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

Lecture – 48
Viscoelasticity – Simple Models

Welcome to this course on polymers where we are looking at uses and properties and concepts associated with polymeric systems as well as we are looking at sustainability aspects. In this week we are focusing on the viscoelasticity of polymers and we have already defined how dynamic testing is used to characterize the response of viscoelastic materials and simple models are very useful for us to compare any realistic macromolecular system that we are characterizing. So, that we can characterize the response of a new material or a engineering material that we have chosen for an application and then compare it with respect to what is the response of a model and there try to understand what are the basic mechanisms which are present in the material. So, our focus remains on understanding viscoelasticity.

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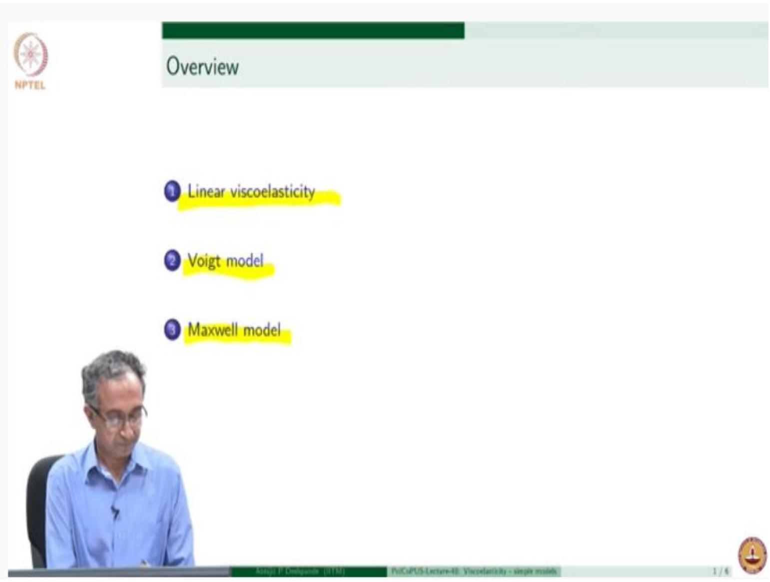

And in this lecture, we will first spend some time looking at linear system response while discussing the viscoelastic response and then the two model which are examples of linear models which means that they are applicable for only small deformations and so we will look at the response of these two models to a creep and stress relaxation.

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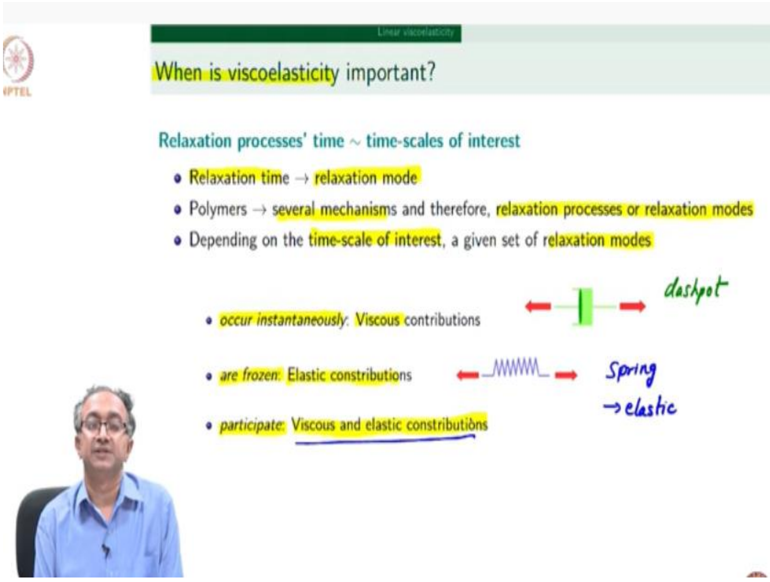

We have already defined it in the last lecture the 47th lecture on viscoelastic characterization. So, one of the questions that you can ask is when is viscoelasticity important why did I say that polymers and viscoelasticity is synonymous and the answer is that if relaxation processes time is similar to time scale of interest then viscoelasticity is important and time scales of interest can be milliseconds to few years that is how many of the phenomena that are associated with applications of polymers that is the time scale we are interested. Sometimes moulding operations happen so fast that milliseconds are time scales of interest and sometimes the plastic structural part may have a service life of 10 years or 15 years. So that is the time scale of interest. So therefore, the relaxation processes and polymers occur over all of these time scales. So therefore, viscoelasticity is always important and given that there are multiple relaxation processes and each relaxation process has a relaxation time we term each of every relaxation process as a mode.

