Mechanical Behavior of Materials

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Module No # 09
Lecture No # 47
Creep – V

Hello I am Professor S. Sankaran in the department of metrological and materials engineering.

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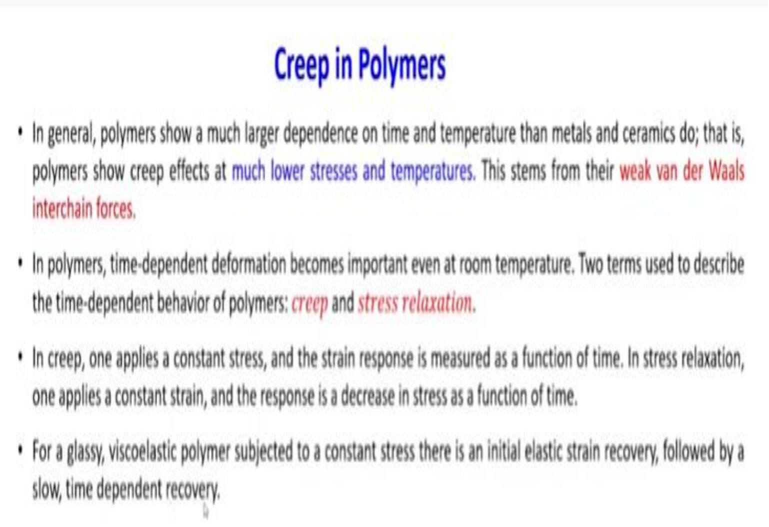

Creep in Polymers

- In general, polymers show a much larger dependence on time and temperature than metals and ceramics do; that is, polymers show creep effects at much lower stresses and temperatures. This stems from their weak van der Waals interchain forces.
- In polymers, time-dependent deformation becomes important even at room temperature. Two terms used to describe the time-dependent behavior of polymers: *creep* and *stress relaxation*.
- In creep, one applies a constant stress, and the strain response is measured as a function of time. In stress relaxation, one applies a constant strain, and the response is a decrease in stress as a function of time.
- For a glassy, viscoelastic polymer subjected to a constant stress there is an initial elastic strain recovery, followed by a slow, time dependent recovery.

Hello everyone welcome to this lecture we have been looking at creep deformation in the last two lectures, of different class of materials and different mechanisms which governs this behavior. Today we will focus our attention to creep in polymeric materials. It is also you know gives an idea about, what happens to the non-crytalline or semi-crytalline materials during creep deformation. So in general polymers show a much larger dependence on time and temperature than the mηls and ceramics do. That is polymer show creep effects at much lower stresses and temperatures this stems from their peak van der Waals interchain forces. So we have a good background to realize all this effects because we looked at polymeric deformation in tensile mode. Also we briefly discussed about the polymeric structure and we also know what; is van der Waals force all that it is a secondary bond?

So all this thing background will have a profound influence on their creep deformation that is what it is? So as compared to mηl and ceramics these materials exhibit a high large dependence on time and temperature. We also looked at this time dependency of, you know these materials in an elastic region that also we have looked at it. In polymers time dependent deformation becomes important even at room temperature.

Two terms used to describe the time dependent behavior of polymers one is creep other is stress relaxation. In creep one applies constant stress and the strain response is measured as a function of time in stress relaxation is one applies constant strain and response is a decrease in stress as a function of time. So these two terms like you know a creep and stress relaxation both are measured in these polymeric materials. We will just look at them and how their behavior is understood that is also we will discuss in the lecture.

For a glassy or viscoelastic polymer subjected to a constant stress there is an initial elastic strain recovery followed by slow time dependent recovery. So that we are now talking about two terms one is initial elastic strain recovery that is instantaneous or immediate, followed by a time dependent recovery. So, we have to distinguish these things and then we look at the total behavior.

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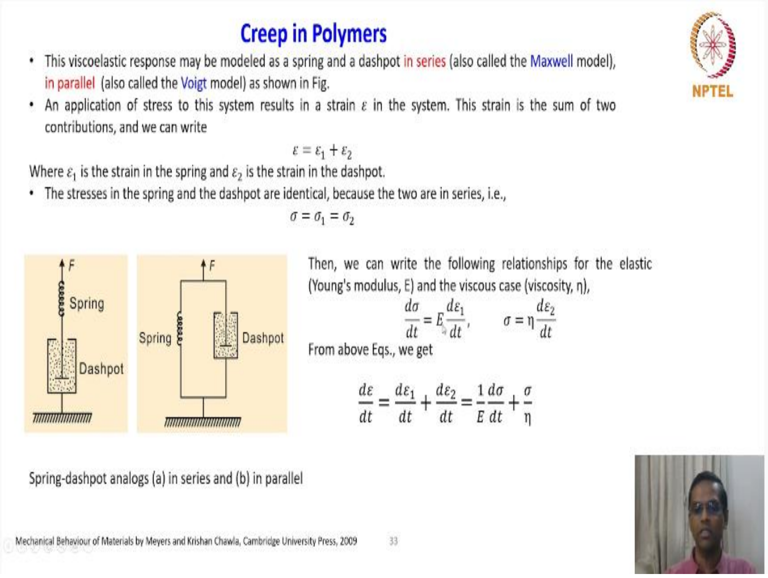

