Simple Concepts Related to Single Macromolecules

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Lecture - 08
Renewable Sources for Polymers

Hello, welcome to this course on polymers. This is week 2, in which we will start learning about single macromolecules. In the past week, we learned basic concepts related to polymers macromolecules. And in this week, we will see that behavior of a single macromolecule or a segment of a macro molecule is very useful in terms of determining properties of various kinds of bulk polymeric systems. So, looking at a single macro molecule will help us understand behavior of a polymer in a solution.

It will help us looking at what happens to macromolecules when a melt is flowing in a mold. It may help us and how segments of rubber deform. And so, behavior of a single macro molecule is very important in terms of describing various phenomena in polymer science. So, in this week, we will focus on some of the aspects of single macromolecule. In the beginning of the course, I mentioned that, we will place a lot of emphasis on sustainability of polymeric systems.

So, in this week before going on to single macromolecules, we will spend 2-3 lectures on looking at some sustainability aspects. And this particular lecture is devoted to renewable resources. So, we are in week 2, where we will start looking at a single macro molecule in much more detail. To begin with let us look at renewable sources for polymers and how macromolecules can be made out of renewable resources.

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And we will do this by first looking at what are renewable resources just defining them and then we will also look at one important set of renewable resources which are used in polymeric systems and those are natural fibers. And then we will end with just couple of examples from about polymers, which have been made from renewable resources or these are polymers which are based on renewable resources.

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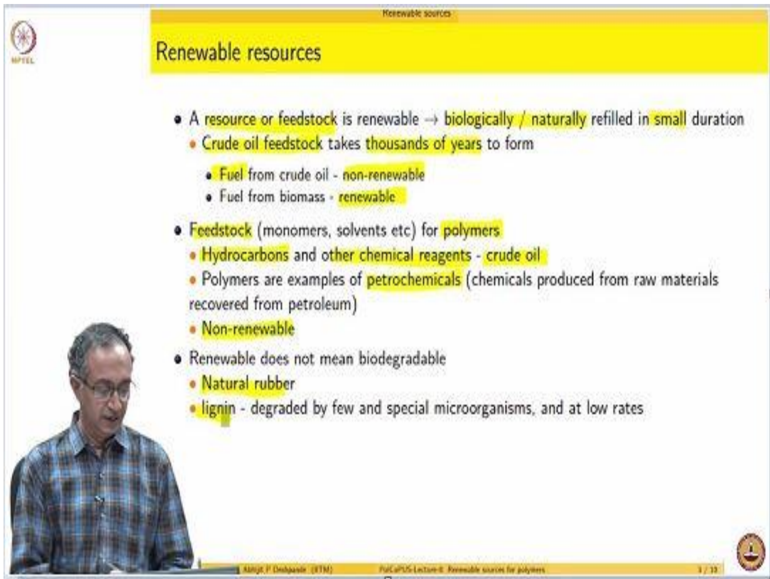

So, what do we mean by renewable resources? So, generally, whenever we think of a material, we need to think of what are the raw material or the feedstock for the material. And that,s where the concept of renewable resources comes from, if the material itself is not renewable. So, a resource or a feedstock is renewable, if it can be biologically or naturally refilled, but the question also is related to how much time. For example, we know that petroleum also comes from biomass.

So, in the end, it is also derived from a naturally occurring system - trees and plants and basically biomass, but it takes large amount of time for it to get converted to petroleum and coal. So, here we do talk about duration which is important and which has to be small. So, in small amount of time, if resource can get renewed due to biological or natural processes, then we will call it renewable and so, crude oil clearly is a non-renewable resource from the point of view if it takes lots of time for it to get made.

And so, generally for example, we think of petrol and diesel if it comes from crude oil then we say it is a non-renewable source if the fuel for driving car or any other transportation vehicle comes from a biomass for example, alcohol which is produced from biomass, then we will call it renewable. So, in case of polymers, we can have renewable resources in terms of feedstock, we can have polymers themselves also are produced in nature.

