Physico - Chemical, Mechanical and Electrical Properties of Polymers

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Lecture - 41
Dielectric Response

Hello, welcome again to this course on polymers, where we are looking at concepts related to polymers, their properties, uses in applications and also overall sustainability aspects. We are focusing on properties in this week and part of the previous week also we looked at mechanical properties, we will continue looking at now the electrical response of polymers by looking at the dielectric properties.

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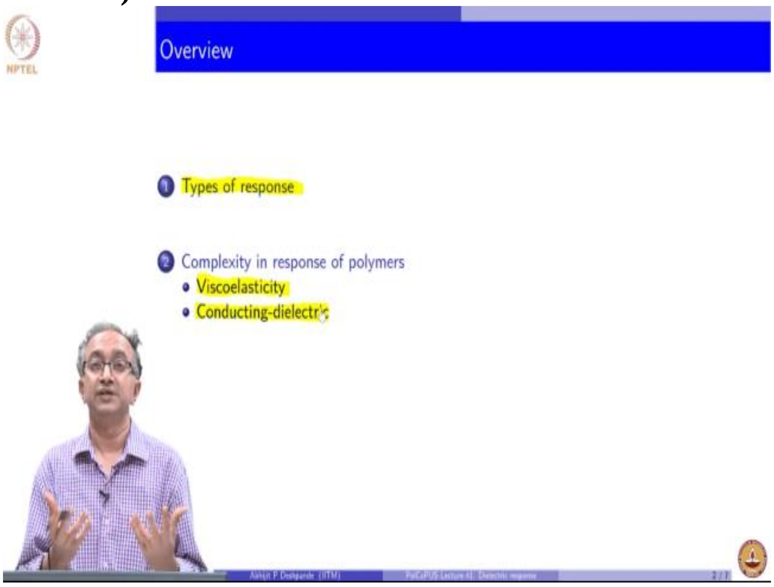

However, before we start looking at dielectric properties, I will spend some time on trying to give a broad overview of the type of responses that we analyze in courses related to polymers and especially in this course, what we will look at. And the surprising aspect that you might find is there are certain commonalities in mechanical domain which is viscoelasticity and the conducting dielectric domain the electrical response and the tools and the analysis methods are quite common in terms of these two seemingly very different types of responses that a polymer can lead to.

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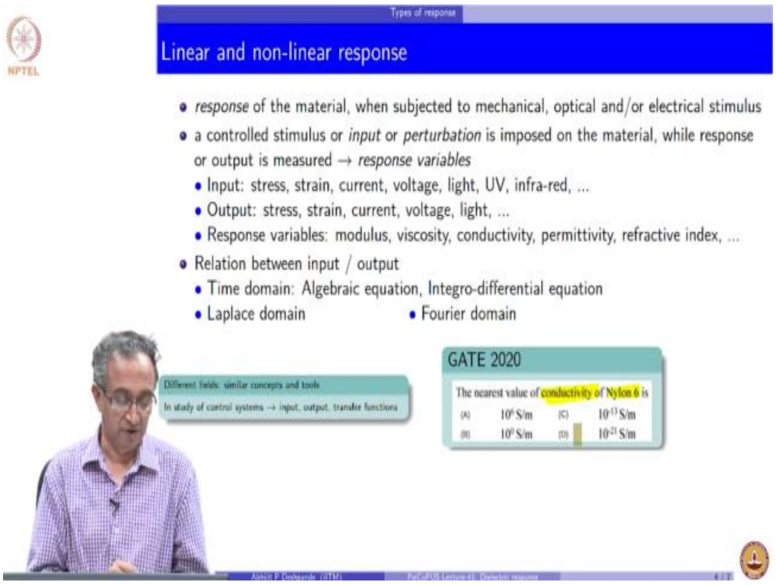

So, one of the first things that I want to highlight is the fact that we will look at most often linear response and there is also the nonlinear response of materials. So, the response of the material of course, we are interested in, if it is related to some stimulus. It could be electrical stimulus, it could be mechanical stimulus, and when we say stimulus here, we are basically saying apply a voltage or put some load on the material or impinge some radiation light or UV radiation on it. So, basically these are stimuli that can be that the material can be subjected to and our interest is in finding out what is the response given by the material and it's not the response and is basically quantifies the relation between two different variables the output and input. So, stress can be the input and then strain is the output or strain rate can be the output, we can have the converse situation also where we deform the material, so therefore, we apply strain or a strain rate and then stress is the output.