So, we say there are several modes in the material and each mode can respond to the given condition. So, given that there are several mechanisms in several modes in the polymer depending on the time scale of interest some modes will respond in a particular way some other modes will respond in another way. So, what do I mean by this for example for water all the relaxation modes are very fast? So therefore, they only dissipate energy for a perfect crystal all the relaxation modes are extremely long. So therefore, they only store energy but for a viscoelastic material we will have combinations of viscous or elastic storage depending on the time scale of interest. So, for example if there are some modes which are very fast then we will only get viscous contributions from them in a macromolecule.

So, for example if the side group rotation is very fast then we just will get pretty much viscous response from it but we can also have temperatures let us say in the glassy state where many of the modes are frozen and so we may then get more dominant elastic contributions also and in some cases when we are intermediate time scales then we may have both viscous and elastic contributions present and generally we understand these viscous and elastic contributions by using some mechanical analogs. And so, for example a dashpot is a mechanical analog while spring is another mechanical analog. Spring is for elasticity and dashpot is for viscous behaviour and generally a viscoelastic material will have combinations of viscous and elastic responses but each of the dashpot and spring comes up with some characteristic time scales associated with it and therefore the overall response of viscoelastic material will depend on the characteristic constants of each of these.

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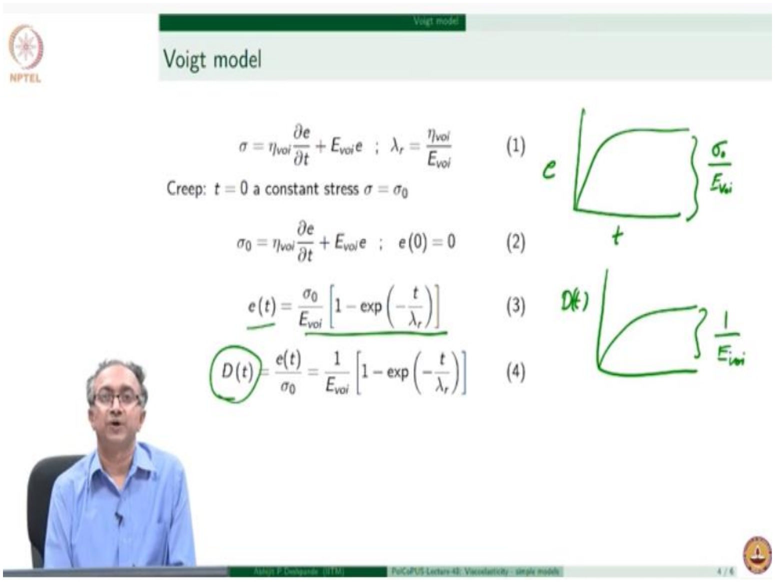


So, let us look at Voigt model which is one of the simpler models of viscoelasticity. So, if we ignore the term which is the derivative of strain then basically, we have stress proportional to strain. So therefore, that just an elastic response which is like a Hookean solid response. On the other hand, if we ignore the second term then this response is nothing but what is the response for Newtonian fluid where stress is proportional to strain rate.

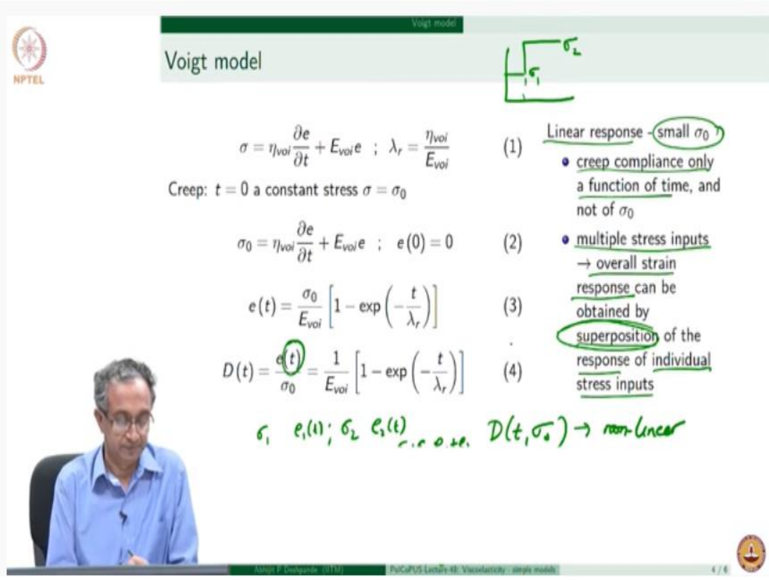
So therefore Voigt model is a combination of viscous and elastic contribution a Hookean solid and a Newtonian fluid combination and the parameters of the model are the modulus like constant which is defining the elastic contributions and then a viscosity like parameter which defines the viscous contributions and it is the ratio of these two which is called retardation time which can tell us about how strong the viscous or elastic responses.