So, we can think of renewability in terms of feedstocks, which are used for making polymers or polymers which are themselves made in nature. So, for example, generally feedstock for polymers, the synthetic polymers that we are so used to in terms of plastics, rubbers and FRP the general feedstock is hydrocarbons and any other solvents and reagents and co-monomers which are used they all come from crude oil. And so, polymers are very important example of petrochemicals, chemicals derived from petroleum and so, these are non-renewable.

And just to carry forward with the definition, renewable does not imply all the time biodegradability. So depending on, for example, natural rubber is produced by trees, but it is not as easily biodegradable. Of course in all of these things you have already noticed that I am talking in terms of qualitative features. And you may ask the question, what is the number when I say small duration or large duration, small time, large time? What is the duration? And so this is a question which answers are not straightforward.

Its clear that petroleum takes so much more time to reform compared to biomass. We see crops getting grown every 2, 3 months. Sometimes trees will take 20 30 years very different amount of time compared to petroleum. So therefore, even though I am not putting a straight number, I hope you get an idea that whenever I say small, most likely it is duration which is less than 10s of years. While when we say very large amount of time you are talking about 1000 and millions of years lakhs of years and so on.

So, therefore, there is a clearly distinguishable feature in terms of what is the amount of time. So even when we think in terms of biodegradation, if it takes 1000s of years for biodegradation, again, it is not of interest from the point of view of new materials which are being brought at a very rapid rate due to our consumption. So clearly, when we think of biodegradation, it has to be achieved within few years for it to be become a process where we produce these materials, we consume or use these materials, and then they get degraded all this within a span of 10s of years.

So therefore, biodegradable is also with this caveat that the amount of time has to be reasonable. So lignin for example, it is a natural polymer, and it is part of wood. And again, it is not something which in fact, again biodegrade very easily. So that is the reason that we have some of the lignin stored and we get petroleum. So therefore, some of these are features, which we have to always question and think carefully before talking about each of these terms.

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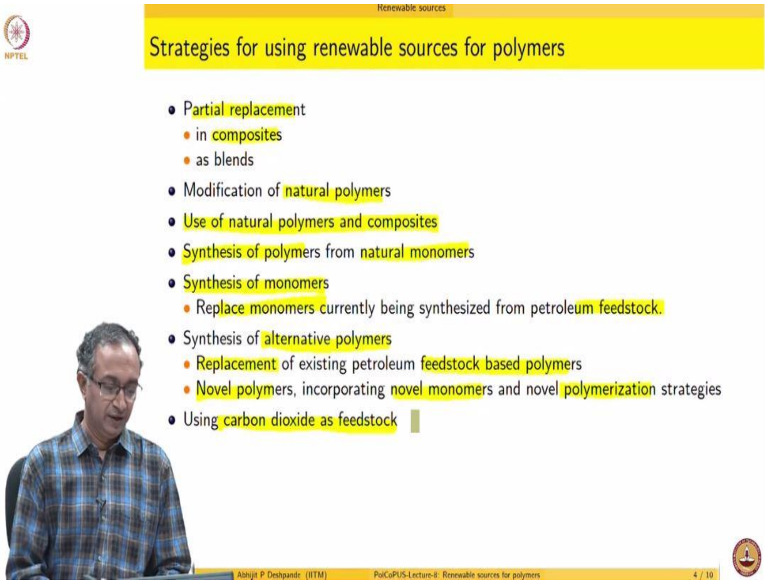

So let us continue and look at you know, what are the options, what are the strategies available to us to try to say that, we will start using polymers, which are more and more based on renewable resources. So what can we do? So the first thing of course, that is easy to do, and that is being done to quite a bit of an extent is we can do a partial replacement. So instead of using a polyethylene material, we can use them mixture of polyethylene and starch and up to 30-40% starch can be incorporated in polyethylene.

And then you can say that you know the amount of plastic waste that I have to deal with is 60%. While the 40% may be accessible, there are issues with this because if starch is embedded in polyethylene is it as biodegradable as pure starch. So, that is something we have to think of. But in general, the idea in this strategy is to say that is to try to use materials which are renewable in combination with synthetic polymers. So you can make starch polyethylene blend you can also use a composite.