Creep in Polymers

- This viscoelastic response may be modeled as a spring and a dashpot in series (also called the Maxwell model), in parallel (also called the Voigt model) as shown in Fig.
- An application of stress to this system results in a strain ε in the system. This strain is the sum of two contributions, and we can write

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

Where ε_1 is the strain in the spring and ε_2 is the strain in the dashpot.

- The stresses in the spring and the dashpot are identical, because the two are in series, i.e.,

$$\sigma = \sigma_1 = \sigma_2$$

Then, we can write the following relationships for the elastic (Young's modulus, E) and the viscous case (viscosity, η),

$$\frac{d\sigma}{dt} = E\frac{d\varepsilon_1}{dt}, \qquad \sigma = \eta\frac{d\varepsilon_2}{dt}$$

From above Eqs., we get

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

Spring-dashpot analogs (a) in series and (b) in parallel

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So in order to describe the creep deformation, people have thought of several models. So, one of the popular model which is most of the textbooks prescribes is this kind of you know a spring dashpot analogs. A spring is there and a dashpot is there with a viscous fluid and piston kind of a thing which is attached to a spring and then you apply a force like this and the one is fixed as it shown here that is called the spring dashpot setup.

This is in a series that means the dashpot or spring is connected in a series and in figure (b), it is connected through a parallel. So now you apply at force from this end and then try to look at, what kind of stress or a strain experience by the dashpot as well as the spring. So these two analogs are compared with the polymeric materials we will see how it is quite interesting but then how much it is relevant to in I mean in real time polymeric deformation that is what is we have to look at it.

This viscoelastic response may be model as the spring dashpot in series which is also called Maxwell model very popularly denoted as Maxwell model. In parallel it is called white model so it is instead of spring and dashpot in series and parallel it is also referred as Maxwell and white model as shown in this figure. An application of this stress to this system results in a strain ε in the system this strain is the sum of two contribution and we can write $\varepsilon = \varepsilon_1 + \varepsilon_2$ where ε_1 is strain in the spring and ε_2 is the strain in the dashpot.

So, the strain experience by the spring and strain experience the dashpot can be additive because it is in the series. So $\varepsilon = \varepsilon_1$ total strain = $\varepsilon_1 + \varepsilon_2$. The stresses in the spring or the dashpot for identical because the two are in series. So, strain is additive but the stress is equal, identical they are not additive here so this we have to understand for this model. Then we can write the following relationship for an elastic and viscous case.

So this is basic Young's modulus equations stress is proportional to strain and $\sigma = e\ \varepsilon$ that kind of equation you can rewrite this equation like this. For a viscous flow because this is a stress is written like this $\sigma = \eta(d\varepsilon_2/dt)$ this is a gradient. This is so basics relations we have already seen it so we can make use of this to analyses this stress strain relationship.

From the above equation we can rewrite those like, $d\varepsilon/dt = (d\varepsilon_1/dt) + (d\varepsilon_2/dt)$ which is can be rewritten as $(1/E)(d\sigma/dt)$ from this relation plus $\eta\ (\sigma/\eta)$ from this relation. So this we are replacing with these two terms which is taken from the basic equations.

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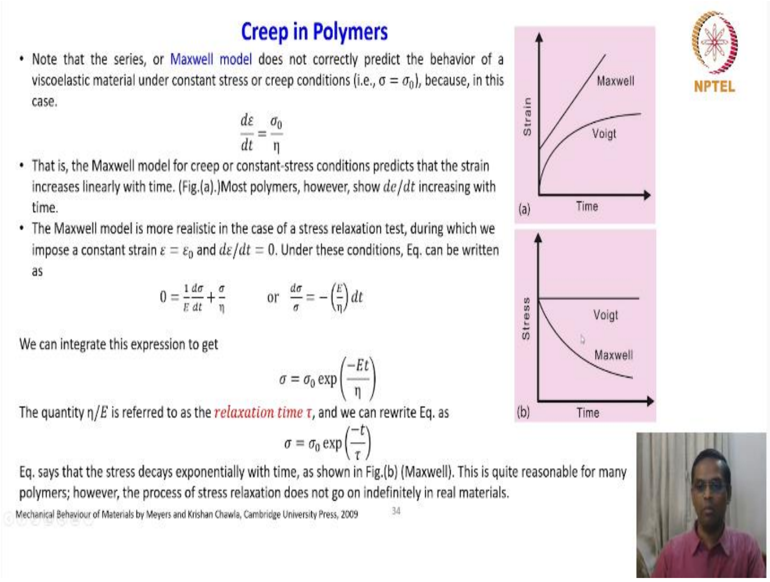

