;;;Polymers: Concepts, Properties, Uses and Sustainability
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

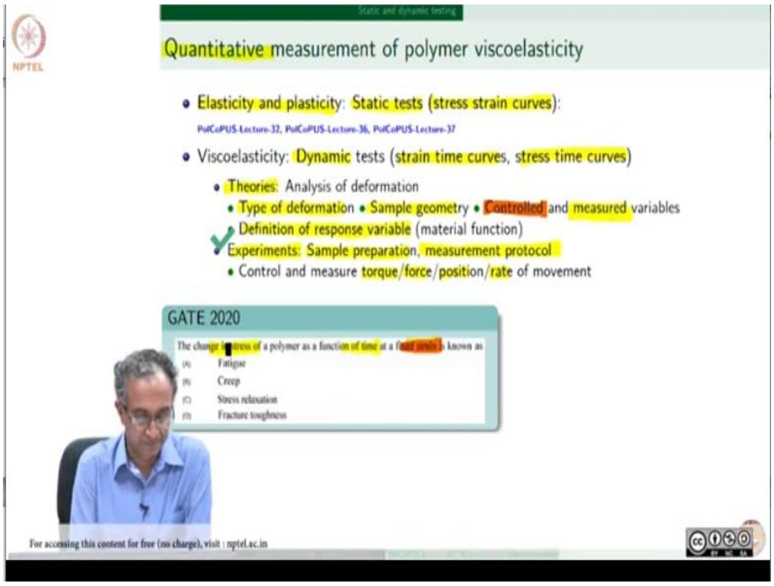
Lecture – 47
Viscoelasticity: Characterization

Hello, we will continue discussion of viscoelasticity and this week we will start looking at clear definitions associated with type of experiments that we do to characterize the viscoelasticity and so characterization of viscoelasticity will be focus of this lecture.

(Refer Slide Time: 00:36)

And the conceptual understanding underlying viscoelastic characterization will be our focus, we look at what is the set of techniques which are used for characterization of viscoelasticity which we will classify as dynamic testing and 2 examples of these dynamic test; creep and stress relaxation we will focus in this lecture and then oscillatory response we will focus on next lecture.

(Refer Slide Time: 01:04)



So, therefore static tests where time is not explicitly recorded are not very useful to characterize viscoelastic materials, so therefore we look at dynamic tests when we characterize viscoelasticity and therefore instead of looking at stress strain curves, we quite often will look at the variation with respect to time and then from there, we will try to gather information about the viscoelastic quantitative response.

And so to do this, we need 2 fold tools, we need on one hand theories, so that we can do a certain set of experiments and then actually achieve the measurement. So, what theoretical formulations do we need? We need theory so that we can analyse the experiments which we are doing. So, for example we first need to find out and talk about what are the different types of idealistic deformation that we can impose on the material.

So, in a real engineering application of course all of this is very complicated, a beam in a building or a bridge or a fluid which is lubricating the joints is subjected to all different kinds of deformation, all different rates of deformation and so therefore to understand the material response in a lab case or when we are trying to begin designing with new materials, we first need to understand the response under much more controlled conditions. And so this is done in dynamic test by first talking about what is the type of deformation that we impose, what should be the sample geometry that we take and what variable should we control and what variable should we measure. If we then specify these things, then based on mechanics we can arrive at definition of a response variable. What do I mean by this process? I can explain this for let us say, Hookean elastic material which is a static test.

