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

Lecture No -86
Biodegradable polymers I

Hello, we continue our discussion of polymers and their presence in environment by way of focusing on biodegradation and in this particular lecture we will look at some examples of biodegradable polymers and the focus will remain on sustainability.

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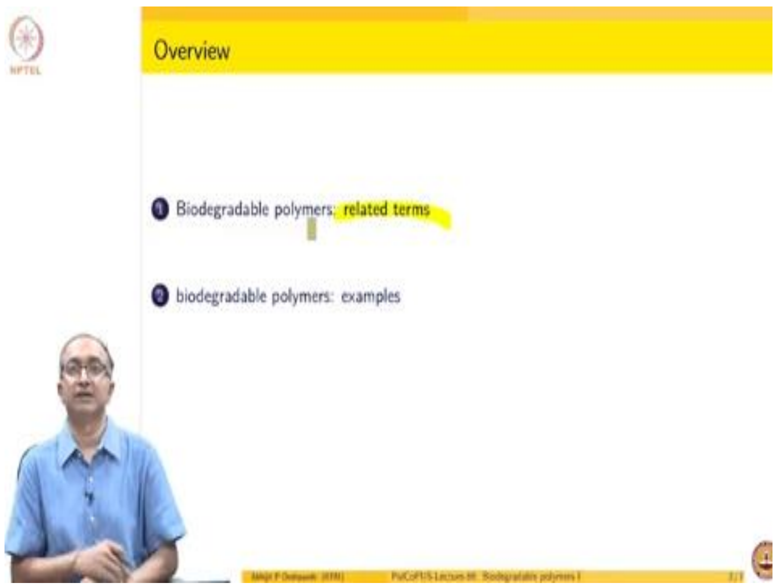

We will first look at some of the related terms associated with description of macromolecules of different kind and the relevance of biological world to the macromolecules and then we will finish by looking at some of the examples of prominent biodegradable polymers.

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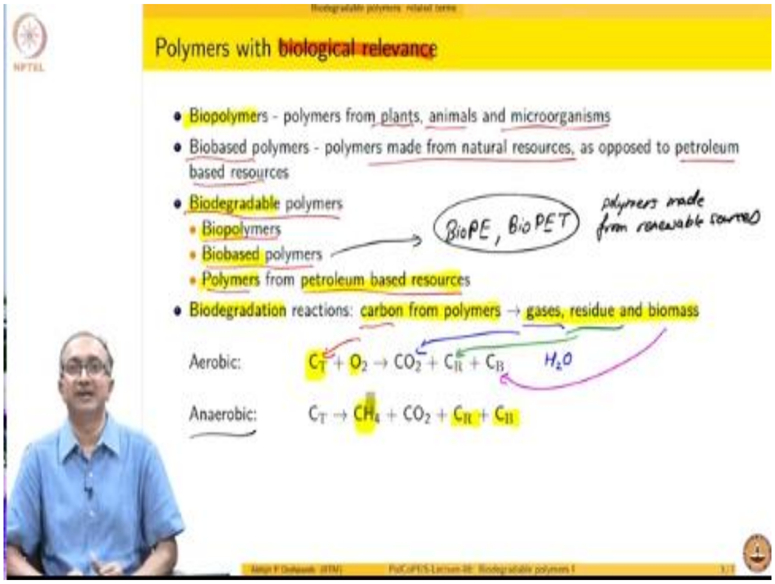

And so if you look at basically polymers with biological relevance, we have already seen that set of polymers which are called biopolymers or bio macromolecules and these happen to be quite often either nucleic acids or proteins or polysaccharides and these are polymers which are macromolecules which are originating from plants, animals or microorganisms. We also talk in terms of a bio based polymer where some amount of transformations are taking place or even polymerization reactions are taking place.

But the original resource is a natural resource as opposed to a petroleum based resource. So these are then called bio based polymers and when we talk of a biodegradable polymer, the polymer has to be degraded in using a biological process, however, they could be bio polymers themselves, they could be bio-based polymers themselves or they could also be polymers which are made from petroleum-based resources.

So all of these three are possible as a source material for generating a biodegradable polymer, given that biopolymers are part of already the biogeochemical cycles, they are naturally biodegradable. Of course, we know that some of them degrade much slowly compared to the others lignin being one example. So there are polymers among the bio polymers which degrade slower than the other.

