Physico - Chemical, Mechanical and Electrical Properties of Polymers

Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology - Madras

Lecture - 40
Conducting Polymers

Hello, as we are looking at all the different properties of polymeric systems, in this lecture, we will look at the electrical properties and we will look at the newfound field of conducting polymers for over last 20 years, many of these polymers have found increasing applications in devices. Traditionally, we have always known polymers as insulating and with the Nobel Prize winning work the conducting polymers have come to the fore. And the advantages of conducting polymers are many as we know about polymeric materials. And can they match up the performance of some of the other conducting materials out there? And that's the question which will determine how many applications these conducting polymers are used for. So, we'll focus on these conducting polymers and their properties. We will also look at the dielectric response of polymers in subsequent lectures.

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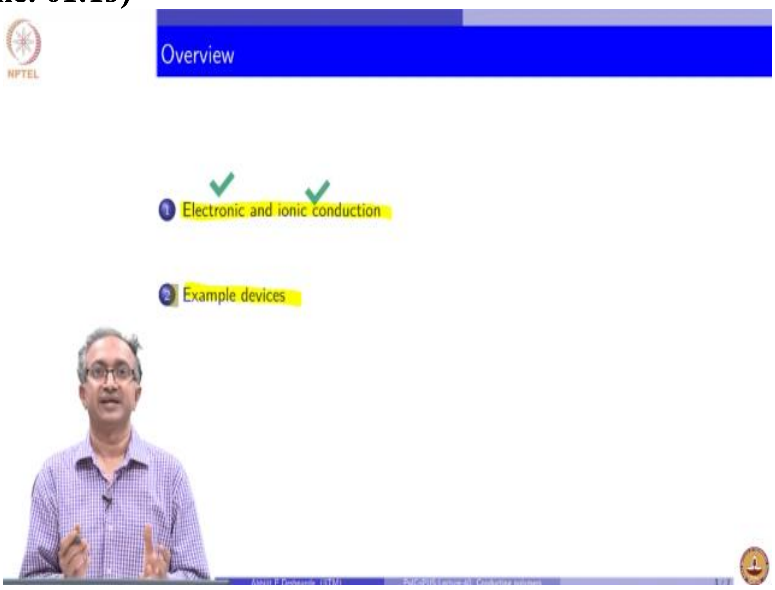

In this lecture, we will first look at both electronic and ionic conduction to emphasize that when we say conducting polymers quite often it is related to the electronic conductivity while DNA and proteins and polysaccharides and polyacrylic acid, these are several polymers which have ionic conductivity. So, both of these mechanisms are present as far as macromolecular conductivity is concerned and we will look at this briefly and then we will just look at a couple of examples of devices in which the polymers can be used. And the target quite often has been on all polymer device. So, we will take a look at couple of examples of such devices.

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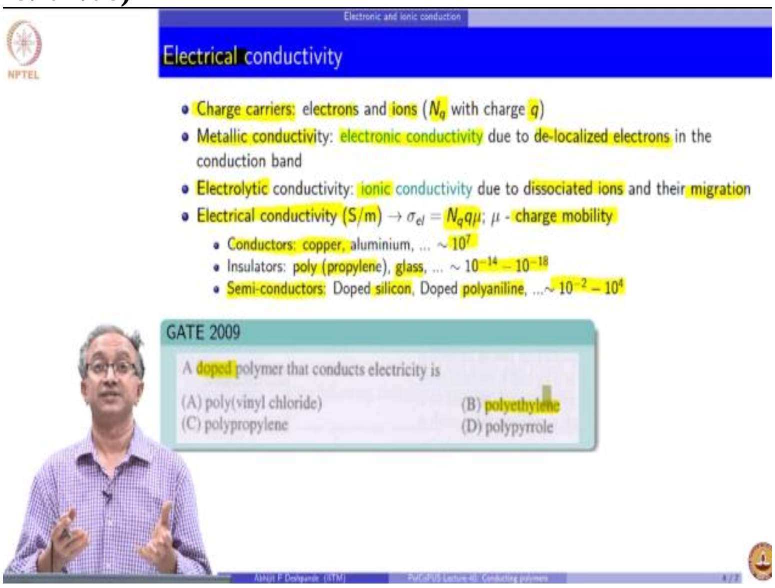