So natural fiber composite, which we will just discuss in this lecture, belong to this class of materials. We could take some of the natural polymers and then modify them for our use, because a natural polymer may serve a certain purpose in the biological domain. This purpose could be structural or any other mechanical. Structural mechanical or any other role. Now, for our purposes when we want to make an engineering component out of it, the properties may not be exactly the same.

So, we may have to modify it sometimes even to process it, because the way nature processes and a tree trunk is grown which can withstand lot of weight, we may not have that capability of producing a column like that. So, we will have our techniques of molding and casting and other techniques which we are familiar with in terms of processing of engineering material. So, we may have to modify a natural polymer so, that we can process it using molding and casting and several other techniques.

So, therefore, modification of existing natural polymer is another strategy. Moving down we could of course, use the natural polymers and composites themselves. So, tree trunk of course, bamboo there are so many such natural materials which are already used and in some form, they can be used for certain applications. The other major strategy is to take monomers which are available from the natural world and then try to polymerize them.

So, we think of synthesis of these in terms of useful polymers. So, right now, lot of synthesis of polymers happens based on petrochemicals, these are byproducts of petroleum refining, and therefore, since they are available in large quantities we have over the decades, with very clever manipulation of reaction conditions and our understanding of chemistry, we have come up with a large set of family of polymers. Now, can we do the same by saying that let us look around and see what are the possible monomers available?

And can we now start synthesizing polymers out of these. We could also go 1 step and say that you know, let us start synthesizing some of the monomers. So, I realized that a monomer like ethylene is not available, let us say in nature or because polyethylene is very important or from nylon I need adipic acid and it may not be available as it is. So, can I use some of the natural materials which are there, can I modify them, so, that they become monomers of my interest?

So, therefore, synthesis of monomers from some of the naturally available chemicals can also be a possibility. So, instead of using monomers which are currently coming from petroleum feedstock, they would be coming from some other sources. We also can continue on this journey and then say that, you know, let us think of alternate family of polymers and novel sets of polymers. So, therefore, can we think in terms of alternate polymers themselves and so, this would imply of course, that we will replace the feedstock based polymers that are being used.

And also they imply that these are going to be novel polymers and they will incorporate monomers they which are themselves novel. And very importantly, we will need a synthesis strategy, we will need a polymerization strategy to do this. So, none of these are easy challenges. And in fact lot of effort worldwide is going on in trying to exploit these thought processes in terms of getting polymers as a set of renewable materials as much as possible.

The last thing that we again can keep in mind is what happens when biomass is produced. And biomass as we have seen is full of macromolecules and biomass comes from carbon dioxide and light. So, can we also think of chemistries by which we can produce polymers from carbon dioxide as a feedstock? So then like what plants are doing, we can also start making polymers from CO2. This again some of these are very engaging sets of research ideas on which lot of work is going on.

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And so let us continue and see what are the first set of options that I talked about in terms of partial replacement and this is done already to quite a bit of extent. A lot of these products are already available. Many of the things which look like wood, but are based on polymer or actually examples of this where a natural fiber has been combined with a polymeric resin or matrix and because of the natural fibers, the look of natural material is there.

But the binding and the rigidity and the overall properties of the material come from a combination of both natural fiber and the polymeric material. And there are several examples of natural fibers which are there. Jute is a prominent example, you can get fibers from bamboo and they can be used. In India Sisal and coir are also very important examples of fiber. And so, some of these are already used in lots of applications.

We could also have silk or wool, which are also examples of some of these natural fiber. And what I have shown here are in fact, a set of products which are being developed and are already out there in the market, which are from jute industries research association, their annual report, I have taken this and you can see that these are very common polymers - polyethylene and polypropylene, but in them jute fiber has been incorporated. And so we have caps of bottles we have caps of pens, syringes, lot of disposable items.

