PolCoPUS
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Lecture No -85
Biodegradation of polymers

Hello, welcome to the course on polymers. In this week we are focusing on the sustainability aspect of polymers and specifically in this lecture we will look at biodegradation of polymers.

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What we will look at initially is the overall degradation processes which happen in the environment and where is biodegradation vis-a-vis other processes that happen and then we will take a closer look at what do we mean by biodegradation and what is it influenced by.

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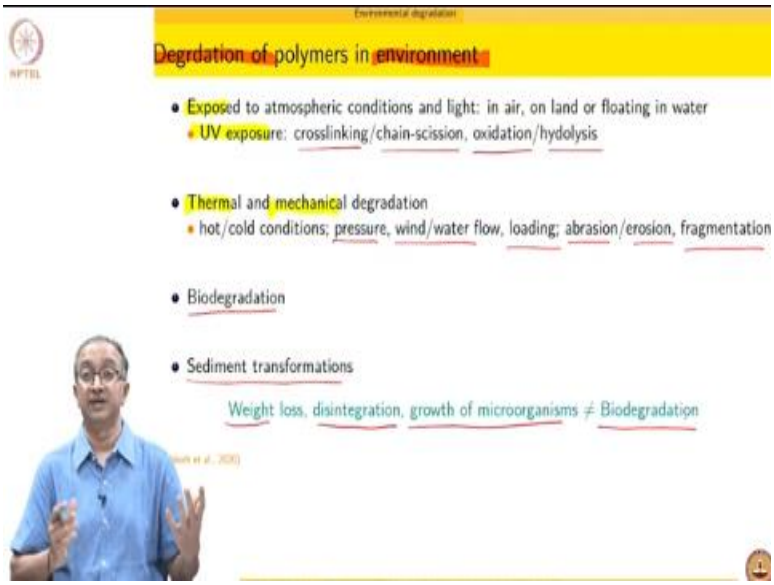

So the polymers and whether they be composites whether elastomers thermosets or thermoplastics are subjected to various degradation processes in the environment and this is due to basically exposure to let us say UV, so in general exposure to atmospheric conditions and this is because they are sometimes floating on water sometimes they are exposed to just air they would also be embedded in soil in that case the UV exposure will not be there, but they will still be subjected to let us say humidity and other additives.

So because of this exposure to radiation we can have processes such as cross linking and chain scission or oxidation and hydrolysis. So presence of radiation which causes free radicals to be generated which causes active centers to be generated in macromolecule and it can lead to breakdown of chains or it can lead to formation of a hydroxyl group in oxidation processes. So therefore all of these processes are possible.

And in fact this is what we prevent by adding lot of additives to the polymeric system, given that its service life is 20 years we do not we would like these processes to be minimized, so that a polymeric part performs according to our expectations. However once disposed it is these processes over time then starts degrading the polymer. The other aspect of degradation that happens is because of the thermal and mechanical loading which this polymer sees depending on the weather conditions it can go from very cold to very hot, also the during flow stresses are subjected.

Sometimes the polymer is getting loaded due to other materials being present in the system, so therefore there is in general pressure there are there is flow conditions, there is mechanical loading, there is abrasion and erosion processes and breakdown. So all of these also lead to degradation of the materials and we also have biodegradation which is what we will discuss from now on which basically implies the involvement of biological species.

It could be microorganisms which are involved and so we will discuss how biodegradation is different compared to these other degradative processes. One other aspect of polymeric transformations that can happen is sediment transformations and we know for example that petroleum is a product is available because of the biomass that got embedded in sediments millions of years ago and then getting transformed.

So therefore under conditions where there is no UV light and even presence of moisture will be less but because of thermal and high pressure conditions, chemical transformations can happen which lead to sediment transformations. So thus, this kind of transformations are also possible in case of polymers. One other key thing to remember in many of these processes the weight will change the polymeric material weight gain may be there or weight loss may be there depending on what kind of degradation reaction that is going on.

Disintegration is certainly there as part of many of these mechanical erosion or because of material becoming brittle due to oxidation and then we can also have growth of organisms on the subs these as substrates on the surface of a plastic material a bacterial colony can grow. However none of these imply that biodegradation is specifically happening. So biodegradation therefore is a much more than just looking at weight loss and disintegration and growth of microorganisms.

In fact these have to be combined together in a way that it becomes a biological process the way several other biological processes are there in our system.