So, therefore, input, output are based on what we define it to be and what is our area of interest, sometimes we may control the current and therefore, just look at voltage as the output, but in other cases, depending on the circuit, the voltage may be a given quantity and current is an output that we are interested in. So, therefore, we have many of these response variables defined as inverse of each other. So, modulus is there, but then inverse of modulus is compliance. Similarly, conductivity is there but inverse of conductivity is resistivity. So, depending on the variables of interest, the response variable will differ. So, therefore, a controlled stimulus or input is applied or we can say that the material is perturbed based on this stimulus and the response is measured as some output and basically these two are related to each other through a response variable.

So, as I mentioned input can be any of these things and output can similarly be many of these variables and then response variables are permittivity, refractive index in case of visible light and so on. And so, the properties, response variables modulus and permittivity and all of these are usually a result of a simplistic model that we have used to capture. What do I mean by this? For example; modulus is the proportionality constant if stress is proportional to strain. However, we can have large classes of materials where stress need not be proportional to strain, not just that stress may depend on not just strain but strain rate or change of rate of change of strain rate; and so on. So, therefore, it is not necessary that stress and strain will always be proportional to each other, but as a way of quantifying and given that there is a large class of material, we call them Hookean elastic material, where stress is proportional to strain. We then choose to define a response variable called modulus. And then what we try to do is for a material which is non-Hookean we can see how it does this modulus differ in which way it’s not going to be a constant anymore because in case of Hookean elasticity, stress is proportional to strain and proportionality constant is modulus. But if for viscoelastic material stress just depends not on strain alone, but other rates of stress change or rate of strain change.

Then clearly if we try to express stress proportional to strain, we will get a modulus, which is going to be a complex quantity. By complex I mean two fold here. The fact that it will not strictly be proportional to each other therefore, it will be a function. Secondly, we will also see that we can use complex notation to describe this modulus, because we can always split the overall response variable into elastic like and something which is not elastic like. So, all this is done by basically analyzing the relationship between input and output. And in this case, let’s say stress and strain. So, the stress and strain can be related to each other by an algebraic equation. So, Hookean law of elasticity is basically that. It could also be a little more complicated like what we saw for a new Hookean model for rubber like material that we saw, when we looked at mechanical properties of polymers. We will soon see that many of the viscoelasticity models are differential or integral equations, because we have rates of quantities involved, rate of change of stress or rate of change of strain are involved. So, the stress is not just related to strain alone, but all the rates quantities are involved.

So, similarly, these time domain equations can be changed to Laplace or Fourier domain. And so, whenever we talk of a linear response, we imply that we are looking at these relations that are linear equations. And so, what do we mean by this linear response, we will continue discussion. But one other thing that you can see, which is a fascinating aspect of science and engineering where we take concepts from different fields and then apply them depending on what the need is. So, many of you who are students of controls would have recognized the terminology that we have used here many times we analyze systems as being linear. And in that case transfer function which is basically like what we are calling here response variable captures the system response. And it''s a relationship between input and output that the transfer function defines. And so, many of the features that we analyze in viscoelasticity or dielectric response of materials are common to control where we are looking at maybe a vehicle control or we are looking at a chemical plant control and so, very complex systems, but in the end, we are interested in relationships between inputs and outputs, so very similar tools can be used.