So in this now, if you replace the polymer and have 30,40,50% of natural fiber, then in the end from a disposable disposal point of view, you only have about 40,50,80,60% of material which is non-biodegradable and also is non-renewable source. So, one of the questions that you have to think of is, we are mixing 2 sets of materials here and this is a question which we will keep on coming up with whenever we mix materials such as blends, where we mix 2 polymers or a composite where we mix a filler or a reinforcement along with a polymer.

So, in this case, jute which is a cellulosic fiber and it has groups such as carboxylic acid and hydroxyl groups. Now, we are mixing this in polyethylene polypropylene which has only CH2-CH2-CH-CH3. So, hydrocarbon based what is the nature of interaction between polyethylene molecule and polyethylene molecule or polypropylene molecule and polypropylene molecule and between a cellulose molecule and a cellulose molecule?

It is very different. Because hydrocarbons will only have van der Waals interactions. While carboxylic acid hydroxyl as soon as you mentioned immediately it should strike you that hydrogen bonding may be involved. And in other terms also we can say that one set of molecules are likely to be hydrophilic with carboxylic acid and hydroxyl while with just hydrocarbons and CH2 and CH3 kind of groups it is going to be hydrophobic.

So, when we are mixing these 2 groups, will they be able to form a good bond at the interface? What is the compatibility? That is the word we use scientifically to try to ask about what is the interaction between 2 materials when we are adding them together. So, therefore generally we use in practice lot of compatibilizers and this is something we will discuss in a lecture much later during the course. So, keep this in mind that whenever we are making composites and we are trying to evolve strategies to make our polymeric materials according to our needs, we will need to work on how to put them together.

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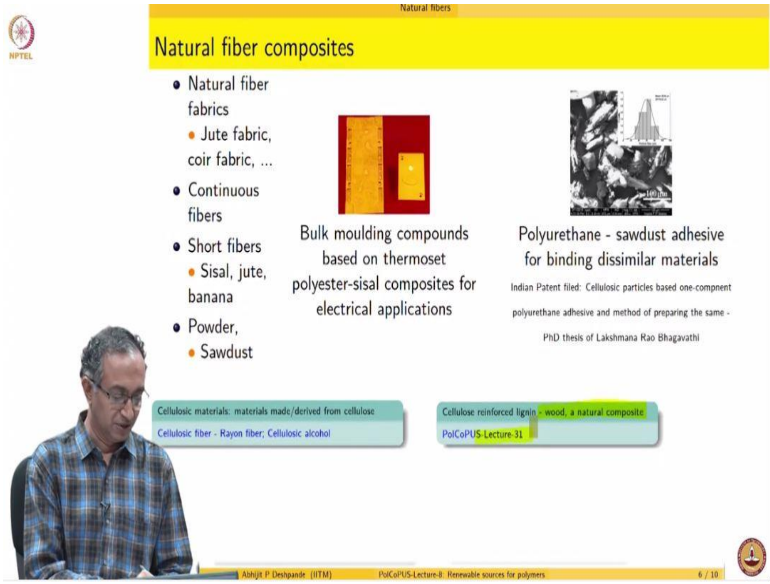

So, continuing on, just show you couple of examples which are from our own work. In one case, we have used a thermoset based so, it is a polyester and sisal fiber and what we did is we made electrical components these are sockets and whenever we have switchboards and even electricity distribution when the board is there in our homes, there are various sockets and things like that. So this is a component which can be made there about 30-40% of sisal fiber was used. Another example where this picture shows actually it is a micrograph.

So, therefore, it shows a very fine view of sawdust. And sawdust is produced in large quantities in sawmills wherever we are cutting wood for using it, a lot of sawdust is produced. So in this example, polyurethane, which is adhesive and it is used in automotive applications in several applications to bond different types of materials. And so, in this case, what we developed is a polyurethane sawdust adhesive. So, again, we use some amount of renewable material in combination with a synthetic polymer.