So as an exercise what you could do is you could divide the terms in Equation-1 by E_{Voi}. So you can have E_{Voi} and then this will get cancelled and you will get 1/ E_{Voi} and then you can try thinking about what happens when λ_r is 0 and what happens when λ_r is infinite so do you get the terminal responses as we described them the terminal viscous response or terminal elastic response.

So, let us look at what happens to Voigt model when creep experiment is done. So, in this case since constant stress is applied the stress value will essentially become σ_o and then creep experiment by definition is measurement of strain. So according to Voigt model then we have an ordinary differential equation in terms of E. So, there is a first order derivative and then strain itself which is related to a constant.

So, the first order ODE the solution is exponential function notice also that this is a linear ODE and we had talked about response of linear viscoelastic or linear dielectric response that the governing equation will be a linear equation. So, this is Voigt model for example. Therefore this is an example of a linear viscoelastic model. So the solution exponential for the strain is just an exponential increase. When time is 0 basically strain is also 0 and when time is infinity then the strain becomes constant.

So, this basically is the strain variation according to Voigt model and the value of this constant strain is nothing but σ_o/E_{Voi}. So, if we were to define the compliance which is the response function then that also will be an exponential function and the constant value reached is one over the parameter of the Voigt model and the rate at which this increase happens. So, for example many of the exponential functions you may think what is the time required for reaching 63% of the maximum value and all of that so all of that depends on basically the rate constant or in this case the relaxation retardation time and so the relation time determines whether this increase in strain is fast or slow. Remember for a Hookean elastic material this is the instantaneous increase and becoming constant.So, you can again try to rationalize the value of lambda r and whether you get terminal elastic response or terminal viscous response. **(Refer Slide Time: 09:09)**



So just to highlight again the aspect related to linearity and linear response. Because these set of analysis that we do will be necessarily valid only for small amounts of stress being applied so that the equilibrium structure of the material is maintained and due to this linearity creep compliance is only a function of time. In case of non-linear response, the creep compliance will be a function of time as well as the load which is being applied. So, this is a non-linear response. And if at all we apply multiple stress inputs because it is a linear system, linear ordinary differential equation which defines it we can actually do overall strain response by superposition of response of individual stress input.

So, I can apply σ_1 find e_1 as a function of time then apply σ_2 find e_2 as a function of time and then I can apply $\sigma_1 + \sigma_2$ and I can just get $e_1 + e_2$ which will be also a function of time and therefore this is called the superposition or scaling of the responses. So, if I double let say σ_2 is double of σ_1 then what will happen is e2 will also be double everywhere. But mind you both of them are functions of time e_1, e_2 and $e_1 + e_2$ everything is function of time.

However, there is a superposition of response possible I can also do an experiment where I can apply value of σ_1 for certain amount of time and then apply σ_2 and again, I can do superposition. So, till certain time the response will be completely based on σ_1 and then later on I can add on the response due to σ_2. So, this superposition of responses is possible because of the linearity of response that we are looking at.

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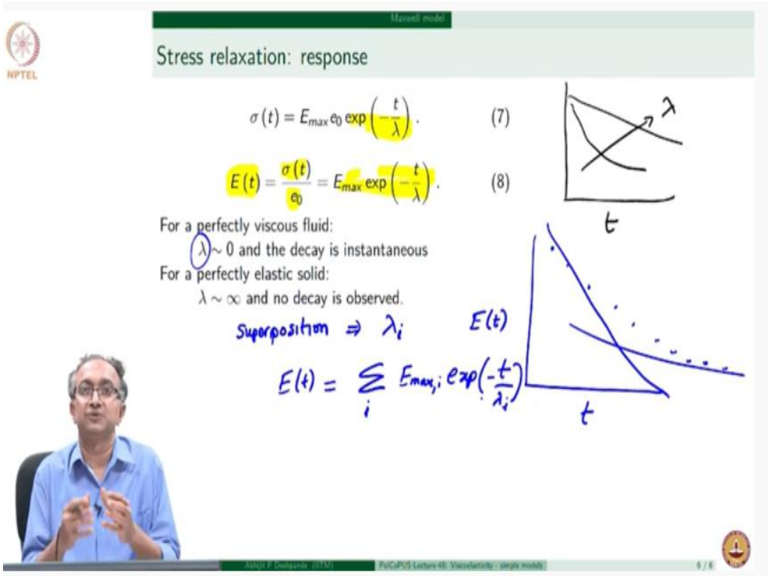


So, the Maxwell model is another example this is useful more for fluid like system and we will see soon that how the response is dominant with more viscous nature while Voigt model had more dominant elastic or solid like nature. This again you can see that if by cancelling this term or cancelling this term you can get both viscous and elastic response you can do that exercise and see which response leads to viscous and which response is related to elastic response. And the characteristic time here is called the relaxation time and this is an indication of how fast the relaxation processes are in the material and both eta and E again are models of Maxwell parameter which determine either viscous or the elastic contributions if lambda is 0 then we have a predominantly viscous response if lambda is infinity then we have predominantly elastic response.

