Polymers: Concepts, Properties, Uses and Sustainability

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Lecture – 45

Viscoelasticity: Introduction

Hello, we will start another week in this journey of understanding polymers and in this week, we are going to focus on viscoelasticity in polymers and the words viscoelastic and polymers are almost synonymous, so much of what we know about viscoelasticity is because we have to describe the all the phenomena which are associated with polymeric materials. So, whenever we say viscoelastic materials, the first material that comes to mind is polymers. And it is the specific macromolecular nature of polymers and the fact that there are so many different time scales and length scales in polymeric material that we cannot ignore viscoelasticity in polymeric materials. Many other materials, an especially engineering materials we could ignore the viscous effects and treat them as elastic materials or many times we ignore the elastic effects and treat them as viscous materials.

However, in case of polymers in the solid state we cannot ignore the viscous nature; in the liquid state we cannot ignore the elastic nature, so that is why viscoelasticity is synonymous with polymers. So, in this week when we are going to focus on the phenomena of viscoelasticity, we will introduce some of the concepts in this lecture and one of the things that you will notice is the field of viscoelasticity is extremely interesting from the point of view of how it explains the real behaviour of polymeric system. At the same time, it is also reasonably complicated, now what do I mean by complicated? Because we cannot ignore either the viscous or elastic effects, everything depends on what is the question we are asking; everything depends on what is our point of interest. So, therefore it is not just a material which is viscoelastic, the type of viscoelasticity and the type of viscoelastic behaviour shown by the material will depend on what is the engineering application in mind, what is the scientific time scale of interest, so based on that then we can understand viscoelasticity.

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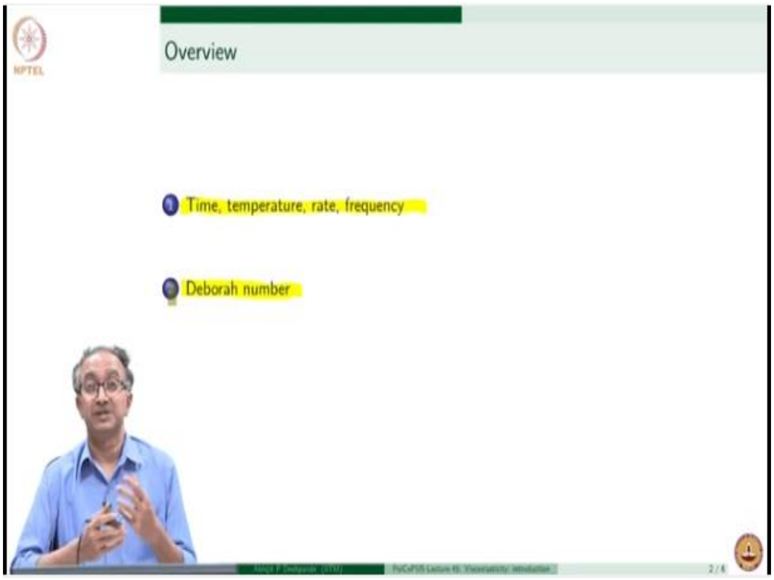

Overview

- Time, temperature, rate, frequency
- Deborah number

So, we will introduce the topic of a viscoelasticity by again focusing a bit more on all these related aspects; time, temperature, the rate of change of quantities or frequency, which is again rate of change of quantities and one of the conceptual way in which we highlight this issue of material time scale and experimental time scale is using Deborah number. So, we will quickly look at what can we learn from understanding Deborah number and its magnitude.