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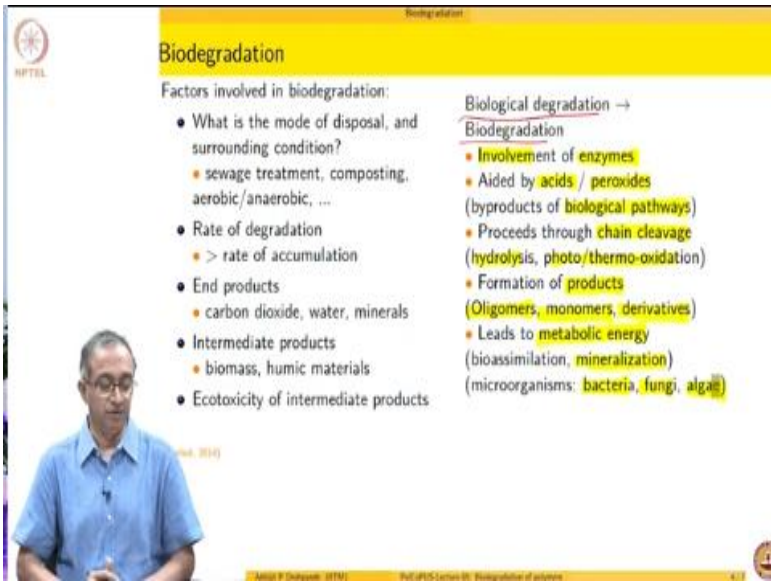

So the factors which are involved before we can look at bio degradation in more detail is for example how is the polymer being disposed and which context are we thinking in terms of bio degradation of polymer. So are we thinking of bio degradation in a compost environment are we treating bio degradation along with sewage and various other waste materials which are coming out from an average settlement of human beings.

So is it being degradation in which context. Similarly is presence of oxygen there or not, so there are several ways in which we can think of biodegradation and each of them is a different mechanism of bio degradation. The other key thing about bio degradation in the context of polymeric material and given our overall emphasis on sustainability and waste management we have to necessarily talk in terms of the rate of biodegradation.

Because the rate of biodegradation should be greater than the rate of accumulation or rate of our use of these materials, because if rate of our use is much higher than biodegradation then it is no use because then any way these materials will get accumulated in the environment and one key feature of how we talk about bio degradation process is by recognizing what are the intermediate and end products.

So the idea here is the fact that we have microorganisms whether it is bacteria or fungi which utilize the polymeric materials as food sources they are responsible for breakage of

macromolecules, sometimes the macromolecular breakage can also be assisted by the other degradation processes that we talked about. So a macromolecule can broken down to smaller fragments and then this gets utilized.

So that the final product of this process are only in terms of carbon dioxide and water which is what happens with all the biomass degradation that happens around us whether it is plant or dead bodies or any biological species basically undergoes degradation to produce carbon dioxide and water and some of the inorganic substances and high molecular weight compounds lead to a residue or minerals.

So these are the only end products that should be there of course as part of the overall biodegradation process biomass can be generated so the number of bio bacteria which are using these polymers as food source can grow and that is how they in fact use the polymeric materials as food source and then of course the overall biomass in combination with soil and other cellulosic materials which are there in the environment can lead to humic materials as the generation.

So only these set of intermediate and end products are considered when we have a biodegradation process and one other key thing when we think of biodegradation of polymeric materials is that none of the intermediate products that are generated whether it is the smaller fragment or oxidized or hydrolyzed version of the fragment this should not be toxic. So none of them should be toxic to the surrounding environment.

And so this is something a key in terms of recognizing the fact that yes, polymer is getting bio degraded in the environment but it is also getting bio degraded in a sustainable manner without impacting the surrounding in a very significant manner. So therefore biodegradation or biological degradation has to have certain number of requisites and this is that first of all enzymes which are of origin from the biological species have to be involved.

So this is one key indicator that it is a bio degradation process as opposed to other degradation processes that we talked about which is like photo degradation and so on and because all of the

biological pathways involve acids and peroxides, the overall process of biodegradation is pretty much helped by the presence of these acids and peroxides. One of the key things is that the breakdown of macromolecule is key for biodegradation, why is that?

Because very large macromolecules cannot be used as food source by a microorganism or any other biological species, so therefore fragmentation as a first step is required before utilization of the carbon source as food can proceed. So chain cleavage is an important aspect so chain cleavage can be enzymatic it can also happen through hydrolysis and oxidation using other means so this can have combinations of steps.

However involvement of enzymes is must when we talk in terms of bio degradation and so generally therefore products will be formed which are oligomers of few monomers may be dimers and then also the derivatives which are oxidized or hydrolyzed versions of these monomers and oligomers and then finally once the formation of these smaller molecular weight products has been achieved then they can get assimilated into the microorganism or lead to basically mineralization.

