Physico - Chemical, Mechanical and Electrical Properties of Polymers

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Lecture – 33
Additives for Polymeric Systems

Hello, and welcome to the course on polymers. In the fifth week, we have switch gears now and looking at the properties after having looked at different kinds of materials, we are looking at mechanical, electrical and physico-chemical properties. And one important influencer in arriving at these properties are a set of additives which are used in polymeric systems, given that we have blends and composites.

So, we always have to formulate a polymeric material and formulations of polymeric materials are proprietary for most industries and they in fact, just saying that it is a polypropylene or just saying that it is an epoxy material is not enough there is so many details associated with not just the macromolecular details of the polymer being used, but what are the different additives being used for the eventual material system, which is used for industrial applications. So, therefore, formulation of a material is an extremely important activity for eventual applications of these materials.

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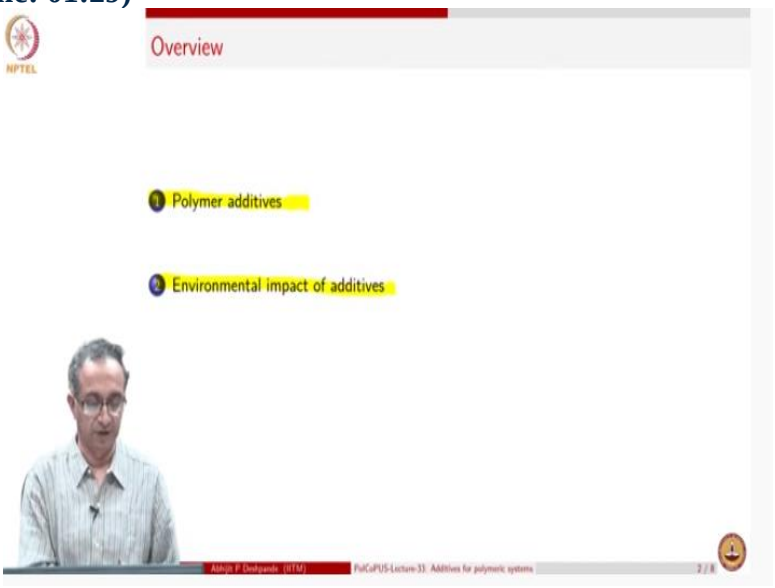

And so, by keeping our focus on the uses, what we will do is first look at the different class of additives, which are normally associated with a polymeric product. And we will close by looking at the impact because these are available in small quantities in the final product, but they can have significant impact given that they are small molecules which can exchange themselves with the surrounding.

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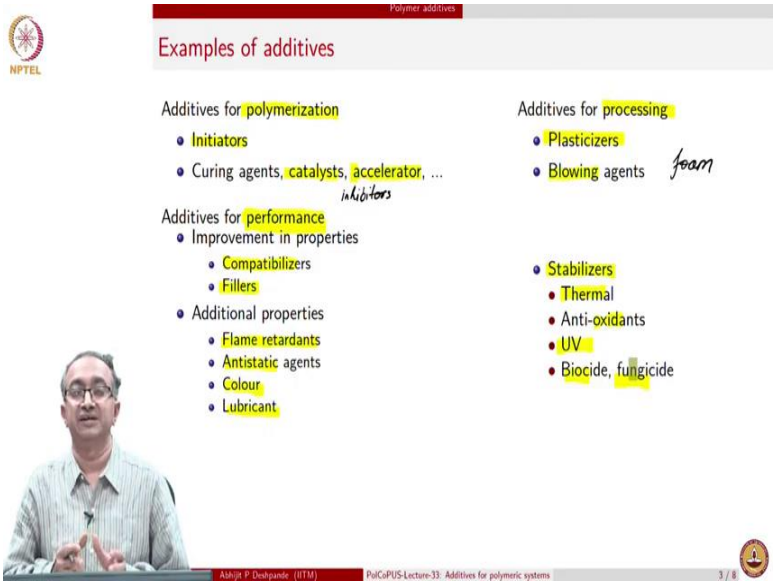

So, the additives can be thought of as being used either during the polymerization itself and once polymerization is done, fabrication and processing of the materials is involved. So, some additives may be required for that stage. Of course, all of this is being done, so, that polymeric material performs a role in terms of its application. So, additives can be used, they are incorporated into the composite or blend or single polymer to enhance performance or to optimize performance.