So, electrical conductivity is basically based on the charge carriers which are present in the material. And so, we can have electrons or ions as the charge carriers and both in case of polymers as well as any other material both of these options are there. And generally the number of charge carriers of course, each with the charge q are present and in many systems and we know for example, in electrolyte, we have sodium chloride, both sodium and chlorine and both of these ion can conduct, but their rates will be different. And therefore, ionic conductivity is dependent on the number of charge carriers of each type of charge that is present. In case of electronic conductivity we have electrons with the charge conduction phenomenon.

So, in metallic materials, that is what happens we have electrons conducting and we know that this is because of the delocalized electrons in the conduction band and we have materials classified as insulating materials because there are no delocalized electrons in their conduction band or they inversely they are there in the valence band. We are also very familiar with electrolytic conductivity which is basically due to ions and these ions are present because we have polar solvents and polar solvent leads to dissociation of ions and therefore, the ions can migrate and set up a current. And in case of macromolecules also we have already seen that ions can be part of the macromolecular chain like in polyacrylic acid or nafion the fuel cell membrane that we have already seen. The other examples are polyethylene oxide-lithium salt system where there is a charge complex between the macromolecule and the salts. In the case of polyethylene oxide-lithium polymer battery kind of an electrolyte, the macromolecule does not really lead to the charge. And so, electrical conductivity is defined as basically the amount of charge carriers and the charges that they have multiplied with charge mobility. So, higher the charge mobility better would be the electrical conductivity. And so, depending on the ions and electrons that are present charge mobilities are different. For example, proton among the ion has a much higher charge mobility compared to many other ionic species. An electron of course, has a very high charge mobility and so, a conductor needs to have sufficient number of charge carriers and the mobility of these charge carriers need to be high for it to have good conductivity. So, this is satisfied let's say in case of metallic materials, where the conductivity in S/m is of the order 10^7, while insulators such as a polypropylene or glass, the conductivity is 10^{-16} or even lower. So, you can see the orders of magnitude difference in terms of what the numbers of charge carriers as well as charge mobilities are in different materials and semiconductor materials fall somewhere in between where they have conductivities of the order of 1. And thereabouts and polyaniline which is a conducting polymer or silicon, of course, which we know is used in many of the semiconductor devices have conductivities in this range.

So, one of the things that induces conductivity in semiconductor material is a phenomena of doping. The idea behind the doping is to make the electrons delocalized. So, in the presence of electronic environment of silicon alone, the electrons are not delocalized.But when a dopant is added the electronic interactions between the dopant and the parent atom silicon induces delocalization and basically it changes valence and conductance band of the host species and something similar is also observed in case of polymer.

So, this question for example, tries to check whether which of these polymers would have electricity conduction possible due to doping and so, even if doping can induce conductivity. The charge carrier still needs to be there and the modification of conductance and valence band needs to be there. So, for example, in polyethylene, we would have no delocalized electrons no matter how much amount of doping we do and therefore, the conduction band electrons will never be there. So, therefore, in such cases conductivity is not feasible even with the doping. However, we should always keep in mind what is the amount of electric field that is being applied? And how are we asking the question related to the conduction? For example, polyethylene is used in its crosslink form as an electrical insulating material for high tension cables and so on. And there the electrical breakdown of polyethylene is of interest. So, with aging, with service life, the polyethylene can start developing defects and these defects can lead to some amount of electricity conduction. However, that phenomena is at extremely high fields and so, which is related to electrical breakdown of a material while here when we are talking about electrical conductivity we are talking about voltages from the range of micro volts to few volts also the conduction is there because of the charge carriers present in the material.