However, there is a biodegradation phenomena in overall the cycling process and the overall sustainability of these materials. The bio based polymers need not be always biodegradable, so therefore some amount of bio-based polymers where there is possibility of chain cleavage there is possibility of enzymatic attack there is possibility of assimilation by microorganisms those set of bio based polymers are biodegradable.

In fact, if you look at commercial systems as well as literature, there are several materials which are called and they go by such names bio polyethylene bio PET. So what these imply is that these are polymers made from renewable sources. So instead of a petroleum refining plant giving you ethylene, if the ethylene comes from a biomass source and biomass by biological conversions or chemical convergence is converted to ethylene which is used as a raw material for polyethylene production.

And similarly bio PET, so the monomers come from such renewable sources. So these kind of polymers are also around, so they play one role of reducing the overall use of the non-renewable sources which are based on petroleum. However, they are not biodegradable. So few bio-based polymers are biodegradable and therefore biodegradable polymer can be bio polymers or bio based polymers and importantly they can be also polymers which are based on petroleum-based resources.

So polyvinyl alcohol for example is a synthetic polymer and but it is biodegradable it is water soluble and then it can be degraded because of the hydroxyl group which is present and because of the micro molecular reactivity chain session can happen and eventually it can get a assimilated and mineralized. So, therefore you have a PVA, which is a synthetic polymer but a biodegradable polymer.

So we have examples of all of these when we consider in terms of biodegradability, but you can see that bio as a phrase is attached to different set of polymers and when we think of biodegradation a bio based polymer need not be biodegradable. And so the key to understanding biodegradation process is to basically recognize that carbon from polymers is getting converted to gases residue and biomass.

So if oxygen is present then the overall carbon which is present in the macromolecule gets converted to the gases, carbon dioxide and of course we also have presence of water as a product and then we have residue and finally of course given that there is a biological process happening we also will have a biomass being formed and this is indicated using C_B. So C_T is the total carbon content which combines with oxygen to give us carbon dioxide and water.

And then we have a residue and biomass as important products. If the overall process is an anaerobic then we also again have residue and biomass but in addition we have formation of methane. So generally in our big condition, we will lead to formation of methane because of less amount of oxygen being present. So this is a key to recognize whether there is biodegradation happening or not.

One the generation of residue and biomass and gases and the involvement of microorganisms in this process and sometimes it is not easy to do this. So, for example, if I take a plastic bottle and let say it is claimed to be a biodegradable bottle. I can put it along with soil and then try to measure the amount of CO2 that is coming off. But the CO2 could be coming off not just because of biodegradation of the polymer, but we have put it in soil environment where there are there is other biomass which is already present which can act as food source.

So therefore whether the CO2 is coming from the plastic bottle, which is there which is a biodegradable polymer or not or whether it is coming from some other sources. So many of these are very difficult issues to address and therefore this definition of biodegradable polymers and how do we classify whether a polymer is biodegradable or not is still under contention and there are several competing interests.

Of course all of us have an interest in moving towards the sustainable future, there are multiple ways of going there and some of them may be good in the short run some of others may be better in the long run. However, they are all ways to proceed towards more sustainable usage of polymeric material and therefore there are lot of competitive definitions and lot of arguments about this is better that is better.

It is a very interesting field right now to not only just look at it from an application and policy point of view but also from research point of view.

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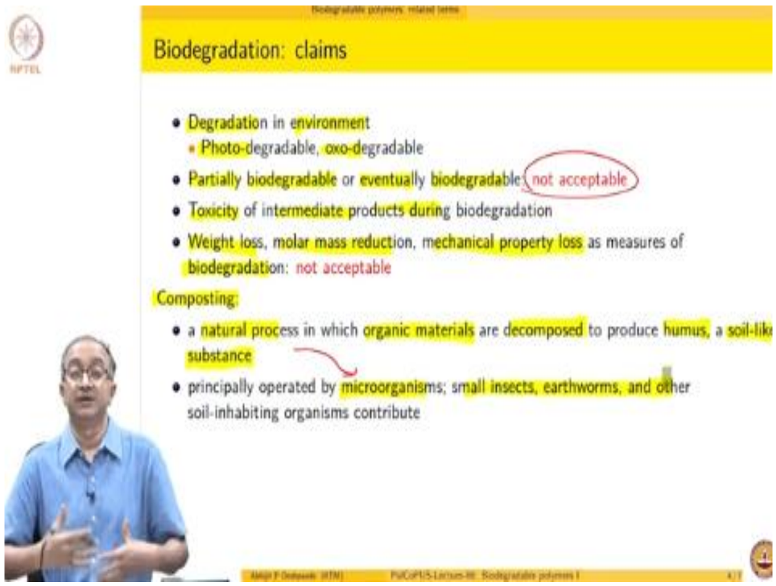