So, we have additives of all at each stage of the material. Of course, in case of polymerization we have initiators, catalysts, accelerators. So, these are materials which take part in reaction or they enhance the rate of reactions or control the rate of reactions. For example, you could also add inhibitors depending on what is the, if you want chemical reaction to be suppressed for a certain amount of time.

Before we want chemical reaction to proceed further, any inhibitor could also be thought of just the accelerator is common ingredient with most of polymeric material formulations because, when we do polymerization, in a practical scenario, you would want the rate to be as high as possible and the additives of processing are mainly to manipulate the flow behaviour. So, plasticizer is a very important component of most product formulations.

So, that viscosity and other rheological properties of polymeric materials are controlled. So, that we can obtain flow efficiently and many times we may want to have not a very high pressure drop, because that leads to its own complication in terms of higher costs, as well as issues related to degradation in properties due to very high amount of stresses. So, therefore, plasticization is very important in terms of manipulating the flow behaviour during processing

Depending on the requirement of the process, for example, if you are making a foam, then we may also add our foaming agent or a blowing agent. So, the purpose of this blowing agent is to create the bubbles and then eventually lead to a porous polymeric material then, once polymer solidifies, it becomes foam and you have seen around us not just Styrofoam, but there are several foam products whether it is in mattresses, whether it is in insulation or false roofing at in residences.

Also, many of the important electronic and electrical components contain lot of foam materials polyurethane or other materials which basically are used as electrical or thermal insulators as

the case may be. So, therefore, foaming and blowing agents are an important class of additives. As far as performance is concerned, if we have blends or composite, then we need compatibilizer sometimes to reduce cost or to achieve electrical conductivity or other properties we may need fillers.

We may also of course, have to worry about the fire resistance of materials. So, can we add some things which will retard the spreading of flames and the burning of the materials? A lot of the times product may accumulate static on the surface and that may be not a good for example for a doorknob we do not want it to accumulate static it is an example which is directly involving us and we getting a shock is usually any discomfort.

So, can we have a doorknob where static does not accumulate, so antistatic properties, so that surface charges do not accumulate. Of course, a static point of view colours, sometimes colour may be an important part of the performance of the material itself and also lubricants. For example, if this solid material that we are using in many times Teflon and nylon components are used in machines, where lubrication also has to be there, so, that the sliding of one material polymeric material over either a metal or another polymer can becomes easy.

So, can surface properties of polymers be modified in such a way that they are self-lubricating. So, that is also So, these are some of the additives that are added to achieve basically a set of performance criteria, we also add, so that whatever performance we design the material for it remains that way. So, that stability of the material, to temperature, to oxygen, to radiation, to attack from fungus or bacteria. So, all of these are important in terms of stability.

So, many times we add additives in polymeric materials, so that they achieve some of this stability, of course, how much of what to add and which components to add depends on several features of miscibility of polymer systems with these additives. The dosage required of these additives to maintain a certain degree of stability. For example, if we have service life, which is let us say 20 years, as supposed to service life, which is 1 year.

Also, within this service life, if the UV exposure is 24 hours a day, 365 days a year, then we will have a certain different requirement, if the exposure to UV light, let us say in sunlight is only maybe can be considered to be about 50 days in a year, then it is a different kind of requirement. So, all these additives, plethora of materials, which are needed for a successful application will have to be decided based on the specific material and specific application.

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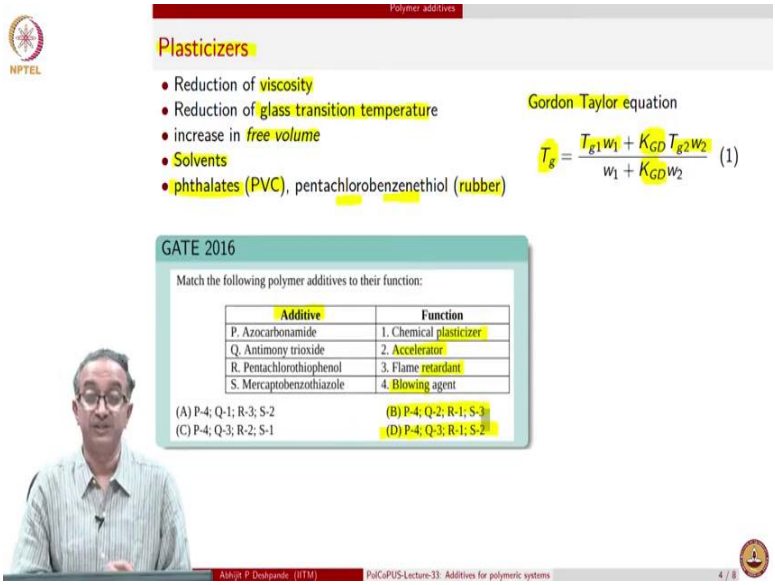