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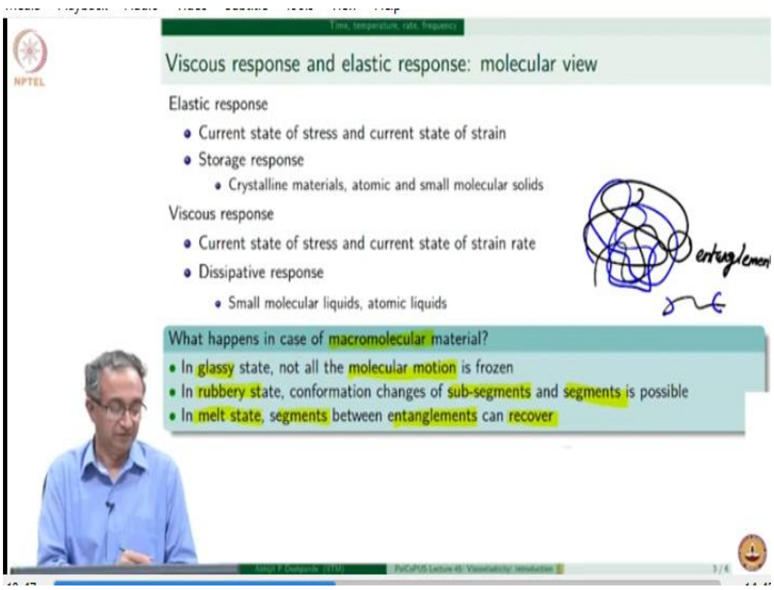

Viscous response and elastic response: molecular view

Elastic response

- Current state of stress and current state of strain
- Storage response
    - Crystalline materials, atomic and small molecular solids

Viscous response

- Current state of stress and current state of strain rate
- Dissipative response
    - Small molecular liquids, atomic liquids

What happens in case of macromolecular material?

- In glassy state, not all the molecular motion is frozen
- In rubbery state, conformation changes of sub-segments and segments is possible
- In melt state, segments between entanglements can recover

So, the viscous response and elastic response; the molecular view is that in case of elasticity we have storage and that is because the atomic and small molecular solids, there is deformation, displacement and recovery and because of this of course, we have said several times that only the current state of both stress and strain are important, the rates are completely irrelevant. It also does not matter whether 10% strain is reached after 5% or after

15%, in the sense I can apply 5% strain, then increase it to 10%, I will observe one stress, I can go to 15% strain and again come back to 10% strain, again I will observe the same stress. So, history, rates are completely irrelevant because what really matters is only the displacement of the atoms and molecules because it is the secondary interaction between atoms and molecules which is overcome in terms of displacing. And the secondary interaction is only dependent on distance between molecules, so therefore as long as distance between molecules is fixed, so at 10% it is one value, at 5% it is less, at 20% it is more, so, therefore stress is completely defined based on strain. However, like we saw in the lecture 43 on plasticity that if phenomena such as twisting, unentangling, orientation, slippage, if such phenomena happen then clearly we will not have this issue of stress being independent of history. Because then it depends on how the slippage happened, how the orientation happened and so the current state is important but what is equally important is how was current state arrived at. Viscous response on the other hand is completely dissipative response and here of course for small molecular liquids or atomic liquids, the idea is molecules are completely randomly anyway going about and then when we impose a stress on the material, the material starts flowing.

And as it starts flowing it continuously dissipates energy because molecules can randomly go about impinging on each other, as they are moving also on an average. So, therefore there is a continuous dissipation of energy and molecular order anyway does not get affected because anyway it was randomly impinging on each other, they continue to collide and bombard each other as well as the walls of the container or pipeline wherever they are flowing.

And so in this case, because a steady state is always reached in terms of when we apply a constant stress, we always reach a constant strain rate, so the current state of stress and current state of strain rate are what are valid. So, if you look at Newtonian fluid as an example, you can see that stress is proportional to strain rate, here in this case also the rate at which energy dissipation happens does not depend on what happened in the past or how did you arrive at the steady state.

So, if let us say shear rate in this case is 5 per second, it does not matter whether it was flowing much faster earlier or it was sheared at 100 per second earlier, 5 per second determines the stress because the current rate of dissipation completely depends on what is the rate at which molecules are being displaced with respect to each other. So, in case of elasticity it is only the displacement which counts.

In this case, since the displacement is happening continuously, molecules are randomly going around and flowing, it is the relative rate of displacement between molecules which leads to dissipation and that is what matters. So, this is a molecular view in case of let us say small molecules. So, now if we have a macromolecular system what can be the features and that is something for us to think about.

So, what happens when we have a macro molecular material? Now, when we have let us say a small molecular elastic solid system; amorphous solid, it mostly happens to be amorphous solid, it will deform little bit and then break, so because up to some extent atoms and molecules can be displaced beyond a certain point crack will start but in case of macromolecules even in the glassy state, not all molecular motion is frozen. So, it is possible for chains to unentangle, it is possible for chains to twist and so therefore, we cannot really consider macromolecular systems to be elastic under all conditions. In the rubbery state in fact conformational changes are easily possible, so sub segment side groups can rotate with respect to each other and segment themselves can also change conformations, so clearly this is more a liquid like system, where there is random motion of molecules possible.