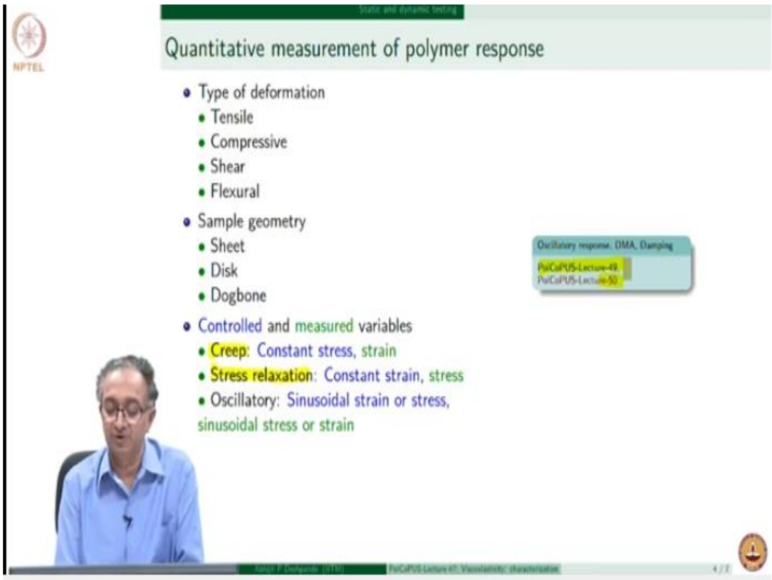
But the whole process has to be done for dynamic test where we are trying to characterize viscoelasticity, so for a static test we say that okay, tensile, tension will be the mode so that is the type of deformation, sample geometry may be a sheet or a film or a dog bone sample and the control variable is strain rate, so the material is being strained at a fixed rate and then the measured variable is let us say stress.

So, I know already what is the amount of strain at each and every instant of time and stress is what is being measured and then by saying that stress will be proportional to strain and then the slope of stress strain graph will be the modulus and that is the response variable we are talking about. So, therefore before we do the experiment we need all these theoretical foundations for us to really make the measurement of modulus.

And so this is the same thing true, when we have so many different ways of analysing viscoelastic response but in each case underlying theory is required and once we have the theory, then we need to prepare sample according to the deformation mode that we have chosen and the sample geometry that we want and then we need to carry out a measurement protocol in the instrument, so that we can do the measurements.

And then basically, arrive at the final goal which is to actually measure the response variable, so the control and the measurement variables more often will be some torque or force or current or voltage in case of electric measurement or position and rate in case of viscoelastic measurement. So, just looking at one of the exam question; the change in stress as a function of time at a fixed strain. So, clearly in this question of course what is not asked is really the type of deformation and the sample geometry because this is not a quantitative, we are not looking at a number itself but idea of doing an experiment of this where we control, so the stress strain is being controlled, it is a fixed strain, change in stress is being observed and that is the measured variable and so all the experiments that we do for viscoelastic characterization, such controlled and measured variables are present.

(Refer Slide Time: 06:30)



So, let us look at the quantitative measurement of viscoelastic response for polymers, we said type of deformation and so it could be tensile, compressive, shear or flexural, torsion depends on the kind of sample geometry what is the engineering application that we have, what kind of loads or the material will be subjected to when it is under the application, so that will decide what is the type of deformation that is of interest.

And of course, if you look at let us say many plastics and their technical data sheet you will see that both tensile and flexural modulus will be mentioned and so clearly the idea is that you know the engineering application may have both of these and both of these properties are important for a given application .You cannot rule out one versus the other. So, this would of course depends on our experience with designing for that engineering application and how to rationalize the application and selection of materials based on these numbers. The other aspect is of course related to geometry whether we may use a disk for a torsional sample or a dog bone sample which is used for attention, so many of these shapes of the samples will have to be specified and these shapes are predominantly based on how the stress transfer happened, how the gripping of the sample can take place. So, many of these sample geometries are for example, standardized based on material standards, testing standards.

So that whatever numbers we use at the end of such measurements we can carry those numbers back and forth between different sets of applications, different sets of people who are working on in the field and the control and measured variable can again be different depending on the type of experiment and this is where the diversity of viscoelastic characterization is involved.

I have listed here only 3 different types in fact, it becomes 4 if you see because we can have a control variable which is constant stress then its creep as we saw in the last lecture, stress relaxation is when strain is constant and we also have the measured variable, which are different. So, in case of creep we measure strain in case of stress relaxation, we measure stress.