So the general claims that are there for example, if there is degradation in the environment due to UV radiation or also many times now in the polymeric materials species catalytic species or species which can generate radicals species which can generate active centers are added. So that cleavage reactions can happen and then these are called oxo-degradable polymers. There is also a claim for example that it is partially biodegradable like the example I gave of starch blend.

So starch at least is biodegradable even with the other polymer which is blended with starch is not biodegradable or the other argument that can be made is eventually it will biodegrade. So of course this is something which is difficult for us to take as an example of biodegradable system in the overall context of sustainability. One other key feature of biodegradation is the toxicity of the products which are present.

So it may be okay for one particular biodegradable polymer to claim that you know, it is biodegradable and therefore it is sustainable, but during the biodegradation process of significant amount of toxic compounds are released and they can influence the overall surrounding biological world then that is not really acceptable. Similarly generally just to talk about the degradation in terms of weight loss, molar mass reduction or mechanical property loss should not be taken as a way of saying that a material is biodegradable.

Again this starch blend film that I talked about what happens is because starch is embedded and if it is available for biodegradation, then it can biodegrade and the overall film will fall apart into smaller fragments and if you try to say that if a particles have to be smaller than let us say 1 millimeter, then of course all the polyethylene from the polyethylene starch blended now available as very small particles which are sub millimeters, but there is no biodegradation of the polyethylene part.

So therefore there are these multiple definitions can be exploited by competing interests to try to market their product as superior compared to others and we as scientists and engineers have to think very carefully before we try to go ahead in terms of certifying before in terms of classifying many of these different phenomena which are involved during degradation of polymers. One common term which is used by several product suppliers and also researchers have tried to focus more on it is in terms of biodegradation in a composting environment.

Because this is something which can be achieved on an industrial scale as well as at a domestic scale, so composting is basically a natural process in which organic materials are decomposed to produce basically humus you make substances and of course this can be then used as a fertilizer for plant growth. And this happens this natural process happens because we have the presence of microorganisms and the several other biological species.

And in a very healthy composting environment requires multitude of these present for an extremely reliable process of converting the carbon sources into the composting biomass.

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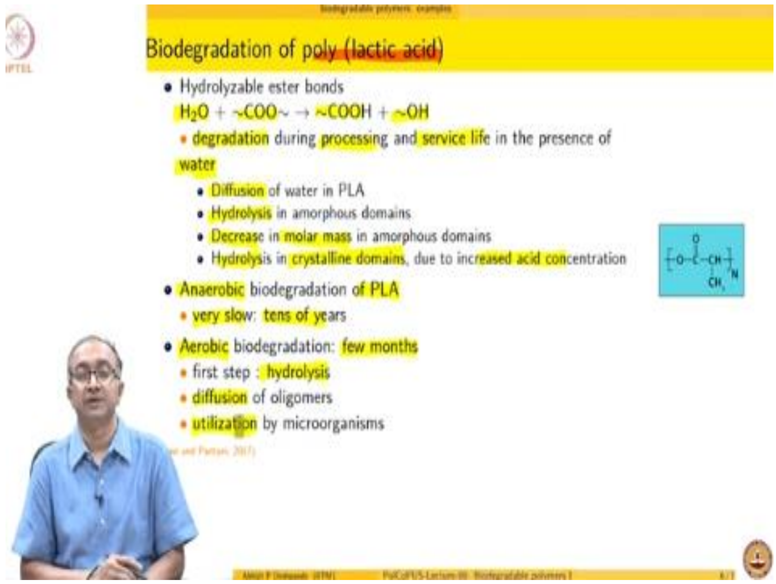

So with this in mind now, let us look at some of the common biodegradable polymers that are out there. We will also look at what are their predominant behavior and so here for example, we look at PHB, this is a microorganism produced polymer, and it basically is a large set of materials which are family of poly hydroxylalkaloids and they are basically degraded because there are hydrolase enzymes.