But you can see that there is a broad range of materials. And there, that is why I said that it is non-trivial to talk about final material which is being used in a product, and it is a formulation, that is why application, people industries, keep this closely guarded, either a trade secret or basically, to intellectual property rights, these are protected, because small variations in these components can have make a big difference in terms of the eventual performance.

And this is how one material formulation is distinguished from the other. And then quite often, a new entrepreneur may come up with an idea to you know, do a replacement of an existing product and sometimes they come saying that, you know, let us say this is a, I am an entrepreneur trying to make a pen. And I will say, I will take an existing pen, and I will try to do some analysis on it, find out all the polymer that is used, and I can then successfully make industry with making pen.

So in terms of finding out the polymer, which is used, let us say the front part of the pen, the cap of the pen, the main body of the pen maybe that is easy to find. But what I am trying to emphasize is that is not be only thing this may be 99% of what the final formulation is, but it is the remaining 1% which crucially determines what the performance of the pen will be. For example, when we grip the pen and we write it, how does it feel? How shiny is the pen surface?

How strong it is if I make it fall once or twice will it break? If I leave it in the sunlight will after 2, 3 days will it start becoming somewhat flaky, if it gets subjected to water and oil does it start becoming so there are several performance related issues and all of these are determined based on not just the polymer itself, but all the additives which are added. So, let us look at plasticizer as a class of additives, because they play a very important role in processing. But I would also like to state here that plasticizers are important from performance point of view also because they determine segmental flexibility in the final part and so plasticisers many times are added also to modify the mechanical properties of the material. So if let us say in case of PVC, we want to have flexible material like what can be used in bags and other materials then we may add plasticizer but if we are interested in making PVC pipes, which is a hard and stiff material, then we may not use plasticizer for performance there.

So, depending on the requirements plasticizer may be added for performance. And so, what plasticizer does is it reduces the viscosity and which is useful for processing, but it also reduces the glass transition temperature, which is relevant if at all we are we have to manipulate glass

transition temperature in a performing formulation. And this is because, one can think in terms of free volume theory and then the rationalization will be that it increases the free volume and because free volume increases the glass transition temperature goes down.

And Gordon Taylor is one empirical semi-empirical equation available, which tries to find out that if you have glass transition temperature of 2 species, which are added in 2 different weight fractions, w_1 and w_2, then knowing this parameter, the Gordon Taylor parameter K, we can then find out the glass transition of the plasticized polymer and, of course, the solvents and also monomers themselves can also play the role of plasticizers.

So, small molecules which are intentionally added as plasticizer, but also residual monomers, residual solvents, which remained behind as a consequence of polymerization or whatever processing that was done earlier. And so, the role of all of these is crucial in terms of determination of the final properties. And as it was highlighted in lectures on mechanical properties in nylon, for example, whether it is dry or wet some amount of water, or condition nylon, the properties are very different.

And that is because water interacts with macromolecule chain is one way of saying it; another way of saying it is water is a plasticizer for nylon. That is another way of saying it. Third way I can say is, water, changes the free volume in nylon, and therefore changes the glass transition temperature. So, all of these are synonymous. It is just different ways in which we describe the underlying mechanism or interaction between water and nylon macromolecules or polyamide macromolecules.

So, phthalates are commonly used for PVC, and also for rubber, we use this benzenethiol. And this exam question. In fact, this is a, I would say, a very popular question in many of the exams, given the range of additives, which are used, a polymer engineer would need to have a good sense of you know, what additive is used for what purpose. And in some sense, you might think that this is pure information, and I can always get it.