One other idea that you need to keep in mind is, there is a large class of materials which are cellulosic materials, and not all cellulosic materials are just directly harvested from biomass. So we have example of rayon fiber, you can search for it and try to read it is a it is a very interesting story of how rayon fiber came about, and how it revolutionized many of the aspects of our fabric usage. And so it is a cellulosic fiber, but we manipulate harvested cellulose and get it into a form in from which we can make a fiber.

And this is still commonly used and it is still a product which is commercially viable product. So cellulosic materials are important class of materials, which are based on cellulose directly as cellulose, like a natural fiber like jute or sisal can be used or we can modify the cellulose which is obtained and then use it for other purposes. In terms of cellulose and lignin combination, one other key thing to keep in mind is it is a natural composite. We have lignin as matrix which is surrounding cellulose fibers.

So, in fact, wood by itself, if you think of is a composite material, and it is a natural composite, so, when we start learning about composite materials, we will try to take some understanding away from wood, which is a material which has been around for lots and lots of years.

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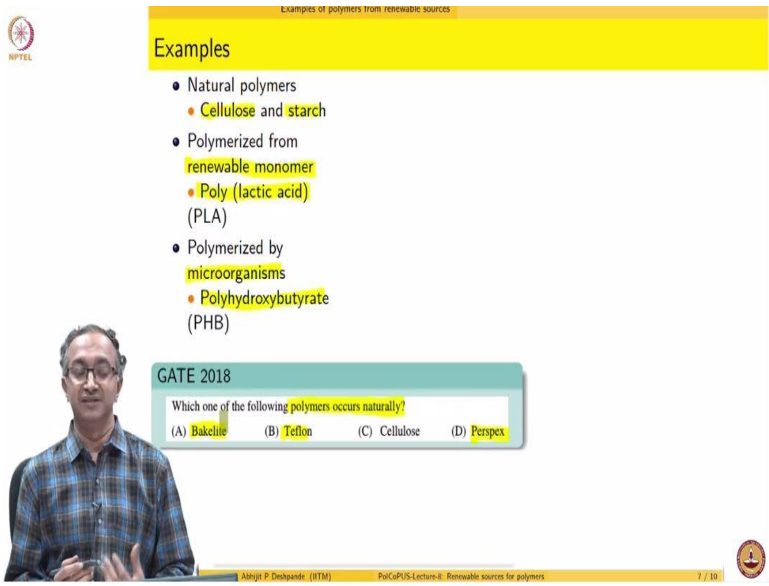

So, let us now finish this lecture by looking at couple of examples of polymers which are based on renewable resource. So, 1 example, which we have already seen are related to natural polymer themselves either cellulose or starch, which can be directly used or they can be used after some amount of modification. Now, we can think of other sets of renewable polymers, which are polymerized from a renewable monomer. So poly-lactic acid is a very important example.

This has been around for many decades but in the last 20 years or so, it has been cited as one of the examples of a biodegradable polymer, which can be used in packaging and several other applications, where large amount of usage will not lead to the plastic waste handling issues that we generally deal with. We will also discuss briefly about a polymer which is made by a microorganism. It is a bacterial polymer and polyhydroxybutyrate again has been known for a long time.

And both of these polymers have been known and there are synthetic synthetic strategies for making both of them and both of them are biodegradable. Both of them have interesting set of properties which are quite close to some of the other polymers that we have. But still there are issues related to the cost of these polymers. Their processibility also the properties being exactly the way we want because if we are trying to use them.

Let us say polyhydroxybutyrate in place of polypropylene 2, 3 properties may match 7,8 properties may match, but there may be 1 or 2 properties where polypropylene is better. So, then how so, therefore, the applications of these are still in are not as large quantities as the promise may be and so, there are still challenges associated with usage of these polymers. Just to think in terms of the distinction between natural and synthetic polymer in the context of renewability.

For example, here is a question and of course, this is a simple question all of you will know answer to that which of the following polymers occurs naturally. And just to remind you in this course, we have already discussed Teflon and Perspex in previous set of lectures, in case you have not heard of, Bakelite, please go and read about it. Again, this is historically very important polymer. You would be surprised to know that when Bakelite was discovered and in some of its initial use, it was first marketed as a material which from which arts art can be made.