Because the only solid residue that remains is these minerals while carbon dioxide and water can escape and so the microorganisms which are involved could be bacteria fungi or algae. So variety of these depending on which polymer we are talking about, depending on which environment we are talking about, depending on which mode are we talking about we have variety of these species which can do the role of biodegradation.

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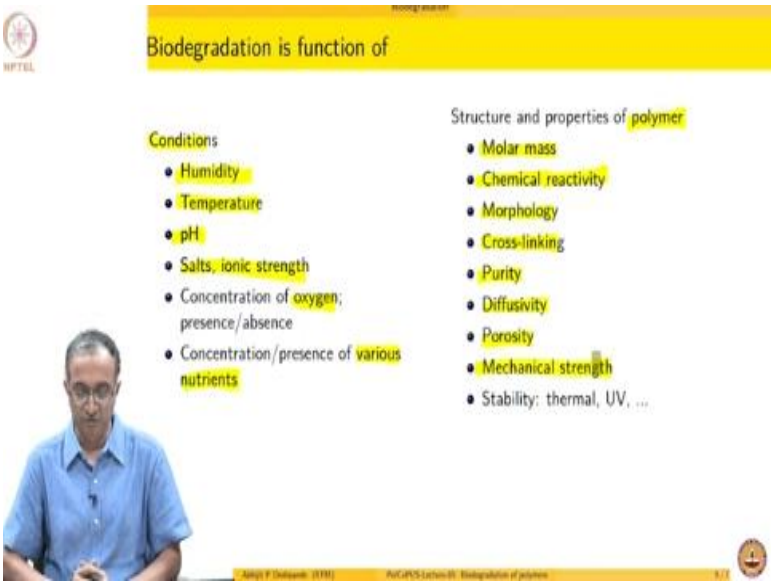

So going further because of this complexity of the overall bio degradation process, the this degradation rate depends on lot of factors. So for example it depends on conditions such as how much is the water present what is the temperature at which biodegradation is happening, what is the pH and as we have seen that there are acids involved there are other intermediates and enzymatic catalysis is involved so all of these depend heavily on the ionic environment.

And therefore pH determines the interaction between these different species which are reacting. We also therefore immediately can recognize that ionic strength and salts can also influence these electrostatic interactions between different molecules which are available and then amount of oxygen because we have oxidative processes we have hydrolytic processes so both amount of water and moisture play a crucial water moisture.

And oxygen play a crucial role in terms of determining the bio degradation rate and given that microorganisms require several other nutrients in smaller quantities which are calcium and other nutrients which are required and so this their presence as well as the amount in which they are present also determines the overall biodegradation and on the other side the polymer itself is a very significant determinant of what the biodegradation will be.

And that is why for example polyethylene is not biodegradable because it does not allow any of the bio degradation processes to take place, it is chains cannot be cleaved by enzymatic waste, it

is chain cannot be even cleaved very easily using photo or thermal degradation processes. Secondly even the smaller fragments may not always act as food source because the smaller fragments are still large enough to be assimilated in the form of minerals and production of carbon dioxide and water by the microorganisms.

And if we have a polymer which is semi crystalline then again access of water to the polymer is much less and so generally basically the structure of polymer is very important in terms of determining the overall biodegradation. So one key determinant is of course the molar mass, I have said this multiple times that larger the molecular weight larger the molar mass more difficult it is to biodegrade.

And that is why chain cleavage is the first set of processes that have to happen before a polymer can be biodegraded. The overall structure in terms of functional groups present on the molecule, the overall set of electronic environments which are there on the macromolecule so that is it susceptible to oxidation or hydrolysis or any other reactive steps. So general reactivity of macromolecule is a big factor morphology in terms of crystallinity;

If it is a blend material what are the different types of domains which are there, whether the material is cross linked are there other additives which can affect the biological processes. For example many times we may add a fungicide for many of the existing polymeric products, so clearly that will prevent biodegradation from happening. So additive and purities are an important source which determines the biodegradation rate.

Diffusion porosity are also very important because smaller molecules have to move in and out either as reactants and products. So water has to go in oxygen has to go in and similarly monomers and oligomers have to move around so that microorganisms can assimilate them so generally diffusion and porosity of these polymeric materials as they are bio degrading influences their bio degradation behavior.

And of course the overall mechanical strength and stability in terms of thermal and UV plays an important role in terms of determining the biodegradation rate.