Creep in Polymers

- Note that the series, or Maxwell model does not correctly predict the behavior of a viscoelastic material under constant stress or creep conditions (i.e., $\sigma = \sigma_0$), because, in this case.

$$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{\eta}$$

- That is, the Maxwell model for creep or constant-stress conditions predicts that the strain increases linearly with time. (Fig.(a).)Most polymers, however, show de/dt increasing with time.
- The Maxwell model is more realistic in the case of a stress relaxation test, during which we impose a constant strain $\varepsilon = \varepsilon_0$ and $d\varepsilon/dt = 0$. Under these conditions, Eq. can be written as

$$0 = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} \qquad \text{or} \qquad \frac{d\sigma}{\sigma} = -\left(\frac{E}{\eta}\right) dt$$

We can integrate this expression to get

$$\sigma = \sigma_0 \exp\left(\frac{-Et}{\eta}\right)$$

The quantity η/E is referred to as the *relaxation time* τ, and we can rewrite Eq. as

$$\sigma = \sigma_0 \exp\left(\frac{-t}{\tau}\right)$$

Eq. says that the stress decays exponentially with time, as shown in Fig.(b) (Maxwell). This is quite reasonable for many polymers; however, the process of stress relaxation does not go on indefinitely in real materials.

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So now note that the series or a Maxwell model does not correctly predict the behavior of a viscoelastic material under constant stress or a creep condition. Where σ is equal to σ_0 because in this case the dε/dt is predicted by this Maxwell model is equal to σ_0/η. That is the Maxwell model for a creep, a constant stress condition predicts that the strain increases linearly with time that is shown in this figure.

But most polymers however the d ε/d t or the de/d t increase with time this is not the real time case. So, we will see, what is that Maxwell model can actually predict the actual model is more realistic in the case of a stress relaxation test. It is not predicting the creep behavior but in the stress relaxation test you can predict how? During which we impose a constant strain which is ε is equal to ε_0 then d ε/d t = 0.

So, in the previous case it is increasing but here it is 0 under these conditions equation can be written as that is d ε/dt = 0 which is equal to (1/E) (d σ/d t) + σ/η, this equation it is there in the previous slide and then we can rewrite them into this form that is d σ/ σ = -(E/η) d t. So we can now integrate this and then we get an expression for σ, $\sigma = \sigma_0 \ \exp\left(\frac{-Et}{\eta}\right)$.

So, the quantity η/E is referred to us as the relaxation time τ so this relaxation time we have already looked at it in the inelasticity chapter we discussed it and there also we looked at how this term comes when we discuss viscoelastic behavior same parameter here. And we can rewrite this equation now replacing this η/E as $\sigma = \sigma_0 \ \exp\left(\frac{-t}{\tau}\right)$, so this is a very standard expression now. Now we can see whether this is going to be useful.

So what I have shown in this plot is the stress versus time and the stress was I mean strain versus time and the stress versus time plot for the both the models and whichever are obeying the actual behavior that we can discuss then and there. Now we just said that Maxwell model does not predict the strain versus time behavior. On the other hand stress relaxation behavior it is predicting so that is what this equation shows.

So, equation says that the stress decays exponentially with time as shown in the figure b. So the stress versus time, Maxwell plot it is almost, it is exponential decay stress decay is shown here. So this model is valid for the stress relaxation behavior this is quite reasonable for many polymers however the process of stress relaxation does not go on infinitely in real time material. So the model predicts that it goes like this.

So if it is not you know touching the time axis then it is infinite right. So which is not the case in the most of the real time material so, that is one drawback with this Maxwell model.