Just to look at the range of possibilities of properties that are present, so, for example, one of the things that we ought to start developing as we learn more about the polymer properties is the fact that you know, conductivity for an insulating material, such as nylon, what order of magnitude it is. So, we already saw that for copper conductivity was 10^7 S/m, and that order so, now among these can you guess what would be the conductivity for nylon, knowing that it is an insulating material?

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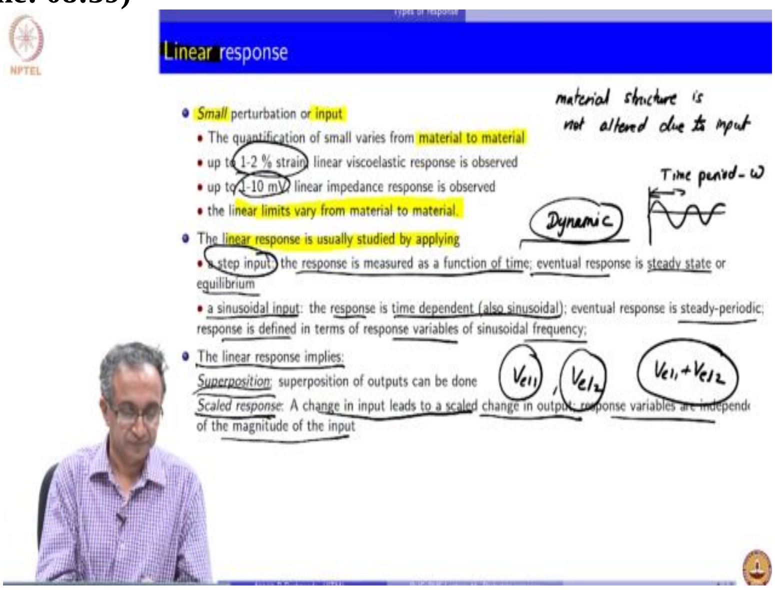

So, let us continue our discussion related to linear response as we said, from a mathematical point of view, the governing equation of input output relationship is a linear equation. So, it can be an algebraic linear equation, it could be linear, ordinary differential equation or so, or in linear integral equation. So, and all of these can be expressed very easily in Laplace domain or Fourier domain. And that is where the linear system response comes about. So, what do we mean by linear when we talk about response of materials for our course purpose? So, the input or the perturbation is small, how small that depends on the material. So, the only thing critical here is that the linear limits vary from material to material, because the assumption when we assume linear response is the fact that material structure is not altered due to input. What do I mean by this?

For example, if we are looking at let's say a thermoplastic sample which is being deformed, if we apply a small amount of strain, then the molecules basically just get displaced with respect to each other, and then they can come back. So, this is a small deformation, but if I apply the strain, which is little larger, then what happens is some of the entanglement points slip, the polymer chain gets oriented, and then when I now release the load, this will not go back to the earlier state. So, now, the deformation is large. So, what is the transition between small to large that depends on material to material. For example, for rubber like materials, small deformation, where linear response is observed is exceedingly small like 4%, 5% and for some other materials, it may even be 0.1%, 0.2% and there are some materials which can be linear all the way up to 15, 20 % also.

So, it depends on the material. So, generally though 1 to 2% strain is usually where linear response is usually observed. In electrical domain also millivolts signal is what is usually there for a linear response to be observed. Anytime we have a higher input than this, that changes the material and therefore, now, the material structure changes and gives us a response, which is an indication of the chain structure of the material. So, there is a very definite structural change that happens, which is due to the applied field. So, in some sense whenever we are looking at linear response, we are looking at the material response in its equilibrium state when there was no input to it. So, by applying this input we perturb the material in a very small way from its equilibrium structure and therefore, whenever we are measuring linear response of the system we are actually measuring its equilibrium structure. Whenever we are measuring nonlinear response of the system, we are taking the material far away from the equilibrium, we are altering its structure quite significantly. So, linear response can be therefore, studied by a variety of ways. And this is now different compared to when we had looked at let's say static testing of mechanical response there. We never brought time into our discussion, even when we define viscosity for a fluid like medium, we just say stress proportional to strain rate. So, whatever is the instant of time it doesn't matter if I know the strain rate, I know the stress or conversely, if I know the stress, I know the strain rate. Even in case of solid if I know the stress, I know the strain, so, time does not come into the factor, but in viscoelasticity or in dielectric response of materials, what we have is rates of various quantities are involved. So, therefore, time is dynamic response is essential. So, this is a word which you will hear quite often, now that we are discussing the properties of polymeric systems to a much greater degree. So, therefore, we can study the dynamic response by not applying a constant quantity, but by changing from one to another. So, therefore, we can do give a, what is called a step input. So, we can change let's say the voltage we can give a step voltage or we can give a step strain and then measure the response as a function of time. And the eventual response can be either steady state or material can go back to equilibrium depending on what kind of material system it is.