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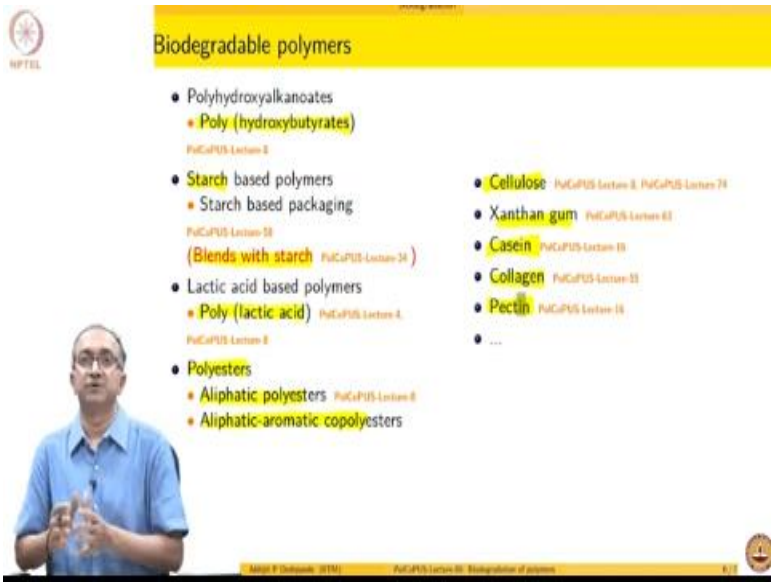

So generally the biodegradable polymer can be thought of in a variety of different families and many of these we have already discussed several times in the course. For example we looked at PHB hydroxybutyrate which is a common example of a bio degradable polymer which is produced by bacteria. We looked at starch based polymers, so cellulose and starch are two most common macromolecules and so the use of starch as materials for polymeric products is being investigated quite significantly.

We also have of course blends of polymers with starch, so let us say polyethylene starch blends so in this case of course this is not a biodegradable material because only starch is biodegradable polyethylene is not and more importantly because of the presence of polyethylene the access to water and oxygen and microorganisms will be severely limited for starch which is present also. So therefore to consider starch blends where the starch is only available in limited amount and the other polymer is not biodegradable is you cannot really have that.

So therefore even though there are a lot of products out there which are starch based blends, the their main function is to say that we are reducing the amount of polymeric materials which are non biodegradable and also which are based on let us say non renewable source such as petroleum based sources. So with this as a justification there are a lot of products out there but if

you think in terms of their impact on the environment lack of biodegradation generation of microplastics being present in the environment over longer periods.

So all of those are still significantly there we also discussed polylactic acid which is a very important polymer, so polylactic acid and PHB are the two most commonly used biodegradable polymers today along with the polyesters, aliphatic polyesters and we also have copolymers where you have combination of aliphatic and aromatic rings in a longer macromolecule backbone.

And of course all throughout the course we have also discussed several polymers which are of natural origin things like cellulose, xanthan gum, casein which is a protein, collagen which is there in tissues and pectin which is there in many plant species and so this is a wide variety of biodegradable polymers some of these are made by microorganisms like PHB, starch which is again made in the biological world.

Lactic acid and polyesters which are actually synthesized but they are biodegradable, they are synthesized using different types of raw materials which could be petroleum origin or non petroleum origin and then we have polymers from the natural world itself which are cellulose, xanthan gum, casein and again these are either made by microorganisms like xanthan gum or they are made like an by animals like casein and then they are available as part of plant world such as cellulose and pectin.

So we have a wide variety of these polymeric systems because of which gradual progressions towards reduction in the usage of polymeric materials which are non-biodegradable to those polymers which are biodegradable is happening. So we have a progression where more and more applications we have started to use these biodegradable polymers.

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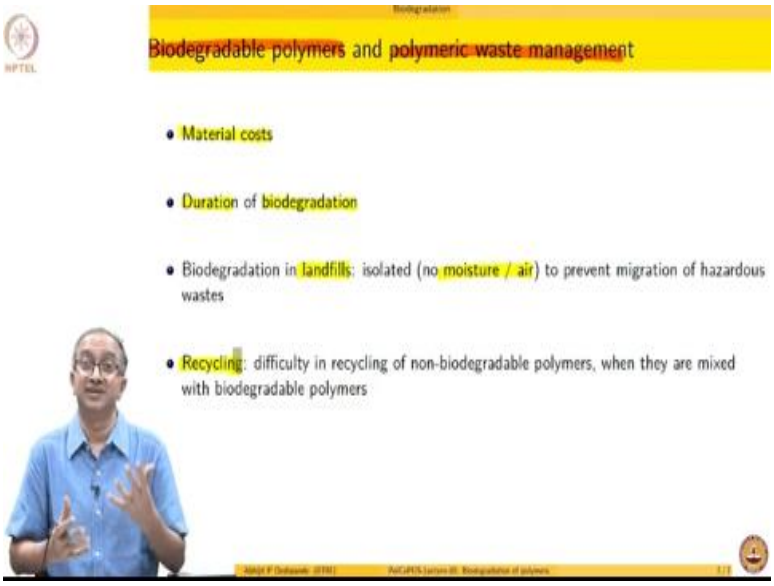