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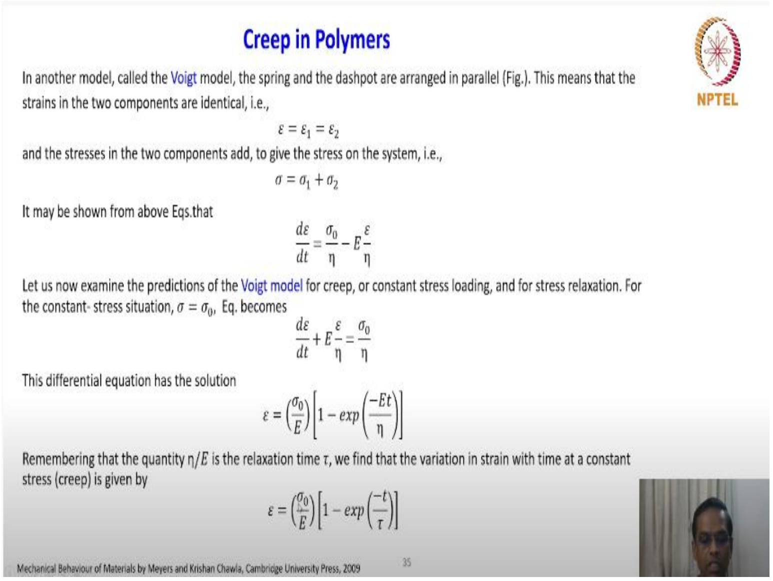

Creep in Polymers

In another model, called the Voigt model, the spring and the dashpot are arranged in parallel (Fig.). This means that the strains in the two components are identical, i.e.,

$$\varepsilon = \varepsilon_1 = \varepsilon_2$$

and the stresses in the two components add, to give the stress on the system, i.e.,

$$\sigma = \sigma_1 + \sigma_2$$

It may be shown from above Eqs.that

$$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{\eta} - E\frac{\varepsilon}{\eta}$$

Let us now examine the predictions of the Voigt model for creep, or constant stress loading, and for stress relaxation. For the constant- stress situation, $\sigma = \sigma_0$, Eq. becomes

$$\frac{d\varepsilon}{dt} + E\frac{\varepsilon}{\eta} = \frac{\sigma_0}{\eta}$$

This differential equation has the solution

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

Remembering that the quantity η/E is the relaxation time τ, we find that the variation in strain with time at a constant stress (creep) is given by

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

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In another model called Voigt model the spring and dashboard are arranged in parallel which is shown in the figure. This means that the strains in the 2 components are identical so there it was a stress was identical here the strain is identical or strains are identical there it is stress. So we can rewrite this and the stresses in the two components add to give the stress on the system that is in a spring dashpot connected in parallel the stress is additive so σ is equal to $\sigma_1 + \sigma_2$, that is what the Voigt model is assumes.

So we can rewrite dot equation like we have written in the previous case it is a very simple substitution you can just look at the previous slide it is the same. So we can rewrite these dε/d t = (σ_0 / η) - E (ε/η). Let us now, examine the predictions of the Vogit model for a creep or a constant stress loading and for stress relaxation. For the constant stress situation σ is equal to σ_0 then equation, has become d ε/d t + E (ε/η) = σ_0/η so this is what it is.

If you put this condition this differential equation has the solution like this form. So whether that is predicting or not that we have to see remember that the quantity η/E, is a relaxation time τ we can replace that. We find that the variation in strain with time at a constant stress is given by ε = (σ_0/E) [1 – exp(- t/τ)] so this is the final expression. So what is this expression say now?

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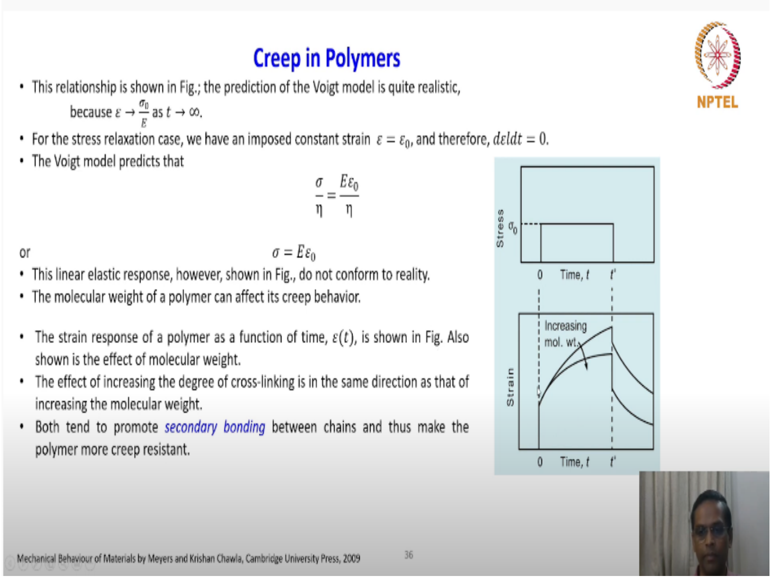