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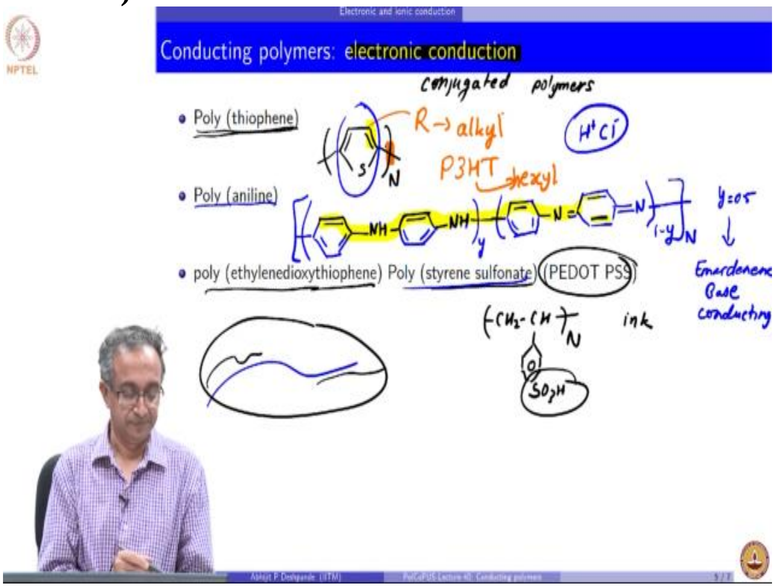

So, looking at some examples of polymeric materials, which can conduct, we have already discussed that electronic conduction is possible for those materials where there is conjugation. So, conjugated polymers are examples of polymers where conduction is possible intrinsically conducting polymer and polyacetylene as we have already seen is one example, where there is an alternating single and double bond present. So, polythiophene is an important class of material which has conducting possibility and this is based on the sulphur linkage which is available in the polymer backbone and so, you can see that when repeating units are there, we have alternating single and double bonds which are present in the polymer and because the next linkage to this will be basically linkages again this same unit, which is the thiophene unit will repeat itself.

Similarly, any of these polymers will have conjugation so, going further looking at polyaniline, so this is also again a polymer which has conjugation possible. And, as the name aniline suggest we have basically these benzyl groups and the polymer has different types of oxidation states possible and depending on these oxidation states, it can be conducting or insulating. So, you can see that because of the conjugation and the presence of the benzyl groups it is quite cumbersome to write the molecular formula for polyaniline and so, depending on y so, for example, y = 0.5 is called the emeraldine base and this is conducting. So, depending on the dopants which are added and for example, HCL hydrochloric acid is a quite common dopant used in many of the conducting polymers, so, that induces the delocalization of electrons across these chains so that you can have conduction of electron along the chain. One of the variations of thiophene is also in terms of side group, which are attached to it. So, if you look at many of the thiophene there will be an attachment of an alkyl group and for example, P3HT where this is a hexyl group is also an example of thiophene. So, 3 is the position specifying where the hexyl group is in hexyl thiophene.

So, thiophenes are generally common materials as part of example of conducting polymers and one of the commercially available polymer is in the form of ink is this PEDOT PSS polymer. So, PEDOT is a thiophene and then there is a polystyrene sulfonate and this also we have seen earlier that this is styrene and in styrene we have sulphonic acid group. So, this is polystyrene sulfonate along with PEDOT. So, if we let's say draw the PEDOT chain as conducting polymer chains, we have the polystyrene sulfonate chains, which are complexed with the PEDOT. So polystyrene sulfonate plays the role of dopant as well as making sure that this PEDOT is dispersible in water as a medium. Many of these conducting polymers with their benzyl groups and largely carbon, hydrogen, nitrogen, sulphur backbone are not soluble in water, but polystyrene sulfonate because of its ionic group is soluble in water. So, this complex of PEDOT and PSS is reasonably dispersible, notice I am using the word dispersible as opposed to be soluble. So, when we say something is soluble, it is molecularly mixed when we say it is a dispersion there will be domains of PEDOT and PSS. However, these domains can remain stable instead of PEDOT completely precipitating out from the mixture.

And so, then this ink as it is called can be used in depositing layers of conducting polymer films and many electrode materials many other applications and devices PEDOT PSS is used like many other natural polymer systems, either pectin or cellulose we have discussed how there is a hierarchy of structures and how they structure from a molecular level all the way to domains and bulk behavior is very complex and PEDOT PSS also has similar very interesting structure.

