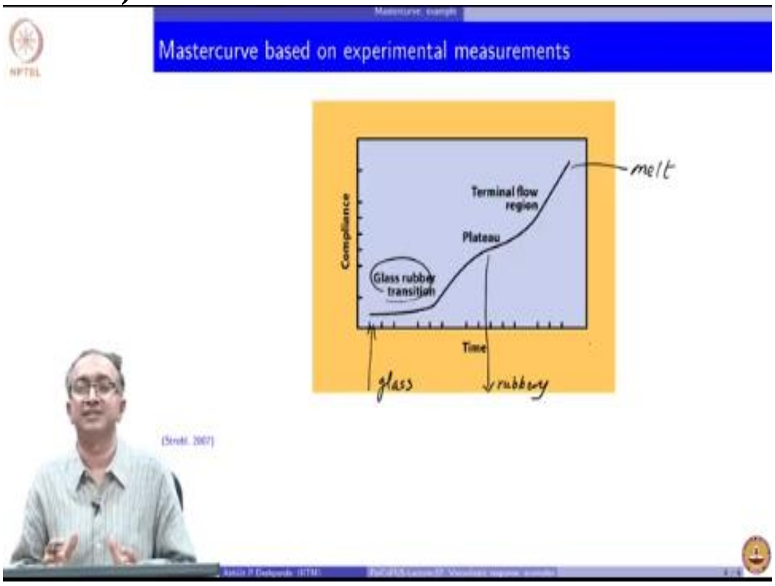

Mastercurve based on experimental measurements

(Strobl, 2007)

So if you construct a master curve based on this is how the response will be so what we have is basically the glassy region, then we have the transition and then we have the rubbery region and then we get the melt region and if these regions are different over basically a time scale which can be about 10^{15} seconds. So that is the range of time over which we can analyze the response of polymeric materials using the master curve approach.

So such master curves are prepared for variety of systems you can go and look at textbooks or other resources and see master curve preparation for frequency E' data or master curves for tan delta and frequency data or we can do dielectric loss and frequency. So any measure of viscoelasticity if we want information over multiple length scales and time scales we can do the time temperature superposition.

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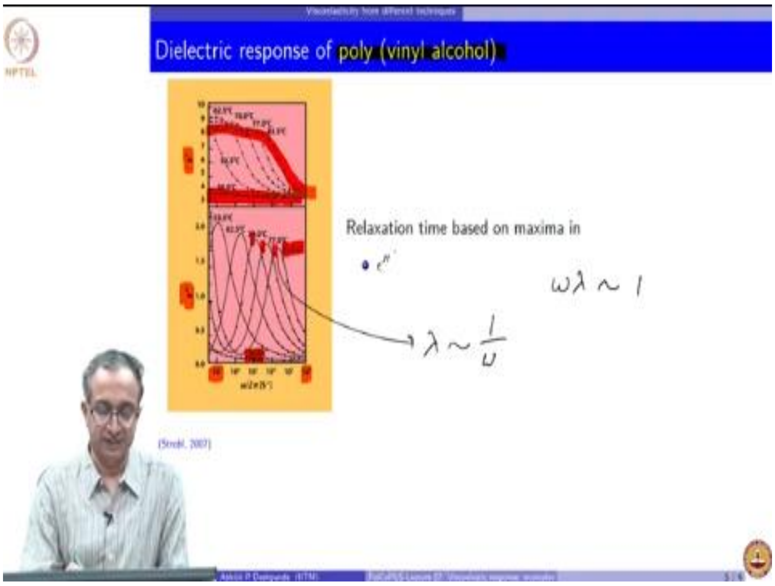

Dielectric response of poly (vinyl alcohol)

Relaxation time based on maxima in

- ϵ''

$\omega\lambda \sim 1$

$\lambda \sim \frac{1}{\omega}$

(Strobl, 2007)

Now let us close by looking at other classic data in this case this is polyvinyl alcohol and its permittivity as well as dielectric loss in the material and again the measurements are done for frequencies for which dielectric spectroscopy is generally used that is millihertz to mega hertz and in this case the measurements are about 1 hertz to 10^6 megahertz and the measurement is done at all different temperatures.

And from 38 to about 85, 83.5 ^{o}C and so what you can see is at higher temperature you can clearly see this debye like response permittivity which is roughly constant and then because of segmental mobility remains frozen because very high frequency is being used for the electric stimulus in this case the dipoles cannot orient and I hope that you can recognize what is the dipole in case of polyvinyl alcohol if you do not please go look at the structure of polyvinyl alcohol and identify what could be the dipole that can orient.