But again, looking at the physio-chemical nature of the additive, we can guess and try to develop a judgement as to what may be its purpose. So, we have already seen that purpose could be a plasticizer, purpose could be enhancing the reaction rate, it could be to prevent fire hazard, or it could be to make foam. So, you can go through each of these compounds, what I would suggest is just look at their chemical structure, look at what are the functional groups which are present?

And then can you make a judgment regarding which of these roles it may perform? And of course, as I have already said, the R is anyway related to a plasticizer. So, you can clearly see that maybe you have to figure out which one of these 2 is the answer. So, try analysing the structure and the role. And we already saw that what is the purpose of each of these additives? So why would it? Why would these compounds play that role?

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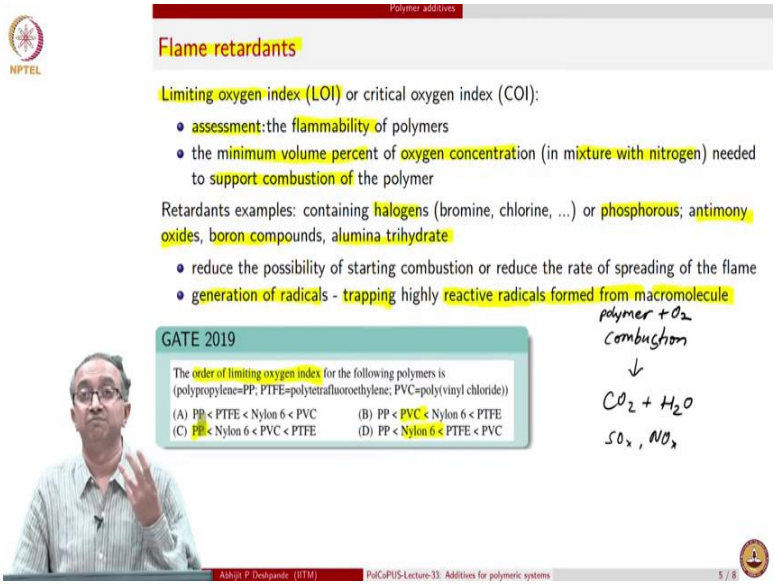

So, think about it as we go along. Fire flame retardants are another important class of materials. And one way to measure flame retardancy is what is called a limiting oxygen index. And basically, this is an assessment of flammability of polymers, how easy or difficult it is for a polymer to burn. And this is the minimum volume percent of oxygen. Of course, in mixture because it is an air of the, we are trying to simulate what is the amount of oxygen required for the combustion to happen.

So, at what percentage of oxygen the combustion is supported. And can you try to reason out will low amount of LOI or COI better or high amount given the definition that it is the minimum volume percent of oxygen concentration needed to support combustion. So, higher amount of oxygen will imply that we need lots of oxygen for combustion to be supported. In other case, we require a very low amount of oxygen. So, which one of these would be desirable? Think about it.
So, retardants, for example can be halogenic compounds, bromine, chlorine related or many of them contain phosphorus antimony oxides, boron compounds and alumina trihydrate are some other common examples of these retardants. Why are these materials used as retardants? And what is the role they play and for that one would have to think you know, what is combustion? How does combustion proceed for a macro molecular case what is meant by combustion?

If you look at let us say, a hydrocarbon based polymers such as polyethylene then it just has C and H and eventual goal of combustion would be for all the C to go to carbon dioxide and all the H to go to water. So, basically, combustion is nothing but a reaction in which finally, we get CO_2 and water. And so, combustion is a process in which polymer plus O_2 will give you CO_2 and H_2O.

Of course, if polymer itself contains nitrogen and sulphur and other hetero atoms, then combustion will also include things like SO_X NO_X and so on nitrogen oxides, sulphur oxides and so, but this is the process of oxidation of a polymer. So, how does this proceed and what we will see is all of these other free radical initiated processes, and if the additive can scavenge can react with those free radicals then basically the rate of combustion is inhibited.

So, that is why generation of radicals by which you can trap the reactive radicals from the macromolecule is the key mechanism by which these flame retardants work and to let you complete your thought process regarding the order of limiting oxygen index in different

polymers, you have to think which one will be better flame resistant material and why? So, if you have let us say, Teflon in which you have CF_2 CF_2, will it have any ability to generate highly reactive radicals from macromolecules.

How easy or difficult will it be as supposed to let us say PVC or nylon or polypropylene? So, think about it, you will have to think both from the point of view of macromolecular groups which are present and in terms of ease of burning of these polymers, what is your judgement. So, just think about it, while we proceed further.