So, generally when we think of sculpture and art, we think of stone and wood carvings and things like that. So, so, but some of the initial discovery of polymeric materials led people to think in terms of set of materials, which are so versatile and nice that they can be used for variety of applications and in this case, art as an application. So, of course, this answer is somewhat straightforward, but it keep this in mind that in any of polymer science discussion, we need to continuously think in terms of these sustainability related issues.

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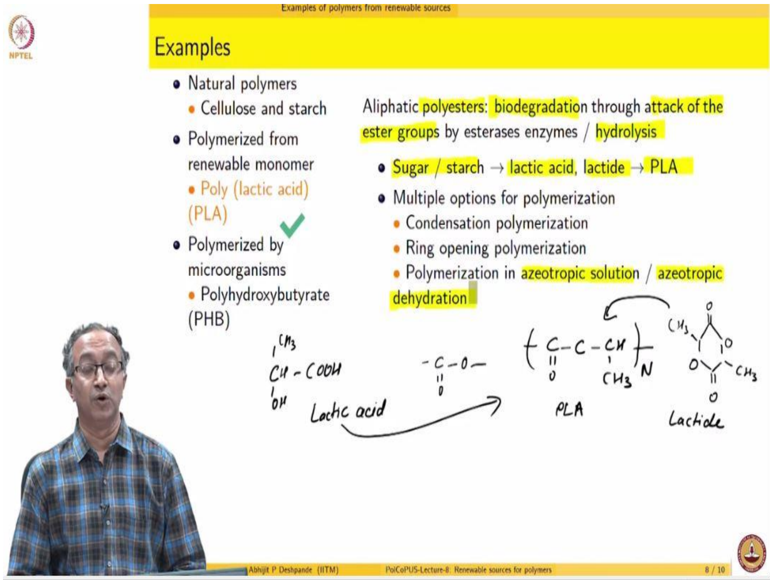

So just going on to look at the 2 examples. So poly-lactic acid is basically a polyester. And we will see that many of the biodegradable polymers are based on this polyester linkage. So, polyester linkage is what is thought is basically enzymes can attack this ester linkage and therefore lead to breakup of a macromolecule. We have already discussed this that building of macromolecules from polymerization is one important strategy that we need, but if you think in terms of sustainability, we need the reverse strategy of breakdown of macromolecules.

So, polyester bond is known to be biodegradable using bacteria and enzymes. So, therefore, this is something where biodegradation is possible through attack of the ester groups and also hydrolysis is possible. So, poly lactic acid is made from renewable resources, such as sugar and starch, lactic acid and it is also converted into lactide and then made into poly lactic acid. And in fact, there multiple options, which are available and both of these condensation polymerization ring opening polymerization are available commercially.

Where in condensation case it is again a reaction which we are familiar with, for ring opening polymerization first lactide is made. So, poly lactic acid, which is this repeating unit is made from lactic acid or it is also made from lactide. And lactide is ring or cyclic compound, which has so this is lactide and so, this ring has to be opened for it to polymerize is as poly lactic acid. Lactic acid on the other hand, is, of course, since it is so, lactic acid. So, you can make poly lactic acid this way or through ring opening polymerization from lactide.

And in all of these cases, removal of water is important. And so, another technique which is followed, in which case, removal of water is implemented using our solution which is azeotropic in case you do not know what azeotropic is, please go and look azeotropic mixtures are useful in vapor liquid equilibria. Azeotropic distillation is something which is quite common, but this is something very similar exploited here in terms of removal of water.