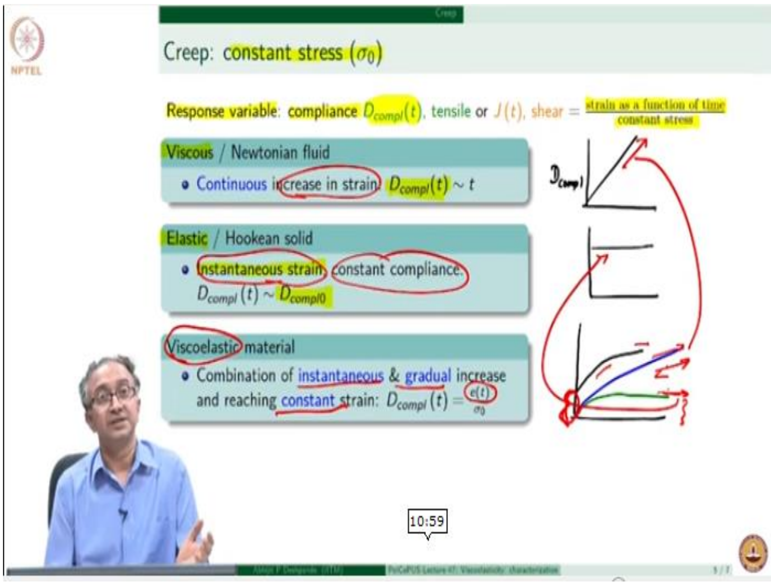
We could do an oscillatory experiment where we apply a sinusoidal strain or control it and we measure a sinusoidal stress alternately, we could also apply a stress and measure strain. So, therefore these are 4 different ways of conducting an experiment and deforming the sample and characterizing its viscoelastic response but however, multiple such combinations can be thought of, how about controlling strain rate, how about doing creep and then recovery, how about doing stress relaxation followed by another stress relaxation.

So, you apply one constant strain then you wait for certain amount of time, apply another strain, double step strain it is called, so therefore there are various possibilities and each of these possibilities is based on what type of viscoelastic response do we want to characterize in the macromolecular system and of course underlying all of this is the macromolecular mechanisms which are responsible for the viscoelastic response.

So, which type of experiment will give me clues regarding what are the mechanisms that are at play, so if I do a creep experiment can I understand how do the entanglements relax in case of an entangled melt, if I do a stress relaxation experiment, what do I understand about how the dissipative mechanisms are there in the solid material. So, therefore all of this depends on what is our understanding.

And some of what we will do in this course, will be trying to understand the relation between the microscopic mechanisms in the overall bulk response of polymeric system and so in this particular lecture, we will look at creep and stress relaxation and define quantitatively what do we measure using these experiments and in 49th and 50th lecture, we will look at the oscillatory response in more detail.

(Refer Slide Time: 10:49)



So, creep is a constant stress experiment, we can also do recovery in which case it is called creep and recovery and the response variable in this case is called compliance which is inverse of modulus. So, stress over strain is modulus, so strain over stress is; so the strain which is changing as a function of time, I hope you remember that for elastic material, strain does not change and strain by stress is a constant compliance. But for a Newtonian fluid, strain will continue to increase because a fluid cannot withstand stress, so if you apply a stress it will continue to deform and therefore it will achieve in fact a steady state and therefore there is a constant strain rate that it will achieve, so strain will continuously keep on increasing. So, therefore we can quantify all of this by capturing compliance as a function of time. So, this is how you can see viscoelastic characterization is very different compared to Hookean or Newtonian fluid characterization, there we characterize a material constant, we say this viscosity or that viscosity for this fluid or that fluid. Similarly, we say modulus for steel is so much; modulus for copper is so much, so there it is a material constant which characterizes the material response.