Another beautiful way to understand the dynamic properties is sinusoidal input, because sinusoidal input by definition is time varying and there is a periodicity associated with its time period. And this time period of course, is related to also the frequency that we are using. And so, by manipulating the frequency we can change the time period of how fast or slow the signal that is being input to the system is and so, the response is also of course, time dependent and sinusoidal. And so, eventual response will be also steady periodic because the input itself is periodic. And so, the responses then define in terms of response variables which are functions of frequency. So, just the way I defined earlier saying that, Hookean law elasticity stress is proportional to strain and the proportionality constant is modulus. Now, we have a complicated material which is a viscoelastic material, a polymer let's say rubber and in rubber sample, the stress and strain and strain rate and stress rate are all related to each other, but we can analyze this response by applying a sinusoidal strain to it and measure the sinusoidal stress which is there. And now by decomposing our output into something which is in-phase with input and something which is out of phase with input, we can in fact, analyze elastic like response and viscous like response.

And so, many of these are ways of looking at the dynamic response of material. And an advantage of looking at linear response in terms of analysis is the fact that we are of course, characterizing the equilibrium structure of the material. So, our understanding of material response becomes much clearer by looking at linear response, but it is also possible that we can do superposition. So, for example, if I apply a voltage 1 and then apply voltage 2 so, let us say I can do an experiment where I apply v l 1 as voltage and then another experiment where I apply voltage 2 and the question that is if I apply this together. And quite often your instinct would be to say that I can take output from first experiment and output from second experiment and just sum them up and I will get output of the third experiment and this is precisely what is meant by a linear response. Linear response does not imply that the variables electric field and current are related to each other linearly, it just means that whenever I have multiple inputs, I can sum them up and get the eventual output. So, therefore, superposition and scale response by which I mean that a change in input leads to change in the scale change in the output and response variables are independent of the magnitude of the input. So, the response variable for example, modulus does not depend on how much is the strain being applied. The overall stress depends on the magnitude of strain being applied, but the response variable itself does not depend.

And so, therefore, conductivity for whenever we say, we talk about conductivity being a material constant we are only looking at the linear response of the system. In fact, if we apply higher and higher currents and higher and higher voltages, then conductivity will start becoming function of the voltage or current. So, then we enter the regime of nonlinear response, because now, the material structure is being altered and it depends on what is the level of electric field being applied or the current being applied on the material.

The other feature which happens is also that a conductor is conductor in a certain range of frequencies, certain range of electric field being applied. If you change this then, there is also a dielectric response possible from the same material. So, this is just like saying that a polymeric melt can be considered a viscous liquid provided we are operating in a certain range, but then it will be a viscoelastic liquid in a certain other range. So, whether we have which phenomena dominate, whether it is dielectric or conducting, or whether it is viscous or elastic depends on which part of the working conditions we are in; however, in all of this superposition and scaled responses possible, provided, we maintain our inputs that are being given the stimulus that is being given to the material that is small. So, therefore, all the discussion in this course that we are going to have will predominantly be focused on the linear response, because this as I have told depends on the equilibrium structure of the material and this way, we will understand what is the connection between polymeric structure and its response? And secondly, it is easier to analyze. The nonlinear phenomena are far more complex to understand, because the input changes the material structure itself.