So, what I have shown here is only the molecular structure then these domains of PEDOT PSS organize themselves and then these domains organize themselves in a particle and then there are several particles floating around in ink. And then when we deposit it all these particles deposit and then they form the coating. And so, the conduction in PEDOT PSS is fairly complex to understand. However, at the background of it, is this conjugated chain of the thiophene which allows electronic conduction.

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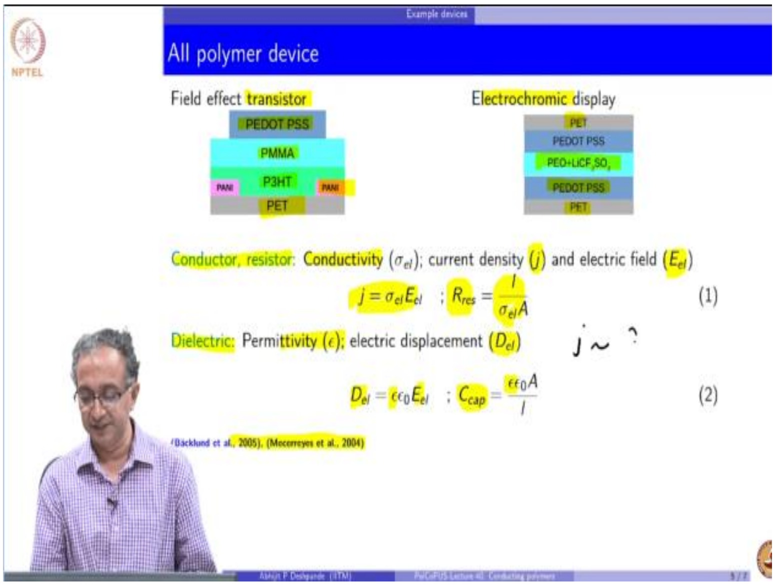

Now let’s look at couple of examples of all polymer devices. These are of course, examples from 15 years ago, but there are several such attempts made to make a device which is completely of polymeric materials. So, in this case for example, it’s this is a transistor where we are there is a PEDOT PSS being used, PMMA is used as a dielectric, P3HT also I mentioned it is a conducting polymer and then there is polyaniline also and the substrate is PET. So, in many devices we have we know that silicon is the substrate of choice. So, here for example PET which is a flexible substrate can also be used. The other example is an electrochromic display and again PEDOT PSS and PET are used for conducting layer as well as for substrate and then the electrolytic layer is a polyethylene oxide charge complex. So, in these cases you can see that the role of polymer is in the form of insulating substrates like PET, it is in the form of a dielectric like PMMA and it is in the form of conducting layers and electrodes and electrolytes like PEDOT, PSS and P3HT and PEO. So, therefore, now polymers in today's age provide all the different diversity of behavior that you can expect from any other class of materials also. And so, they do exist as conductor or resistors or as dielectric materials.

So, in case of conductor, we are interested in either their conductivity or the resistance of these materials. So, if we have current density and the electric field then basically conductivity is just related to the current density in a proportional sense, this is nothing but Ohm’s law, you can define based on how current density is related to current? And how electric field is related to potential? You can transform this relationship based on the geometry of whatever is the measurement being made and show that resistance is nothing but the related to the length of whatever is being measured and the cross sectional area across which the conductivity is being measured. Similarly, for a dielectric permittivity is important and permittivity is basically proportional constant when electric displacement and electric field are related to each other linearly. Electric displacement is basically the response of material or polarization of the material to electric field. So, in this course, we will see this response variable relating basically two different functions. So, stress strain-modulus, stress strain rate-viscosity. Similarly, electric displacement electric field we have permittivity, current density electric field we have conductivity, so, we have all of these variables of interest depending on whichever properties we are interested in and then we define a response variable to capture the performance of the material, where electric displacement can be related to current and electric field can be related to potential and one of the things that we ought to remember is the current density is basically related to the derivative of the dielectric electric field electric displacement.