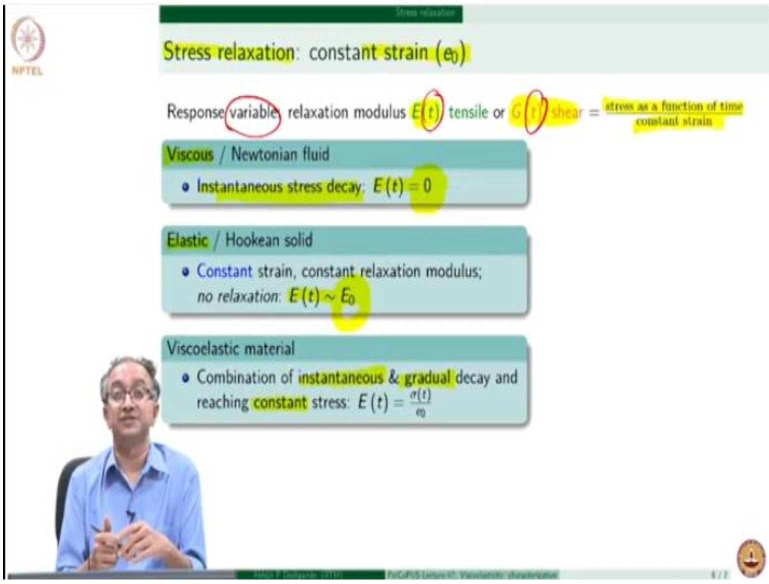
In this case we have a response function because compliance is a function of time and how to show different variation with respect to time implies the different contributions of viscous and elastic response in those 2 materials. So, therefore it is not sufficient for us to capture the response statically but it is a dynamic response as a function of time what happens to the polymeric sample. So, just to summarize again for a viscous sample a steady state is reached when a constant stress is applied and strain continues to increase linearly with time because strain rate is constant and therefore compliance is also proportional to time. For an elastic material as soon as stress is increase, strain will also jump instantaneously because remember for an elastic material instantaneous value of stress determines what is the instantaneous value of strain and vice versa.

So, therefore since stress is constant, the strain also is constant throughout and then it is a constant compliance, so if you were to look at these variations what you have in case of fluid is just a constant increase, in case of a solid you have a constant and in case of a viscoelastic material, you may have some initial jump and then it becoming constant, it is possible that there may not be any jump and then it may continue to increase. It is also possible that there is no jump but it will become constant, so all possibilities are there and you can see that this has features of both viscous and elastic responses. So therefore viscoelastic material has a combination of instantaneous increase, gradual increase or constant strain. So, all of these possibilities are there and therefore we can only characterize the viscoelastic material, the macromolecular system at hand if we characterize strain as a function of time and then based on this we can say how much is the contribution of elastic or viscous response. So, clearly between this black sample which has an instantaneous jump we know that there is contribution of elasticity while the blue and the green samples have no instantaneous jump and so which is an indication of instantaneous strain is absent in those 2 materials.

So, therefore we can get an idea about what is the nature of this material on the other hand, if you look at the green it becomes constant, so which is again a constant compliance which is related to solid however, the blue continues to increase which is increase in strain analogous to a fluid like material. So, some of these may be classified as viscoelastic fluid like or viscoelastic solid like material depending on our characterization.

But the key here is to characterize the dynamics of response to look at it as a function of time and to look at the whole function itself and of course, since I have talked about an increase and then becoming constant an exponential function is one of the easiest one and we will see that Voigt model which is the simplest model to describe creep shows an exponential increase and then becoming constant.

(Refer Slide Time: 16:00)

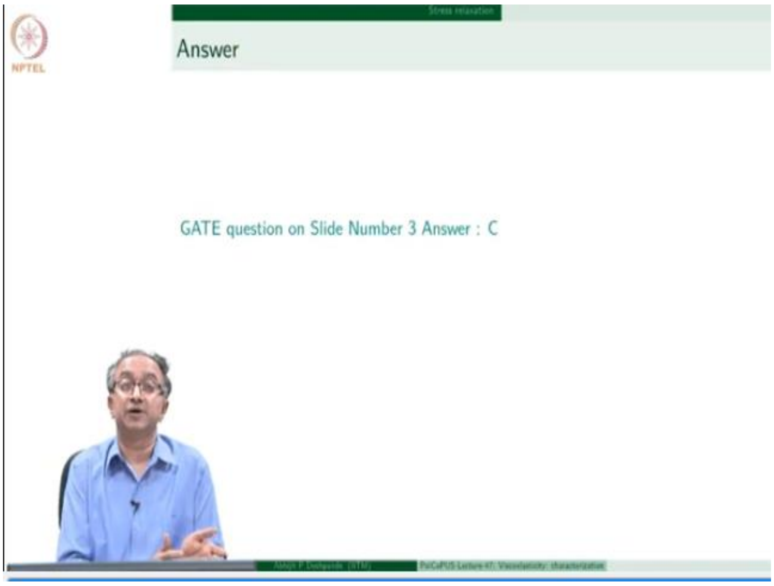


Let us look at the other experiment which is stress relaxation and where we apply a constant strain and again there is a response variable and again it is a function of time. I have also mentioned basically the symbols which are used in shear or in tension, so in largely solid like systems we use tension as a predominant mode or sometimes flexural mode but for fluid like systems, we use largely shear mode.