Creep in Polymers

- This relationship is shown in Fig.; the prediction of the Voigt model is quite realistic, because $\varepsilon \rightarrow \frac{\sigma_0}{E}$ as $t \rightarrow \infty$.
- For the stress relaxation case, we have an imposed constant strain $\varepsilon = \varepsilon_0$, and therefore, $d\varepsilon/dt = 0$.
- The Voigt model predicts that

$$\frac{\sigma}{\eta} = \frac{E\varepsilon_0}{\eta}$$

or

$$\sigma = E\varepsilon_0$$

- This linear elastic response, however, shown in Fig., do not conform to reality.
- The molecular weight of a polymer can affect its creep behavior.

- The strain response of a polymer as a function of time, $\varepsilon(t)$, is shown in Fig. Also shown is the effect of molecular weight.
- The effect of increasing the degree of cross-linking is in the same direction as that of increasing the molecular weight.
- Both tend to promote *secondary bonding* between chains and thus make the polymer more creep resistant.

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This relationship shown in the figure we will go back to the figure now the prediction of Voigt model is quite realistic because when ε tends to σ/E as t tend to infinity this what that plot also predicts what is that plot? Now we will go back to this plot.

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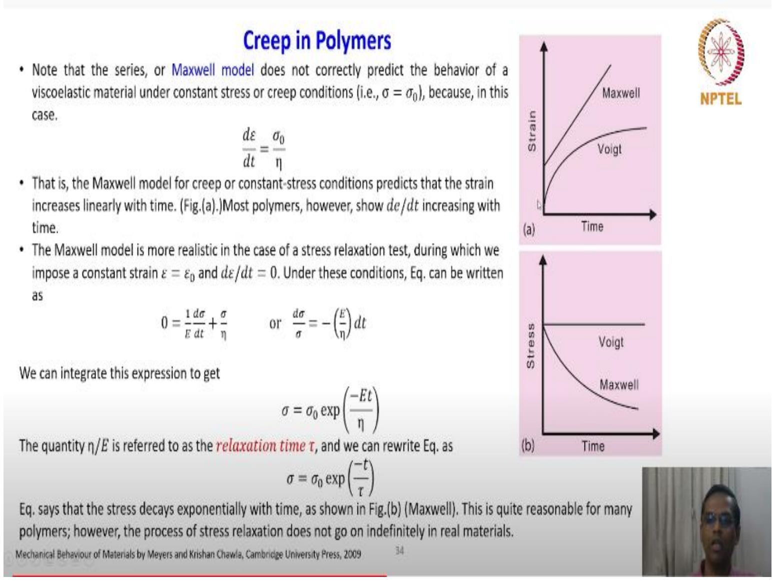

Creep in Polymers

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- That is, the Maxwell model for creep or constant-stress conditions predicts that the strain increases linearly with time. (Fig.(a).)Most polymers, however, show de/dt increasing with time.
- The Maxwell model is more realistic in the case of a stress relaxation test, during which we impose a constant strain $\varepsilon = \varepsilon_0$ and $d\varepsilon/dt = 0$. Under these conditions, Eq. can be written as

$$0 = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} \qquad \text{or} \qquad \frac{d\sigma}{\sigma} = -\left(\frac{E}{\eta}\right) dt$$

We can integrate this expression to get

$$\sigma = \sigma_0 \exp\left(\frac{-Et}{\eta}\right)$$

The quantity η/E is referred to as the *relaxation time τ*, and we can rewrite Eq. as

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Eq. says that the stress decays exponentially with time, as shown in Fig.(b) (Maxwell). This is quite reasonable for many polymers; however, the process of stress relaxation does not go on indefinitely in real materials.

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So this is the plot we are talking about. So the Voigt model predicts. So for a constant stress relaxation case we have an imposed constant strain that is ε is equal to ε_0 and therefore d ε/d t = 0. So for the constant stress the Voigt model predicts quite realistic behavior of polymer for the stress relaxation case. We have to impose this condition that is dε/dt = 0 then Voigt model predicts that $\sigma/\eta = E\varepsilon_0/\eta$, which is a linear behavior right.

Whether, this is okay or not this linear elastic, response over shown in this figure do not conform to reality. So, these two models are you know predicting the and only one condition either the stress relaxation or the constant stress or creep these are the two models but they predict only under either one of them in the both the deformation cases. So, what is shown in this plot the molecular weight of a polymer can affect its creep behavior.