So there are specifically PHA depolymerases in many of the microorganisms present they could be within the cell or they could be extracellular and then they lead to cleavage of these PHB chains. And so because of this cleavage then oligomers dimers and monomers can be generated and once these oligomers and the monomers are generated they can be utilized by microorganism to produce energy, carbon dioxide and water and of course biomass and residue as we discussed earlier.

So therefore PHB is a classical polymer which can be biodegraded because of the environment of enzyme as well as the key aspect of the products being carbon dioxide, water, residue and biomass. And if we have the anaerobic condition of the biodegradation, then we have a methane being produced in larger quantities compared to carbon dioxide. And generally duration if you look at it takes a few days for it to degrade in environment such as tap water, this is mainly based on some of the research that is being done.

And very careful work has to be done in order to show that yes indeed what we are measuring is due to biodegradation you have to look at the macromolecule and its several products you have to look at gases and where do they come from and you have to look at the energy and material flow into this overall system. So very careful work is done to analyze the biodegradation of polymers such as PHB.

And we generally agree that it takes few months if biodegradation is done in anaerobic condition, and if it is in marine condition, then it takes a few years. But still this is much better than the kind of fate and transport that we have seen for many of the other synthetic polymers that we spoke about during this course. The other prominent example of biodegradable polymer is poly lactic acid.

And again, so this is a synthetic polymer but made from renewable resources and this basically has the hydrolyzable ester bond. So in the presence of water, it can break down into the acid and alcohol and so in fact this degradation reaction can happen during process and service life also as long as water is there. And generally, this would happen based on the processes that we discussed when we discussed diffusion absorption leaching swelling.

So basically, we have to have the small molecule diffusion then we have to have hydrolysis happening in the amorphous region because amorphous region is more accessible to moisture with the free volume present there and also random arrangement of macromolecules. And then because of this chain cleavage and this hydrolyze hydrolysis reactions happening, we have decrease in molar mass and overall PLA stability becomes quite low.

Finally, hydrolysis also starts happening in crystalline domain. This is also aided because the acid which is formed and acid leads to dissolution of the crystals and therefore now degradation in the crystallization domain can begin. So you can see that if you have a semicrystalline polymer the response of, Amorphous and crystalline regions will be very different because these two regions behave very differently in from starting from diffusion absorption phenomena like these two accessibility of enzymes accessibility to microorganisms.

So these biodegradation behavior can be very significantly influenced by the overall morphology of the polymer. And the anaerobic biodegradation of poly lactic acid on the other hand is much slower and it can take tens of years for this to happen. Aerobic biodegradation on the other hand takes only few months and as we have seen first step is hydrolysis breakdown of chain and then we have diffusion and then finally utilization.

So poly lactic acid, you can see is how biodegradable in most conditions which may be prevailing once it comes in the environment.

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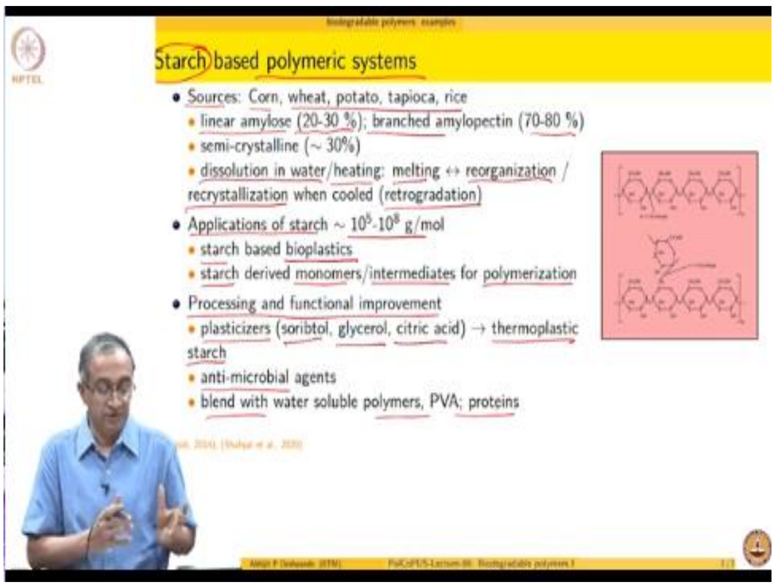