However, in the rubbery state the overall macromolecule cannot move but only parts, segments can move and so therefore, rubbery state seems to have properties which are associated with solid as well as liquid state and therefore, it also is viscoelastic. In the molten state, in the liquid state of macromolecules now there is sufficient thermal energy for whole molecule to also move about.

But one macromolecule is entangled with another macromolecule, so even though this whole molecule of course segments can move about because let us say for PET, melt temperature is 250, moulding happens let us say at 270 degree Celsius of course, these macromolecules can move about the segments also can certainly move about but the motion of macromolecules is hampered because of the entanglement which are there. And so if you look at a segment, it is almost like it is stopped or anchored at 2 location due to entanglement with 2 other chains, so it is as if there are temporary junctions in the polymeric molten material and these between these junctions the segment can stretch and again can recover; recovery implies elastic response because material can go back to its earlier state and so segments in molten state because of entanglements can also recover. So, elasticity is there in the molten state, so that is the fascinating aspect of dealing with mechanical response of polymeric system that in the solid state, we still have to worry about molecular movement, chain orientation, chain untwisting and in the molten state we have to worry about elastic recovery. So, therefore viscoelasticity is always important whether we are worried about glassy state, rubbery state or molten state of polymers. And that is why at the beginning of the lecture when I said that viscoelasticity and polymers are synonymous, now you can see how macromolecular nature how closely it is linked to the behaviour of viscoelasticity.

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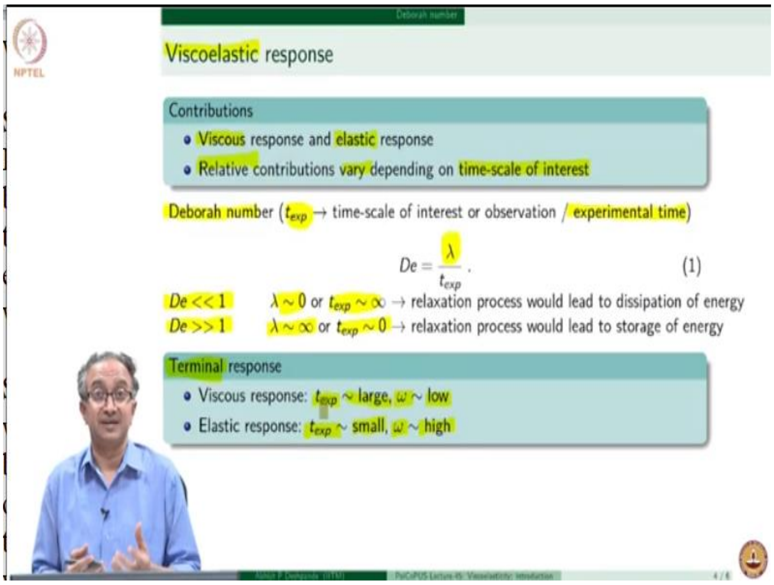

Deborah number

Viscoelastic response

Contributions

- Viscous response and elastic response
- Relative contributions vary depending on time-scale of interest

Deborah number ($t_{exp} \rightarrow$ time-scale of interest or observation / experimental time)

$$De = \frac{\lambda}{t_{exp}}. \qquad (1)$$

$De << 1$ $\lambda \sim 0$ or $t_{exp} \sim \infty \rightarrow$ relaxation process would lead to dissipation of energy

$De >> 1$ $\lambda \sim \infty$ or $t_{exp} \sim 0 \rightarrow$ relaxation process would lead to storage of energy

Terminal response

- Viscous response: $t_{exp} \sim$ large, $\omega \sim$ low
- Elastic response: $t_{exp} \sim$ small, $\omega \sim$ high

So, let us look at viscoelasticity in little more detail, so basically viscoelasticity means that we have both viscous and elastic response however, the relative contributions will vary depending on the time scales of interest and this is what I meant when I said in the; again the beginning of lecture that viscoelasticity can be complicated and the reason is this that it depends on the time scale of interest.