So the strain versus time plot you can see that with increasing the molecular weight it is having some influence on the creep behavior right. The strain response of the polymer as a function of time that is strain as a function of time is shown in the figure. also shown the effect of molecular so strain is here it is a constant stress and then you can see the strain and this is a strain versus time so that is what it shown here.

The effect of increasing the degree of cross linking is in the same direction as that of increase in the molecular weight. So the degree of cross linking has the same effect like the molecular weight increase so both are interconnected anyway. Both tend to promote secondary bonding between chains and thus make the polymer more creep resistant. So the higher molecular weight polymer will have better creep resistant so that is what this, I mean these models explain.

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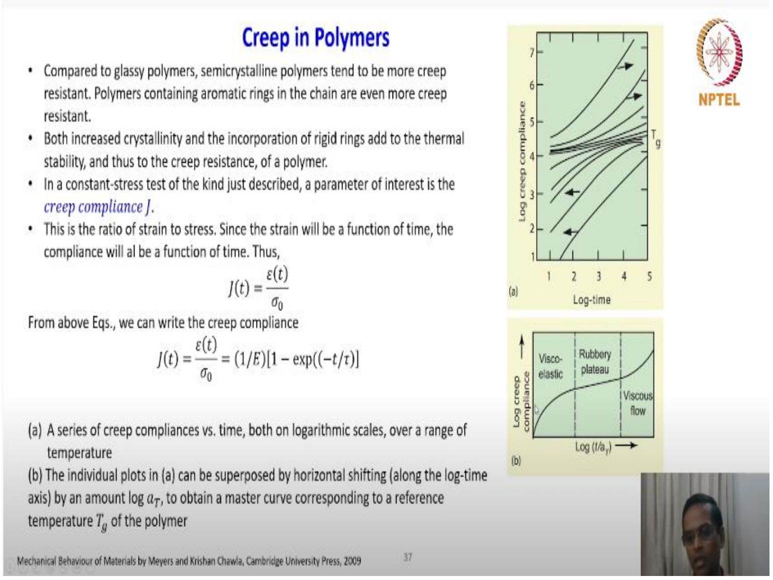

Creep in Polymers

- Compared to glassy polymers, semicrystalline polymers tend to be more creep resistant. Polymers containing aromatic rings in the chain are even more creep resistant.
- Both increased crystallinity and the incorporation of rigid rings add to the thermal stability, and thus to the creep resistance, of a polymer.
- In a constant-stress test of the kind just described, a parameter of interest is the *creep compliance J*.
- This is the ratio of strain to stress. Since the strain will be a function of time, the compliance will al be a function of time. Thus,

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

From above Eqs., we can write the creep compliance

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} = (1/E)[1 - \exp((-t/\tau)]$$

(a) A series of creep compliances vs. time, both on logarithmic scales, over a range of temperature

(b) The individual plots in (a) can be superposed by horizontal shifting (along the log-time axis) by an amount log a_T, to obtain a master curve corresponding to a reference temperature T_g of the polymer

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Compared to glassy polymers semi-crystalline polymers tend to be more creep resistance or creeprsistent. Polymers containing aromatic rings in the chain are more creep resistant. Both increased crystallinity and incorporation of rigid rings add to the thermal stability and thus to creep resistance of a polymer so these are some general characteristics. In a constant stress test of a kind just described a parameter of interest is creep compliance J.

What is compliance? Compliance is inverse of E, that means ratio of strain to stress. This is the ratio of strain to stress since the strain will be a function of time the complements will also be a function of time thus you can write like $j(t) = \varepsilon(t)/\sigma_0$ so, this parameter is called creep compliance. From the above equations we can use this and then the previous equation we can rewrite this equation for the creep components which $j(t) = \varepsilon(t)/\sigma_0 = (1/E)[1- \exp(-t/\tau)]$.

So, what is now shown in this figure is the creep compliance are plotted versus time but in a log-log scale. You can see that it is very interesting plots, we will try to explain this series of creep compliances versus time both on logarithmic scales over a range of temperatures. So for a different temperature range of temperatures, the creep compliance curves are drawn here and one can build a master curve from these kinds of experiments and this is a master curve one can build it from that.

So how do you build this master curve? the individual plots in a can be superimposed by an horizontal shifting (along the log time axis) by an amount log a_T, to obtain a master curve corresponding to a reference temperature T_g of a polymer. You see this creep compliance versus log time has this kind of a variation with the reference temperature T_g. In semi crystalline or glassy material or dimmers T_g is a very important temperature.