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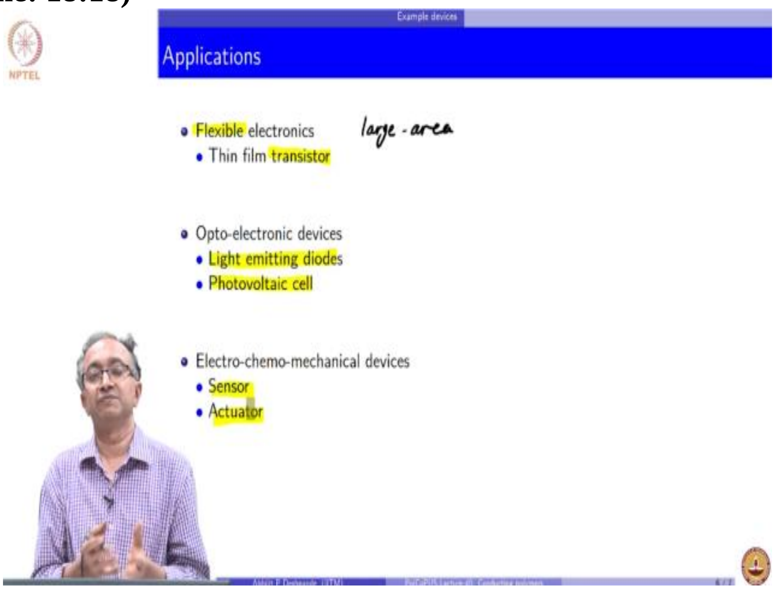

So, the range of application because of this conducting polymers is quite large we have basically applications in flexible also large area. What do we mean by large area? Basically we can carry out the device manufacturing and meters of length because of the kind of processing methods printing, for example, can be used as opposed to let's say the silicon manufacturing which happens over a wafer which is a 10 cm diameter wafer as opposed to that we can have very large area printing and we can make devices over a very large volume. So, many of the advantages which are there for polymers are present here also such as flexibility and so, transistor can be made, light emitting diodes and photovoltaic cells can be made and similarly, sensors and actuators can be made. So, conducting polymers therefore is a very interesting new area in which we have seen lots of applications in many of the devices and that goes from electronic devices to soft robotic applications many of these field conducting polymers have seen very interesting features.

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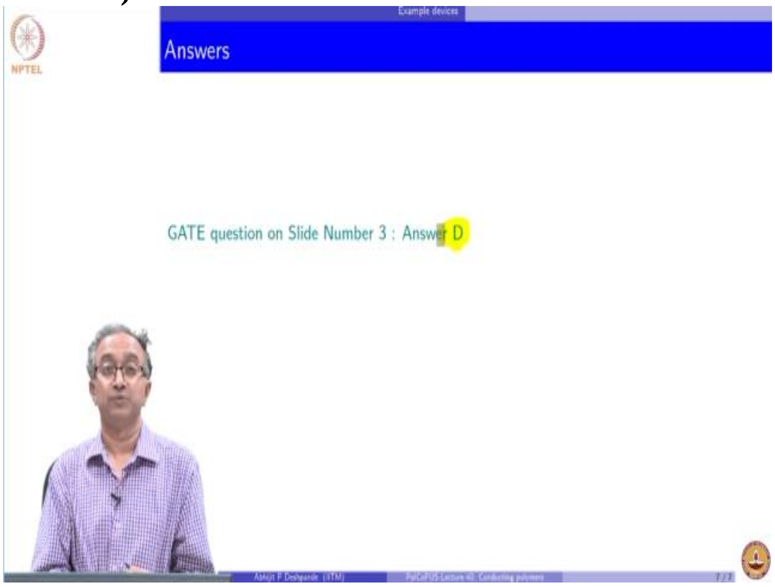

So, with this, we will stop. I am sure you are able to get most of the polymers that were listed in the question are in fact insulating polymer. It’s only polypyrole with doping that can conduct the electricity. So, with this we will close this lecture and in the next couple of lectures, we will look at the dielectric response of polymeric materials.

Thank you.