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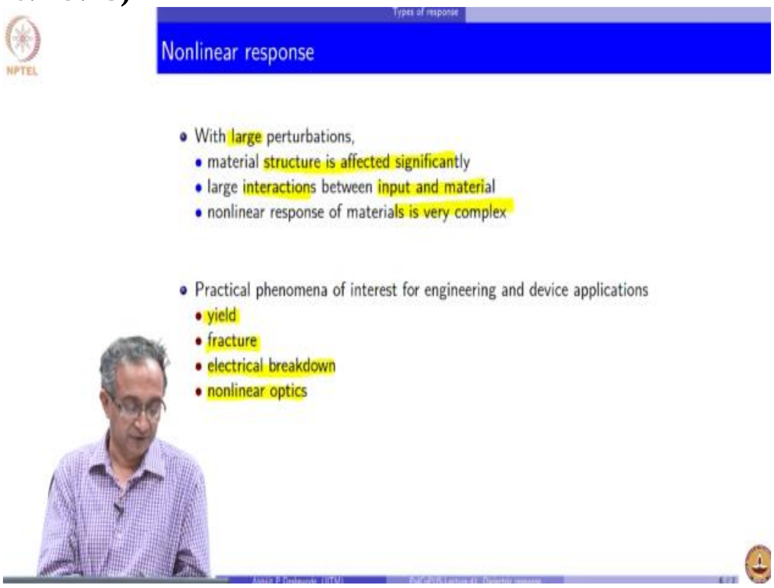

So, nonlinear response though is practically very relevant, with large perturbation material structure is affected significantly, there is a large interaction between input and material and therefore, the response is fairly complex. But things like yielding and plasticity breaking down of material electrical breakdown in case of insulation for high tension cables or nonlinear optics, so, these are all examples where the nonlinear response of material is very crucial. And many of the advanced students of properties of polymers we will be focusing on these phenomena, not just from a theoretical viewpoint or a conceptual understanding point of view, but practical applications, because each of these phenomena is involved in the direct application of polymeric material in a real world scenario.

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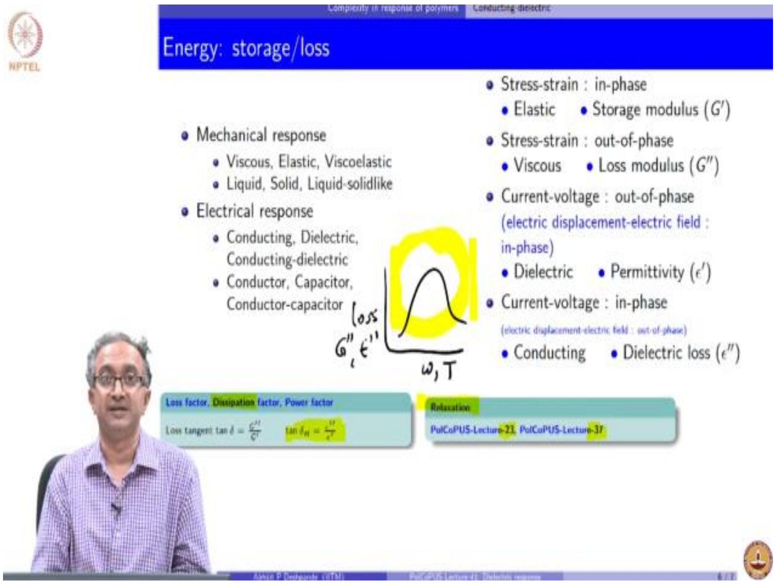

So, let’s finish this lecture by trying to summarize what is the range of complexity that is present when we analyze the polymer response and especially with respect to the conducting and dielectric part. So, when we have the mechanical response, we have seen that we could think of viscous, elastic and viscoelastic response which is a combination of these and from lecture 44, 45, 46 we will start discussing viscoelasticity more and more. And we will see that viscous is mapped on to the liquid like response, elastic is more solid like response and therefore, viscoelastic is liquid solid like or solid liquid like depending on the working conditions and the type of material we have.