So that is why if you look at different books or different resources, you may find different symbols being used generally, E is used for tensile mode and G is used for the moduli associated with shear mode. So, here now stress as a function of time is being measured and divided by the constant strain if this is basically a modulus but the modulus is a function of time. So, modulus depends on time, so again it is a response variable but it is a function of time, so it is not one value but we have to look at how this varies as a function of time and then look at the overall characterization. So, in case of viscous fluid the stress falls off immediately to 0 because the constant deformation when it is applied on a fluid nothing happens, it deforms and then it stays there. On the other hand, the elastic solid as soon as we apply the strain, the atoms molecules will be pulled apart and they will remain in that position by storing the strain energy and then when we release it, it will come back. So, therefore in case of solid materials there is no relaxation, there is no dissipation of energy in case of fluid, there is complete dissipation of energy, whatever strain was applied all that mechanical energy is completely gone and dissipated in the material.

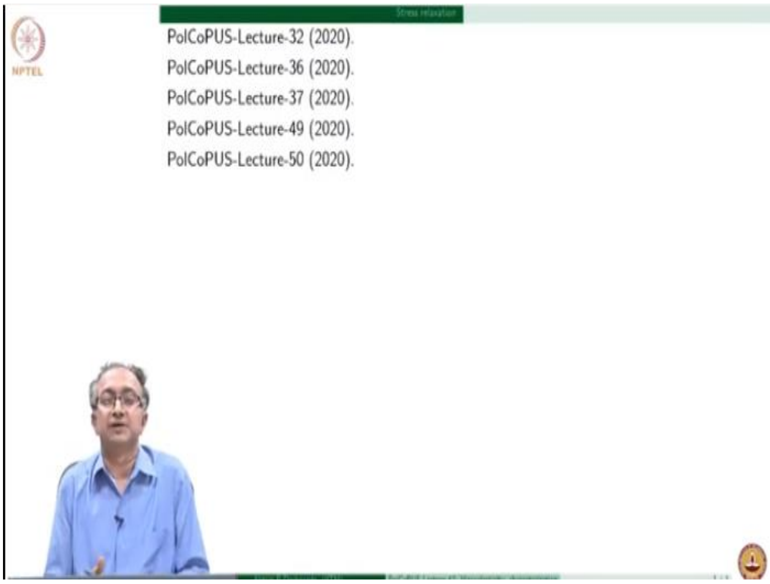
But viscoelastic material on the other hand will have combination of some decay which is instantaneous or may be gradual and eventually it may reach a constant stress, it may reach zero stress. If it reaches a zero stress then it is more like a fluid like response, if it reaches some constant stress then it is more like a solid like response, so different viscoelastic materials will have different properties. And we will see that the simplest model which is Maxwell model for viscoelastic materials which can explain stress relaxation shows an exponential decay and in all of this, the time scale of the material and the time scale of the experiment will determine how fast or slow the decay is. So, same viscoelastic material if I do experiment over much shorter amount of time, I will see more elastic response or decay will be less. If I do experiment over much longer period of time or also at higher temperature, then I will see more viscous response or lot of decay in stress.

(Refer Slide Time: 19:05)



So, therefore viscoelastic characterization is feasible when we do such dynamic tests and characterize the response functions which are basically either creep compliance or stress relaxation later on, we will define storage modulus and loss modulus and the loss tangent and all the other variables associated with different dynamic tests. So, with this we will close this lecture and I hope that given the definition of stress relaxation that we have already seen, you have got the answer to the question which was posed on the slide number 3.

(Refer Slide Time: 19:39)



So, we will continue this discussion of viscoelastic characterization in the next couple of lectures, thank you.