While we do this there are few things that we should consider as scientists and engineers and that is basically the overall idea of biodegradability and how does it integrate with our current practices of waste management. So one of the key thing related to biodegradable polymers is of course the cost associated with it, cost is not in only in terms of let us say the final product the raw material costs and the processing costs which will of course get reflected in the final material cost.

But also impact in terms of what is the reagents and substances which are used in manufacture of these biodegradable polymers, so given the main emphasis on sustainability we have to look at various aspects before we can conclude of their overall impact being less in terms of overall biogeochemical cycles and also as I mentioned already duration of biodegradation is a key factor, we said that you know the biodegradation rate has to be higher than the use rate so that accumulation in environment is not there.

And sometimes this is not very easy to achieve an example is let us say biodegradation in landfill where we have a stack of wastes of all different kind and generally many of these landfills are designed so that you know no moisture or air it is subjected to and contact with surrounding is minimized because landfills will contain all different kinds of wastes including hazardous substances also.

So to prevent the migration of hazardous substances to the air or soil or water which is surrounding we would tend to try to make sure that the landfill is isolated and given that is isolated then can biodegradation happen in such a situation even the pH or the other conditions of this landfill are they appropriate for biodegradation and it is no good if we say that biodegradation under certain condition happened in 15-20 days or happened in 2 months but when we put it in a landfill it takes 400 years to biodegrade.

Then again we are back to square one so therefore we have to think in terms of bio degradation under what condition and one other key feature is given that we have so many other materials which we are attempting to recycle more and more and we have mechanical and chemical recycling methods. So that our impact on environment and is minimized and sustainability is improved what happens when we add biodegradable polymer in this mix.

And biodegradable polymer because the way they micro molecular nature is are not suitable for recycling. So now if we have a stream where there is polyethylene polypropylene and a biodegradable polymer how do we then take care of recycling of this mixed waste, in which case we have a biodegradable polymer but we cannot leave it for biodegradation because it is mixed with polyethylene and polypropylene.

We cannot recycle it even though there is large amount of polyethylene polypropylene because there is some amount of biodegradable polymer, so do we then end up complicating the overall waste management scenario and so these are some of the things that we have to think of while we consider looking at biodegradation of these polymeric systems.

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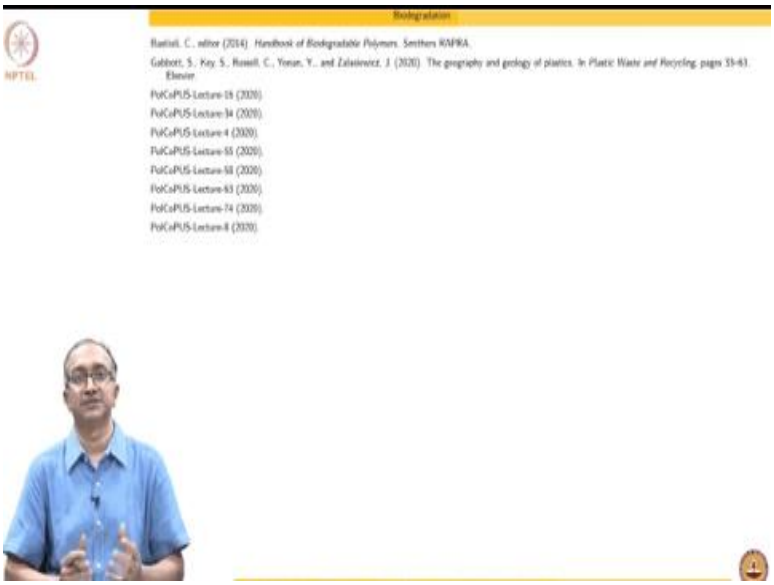

So with this thought we will stop here and look at a few examples of biodegradable polymers in subsequent lectures, thank you.