Like our recrystallization behavior right, in metals we talk about our ceramics we talk about right we were also talking about critical temperatures, recrystallization temperature right. So here in polymeric material this is T_g is the reference temperature. So but these plots are one over the other to generate this kind of a master plot to have an overall understanding that is we need some a constant that is called you know shifting constant. A shifting constant a_T is required, so if you shift each of this, curve to by this constant a T then you get this kind of master curve. What does this master curve show? It shows that the polymeric deformation as a function of time but it will now show that different regions like score elastic rubbery pladeu and then completely viscous flow. So these kinds of mechanisms all the mechanisms are nicely revealed if you do this a master curve construction.

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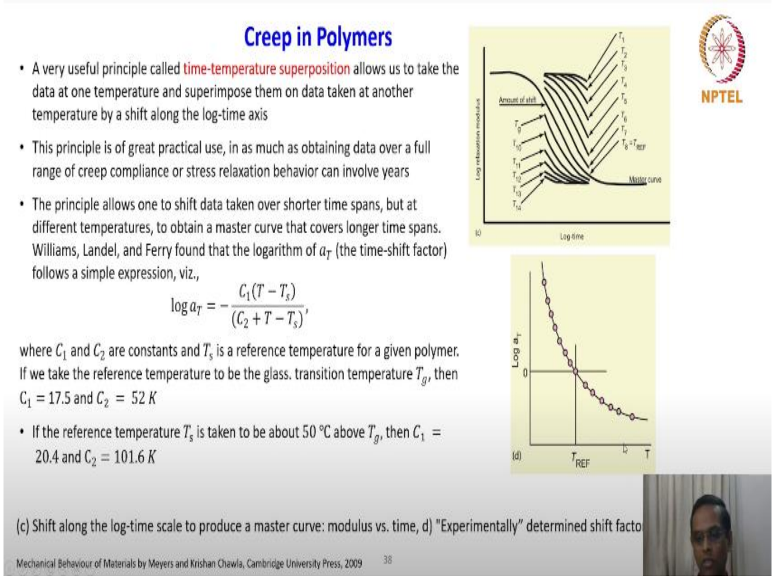

Creep in Polymers

- A very useful principle called time-temperature superposition allows us to take the data at one temperature and superimpose them on data taken at another temperature by a shift along the log-time axis
- This principle is of great practical use, in as much as obtaining data over a full range of creep compliance or stress relaxation behavior can involve years
- The principle allows one to shift data taken over shorter time spans, but at different temperatures, to obtain a master curve that covers longer time spans. Williams, Landel, and Ferry found that the logarithm of a_T (the time-shift factor) follows a simple expression, viz.,

$$\log a_T = -\frac{C_1(T-T_s)}{(C_2+T-T_s)},$$

where C_1 and C_2 are constants and T_s is a reference temperature for a given polymer. If we take the reference temperature to be the glass. transition temperature T_g, then $C_1 = 17.5$ and $C_2 = 52\ K$

- If the reference temperature T_s is taken to be about 50 °C above T_g, then $C_1 = 20.4$ and $C_2 = 101.6\ K$

(c) Shift along the log-time scale to produce a master curve: modulus vs. time, d) "Experimentally" determined shift facto

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So we will see little more on this master curve. A very useful principle called the time temperature superposition, allows us to take the data at one temperature and superimpose them on data taken at another temperature by shift along the log time axis. So this experiment is done to generate these kinds of a master curve. So one of the, I mean models, people have tried to plot this relaxation modulus versus time.

And then you generate these kinds of curve and then shift them by the method just look at it and you plot them then you get this master curve like this. We will look at it how there are particular model which are used to obtain this the constant shifting constant. This principle is of great practical use in as much as obtaining a data over a full range of pre-compliance or stress relaxation behavior which can involve even year's.

So which is very important because when you say stress relaxation that time is you know quite large depending upon the material what kind of material we are looking at it. So the stress relaxation in the context of stress relaxation behavior this relaxation modulus is also very important parameter. The principle allows one to shift data taken over a short time spans but at different temperatures to obtain a master curve that covers long time spans.

So you take a data from short time and then extrapolate to a long time so for that Williams, Landel and Ferry found that the logarithm of a T that is a time shift factor follows a simple expression like this log a T = -C_1 times T - T_s divided by C_2 + T - T_s. Where C_1 and C_2 are constants and T_s is a reference temperature for a given polymer. If we take the reference temperature to be the glass the transition temperature is T_g then C_1 is 17.5 and C_2 is 52K something like that.

So if the reference temperature is T_s is taken to be about 50 degree above T_g then C_1 is 20.4 and C_2 is 101.6 K. So, these are some of the examples how this you know time shift factor is being adopted to arrive at a master curve in a relaxation modulus versus time clock. So what is shown here in C in continuation with the previous slide is the shift along the time scale to produce master curve modulus versus time. The bottom one is experimentally determined shift factor so we can one can also find the shift factor experimentally.