Now, let us look at the third material which is very common as an example of biodegradable polymeric system, these are basically starch based polymeric systems. There is different ways in which starch is utilized for these polymeric systems. So that is why we look at you know, what ways is starch present in many of the commercial systems today? So generally the source for starch is variety of crops, corn is major source worldwide.

But there are the various sources like tapioca and potato and rice also present. And generally starch has linear and branched molecules there is amylose which is about 20 to 30% and amylopectin which is 70 to 80% and generally when we use this starch and in fact, this is what is used in cooking while thickening and variety of others dishes that we prepare we have resolution in water and heating and this generally leads to processes where starch undergoes melting and then again it undergoes reorganization and process which is called retrogradation.

So when you heat it, it melts and then starch macromolecules can acquire different conformations and they can become coil like and then when you again cool then they again get assembled into crystalline domains and these recrystallized domains then lead to thickening and formation of a gel-like substance and that is what we see whenever we used starch in many of the thickening applications in kitchen.

So applications of starch basically the molecular weight varies a lot it is about 10 to the power 5 for the linear molecules to 10 to the power 8 for the branch molecules. So you can see there is a very large variation in terms of molar mass and we have basically starch based bioplastics and we could also break down starch to arrive at smaller molecules which can then be polymerized. So therefore starch is used in both of these ways, you can just use starch by some modification by adding some additives to it or blending it with another polymer, which is biodegradable.

And then this is starch based bioplastics or you could carry out certain transformations of starch, break it down to smaller molecules which can become effective intermediate or monomers. And if you look at starch system and it is used there are several additives which are very commonly used and they belong to plasticizers. In fact, if we add these plasticizers like soribtol and glycerol and citric acid, we get what is called thermoplastic starch.

And like many other thermoplastic materials, we know polyethylene, PET, nylon which can be molded which can be extruded. So many of these processes can be done with starch also. We of course have to add certain anti microbial agents because we would want to prevent biodegradation for certain amount of time which is the service life of the part and we would also blend it with other polymers to improve the film forming capability or flexibility or barrier properties.

So depending on the applications you can add it with other polymers which are also biodegradable and so this way starch based polymeric systems in fact are used quite a lot in today's world.

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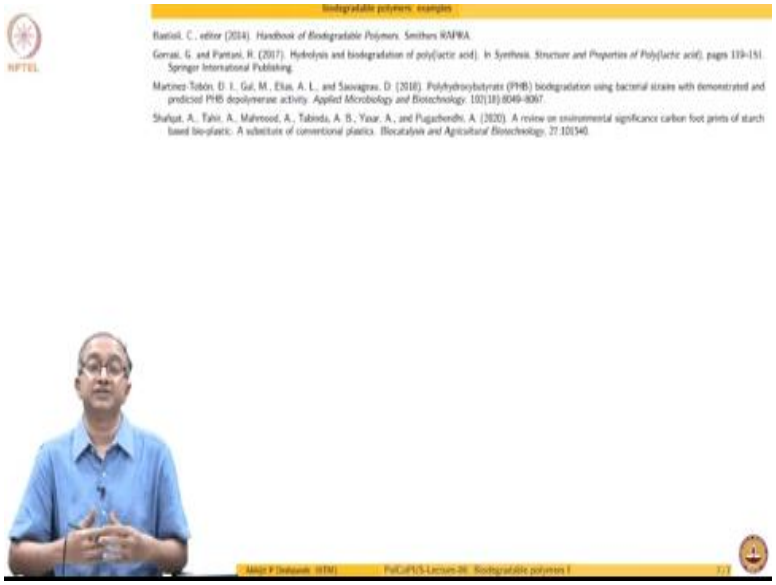

So with this we will stop the discussion related to these different examples of the polymers that we have seen which can be biodegraded. In the upcoming lecture we will look at some of the applications associated with many of these polymers, thank you.