Is it part of a side group? Is it part of the backbone? Try to answer those questions and so but as we change the temperature and as we go to lower and lower temperature what happens is, the overall dipoles actually lose the ability to orient themselves because macromolecules themselves become very inflexible because of reaching the glassy state. So clearly what you can see is we again have a glass to rubber transition and that is also represented by the peak in dielectric response.

So you can recognize that we discussed this during Maxwell model response that frequency at which you observe the peak is usually where $\omega\lambda$ is 1. So this peak frequency is where λ can be estimated as inverse of this ω so based on this we can calculate or estimate relaxation times in the material and in this case since there is a maximum in dielectric loss we can get the relaxation times.

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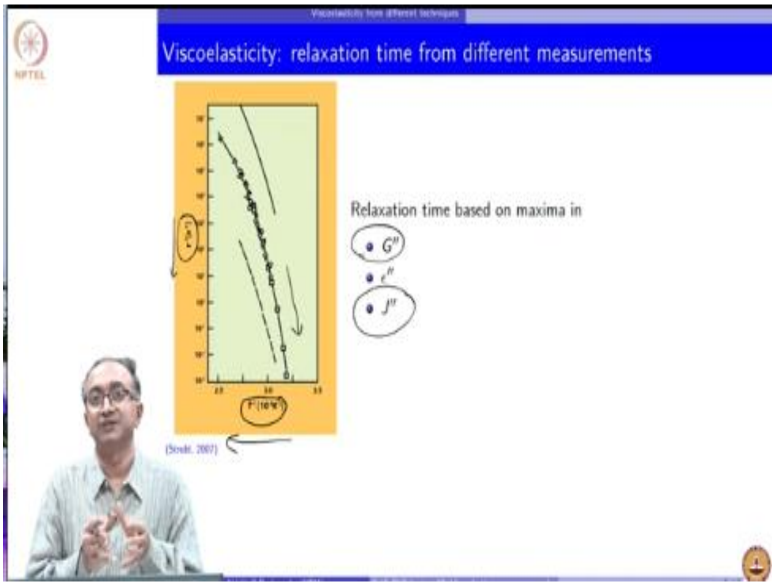

Viscoelasticity from different techniques

Viscoelasticity: relaxation time from different measurements

Relaxation time based on maxima in

- G''
- ϵ''
- J''

(Strobl, 2007)

And the same exercise can be carried out by doing sinusoidal variation and calculating compliance or sinusoidal variation in calculating the modulus and in this graph for same polyvinyl alcohol the data is summarized where the relaxation time and in this case it is the inverse of relaxation time is plotted with inverse of temperature. So temperature is increasing as we go along here and time is also similarly increasing as you go along here.

So lower and lower temperature implies higher and higher time and you can see that there is an order of magnitude difference in terms of relaxation times when you go from one technique to the other because in one case you are measuring far local phenomena. In case of dipole in the other cases it may be different phenomenon but you can see that overall qualitative response matches and this is something which we always do in terms of looking at viscoelasticity from different perspectives and then try to rationalize the overall response of materials.

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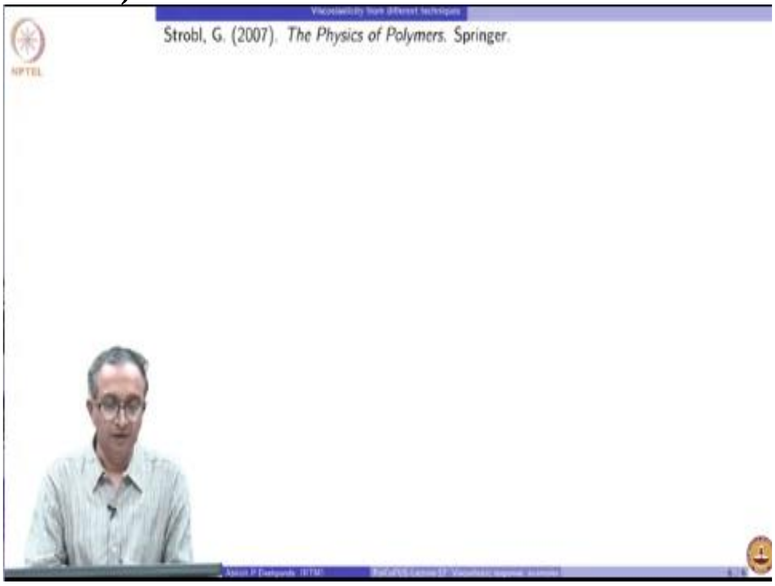

Viscoelasticity from different techniques

Strobl, G. (2007). *The Physics of Polymers*. Springer.

So with this we will close this lecture we have summarized the overall viscoelastic response using a master curve or using multiple techniques to analyze the viscoelastic response in materials, thank you.