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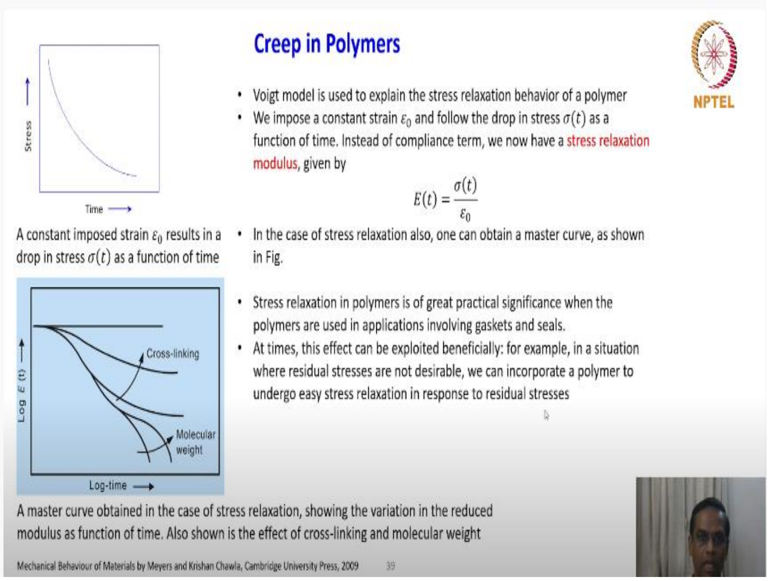

Creep in Polymers

- Voigt model is used to explain the stress relaxation behavior of a polymer
- We impose a constant strain ε_0 and follow the drop in stress $\sigma(t)$ as a function of time. Instead of compliance term, we now have a stress relaxation modulus, given by

$$E(t) = \frac{\sigma(t)}{\varepsilon_0}$$

- In the case of stress relaxation also, one can obtain a master curve, as shown in Fig.
- Stress relaxation in polymers is of great practical significance when the polymers are used in applications involving gaskets and seals.
- At times, this effect can be exploited beneficially: for example, in a situation where residual stresses are not desirable, we can incorporate a polymer to undergo easy stress relaxation in response to residual stresses

A constant imposed strain ε_0 results in a drop in stress $\sigma(t)$ as a function of time

A master curve obtained in the case of stress relaxation, showing the variation in the reduced modulus as function of time. Also shown is the effect of cross-linking and molecular weight

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So now we will come to one more important point the Voigt model is used to explain the stress relaxation behavior of the polymer. That is what we have just seen that Voigt model is useful but it was not explained in the other parameter. We impose a constant strain ε_0 and follow the drop in stress as a function of time. So stress relaxation means what you impose a constant strain and allow the material to relax and observe the stress that is stress relaxation.

So instead of compliance term we now have a stress relaxation modulus which is given by E(t) which is equal to σ (t)/ε_0. In the case of stress relaxation also one can obtain a master curve as shown in the figure. So this is a stress relaxation curve typical stress relaxation at a constant input strain ε naught results in a drop in stress σ as a function of t and the master curve is shown here typical master curve. Log E versus log t so this is relaxation modulus. A master curve obtained in the case of stress relaxation showing the variation in the reduced modulus as a function of time, also shown is the effect of cross linking and molecular weight. So these plots are very interesting because they have a complete practical relevance we are talking about reduced modulus. That means as a function of as the time passed by the more the modulus relaxed so it is called reduced models. So, this is also function of molecular weight and then cross linking so it is completely based upon the structural information structural aspects of the polymeric material that is what we have to understand. Stress relaxation polymer is of great practical significance when the polymers are used in application involving gaskets and seeds this is very interesting point you have to realize and this in fact we observe in the day-to-day life gaskets and seals.

They are after some time they will lose their function functionality for example the gasket in the pressure cooker the seals we use it in most of the know simple boxes now people use with seals you know they after some time that seal will become loose or it will brittle or it becomes first it will become loose that means it has completely relaxed. At times this effect can be exploited beneficially how can, we exploit this stress relaxation that is another important and applied in the reality. For example, in a situation where the residual stresses are not desirable we can incorporate a polymer to undergo easy stress relaxation in response to residual stresses so this is very important. So if you have an issue with the residual stresses then incorporating the polymer and then allow them to relax that will take care of the effect of residual stress so this is also very interesting application to realize the stress relaxation behavior of polymers.