So, therefore for certain design of engineering polymers, we may be able to assume elasticity because that is the time scale of interest that we are working with and those are the numbers with which we will do our design, does not mean that the material itself may not be showing some viscoelastic aspect but the overall practice of engineering and technology happens in such a way that we can get away by assuming elastic response.

Same thing is true about let us say transport in huge pipelines of materials, which are non-Newtonian or viscoelastic fluids, again there we can assume that they are largely viscous fluids and again get away with engineering empiricism. However that does not imply that the viscoelastic melt itself is not showing any viscoelastic behaviour. So, this quantification of how do we assess whether viscoelastic effects are important or not is done using a hypothetical number called Deborah number which is a ratio of the experimental or the engineering time scale of interest. And which is also basically the experimental time with respect to the relaxation time of the material that we have discussed several times. So, the relaxation time is the characteristic of polymeric material of course, we know that there is not a single relaxation time in polymer, there is a relaxation time associated with side group, there is relaxation time associated with segment, there is relaxation time with overall macromolecules, so of course we have a relaxation time spectrum in the material.

But in general, when we want to think about what is the relation between the material time scale and experimental time scale what we need to look at, the ratios of these 2 and if Deborah number is very small, it implies that either lambda is very small or experimental time scale is very large and generally, while introducing topics of viscoelasticity, we talk often about example of from geology.

And geological time scales are basically, lakhs and crores of years, millions of years, so therefore in those time scales even plate tectonics and geological basically deformation that happens on the earth's crust surface, the models can be viscous fluids or viscoelastic fluid like models, so that is the idea behind Deborah number. So, if our time scale of interest is so large, then the viscous phenomena, the dissipative phenomena will start happening and something like a rock which for a few seconds or hours or even hundreds of years seems like a solid object, over crores of years seems like a fluid like object.

And so opposite case is there when we have Deborah number much greater, in which case now the experimental time scale is very small or the relaxation time of the material is very large which is the case let us say, when we observe the rock for a 5 year or 10 year period because in the time scale associated with the material itself is extremely large compared to the experimental time scale of interest.

And so generally, when we are analysing the viscoelastic response it is helpful sometimes to look at the terminal response. What do I mean by terminal response? We can look at either a short time or a long time response, we can say that okay, polymeric melt material has certain aspects of elastic recovery due to segments and entanglements but if i make the polymeric melt flow very slowly, then it ought to show certain amount of viscous behaviour which is dominant and therefore I can ignore elastic response. So, therefore terminal response of a polymeric melt under extremely slow strain rate conditions will be a viscous response. We can also think in terms of polymeric solids that if I do an extremely fast experiment, where I apply the load the polymeric molecules do not get a chance for untwisting or conformation change or any of the features which are associated with dissipative response.

So, then a polymeric material which even if it has segmental mobility at room temperature, if I do the deformation extremely fast, then none of the segmental mobility will be relevant because deformation is done so fast, so then the material would appear to be elastic. So, therefore terminal response is always useful for us to guide in terms of can we see the extremes of behaviour, the viscous dominating behaviour or elastic dominating behaviour as we change the conditions.

So, I already explained about rate or time of observation, we could also do the same thing if we are doing a sinusoidal loading, then if we do a very fast sinusoidal loading, then we are basically not giving material enough time, so it is associated with small time, high frequency or very low frequency which is more gradual implies that we are giving material sufficient time. So, generally low frequency response will be viscous like and high frequency response will be elastic like in a viscoelastic material.

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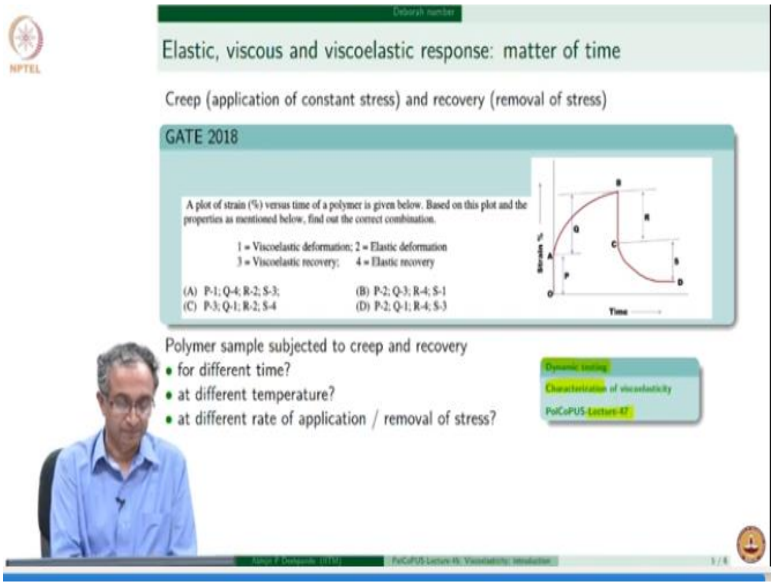