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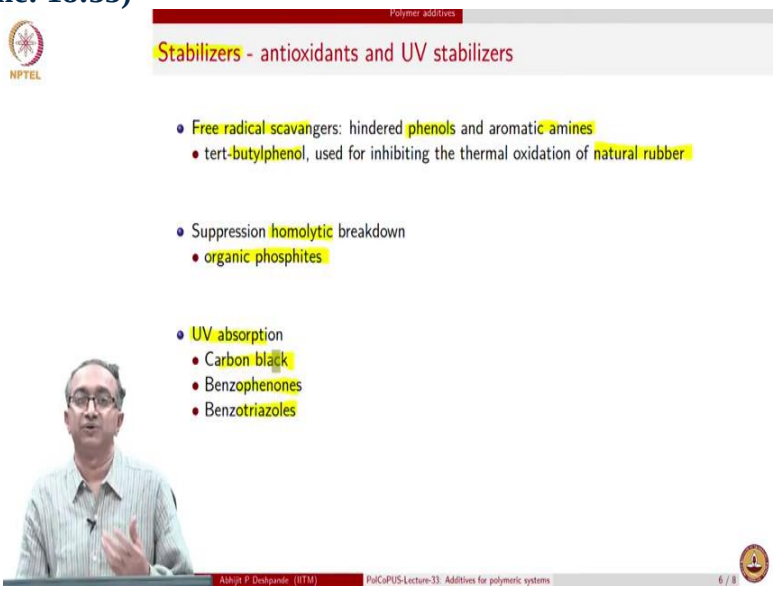

And look at the other class of important additives, which are stabilizers and these again, stability is mainly in terms of basically trying to capture whatever active species are formed. So, that these active species do not react with macromolecules, but end up reacting with these additives and generally phenols and amines are a very important class of stabilizers and so butylphenol is used in rubber for example.

And so, this is a commonly you will see that when you look at the rubber formulation, there will be at least 8 to 10 substances which will be mentioned some of them will be related to the plasticizing action some of them will be related to the manipulation of rates of curing or rates of crosslinking and some of them will be related to stability once the final part is made. And of course, sometimes there can be a homolysis or breakup of the chain and that can be prevented using phosphites.

And UV absorption can also be done using some of the phenones or triazoles but also carbon black and so, UV absorbing materials basically can absorb the UV radiation, they can dissipate it in the form of heat, but they will not get chemically altered. So, the energies of the bond formation and breakage in these materials are not similar to what is the kind of radiation energy that comes from UV. So, therefore, these materials are stable and they will absorb the radiation and therefore, prevent macromolecules from degrading because of the UV radiation.

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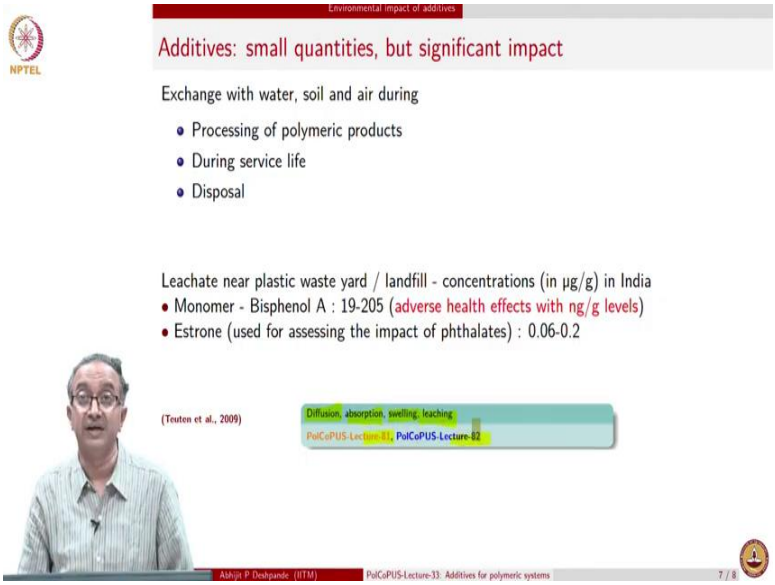

So, in terms of these additives and given their large numbers, the amount may be small, but we have large number of physical chemical species which are used as additives. And so, they are used in small quantities, but they have a very significant impact because they are exchanged with the surroundings. So, you can have an additive leach out to polymer and so in food for example, this is a very common concern and we will often hear of food grade and PET and that implies that the PET has a set of additives which first of all may not leach to the food which is being stored or secondly even if they leach, they are safe for consumption and they are safe for human consumption. So, that is right then it will be called a food grade polymer. And so, this exchange of PET can happen not just during service life, it can happen also during processing itself. So, if we are using let us say, a plasticizer, during processing, we will have to worry about occupational health and safety of the personnel which are doing moulding operations.