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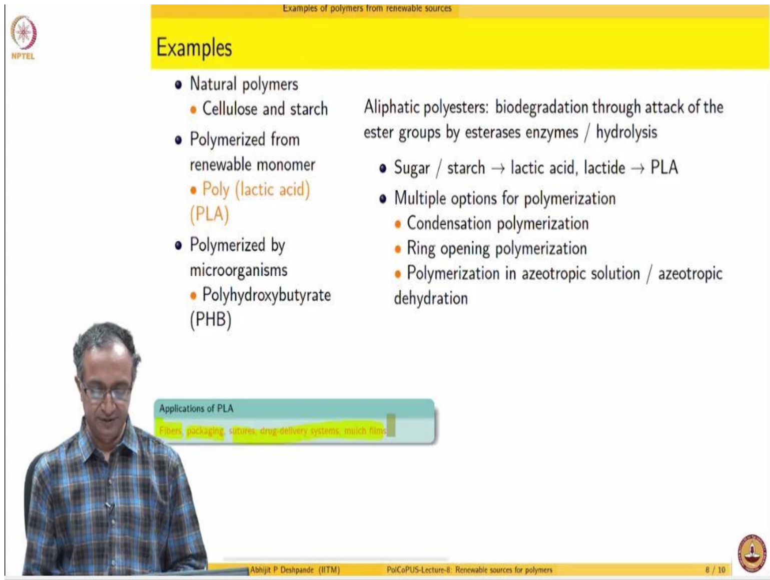

So, the application of PLA are plenty. It is used in packaging fibers, in several biomedical applications as well as much films which are used in agriculture.

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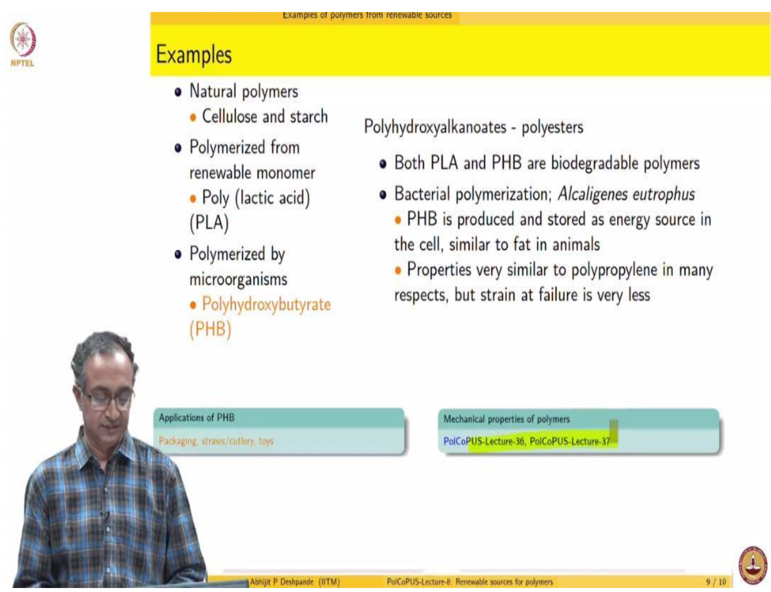

The other example is polyhydroxybutyrate, which is a family of polymers and again polyesters as I mentioned, and so, both of these are biodegradable polymers because of the ester linkages. And this is based on bacteria, and it is Alcaligenes eutrophus bacteria and what is very interesting is PHB is produced and stored by this bacteria, like what we do in terms of fat storage, we think of fat as energy storage, in case of animals.

So something very similar strategy is used. But this polymer can be useful in terms of its properties, which are very closely related to polypropylene. So, PHB properties are very close to polypropylene, but one key difference is in terms of strain at failure being very less. So many times we would like these materials to not be brittle and break with very low amount of deformation. And so that is something which is very different in case of PHB, as compared to polypropylene.

Applications of PHB again are similar in terms of packaging, and toys, and cutlery and things like that. Again, there are commercially available grades of these materials and some of these materials both poly lactic acid and PHB are used, but because of their cost, the usage is very limited. I just mentioned also related to strain at failure. So, in 2-3 lectures on mechanical properties of polymers, we will spend a lot more time talking about strength, toughness, strain at failure, and various other aspects which are related to mechanical properties of polymeric materials.

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And, of course, the question that was there, I am sure all of you know the answer. So, maybe in this case, you do not even need to go back and look at what the question was. But I hope this gives you an idea of the challenges associated with making polymers as a renewable materials. Thank you.