Deborah number

Elastic, viscous and viscoelastic response: matter of time

Creep (application of constant stress) and recovery (removal of stress)

GATE 2018

A plot of strain (%) versus time of a polymer is given below. Based on this plot and the properties as mentioned below, find out the correct combination.

1 = Viscoelastic deformation; 2 = Elastic deformation
3 = Viscoelastic recovery; 4 = Elastic recovery

(A) P-1; Q-4; R-2; S-3;
(B) P-2; Q-3; R-4; S-1
(C) P-3; Q-1; R-2; S-4
(D) P-2; Q-1; R-4; S-3

Polymer sample subjected to creep and recovery

- for different time?
- at different temperature?
- at different rate of application / removal of stress?

Dynamic testing
Characterization of viscoelasticity
PolCoPUS Lecture 47

So, let us just look at this question from exam to try to discuss little more about you know elastic response, viscous response and viscoelastic response and how it is a matter of time as to which one of these will be more dominant, we will soon define an experiment where we try to look at viscoelasticity in a material by doing creep and recovery experiment. So, we apply a constant stress on the material and then we remove that stress. So, if you were to just look at what is the experiment and look at what is happening to a stress as a function of time, so at time t is equal to 0, a constant stress is applied and after certain time suddenly that stress is again brought to 0. So, this part of it is called recovery and this part of it is called creep. So, because this application of the stress, the material starts deforming and so we measure strain as a function of time.

So, this question is asked where plot of strain versus time for a polymer is given and based on this plot, we have to find whether we have viscoelastic deformation happening, elastic deformation happening, is there a recovery which is viscoelastic or is there a recovery which is elastic and so what we need to think of is what would happen if we had a completely viscous material in this experiment or what would happen if we have a completely elastic material in this experiment.

So, if we assume that this is the load which is being applied, now what would happen in case of elastic material which is let us say, a Hookean elastic material. So, clearly strain in this case as a function of time because the load is constant, strain will also be constant and in fact this strain will be equal to sigma0 by E which is the modulus of the material and as soon as we remove the load, again strain will fall to 0. So, this is strain as a function of time for an elastic solid, you can look at this similar analogy you can do for a viscous Newtonian fluid and what you will be able to show is that strain will increase linearly during creep and when the load is removed, there is no recovery in the material. So, you can think about how to arrive at the shape that I described and rationalize how the response for a Newtonian fluid would look something like this. So, now we can look at the graph and then you can try to see whether there are elements of both of these responses in this creep and recovery test and you can see that yes it neither looks like elastic nor looks like viscous but it seems to be a combination of the 2 and that is the characterization of viscoelasticity and that is why for example, creep which is a dynamic test because time is involved is used to characterize viscoelasticity in the material.

The question that I have been trying to emphasize is viscoelasticity depends on the conditions under which we are observing the material. So, the same polymer sample let us say which is shown in this graph instead of doing experiment over the time whatever is given here, what if I do it at very short amount of time. So, instead of applying stress for let us say 1 minute or 2 minutes what if I apply for micro second and then leave it. So, I take the material, apply stress for an extremely small amount of time and then leave it, will I observe an elastic response? For example, will I see because the strain is being applied for a very, very short amount of time, creep is being applied for a very short amount of time, will I see strain pretty much like an elastic solid, think about it. On the other hand, if I the creep experiment is conducted for years, what is the response that we will see.