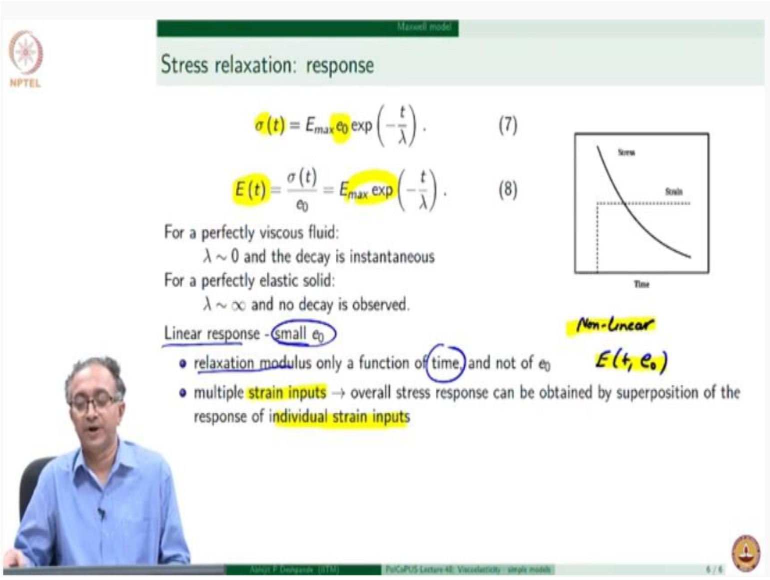
So now let us look at what happens to Maxwell model in case of a stress relaxation experiment. So, if we take maxwell model and apply condition which is valid when a stress relaxation experiment is done what we have is a strain is constant. Since strain is constant this $\dot{e}$ which is derivative of strain will go to 0 and therefore, we have again an ordinary differential equation in σ= 0 and again solution of this is also going to be an exponential function. But it is going to be an exponential decay in this case and so the decay depends on whatever is the magnitude of lambda and you can again look at the magnitudes of lambda and justify to yourself that if the lambda is very large then decay will be much slower and if lambda is very high you will have faster decay and so this is these curves are being drawn with increasing lambda.

So more and more elastic like response as lambda is increasing and so in this case the response variable is the relaxation modulus which is stress as a function of stress divided by strain and it is again an exponential function. So, characterization of viscoelasticity involves looking at such functions and now the challenge of course will be is when I do a real material and look at the response of that real material how do I rationalize what its response is.

So for example let us say I measure relaxation modulus for an unknown or new material which I have decided for an application and then I get data points which seem to indicate some variation so it seems to be decaying now the question is whether this is a Maxwell kind of a material is this so how do I start doing so what I can do is I can just start fitting an exponential and try to see if I fit it so let us say if I try fitting and if I can fit only a part of the curve or I can fit another part of the curve then I clearly know that one single exponential is not sufficient to explain the behaviour of this real material.

So, then I have to start thinking in terms of saying that oh maybe there is more elastic contribution maybe there is more viscous contribution than what Maxwell model suggests. So, therefore I need to modify my model other possibilities to say that look instead of having one lambda in the material maybe there are several lambdas and again because of superposition if there are λ_i relaxation processes in the material the overall relaxation modulus is nothing but summation of all of these individual relaxation processes.

So therefore I can have a set of exponential functions which I can try to fit to this overall set of data that I have observed and if that if it works good then I know that the material has several relaxation processes and some of them could be related to side groups some of them could be related to segmental motion and so on. So, I can try interpreting the viscoelastic response and the microstructure together to understand the viscoelasticity origins quite clearly. **(Refer Slide Time: 16:02)**



So therefore the stress decay as we have seen with exponential function for a constant strain is the response that a Maxwell model gives and just to highlight again that this is because we are looking at only small strain response and relaxation modulus is only a function of time and for a non-linear response E will be a function of time as well as e_o remember in all of this stress is always a function of strain but the response variable is not a function of strain there is no strain in the function.

So, that is what is linear response while in a non-linear response even the relaxation modulus itself will depend on the amount of strain because the material structure has changed due to the application of very large amount of strain and again as we discussed earlier in case of creep by multiple strain inputs we can actually superimpose and obtain the overall strain inputs.

So with this we will close this lecture where we have looked at the response of Voigt and Maxwell models and we will see that for to describe rubber like model materials we need a standard linear solid which is the simplest possible model that can describe the rubber like response because it has more solid like feature at under short time scales as well as large time scales while Voigt model and Maxwell model are more suited for only solid like sample or only liquid like sample. So, we will use standard linear solid which is much more applicable for rubber like samples these are just few text books examples of models over the last 30, 40 years we have lots and lots of models which can each capture the response of different materials under differing conditions. Thank you.