So, similarly, for electrical domain also, we saw conducting polymers in which case we only talked about electrical conductivity, but are the conducting polymers perfect conductors in the sense that they do not store energy at all? And so, this is a key idea behind different fields, mechanical, electrical or any other stimulus that we are talking about, but if we think in terms of whether the material is leading to more energy storage, or is it leading to relaxation? Relaxation implies dissipation or loss. So, depending on these kinds of phenomena and mechanisms that are at play in the material, we can look at all of them using similar set of tools. So, viscous for example, is related to loss, while elastic is related to storage. And so viscoelastic of course, has both of those.

So, similarly conducting material can you guess whether it’s going to be storage or whether it’s going to be energy consuming, energy dissipating? And to answer this question, you might think of what happens to the heating of the wire when a current is passed. So, as a corollary to Ohms law, we also learned that what is the amount of heat that is generated when a current passes through a conductor or a resistor? So, as you have guessed it, conducting phenomena is related to transport of charges, just the way viscous phenomena is related to motion of molecules and these are dissipating phenomena, while capacitor on the other hand, we know stores charge. We usually think of capacitor as a set of dipoles material, which has dipoles which can orient and when electric field is applied, the dipoles get oriented and when electric field is removed, the dipoles come back. So, this is an energy storage phenomena where electric field which is applied in the form of voltage gets stored in the material by way of dipole orientation. So, therefore, we can think of very different phenomena by analyzing this energy storage and loss. In case of elastic materials, basically, atoms and molecules get displaced by changing the interaction energy between these atoms and molecules and store the mechanical energy which is applied, and when we release the strain, basically, the strain energy gets back and we get the equilibrium structure back.

So therefore, most common materials are in fact, combination of storage and loss. It just so happens that for our preliminary analysis, many times we ignore the other aspect. So a perfect conductor, we ignore the dielectric response that it has or a dielectric, we ignore the conductivity that it might have. But many of the polymeric materials incorporate mechanisms which are both storage and loss type. And so that is the key why in case of polymeric materials, we always have to discuss both of these phenomena together. And this is of course, done using dynamic testing and I have already talked about sinusoidal testing. And so, for example, stress and strain, when we apply a sinusoidal strain if they are in phase then it’s elastic or energy storage phenomena, and the modulus that we will define for such an input condition will be called storage modulus.

Similarly, if stress and strain are out of phase, because for a Newtonian fluid stress is proportional to strain rate, strain and strain rate are of course, out of phase with each other. So, therefore, stress and strain rate are also out of phase. And so, the modulus in this case will be called a loss modulus because, it is associated with energy dissipation in the material. Similarly, we can think in terms of current voltage when they are out of phase, then we have energy storage in the material. And in fact, then the material is called dielectric and we define its performance using permittivity. Formally, instead of talking current voltage, we actually define the variables of interest or electric displacement in electric field some of you may not be familiar with it. So, you can read a little bit about the electric displacement and electric field and in fact, these two are proportional to each other in a linear dielectric or a perfect dielectric. And the proportionality constant is permittivity, just the way here, stress and strain are related to each other linearly for Hooke's law, and then the proportionality constant is called the modulus.

So, generally the relationship between permittivity and capacitance or conductivity and resistance, all of these are related to basically one is material properties. So, conductivity, permittivity these are material properties it does not depend on what is the material shape. While conductance or resistance or capacitance they depend on what is the shape of the material being measured? Very true in case of mechanical response also, stress and strain are again, relationship between stress and strain is the material property. So, modulus is a material property, but, the specific amount of load that has to be applied a force that has to be applied and the displacement that happens between two ends of the rod let us say if I take a rod. And if I pull it and I measured the displacement between these two ends, that will depend on what is the size of the rod, what is its cross sectional area? So, all of that will determine the relationship between displacement and load in force Newton that is being applied. So, when we talk of current and voltage, it is more like an element or a component being tested, when we talk about electric displacement and electric field we are talking about material response, just the way when we say stress and strain, we are discussing material response.