And so, the staff there should not be exposed to the plasticizer if it is toxic, or it has certain health consequences. So, we have to worry about exchange not in terms during service life, we have to worry about during processing. And of course, given the questionable sustainability that is being raised about many of these polymeric materials, we have to also worry about exchange with surrounding whether it is air or soil or water during the disposal and eventual whenever service life is over.

And a couple of examples that I have given here is basically if you have a plastic waste yard, and this is a measurement from India from a research paper and you can see that Bisphenol A which is used in polycarbonate epoxies and so, it is an important industrial chemical, and you can see that, in some cases near landfill, the quantities are very high compared to what is permissible in terms of what might have an health impact.

And so, this is something very crucial, because what eventually will happen is this, this is near the landfill itself or near the yard itself, but eventually because all water sources are connected to each other, it can then get transported. So, the fate and transport of Bisphenol A in this case is very important in terms of determining the overall impact of the polymers and therefore additives, being sustainable is also become an important issue.

So, can we use a set of additives which do not have health consequences when they leach out or get exchanged with the surrounding, and that is an important area? So, not only do we have to make polymeric macromolecules themselves sustainable, we have to make the final product

sustainable. And since additives are an important part of the overall product, we need to make sure that many of these additives are also less harmful, they require less footprint to make, and they are based on renewable resources and so on.

And so, the another example is just measurement of a Estrone, which basically gives us an idea of the amount of phthalates present and that is also significant in many of these places. So, this is an important determinant of the overall sustainability of polymeric materials. And as we look at macromolecular sustainability, we need to look at additive sustainability as well. So, this idea that there is an exchange in terms of diffusion of species in terms of absorption., because these polymers could take up material from the surrounding also it could leach which is giving out to the surrounding and there may be swelling because the polymer is absorbing. So, all of these interrelated phenomena, we will look in lectures 81 and 82.

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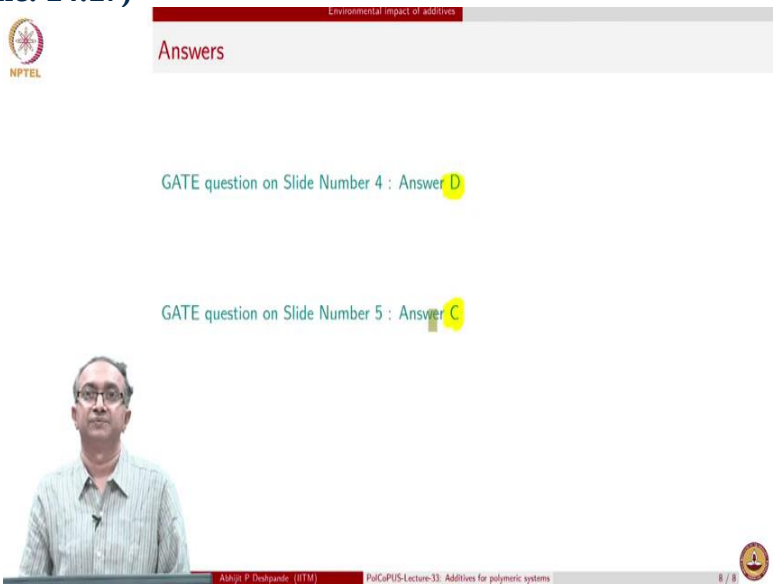

So, with this, we come to the end, I hope through your survey of those molecules, and by thinking you know that, for example, Teflon would have a difficulty in generating the active species, while polypropylene on the other hand will be easily flammable. So, you can look at the structure and then try to justify the results that are there for those questions. So, with this, we will close this lecture on additives that are used in polymeric products, and then we will continue our journey towards looking at different properties. Thank you.