So, therefore depending on different times, the same polymeric material may show different behaviour, in the sense that elasticity may dominate when we do creep and recovery for very short amount of time and viscous nature will dominate when we do creep and recovery for much longer periods of time. What if we change the temperature on the material? So, let us say if this is nylon and this experiment was being done at 45 degree Celsius, now the temperature is changed to 65 degree Celsius, so about 20 degree Celsius higher. So, what can we expect in terms of creep and recovery; so because the temperature is higher we would expect that strain to be more but is qualitatively also anything changing and what will be the response of the material and so clearly when we change the temperature, what are we changing with respect to material, we will keep the time the same. So, the experimental time scale now remains the same but because we have change the temperature, the relaxation time in the material changes and so again, therefore Deborah number changes.

Now, we could also, if we are not applying a constant stress, if we are applying strain rather than applying a constant strain, we could apply a constant strain rate, more importantly as we are doing many of these viscoelastic experiments, we have to be careful while what can be done in reality and what we draw for some simple understanding in the beginning. So, for example I talked about the stress being manipulated this way where we say that stress as a function of time for creep and recovery initially, it σ_0 and then it is brought down to 0. So, how does it go from at time t is equal to 0 to σ_0? A real instrument will always do this in finite amount of time, it is not going to happen at time t is equal to 0 and immediately the stress becomes σ_0. So, it has to actually take certain amount of time before it can reach σ_0, so the rate of increase of stress is an instrument feature and therefore 2 different instruments in which you do this creep and recovery experiment, if the initial rate of increase is very different in the 2 cases, you will get a different response. Because the rate of change of stress in the beginning period is also important, so therefore rate of application of stress or rate of removal of the stress, each of these can be features which will influence the viscoelastic response and that is what one really needs to understand that viscoelasticity depends a lot on how we are looking at the material response and so dynamic testing and looking at time, temperature, rate variations are very crucial when we look at the viscoelastic behaviour in much more detail.

And that is what we will do in the 47th lecture; we will look at the type of dynamic tests which are used to characterize the viscoelasticity.

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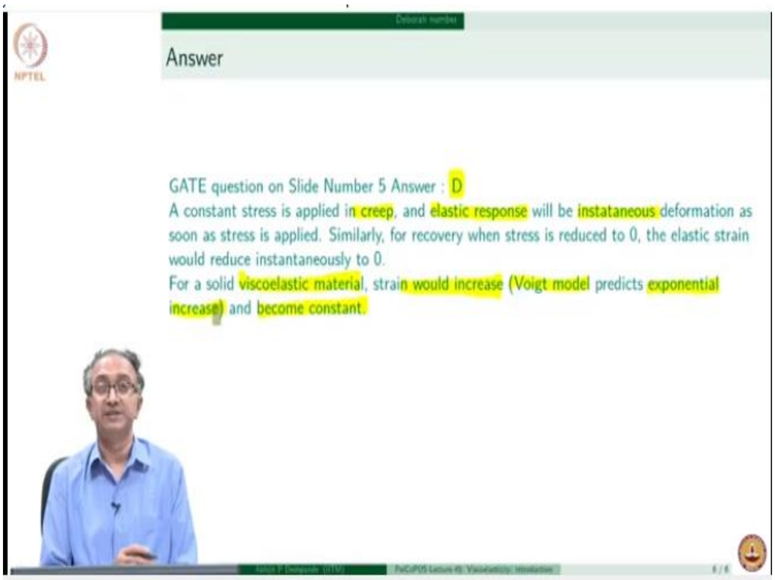

Answer

GATE question on Slide Number 5 Answer : D
A constant stress is applied in creep, and elastic response will be instataneous deformation as soon as stress is applied. Similarly, for recovery when stress is reduced to 0, the elastic strain would reduce instantaneously to 0.
For a solid viscoelastic material, strain would increase (Voigt model predicts exponential increase) and become constant.

So, with this we will close this lecture given that constant stress is applied in creep and elastic response is basically, instantaneous deformation as we saw earlier, so I am sure all of you can then try to get the answer because for a viscoelastic material, strain would increase first and then it would become constant. So, this is an elastic feature that it becomes constant while increasing implies it is a viscous behaviour.

So, as we will see later on Voigt model which is one of the simplest model to describe viscoelasticity predicts in fact an exponential increase in strain. So, with this we will close this introduction on viscoelasticity and in the next set of lectures, we will start defining quantities which can characterize viscoelasticity as response variables, thank you.