So, therefore, in case of polymers, the challenge is that we have these phenomena of energy storage and loss happening, they both of them exist and very rare cases of short timescales or very rare cases of extremely high temperature, we may encounter predominantly one phenomena and get away by assuming just either storage or just dissipation. But, for most challenging situations, we have to consider polymers as viscoelastic or conducting dielectric materials.

And one way to also measure the loss and dissipation that happens in these materials is by looking at the ratio instead of looking at these variables by themselves, we can look at the loss to the storage ratio and these are called loss factors or dissipation factors and both in mechanical domain and electrical domain we use them. So, you can see how there is a similarity in terms of when we look at the overall response as just relation between input and output, we can use similar set of tools to look at both mechanical and dielectric response. And underlying all of this in case of polymer is the phenomenon of relaxation, which we have already discussed in lectures 23 and 37, relaxation phenomena, whether it's associated with a segment moving or whether it's associated with a macromolecule moving, basically, these are liquid like molecular motions, which lead to dissipation in case of a polymeric materials.

So, the understanding of relaxation is central to understanding what happens to material in case of how dissipative it is or how much dielectric loss is there in the material. Because, if we have let's say segmental motion possible, then we will have possibility of loss if segmental mobility is too high, then again dissipation will be less. If segmental mobility is not there material is frozen, then again dissipation is not there. So, quite often, we will see that the loss quantities such as G′ or ε″ may show some peak like this as a function of either frequency or as a function of temperature.

And this indicates that at one end of the condition in some frequency or in some temperature, very little dissipation was possible. Similarly at a higher frequency or temperature again, dissipation is not as high and so it's in between where the dissipation is maximum. So, this is like a phenomena of resonance and so, this is also the idea behind spectroscopy of these materials. So, we can apply different frequencies and we can therefore, study the overall set of relaxations which are present in these materials. And we will do this both for dielectric response as well as viscoelasticity.

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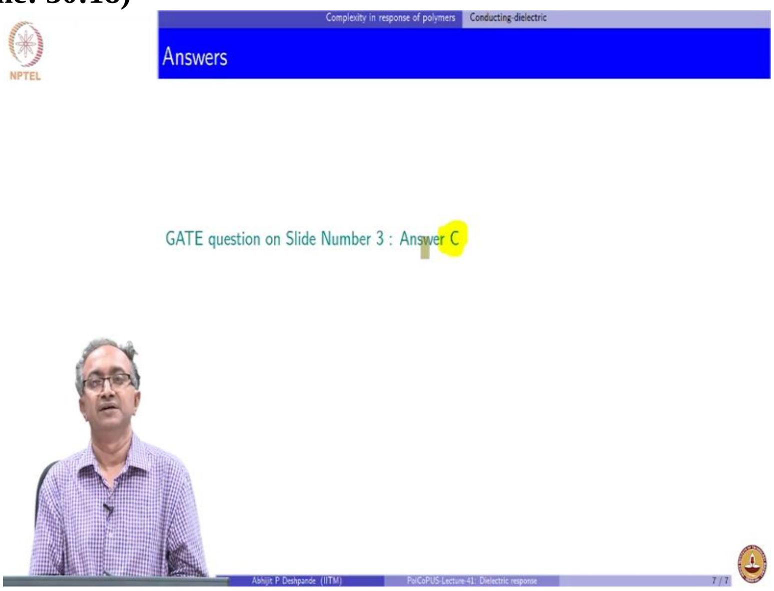

So, with this we will close this lecture and the question related to the conductivity of nylon, I am sure many of you would have been able to guess that it is of the order of 10^{-14}, which is where many of the insulating materials conductivities are. So, with this, we will close this lecture. Thank you.